



SOL-GEL '97



ABSTRACTS

9th International Workshop on
Glasses, Ceramics, Hybrids
and Nanocomposites from Gels

31 August - 5 September 1997
Sheffield, UK



FOREWORD

9th International Workshop on Glasses, Ceramics, Hybrids and Nanocomposites from Gels.

SOL-GEL '97

The 9th International Workshop, is the premier conference for discussion of the latest developments in the rapidly growing multidisciplinary field of sol-gel science and technology. An important objective of the 9th Workshop is to bridge the gap between the scientific understanding and industrial applications so that the enormous future potential of sol-gel methods for innovative materials technologies is realised. Emphasis is given not only to glasses and ceramics but also to the exciting area of organic-inorganic hybrids and nanocomposites

Sol-Gel '97 is taking place at Ranmoor Conference Centre, University of Sheffield. Sheffield is the fourth largest city in England and is world famous for its steel and cutlery industries. The University founded the first Department of Glass Technology in 1915 and the 9th Workshop is being co-organised by the Centre for Glass Research, which is a direct descendant of the Department of Glass Technology. The City is on the edge of the magnificent Peak District National Park.

The 9th Workshop comprises one oral session running 31 August to 5 September 1997. The invitation keynote lecture will be given by Professor David Avnir of the Hebrew University of Jerusalem, Israel, and there are 22 invited papers and 57 other oral papers. There are also two separate poster sessions of 184 papers in total. About 300 delegates are attending the Workshop from 33 different countries.

We should like to thank: our Deputy Chairman, Dr Russell Hand, and the Local Organisation Committee for their hard work; Jill Costello, Christine Brown and Sara Lindley of the Society of Glass Technology for the splendid conference administration and the International Advisory Committee for awarding us the honour of bringing the 9th Workshop to Sheffield. We are exceedingly grateful to our financial Sponsors, who are listed herewith, for making the Workshop possible. As Chairmen of Sol-Gel '97 we bid you a very warm welcome to Sheffield.

Peter F. James *Angela B. Seddon*

Peter F. James and Angela B. Seddon, Co-Chairmen of Sol-Gel '97.

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INVITED SPEAKERS

A1 D. Avnir (The Hebrew University of Jerusalem, Israel)
'Sol-gel materials doped with organic molecules. Applications across chemistry and recent advances'

A3 F. Babonneau (Universite Pierre et Marie Curie, France)
'Structural chemistry of siloxane-oxide hybrid materials'

A6 R C Mehrotra (University of Rajasthan, India)
'Molecular design of novel alkoxide systems as precursors for oxide ceramic materials by sol-gel process'

A7 R.M. Almeida (Instituto Superior Tecnico, Portugal)
'Spectroscopy and structure of sol-gel systems'

B1 A. Atkinson (Imperial College, UK)
'Some recent developments in aqueous sol-gel processing'

B3 B.E. Yoldas (Carnegie Mellon University, Pittsburgh, USA)
'Sol-gel coating media for ink-jet printing'

B4 D.R. Uhlmann (University of Arizona, USA)
'Sol-gel science and technology, how bright is the future?'

C1 S. Mann (University of Bath, UK)
'Sol-gel synthesis of organised matter'

C4 E.J.A. Pope (MATECH, USA)
'Sol-gel bioartificial organs for the treatment of Diabetes Mellitus'

C5 L.L. Hench (Imperial College, UK)
'Molecular control of bioactivity in sol-gel glasses'

DI J. Fricke (Physikalisches Institut, Würzburg, Germany)
'Aerogels - recent progress in production techniques and novel applications'

E1 J.D. Mackenzie (UCLA, USA)
'Structures, properties and potential applications of ormosils'

INVITED SPEAKERS (continued)

E5 H. Schmidt (Institut für Neue Materialien, Germany)

'The sol-gel process for nanotechnologies: new nanocomposites with interesting optical and mechanical properties'

F1 R.R.A. Syms (Imperial College, UK)

'Development of the SC-RTA process for fabrication of sol-gel based silicon-silicon integrated optic components'

F11 F. Gan (Shanghai Institute of Optics and Fine Mechanics)

'Optical nonlinearity of the hybrid and nanocomposite materials prepared by sol-gel'

F12 B.D. MacCraith (Dublin City University, Ireland)

'Optimisation of chemical sensors using sol-gel derived materials'

G1 H. Dislich (Consultant, Germany)

'Technological development of sol-gel coating materials in the last three decades'

G7 C.J. Brinker (Sandia National Labs., USA)

'Surfactant-templating of sol-gel silica films'

G11 S. Sakka (Fukui University, Japan)

'Sol-gel preparation of noble metal colloids-containing oxides'

H1 I.M. Reaney (University of Sheffield, UK)

'Ferroelectric PZT thin films by sol-gel deposition'

I1 K. Nakanishi (Kyoto University, Japan)

'Structure design of double-pore silica and its application to HPLC'

J1 G.W. Scherer (Princeton University, USA)

'Sintering of aerogels'

9TH INTERNATIONAL WORKSHOP ON GLASSES,
CERAMICS, HYBRIDS AND NANOCOMPOSITES
FROM GELS

SOL-GEL '97

ABSTRACTS

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SECTION 1

**ORAL
PRESENTATIONS**

**SOL-GEL MATERIALS DOPED WITH ORGANIC MOLECULES -
APPLICATIONS ACROSS CHEMISTRY AND RECENT ADVANCES**

David Avnir

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In the introductory part of the lecture I provide an overview of the field of sol-gel ceramic materials doped with organic molecules and with proteins. It has been found that most molecules can be entrapped in these matrices while retaining their characteristic physical and chemical properties. The doped materials are highly suitable for a wide variety of optical applications; and for a wide variety of chemical reactive applications due to the accessibility of the dopant to external reagents through the pore network. Optical applications include filters, laser components, light-guides, photochromic glasses, luminescent and phosphorescent materials, optical memory and other information recording materials. Reactions of doped sol-gel materials include catalysis, photochemistry, redox reactions, complexations, enzymatic processes, antibody-antigen interactions, electrochemistry, a wide variety of sensing reactions and materials for use in chromatography.

After summarising the achievements of this 15 years old field as has emerged from the activity of well over 100 laboratories, I will describe 1996/7 advances from our own laboratories, including:

- The sol-gel co-entrapment of indicating dopants with surfactants.
- The polarity of Ormosils and their sensors-applications.
- Fractal and other structural properties of Ormosil
- Catalysis with entrapped organometallics
- Novel sol-gel fibre optics configurations
- The entrapment of antibodies.

STRUCTURE CONTROL IN SOL-GEL SILICA SYNTHESIS USING IONENE POLYMERS

J. N. Hay* and M. J. Adeogun

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Hybrids of silica with main chain (ionene) viologen (bipyridinium) polymers have been prepared by the low temperature sol-gel route from tetra-alkyl orthosilicates. The viologens are reduced reversibly to radical cation species which are deep purple. The hybrid glasses therefore have potential as colorimetric redox sensors (e.g. for oxygen). The synthesis and characterisation of these novel hybrids have been reported. In this presentation, we will focus on the effect of the ionene polymers on structure development in the silica during the sol-gel transformation.

The viologen ionene polymers exhibit interesting amphotropic liquid crystalline (LC) properties i.e. they can exist in a lyotropic LC phase in aqueous solution or in a thermotropic LC phase at elevated temperatures (above 80°C). Either or both these phases may therefore exist during the sol-gel formation of the silica phase. Silica hybrids have been synthesised from precursors where the polyviologen is in respectively an isotropic or a lyotropic solution phase and the resulting sol-gel hybrids studied using DSC, TGA, FTIR and small angle X-ray scattering (SAXS). In addition, the development of structure in the hybrids immediately after gelation was followed in real time using combined SAXS-WAXS (wide angle X-ray scattering) and also FTIR. The ionene polymers can lead to formation of silica with surface fractal geometry rather than the mass fractals more commonly observed for acid catalysed hydrolysis and condensation of the silicates. There is evidence that the use of a lyotropic LC system in the sol-gel reaction influences structure formation in the silica. The LC polymer may be acting as some kind of template for the silica network formation. In this presentation, we will present the results of recent work aimed at elucidating the nature of this effect on the silica structure. The effect of an LC phase on the structure will be compared with silica structure development in cases where no LC component is present.

**SYNTHESIS AND STRUCTURAL STUDIES OF MICROPOROUS
ORGANO-BRIDGED POLYSILSESQUIOXANE AMORPHOUS
POWDER**

A. C. Sullivan, D. L. Ou* and S. W. Carr

Department of Chemistry, Queen Mary and Westfield College

Hydrothermal reactions are normally used to synthesise zeolite materials. Hydrolysis of organotrichlorosilanes (eq. phenyltrichlorodilane) have been studied extensively and cage like organic functional siloxane molecules have been observed among the products. We have studied the hydrolysis of bis(trichlosilylmethy)arenes and observed the presence of the arenes spacers within the siloxane network of the hydrolysis products. In this work, we have investigated use of hydrothermal methods for the hydrolysis of bis(trichlosilylmethy)arenes to see if organo bridged siloxane cages might be formed under these conditions. Both aqueous and non-aqueous media have been used in these reactions. However, the resulting materials were highly amorphous materials, and no crystalline phases were observed. Nevertheless, the internal structure and the microporosity of these organo-bridged silicate amorphous powders are still of great interest, and have been studied by means of N₂ sorption porosity measurement, solid-state NMR, SEM and thermal analysis.

A4(I)

STRUCTURAL CHEMISTRY OF SILOXANE-OXIDE HYBRID MATERIALS

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Sol-gel processing of hybrid siloxane-oxide materials is an area of rapid growth due to the wide variety of potential applications of these systems. The flexibility offered by this synthetic approach - large variety of precursors, low temperature - could allow real molecular engineering of the final materials that could eventually lead to controlled nanostructures.

These systems are usually prepared from organosilanes $R'_xSi(OR)_{4-x}$ ($x = 1, 2$), and metal alkoxides, $M(OR)_4$ with $M = Si, Ti$ or Zr . The chemical reactions occurring in solution (hydrolysis and condensation), during the ageing process before gelation, and then during drying will strongly influence the chemical homogeneity of the final materials, and thus their properties.

The objective of this work is to show that appropriate use of NMR techniques both in solution and in solid state, can provide unique information to describe structural aspects of such systems. The paper will discuss the use of ^{17}O NMR in solution, which can provide unique information on the formation of co-condensed species and their stability versus time, but can also present some limitations depending on the systems. It will also focus on the use of cross-polarisation (CP) and related techniques to probe by ^{29}Si MAS-NMR the local environment of the various Si sites through the dipolar interactions between ^{29}Si and ^1H nuclei.

Examples will be given to show how 2D ^{29}Si - ^1H heteronuclear NMR correlation can provide information on the distribution of Si units throughout the gel matrix.

**ON THE EXISTENCE AND HYDROLYTIC STABILITY OF
TITANOSILOXANE BONDS IN THE SYSTEM:
GLYCIDOXYPROPYLTRIMETHOXY-SILANE-WATER-
TITANIUMTETRAETHOXIDE**

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Glycidoxypropyltrimethoxysilane (GPTS) and titanium alkoxides are frequently employed for the preparation of heterometal hybrid polymers which are used e.g. for hard coatings of organic polymers and contact lens materials in the optical industry. In spite of the importance of these materials a considerable lack of knowledge exists concerning the existence of oxygen bridged heterometal bonds and the ring opening reaction of the epoxy group which should influence the homogeneity in a molecular scale and the structure of these materials. Investigations by means of ^{17}O , ^{29}Si and ^{13}C NMR show that Si-O-Ti bonds are built up after the addition of Ti-tetra-ethoxide to an acid catalysed prehydrolysate of GPTS (Ti:Si=1) with a low water content (0.1 mole $\text{H}_2\text{O}/\text{OR}$ free water). Additional amounts of water (0.1 in HCl) up to a molar ratio $2\text{H}_2\text{O}/\text{OR}$ at a whole leads to the degradation of the oxygen bridged heterometal bonds and the building up of polymeric silsesquioxanes. The presence of the Ti-ethoxide or methylimidazol (MI) as catalyst does not have a significant effect on the ring opening reaction of the epoxy group in the sols. This reaction only occurs after a temperature treatment at 130°C . The influence of the MI on the siloxane and titanasiloxane condensation reaction is discussed. The work improves the NMR spectroscopic identification and characterisation of hybrid sols, summarises and compares the different reactions in the two component system and contributes to the better understanding of basic reactions in a heterometal hybrid system and of the relations between structure and properties of hybrid materials.

A6(I)

**MOLECULAR DESIGN OF NOVEL ALKOXIDE SYSTEMS AS
PRECURSORS FOR OXIDE CERAMIC MATERIALS BY SOL-GEL
PROCESS**

R. C. Mehrotra* and A. Singh

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The increasing interaction between alkoxide chemists and ceramists during the last decade has led to more suitable precursors (alkoxides including heterometallic and other derivatives), resulting in a synergic development in both the fields.

The difficulties involved in handling highly moisture sensitive metal alkoxides have been partially overcome by replacement of alkoxo groups with ligands like β -diketones, amino- as well as alkoxy-alkanols, and more recently some special glycols (e.g., 2-methyl-2,4-pentanediol, commonly called hexylene glycol, which tends to give soluble/volatile products). The isolation of an interesting variety of oxo-alkoxides and heterometallic alkoxides is throwing fresh light on the S-G process itself, in addition to providing new precursors for the same.

The synthetic routes developed for a large number of soluble heterometallic alkoxides involving even bivalent metals like copper and barium have opened up possibilities for molecular design of single source precursors for targeted materials.

SPECTROSCOPY AND STRUCTURE OF SOL-GEL SYSTEMS

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Sol-gel systems differ from conventional melt quenched glasses owing to the peculiar microstructures existing at the gel state and, even after gel densification, some differences may remain relatively to the composition and the molecular structure. Spectroscopic methods are some of the most powerful tools to detect and characterise such differences and to investigate the nano-structure of gel systems in general.

This paper discusses structural characteristics of oxide gels and glasses in bulk, thin film and nano-crystallised film forms, with a special emphasis on SiO_2 - TiO_2 based systems, which are of particular interest for sol-gel optics and integrated optics. Results are presented for infrared spectroscopy measurements (including a discussion of the relationship between IR absorption and porosity), Raman measurements and X-ray photoemission (XPS) and photoabsorption (EXAFS, NEXAFS) spectroscopies, dealing in particular with the issue of homo vs. hetero-condensation in the SiO_2 - TiO_2 system and the structural incorporation of co-dopants such as P or Al into silica-titania gels and glasses. Some NMR data are also presented, for studying the degree of chemical homogeneity in such systems.

The structure of undoped and rare-earth doped nanocrystalline films prepared by sol-gel is also discussed, based on grazing incidence X-ray diffraction, transmission electron microscopy and techniques are compared in detail.

SULPHIDE GELS AND FILMS: PRODUCTS OF NON-OXIDE GELATION

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The inorganic sol-gel process generally proceeds through the controlled aggregation of colloidal particles. A limited reactivity, leading to a gel instead of a precipitate, can either be obtained through electrostatic repulsion or by partial passivation of the surface of the particles. So far, this process has been mainly restricted to oxides. We present here a new reaction scheme for the synthesis of non oxide CdS gels starting from highly concentrated colloids. This allows the synthesis of new transparent nanocrystalline materials, either as thin films or monoliths.

In a first step, concentrated CdS colloids are obtained from particles made either in microemulsions or by direct precipitation in the presence of a complexing molecule. Depending on the experimental conditions, the size of the nanoparticles can be tuned from 1 to 10 nm. High concentrations up to 5 mol.l^{-1} in acetone or tetrahydrofuran can be obtained due to the efficient complexation of the surface of the nanoparticles by a thiolate complex. Extensive NMR characterisation of the structure of this surface complexation will be presented.

Starting from such colloidal solutions, the random aggregation of the particles, leading to the sol-gel transition, is achieved by a progressive depassivation of the particles through oxidation of the thiolate molecules into dithiols. The effect of some parameters such as the CdS concentration or the oxidised thiol fraction on the gelation time, the optical transparency of the gels and its further ageing will be discussed. Structural characterisation of the gels by small angle X-ray scattering show a fractal dimension of 1.9 consistent with a cluster-cluster aggregation model.

Drying of the gels allows the obtention of transparent materials which can be processed either as thin films or monoliths just as it is usually done in oxide systems such as silica. For example, one-micron thick films have been obtained free of crack, and exhibit an optical index of 1.95 at 633 nm. High resolution electron microscopy show that the materials are nanocrystalline with a blende or wurtzite structure depending on the size of the primary nanoparticles.

In conclusion, we propose a new synthesis scheme to obtain transparent chalcogenide gels or films. The principles of our method could be applied to other systems and open the way to new transparent nanostructured materials.

SYNTHESIS OF POLYVANADATES FROM AQUEOUS SOLUTIONS

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A wide range of polyvanadates can be synthesised from aqueous solutions. Vanadium oxide gels $V_2O_5 \cdot nH_2O$ are formed around the point of zero charge ($pH \approx 2$). They exhibit a ribbon-like structure. Weak interactions between these ribbons lead to the formation of mesophases in which vanadium oxide gels or sols behave as nematic liquid crystals. Organic species can be easily intercalated between these oxide ribbons leading to the formation of hybrid nanocomposites made of alternative layers of organic and inorganic components. Hybrid nanophases can also be formed above the point of zero charge, in the presence of large organic ions such as $[N(CH_3)_4]^+$. They often exhibit layered structures in which organic cations lie between the polyvanadate planes. Cluster shell polyvanadates have been obtained in the presence of anions such as Cl^- or I^- . They are made of negatively charged polyvanadate hollow spheres in which the anion is encapsulated. Organic cations then behave as counter ions for the formation of the crystal network.

B1(I)

SOME RECENT DEVELOPMENTS IN AQUEOUS SOL-GEL PROCESSING

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D. Segal

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Since its initial application to the fabrication of nuclear fuels during the late 1950s, aqueous sol-gel processing has become an increasingly popular method for the preparation of ceramic materials in a variety of forms. Its main advantages over the alkoxide sol-gel process are lower cost and avoidance of organic solvents. In this overview we first give an outline of the process and then describe the recent use of aqueous sol-gel processing for the preparation of ceramics that have very different end-uses. Ceramic stains (e.g. chrome alumina pink) for decorating ceramic bodies have been produced using this method; not only in powder form but also for direct application to ceramic ware by a novel use of inkjet printing technology. Cathodoluminescent phosphor powders, based on the doped-yttrium aluminium gallium oxide system, have been developed for high resolution displays using a combination of aqueous sol-gel precursors and aerosol techniques to produce particles of controlled size and shape. Zirconia nanofiltration membranes have been produced by use of zirconia sols and evaluated on the pilot-plant scale for the treatment of waste brine produced during refining of cane sugar. Finally, microporous zirconia-pillared clay minerals having a large and hydrothermally stable interlayer spacing have been produced using aqueous sols for catalytic applications. These examples illustrate the versatility of aqueous sol-gel processing for the preparation of a wide range of ceramic compositions.

INORGANIC-ORGANIC HYBRID POLYMERS WITH BARRIER PROPERTIES FOR WATER VAPOUR, OXYGEN AND FLAVOURS

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In recent years polymeric packaging materials have become increasingly important, especially in the food packaging industry due to their numerous advantages over other materials with respect to convenience, economy and even ecology. However unlike materials such as ceramics or metals, polymers are permeable to gases, water vapour and volatile organic compounds like hydrocarbons or food flavours.

New inorganic-organic hybrid polymers developed at the Fraunhofer Institute can be used to obtain high-barrier coatings which are able to reduce drastically the permeation rates of oxygen, water vapour and volatile organic compounds.

The hybrid polymers are accessible via the sol-gel technique. The inorganic-network is formed as a result of controlled hydrolysis and condensation of alkoxides, organoalkoxysilanes, metal alkoxides or acrylate alkoxides. The organic network results from subsequent thermal or ultraviolet induced polymerisation of organo-functional groups.

Due to the control of the inorganic and organic network densities and the insertion of specific functional groups to control the polarity of the material it was possible to develop high-barrier coatings with excellent adhesion properties on a wide variety of polymer substrates. Further investigations showed that by using special morphology types of inorganic-organic hybrid polymers the barrier properties can be improved further.

These high-barrier coatings are also suitable as laminating agents. The properties of such multilayer constructions can be conserved even under high mechanical and thermal stress.

B3(I)

SOL-GEL COATING MEDIA FOR INK-JET PRINTING

Bulent E. Yoldas

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Image transfer and image recording is an important part of everyday life in the age of communication. Inkjet printing is used to transfer multicolour images on paper and on transparencies for presentations and for record keeping. This technology, which is rapidly growing, suffers from the shortcomings of the coatings designed to receive the ink in high speed. The shortcomings include: ink dry time, edge acuity of ink patterns, colour fidelity, light and water fastness of the prints, haze and abrasion resistance of the film, etc.

We have engineered a single layer sol-gel coating which is clear, dense and provides virtually instantaneous drying of the print. The coating exhibits an excellent ability to maintain edge acuity and colour fidelity resulting in photographic quality images. It is coatable to all substrates and not printer specific. In this presentation factors involved in the engineering of such an inkjet receiving film will be discussed.

B4(I)

**SOL-GEL SCIENCE AND TECHNOLOGY, HOW BRIGHT IS THE
FUTURE?**

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This paper represents a follow-on to the paper presented at the previous Symposium held in Portugal in 1995 on the current state and future prospects for sol-gel processing. The present report will discuss the results of an updated questionnaire sent to leading practitioners in the field of sol-gel science and technology, as well as to prospective users of the technology, with an expanded base of respondents. The present questionnaire focused more on future prospects than on past accomplishments, and more on the potential for commercial applications than on scientific advances. Besides summarising the views of the community, the paper will also present the opinions and perspectives of the authors.

C1(I)

SOL-GEL SYNTHESIS AND ORGANISED MATTER

Stephen Mann

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The study of biological silicification in unicellular organisms such as diatoms and radiolaria, is providing new ideas and inspirations for the synthesis of organised inorganic matter. This lecture describes recent approaches to the 'synthesis-with-construction' of silica-based materials with structural and morphological organisation across a range of length scales. Several themes are addressed. These include the template-directed synthesis of covalently linked organosilicate hybrid clays with lamellar structure, and of ordered mesoporous MCM-41-type hybrid materials. The former are produced by reaction of organosiloxanes in the presence of inorganic templates (mono-octahedral Mg/OH/O brucite layers), whereas the latter are synthesised by co-condensation of siloxanes and organo-siloxanes in the presence of cylindrical micellar templates consisting of long chain surfactant molecules. In addition, the use of larger templates, such as ordered arrays of bacterial cellular filaments, in the formation of ordered macrostructures of amorphous silica or mesoporous silica, is described. Finally, a new method for synthesising silica with microkeletal architecture is discussed. The approach employs condensation reactions in compartmentalised liquids as a means of generating organised patterns of inorganic matter.

BIOACTIVE GEL COATINGS DERIVED FROM VINYLTRIMETHOXYSILANE

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Most organic polymers in clinical use are only biotolerant as other common materials like ceramics and metals and are encapsulated by fibrous tissue when embedded in human bodies. A few ceramics like Bioglass®, however, can chemically bond to soft or hard tissue through a biologically active apatite layer that forms spontaneously on their surface. Calcium ions and silanol groups (Ca^{2+} and Si-OH) are two of the essential chemical species providing bioactivity. One can therefore expect that gels even with organic skeletons show bioactivity if they are incorporated with those ions and groups, and that the gels serve flexible bioactive coating which prevents blood coagulation due to the newly depositing apatite layer.

The present study is concerned with sol-gel preparation of Ca-containing bioactive gels derived from vinyltrimethoxysilane and gel coatings on a polyamide (Nylon 6®), one of the most common polymers in clinics. Vinyltrimethoxysilane (VTMS) was polymerised under N_2 atmosphere at 150°C for 2h with an initiator di-t-butylperoxide (5 mol%/VTMS). The polymerised VTMS (PVTMS) was about 20-mers due to GPC analysis. An ethanol solution of PVTMS was mixed with an aqueous solution of calcium acetate ($\text{Ca}(\text{OAc})_2$) and refluxed in N_2 for 1h: the composition of the mixture was VTMS: H_2O : EtOH: $\text{Ca}(\text{OAc})_2$ = 1: 8: 9: 0.05 (mol). Thus obtained sol set in 24h at 40°C into a transparent bulk gel. The sol was dip-coated on the polyamide and was gelled at 40°C : the coating was anchored to the substrate strongly enough for a Scotch® tape test. ^{29}Si CP-MAS NMR analysis indicated that a half of the Si atoms was in $\text{C-Si}(\text{OMe}, \text{OH})-(\text{O-Si})_2$. The bulk gel and the coated substrate were soaked in a simulated body fluid at 36.5°C . Thin film X-ray diffraction and IR reflection spectroscopic analysis indicated that the bulk gels deposited apatite on whole surfaces in 1d while the gel coating deposited apatite within 7d, indicating the present gel was bioactive and applicable to bioactive coating on the polyamide.

ELECTRIC WIRING OF OXIDOREDUCTASES TO SOL-GEL DERIVED COMPOSITE MATERIALS

O. Lev*, J. Gun, S. Bharathi, Z. Wu and S. Sampath

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Sol-gel technology is emerging as a powerful technology for the encapsulation of enzymes and other biochemicals in porous inorganic materials. Amperometric biosensors employing oxidoreductase enzymes (such as, glucose oxidase, GOx) require means for long range charge transport from the enzyme cofactor to the conducting transducer. This can be accomplished by diffusing mediators, which however tend to leach out of the active membrane of the biosensors during prolonged operation.

Three approaches for the construction of sol-gel composite bioceramics, which facilitate charge transport between the active centre of the enzyme and the electrode are demonstrated. All three approaches are based on graphite - silicate composite materials in which the graphite powder provides long range electron conduction by electron percolation mechanism and the silicate or organically modified silicate backbone contributes the rigid skeleton and encapsulates the enzymes. Electric 'wiring' of the oxidoreductase is accomplished by one of the following three ways: 1. Formation of redox - modified silicate backbone which transduces the electrons by self exchange (electron hopping) mechanism; 2. Covalent bonding of the redox mediators onto the oxidoreductase enzyme, which facilitates electron tunnelling through the enzyme bound moieties and 3. Modification of the graphite powder by thiol-anchored monolayer of charge mediators (ferrocene) and encapsulation of the modified graphite in the sol-gel silicate matrix.

All three methods yield reagentless, leaching free, Amperometric biosensors. Metrological characteristics of the biosensors are compared.

C4(I)

SOL-GEL BIOARTIFICIAL ORGANS FOR THE TREATMENT OF DIABETES MELLITUS

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The primary objective of this work is to evaluate the potential of silica gel encapsulated pancreatic islets of Langerhans, or islet tissue, as a means by which insulin secretory capacity might be restored to individuals with insulin dependent, type 1, diabetes mellitus. The encapsulation material under investigation is comprised of sol-gel derived silica ceramic that hardens under conditions of pH, salinity, and temperature that are not harmful to living cells and organisms. Preliminary efficacy has been demonstrated by measurements of insulin secretory response of silica gel encapsulated pancreatic islets in vivo and blood glucose levels of nonobese diabetic mice in vivo. In NOD and streptozotocin-induced diabetic mice, symptoms of diabetes have been eliminated for over 3 months (14 weeks). The sol-gel method can be used to generate spheres of varying dimensions. The optimal sphere size and optimal encapsulation method for islet encapsulation have been addressed. Our approach addresses two of the three major causes of graft rejection: inadequate protection of engrafted islets from damage by the patient's immune system; and toxic effects of the drugs used for immunosuppression.

C5(I)

MOLECULAR CONTROL OF BIOACTIVITY IN SOL-GEL GLASSES.

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Seven steps are involved in making bioactive calcia-phosphate-silica glasses, by the alkoxide-based sol-gel method. Step 1 - mixing; Step 2 - casting (when monoliths such as substrates for tissue engineering are desired); Step 3 - gelation (powders or fibres can be made during this step); Step 4 - ageing (control of hierarchical structures can be achieved at this step); Step 5 - drying (highly dependent on whether monoliths, powders or fibres are being made); Step 6 - stabilisation (molecular control of isoelectric point and surface charge is established by varying the thermal and chemical history of the porous material). Following a thermal stabilisation treatment of 700 to 1000°C the surface of the porous gel-derived glasses is composed almost entirely of siloxane bonds and can withstand atmospheric exposure and liquid environments indefinitely. Alkoxide-derived gel-glasses made with a proper stabilisation treatment contain a large volume fraction of stable, interconnected porosity which can be impregnated with optically and biologically active second phases. Porous gel-silica optical matrices made in this manner are termed Type VI silica, porous calcia-phosphate-silica glasses are termed bioactive gel-glasses. The compositional range of the porous calcia-phosphate-silica gel glasses that exhibit bioactivity is considerably larger than exists for melt-derived glasses.

The chemically stable porous matrices made by the sol-gel glass process offer a unique approach towards achieving molecular control over bioactivity. Animal experiments show that bioactive gel-glass powders stimulate bone to fill bone defects and resorb from the defect site more rapidly than synthetic calcium phosphate ceramics or melt-derived glasses. The proposed mechanism responsible for the enhanced osteogenic behaviour of bioactive gel-glasses is described in this paper. An important aspect in rapid bone proliferation is that biological molecules can adsorb and desorb from the interconnected pore network without loss of conformation and biological activity. Control of the pore size of the bioactive gel-glasses is also important because of the effect of radii of curvature on the rate of surface nucleation of biological hydroxy carbonate apatite in the pores of the material and the rate of dissolution of soluble silica from the gel-glass network.

AEROGELS - RECENT PROGRESS IN PRODUCTION TECHNIQUES AND NOVEL APPLICATIONS

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Aerogels are sol-gel derived nanostructured materials with extraordinary properties according to their high porosity. In principle, nearly every organic or inorganic precursor which condenses to form a three-dimensional gel network can be transformed into an aerogel via supercritical drying in an autoclave. Recently considerable activities are devoted to ambient pressure drying. This is a prerequisite for a cheap large-scale commercial production presumed that the low-density open-porous structure and thus the material properties can be preserved. Though first prepared more than 60 years ago, silica aerogels became widely known only in the late 1980s when they were used in Cerenkov detectors and their potential was recognised as catalytic substrates and high performance thermal insulants. Nowadays aerogel research has attracted a lot of scientists from different fields, resulting in some hundred publications per year and the fifth aerogel symposium soon to take place.

This review will focus on recent developments made in the field of sol-ambient pressure drying processes. The state of the art with respect to structural characterisation and measuring the material properties is reported including non-destructive techniques and alterations induced by invasive methods. A brief survey is given on modelling the aerogel structure and simulating mechanical, thermal and (di)electric properties as well as sintering and transport processes within bulk, surface and pores.

The progress in the field of non-silica and multicomponent aerogels is reviewed as well as organic modification and doping by chemical vapour infiltration. The ongoing development in preparation and the understanding obtained by non-destructive characterisation allow to optimise the material properties for several applications. Additionally, also novel utilisations are pursued such as smart sensor systems, low-impedance piezo-electric transducers or high-temperature thermal insulants. Special attention will be electrical conductivity of their graphitic backbone and the large specific inner surface areas, carbon aerogels can be considered ideal electrodes in supercapacitors and fuel cells.

D2

SYNTHESIS OF HYBRID ORGANIC/INORGANIC AEROGELS BY AMBIENT PRESSURE SOL-GEL PROCESSING

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Aerogels are typically made by extracting solvent from wet gels through supercritical drying. Under this condition, the liquid-solid interface is eliminated and the stress exerted by liquid on the gel network is essentially zero, thus little or no shrinkage will occur. But this method is expensive and also rather dangerous. In addition, this method is not adaptable for making aerogel thin films, which constitute some very important applications. One alternative approach is to prepare aerogels and films at ambient pressure by fluid exchange. Drawbacks of the fluid exchange approach are the laborious process and consumption of large quantity of chemical solvent.

This paper reports the synthesis of hybrid organic/inorganic aerogels and films by ambient pressure sol-gel processing. It is to copolymerise organic and inorganic precursors so as to incorporate organic ligands into the solid skeleton. The organic ligands incorporated into the solid gel network modifies the surface chemistry and, thus, the surface tension and wetting angle are changed such that the collapse of the gel network is prevented upon the removal of pore fluid during drying. Experiments have shown that processing parameters such as, precursors, Si:H₂O ratios, pH values, solvent, and ageing time are very important for preventing phase segregation and obtaining highly porous structures. Hybrid organic/inorganic aerogels with BET surface area above 1250 m²/g, porosity above 80%, and pore size of ~50 nm have been synthesised using the ambient pressure sol-gel processing. In addition, hybrid organic/inorganic aerogels and films possess another unique property, i.e., hydrophobicity and, thus, are not moisture sensitive.

SCHNELL GEL. RAPID ROUTE TO ULTRALOW DENSITY GELS WITH NO CATALYST REQUIRED

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A new family of simple precursors to silica gel has been developed. The gel precursors are tetra(polyfluoroalkoxy)silanes, the prototype being $\text{Si}(\text{OCH}_2\text{CF}_3)_4$. Rapid formation of transparent monolithic gels is possible even at very low concentrations in water/alcohol solvents with no added catalyst. Pore sizes in the wet gels were estimated from hydrodynamic relaxation in a beam-bending experiment on cylindrical logs. In a gel at 1% solids, the pore size was approximately 100 nm. At this concentration gels can easily be generated in seconds; gelation rates are at least four orders of magnitude higher than that for TEOS at the same solids content and pH*. Monolithic - and very fragile - gels can be created at concentrations at least as low as 0.2% solids. Syneresis occurs rapidly in the sparse gels although the corresponding TEOS-derived gels show no syneresis below 4% solids. Mechanistic evidence from NMR, GC/IR and mass spectrometry will be presented for intermediacy of novel polysilicates with low percolation thresholds for gelation.

FUNCTIONALISED SILICA AEROGELS

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The incorporation of functional groups is one of the prerequisites to broaden the range of possible applications for silica aerogels into the field of sensors or catalysts etc.

Organically functionalised silica aerogels of the idealised composition $(A-(CH_2)_n)_x-SiO_{(2-0.5x)}$ were prepared by sol-gel processing of $A-(CH_2)_n-Si(OR)_3/Si(OR)_4$ mixtures followed by supercritical drying of the obtained alcogels. A wide variety of functional groups A was employed, such as epoxy, methacrylate, chloro, phosphino, amino, ethlendiamino, carbamato or metcapto groups.

The steric, electronic, and Lewis acid or basic properties of the functional organic group influence the hydrolysis and condensation reactions and therefore the microstructure of the resulting aerogels. Different analytical methods such as IR and Raman spectroscopy in combination with thermal and elemental analysis were employed to follow the elementary steps of sol-gel processing and get information whether the organic group is destroyed during hydrolysis and condensation or drying. Structural investigations by nitrogen sorption and small angle X-ray scattering allow a correlation between the first network forming steps and the final microstructure of the modified aerogels.

Additionally, some macroscopic properties, such as the mechanical behaviour and the hydrophobicity of the resulting aerogels in dependence of the functional group, will be discussed.

DRYING OF AEROGELS BETWEEN ATMOSPHERIC AND SUPERCRITICAL PRESSURES

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The sol-gel derived wet gels are usually dried by two fundamental processes. In the first process, the liquid in the gel pores is evaporated at atmospheric pressure to yield so-called xerogels. The formation of capillary pressure during this process causes shrinkage of the gel network and thereby reduces the pore size. This pressure may necessitate a slow, careful drying to avoid cracking of the gel.

In the second process, the wet gel is rapidly dried above supercritical pressure and temperature. Under these conditions, there is no interface between vapour and liquid and the destructive effects of capillary pressure are therefore avoided. The dry-gel or so called aerogel has larger pores, because the drying shrinkage is relatively small. However, the supercritical pressures are usually so high (for example, 63.1 atm at 243.1°C for ethanol) that expensive autoclaves are necessary for this process.

It is of interest to investigate whether gels can be dried between atmospheric and supercritical pressures with minimal shrinkage. Minimisation of shrinkage allows pores to remain large and open after drying. This helps the sintering process. Equipment costs may also be reduced substantially because of low pressure drying operation.

The purpose of this investigation is to show feasibility of producing aerogels at subcritical conditions and understand the drying behaviour. SiO₂ wet gels were prepared using tetraethoxysilane (TEOS) as precursor. The drying pressure was controlled by the total solvent amount in the drying equipment. Crack-free dry gels with negligible shrinkage (<2 %) were obtained at conditions considerably less than supercritical pressure. For example, one gel, with ethanol as the pore fluid, was dried at 30.8 atm and 239°C. Its average pore radius was 91 Å, surface area 705 m²/g and pore volume 3.2 cm³/g. The same gel, dried supercritically at 72.5 atm and 250°C, had average pore radius of 88 Å, surface area 683 m²/g and pore volume of 2.99 cm³/g. Thus, the gels had very similar microstructure.

In conclusion, it was shown that aerogels can be obtained at moderate pressures which may make this drying process economically feasible.

E1(I)

STRUCTURES, PROPERTIES AND POTENTIAL APPLICATIONS OF ORMOSILS

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Ormosils are organic-inorganic hybrid solids in which the organic component may be chemically bonded to a silica matrix. Somewhat similar to inorganic silicate glasses, the structure of the silica network can be modified by the presence of organic groups. The resulting properties of the Ormosils are then governed by the type and concentration of the organics used. Examples are presented in which the mechanical, electrical and optical properties of selected Ormosils can be influenced by organic groups. For instance, small amounts of polydimethylsiloxane (PDMS) added to a solution of TEOS will give an Ormosil about ten times harder than the hardest organic polymer. Larger amounts of PDMS (20%) will organics used. Examples are presented in which the mechanical, electrical and optical properties of selected Ormosils can be influenced by organic groups. For instance, small amounts of polydimethylsiloxane (PDMS) added to a solution of TEOS will give an Ormosil about ten times harder than the hardest organic polymer. Larger amounts of PDMS (20%) will now yield an Ormosil which is as rubbery as organic rubber. The thermal stability of Ormosils is greatly enhanced by small amounts of iron ions. The mechanical properties and microstructure of Ormosils are significantly altered by small concentrations of carbon. The potential applications of some Ormosils are discussed.

STRUCTURE DEVELOPMENT IN SIMPLE CROSS-LINKED ORGANOPOLYSILOXANES

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^{12}C CP and CPPI MAS NMR have been carried out on cured samples of simple polymethylvinylsiloxane and polydimethylsiloxane prepared by hydrolysis and condensation of dichloromethylvinylsilane and dichlorodimethylsilane. Curing of the siloxanes was achieved thermally and the degree of cure could be controlled to give brittle or elastomeric polymers.

By varying the CP contact time for the ^{12}C CP MAS spectra of the polymethylvinylsiloxane, the α and β vinyl carbons and the methyl carbon of the $-(\text{CHCH}_2)(\text{CH}_3)\text{SiO}-$ species could be identified. A further methyl carbon was detected which was less mobile and which we assign to methyl groups attached to silicon species on which the vinyl group has reacted to form a cross-link.

Resonance from $-\text{CH}_2-$ carbons was observed in the 30–40 ppm range, and these species arise from vinyl-vinyl cross-linking to give $-(\text{CH}_3)\text{OSiCH}_2\text{CH}=\text{CHCH}_2\text{SiO}(\text{CH}_3)-$ links between chains. Further evidence for this comes from the temperature insensitivity of the β carbon resonance under CPPI, indicating that it is in a $-\text{CH}=-$ rather than a $=\text{CH}_2$ environment.

There was also evidence of $-\text{CH}_2-$ carbons in the polydimethylsiloxane material, suggesting that thermally activated, methyl-methyl cross-linking can occur to give $-(\text{CH}_3)\text{OSiCH}_2\text{CH}_2\text{SiO}(\text{CH}_3)-$ links between chains.

**KINETIC INVESTIGATIONS OF HYDROLYSIS AND
CONDENSATION OF THE
GLYCIDOXYPROPYLTRIMETHOXY-SILANE/
AMINOPROPYLTRIETHOXY-SILANE SYSTEM BY
MEANS OF FT-RAMAN SPECTROSCOPY**

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FT-IR Raman spectroscopy is a valuable tool for in situ measurements of the base catalysed sol-gel process in the system 3-glycidoxypropyl-trimethoxysilane/3-aminopropyl-triethoxysilane. This system is highly interesting for the production of hybrid (inorganic-organic) polymers. Raman bands of the trimethoxysilyl- and the epoxy-moieties monitor the kinetic behaviour of the hydrolysis reaction and the ring cleavage, respectively.

An unexpected slowdown of the hydrolysis of the epoxy silane recorded at higher temperatures can be attributed to a deficiency of water and a multiple hydroxylation on each silicon atom. This is a straightforward proof for the formation of a pentacoordinated transition state with a negative charge at the silicon atom during base catalysed hydrolysis. The shortage of water results in a shortage of hydroxyl-ions, the silicon attacking agent in base catalysed hydrolysis. After the slowdown a reacceleration of hydrolysis takes place due to the beginning water condensation after an induction period, which liberates new water molecules.

The opening of the epoxy-ring depends strongly on the amount of aminopropyltriethoxysilane as the amount of opened rings in the first part of the reaction is proportional to the concentration of the amino-groups.

ENCAPSULATION VERSUS TETHERING IN THE INCORPORATION
OF $C_5H_5Rh(CO)_2$ INTO HYBRID INORGANIC-ORGANIC CUBANE
{ Si_8O_{12} } COPOLYMERS

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Controlled pore inorganic solids play a key role in modern chemical technology as *inter alia* heterogeneous catalysts, absorbents, and porous membranes. We have previously demonstrated that porous materials may be obtained by the copolymerisation of cubane octavinylsilsesquioxane, $\{Si_8O_{12}\}(CH=CH_2)_8$, with the cubane silsesquioxane hybrids, $\{Si_8O_{12}\}H_8$ and $\{Si_8O_{12}\}(OSiMe_2H)_8$, under mild conditions. The copolymer resulting from $\{Si_8O_{12}\}H_8$ exhibits a remarkably high BET surface area of around $500\text{ m}^2\text{ g}^{-1}$.

The complex $C_5H_5Rh(CO)_2$ may be incorporated into this polymer structure either by impregnation of the previously prepared polymer using a solution of $C_5H_5Rh(CO)_2$ in toluene, or by performing the copolymerisation in the presence of the complex. Although very similar in appearance, these two polymers differ substantially in their BET surface areas ($275\text{ m}^2\text{ g}^{-1}$ for the sample obtained by impregnation versus $656\text{ m}^2\text{ g}^{-1}$ for that obtained by copolymerisation). Similar polymers are also obtained from $\{Si_8O_{12}\}(OSiMe_2H)_8$. Spectroscopic data including MAS-NMR and infrared using $^{12}CO/^{13}CO$ isotopomers will be presented to distinguish between the possibilities of whether the rhodium complex is incorporated into the polymer structure as an intact molecule or whether the rhodium becomes tethered to the polymer structure.

E5(I)

**THE SOL-GEL PROCESS FOR NANOTECHNOLOGIES: NEW
NANOCOMPOSITES WITH INTERESTING OPTICAL AND
MECHANICAL PROPERTIES**

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Sol-gel synthesis reactions have been investigated with respect to the formation and processing of nanoparticles. It has been found out that by controlling the growth reaction by growth controlling agents (GCA) stable sols could be obtained from various oxides (Al_2O_3 , ZrO_2 , Y-ZrO_2 , SiO_2 , Fe_2O_3 , TiO_2 and others). As GCA's either functional or non-reactive components have been chosen. Functional components have been used to introduce the nanoparticles into organic polymer matrices and the nanoparticles themselves have been investigated with respect to their catalytic activity for polymerisation and polycondensation enhancing effects.

It could be shown that nanoparticles can act very similar to alkoxides in polycondensation reactions for building up inorganic backbones, but can also act as organic network forming catalysts. Based on these findings, a series of new nanocomposites (Nanomers®) has been developed for hard coatings, waveguides or binders for glass fibres. In the paper, the basics of the chemistry, material properties and various applications are given.

STRUCTURAL AND DYNAMICAL STUDIES OF HYBRID SILOXANE-SILICA MATERIALS

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Hybrid siloxane-silica coatings with second-order nonlinear optical (NLO) properties have been prepared by hydrolysis and condensation of N-[3-triethoxysilylpropyl]-2,4-dinitrophenylamine (TSDP) and tetramethoxysilane (TMOS) precursors. Hetero- and homo-condensations between both precursors have been demonstrated to occur in the early stages of the process via ^{17}O and ^{29}Si nuclear magnetic resonance (NMR) in solution. These hybrids can be described as nanocomposites made of polysiloxane-based domains cross-linked by silica-based nanoparticles, as evidenced by solid-state NMR, differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR). Moreover, the high degree of interpenetration occurring in these materials is evidenced by the presence of some Q and T subunits sequestered within these polysiloxane and silica-based domains, respectively. The mobility of the NLO chromophores, as observed by high-resolution solid-state ^{13}C NMR, is correlated with the glass-transition phenomenon of the matrix. Dielectric relaxation experiments in a large frequency range were also carried out to improve the understanding of the relationships between the structure and the dynamical behaviour of NLO chromophores in these hybrid systems.

**CERAMERS BASED ON CROSSLINKED EPOXY RESINS-SILICA
HYBRIDS: ASPECTS OF STRUCTURE/PROPERTIES
RELATIONSHIP**

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There are basically two ways of preparing organic-inorganic hybrids by the sol-gel method. These differ from each other with respect to the molecular state of the organic component, which can be either in the form of a linear polymer or as a network involving some of the metal oxide units from the inorganic component in the interfacial regions. Organic networks are produced from oligomers containing alkoxy silane terminal groups which are capable of reacting with the metal alkoxide, usually tetraethoxy silane (TEOS) and the morphology is controlled by adjusting the reaction/processing conditions.

So far only one study has been reported for hybrids based on epoxy resin. This does not fall, however, within the general category of ceramers in so far as the silica phase is present as dispersed particles rather than as co-continuous domains. The only feature that is in common with ceramers is the use of the sol-gel method to produce the silica particles and the use of an organofunctional trialkoxysilane (an amine type) with the TEOS to enhance its bonding to the epoxy resin matrix.

In the present study cured epoxy resin-silica hybrids were prepared through telechelic functionalisation of a bisphenol-A epoxy resin using different types of reactive trialkoxysilanes, at various molar ratios and always ensuring that a major amount of epoxy groups remain for crosslinking with hardeners. In this case methyl nadic anhydride (MNA) and diamino diphenyl sulphone (DDS) were used. The partially functionalised glycidyl ether resin with alkoxy silanes was also used as compatibilising agent for a multifunctional epoxy resin (novolac type) to produce epoxy ceramers with a higher glass transition temperature.

These systems were also compared with ceramers produced from prehydrolysed solution mixtures of TEOS with minor amounts of a glycidyl trialkoxysilane which is expected to enter the epoxy resin network through copolymerisation with the hardener.

A particular feature of this work is the study of the effect of the molecular weight of the epoxy resin on the morphology or the resulting ceramer.

COATING OF TEOS/VTES HYBRID SOLUTION ON POLYMER FILMS

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Inorganic-organic hybrid materials can be used for transparent functional coatings on polymer substrate such as abrasion resistant and gas barrier coatings. VTES(vinyltriethoxysilane) was used as the organic part to enhance the adhesion between the coating and the substrate. Because the VTES has been widely employed as a coupling agent having dual chemical functionality capable of interlocking the inorganics and organics by reacting with the molecules of both substances. The hydrolysis and condensation reactions in TEOS/VTES hybrid solution were examined using ^{29}Si NMR and chromatography. The optimum process parameters, TEOS/VTES ratio, drying temperature, and pretreatment of the films, was investigated for the solution to be coated on PP or PET films. Also microwave heating was applied to get better adhesion by efficient drying. Then, it was found that the gas barrier characteristics of the films were enhanced by hybrid solution coating.

F1(I)

**DEVELOPMENT OF THE SC-RTA PROCESS FOR FABRICATION
OF SOL-GEL BASED SILICA-ON-SILICON INTEGRATED OPTIC
COMPONENTS**

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A method of fabricating silica-on-silicon integrated optical components from sol-gel glass has been developed, based on the repetitive use of spin-coating and rapid thermal annealing (SC-RTA) to deposit very thick ($> 30 \mu\text{m}$) films as multilayers. A variety of compositions can now be deposited, including silica, silica-titania, phosphosilicate glass, borosilicate and borophosphosilicate glass and germanophosphosilicate glass. Process temperatures have gradually been reduced as compositions have been optimised, and waveguide components fabricated by reactive ion etching, reflow and burial of channel guide cores have shown steadily decreasing loss. Propagation losses are now $\approx 0.1 \text{ dB/cm}$ at $1.523 \mu\text{m}$ wavelength in a high Δn system based on germanophosphosilicate glass, and a range of passive channel waveguide components has been demonstrated including tree-structured power splitters and interferometric thermo-optic switches.

STRIP-LOADED HIGH-CONFINEMENT WAVEGUIDES FOR PHOTONIC APPLICATIONS

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Sol-gel provides a potentially valuable alternative to other deposition techniques for the fabrication of silica-on-silicon photonic components. Buried channel waveguides have been demonstrated with excellent optical fibre compatibility and low propagation loss. However, such guides have not been successfully fabricated with silica-titania composition. Titania doping provides large index differences, and thus strong mode confinement, which is desirable for photonic devices, particularly optical amplifiers. However, titania-doped silica is resistant to reactive ion etching, and etched ridges cannot be reflowed without inducing crystallisation.

We have developed channel waveguides for passive and amplifying components, based on phosphosilicate strip loads over high index titania-doped guiding layers. Here we demonstrate that low propagation loss can be obtained in such guides at optical communication wavelengths, and consider the relevant loss mechanisms and how they are overcome, including OH impurity, crystallisation, inhomogeneity, substrate loss, and strip profile and surface quality. We also give results and prospects for component applications.

F3

**PHOTOCURABLE SOL-GEL COATINGS: CHANNEL WAVEGUIDES
FOR USE AT 1.55 μm**

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The focus of our research is to implement new strategies based on wet-process, low temperature sol-gel chemistry to deposit glass waveguides. This paper deals with the development and characterisation of channel waveguides which are the basic function of all integrated optic components.

We studied two structures. The first one is a one-layer structure, composed of a sol-gel solution which is a mixture of photopolymerisable organosilicate and organozirconate precursors. The other is a multilayer structure with a buffer under the guide and a protective coating. The layers are deposited by the dipping technique. The devices are obtained by UV-light exposure of the coating through a redefined mask (channel waveguides). The refractive index increase is sufficient enough to allow the use of waveguides in the 1.55 μm telecommunication window.

These waveguides are thick enough to reduce the coupling losses with an optical fibre below 0.5 dB. Also, because of our sandwich structure, the propagation losses are less than 0.1 dB.

STRUCTURAL AND OPTICAL PROPERTIES OF SOL-GEL DERIVED ALUMINOSILICATE PLANAR WAVEGUIDES DOPED WITH Er^{3+} IONS

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Er^{3+} doped aluminosilicate thin films were prepared on silica and silica/Si substrates by sol-gel process and dip-coating technique. The method followed to prepare sol-gel aluminosilicate planar waveguides is based on the use of silicon and aluminium alkoxides. The Er ion concentration was varied from 0.125 to 1-at%. These films were prepared at different annealing temperatures and their thickness and refractive index were measured. Their structural characterisation was carried out by Raman spectroscopy and the scanning electron microscopy. The optical properties were investigated by fluorescence spectroscopy in the visible and infrared region. Green and red upconversion fluorescences centred at 548 and 655 nm for, respectively, the $(^2\text{H}_{11/2} + ^4\text{S}_{3/2}) \rightarrow ^4\text{I}_{15/2}$ and $^2\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ have been observed. A broadband peak was observed at 1531 nm corresponding to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition with the full width at half-maximum (FWHM) of 47 nm comparable to those prepared by other methods. The fluorescence lifetime of the $^4\text{I}_{13/2}$ excited state was found to be constant and equal to 3.5 ms until a high Er-doping of 0.5 at%.

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FABRICATION AND CHARACTERISATION OF SOL-GEL $\text{GeO}_2\text{-SiO}_2$ ERBIUM-DOPED PLANAR WAVEGUIDES

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Erbium-doped optical waveguides are very interesting for applications in integrated lasers or amplifiers for telecommunications. $\text{GeO}_2\text{-SiO}_2$ sol-gel planar waveguides doped with Er^{3+} were deposited by spinning on silica substrate. Waveguide properties and fluorescence performances were tested. The effects of heat treatment on crystallisation and OH content were investigated. Heat treatments at higher temperature or in CCl_4 reduce the OH content, narrowing the fluorescence spectra. P_2O_5 or Al_2O_3 were used as co-dopants to improve erbium dissolution in the $\text{GeO}_2\text{-SiO}_2$ matrix. Their concentration affects the fluorescence and the Er dissolution. It was demonstrated that addition of Yb enhances the fluorescence efficiency. Er in the planar waveguide pumped at 980 nm, showed fluorescence around 1530 nm with lifetimes higher than 6 ms.

PERSISTENT SPECTRA HOLE BURNING OF SOL-GEL DERIVED Sm²⁺-DOPED GLASSES

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Sm²⁺-doped glasses in the system of Al₂O₃-SiO₂ were prepared by the sol-gel processing of metal alkoxides and the reaction with H₂ gas at 800°C, of which hole burning properties were investigated. Al₂O₃-SiO₂ glasses enable Sm to be doped in the Sm²⁺ state of which the 4f⁶ (⁷F₀) → 4f⁵5d band does not overlap with the ⁵D₀→⁷F₀ line. The fluorescence properties of Sm²⁺ ions incorporated in glasses were measured using steady-state and laser-induced line narrowing techniques and the effect of Al³⁺ ions to the local structure around the Sm²⁺ ion was investigated. The energies of the three Stark levels of the ⁵D₀→⁷F₁ transition were analysed using C_{2v} symmetry. The addition of Al³⁺ ions facilitates dispersion of the Sm²⁺ ions and increases the coordination number of the Sm²⁺ ion due to the long distance between the Sm²⁺ and O²⁻ ions, resulting in the increased fluorescence intensity. The fluorescence intensity of the Sm²⁺ ions considerably increases in glasses containing more than 5 mol% Al₂O₃.

The hole was burned in the ⁷F₀→⁵D₀ line of the Sm²⁺ ions using a DCM dye laser at 77K and the dependence of the burning efficiency on the laser power and burning time was measured. The hole depth increased with increasing the laser irradiation time, reaching up to ~ 30 % of the total intensity within a few hundred seconds. Neither an anti-hole around the burned hole nor a change in the fluorescence line narrowing spectrum were observed after hole burning. The hole depth linearly increased with increasing the incident laser power up to ~1 W/mm², indicating a single-photon process of hole burning. the dependence of hole area and width on the temperature was also investigated.

**INTERMOLECULAR ENERGY TRANSFER FROM COUMARIN-120
TO RARE EARTH IONS (Eu^{3+} , Tb^{3+}) IN SILICA XEROGELS**

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The photophysical processes of energy transfer among rare earth ions in oxide glasses and intramolecular energy transfer in rare earth chelates have been the subject of extensive research. The intermolecular energy transfer between rare earth ions and organics in solutions has also been widely investigated. However, it seems that few studies have been done on the energy transfer from organic molecules to rare earth ions in an inorganic transparent solid.

In this work, we co-doped with coumarin-120 (C120) and rare earth ions (Eu^{3+} , Tb^{3+}) in silica xerogels via sol-gel technique, and studied the energy transfer process between C120 and rare earth ions. The fluorescence intensities of europium and terbium ions can be increased by a factor of 35 and 8, respectively, because of being sensitised by the C120 absorption at 344 nm. The results show that no complex species between C120 and rare earth ions form in co-doped xerogels. The sensitised emission of rare earth ions is through intermolecularly resonant exchange interaction. Resonance energy transfer can occur over distances as great as 50 100Å. As a result of decreasing the energy transfer efficiency by C120 concentration quenching, the fluorescence intensities of Eu^{3+} and Tb^{3+} increase to maximum when the C120 doping concentration is of 0.1 mol % (mole percent referred to SiO_2).

SOL-GEL PREPARED GLASS FOR REFRACTIVE AND DIFFRACTIVE MICRO-OPTICAL ELEMENTS AND ARRAYS

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Volume reduction typical of sol-gel processes results in cracking, unless sufficient relaxation is allowed to take place. The shrinkage, typically by factors of 2.5 and higher, imposes great difficulty to obtain dimensional accuracy in thus prepared micro-optical elements.

The new fast sol-gel method enables facile preparation of siloxane-based glassy materials in which polymerisation is completed within minutes and volume changes upon curing are less than a few percent. These features and the resulting optical quality make this method technologically and economically attractive for micro-lenses and micro-optical arrays by replication.

Micro-optical elements and arrays are highly patterned. Two primary aspects of the replication process were studied: a. The sol-gel chemical constitution and reaction pathway that ensure prompt adhesion to the template until curing is completed. b. The chemical constitution of the template material, that allows for prompt replication and release of the produced elements.

The results of this study and the fabrication of refractive and diffractive micro-optical arrays are presented. Further, the characterisation of thus produced micro-optical arrays is described. Finally, various approaches to stress-release in accurate-replications in sol-gel matrices are discussed.

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PHOTOSTABILITY OF PYRROMETHENE-567 IN AMINOSIL HOSTS

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Pyrromethene-567 (PM-567) laser dye has been incorporated within Aminosils synthesised from 3-aminopropyltriethoxysilane (3AS) and tetramethoxysilane (TMOS) precursors to yield optically transparent monoliths and films. The addition of H₂O to a mixture of a basic (3AS) and an acidic (TMOS) alkoxide leads to rapid gel formation which is thermoreversible. This phenomenon is described as a function of the sol-gel processing parameters and host composition and related to the structural properties of the gel determined by Cross Polarisation (CP), Magic Angle Spinning (MAS) ²⁹Si NMR. The photostability of the samples were measured by monitoring the drop in the dye absorption upon irradiating the films with a UV lamp. The photostability of PM-567 was found to improve in basic environment and upon the addition of certain antioxidant additives. A PM-567 doped Aminosil film was synthesised as a planar waveguide, and guided fluorescence was demonstrated upon prism coupling laser light from an Argon laser at 488 nm.

AN OPTICAL SOL-GEL-BASED DISSOLVED OXYGEN SENSOR: PROGRESS TOWARDS A COMMERCIAL INSTRUMENT

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Sol-gel-derived films offer many advantages for optical sensor applications. In particular, the films are relatively easy to fabricate, offer considerable flexibility in processing and because of their porous nature, enable optically-active analyse-sensitive dyes to be immobilised in the film matrix while remaining accessible to the analyse. A dissolved oxygen (DO) sensor based on fluorescence quenching of the oxygen-sensitive ruthenium complex, $[\text{Ru(II)tris(4,7-diphenyl-1,10-phenanthroline)}]^{2+}$, which has been immobilised in a porous silica sol-gel-derived film, has recently been developed in this laboratory and has been reported in the literature. The further development of this sensor towards a commercial instrument is now reported here.

The films were fabricated using modified precursors of silica such as methyltrimethoxysilane (MTEOS) and ethyltriethoxysilane (ETEOS) and were dip-coated onto planar glass substrates. Quenching behaviour was characterised using a blue LED, photodiode and a flow cell through which water containing calibrated dissolved oxygen concentrations was flowed.

The sensor was optimised for commercial use and progress is reported under the following headings: (a) optimisation of sol-gel film parameters including the use of organically modified silica precursors, (b) incorporation of barrier layer, (c) minimisation of dye leaching and photobleaching, (d) long-term stability. In the course of this work, considerable enhancement of quenching response was achieved by tailoring the fabrication process of the organically modified films. Dye leaching was minimised by tailoring the sol-gel fabrication parameters to improve dye immobilisation and also by incorporating a polymeric barrier layer on the organically modified film. The sensor exhibits excellent repeatability and has limit of detection and resolution comparable with other recently developed optical DO sensors. This overall good performance has confirmed the suitability of dye-doped sol-gel films for both DO sensing and for other sensor applications. The use of high-brightness LEDs, combined with miniature photodiode detection systems, highlights the potential for low-cost, high performance, portable sensors for use in many applications.

F11(I)

OPTICAL NONLINEARITY OF THE HYBRID AND NANO-COMPOSITE MATERIALS PREPARED BY SOL-GEL

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Nonlinear optical effects, such as nonlinear optical absorption, second and third optical nonlinearities, can be applied for making optical limiters, optical modulators, as well as laser second and third harmonic generations. Nonlinear optical hybrid and nano-composite materials prepared by the sol-gel process are paid more attention in recent years. The research progress of these hybrid and nano-composite materials for nonlinear optical application are reviewed in this paper.

Research on doping an active organic phase into a inorganic host matrix to prepare these hybrid materials has been intensified in recent years. Our recent experimental results of dye-doped ormosils are reported. The organic dyes, such as phthalocycline, pyrylium, acridine, fluorescein, coumarin and malachite, et al, were doped in silica and TiO_2/MMA ormosil matrix by in-situ sol-gel synthesis. The condition of in-situ synthesis and molecular structure of in-situ complex were studied.

The preparation of nano-composite materials is a promising alternative to obtain new and competitive products for optical nonlinearity application. Semiconductor clusters, such as ZnS , CdS , PbS , Sb_2O_3 , Bi_2O_3 , as well as CuI and CuBr doped silica gels and glasses were prepared by the sol-gel process and in-situ growth technique. Nano-particles of SnO_2 , In_2O_3 and Bi_2O_3 were coated by stearic or sulphonic acid salts for surface modification. Hybrid materials connecting with fullerene were also derived by sol-gel. The quantum confined effect and dielectric confined effect of nano-composite materials were studied.

The third-order optical nonlinearity were determined with the Z-scan technique or from degenerate four-wave mixing (DFWM). The optical limiting properties and electric field induced second-order nonlinear optical effect of nano-composite materials were also investigated.

OPTIMISATION OF OPTICAL CHEMICAL SENSORS USING SOL-GEL DERIVED MATERIALS

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The use of sol-gel process to produce materials for use in optical chemical and biochemical sensors is attracting considerable research interest. This interest derives from a number of advantages of the process, chief among which is the design flexibility which enables tailoring of the physico-chemical properties of the final material. In most sensor applications the sol-gel process is used to produce microporous transparent oxides, such as silica or titania, in which analyte - sensitive reagents - are entrapped. The controlled porosity provides access for the target analytes to the reagents. Although many configurations have been demonstrated, the most attractive of these employ thin films which yield rapid response. Such films are usually interrogated by evanescent wave interactions on optical fibres or planar waveguides. A wide range of examples of sensors based on these principles is presented in this paper, together with strategies for optimisation of sensor performance. The strategies include adjustment of process conditions and selection of appropriate precursors, to yield stable materials with acceptable response times, minimal leaching and reduced interference.

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**A NEW SOL-GEL DERIVED OPTICAL FIBRE SENSOR FOR HIGH
ACIDITY MEASUREMENTS: APPLICATION IN NUCLEAR FUEL
REPROCESSING**

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Nuclear fuel reprocessing requires high acidity levels that must be accurately and fastly controlled in order to optimise extraction yields and process efficiency. To improve a remote and on-line monitoring, a new optical fibre sensor based on a sol-gel film doped with an acidic indicator has been developed.

The organic dye was physically incorporated in an acid-catalysed sol-gel silicate matrix and coated onto the core of a denuded 600 µm optical fibre. The absorption properties of the sensor were evaluated in several nitric acid media, ranging from 0,1 N to 10 N. When used in nuclear medium, the properties were modified but no change in efficiency of the sensor was occurred.

Performances of the sensor are reported with respect to dynamic acidity range, response time and reversibility. Study of interfering elements, such as uranium, plutonium and americium has been under consideration. The photochemical stability and the behaviour under irradiation have also been investigated.

MATRIX EFFECTS ON SELECTIVE CHEMICAL SENSING BY SOL-GEL ENTRAPPED COMPLEXING AGENTS

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Molecular recognition by complexing agents and selective receptors is a very active research area and provides many opportunities for the development of chemical sensors. This paper describes our recent results on the modifications of receptor selectivity arising from sol-gel entrapment of molecular recognition systems.

Thermodynamic effects of entrapment are exemplified by studies of the metal-ion complexing agent Eriochrome Cyanine R (ECR). In aqueous solution this binds strongly and selectively to Al^{3+} , whereas in a TMOS-based sol-gel matrix it is selective for Cu^{2+} . Experiments with sol-gel entrapped 3,5,7,2',7'-pentahydroxyflavone showed that it was able to form a fluorescent complex with Al^{3+} , so the change in selectivity of ECR could not be explained by complexation of Al^{3+} , so the change in selectivity of ECR could not be explained by complexation of Al^{3+} with surface OH groups of the sol-gel. Thermodynamic effects of complexation within small pores can, however, explain the observations. The restricted translational freedom of water molecules in small pores prevents development of the full entropy change when the ion hydration sphere is displaced by multidentate ligands. Enthalpy changes due to different solvent structure within pores, ligand conformational changes, and isolation of ligands within pores so that the normal complex stoichiometry cannot be obtained, all play an additional role. Effects of changes in receptor conformation on entrapment have been studied using a tris-terminated PAMAM dendrimer. The dendrimer conformation and complexation with Cu^{2+} changes on entrapment, and differences in binding of aromatic carboxylic acids such as Ibuprofen can be detected by changes in visible absorption and surface plasmon resonance using spun films of the sol-gel composite.

These effects show that in addition to providing a porous entrapment matrix of good optical quality, sol-gels provide a means of fine-tuning the experiments varying pore size and pore wall chemistry.

FABRICATION AND PROPERTIES OF DOPED POROUS POLYSILOXANE SOL-GEL LAYERS ON OPTICAL FIBRES

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Polysiloxane porous layers doped with ZrO-, TiO- and phenyl- groups have been fabricated by the sol-gel method with the aim of tailoring the thickness, refractive index, porosity of the layers and their sensitivity to gaseous or liquid chemicals. Starting sols were prepared from alkoxides under the acidic catalysis of HCl or HF which have also been studied as means for changing the layer porosity. Stable SiOTiO-sols have been obtained by using HF. Porous gel layers with thicknesses of from 0.3 to 1 μm were coated by a single or multiple dip-coating process on fibre surfaces, silicon wafers and silica rods.

Layers with the refractive index of from 1.38 to 1.7 have been prepared (measured on planar wafers and on silica rods). On the basis of these data the porosity of the layers was estimated to be from 10 to 40% depending on the type of the catalyst, water content and the concentration of the sol.

The interaction of the layers with gases, vapours and liquids has been studied in immersing experiments by measuring the output light intensity from the fibres in the wavelength range of from 400 to 1600 nm. The observed changes of the output intensity could be correlated to changes of the refractive index of the layer caused by the penetration of tested chemicals into pores and interaction with the material of the layers. An increased effect of aromatic hydrocarbons on the layers doped with phenyl- groups has been observed. The observed effects can be used for tailoring sensitive parts of evanescent-wave fibre optic sensors for the detection of gases and liquids.

G1(I)

**TECHNOLOGICAL DEVELOPMENT ON SOL-GEL COATING
MATERIALS IN THE LAST THREE DECADES**

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After short remembering you to some basics of Sol-Gel (Duran 50, Ceramics, UV-light guides) I will show you some car rear view mirrors and remembering you at the interest of Bayer AG in going into the field of substitution glass by polycarbonate.

After switching over to non reflective show window glass Amiran® I shall report about IROX® (Pd in titania) and for other Schott-products and in the last years Merck products (Iriodin®) which allows to use aqueous solutions. But this is only in the beginning following the route from Meerwein to the Sol-Gel of today.

CHARACTERISATION OF ELECTROCHROMIC WO₃ LAYERS PREPARED BY SOL GEL NANOTECHNOLOGY

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Stable tungsten oxide coating sols were prepared by a modified peroxotungstic acid route. Layers up to 250 nm thickness could be deposited on ITO-coated glass substrates in a single dip-coating process. The influence of various coating parameters such as the chamber humidity, curing temperature and the duration of heat treatment on the electrochromic properties (change in optical density, switching times) of the layers was investigated by optoelectrochemical measurements. High resolution transmission electron microscopy (H-TEM) has shown that the optimised layers possess a partially crystalline morphology with nanocrystalline regions 2–3 nm in size. The chemical diffusion coefficient as determined by electrochemical impedance spectroscopy (EIS) was found to lie between 10^{-11} and 10^{-12} cm² s⁻¹, which compares favourable with values reported for sputtered and thermally evaporated films.

Electrochromic cells were constructed in the following laminated arrangement: glass/ITO/WO₃/nanocomposite elect./CeO₂-TiO₂/ITO/glass. The CeO₂-TiO₂ ion storage layer was also prepared by a sol-gel route. The novel nanocomposite electrolyte system is based on organically modified silanes. This has a high ionic conductivity, $\sigma_{25^\circ\text{C}} = 10^{-4}$ – 10^{-5} S cm⁻¹ depending on composition, and also acts as a binder between the halves of the device. Reversible optical modulation (10^4 – 10^5 cycles) between 80% and 20% transmission was achieved. The switching times depend on the geometric area of the devices, whereby colouration times less than 5 minutes could be obtained for electrochromic devices up to 0.1 m² in area.

PREPARATION OF ELECTROCHROMIC COATINGS BY SOL-GEL TECHNOLOGY

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The manufacturing of electrochromic devices represents a technology with a broad perspective of commercially attractive applications, like smart windows, optical switching devices and rear-view mirrors. Nowadays, electrochromic devices are generally produced by PVD techniques. Electrochromic coatings have been prepared by sol gel technology, but usually on relatively small coating areas. In the same work of a Joule project TNO studied in collaboration with a large glass manufacturing company the feasibility of sol gel/dip coating technology as production technology for electrochromic coatings on large substrate areas.

In this paper we will report on the preparation of WO_3 and V_2O_5 coatings by sol gel technology. The electrochromic device (smart window) developed in this study consists of: glass/F:SnO₂/WO₃/electrolyte/V₂O₅/F: SnO₂/glass. Very homogeneous V_2O_5 and $\text{V}_2\text{O}_5\text{-TiO}_2$ coatings with good electrochromic properties (Charge capacities up to 45 mC/cm²) on large area sheets (up to 400 cm²) were prepared using VO(OⁱPr)₃/alcohol solutions. Homogeneous WO_3 coatings with reasonable electrochromic properties (coloration efficiency up to 34 cm²/C and transmission change up to 5:1) were prepared using W(OEt)₅ and W(OEt)₃Cl₂/alcohol solutions.

OS AND PD MODIFIED TIN OXIDE FILMS FOR SENSORS BY THE SOL GEL PROCESS

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Pd and Os modified SnO_2 films were prepared by the sol gel process and used as active materials in gas sensing devices. The films have been prepared starting from tin chloride in alcoholic solution hydrolysed with water, the modifier was added to the sol as inorganic salts: Pd acetate and Os chloride were the Pd and Os precursors respectively. A structural and morphological study was carried out by means of scanning electron microscopy (SEM), secondary ion mass spectrometer (SIMS), X-ray diffraction (XRD), to characterise the materials. The electrical conductivity variations as a function of various gaseous atmospheres and temperature were measured to evaluate the sensing properties of the films. Among the others CO , CH_4 , CH_3OH gases were used for the tests. Following results were obtained: Pd is present in the form of PdO nanocluster in the polycrystalline SnO_2 matrix as evidenced by XRD spectra whereas Os is a cationic modifier uniformly dispersed as evidenced in SIMS studies. Both modifiers enhance the low temperature sensing behaviour whereas the sensitivity variations, with respect to the undoped films, differ according to the gaseous species. It looks therefore promising to use inexpensive, all sol gel derived, array of films in smart gas sensing devices that are able to recognise gas species and concentration.

SOL-GEL DEPOSITED SB-DOPED TIN OXIDE FILMS

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Sol-gel derived antimony-doped tin oxide (ATO) films have been deposited on glass substrates by the spin-coating method. The structural, electrical and optical properties have been measured. The reproducibility of both the preparation and the characterisation procedures have been tested by a round-robin experiment within a CEA project. The above properties have been measured by different groups on samples prepared by the same chemical and deposition procedures in three different laboratories and on samples having an antimony concentration ranging from 2 mol % to 15 mol %. The comparison of the electrical properties evaluated from the optical behaviour and those derived from electrical measurements, together with structural characterisation allow the formulation of some hypothesis to explain the different performances obtained in sol-gel derived films with respect to films prepared by other methods.

SYNTHESIS AND OPTICAL PROPERTIES OF Mn-DOPED ZnS NANOPARTICLES IN SOLUTIONS AND COATINGS

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Nanosized semiconductor particles of Mn^{2+} doped ZnS have been synthesised in solutions and coatings. Their optical and structural properties have been characterised by means of UV/VIS-spectroscopy, fluorescence spectroscopy and high resolution transmission electron microscopy (HRTEM).

Mn doped ZnS nanoparticles from a precursor solution containing 0.01 M $\text{Zn}(\text{CH}_3\text{COO})_2$ were formed by precipitation with H_2S gas in the presence of hydroxypropyl cellulose (HPC) as stabiliser. Doping of Mn^{2+} ions into ZnS nanoparticles was realised *in situ* during the precipitation procedure. Thereby the Mn concentration has been varied from 1 mol% to 8 mol% with respect to the total concentration of metal ions. With a concentration of 0.01 M, all colloidal solutions were transparent and colourless. Coatings up to a thickness of 50 μm containing 0.4 vol% Mn doped ZnS nanoparticles were obtained on silica glasses by multiple dip-coating from the colloidal solutions.

The absorption spectrum of ZnS nanoparticle containing solutions exhibits an absorption peak at 273 nm, resulting from the excitonic transition of ZnS nanoparticles due to the quantum confinement effect. The absorption peak is broadened and has a blue shift of about 5 nm from 2 mol% to 8 mol% Mn concentration. The coatings still show the excitonic absorption shoulder, which is broadened with 4 nm in FWHM and red-shifted with 7 nm of the peak position compared to the solutions. Furthermore solutions and coatings exhibit a strong fluorescence at 595 nm when excited with UV light; showing that Mn^{2+} is incorporated into the ZnS-nanoparticles. The highest fluorescence intensity is obtained with a Mn concentration of 2 mol% respect to cations. HRTEM investigations show that the particles are crystalline and exhibit sizes of 3 ± 0.5 nm. Currently additional SAXS measurements are performed to determine the particle size distribution.

SURFACTANT-TEMPLATING OF SOL-GEL SILICA FILMS

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The practical use of surfactant-templated mesoporous materials for applications such as membranes, catalysts and sensors requires the formation of homogeneous supported films with uni-modal pore size and pore accessibility. We report the formation of a family of homogeneous mesostructured films exhibiting interfacial liquid crystalline order (hexagonal, cubic, lamellar (via a continuous, steady state dip coating process with timescale of several seconds. Our process begins with a homogeneous sol with initial surfactant concentration $c_0 \ll$ the critical micelle concentration cmc. We rely on surfactant enrichment by solvent evaporation to exceed cmc only within the depositing film allowing us to access a continuous range of silica/surfactant/solvent phase space. Whereas self assembly in bulk solution has resulted so far only in hexagonal mesophases, by varying c_0 (while maintaining $c_0 \ll$ cmc) we can continuously vary the final film structure, providing the first evidence for an interfacially-organised cubic phase. Optically transparent 100–500 nm thick films exhibiting unique microstructures and uni-modal pore sizes are formed in seconds in a continuous coating operation. An in situ optical probe technique, fluorescence depolarisation, is used to monitor the progressive evolution of structure (homogeneous $\rightarrow$ micellar $\rightarrow$ liquid crystalline) induced by surfactant enrichment during film deposition. Surface acoustic wave (SAW)-based N_2 -sorption is used to directly evaluate the pore size and pore accessibility of supported films.

PREPARATION OF THE TiO_2 THIN FILM PHOTOCATALYST BY THE DIP COATING PROCESS

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NO_x is a major air pollutant, is expected to be removed effectively by photocatalytic oxidation using titanium dioxide. Desorption control of the NO_x on the photocatalyst is one of the important factors for the development of the efficient photocatalytic environmental purification materials. The larger surface area of the thin film photocatalyst is expected to suppress desorption of NO_x from the photocatalyst.

The effect of polymer for doping was expected to increase surface area of the thin film catalyst, because the doped polymer is possible to leave the porous structure on the thin film after calcination. However, polymer doping effect into the thin films by the dip-coating method is not well understood. In this study, we examine how to influence the polymer doping process to the surface structure, and the photocatalytic ability of the thin films. Preparation of the TiO_2 thin film photocatalyst was carried out by the dip coating method using titanium alkoxide with a various size of polymer (polyethyleneglycol 300 to 1500).

The obtained thin films were either transparent or opaque depending on the molecular weight of the doped polymer, smaller size of polymer doped thin film was transparent. We had a very interesting observation on the transparent and opaque films by atomic force microscope as follows: the surface of the transparent thin films looked plain consisting of uniformly aggregated nanometer size TiO_2 single crystal, while the opaque thin films were formed with cubic system TiO_2 at micrometer level. This striking difference between two samples was explained by the presence of phase separation between titanium alkoxide and doped polymer.

With respect to the activity, that of the obtained film was more than the commercial photocatalyst P25. That is, elimination of NO in dry air (flow rate = 1.5 L/min, light intensity = 0.38 mW/cm^2 ($\lambda = 360 \text{ nm}$)) by the thin film photocatalyst was successfully carried out. From this result, NO_x is eliminated by these thin films without desorption. Photocatalytic ability of transparent and opaque thin films was almost to equal. The result of the surface area measurement, these two type films have similar surface area in spite of the different surface structure of two. The surface structure of the TiO_2 thin film is strongly depended on the doping of the polymer size, and these thin films have high photocatalytic ability for DeNO_x .

GLASS STRENGTHENING USING ORMOSIL POLYMERIC COATINGS

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Ormosil polymeric coatings comprised of an epoxy resin, an amine hardener and a silane have been applied to glass samples containing large, controlled defects introduced by Vickers indentation. The coatings can completely overcome the defects. The strengthening effect is due to penetration of the defects by the coatings and thus the reactions between the components of these hybrid materials and the glass substrate are of crucial importance in determining both the degree of strengthening that is achieved and the hydrolytic durability of the coatings.

Studies on silane primed systems clearly show that the effective amount of silane at the glass coating interface has a marked effect on both the mechanical properties and hydrolytic durability of the coatings. Although silanes are expected to improve the adhesion of coatings to glass, with silane primed coatings excess silane leads to poor mechanical properties and low hydrolytic durability, because the overall bonding of the coating to the glass is via an interlayer with poor cohesion even though this interlayer itself has good adhesion to the glass.

In the hybrid ormosil polymeric systems the silane reacts with both the epoxy resin and the glass surface. The maximum strengthening effect of these ormosil polymeric coatings is obtained when 25% of the active hydrogen was supplied by the silane. If more silane than this is present then a relatively loose network structure is formed and this more than counteracts any improved adhesion of the coating to the resin. Hydrolytic ageing of these coatings leads to further increases in strength because during ageing hydrolysis and condensation take place leading to a tighter network structure in the coating. Therefore the strengthening effect of an individual coating is controlled by both the adhesion of the coating to the glass and also by the cohesion within the coatings. With good adhesion and cohesion strength increases of up 235% are achievable with ormosil polymeric coatings.

G10

**CONTROLLED RELEASE ABRASION RESISTANT COATINGS
WITH PERMANENT WETTABILITY AND ANTIFOGGING
PROPERTIES FOR GLAZINGS**

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Objective of the investigations was the development of coatings on glazings with a good wettability and a permanent antifogging effect.

As a baseline inorganic-organic nanocomposites (Nanomers) functionalised with hydrophilic compounds were chosen.

The use of only hydroxyl- or aminocontaining compounds incorporated into the matrix results in high-surface energies ($> 65 \text{ mN/m}$) and led to materials with hydrophilic properties (contact angles against water $< 30^\circ$).

To obtain lower contact angles combined with long term hydrophilicity, non ionic surfactants have been chemically modified in two ways. The first modification led to molecules to be anchored to the backbone and the second to molecules compatible to the inorganic organic matrix but not being anchored to the backbone. The combination of this matrix modification led to hydrophilic coating systems showing a high abrasion resistance (ΔH 8–10 % after 1000 cycles Taber-Abraser test) as well as permanent hydrophilic properties (contact angles $< 30^\circ$).

The characterisation was carried out by ^{13}C -NMR-, ^{29}Si -NMR-spectroscopy and IR-spectroscopy. The release behaviour of the surfactants was investigated by GC-MS, ionselective titration as well as gel permeation chromatography (GPC).

It was found that only the non-anchored surfactants could be extracted.

SOL-GEL PREPARATION OF NOBLE METAL COLLOIDS- CONTAINING OXIDES

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Coating films containing fine metal particles are attracting a considerable attention for the colouring, light-reflecting and nonlinear optical properties. In this review paper, we present our works on sol-gel preparation of silica and/or titania coating films containing Au, Ag, Pd or Pt metal colloidal particles. The effects of the preparation condition on the size of metal particles precipitated in the films will be described. Also, the shift of the absorption peak due to the change of the kind of the matrix oxide will be discussed in some detail on the basis of the theory of plasmon resonance.

It is shown that metallic Au particles are precipitated at about 200°C in both amorphous silica and crystalline titania matrices, whereas heating up to 600°C is needed for precipitation of metallic Ag particles. On the other hand, no direct formation of metallic particles are found for palladium and platinum. Palladium oxide and platinum oxide particles are precipitated in titania matrix at about 800°C and reduction of these oxide particles as a result of heating in hydrogen-argon gas at 500°C leads to the formation of Pd and Pt colloidal metal particles.

OPTICAL VISCOMETRY OF SPINNING SOL COATINGS

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As sol-gel coatings, due to their wide flexibility in composition and microstructure, have increasingly shown applications in opto and microelectronics, their viscosity at formation stages still remains a key parameter for process control and reproducibility.

For spin coating in open air, optical interferometric monitoring has allowed us to distinguish four main stages of evolution: (I) pre-spinning oscillations in the sol, (II) ultrafast convective mass flow, (III) convection-evaporation, and (IV) limited evaporation. These two last stages are greatly simplified when spin coating is performed in a saturated solvent atmosphere, which reduces the role of evaporation to negligible values, and therefore allows analytical modelling of the process.

Experimentally, analysis is made of a laser beam reflected from the film on a silicon wafer or glass substrate, at speeds in the range of 700–3000 rpm, with 100 Hz data acquisition. The resulting kinematic viscosities for sols based on tetraethylorthosilicate to produce silica films, with varying pH, ageing period and dilution in ethanol, are in the range of 20 to 60 cS.

Validity of the method was tested with a standard (mineral oil OP20) with nominal kinematic viscosity $\nu=37\pm1$ cS (temperature fluctuation of $\pm0.5^\circ\text{C}$), for which the above 'optospinography' method, combined with Abbe refractometry, provided $\nu=36.1\pm0.1$ cS (angular speed uncertainty of ±5 rpm). While further tests are needed to determine its limitations, this is an indication that we might now have available a contactless optical viscometry method for thin (thickness less than 10 μm) sol, or other, liquid films.

POROUS SILICA FILMS AS EFFECTIVE ANTIREFLECTIVE MEDIUM

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Various concepts exist to suppress reflection on glass. However, most of them successfully reduce reflection only in the visible range. Furthermore, they require a large technical expenditure (e.g. the manufacture of interference layers) and are therefore expensive. Both the narrow waveband in which the anti-reflection is effective and the high cost limit the fields of application.

A single layer on glass which may be cost-efficiently manufactured by dip-coating can lead to a very good broadband anti-reflectance at the glass-air boundary if its refractive index is adjusted to the substrate. In our work the required low refractive index was achieved by using a porous thin silica film on the glass surface.

Coating solutions are essentially water based and contain nanosized silica particles prepared by the sol-gel method and a soluble organic polymer. The solutions have a shelf life time of more than one month. Float glass substrates of $30 \times 30 \text{ cm}^2$ size have been dip-coated with this solution. The resulting films have a refractive index of 1.22 and thicknesses of 110–150 nm after a short treatment of the coated glass at temperatures of 500°C. On glass with low Fe content a transmission of 99.6% in the visual range and a transmission of 97.0% in the solar range have been achieved. The porous inorganic silica films show a satisfactory abrasion resistance and an excellent stability against environmental influences.

G14

**AERIAL OXIDATION OF TETRAETHYL SILICATE AND EFFECT
ON AMMONIA CATALYSED HYDROLYSIS**

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Colloidal suspensions of SiO_2 ethanol prepared by the ammonia catalysed hydrolysis of tetraethyl silicate (TEOS) in ethanol (Stober process) have been routinely used for over 10 years to prepare antireflective coatings on the fused silica optical components of high power fusion lasers. Very high purity coatings are required to avoid laser damage and the TEOS is fractionally distilled under nitrogen prior to use.

Recently we have found that the impurities caused by aerial oxidation of distilled TEOS have a significant effect on the particle size of our coating suspensions to the detriment of the optical performance. We require particle size to be in the range 20–30 nm to avoid light loss due to scatter in the coatings and contaminated TEOS has given suspensions with particle sized much higher. Oxidation products include acetaldehyde and acetic acid and these are readily formed in nominally pure TEOS stored in sealed containers with a large air space or imperfectly sealed containers which allow air access over time.

It is likely that these impurities cause premature nucleation sites and consequently larger particles.

FERROELECTRIC PZT THIN FILMS BY SOL GEL DEPOSITION

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Recent advances in deposition techniques have led to great interest in the potential integration of ferroelectric thin films into Si-based technology. Integrated ferroelectric thin films can be utilised in many ways, e.g. memories make use of their switching characteristics under applied field to record binary information, the pyroelectric effect is employed to make infrared sensors and the piezoelectric effect is used to fabricate pressure sensors and micro-pumps and motors. Sol-gel spin coating has a low 'thermal budget' (ideal for integration), relatively low development costs compared to vacuum-based techniques and is now routinely used to produce dense, pore-free films. The solid solution, $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$ (PZT) is utilised in most applications because it has a large remanent polarisation, high piezo- and pyroelectric coefficients and optimised electromechanical coupling factors, depending on precise composition.

This paper will review some of the principles and applications of PZT films and highlight using transmission electron microscopy some of the basic problems and solutions involved in producing device-quality material on Si-substrates.

H2

DEVELOPMENTS IN SOL-GEL ROUTES FOR THE FABRICATION OF FERROELECTRIC THIN FILMS

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Results are presented showing the sequence of experimental steps in the development of a sol-gel route for the production of $\geq 1\mu\text{m}$ thick films of lead zirconate titanate deposited on platinised silicon substrates. The films, of composition $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$, were prepared from the solutions formed from $\text{Pb}(\text{OOCCH}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ti}(\text{OC}_3\text{H}_7)_2(\text{CH}_3\text{COCHCOCH}_3)_2$, $\text{Zr}(\text{OC}_3\text{H}_7)_2(\text{CH}_3\text{COCHCOCH}_3)_2$ and various polyfunctional alcohols. Solution NMR and crystallisation data are presented for the precursor systems. Information on molecular structures is related to film properties.

PREPARATION OF A THICK CERAMIC FILM BY AN INTERFACIAL POLYMERISATION

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The formation of a ceramic film of 20-100 micrometer in thickness via an interfacial polymerisation of metal-organic precursors has been studied. Titanium butoxide or a commercially available precursor solution for PZT was mixed with an equal amount of hexane under stirring. A 5 ml of the solution was poured on water contained in a teflon reaction container of 88 mm inside diameter. Inside the container, an exchangeable ring of 76 mm inside diameter was placed to keep the container wall unattacked with an organic solvent. The reaction of the metal organic precursor at the interface between the two immiscible phases, i.e., organic phase consisting of metal organic precursor diluted with hexane and inorganic phase of water, began in a few minutes to form a translucent gel film at the interface. The gel film began to shrink in 20-30 minutes as the coagulation and the polycondensation of the colloids advanced. A careful separation of the gel film from the wall of exchangeable ring was necessary to allow further shrinkage with the evaporation of hexane to a size less than the half of the original diameter. The gel film thus prepared was gently placed on a silicon wafer which had been placed near the bottom of the reaction container in advance, followed by drying in an oven.

H4

PREPARATION OF LEAD ZIRCONATE-TITANATE FILMS BY A WATER BASED CHEMICAL DEPOSITION METHOD

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Precursor powders for $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) thin films have been produced by the reaction of zirconium- and titanium-n-propoxides with acetylacetone and lead acetate trihydrate. The subsequent complete removal of volatile components yielded powders that can be handled in air and are stable indefinitely under ambient conditions.

High molarity ($> 2\text{M}$) coating sols are prepared by dissolution of the precursor powders in mixtures of triethanolamine (TEA) and water. Over-stoichiometric amounts of lead for the compensation of lead loss during firing and dopants are easily introduced into these solutions.

Solutions containing equal-mass fractions of TEA and water lead to homogeneous ceramic films of $1.6\text{ }\mu\text{m}$ thickness after one spin coating and firing at 600°C for 5 minutes on steel substrates. The surface of the films is dense, but considerable porosity was detected in the interior. A dielectric permittivity ϵ_r of about 300 was measured at 1 kHz. Large signal dielectric measurements were carried out at 50 Hz. For a sinusoidal field amplitude of $60\text{ V}/\mu\text{m}$ a remanent polarisation of about $20\text{ }\mu\text{C}/\text{cm}^2$ and a coercivity of about $12\text{ V}/\mu\text{m}$ was obtained. The films are stable against dielectric break-down up to $80\text{ V}/\mu\text{m}$.

ACETIC ACID BASED SOL-GEL PLZT THIN FILMS: PROCESSING AND CHARACTERISATION

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Ferroelectric materials in thin film form such as PZT ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) have been extensively studied due to their possible microelectronic and micromechanical applications. The functional properties of La doped PZT solid solutions (PLZT) greatly depend on the stoichiometry, ranging from ferroelectric, antiferroelectric or relaxor-type response, offering therefore a wide range of possible applications.

PLZT x/65/35 ($x = 4, 8, 10\%$ La) thin films were prepared by acetic acid based processing with lanthanum acetate or nitrate as lanthanum sources with formamide as DCCA. PbO rich PLZT sols were prepared for top layers. The sols were spin-coated on various substrates ($\text{Pt/Ti/SiO}_2/\text{Si}$, $\text{TiO}_2/\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$, $\text{PbTiO}_3/\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$) and rapid thermally annealed. Thermogravimetric analysis, X-ray diffraction, scanning and transmission electron microscopy as well as ferroelectric properties measurements of selected samples were performed in order to characterise the thin films in view of La content, stoichiometry and substrate effect.

According to XRD perovskite phase is obtained for all La contents at 650°C , 5 min. PLZT thin films on Pt/Ti coated substrates exhibit random orientation when prepared from La-acetate and preferred (111) orientation when prepared from La-nitrate. The La-source effect on orientation is found on other substrates too and is correlated to different thermal decomposition paths of these films.

Ferroelectric response of PLZT thin films with 4, 8 and 10% La (on Pt/Ti coated substrates) decreases with increasing La content, in agreement with reported data.

H6

SOL-GEL PROCESSING OF MESOPOROUS TiO₂ ELECTRODES FOR PHOTOVOLTAIC APPLICATIONS

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During the past five years, we have developed in our laboratory a new type of solar cell based on a photo-electrochemical process. In opposition to conventional solar cells the light adsorption and charge separation steps are differentiated. The light absorption is performed by a monolayer of dye (i.e. a Ruthenium complex) adsorbed chemically at the surface of the semiconductor (i.e. TiO₂). Upon excitation by a photon the dye is able to transfer an electron to the semiconductor. The electric field inside the material allows extraction of the electron and the positive charge is transferred from the dye to a redox mediator present in solution. The simplicity of the cell design as well as its respectable efficiency (i.e. 10%) promise significant cost reduction of solar cells.

This respectable photovoltaic efficiency is obtained by the use of porous, nanostructured films. The TiO₂ electrode microstructure, thus the film synthesis, influences the photovoltaic response of the cell. More precisely some relationships can be established between the particle size, the surface area, pore size distribution and the current delivered by the solar cell. To carefully control the microstructure we devised two new synthesis routes involving amphiphilic molecules. In the first one, monodisperse particles synthesised from modified titanium alkoxides are mixed with alkyl ammonium salts. After a mild hydrothermal treatment, micron-size particles with high surface area and narrow pore size distribution are obtained. In the second route, the titanium alkoxides are reacted with long chain acetylacetonates. Hydrolysis of this solution leads to self assembly of the mineralised micelles and production of tailored nanoscale materials.

COMPARISON OF HIGHLY ORIENTED BIT ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) THIN FILMS PREPARED FROM SOL-GEL PROCESS AND CVD METHOD

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BIT has a Curie temperature of 675°C, allowing poled polycrystals to maintain a remanent polarisation state up to at 400°C. Bismuth titanate BIT is a ferroelectric oxide with a layered structure with exhibits the polarisation-electric field (P-E) switching behaviour necessary for memory application in bulk ceramic form. The spontaneous polarisation vector of BIT lies in the b-c plane at an angle of 4.5 to the b-axis. As a result, two independently reversible components are observed, one with a remanent polarisation of 50 $\mu\text{C}/\text{cm}^2$ along the b-axis, and one with 4 $\mu\text{C}/\text{cm}^2$ along the c-axis. In the present study, an attempt is made to prepare a highly c-axis oriented thin film with the composition of BIT. The thin film was a single phase of BIT completely oriented along the c-axis on Pt substrate with good ferroelectric properties at room temperature: coercive field of 25kV/cm, remanent polarisation of 2.5 $\mu\text{C}/\text{cm}^2$, dielectric constant of 130. On the other hand, thin films by MOCVD method were prepared to completely c-axis oriented BIT thin film and showed good ferroelectric properties: remanent polarisation of 1.0 $\mu\text{C}/\text{cm}^2$, coercive field of 18kV/cm. But CVD method contained a very complicating treatment on raw materials and procedure.

STRUCTURE DESIGN OF DOUBLE-PORE SILICA AND ITS APPLICATION TO HPLC

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Pure silica gel monoliths with micrometer range interconnected pores can be prepared by hydrolysing alkoxysilane in the presence of a certain kind of water soluble organic polymer which induces a phase separation during the polycondensation and gel formation reactions. The mesopore structure of gels thus obtained can be modified by ageing them under the conditions where dissolution-reprecipitation of silica is enhanced. After appropriate solvent removal and heat-treatment processes, gels having fully open pores in discrete size ranges, i.e. those of micrometer and nanometer, are obtained.

As the first example of a practical application of the double pore silica, a new type of silica gel column for liquid chromatography (LC) has been developed. After preparing a rod-shaped gel monolith which has 2 μm of interconnected through-pores and mesopores being distributed around 10 nm via the process described above, the side wall of the rod was clad with a resin, then equipped in a LC apparatus. The reversed phase column was prepared by octadecyl silylation and methyl silylation.

Rod columns with up to 80% total pore volume have been obtained, and they required only 1/2 to 1/3 of applied pressure compared with conventional ones. The dependence of plate height on linear flow velocity for the rod column was several times weaker than that for the conventional columns, and the calculated separation impedance for amylbenzene was an order lower than that of the best commercially available columns. These indicate that in the rod columns the thin continuous gel skeletons associated with the high pore volume serve as a highly efficient stationary phase for high-speed separation.

NET-SHAPE MANUFACTURE OF LOW-COST CERAMIC SHAPES BY FREEZE-GELATION

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The sol-gel process is capable of producing a wide range of engineering ceramic materials very economically. It is a flexible process that may be carried out at low temperatures, able to take advantage of the use of liquids of controlled, low viscosity for wet processing to near-final shape. The initial forming stage may be followed by consolidation at relatively modest commercial heat treatment temperatures, but in many cases even this is unnecessary since the green strengths of sol-gel products can be very high. The disadvantage of the process is the inherently large shrinkage of typical gels, usually 20-25 vol%, but reducing to ~5% is appropriate proportions of fillers are used. The use of freeze-gelation overcomes many of the familiar limitations of sol-gel processing and permits the formation of low-cost, crack free, essentially zero-shrinkage ceramic bodies of complex shape.

Industrial applications involving the manufacture of complex shapes by the freeze-gelation (or freeze casting) process, investigated at the University of Bath, are discussed. This paper presents the results of a wide ranging investigation into the effects of materials and processing parameters on the performance, properties and microstructures of the ceramics produced. In particular the effects of, the type and composition of sol, use of different refractory fillers, thermal characteristics of mould materials, and variable freezing conditions, have been investigated.

MICROLENSSES FABRICATION BY INK-JET PROCESS

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Ink-jet processes are today commonly used for printing paper, plastic, glass and metal. A commercial drop-on-demand printing system using a 50 μm diameter nozzle driven by a piezo electric device has been adapted for the fabrication of plano-convex refractive microlenses array on glass substrate. Hybrid organic-inorganic sols have been used. They have been prepared by hydrolysis of methacryloxypropyltrimethoxysilane (MPTS) mixed in an ethanolic solution of tetraethyleneglycoldimetacrylate (TEGDMA) and a UV photostarter. After deposition the drops have been polymerised by UV light irradiation. Viscosity, solvent evaporation, drop-substrates, wetting condition, drop and substrate temperature are the main parameters which govern the obtention of a reproducible shape of the microlenses. The shape and surface roughness of the lenses have been characterised by atomic force microscopy and profilometer. Their optical properties (focusing length, transparency) have been determined by light microscopy and spectrometric technique respectively. Typical diameters of the lenses are 50 to 150 μm to 1 mm.

Application can be foreseen for collimation or focusing (detector arrays, fibre optics, sensors) for illumination (flat panel displays, TV projection) imaging (photocopier, optical fibre coupling, lithography) etc.

INDUSTRIAL APPLICATION OF HYBRID SOL-GEL COATINGS FOR THE DECORATION OF CRYSTAL GLASSWARE

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The colouration of glass via melting techniques presents some unique problems with respect to the availability, reproducibility and toxicology of different colours, especially if the market demands are highly variable. This is also the case for crystal glass and tableware as consumer products. Traditionally, the decoration of crystal glasses is performed by laborious manual techniques, which are costly and do not meet modern market requirements. Alternatively, spraying of coloured lacquers is a highly flexible and valuable tool for the development of new products.

Sol-gel type hybrid coatings provide several advantages compared to conventional organic systems like high abrasion resistance, almost perfect adhesion, refractive index matching and high stability in dishwashing procedures. The solubility of organic dyes in the hybrid matrix is sufficient for intense colours even at rather low layer thicknesses, which on the other hand convey the high brilliance of the base material.

The development of transparent, translucent and opaque hybrid coatings for crystal glass has been completed in the last few years and the production of partially coated articles has started recently. The synthesis of the coating material and its structural elucidation via spectroscopic means and the application oriented properties of the cured coating are reviewed and discussed. The industrial process and the first market results will be outlined.

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SINTERING OF AEROGELS

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There have been numerous studies of the sintering of aerogels, many of which have yielded surprising results. For example, some have reported densification without change in pore size, and others claim that large pores contract before small ones, in contradiction to the prediction of the theory of viscous sintering; at the same time, several studies have yielded results that are completely consistent with theory. We review the previous work and show that the unusual results follow from misinterpretations or inappropriate methods of characterisation. The theory of viscous sintering of a body with a distribution of pore sizes will be reviewed and tested using new data for sintering of a silica aerogel. We find that the theory correctly predicts the changes in surface area, as well as the kinetics of densification. A key element in correct application of the theory is accurate characterisation of the initial pore structure. We have developed a novel method for interpreting adsorption/desorption isotherms for aerogels that provides an accurate pore size distribution.

LARGE SILICA OVERCLADDING TUBES FOR OPTICAL FIBRE PREFORMS VIA A SOL-GEL PROCESS

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We have developed a process to fabricate large (4500g), precision, monolithic tubes of optical quality silica via a sol-gel process. These are critical components for the hybrid rod-in-tube process of making fibre preforms. These tubes presently constitute about 90% of the fibre's mass.

The starting sols are comprised of 50 m²/gram fumed silica dispersed in a solution of water, an organic base and other additives. The addition of an ester, which undergoes base-catalysed hydrolysis, lowers the pH, collapses the double layer and initiates gelation. Precision molds and alignment procedures result in net-shape tubes that require no further etching nor grinding to meet demanding dimensional specifications. The relatively highly loaded sol (46 wt.% silica) reduces shrinkage and eliminates cracking during drying. The relatively large size of the silica particles, 50 nm average diameter, produces a percolated pore structure that facilitates drying and purification. Subsequent to drying, the tubes are heat treated to remove excess water and residual organic materials. Following this, the refractory oxide particles and transition metal ions are chemically removed. The tubes are then sintered to transparent, bubble-free silica in a helium atmosphere.

A three pronged approach of clean room processing, centrifugation and chemical treatment has reduced tube-induced fibre breaks, resulting from included particles, to less than one per fibre megameter at 100 kpsi proof-test. The spectral loss measurements at 1310 nm are routinely below 0.35 dB/km and vary in response to minor changes in formulation, purification, and sintering conditions. The sol gel based tubes produce optical fibre meeting current commercial standards.

INFLUENCE OF COLLOIDAL SILICA PARTICLES ON THE DENSIFICATION BEHAVIOUR OF METHYL-MODIFIED SILICON-ALKOXIDE MATRICES

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To realise crackfree coating thicknesses $>1\text{ }\mu\text{m}$ with sol-gel SiO_2 -systems several requirements have to be fulfilled. First, the coating solution must have a high solid content to reduce shrinkage during the coating drying step and second the coating material must be able to relax the stresses which are developed during the sintering step.

It was found, that colloidal silica particles are able to increase the critical thickness of a methyl-modified silicon-alkoxide single step coating up to $16\text{ }\mu\text{m}$ after 500°C firing.

It was shown by photon correlation spectroscopy, NMR and viscosity-measurements, that colloidal silica particles of about 10 nm size together with TEOS and methyltri(m)ethoxysilane react to well defined $30\text{-}50\text{ nm}$ particles, whereas in the absence of colloidal silica polymer type of structures are built up, which entangle during the coating step, leading to much lower green densities compared to the compositions with colloidal silica.

The densification behaviour of such coatings was investigated by means of BET, NMR, DTA/TG and IR measurements. They indicate, that the thermal decomposition of the methylgroups is significantly shifted by almost 100 K to higher temperatures. This leads to a better stress relaxation behaviour of such coatings, which was proven by microhardness measurements.

These results have been used to develop coatings for waveguides and flame retardation.

SILICON OXYCARBIDE GLASSES DERIVED FROM POLYMER PRECURSORS

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Silicon oxycarbide glasses on ceramics are readily derived from the pyrolysis of organosilicon preceramic polymers. The composition of silicon oxycarbide (SiOC) ceramics play a large role on the microstructure and therefore the properties and ultimately the utility of the ceramic or glass. For example SiOCs with relatively low levels of carbon display inherently good stabilities in air at elevated temperatures. This attribute has allowed for the use of these ceramics as structural materials: ceramic fibre and matrices for ceramic matrix composites. While SiOCs with relatively high carbon contents have shown utility as intercalation matrices for elements such as lithium. This property has allowed for the use of these materials as anodes for rechargeable lithium ion batteries.

The compositions of silicon oxycarbide ceramics can be controlled by tailoring the chemistry and the pyrolysis conditions of the polymeric organosilicon precursor. Over the past 8 years our labs and others have studied the relationship between preceramic polymer structure and SiOC ceramic composition. Combined, this work has led to a qualitative understanding of the relationship between polymer structure and SiOC composition. In this paper we will describe our results from modelling the relationship between polymer structure and SiOC composition and show the importance of this relationship with respect to the applications described above.

CRYSTALLISATION OF GELS IN THE APATITE - MULLITE SYSTEM

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The crystallisation processes of gels in the apatite - mullite system have been studied in order to obtain the information necessary for the synthesis of bioglass-ceramics and composite materials.

For sol-gel synthesis as precursors have been used SiO_2 -sol, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and CaF_2 (added before and after gelling). The composites are prepared by mixing of mullite gel-glass and fluorapatite (from 10 to 90 mol %). The obtained samples are heat treated from 950°C to 1250°C and the structural changes are investigated using X-ray diffraction analysis, IR-spectroscopy, TEM and TEMD.

The main crystalline phases are fluorapatite and mullite when the gels are treated at 1050°C and 1150°C, independently of the CaF_2 content and the way of its addition. At higher temperature (1250°C) the intensity of the fluorapatite and mullite diffraction peaks decreases and some diffraction maxima of gehlenite appear. From the electron micrographs of the gels and their corresponding electron diffraction patterns the formation of crystals, which are dispersed in an amorphous matrix, starts at 950°C. The sizes of the crystals vary from 0.05 μm to 1 μm . It is found that the composite materials containing fluorapatite and mullite as main crystalline phases can be obtained only when the content of mullite gel-glass in initial mixture is more than 60 mol %.

From the results of X-ray diffraction analysis and IR-spectroscopy it is established that three main composite glass-ceramics can be synthesised depending on the chemical composition and the heat treatment of the studied samples:- with only one crystalline phase-fluorapatite and amorphous phase of mullite composition;- with two or three crystalline phases-fluorapatite, gehlenite, anorthite or mullite;- with only silicate crystalline phases. In this case P_2O_5 remains in amorphous state.

PRODUCTION OF TITANATE MICROSPHERES BY SOL-GEL AND SPRAY-DRYING

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Multi-component titania/zirconia sols have been prepared on a 60 kg scale by hydrolysis of an alkoxide and subsequent peptisation with acidic zirconia sol. After incorporation of Ca, Ba and Al, the resulting sols were spray-dried to produce micro-spheres (20–60 micron) with controlled porosity and morphology.

The properties of the spray-dried powder were very dependent upon the chemistry of the precursor sol. In particular, hollow spheres were produced from well dispersed sols, whereas solid spheres could be produced from partially-aggregated sols. The multi component sols were characterised by density, viscosity, pH and conductivity measurements.

The powders produced by spray drying were characterised by scanning electron micrographs, porosity, surface area and particle size measurements. The microspherical particles were readily impregnated with 20 wt % simulated high-level nuclear waste solution. They were then calcined at 1023 K and subsequently hot-pressed to produce dense Synroc.

The paper discusses preparation of the micro-spherical precursor particles by spray-drying, their physical properties and the influence of sol aggregation and drying rate on their morphology.

K2

HIGH DENSITY CERAMIC MILLING BALLS PRODUCED BY A SOL-GEL PROCESS

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Trends in ceramic milling ball development have recently been moving toward increasingly high quality and an ultra spherical shape.

The object of the recent development was to find a method for producing ceramic grinding media with very high density, a uniform spherical geometry and a narrow grain size distribution.

Materials chosen were the oxides of Aluminium, Zirconium, and Hafnium. The theoretical densities of the oxides are increasing from Al_2O_3 ($\alpha\text{-Al}_2\text{O}_3$: 3.9 g/cm^3) via ZrO_2 (cubic: 5.6 g/cm^3) to HfO_2 (cubic: 9.68 g/cm^3).

Aqueous solutions or sols of Hf, Zr or Al preneutralised with ammonia are the precursors to get high density microspheres. The liquid is gently pumped through a vibrating nozzle system where upon exiting the fluid stream breaks up into uniform droplets. The surface tension of these droplets moulds them into perfect spheres in which gelation is induced during a short period of free fall. Solidification is induced in a ammonia gaseous and liquid medium through chemical reaction. Amplitude and frequency of the nozzle oscillation or the liquid oscillation are held constant to attain a monodisperse grain size distribution.

The as moulded microspheres are treated by subsequent washing, drying, calcimining, and sintering. Sintering in an hydrogen atmosphere at 1700°C or in air at 1500°C leads to microspheres of very high density (95 % to 98 % of theoretical density) without any cracking. ZrO_2 and HfO_2 were stabilised by addition of B_2O_3 . The microspheres attain diameters from 3 mm down to $50 \mu\text{m}$. Unusually effective and abrasion resistant microspheres for grinding other materials were made from sintered HfO_2 , ZrO_2 , Al_2O_3 , and mixed oxides as $(\text{Hf}, \text{Zr})\text{O}_2$.

WOOD/SiO₂ COMPOSITE PREPARED BY SOL-GEL PROCESSING

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Synthesis properties and micromechanism of a novel organic/inorganic composite, Ceramic-Wood, were discoursed. The procedure involved the impregnation of alkoxysilanes precursor into wood and the sol-gel process of the precursor to form silica gel within wood cell walls. The changes of properties (including dimensional stability, heat stability and physical mechanics) and micro-structure have been investigated after wood was turned into ceramic-wood nanocomposites.

SECTION 2

**POSTER
PRESENTATIONS**

¹⁷O-NMR OF A TWO-STEP SOL-GEL PROCESS OF TEOS

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²⁹Si-NMR is a very powerful tool to monitor the hydrolysis and condensation reaction of a two step sol-gel process of TEOS. However, not many analytical techniques are suitable to follow the water consumption and formation. Water is one of the major reaction components in the sol-gel process. By using ¹⁷O-NMR it is possible to determine this component quantitatively as a function of reaction time. For this analysis a hydrolysing TEOS mixture is used. The water concentration is followed for TEOS, ethanol, and water mixtures starting with a, for hydrolysis, substoichiometric water amount. The effect of several process parameters on the residual amount of water is investigated.

It is found that this residual water concentration is dominated by the reaction volume in which the hydrolysis is performed.

AP2

NMR MONITORING OF THE AGGREGATES GROWTH DURING SOL-GEL POLYMERISATION

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We report on a new method of *in vivo* monitoring of growth of aggregates during sol-gel polymerisation based on spin-echo NMR spectroscopy. The idea is that the Brownian rotational diffusion of the aggregates becomes slower with growth of their size in the course of polymerisation. The correlation time τ of the diffusion can be directly determined from the nuclear spin-echo measurements of the transversal relaxation time T_2 . Experimental τ as a function of time allows to determine a size of the aggregates as a function of the polymerisation reaction time. For the case of sphere-like aggregates this is done using Stokes formula $\tau = \eta V/kT$, where η is the solvent's viscosity, V is the volume of an aggregate, k is the Boltzmann constant and T is the temperature.

We tested this approach for two model systems of the stable colloidal silica LUDOX consisted of monosized spheres with diameters of 7 and 11 nm. We found the diameters determined from spin-echo of ^{29}Si in Q^3 species to be close to these values. The next system studied was TEOS polycondensation under acid conditions with the growth of fractal-like silica aggregates. The same system was studied by small angle X-ray scattering to measure the time evolution of the gyration radius and to compare it with NMR results on the aggregates size. We also started studies of more complicated system with amino-epoxy-silane precursor. An evident advantage of NMR method in comparison with small angle scattering and chromatography standard methods is that in the same experiment we acquire both information on the chemical kinetics and growth of aggregates.

NMR STUDIES ON HYDROLYSIS AND CONDENSATION REACTIONS OF MODIFIED ALKOXIDES CONTAINING Si-H GROUPS

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Hybrid silica xerogels containing Si-H and Si-CH₃ groups have been prepared as precursors for silicon oxycarbide glasses. Such glasses exhibit improved physical and mechanical properties compared to silica glasses and are excellent candidates for high temperature materials. We have found that the introduction of Si-H groups together with Si-CH₃ groups in a silica gel network can favour, after pyrolysis under argon, the formation of a carbon-rich silicon oxycarbide network, and strongly reduce the presence of free carbon.

The preparation of these gels involves usually the co-hydrolysis of two organosilanes, which serve as sources for Si-H and Si-CH₃ groups. Hydrolysis and condensation reactions of four different precursors have been followed by ²⁹Si NMR, and the study shows that these processes are extremely fast for trimethoxysilane (HSi(OEt)₃) and methyldiethoxysilane (MeHSi(OEt)₂), compared to methyltriethoxysilane (MeSi(OEt)₃) and tetraethoxysilane (Si(OEt)₄). Co-hydrolysis reactions between different pairs of precursors, including MeSi(OEt)₃ / Si(OEt)₄ : MeSi(OEt)₃ / HSi(OEt)₃ : MeHSi(OEt)₂ / Si(OEt)₄ : and MeHSi(OEt)₂ / HSi(OEt)₃ have been investigated by solution and solid-state NMR, which probe structural features of the reacting components at a molecular level. Despite significantly different activities between precursors in several systems, evidence for co-condensation reactions has been found in all cases. Moreover, the chemical homogeneity in each of the final gels has been clearly demonstrated by 2D ²⁹Si-¹H heteronuclear correlation MAS-NMR spectroscopy.

ON AGEING OF ACID-CATALYSED SILICA SOLS - A DYNAMIC LIGHT SCATTERING STUDY

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Exact scattering analyses for determination of particle sizes by MIE theory and its approximations are based on spherical particles. Consequently, dynamic light scattering (DLS) measurements for characterisation of alkoxide derived sol-gel processes have only been used in base- or acid/base-catalysed systems because of the sphere-like shape of their particles. Acid-catalysed sols show rather linear or branched structures. In this study, the meaningfulness of DLS experiments for this case is exemplary discussed.

Various acid-catalysed silica sols made from $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{C}_2\text{H}_5\text{OH}$, H_2O , and HCl in molar ratios of 1 : 4,5: (3...10): 0,007 at 293 K and 350 K, respectively, and kept at 290 K were investigated by means of DLS from the early stages of the sol-gel process to the stages just before gelation. A 'ZetaSizer 3' of MALVERN Instr. modified with a Nd:YAG laser (200 mW 532 nm) allowed the detection of particles from the size of 2 nm up.

It is shown that in spite of limited determinability of parameters (indices of refraction of the particles and the dispersion media) and limited absoluteness of the particle sizes, the scattering data of the various series are comparable with one another and give information about structural differences. In agreement with measurements of viscosities and degradation of the silica species by means of molybdate reagent three ranges of different development of the particles until gelation were found. They correspond to the range of Newtonian behaviour, shearing thinning, and thixotropic behaviour. In contrast to sols made at 293 K, boiled sols show a distinct increase of their particle sizes as a function of the water/alkoxide ratio in all ageing stages. From the higher reliability of their scattering data a more dense, less branched structure of their particles are deduced compared to unboiled sols. Thus, in the final ageing stages even smaller clusters can be formed in boiled sols than in unboiled ones presupposed the same starting composition. Multiangle measurements indicate nearly isotropic particles in final ageing stages and allow the estimation of gelling times before gelation.

**ON THE MICROSTRUCTURE OF HYALITES AND GEYSERITES,
NATURAL HYDROUS FORMS OF SILICA**

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The submicron structure of some natural hydrous forms of silica (hyalite from Valec, geyserites from Iceland) has been investigated with scanning electron microscopy, small-angle X-ray scattering and X-ray diffraction.

All investigated geyserites are composed of colloidal particles of silica with a non-uniform size distribution. These particles are arranged either like clusters of grapes or in a chain-like manner. Some of these chains form characteristically helical patterns with extensions up to 50 μm . The average diameters of the spherical particles having rough or smooth phase boundaries range between 200 nm and 2 μm depending on the consistency of the samples. The SAXS experiments have shown the porous nature of the particles with inhomogeneities smaller than 10 nm inside and hydrated surfaces. The hyalite is characterised by a homogeneous microstructure and smooth phase boundaries. Traces of crystalline silica (α -quartz) could be detected in the hyalite sample and only in some of the geyserites.

Based on the structure of the geyserites their origin is discussed as a process of condensation of silicic acid in aqueous environment, sedimentation and particle agglomeration. The structural development including the textures is determined by the dynamics of the underlying processes: fast decompression and cooling of the parent solutions and their rapid transport.

AP7

RHEOLOGICAL PROPERTIES OF MODIFIED SILICA SOLS

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The rheological behaviour modified of silica sols has been investigated by gel formation kinetics and dynamic flowing in dependence on the pH range 3–7 and the temperature range 20–50 °C. At low shear-rates the sols show pseudo-plastical and below 100 s⁻¹ Newtonian behaviour. Oscillation measurements reveal that the gelation starts with a significant decrease of phase difference $\delta < 10^\circ$ due to a strong increase of the elastic parts. After solidification the values of phase difference increase which indicates a partial destruction of the gel structure during stress influence.

The gelation time decreases with increasing storage temperature, increasing SiO₂ and water content increasing amounts of organic acid and added polymers like PEO and cellulose derivatives. Otherwise, the gelation time increases with the substitution of EtOH by aprotic solvents like dioxane and by increased substitution of silica by Me-SiOn. The influence of added surfactants and plasticisers was negligible when their concentrations are smaller than 1 % within the sols.

The relations between the rheological parameters of the modified silica sols and the coating parameters were investigated for dip coating and for continuous coating with a slide coating unit.

SILICA-SURFACTANT COMPOSITE MATRICES AND THIN FILMS

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Silica-surfactant composite matrices have been made by the sol-gel method by adding partially hydrolysed tetramethoxysilane or tetraethoxysilane to aqueous micellar solutions (ref. M. Ogawa, J. Am. Chem. Soc., 1994, 116, 7941; M. Ferrer and P. Lianos, Langmuir, in press). Micellar solutions were made by trying three surfactants: a cationic, cetyltrimethylammonium bromide (CTAB); an anionic, sodium dodecylsulphate (SDS); and a non-ionic (Triton X-100). Monolithic gels and xerogels were obtained by slow drying of the original sols. Thin transparent films were obtained by dip-coating at an early stage of gelation. Both materials have been characterised by various methods with particular emphasis on fluorescence probing. For the latter, we have studied steady-state absorption and fluorescence spectra and performed time-resolved analysis of fluorescence decay profiles. In this respect, we have exploited the sensitivity of pyrene spectra to its environment, the pyrene excimer formation, the solvatochromic effect on coumarin-153, the resonance energy transfer between pyrene, acting as a donor, and coumarin, acting as an acceptor and the electron transfer quenching between $\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} . Models compatible with the results for the structure of both films and matrices will be presented. Beyond the interest on their structure, these materials were studied by bearing in mind the following applications:

- (1) they can be used as transparent matrices for optical applications. Results will be presented on the observation of light enhancement (laser action) phenomena;
- (2) their nanostructure creates low-dimensional domains. Results will be presented on restricted particle growth and low-dimensional electron transfer;
- (3) contrary to pure silica matrices, they allow diffusion of molecular and ionic species. Results will be presented on conductivity measurements in blocks and films charged with Li^+ ; and finally,
- (4) they allow slow release of embedded molecular species. Results will be presented on the study of controlled release of selected fluorophores. Relevance to drug delivery will be stressed.

INORGANIC GELATION IN LYOTROPIC LAMELLAR PHASE

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Silicon tetramethoxide has been polymerised within a lyotropic lamellar phase composed of a mixture of non ionic commercial surfactant (Triton X100 and Triton X35), water and decane.

Gelation of TMOS in the lamellar phase is estimated by visual observation of the fluidity of the sample. The structure is characterised by High Resolution Small Angle X-ray Scattering, polarising optical microscopy and Nuclear Magnetic Resonance of ^{29}Si . At the end of the polymerisation, HR SAXS pattern of the gel presents Bragg peaks characteristic of a layered structure. The birefringence is preserved which is in favour of a lamellar phase. On the other hand, the optical observation reveals no segregation at the microscopic scale. All these experimental observations, and the evolution of the intensity of Bragg peak seem to indicate that the silica is located in the lamellar structure.

**A SPECTROSCOPIC STUDY OF AN ANHYDROUS TETRAETHYL
ORTHOSILICATE-BORIC ACID-ETHANOL SYSTEM**

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Hydrolysis and condensation reactions of tetraethyl orthosilicate (TEOS) in a novel anhydrous TEOS-boric acid-ethanol sol-gel system have been studied using X-ray diffraction and NMR, Raman and IR spectroscopies, and similarities and differences with the more traditional aqueous system are discussed. Similar to the effect of water, boric acid can hydrolyse TEOS directly with its OH groups, but unlike in an aqueous system, condensation reactions form borosiloxane ($\equiv\text{B}-\text{O}-\text{Si}\equiv$) linkages in preference to siloxane ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) linkages. In an aqueous system, borosiloxane linkages are unstable to hydrolysis and are formed only upon heat treatment of the dried gel. The anhydrous mixture is stable indefinitely against gelation, but can be readily gelled by addition of NaOH in ethanol. This novel sol-gel system may be useful for preparing borosilicate glasses with a high degree of homogeneity.

AP11

PREPARATION OF INORGANIC OXIDES VIA A NON-HYDROLYTIC SOL-GEL ROUTE

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Both single and binary inorganic oxides have been successfully synthesised under mild reaction conditions using the non-hydrolytic sol-gel process. This alternative route to traditional hydrolytic sol-gel synthesis was based on the direct condensation reaction between metal and non-metal chlorides and various oxygen donors such as alkoxides and ethers. Iron (III) chloride was used as a catalyst and the use of volatile additives was avoided.

Single oxides prepared were silica, alumina and titania. Combinations of the respective precursors were used to form the binary oxides, demonstrating both the generality and simplicity of this route. Product yields were high and the gels were characterised by thermogravimetric analysis (TGA), Fourier transform infra-red (FTIR) spectroscopy, Brauner-Emmett-Teller (BET) surface area analysis, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

Calcination studies on the silica based gels showed these materials to be amorphous up to at least 700°C. The crystallisation of selected oxides was studied by X-ray powder diffraction.

CONTROL OF THE POLYMERISATION PROCESS OF Si-Ti AND Si-Ti-Zr SYSTEMS USING ISOEUGENOL

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The preparation and study of mixed Si-Ti, Si-Zr and Si-Ti-Zr systems is important because of the incorporation of new properties that are not usually found in the single systems. The homogeneous incorporation of Ti and Zr into a SiO₂ matrix is important to obtain materials that exhibit chemical, thermal and mechanical stabilities. These properties are essential in applications such as thin films and membranes.

Isoeugenol (2-methoxy-4-propenylphenol) is a polymerisable organic ligand that can be used as chelating agent with transition metals via the phenolic OH group and the oxygen of the methoxy substituent. Isoeugenol can be used to functionalise an oxidic material, offering the possibility of obtaining inorganic-organic hybrid materials.

We have used isoeugenol to chelate Ti in Ti isopropoxide and Zr in Zr n-propoxide (monomeric precursors) in order to modify the polymerisation process of the alkoxides via the sol-gel method. In this way, the homogeneity of the resulting sols and gels has been accomplished. Using this chemical strategy we have also obtained homogeneous, stable and clear Si-Ti and Si-Ti-Zr polymeric systems.

The sols have been studied by FTIR and UV-Vis spectroscopies during the gelation step. Both techniques indicate that isoeugenol is effectively chelated to Ti and to Zr, controlling the polymerisation process. Small Angle X-ray Scattering (SAXS) study of the sols will be performed. The xerogels and oxides will be characterised by surface area measurements.

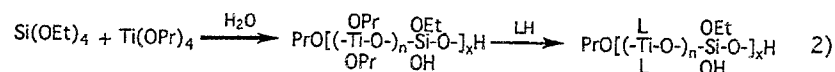
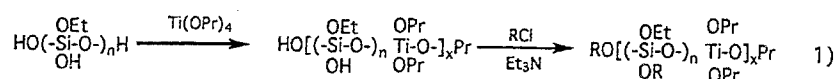
THE STUDIES ON THE ISOLATION AND CHARACTERISATION OF INTERMEDIATE SOLS IN SOL-GEL WITH Si AND Ti ALKOXIDE

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Sol-gel process is a potential method to prepare the materials such as coating and oxide ceramics. However, the chemistry of the process from sol to gel and/or the reaction of hydrolytic polycondensation has not been investigated in detail, especially from the viewpoint of isolation and characterisation of intermediate sols. It is of value to investigate this because the study on the structure of sols and the control of the reaction may provide more preferable process to prepare better oxide ceramics.

We have investigated 'the controlled sol-gel process' to synthesise polytitanosiloxanes as a precursor for $\text{SiO}_2\text{-TiO}_2$ fibres, which is not concerned with 'the real sol-gel process'. In this work, we tried to isolate and characterise the sols formed in the sol-gel process of eqs. 1) and 2).



where $\text{R}=\text{SiMe}_3$ and $\text{L}=\text{acac}$.

In eqs. 1) and 2), the sols were isolated as polytitanosiloxanes with ca. 2000–3000 and molar compositions $\text{Si/Ti}=0.5\text{--}1.5$ consisted of the unit structures Q2, Q3, and Q4 and back bone linkages Si-O-Si , Ti-O-Ti , and Si-O-Ti which are stable to self condensation and soluble in organic solvents. The sols may be a block or random copolymer.

TiO₂ BASED POLYMERS PREPARED BY SOL-GEL METHOD

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Synthesis of titanium oxopolymers by hydrolysis-condensation of titanium alkoxides is a widely studied subject. However calorimetry and water titration provide new informations on the hydrolysis reaction. Furthermore ¹⁷O experiments performed on sol, gel and precipitate give informations on the nature of the polymers, from the hydrolysis step to the final xerogel; Small Angle X-ray Scattering give informations on the structure of the polymers.

Two different methods have been used in order to avoid precipitation during the synthesis of polymers. The first one consists in using acidified water during the hydrolysis step. The second one uses modified precursors whose reactivity is lowered by the complexation of the metallic centre by a bidentate ligand such as acetylaceton. Sols, gels or precipitates are obtained depending on the hydrolysis ratio $H=[H_2O]/[Ti]$ and inhibitor ratio $a=[Acac]/[Ti]$ or $p=[H^+]/[Ti]$. The synthesis of monodispersed nanosized cristalline particles in a range of 1–5 nm has been performed by using this two inhibitors simultaneously.

All these titanium oxopolymers have been characterised from the hydrolysis step to the xerogel using different methods: Karl Fischer titration is used to demonstrate the reversibility of the hydrolysis-condensation reactions. The enthalpy of hydrolysis reaction, estimated using calorimetric measurements, shows the paramount importance of coordinence insaturation in the high reactivity of titanium alkoxides. ¹⁷O NMR is used to establish the nature of the oxopolymers present in the sol (liquid state NMR) the gel and the xerogel (solid state NMR). It demonstrates that the whole chemical composition of the systems depends only slightly on the inhibitors and hydrolysis ratios. The presence of surface Ti–OH groups has been demonstrated on both xerogels and nanosized particles using ¹⁷O CP NMR. SAXS experiments show the presence in all the sol and gels of a common subunit which radius of gyration is about 20 Å. Moreover the aggregation of these subunits strongly depends on the inhibitor and hydrolysis ratio: increasing the hydrolysis ratio (or lowering the inhibitors ratio) gives rise to an increase of the size of the aggregate.

STRUCTURE AND STABILITY OF MODIFIED $\text{Ti}(\text{OPr}^i)_4$ WITH ORGANIC ADDITIVES

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Chemical modification of metal alkoxides with organic additives such as β -diketones and β -keto-ester is known to be very effective to control the reactivity of metal alkoxides. The structure of these modified alkoxide affects the properties and structure of prepared gels after hydrolysis and polycondensation. It is very important to investigate the structure of modified alkoxide and its effect on the properties of gels. Livage et al. had reported the structure of modified Al and Ti alkoxide with ethylacetoacetate and p-diketones with ^{13}C -NMR, ^{27}Al -NMR and IR[2-3]. However, few systematic studies have reported about the quantitative hydrolysis-condensation rate and stability of modified metal alkoxides. In the present study, the structure of modified Ti alkoxides with organic additives such as acetylacetonate(AcAc), ethyl acetoacetate(EAcAc) and methyl acetoacetate(MAcAc) was characterised by ^1H -NMR, ^{13}C -NMR, IR, UV-Vis and XANES/EXAFS. The hydrolysis and condensation rates of these modified metal alkoxides were obtained by NMR spectroscopy. The effect of organic additives on the properties of prepared sol/gel was also discussed.

The structure of modified $\text{Ti}(\text{OPr}^i)_4$ with organic additives such as EAcAc, AcAc and MAcAc was identified with ^1H -NMR and ^{13}C -NMR and the octahedral structures were confirmed after modification. The pre-edge peaks of XANES spectra of modified metal alkoxides also denoted the mixture of five-fold and six-fold structure. The EXAFS fitting results showed the local structure around Ti atom after alkoxide modification. $\text{Ti}(\text{OPr}^i)_4$ modified with AcAc was less reactive toward hydrolysis-condensation reaction than other alkoxides, which could be attributed to the stable ligand structure between $\text{Ti}(\text{OPr}^i)_4$ and AcAc. The small particle size of modified $\text{Ti}(\text{OPr}^i)_4$ sol with AcAc was also obtained.

THERMOCHEMICAL AND ELECTRON MICROSCOPY STUDY OF HYDROLYSIS OF $\text{Ti}(\text{OR})_4$

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The present work concerns physico-chemical study of hydrolysis of $\text{Ti}(\text{OR})_4$. These data are essential for the variety of sol-gel processes and are of major importance for preparation of fine monosized powders. We performed the calorimetry study and obtained the following values for thermal effects of the hydrolysis reactions of $\text{Ti}(\text{OR})_4$, $\text{R}=\text{Et}$, i-Pr , n-Bu , $\text{C}_2\text{H}_4\text{OCH}_3$: $-\Delta\text{H}=13.8\pm0.6$, 64.9 ± 2.6 , 19.2 ± 0.8 , 5.4 ± 0.2 kJ/mol respectively. The heats of the reactions increase linearly in the range of the reagents ratio $\text{R}=[\text{H}_2\text{O}]:[\text{Ti}(\text{OR})_4]$ from 0 to 1. Further increase of R practically does not change the ΔH values. Presumably alongside with the quick reaction of substitution of alkoxy by hydroxy groups condensation occurs; in accordance with the recent data the latter should be also considered a quick process. Oxoalkoxides thus formed hydrolyse with much lower heat evolution.

The particle size distribution curves for the hydrolysis products of $\text{Ti}(\text{OEt})_4$ and $\text{Ti}(\text{OBu})_4$ were calculated from the TEM data for different reaction times. The mean size of the first particles registered was about $0.2\text{ }\mu\text{m}$, which is in good agreement with the data for hydrolysis of $\text{Ti}(\text{OEt})_4$. The uniform particles growth is preserved for a few hours however later on distribution broadens both due to the growth of the particles as well as to the appearance of new ones. The latter presumably are the hydrolysis products of oxoalkoxides. Thus the nonuniformity in the particle size distribution is due to the drastic difference in the rates of hydrolysis of the initial titanium alkoxides and oxoalkoxides formed on the first step of hydrolysis.

Formation of oxoalkoxides as the first hydrolysis products allowed us to regulate the sizes of the TiO_2 particles obtained on hydrolysis of $\text{Ti}(\text{OBu})_4$. TiO_2 powders with different mean particle sizes are used as models for study of sintering kinetics and microstructure of ceramics.

AP17

MECHANISM AND NANOSTRUCTURE FORMATION IN A NON-AQUEOUS TITANIUM ALKOXIDE SYSTEM

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Alkyl titanates can be converted into gels under non-aqueous conditions by the action of formic acid in the presence of an optional solvent. Despite the well-known effect of acetic acid to moderate titanate reactivity in aqueous media, reactions of Ti(OR)_4 with formic acid can lead to rapid gelation.

The reaction pathways of titanium ethoxide and titanium butoxide in formic acid and aqueous media have been studied with several time resolved techniques. A rapid mixing-continuous flowing technique is used in conjunction with FTIR and SAXS to monitor the chemical and physical changes that occur during the very early stages (i.e., reaction times as small as 80 ms) of the reaction. The effect of acid and water concentration, temperature and solvent on the reaction kinetics can be determined from FTIR. Then the influence of reaction kinetics and modality on nanostructure formation can be inferred from SAXS measurements relating to fractal scatterers and radii of gyration.

**NEW ORGANOFUNCTIONAL TITANIUM AND ZIRCONIUM
ALKOXIDE DERIVATIVES, AND STRUCTURAL
CHARACTERISATION OF PRIMARY HYDROLYSIS PRODUCTS**

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Organofunctional alkoxides of the type $[(RO)_3E\text{-Ch-X-A}]_n$ ($E = \text{Ti, Zr}$), in which Ch is a chelating group, X a spacer and A a functional organic group, are required for the preparation of inorganic-organic hybrid materials based on titania or zirconia. Previous work on organofunctional carboxylate derivatives was extended to sulphonates and hydroxamates.

In particular, derivatives with $A = \text{PPh}_2$ were prepared by reaction of phosphino-substituted carboxylic, sulphonic, or hydroxamic acids with $E(OR)_4$. They can be coordinated to metal complex moieties (ML_n) via the PR_2 group and thus allow to heterogenise metal complexes on TiO_2 or ZrO_2 -based solids.

An understanding of the structural organisation of the building blocks from which the hybrid materials are composed, and the arrangement and bonding of the functional organic groups is the key for their deliberate design, because the microstructure determines their properties. Part of this information is obtained by the structural characterisation of crystalline primary hydrolysis products as model compounds. The clusters $Zr_6(OH)_4O_4(OMc)_{12}$, $Zr_{12}(OH)_8O_8(OMc)_{24}$, $Zr_4O_2(OMC)_{12}$ ($OMc = \text{methacrylate}$), $Zr_6O_2(OPr)_{18}(NpOH)_{12}$ ($NpOH = 1\text{-hydroxy-2-naphthoate}$) and the polymeric compound $[Zr(OPr)(O_3SMe)_3]_\infty$ were obtained by reaction of the corresponding acids with $Zr(OR)_4$. Comparison of these and related compounds allows the elaboration of the factors that influence the structural properties of hybrid inorganic-organic solids.

THE STRUCTURE OF MULTICOMPONENT (TITANIA/ZIRCONIA) NANOPARTICLES

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The structure of titania/zirconia colloids has been investigated using small-angle neutron scattering (SANS). The colloids were produced by:

- hydrolysis of a mixture of titanium and zirconium alkoxides, and peptisation of the resulting hydrolysate with nitric acid (homogeneous);
- hydrolysis of a titanium alkoxide, and peptisation of the resulting hydrolysate with aqueous zirconium (IV) nitrate solution (heterogeneous).

The sols were concentrated by evaporation, dried under controlled condition and re-dispersed in D_2O/H_2O mixtures. Raman spectra of the sols, and XRD powder patterns from the gels, showed that the material was crystalline anatase and amorphous zirconia. Both TEM and XRD line broadening indicate that crystallite size of the dried titania gels is ~ 8 nm.

The SANS contrast variation experiments showed that the minimum contrast points for the homogeneous and heterogeneous colloids, determined by two different methods, gave similar results which differed significantly from the expected value, due to the sorption of nitrate counter-ions and hydroxyl species on the surface of the colloids. The homogeneous colloids exhibited a smooth solid/solution interface at full contrast (on length scales < 10 nm), while no such interface was observed for the heterogeneous colloids. In both cases, the scattering at minimum contrast was consistent with a fractal network of unidimensional zirconia, with a typical diameter of ~ 1.5 nm. At full contrast, the homogeneous colloids have fractal dimensions (d_f of 1.6) similar to those from static light scattering, i.e. consistent with an open, extended, chain-like aggregate structure. The heterogeneous colloids have higher fractal dimensions (d_f of 2.2 to 2.9), due to zirconia crystallites packing the interstices between the titania crystallites, i.e. consistent with an loosely packed, spherical structure.

These results infer that in the homogeneous colloids, the zirconia is segregated within the matrix of the titania crystallites (on ~ 1 nm scale), whereas in the heterogeneous colloids, the zirconia is segregated on the surface of the titania crystallites (on ~ 10 nm scale).

**MECHANISM OF HYDROTHERMAL SYNTHESIS IN FLUORIDE
MEDIUM: HYDROTHERMAL SYNTHESIS OF ZIRCON**

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The hydrothermal synthesis of zircon in a fluoride medium leads principally to two kinds of zircons, differentiated by their morphology, their chemical composition, their thermal stability and their solubility. Differences in the thermodynamic parameters of the solution (pH, temperature, [F]) could explain the formation of these two kinds of zircons.

The main hypothesis involves two crystallisation mechanisms. Both include a step of gel dissolution with formation of soluble species that are responsible for the crystallisation. In each case, the silicic species seem to be monomeric without fluorine. However, the nature of soluble zirconium species depend on the thermodynamic parameters of the solution.

At acid pH and with fluoride ions, the reactive species for the crystallisation seem to be fluorine rich zirconium complexes. In this case, the zircon obtained, contains a large amount of fluorine presumably located in silicic sites (Zircon A).

At basic pH and whatever the concentration of fluoride, the reactive species for crystallisation seem to be linear polymeric entities. In this case the zircon obtained, shows a typical morphology in the form of layered aggregate and a high specific surface area (Zircon B).

UREA-FORMALDEHYDE AS PRECURSOR FOR THE PREPARATION OF ZIRCONIA BY SOL-GEL POLYMERIC ROUTE

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The polymerisation reaction between urea and formaldehyde was utilised to prepare zirconia powder. Zirconium chloride solution was added to the resin during formation. Optimisation of the conditions of preparation namely concentration, temperature, time and pH of solution was concerned to obtain a clear transparent gel. Zr^{4+} hosted in the structure of the resin was equivalent to 4 molecules of zirconium oxide. IR showed that Zr^{4+} is octahedral coordinated and is bonded with the different groups CH_2 , OH, CN preserving the structure of the hosting resin arranged in rings and branches. DTA showed a combustion reaction at 260°C and complete dissociation of the organic part is ended at about 600°C. TEM and SEM showed the grains of powder calcined at 500°C to be equigranular and spherical in shape of uniform size about 12 nm. XRD showed that the Tetragonal phase exists at 300°C and is totally transformed into the monoclinic phase at 1000°C with conspicuous grain growth. Pore are concentrated in the micro capillary fraction as determined by Hg porosimetry.

STRUCTURAL STUDIES OF ZIRCONIUM OXIDE GELS

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Pure zirconium oxide and zirconium oxide based materials have earned much interest because of the mechanical and chemical properties. For industrial utilisation ZrO_2 is often required in a determined amorphous or crystalline structure. The sol-gel method can be a method to produce amorphous ZrO_2 as the initial point for a thermal treatment to obtain a defined crystalline structure.

Zirconium oxide gels were prepared by controlled hydrolysis and condensation of zirconium- η -propoxide in alcoholic solution. After completion of the gelation the ageing and drying of the alcogel was observed in situ by Small and Wide Angle X-ray Scattering experiments at room temperature. The xerogels obtained have been annealed at different temperatures to crystallisation. The structural changes were observed by using SAXS and WAXS. Structural models reproducing the experimental WAXS data have been simulated by the reverse Monte Carlo method.

The structural changes from alcogel to xerogel have been understood very well by using SAXS. The ZrO_2 alcogel consists of primary particles which form clusters giving this system fractal properties. During the drying, the gel network collapsed because of the capillary forces as well as the interfacial stress, and the fractal properties are lost. One can not find a gel glass transition. The system is noncrystalline because of the high internal surface area.

The local atomic ordering in the dried ZrO_2 xerogel resembles crystalline monoclinic ZrO_2 , and the xerogel annealed at elevated temperatures that in crystalline tetragonal ZrO_2 . A comparison between zirconium oxide xerogels obtained under different preparation conditions was made and evidence was found that thermal treatment at higher temperatures and preparation conditions affect the atomic arrangement of these amorphous gels.

ALKOXIDE PRECURSORS FOR Er-CONTAINING GLASSES AND CERAMICS

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Heterometallic alkoxides are good precursors for sol-gel preparation of advanced ceramics, especially homogeneously distributed in the oxide. The sol-gel technique also allows for films, fibres and nano-powders to be prepared and low temperatures for conversion of the gel to oxide to be used. Rare-earth containing oxides are present in many commercially important fine ceramics such as solid electrolytes, high-Tc super-conductors, catalysts, lasers and frequency up-conversion devices. A good knowledge about the steps involved in the sol-gel process is vital to optimise the properties of the product ceramics. Knowledge about the precursor alkoxide with its atomic composition, physical and chemical properties is the first important step.

In this article, we investigate alkoxides obtained in the systems; Er-Al, Er-Zr, Er-Ti, Er-Pb and Er-Bi, as well as some related alkoxides. The alkoxides have been studied with techniques, such as single crystal X-ray diffraction, EDS, FT-IR and UV-Vis.-spectroscopy.

FLUOROALKOXIDES AS MOLECULAR PRECURSORS OF FLUORIDE MATERIALS BY SOL-GEL PROCESS

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Numerous works have reported the access to pure oxide materials using the sol-gel process. The purpose of this paper is to show that it is possible to obtain pure fluoride homometallic or heterometallic materials at room temperature by the hydrolysis of tailored molecular precursors.

We focused our work on alkaline-earth and lanthanide fluoroalkoxides ($[M(OR)_n]n'$ wherein OR = fluoroalcoxo group) and the characterisation of the final products of their hydrolyses. The molecular precursors were characterised by FT-Raman and the final powders were characterised by XRD and EDXRMA.

The mechanism of formation of these fluoride materials involves the formation of fluoride organic by-products. The reactivity of these organic compounds on variable substrates in terms of surface modification has been studied. This technology, due to its high flexibility, could be very useful in membrane technology. This last point will be discussed.

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SOL-GEL PROCESSING TO PRODUCE NANO-ENGINEERED SCANDIA

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Scandium is the lightest of the d-block elements and exists as only one oxide (Sc_2O_3) which has a cubic structure that converts to monoclinic above 1273K and 13GPa. It possesses a high melting point (2753K), refractive index (1.91) and band gap (5.7eV). The formation and properties of scandia sols and sol-gels have not been intensively investigated to date.

Scandium chloride (99.9%; Aldrich) in dry butanol can be converted to gelatinous white $\text{Sc}(\text{OH})_3$ by the addition of dry NH_3 with precipitation beginning at pH 4–7 to give average particle sizes of 10–100 nm.

It is shown here that sol-gel chemistry based upon $\text{SC}(\text{m})$ -acetylacetonate in ethanol can produce scandia particles 5–10 nm in size, that could be purified thermally or by sohxlet extraction. Such sols were stable for several months and were characterised by TEM. Xerogels derived from these were characterised by FTIR, XPS, TGA, X-ray and electron diffraction; their surface areas were about $300\text{m}^2/\text{g}$. Particles showed no growth up to the temperature of their recrystallisation.

SYNTHESIS OF THORIUM PHOSPHATE-DIPHOSPHATE FROM GELS

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Thorium phosphate-diphosphate $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ is a very less soluble compound. This matrix can be used for radioactive waste storage. Leaching studies of solid solutions labelled with ^{85}Sr , ^{227}Th , ^{230}U ... led to $\approx 10^{-3}$ % of release these radionuclides (ten times less than monazites).

Thorium phosphate-diphosphate can be synthesised either by dry or by wet way but soft chemistry routes allow easier to dope it. For this we used 1 M solutions of a thorium salt (chloride, nitrate..) and phosphoric acid or ammonium hydrogen phosphate. A gel is formed when the pH value vary the range from 0 to 4. This gel was heated at 150–160°C in order to evaporate the major part of water and volatile acid (HCl , HNO_3), washed with water to remove the remained acids, then heated at 400°C and finely calcinated at 1100–1250°C. In this way a very homogenous powder of $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ is obtained, provided the mole ratio $r = \text{PO}_4/\text{Th} = 3/2$.

BIMETALLIC ALKOXIDES OF TANTALUM

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There has been carried out a systematic study of tantalum alkoxides interaction with the alkoxides of Li, Mg, Ba. The physicochemical properties of obtained bimetallic complexes, that are molecular precursors of ferro- and piezoelectric materials, were investigated.

Existence of crystalline alkoxotantalates, e.g. LiTa(OR)_6 ($\text{R} = \text{Me, Et, } ^{11}\text{Bu}$), $\text{MgTa}_2(\text{OEt})_{12}2\text{EtOH}$ and $\text{BaTa}_2(\text{O}^i\text{Pr})_{12}2^i\text{PrOH}$, was established. Infinite chains of intermitting $[\text{Ta(OR)}_6]$ octahedra and $[\text{Bi(OR)}_4]$ tetrahedra, sharing common edges (analogous to that known for LiNb(OEt)_6) were found in the structures of LiTa(OMe)_6 , and LiTa(OEt)_6 . Chains of three octahedra, sharing common edges were found in the structures of $\text{trans-MgTa}_2(\text{OEt})_{12}2\text{EtOH}$ and $\text{cis-BaTa}_2(\text{O}^i\text{Pr})_{12}2^i\text{PrOH}$.

For the $\text{M(OR)}_n - \text{Ta(OR)}_5 - \text{ROH}$ ($\text{R} = \text{Me, Et, } ^i\text{Pr, } ^{11}\text{Bu}$, $\text{M} = \text{Li, Ba, Mg}$) systems solubility isotherms, 25°C , were studied. In the systems, including LiO^iPr , Mg(OMe)_2 , Ba(OMe)_2 , Ba(OEt)_2 no crystalline complexes but the isotherms indicate that the formation complexes of $\text{M:Ta}=1:1$ for Li and $1:2$ for Mg and Ba takes place. No interaction was observed in the case of barium butoxide.

The existence of $\text{Li:Ta}=1:1$ and $\text{M:Ta}=1:2$ ($\text{M} = \text{Mg, Ba}$) complexes in the title systems (including those, where the crystal complexes were not isolable) was confirmed by viscosity and conductivity studies in the corresponding isomolar series, and by mass-spectral investigation of the gas phase. Fragmentation of $[\text{LiTa(OR)}_6]_n$ ($n = 1, 2$) and $\text{MTa}_2(\text{OR})_{12}$ occurs via loss of Ta(OR)_5 , R_2O and RO .

The storage of alkoxotantalate solutions leads through the uncontrolled microhydrolysis and oxidation and possibly ether elimination pathways to crystallisation of oxoalkoxides, such as $[\text{LiTaO(OEt)}_4(\text{EtOH})]_2$, $\text{LiTa}_9\text{O}_{13}(\text{OEt})_{20}2\text{ROH}$, and cubane-like $[\text{BaTaO(OMe)}_5(\text{MeOH})_{2.5}]_4$, $[\text{BaTaO(OEt)}_5(\text{EtOH})_{1.5}]_4$, $[\text{MgTaO}(^{11}\text{Bu})_5(^{11}\text{BuOH})]_4$. (X-ray crystal study was fulfilled by A. I. Yanovsky and Z. A. Starikova at INEOS, Moscow.)

SOL-GEL FORMATION OF SILICATE FOAMS BY HYDROGEN PEROXIDE DECOMPOSITION

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A new method for the formation of silicate and organically modified silicate foams is introduced. Monoliths were prepared by incorporating a few percent hydrogen peroxide in the sol-gel starting solution. For example, incorporation of 6-10% (v) hydrogen peroxide in base catalysed sol-gel precursors of methyl-Ormosil yielded macroporous monoliths with bi-modal pore size distribution. The average characteristic pore diameters were approximately 1.0 nanometer and 0.7 micrometer, depending on the sol-gel precursors and preparation protocol. The specific surface area was approximately 160 m²/g, contributed mainly by the microporous structure. Foams of similar macrostructure were formed also under acid catalyses.

The monolith foams were stable and did not crack upon repeated water wetting and drying cycles. Similar preparation procedure without hydrogen peroxide yielded only powdered or highly fractured materials. Presumably, the decomposition of the hydrogen peroxide yielded microbubbles which formed templates for the polycondensation reaction.

SEM, nitrogen absorption isotherms, small angle X-ray spectroscopy and mercury porosimetry were used to characterise the foamy materials.

BP2

CERAMIC FOAMS FROM A PRECERAMIC POLYMER AND POLYURETHANES

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Ceramic open-cell foams were obtained from a preceramic polymer (SR350 silicone resin, GE, USA) and blown polyurethanes. The preceramic polymer, which crosslinks by condensation of silanol groups, was dissolved in CH_2Cl_2 and added as a filler to a liquid polyol containing the surfactant and the amine catalyst. The mixture was added to isocyanate and foamed using as blowing agents the dichloromethane present and the CO_2 deriving from the reaction between the isocyanate and water coming from the condensation of the Si-OH groups in the silicone resin. The morphology of the expanded polyurethane, which can be flexible or semi-rigid, characterises the final structure of the ceramic foam. In the first case the polyurethane morphology is designed to be completely open-celled. In the second case, structures with pores (pin holes) in cell windows are obtained. Obviously, different structures imply different physical-mechanical properties of the foam. The materials obtained were pyrolysed in a nitrogen flux at temperatures of $1000^\circ\text{C} \div 1200^\circ\text{C}$, thus allowing for the polymer-to-ceramic transformation to occur in the preceramic polymer.

The ceramic foams produced in this way are constituted by an amorphous silicon oxycarbide ceramic (SiOC). They have a density ranging from 0.1 to 0.3 g/cm^3 and CTE ($20\text{--}200^\circ\text{C}$) of about $1.1 \times 10^{-6}/\text{K}$. The average pore diameter ranges from 100 to 200 μm and they possess 80 to 90% porosity. The ceramic foams have an elastic modulus ranging from 20 to 80 MPa, and a compression strength σ_{max} of $1 \div 4 \text{ MPa}$. They display an excellent thermal and dimensional stability up to their heat-treatment temperature.

SOL-GEL SYNTHESIS OF Bi_2O_3 AND $\text{Bi}_4(\text{SiO}_4)_3$ THIN FILMS

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Bismuth oxide and silicate films show many interesting properties which make them very appealing for potential applications as catalyst, scintillators or part of sensing devices. Bi_2O_3 thin films were prepared by dipping silica slides in ethanolic solutions of tris (2,2'-6,6'-tetramethylheptane-3,5-dionato) bismuth (III) $[\text{Bi}(\text{dpm})_3]$ and heating in air at temperatures $\leq 500^\circ\text{C}$. Homogeneous bismuth silicate films were obtained from the reaction of the bismuth oxide coating with the silica glass substrate upon heating at high temperatures. Bi_2SiO_5 coatings formed for heat treatments at temperatures between 550 and 700°C , while $\text{Bi}_4(\text{SiO}_4)_3$ thin films developed when annealing at temperatures higher than 700°C .

The chemical composition of the films was determined by Secondary Ion-Mass Spectrometry (SIMS) and X-ray Photoelectron Spectroscopy (XPS) while their microstructural evolution was studied by Glancing Angle X-ray Diffraction (GA-XRD). Further information were obtained by UV-Vis Spectroscopy.

We demonstrated that the adopted synthetic procedure was reproducible and allowed the control of the Bi_2O_3 phase composition. Moreover, we were able to correlate the variations of the experimental conditions, i. e. heating time and temperature, with the formation of bismuth silicates thin films.

SOL-GEL DERIVED TiO_2 /LEAD PHTHALOCYANINE PHOTOVOLTAIC CELLS

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Despite their environmental advantages, the widescale introduction of photovoltaic devices has not occurred. One of the principle drawbacks of conventional Si-based cells are the high material and processing costs. Consequently, a number of alternative material and device structures have been considered, including both organic and hybrid organic/inorganic systems. Research has shown that organic dyes can be used to spectrally sensitise wide band gap metal oxide semiconductors, resulting in an organic/inorganic photovoltaic (PV) cell. The successful development of such a novel device structure would result in a cheaper alternative. The Sol-Gel process is particularly attractive for fabricating such thin film heterostructures. Due to the relatively low cost, versatility and ease of manufacture. This paper describes the development and results obtained from such a cell, which is in the form; Au/Lead Phthalocyanine (PbPc) / TiO_2 /ITO.

Transparent TiO_2 films were deposited onto a base electrode comprising an ITO glass substrate using the (alkoxide) Sol-Gel technique. Following heat treatment at 500°C , the TiO_2 was shown by X-ray diffraction to be anatase in structure. Lead Phthalocyanine (PbPc) films were subsequently vacuum sublimed onto the TiO_2 surface. A gold counter electrode was evaporated onto the PbPc surface.

The short circuit current and open circuit voltage were measured as a function of wavelength in the range 300–900nm. A good spectral match between these photoelectrical measurements and the PbPc absorption spectra were found, indicating that the Sol-Gel derived TiO_2 had been sensitised into the visible region. Dark and illuminated I(V) and spectral characteristics of the resulting TiO_2 /PbPc heterojunction were also investigated to study its potential as a dye sensitised PV cell. The ideality factor (n) and saturation current density (J_0) were determined from the I(V) measurements. Typical photovoltaic characteristics were obtained indicating the devices potential for solar cell applications, however efficiency improvements are required.

ELECTRICAL PROPERTY OF POLYCRYSTALLINE LITHIUM CHLOROBORACITE PREPARED BY THE SOL-GEL METHOD

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Lithium boracites, $\text{Li}_4\text{B}_7\text{O}_{12}\text{X}$ (X=halogen), are lithium-ion conductors, having a potential application to solid electrolytes in thin film batteries. It is difficult to prepare not only $\text{Li}_4\text{B}_7\text{O}_{12}\text{X}$ films but also their sintered bodies, because $\text{Li}_4\text{B}_7\text{O}_{12}\text{X}$ decompose at high temperatures. Recently we have prepared lithium chloroboracite, $\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}$, powders and polycrystalline films by the sol-gel method. However, the surfaces of the prepared films were too rough to examine their conductivity. In this study, the conductivity of polycrystalline $\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}$ pellets was measured using the complex impedance method. The results are discussed with relation to the presence of grain boundaries and by-products.

Precursors of $\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}$ were prepared in a way similar to that in the preparation of $\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}$ powders. Ammonium chloride or hydrochloric acid was added as a chlorine source to a sol solution in the molar ratio of Cl/Li (R_c) of 0.6 to 0.75, and 0.6 to 0.9, respectively. The resulting sol solutions were dried and preheated to obtain the precursor powders. The powders were molded into pellets. The pellets were heated at 973 K for 1h, leading to crystallisation and sintering. $\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}$ formed as a major component in all the heated pellets, with a trace amount of LiCl or $\text{Li}_2\text{B}_4\text{O}_7$ as a by-product. When prepared from the precursors in R_c of 0.675 or above with hydrochloric acid, LiCl formed. In the other cases, $\text{Li}_2\text{B}_4\text{O}_7$ formed. The densities of the pellets were between 56 and 61% of the theoretical value of $\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}$. Nevertheless, one of these pellets showed a conductivity of $1 \times 10^{-3} \text{ S/cm}$ at 573 K, which is approximately one order lower than the single crystal. The formation of $\text{Li}_2\text{B}_4\text{O}_7$ decreased the conductivity, while LiCl produced little difference in the conductivity.

BP8

TEM ANALYSIS ON MICROSTRUCTURES IN HIGH-T_c BI-BASED SUPERCONDUCTORS

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Microstructure evolutions during the heat treatment of high-T_c Bi-based superconductors have been examined using transmission electron microscopy (TEM). In the specimens, which were prepared using the starting powders by the sol-gel method, the density of the synthesised superconducting grains was high with few voids among them. The Bi-2212 and Bi-2223 grains grow in rather short time of heating and, accordingly, the critical temperature T_c increases rapidly. However, T_c starts to decrease soon on the succeeding heating (e.g, 870°C-95 hrs for Bi-2223). This is due to the formation of amorphous phase at the surface of grains or their boundary. On the other hand, in the specimens, which were prepared using the conventional starting powders, the reaction to form superconducting grains was slow on heating. Obtained grains are in a large thin plate form so that large holes occur among them. The increase of T_c is therefore slow on heating but the amorphisation of grains is rather suppressed.

SYNTHESIS OF HIGH-T_c SUPERCONDUCTORS USING THE SOL-GEL METHOD

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The sol-gel method is thought to be effective to synthesise high-T_c superconductors under soft conditions. We have made efforts to synthesise oxide superconductors of $(\text{Cu},\text{M})\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$, $\text{CuSr}_2(\text{Y},\text{Ca})_{n-1}(\text{Cu},\text{Re})_n\text{O}_y$, $\text{NdBa}_2\text{Cu}_3\text{O}_y$ and so on and oxyfluoride superconductors of $(\text{Ba},\text{La})_3\text{Cu}_3(\text{O},\text{F})_y$ and $(\text{Sr}, \text{La})_2\text{Cu}(\text{O},\text{F})_{4\pm\delta}$ using contrived sol-gel methods. These superconductors were produced in the style of bulk or film.

$(\text{Cu},\text{Ga})\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ sample showed an anomaly like a superconducting flux trapping behaviour from 150K. The tetragonal superconducting phase $(\text{Y},\text{Ca})\text{Sr}_2\text{Cu}_3\text{O}_2$ which is thought to form under the limited condition of high pressure was obtained under atmospheric pressure. This phase was confirmed to be stabilised by displacing a part of Cu with Re, and also superconducting properties of them were improved by doping Ca. A tetragonal phase $(\text{Ba},\text{La})_2\text{Cu}(\text{O},\text{F})_y$ with K_2NiF_4 structure was found to be obtained at 600C in films from the system $(\text{Ba},\text{La})_3\text{Cu}_3(\text{O},\text{F})_y$. This phase performed an anomaly from about 50K in a measurement of magnetisation. A tetragonal phase $\text{Sr}_2\text{Cu}(\text{O},\text{F})_{4\pm\delta}$ was first obtained in film not via Sr_2CuO_3 by heating coated film in flowing gas controlled with O_2 . This phase showed superconductivity from about 45K.

It is considered that sol-gel method is a useful route to synthesise high-T_c superconductors under soft conditions.

This work was supported by NEDO of Japan

BP11

**RIETVELD ANALYSIS OF LA- β -ALUMINATE/ALUMINA
COMPOSITES PREPARED FROM BOEHMITE GELS**

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Alumina ceramics were self-reinforced by homogeneous distributions of in-situ growth La- β -aluminate (LBA) platelets. These composite materials were prepared by a sol-gel processing from alumina seeded boehmite sol and lanthanum nitrate.

Rietveld and line-profile analysis of X-ray diffraction data have been used to monitor the crystallisation process, emphasising the LBA formation and its dependence on the temperature. It has been observed that the formation of the LBA phase occurs at a lower temperature than when it is prepared by conventional reaction in solid state of commercial alumina powder and the same La precursor.

**SOL-GEL; POTENTIAL CREATIVE APPLICATIONS FOR THE
ARTIST, FOCUSING ON THE COLLOIDAL ALKALI SILICATE
ROUTE**

Ed Smy

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The development of the colloidal alkali silicate gelation process (the Shoup Method) has established that intrically shaped large size monolithic glass samples are achievable without the need for long drying procedures or the use of a critical drying process. The ability to fabricate gels with large pores (diameter range of 100–300 nm) and the ability to dry them simply and quickly (with the use of a micro wave oven), has made sol-gel technology accessible to the artist and with it new creative possibilities.

Purity, a principal goal of the scientist, is not a precondition for the artist, allowing for the exploration of fused bodies at much lower temperature ranges. This freedom, linked to the potential to dope with colour and interactive materials as a formative ingredient and to cast near net shapes without major finishing, establishes new horizons for studio practice.

Through out the development of glass, from its origins in Mesopotamia, through the industrial revolution, glass has benefited from the interaction of the scientist and artist. Sol-gel, has from its inception been in the domain of the scientist, can the artist play a part in its development ?

BP13

MULLITE-ALUMINA COMPOSITES PREPARED BY SOL-GEL

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Ceramic composite gels in the mullite-alumina system (with mullite phase content ranging from 100 to 20 wt%) were prepared by sol-gel. The preparation of gels was done in acid media and for a molar ratio water/alkoxide equal to 4. Composite powders obtained by controlled milling of gels were uniaxially pressed to obtain discs.

The thermal evolution of the various materials was followed by thermal analysis and X-ray diffraction.

The crystalline phases formed on gels are related with the thermal treatment. The crystallisation of mullite and transient phases of alumina were observed in gel samples after heat treatment at temperatures equal or higher than 900°C.

The density, the morphology of the sintered materials and their mechanical properties were studied.

**PREPARATION AND PROPERTIES OF RHODAMINE B
DERIVATIVES WITH ETHOXY SILANO GROUPS AND ITS
APPLICATION FOR CATHODE RAY TUBES (CRT)**

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Rhodamine B derivative with ethoxy silano group has been prepared from a reaction of Rhodamine B sulphonyl chloride with aminopropyltriethoxysilane in dry pyridine. This new Rhodamine B derivative reacts with SiO_2 sol to connect directly with a network of silica matrix. We prepared wavelength selective absorption film for CRT by use of SiO_2 sol solution containing the new derivative. This sol solution was spin coated on a face plate of a CRT, followed by heat-treatment (100°C) to form a thin film. The organic dye bonds to the inorganic skeleton. This film has good performance (contrast enhancing performance) since organic dye is heavily incorporated in a high concentration in the film.

CP1

**NUCLEATION OF HYDROXYAPATITE ON SILICA-GEL:
EXPERIMENTS AND THERMODYNAMIC EXPLANATION**

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Silica gel have been prepared from ethanol, TEOS and water, through nitric acid catalysed sol-gel processing; after slow drying, the gel has been heated in air up to 900°C. Then, platelike shaped pieces of heat treated silica-gel have been selected and used for the hydroxyapatite nucleation - experiments in a simulated fluid body (SBF).

After seven days in the SBF, 1: hydroxyapatite on the surface of the silica-gel samples has been observed and identified through scanning electron microscopy. Confirmation by FTIR, and X-ray diffraction has also been carried out. Some hydroxyapatite growing experiments has been performed renewing the SBF each two days through the duration of the test. The results obtained are in good agreement with those of previous authors.

The new contribution to the subject consisted of a thermodynamic explanation for this nucleation and growth of the hydroxyapatite on the silica gel surface. Sol-gel processing gives the silica an active surface. Dense silica could get an active surface through surface

THE FORMATION OF A TRANSPARENT GEL WITH A HYDROXYAPATITE OXIDE COMPOSITION

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The well understood sol-gel chemistry of silicate systems leads to various sol-gel derived materials. However, phosphate systems, also a kind of important materials, are rarely involved among the publications about the sol-gel processes. Hence, the work on the sol-gel process in the system $\text{CaO}-\text{P}_2\text{O}_5$ is interesting because of its significance in chemical and biological engineering. It is well known that the control of a system to form a transparent gel can be helpful to understand the corresponding sol-gel process. In this work, a biologically interested hydroxyapatite oxide system was chosen. Ca glycolate and phosphoric acid were used as the precursors and acetic acid was used as a modifier to retard the reactions between the precursors. A transparent gel could be obtained when the as-prepared mixture of Ca glycolate and phosphoric acid with an acetic acid/Ca ratio of 6 was not stirred for a long time. The gel could be directly transformed to a pure and well developed hydroxyapatite phase when it was calcined at a temperature of more than 500°C . The formation conditions of a transparent gel, and its gelation process were characterised and discussed.

PHASE FORMATION IN THE GELS OF APATITE - ANORTHITE SYSTEM

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The phase formation in the heat treated gels of apatite-anorthite system has been investigated using X-ray diffraction analysis, IR spectroscopy, TEM and TEMD. The short range order of anorthite gel glasses has been determined by X-ray diffraction structural analysis. For sol gel synthesis TEOS, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and CaF_2 have been used as precursors.

The obtained gels are treated from 200°C up to 1250°C. It is found that the gels of apatite-anorthite system and gels of anorthite stoichiometric composition remain in amorphous state up to 950°C.

From the X-ray diffraction structural analysis of anorthite gel-glasses heat treated at 600°C and 800°C it is found a shift of the first maximum from 1.85 Å to 1.77 Å, which could be interpreted as one densification of the anorthite gel-glass structure with the increasing of temperature.

During the heat treatment of gels from the apatite-anorthite system it is found that the apatite and anorthite are formed as main crystalline phases at 1050°C and 1150°C. At lower temperature (950°) fluorite presents in the studied gels. The intensity of fluorapatite diffraction peaks significantly decreases at 1250°C and a new crystalline phase (gehlenite) is formed.

The phase formation has been also studied in composites synthesised from anorthite gel-glass and fluorapatite. On the basis of the experimental results received from the studying of the phase formation in samples of the system fluorapatite-anorthite it can be concluded that it is possible to obtain the next composite materials containing: - only one crystalline phase fluorapatite and amorphous phase of anorthite composition;- three crystalline phases fluorapatite, gehlenite and anorthite;- two crystalline phases gehlenite and anorthite and amorphous phase with P_2O_5 oxide mainly.

SOL-GEL DERIVED CALCIUM PHOSPHATE COATINGS FOR BIOMEDICAL APPLICATIONS

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Hydroxyapatite (HA) coatings have received considerable attention in recent years because they exhibit bone bonding capabilities. Unfortunately the common forms of coating production result in cracking and degradation of HA due to the thickness of the coatings and the elevated temperatures employed. This study demonstrates the production of sub-micron, crack-free calcium phosphate coatings using a sol-gel dip-coating technique and firing temperatures below 1000°C.

Calcium ethoxide and triethyl phosphate precursors in ethanediol and ethanol solvents have been used to prepare coating solutions. Coatings applied to quartz glass substrates have been examined using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Reactions with simulated body fluid (SBF) have also been investigated.

Diluting the Ca/P/ethanediol sol with ethanol allowed the production of uniform coatings with reproducible morphology. SEM showed the coating microstructure appeared as two phases, and this was supported by XRD findings indicating that coatings fired at 1000°C comprised a mixture of hydroxyapatite (HA) and tricalcium phosphate (TCP). XPS analysis of the coating surface showed that the Ca/P ratio lay in the range 1.5–1.67, and that there was a contribution from carbon in the form of carbonate. Immersion of fired coatings in SBF resulted in a decrease in the calcium ion concentration in solution, indicating deposition of a CaP phase. The characteristics of the deposited phase were different to those of the underlying coating, as evidenced by morphological changes after SEM examination. After immersion in simulated body fluid, XPS showed that the carbonate ion contribution at the surface was increased and the Ca/P ratio decreased compared to unimmersed coatings.

It is proposed that the sol-gel coatings comprising a resorbable (TCP) and an insoluble (HA) phase have potential benefits in certain implant applications.

CP5

TITANIUM- AND ZIRCONIUM-ALKOXIDE BASED SOL-GEL-COATING AS BIOCOMPATIBLE SURFACE MODIFICATION

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For many years titanium has been used as implant material in different areas of implantology. The biocompatibility of titanium is due to a tight, semiconducting oxide layer, formed spontaneously within body fluid. A suited surface energy, a low surface charge and the inhibition of electrochemical reactions with compounds of the extracellular fluid leads to an adsorbed film of conformational unchanged proteins - one precondition-for biocompatibility.

For further improvement of materials for orthopaedic or dental implants, biocompatible surfaces are chemically modified, to direct the adsorption of proteins, stimulating the adhesion of load bearing cells, like osteoblasts. In respect, fibronectin and vitronectin serve as model proteins.

The modification is performed by dip-coating with a sol consisting of synthesised titanium or zirconium-alkoxide derivatives in alcoholic solution. The alkoxide precursors react with organic molecules, like amino acids, short peptides or polycarboxylic acids with the advantage of a wide selection of functional groups, like thiol, amino, carboxylic acid or hydroxy. At least one of the functional groups of the reacting molecule is not involved with the complexation of the precursors. After gelation the resulting sol-gel-coatings have adjusted biological surface characteristics.

The method described is applied to titanium samples, which are preliminarily heated to 700°C to create a dense titanium oxide layer. The coatings are characterised by FTIR-spectroscopy using diffuse reflection techniques and tested molecular biologically to prove the selective protein adsorption.

BIODEGRADABLE SILICA FIBRES FROM SOLS

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Resorbable materials for medical implants provide a good alternative to conventional metal implants, because they degrade in the body and decompose. A second operation for removal of the implants after regeneration of tissue is unnecessary in this case. The majority of degradable biomaterials are organic polymers such as PLA (polylactid) or PG (polyglycolid), which are already used for small implants in certain bone surgery. The disadvantages of degradable polymers are their low mechanical strength and Young's modulus which do not allow their use for weight-bearing bones. Biodegradable polymers therefore need reinforcements.

Such reinforcement can be biocompatible, biodegradable silica gel fibres, which were successfully prepared by a sol-gel route. We have developed a novel three-step synthesis using TEOS, EtOH, H₂O and HNO₃ which leads to spinnable, homogeneous sols. A comparative study of particle growth and rheological behaviour reveals the structure of the sols, consisting of particles with radii up to 2.5 nm that form a non-covalent, supramolecular network with a defined rheological behaviour.

This allows a continuous multifilament drawing process with spinning velocities of about 2.5 m/s. Suitable atmospheric parameters during the spinning process lead to round, homogeneous and dense silica fibres with diameters from 15 to 20 µm. A drying process at 20°C which converts the fibres consisting of $[\text{Si}(\text{OEt})_x(\text{OH})_{2-x/2-y/2}]_n$ to "silica" fibres $[\text{SiO}_{1.9}(\text{OH})_{0.2}]$ is necessary to strengthen the fibres. This conversion is monitored by IR, NMR and thermoanalysis. The fibres have a tensile strength up to 300 MPa with Young's modulus up to 20 GPa. Dissolution tests of these fibres show dissolution rates between 10 nm and 100 nm fibre-radius per day.

Using the injection molding technique, the fibres were embedded into PLA matrices. Toxicological results will also be presented allowing to evaluate the potential of the silica fibres as medical material.

CP7

**PRODUCTION OF VALUABLE DRUGS FROM PLANT CELLS
(CATHARANTHUS AND TAXUS) IMMOBILISED BY HYBRID
SOL-GEL SiO_2**

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The production of complex metabolites from cellular cultures of superior plants can be improved by industrial methods exploiting the advantages of an immobilised cellular load. This approach may be the unique option in case of large scale production of valuable drugs such as taxanes and Catharanthus alkaloids, which can be extracted or can hardly be prepared by artificial chemical synthesis.

Cell suspension cultures of mentioned species are inoculated on porous supports, such as polyester disks obtained from a sponge-like blanket; cells are grown till a dry cellular mass of $0,02\text{g}/\text{cm}^3$ of support. This supported cellular dispersion is reacted with a mixture of $\text{Si}(\text{OEt})_4$ and $\text{CH}_3\text{SiH}(\text{OEt})_2$, according to the Biosil method, providing the formation of a 1–3µm layer of hybrid SiO_2 , directly laid on the living cellular surface. This permanent and porous deposit does not prevent from cellular viability and metabolite release.

Production of Catharanthus total alkaloids is shown in the figure, with reference to free cells of the same cellular line, for some production cycles of the same cellular mass.

The same method applied to Taxus B. allows the continuous production of metabolites, being Taxol and Baccatin III the major products.

These results can be discussed in terms of effectiveness of the hybrid SiO_2 deposit to control and increase the productivity of the immobilised cellular load.

SOL-GEL CARRIER SYSTEMS FOR CONTROLLED DRUG DELIVERY

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To evaluate the suitability of metal oxide gels as carrier matrix in controlled release systems, the calcium antagonist Nifedipin (dimethyl-[1,4-dihydro-2,6-dimethyl-4-(2-nitrophenyl)-3,5-pyridine-dicarboxylat]) was embedded in different modified silica gels.

For this, the Nifedipin (I) was dissolved in different silica sols prepared by acid hydrolysis of $\text{Si}(\text{OEt})_4$ or $\text{Si}(\text{OEt})_4:\text{MeSi}(\text{OEt})_3$ mixtures in $\text{EtOH}/\text{H}_2\text{O}$. After gelation by neutralisation and heating the gels were dried, ground and sieved. The liberation of the embedded (I) into water was determined by soaking of the sieve fractions under standard conditions in a Paddle device combined with HPLC analysis. It was shown that the releasing behaviour of Nifedipin within the silica matrix can be controlled by the sol-gel technique to a high degree:

- The liberation of (I) bulk composites increases reverse proportional with decreasing grain size
- The releasing rate decreases with increasing amounts co-hydrolysed $\text{MeSi}(\text{OEt})_3$. Bulk products and films (by coating of (I) containing sols onto cellite foils) show a different dependence on the $\text{MeSi}(\text{OEt})_3$ content due to different mechanisms of the gelation and drying process
- The liberation of (I) can accelerate by added penetration agents like sorbitol and retard by some polymeric compounds like PEG 600.

Kinetic analyses point to a diffusion-controlled liberation mechanism, i.e., the rate depends on the diffusion coefficient of (I) within the silica pores and their diameter.

ENCAPSULATION OF MICROBIAL CELLS INTO SILICA GEL

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Recently it has been shown that whole cells immobilised in sol-gel preserve their full metabolic activity. This work deals with changes in cells respiratory and phenol degradation activity caused by immobilisation into silica gel. Silica layers with cells were prepared by withdrawing a polyester mesh from the suspension of cells in prepolymerised tetraethoxysilane (TEOS) or colloidal SiO_2 . Connecting the cells in silica layers with an oxygen electrode made possible for us to study the influence of the immobilisation procedure on microbial respiration. Comparing the prepolymerised TEOS and colloidal SiO_2 as immobilisation materials, TEOS had a significantly higher stress impact on cells respiration activity. Overcoating the cells in silica layer with an additional pure silica layer, made of prepolymerised TEOS, resulted in extended pre-conditioning time. Encapsulation in organic prepolymer - polyurethane - in comparison with immobilisation by sol-gel process impaired cells what decreased the phenol degradation rate. Growth of cells immobilised in silica layers was observed by optical microscope for one week.

The cells in silica gel (biological-probe) connected with an oxygen electrode (transducer) was used as a biosensor. The signal output of the sensor made of cells in prepolymerised TEOS and colloidal SiO_2 layers was constant for 3 and 5 days respectively. A linear response of the probe was observed in the range of phenol concentration from 2 to 10 mg/l. Advantages of the sol-gel immobilisation technique for construction of biosensors are its simplicity, and the fact that it is not necessary to overcoat the cell layer on the electrode with an additional dialysis membrane.

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**THE APPLICATION OF SOL-GEL IMMOBILISATION TECHNIQUE
FOR PREPARATION OF HEAVY METAL BIOSORBENT FROM
YEAST CELLS**

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The encapsulation of biomaterials by sol-gel process for fabrication of biosorbents can be foreseen from chemical stability and high porosity of silicates from gels. In this work we compared biosorbents obtained by encapsulation of polysaccharide parts of waste brewing derived silicates and in organic polymers.

Biosorbents were prepared by mixing crosslinking-agents - organic or siliceous - with dried cell envelopes. Siliceous prepolymers have been synthesised via transesterification and hydrolysis from tetraethoxysilane (TEOS) and methanol. Dried monoliths with and without biomaterial were characterised by determination of surface area and distribution of pores.

Sorption of Cd, Cu and Ag by biosorbent granules (0.25–0.6 mm) was tested in batch and in packed column. The sorption behaviour of biosorbents was investigated by electron microprobe analyser and described by Freundlich and Langmuir isotherm. The biosorbent prepared by transesterification of TEOS showed higher sorption capacity than the biosorbent crosslinked with epichlorhydrine (the most effective crosslinking organic agents).

The influence of immobilisation procedure, surface area, distribution of pores, covalent bonding with biomaterial on preservation of sorption capacity of biomass immobilised by encapsulation in sol-gel derived matrix was discussed.

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CP11

**SOL-GEL IMMOBILISATION GLUCOSE-OXIDASE -
CALORIMETRIC INVESTIGATIONS OF ENZYME ACTIVITIES**

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The calorimetric approach offers a rapid, uncomplicated opportunity to determine and compare enzyme activities.

We used the Enzyme Thermistor, a flow microcalorimeter, to estimate the influence of several additives and precursors to the efficacy of sol-gel immobilised glucose-oxidase. For the investigations dried xerogels and films on different carrier materials were prepared.

It could be shown that in the flow-injection mode peak heights and area are correlating with the activity of immobilised enzymes.

Using tetraethoxysilane as precursor of the enzyme carrier gel the enzymatic activity decreases slowly in the course of time. The addition of glutardialdehyde, veratryl aldehyde or aminocaproic acid to the sol creates higher enzyme activities in the silica gels. The influence of additive concentration to the activity of the entrapped glucose-oxidase was investigated.

Furthermore sol-gel materials can be optimised via precursors with functional groups (RSi(OR')_3). Aminopropyltriethoxysilane gave interesting results.

THERMAL AND TEMPORAL AGEING OF SILICA GELS IN MONOMER SOLUTIONS

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Silica aerogel is a nanostructural material with porosities up to 99.8% with an open structure and a large inner surface area (500–1200 m²/g). The great interest for silica aerogels is mainly due to the materials excellent heat insulating properties. However, for this application it is necessary to circumvent the high costs and risk of supercritical drying and in recent years processes for preparing monolithic aerogels by ambient pressure drying have been developed. In previous work, we have shown that gels can be strengthened and stiffened by providing new monomers to the alcogel giving xerogels dried at ambient pressure with similar properties as aerogels. The new monomers are provided through ageing the wet gels in a solution of monomers. During this ageing, the nanostructure of the wet gels will be altered which is also of interest for design of dried gels with desired properties.

However, for our previous work rather expensive alkoxide precursors have been used for the wet gel preparation as well as for the ageing solution. The present work elucidates the possibilities to obtain aerogels by drying at ambient pressure using cheaper precursors than the alkoxides i.e. water soluble sodium silicate (water glass). The strength and stiffness of the wet gels will be reported as well as the properties of the ambient pressure dried gels.

DP2

SYNTHESIS AND CHARACTERISATION OF AEROGELS USING DIFFERENT SOLVENT EXTRACTION METHODS

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In view of the importance of aerogels (both the inorganic and organic) for several scientific and technological applications, the experimental results on the effect of various supercritical drying methods such as high temperature ($\approx 260^\circ\text{C}$) solvent, low temperature liquid CO_2 and direct supercritical CO_2 ($\approx 38^\circ\text{C}$) evacuations on transparency, monolithicity and other physical properties of silica and resorcinol-formaldehyde (RF) aerogels, are reported. The aerogels were prepared by sol-gel polymerisation followed by supercritical solvent extraction. It has been found that the high temperature solvent evacuation method resulted in powdered RF aerogels and shrunk (2 to 5%) silica aerogels, whereas liquid CO_2 exchange and supercritical extraction gave monolithic but opaque RF and translucent SiO_2 aerogels. The best quality of both the aerogels in terms of monolithicity, transparency ($>90\%$ for SiO_2 and $>60\%$ for RF) and large surface area ($> 900 \text{ m}^2/\text{gm}$ for both the aerogels) with negligible shrinkage ($<1\%$), were obtained using direct supercritical CO_2 solvent exchange as well as extraction. However, it has been found that the high temperature solvent extraction method is the fastest (<12 hours) compared to the CO_2 methods (>36 hours), to obtain the aerogels. The aerogels have been characterised by density, refractive index, BET analysis, optical transmission and scanning electron microscopy techniques. The results have been discussed by taking into account the porosity, permeability and drying stresses.

THE SUBCRITICAL PREPARATION OF AEROGELS ON THE BASIS OF SODIUM WATERGLASS

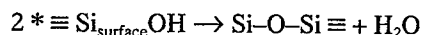
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In general, aerogels are prepared by drying under hypercritical conditions with respect to alcohol or CO₂. In this way, the solid matter framework of the wet gel is conserved.

A procedure will be presented which involves working below the hypercritical temperature and pressure and which conserves the structure of the wet gel as well.

The fundamental step of the subcritical preparation of aerogels is the prevention of the condensation reaction of the $\equiv \text{Si}_{\text{surface}}\text{OH}$ groups at the inner surface of the gel during drying. The reaction



is avoided by occupation of the surface with a stable chemical group which does not condense.

An esterification $\equiv \text{Si}_{\text{surface}}\text{OH} + \text{ROH} \rightarrow \equiv \text{Si}_{\text{surface}}\text{OR} + \text{H}_2\text{O}$ is a simple method of sealing the inner surface. This reaction is an equilibrium reaction.

The equilibrium is shifted in favour of $\equiv \text{Si}_{\text{surface}}\text{OR}$ by removal of the water.

An ion exchanger was applied to a sodium water glass solution (Na:Si=0.6; Si concentration 2-8 mol/l) in order to achieve a substitution of sodium ions by protons. The gelation was carried out in the range of pH 5-6. The solvent exchange take place after a short ageing. Because the time required for each step scales with the square of the smallest dimension granules of the wet gel having the size in the range of 3-6 mm were used. The best esterification was obtained by use of n-butanol.

Densities of the aerogels prepared under subcritical conditions lower than 0.1 gcm⁻³ were got.

The changes in the structure of the gel during all procedure steps are studied by small angle X-ray scattering, transmission- and scanning electron microscopy.

DP4

EVOLUTION OF THE ACOUSTICAL PROPERTIES OF SILICA ALCOGELS DURING THEIR FORMATION

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Silica aerogels, highly porous materials of very low density, are nowadays the object of many studies. Since they have been considered as a good candidate for quarterwave layers on ultrasonic transducers, it becomes essential to well know the structure and the mechanical characteristics of the aerogels. From this point of view, it seems interesting to enquire into their formation process.

The first step consists of the formation of a silica alcogel, obtained by dissolution in an alcohol of an organic silica compound, the tetramethoxysilane (T.M.O.S.). After hydrolysis, a spontaneous polymerisation in microscopic clusters occurred, driving finally to a solid system whose pores are filled with alcohol. The second step, allowing to replace in pores alcohol by air without collapsing the structure, is executed by supercritical drying.

The formation of the alcogel has been studied in emission-reception in the frequency range 20 -220 kHz with the help of longitudinal and transverse transducers, during the sol-gel process.

These measures allow to visualise the evolution of the velocities and attenuations of longitudinal and transverse waves propagating in the material:

- a transverse wave appears immediately, with a very weak amplitude, that is clearly amplified after 90 min, indicating the passage of a fluid structure (sol) to a viscous structure (gel);
- in the first quarter of an hour, the longitudinal velocity decreases and stabilises after;
- spectrograms of signals at different times allow to study the type of dispersion into the alcogels.

The first point confirms the gel solidification; the second allows to follow the physical characteristic changes that happen, linked to hydrolysis and polycondensation: it becomes possible to display the emergence of alcohol and water during the transformation. We will present experimental results obtained for different concentrations of the organometallic precursor, different velocities of gelification as well as implications of measures for phases study of the aerogels derived from the present alcogels. The third point leads to study the links between frequency, velocities and attenuation not even in alcogels, but also in aerogels; the results will be compared with the predictions of Biot's theory for porous media.

We will there discuss differences linked to the fluid and especially the fact that the same structures conduct in the case of alcohol to velocities of propagation always superior that in the fluid while one obtains for the air velocities up to four inferior times.

FRACTURE OF AEROGELS: CRACK PROPAGATION SPEED AS A FUNCTION OF THE STRESS INTENSITY FACTOR

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In previous works, dynamic fatigue tests calculated that in an aqueous environment (50% HR), « as prepared » aerogels, which are known to show an hydrophobic behaviour, did not have any slow crack propagation. After an oxidation treatment aerogels became hydrophilic and exhibit then, a stress corrosion phenomenon.

However, behind the dynamic fatigue method simplicity, an approximation is implicitly admitted which can introduce some non negligible errors: we assumed a power law dependence and the limits of this power law dependence are not defined (they depend on the defect size).

Moreover, stress corrosion parameters as A and n are not sufficient to completely characterise the brittle behaviour of materials. Slow crack propagation appears only when stress intensity factor reaches an under limit (K_{II}). So its study is particularly of interest to prevent stress corrosion.

In this work, we have precisely determined the crack propagation speed as a function of the stress intensity factor (K_I - V curve) by the DCDC (Double Cleavage Drilled Compression) technique. Experiments on oxidised aerogels confirm the results previously published but in the case of « as prepared » aerogels, a slow stress corrosion phenomenon can be measured which put in evidence the interest of this method.

DP8

AEROGEL - A PIONEER MOULD MATERIAL FOR CASTING AND CRYSTAL GROWTH?!

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The application of aerogels as mould materials for the investigation of solidification of metal alloys and crystal growth is based on their unique properties which are distinct from the properties of conventional mould materials.

Their extremely low thermal conductivity leads to a nearly one-dimensional cooling and solidification since it offers the possibility to reduce drastically radial heat losses, irrespective of those due to radiation. However exactly this addition together with the optical transparency of silica aerogels lead to the possibility to measure temperatures at the sample surface with optical methods with high space and time resolution. Series of experiments carried out by the authors et al. showed that metallic alloys and semiconductors do not react chemically with silica aerogels. Today the crucibles are shaped mechanically from sheets of 20×20×3 cm provided by AIRGLASS AB. This production method has advantages and disadvantages which will be outlined. For future experiments also aerogels based on alumina, carbon or zirconia would however be of particular interest for solidification of e.g. turbine blades and crystal growth of compound semiconductors (e.g. GaAs, InSb). Because their temperature range for operation will probably be higher than that of silica aerogels (800°C).

The paper will especially address with respect to recent experimental evidences the potential aerogels could offer for laboratory and industrial solidification processes as well as growth of semiconductors. The potential could even be broader if aerogels stable at high temperatures in arbitrary shape could be provided on an industrial level.

These principles of the new techniques are treated in this presentation.

MERCURY POROSIMETRY APPLIED TO LOW DENSITY XEROGELS

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Xerogels contain small size pores (generally less than 25 nm). They have a high density and a large resistance to compression. During a mercury porosimetry experiment, they are intruded by mercury.

Aerogels are characterised by large size pores, a low density and a weak resistance to compression. Submitted to the mercury pressure, they are not intruded by mercury, but they shrink or collapse. In a previous publication, we have shown that the pore collapsing of aerogel is irreversible and follows a buckling law. At mercury pressure P , all pores of size L larger than $KP^{-0.25}$ are collapsed and pores of size smaller stay unaltered. If the K constant characteristic of the material is known, the pore volume distribution can be obtained.

Drying, at room temperature and pressure, of gels synthesised with TEOS leads generally to xerogels. Additions of amino-ethyl-amino-propyltrimethoxysilane in small amount with the TEOS improves the resistance of the mineral skeleton of gel and limits the shrinkage during the solvent evaporation. The density of such a material, called low density xerogel is about 0.3 g/cm^3 which is intermediate between xerogels and aerogels.

Submitted to mercury porosimetry, these materials have a behaviour intermediate between xerogels and aerogels and exhibit a hybrid curve with a sudden slope change corresponding to a change of mechanism from buckling at low pressure to intrusion at high pressure.

The pressure at which the change of mechanism occurs, leads to an easy and accurate determination of the K characteristic of the sample. The representation of K in function of the particles size, measured by TEM, shows a proportionality which confirms the buckling mechanism as described by the Euler's law.

PARAMETERS INVOLVED IN THE SOL- GEL TRANSITION OF TITANIA IN REVERSE MICELLES

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An attractive way for the synthesis of titanium dioxide nanoparticles and gels is from the hydrolysis of titanium alcoxide precursors in reverse micelles. The size and structure of water cavities inside micelles is determined by the surfactant structure, the water to surfactant ratio, and temperature. The addition of a titanium all oxide to these systems leads first to the formation of nanoparticles followed by gelation. The kinetics of the sol - gel transition is complex and depends on the size and the structure of water cavities as well as on the alcoxide and the nature of the organic phase.

Here we present results for the sol - gel kinetics of titania at 30°C in micellar systems formed by either ionic and non-ionic surfactants, with different water/surfactant ratio in the 1-7 water pH range. Linear and nonlinear C_6 to C_{12} alkanes were used as continuous media. Titanium butoxide and isopropoxide were employed as precursors for different alcoxide/water ratio. The kinetics was monitored by turbidimetry at 800 nm.

The sol - gel transition depends on the composition of the continuous medium, being slower as the chain length decreases and for the more ramified alkanes. Alcoxide precursors and pH affect the kinetics in the same way that titania obtained in aqueous media.

The chemical nature of the hydrophilic part of the surfactant molecule, ionic and non ionic, interacts with the water cavities and the hydrophobic part is located in the continuous medium This arrangement forms the water cavity shell. The kinetics of the sol-gel transition depends stongly on the structure of this shell being slower for the non-ionic surfactant (Triton[®], X100) than for ionic surfactant (sodium dioctyl sulphosuccinate, AOT).

**MICROSTRUCTURAL DIFFERENTIATION BETWEEN THE GREEN
AND TURKISH BLUE SOLID SOLUTIONS OF V IN ZIRCON
LATTICE OBTAINED BY SOL-GEL PROCESS.**

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Vanadium forms two types of solid solutions in zircon: a Turkish blue coloured based on V^{4+} and F^- ions entering in $ZrSiO_4$ lattice, and a green solid solution due to zircon doped by both V^{4+} and V^{5+} ions. Normally, proceeding without fluoride addition and by sol-gel process, a green material is obtained at low firing temperatures, but a blue solid solution is stabilised at high temperatures. Blue solid solution becomes an important commercial ceramic pigment, and their greenish behaviour must be avoided in industrial manufacture.

In this sense, operating in aqueous media and with fluoride presence, it is possible to allow the green solid solution simply altering the adding order of zirconia and silica precursors or varying them. In effect, when a chelated NH_4VO_3 in 0.5 M aqueous tartaric acid solution, continuously stirred, is impregnated by zirconia during an hour and neutralised to pH=6 by concentrated NH_3 dropwise, a deep blue turquoise is obtained when the dried sample, is milled with quartz and fluoride mineralisers and fired at 750°C/2h. In the other hand, if quartz is changed into colloidal silica, or zirconia into $ZrOCl_2 \cdot 5H_2O$ a deep green colour is obtained.

In order to analyse the microstructural differences between green and Turkish blue solid solutions, the chelated samples has been compared with the solid solutions obtained by hydrolysis-condensation of a mixture of prehydrolysed TEOS, $VO(acac)$, and $Zr(IV)$ n-propoxide: adding fluoride (blue) and without addition (green). IR spectroscopy, DRX, V etching analysis, SEM-EDX technique and lattice parameters measurements has been performed.

DP13

**STUDY OF THE INFLUENCE OF ALKALINE IONS ON THE STRUCTURE
OF THE SILICATE ENTITIES IN SILICO ALKALINE SOL AND OF THE
SILICO-CALCO-ALKALINE GEL.**

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The concrete is a porous material constituted of aggregates immobilized in a cement paste. The interaction between these aggregates, containing reactive silica, and various ions present in the interstitial solution of the concrete (hydroxide, alkaline, calcium...) induces the formation of calcium alkaline silica gels (alkali-reaction) which could thereafter induce the cracking of the concrete. In our laboratory, system is simulated by destabilisation of alkaline silicate sols by a salt of calcium (Ca(OH)_2 portlandite). In sols, the degree of polymerisation and ionisation of silicate oligomers, at constant silica concentration, depends on the molar ratio ($R_m = [\text{SiO}_2]/[\text{A}_2\text{O}]$ with $\text{A} = \text{Li, Na or K}$) and on the alkaline ion. The distribution of the silicate entities present in sols is determined by ^{29}Si NMR, according to the assignment established by Knight, in function to these two parameters. The degree of connectivity of silicate entities in sols increases with the molar ratio (R_m). In the case of R_m higher than 2, the lithium allows to obtain a state of condensation more important than in the case of the sodium and the potassium. After addition of calcium ions in sols, aggregation takes place by condensation of silanol groups that form siloxane bonds (SiOSi) leading to a gel ($R_m > 2$). In the case of R_m lower than 2, as entities of sol were less polymerized than for the $R_m > 2$, a precipitate is formed instead of a gel. According to Iler and works on ^{43}Ca NMR, calcium ion allows bringing together two silicates entities and then leaves the place to a siloxane bond. It is going therefore to play the role of a "catalyst". In order to study the gels structure, Small Angle X-ray Scattering (LURE) and Elastic Light Scattering (LRRS) experiments have been realised. The kinetic of gelation has been followed in situ. The spherical particle model of Guinier applies in our case and allows to obtain the average diameter of scattering particles and their number. In these two observation windows (SAXS and ELS), the system tends to an equilibrium state even after the gel point. The particles of diameter in the order 15 to 35 nm (SAXS) seem to feed the bigger ones, which diameter in the order 150 to 350 nm (ELS).

PREPARATION AND CHARACTERISATION OF FORSTERITE (Mg_2SiO_4) XEROGELS

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Mg_2SiO_4 gels were prepared from alkoxide precursors, and the formation of the forsterite crystal phase was studied after heat treatments up to 1200°C.

Gels with forsterite stoichiometry were prepared by mixing solutions of partially pre-hydrolysed TEOS in 2-methoxyethanol with solutions of $\text{Mg}(\text{OEt})_2$ in 2-methoxyethanol. The solutions were then hydrolysed using excess H_2O . The resultant gels were dried to form xerogels, which were subsequently powdered. These powders have been characterised using infrared spectroscopy (FTIR), thermal analysis (DTA and TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface area analysis. Aerogels were also made by drying wet gels supercritically.

FTIR indicated that the amorphous gels contained Mg–O–Si bonds, suggesting a high degree of homogeneity and not a two-phase powder of MgO and SiO_2 . DTA and XRD showed that forsterite began to form at 790°C, and at 1000°C the powders were predominantly crystalline. However, at 1200°C a significant amount of MgO was detected, along with trace amounts of enstatite (MgSiO_3). TEM showed angular primary particles, with sizes ranging from 200 to 500 nm, which formed large agglomerates up to 2 μm in size. The agglomerate size increased to a maximum of 6 μm when heated at 1200°C. Surface areas of the xerogel powders ranged from 50 to 120 m^2g^{-1} compared to values of around 320 m^2g^{-1} for the aerogels.

DP15

VARIABLES IN NONHYDROLYTIC ALUMINA XEROGELS SYNTHESIS

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Nonhydrolytic sol-gel processes of aluminium chloride and aluminium bromide with isopropyl ether and aluminium sec-butoxide were performed at various temperatures. Based on the Arrhenius type variation of the gelation time with temperature, activation energies for the gelation were found to be in the range 19–25 Kcal/mol range. The energies were found to be sensitive to the nature of the aluminium ligands and the chemical scheme. Small angle X-ray scattering (SAXS) of sols from the $\text{AlCl}_3/\text{P}^i_2\text{O}$ system shows unique development of a fractal like structure with nanometer scale order, demonstrated by discrete peaks in the SAXS data. A fractal dimension $D=1.64$ was found. An aggregation scheme is proposed to explain this phenomenon. Due to the polymeric network of the primary particles and the high activation energy for the gelation process, the xerogels morphology is highly sensitive to the drying process. Mass or surface fractals can be obtained depending on the drying procedure used. Xerogels dried at room temperature followed by heat treatment at 150°C show closed porosity which is reopened after calcination at 650°C .

**EFFECT OF COMPOSITION ON THE GLASS-FORMING TENDENCY
OF BARIUM ALUMINOSILICATE GELS DERIVED FROM METAL
ALKOXIDES.**

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Barium aluminosilicate (BAS) glass-ceramic is a useful matrix material for fibre- or whisker-reinforced refractory glass-ceramic matrix composites. The glass-forming characteristics of BAS gels are important to the development of the materials.

The effect of composition on the glass-forming tendency of barium aluminosilicate gels derived from metal alkoxides with compositions near the theoretical composition of barium feldspar was studied. Prepared by hydrolysis and polymerisation of metal alkoxides of aluminium, barium, and silicon, the gel powders were cold pressed into tablets, which were heat treated at 950°C for half an hour and analysed for glassy and crystalline phases through X-ray diffraction. The coordination status of aluminium in the gel glasses was determined by Raman spectroscopy. Results indicated that, in the experimental range, higher SiO₂ content and higher BaO/Al₂O₃ ratio were advantageous to glass formation. According to the behaviour of each component in the glass structure, a criterion for glass formation under the experimental conditions was established as the follows:

$$(0.5b+1.5-2y)/(y+s(1+b))/(200-2s) < C$$

where b is the BaO/Al₂O₃ ratio, s is the mol percentage of SiO₂, y the fraction of four-coordinated aluminium over the total amount of aluminium, and C is a constant for a definite experimental condition. The criterion showed good fitness with experimental results.

DP17

**SYNTHESIS AND CHARACTERISATION OF Al_2O_3 - TiO_2 BINARY
OXIDES PREPARED BY THE SOL-GEL METHOD**

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In the present study sol-gel Al_2O_3 - TiO_2 binary oxides were synthesised at 10 and 20 wt% of titania content. The sol-gel binary oxides were prepared using aluminium tri-sec-butoxide and titanium isopropoxide as starting metal alkoxides, likewise acid (HCl, pH3) and base (NH_4OH , pH9) preparations were obtained.

The specific surface area of the samples determined by the BET method, show that the samples are mesoporous ones and with BET areas between 250 and $380 \text{ m}^2/\text{g}$.

By FT-IR spectroscopic was observed the characteristic band of hydroxyl groups. The band is broad and of high intensity and is assigned to the O-H stretching vibration frequency and its intensity is maintained even when the oxides were treated at temperatures higher than 500°C . Ammonia and CO_2 thermodesorption study show that acid and basic sites co-exist in both preparations. The oxides were tested in the CO and NO non selective reduction and ammonia is obtained as main product. This unexpected result is explained by a mechanism in which the hydroxyls bonded to the mixed oxides acts as reducing agents. Applications of the sol-gel Al_2O_3 - TiO_2 binary oxides as whascoat of ceramic monoliths is discussed.

ROOM TEMPERATURE DENSIFICATION OF AEROGEL BY ISOSTATIC COMPRESSION

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An alternative to sintering for densification of aerogels is compaction by isostatic compression at room temperature. To improve and control the amplitude of the volumic shrinkage during the compression, it is important to know precisely the different mechanisms responsible for the densification. A porosimeter is used to isostatically compress the aerogel and, at the same time, to measure the amplitude of the shrinkage.

Previous works have investigated the influence of physico-chemical parameters such as the chemical nature (hydroxylated or esterified) of the surface. In this study we focus our study on the time dependent mechanisms such as densification kinetics and relaxation effects. These two mechanisms respectively increase or decrease the total densification.

The densification kinetics are revealed by two properties: the volumetric shrinkage and the stiffening with time. Hydroxylated and esterified aerogels, which exhibit at low pressure almost the same shrinkage evolution, have a completely different behaviour as far as the stiffness is concerned. The hydroxylated aerogels stiffen during compaction while the elastic bulk modulus of esterified aerogels decreases. This result shows that shrinkage is due to two antagonistic mechanisms: the formation of new siloxane bonds which freezes the strained network but also the breakage of links between clusters which allows the restructuring of the solid phase.

Relaxation is attributed to the disentanglement of the clusters when the pressure is released (40% of the shrinkage can be recovered). However, if during the compression run a large number of siloxane bonds is formed (compression run + a kinetic step), relaxation is not observed.

POROUS SILICA OBTAINED FROM BIODEGRADABLE AND BIOCOMPATIBLE INORGANIC-ORGANIC HYBRID MATERIALS

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Porous materials, such as silica are emerging as a new area of great technological and scientific interest. Materials with tailor-made pore shapes and sizes are particularly important in applications such as shape-selective catalysis, molecular sieving, chemical sensing, and selective adsorption. Porous silica can be obtained from the supercritical drying of highly crosslinked silica gel prepared by sol-gel process. However, the final texture of these aerogels depend on several independent parameters, such as the amount of catalyst, the dilution of the gel, drying process, etc. Obviously, is not easy to tailor the pore shapes, size and size distribution by this method which is particularly important in the potential applications. The other method is template-based approach to the preparation of porous silicas in which porosity is created by removing the incorporated template from silica network. The tailor-made porosity is expected by control of the incorporated template.

We have reported a novel biodegradable and biocompatible inorganic-organic hybrid materials prepared by the sol-gel process. Poly((-caprolactone) (PCL), well-known for their biocompatibility, permeability and biodegradability, has been incorporated into the silica network. In this paper, we study the texture of porous silica obtained by removing the PCL. The PCL functional end-groups, the number of functional end-groups per PCL chain and the PCL molecular weight and content, were varied. This material has been characterised by nitrogen adsorption-desorption, small angle X-ray scattering and atomic force microscopy.

EFFECTS OF ORGANIC ADDITIVES ON THE GELATION PROPERTIES OF TETRAETHOXYSilANE SOLUTIONS

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This study has arisen from the need to understand the effects of several variables on the characteristics of hydrolysed tetraethoxysilane (TEOS) solution mixtures, as precursors for the production of organic-inorganic hybrids based on polyimide-silica systems, for use as matrices for carbon fibre composites.

A special feature of these systems is the use of organofunctional trialkoxysilanes as coupling agents for the two phases and for controlling the resulting morphology. In the production of composites the fibres have to be pre-impregnated with a solution of the matrix material, whose gelation characteristics have to be controlled in order to be able to perform the subsequent moulding operation.

Owing to the very large surface area to volume ratio of the matrix solution in fibre prepreps it is particularly difficult to control the rate of evaporation of essential components, such as the solvent and the acid used to catalyse the hydrolysis and to regulate the condensation reactions of the siloxane component. Another difficulty arises from the fact that any additional components, such as coupling agents and organic precursors, may interact with the catalyst and bring about premature gelation of the alkoxy silane component.

The parameters that were investigated in this study are the following:

- Volumetric fill-factor of the closed container used to prepare the precursor alkoxy silane solution, taking into account also the exposed area to volume ratio.
- Nature of the solvent, i.e. DMF and ethanol
- Nature of the acid, i.e. HCl and HNO₃
- Type of coupling agent, i.e. various organofunctional trimethoxysilanes
- Nature of the polyimide precursor, i.e. polyamic acid and an acetylene terminated aromatic isoimide oligomer.

The changes in rheological behaviour of the siloxane solution and the morphology of the resulting ceramics were used to monitor the effects of the above variables.

**PREPARATION OF SACCHARIDE-SILICA COMPOSITES BY
SOL-GEL METHOD AND ITS APPLICATION FOR OPTICAL
RESOLUTION OF METAL CHELATE COMPOUNDS.**

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A novel organic-inorganic composite was prepared by the sol-gel process, which is via hydrolysis and condensation process of tetraethoxysilane (TEOS) reacted with a saccharide. During the process, ethoxy groups of TEOS were replaced with hydroxy groups of a saccharide, consequently, saccharide molecules were combined with silica through their hydroxy groups. Samples obtained at different reaction conditions were applied for optical resolution of metal chelate compounds. As a result, the composites showed good ability in optical resolution. The resolution performance of the composites was affected by the amounts of water added for hydrolysis and the saccharide used, respectively. Especially, the amount of water drastically influenced on the optical resolution performance. With the composites obtained at higher $H_2O/TEOS$ ratios, the optical rotary power of metal chelate compound eluted was lower, on the other hand, at lower $H_2O/TEOS$ ratios, that of metal chelate compound eluted was higher. Moreover, three types of the composites with the same compositors were prepared by kneading, impregnation and the sol-gel methods, and their abilities were compared. The sol-gel one showed the best optical resolution. From these results, it was found that the performance of the optical resolution was closely related to the dispersibility of a saccharide on silica.

STUDY OF HYBRID SILICA-POLYETHYLENEGLYCOL XEROGELS BY Eu^{3+} LUMINESCENCE SPECTROSCOPY

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Over the past few years, there has been a great deal of spectroscopic studies in the field of hybrid organic-inorganic materials (Ormocers) doped by rare earths or organic dyes. The luminescent, photocromic and non-linear optical properties of such doped nanocomposites is a promising research field. Nevertheless, there are only few spectroscopic studies on the preparation and structure of hybrid materials. This knowledge should be essential to optimise their properties.

In this work, Eu^{3+} luminescent spectroscopic properties were used in probing the changes in the preparation of such hybrid xerogels presenting covalent bonds between the organic (polymer) and inorganic (silica) phases. The samples have been prepared from mixtures of 3-isocyanatopropyltriethoxysilane (IsoTrEOS), O,O'Bis(2aminopropyl) polyethyleneglycol (PEG) and Europium Chloride (up to 8%mol). The sol-gel transition and the drying have been followed in this complex system as a function of time.

A broad fluorescence band is observed in the visible under UV excitation. This band is not observed in the organic or in the inorganic phase separately. Eu^{3+} emission could be easily followed with continuous and pulsed Xe lamp broad band excitation. During the sol-gel transition no important change has been observed, with Eu^{3+} ions distributed preferentially in the organic phase. With drying, interesting features could be observed. By using Eu^{3+} doped PEG and Eu doped silica xerogels as standards, we could follow the structural evolution in the rare earth ion neighbourhood. Interesting enough, the relative concentration of Eu^{3+} adsorbed at the silica phase increases with solvent extraction, suggesting structural rearrangements not detectable by other technique.

EP5

HYBRID SILICA GEL-POLYTETRAHYDROFURAN THIN FILMS

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Hybrid silica gel-polytetrahydrofuran (PTHF) films have been prepared from tetraethoxysilane (TEOS), under acid-catalysed conditions. Comparison was made with equivalent pure silica gel films.

A parallel investigation was carried out on the ageing solutions and on the corresponding films obtained by spin coating on silicon and glass wafers. Solutions were characterised by FTIR and NMR spectroscopies and films by optical microscopy, FTIR, profilometry. BET surface area measurements and SEM.

In order to explore the chemical interactions between TEOS and PTHF, three routes were rehearsed concerning the addition of the polymer to the initial mixture: simultaneous addition of water, addition of water after a two hour period at 50°C and no addition of water at all. It has been shown that whenever there is water in the system, it is responsible for the hydrolysis of TEOS, no evidence for Si-O-C bonds having been obtained in these cases.

The comparison of ethanol and tetrahydrofuran as solvents showed that the solvent has a determinant effect on film properties: when ethanol is used, the films are thicker, more homogeneous and with better adhesion to the substrate.

Other parameters influencing the film characteristics were also studied, namely initial pH, the polymer molecular weight (650 to 2900 g mol⁻¹) and its concentration (0.01 to 0.06 molar fractions relative to TEOS).

PHOTOLUMINESCENCE STUDY OF FUNCTIONALISED POLYSILOXANE GEL

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Photoluminescent properties of polysiloxane gel functionalised by Polyether Xylylidene (PEX) are investigated. Polymethylhydrosiloxane (PMRS) is used as start material. PMRS was functionalised by conjugated organic polymer via hydrosilylation reaction and deposited by dip-coating method over glass slides.

Photoluminescence spectra were carried out at various λ_{ex} at 2K. The results show that:

- The gel has not modified the structure of the PEX.
- The hydrosilylation reaction have affected the length of the PEX chain. This effect is due to the reaction of Si-H groups with internal double bond of PEX.
- The structure of the system is improved when the PEX is linked to the PMHS.

Radiative energy levels implicated in the photoluminescence phenomenon was evidenced from the recorded spectra.

EP8

SILICA-PDMS SOL-GEL MATERIALS: PROPERTIES AND APPLICATIONS.

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Hybrid organic-inorganic materials are of considerable interest as their properties may bridge the gap between traditional polymers and ceramics. The sol-gel method has several advantages for the preparation of these materials, such as the high purity of starting materials, low temperature processing and the ability to fabricate thin films.

This abstract reports our recent studies of the preparation of composite materials of PDMS and silica using sol-gel processing to fabricate transparent, monolithic xerogels. A range of materials were prepared by crosslinking hydroxy terminated PDMS chains with tetra-alkoxysilanes. Two complementary synthetic procedures were employed: a tin-catalysed condensation and a 'non-aqueous', formic acid cure.

The tin-catalysed route allowed the preparation of composite materials with relatively large amounts of PDMS with a high degree of polymerisation (DP of up to 243). These materials were optically clear elastomers. However, when small amounts of PDMS were used monolithic samples could not be produced.

The formic acid cure allowed the preparation of composite materials with lower concentrations of PDMS with a low degree of condensation (DP = 20-27).

The properties of these materials are different to those of room temperature processed, inorganic sol-gel materials. They are substantially less brittle and more robust than conventional materials, and this makes them suitable hosts for more fragile molecules with interesting properties. Further investigations are under way to examine new applications for these materials.

PROCESSING AND PROPERTIES OF INORGANIC-ORGANIC HYBRIDS CONTAINING VARIOUS INORGANIC COMPONENTS

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Inorganic-organic hybrids containing various inorganic components have been synthesised in order to study the effect of inorganic species on the properties of the hybrids. Al, Ti and Ta alkoxides modified with ethyl acetoacetate were mixed with silanol terminated polydimethylsiloxane (Mw=3000) in ethanol separately. The alkoxides in the solutions were hydrolysed by the addition of water. The hydrolysed solutions were allowed to gel and then heat-treated to yield monolithic hybrids.

The storage modulus of the hybrids around the room temperature depended on the inorganic components. It increased in the order of Al, Ti and Ta. This suggests that metallic element with higher valence can form denser three-dimensional network in the hybrids.

As a result of a stress-strain experiment, the elongation at break of these hybrids was also dependent on the inorganic components. The hybrid containing Ti exhibited the elongation of 300%, which was the highest among them. The interaction between inorganic component and PDMS is considered to be the highest in the hybrid containing Ti.

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EP10

**BRILLOUIN SPECTROSCOPY: A CONTACTLESS TECHNIQUE TO
PROBE THE STRUCTURAL, MECHANICAL AND OPTICAL
PROPERTIES OF ORMOSILS.**

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Monolithic and film-like pieces of ormosils have been obtained from ultrasounds-assisted polycondensation of tetraethoxysilane (TEOS) and polydimethylsiloxane (PDMS). These sono-ormosils were studied by means of high resolution Brillouin and NMR spectroscopies and their textures were analysed from adsorption isotherms and SEM micrographs. The results evidence the occurrence of organic and inorganic phases microseparation in samples with high polymer concentration. Brillouin spectra reveal the influence of the microstructure of these materials on their elastic and optical properties.

On these basis, a three component mechanical model is proposed, which quantitatively explains the observed variations of the elastic constant c_{11} with the molar fraction of dimethylsiloxane in these vitreous systems. Finally, a structural model that accounts for the observed dynamical behaviour was developed.

XEROGEL STRUCTURE AND MOLECULAR GUESTS DYNAMICS

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In the last ten years, there has been an increasing interest for hybrid organic-inorganic materials, in particular for their potential applications in optics. It is now clearly identified that the optical properties depend on the guest chemical and physical environment, which also determine the dynamical behaviour of the molecules.

We have studied the dynamics of various guests, according to their ability to create H-bond with the host matrix. The case of deuterated adamantane ($C_{10}D_{16}$) appeared of special interest, due to its high symmetry and lack of H-bond possibility. The deuterium NMR data provides information concerning the gel topology, which is peculiarly useful when the porosity is closed so that classical picnometry is forbidden. We present here results during ageing and drying of different matrices, with various proportions of TEOS and MTEOS. The molecular probes are introduced before gelation, and NMR relaxation times and linewidths are followed during ageing and drying.

In the case of MTEOS, the relaxation time T_1 informs on the activated molecular reorientations (3 kcal/mol) while the linewidth, dominated by the dipolar broadening with the organic part, reveals the molecular diffusion. The temperature behaviour of the linewidth is striking: a net cross-over temperature around 40°C is observed. This temperature shifts towards higher values as the drying completes. At a low temperatures, the linewidth is almost constant while at high temperatures appears a very strong activation behaviour (18 kcal/mol). This can be due to a cross-over in the translational diffusion from a quasi-1-D to a 3-D regime. It reveals that the guest molecules diffuse in an organic-rich phase which defines a 3-dimensional network. The typical length between connections of this internal network varies with the drying time of the xerogel.

**X-RAY DIFFRACTION STUDIES OF SOL-GEL DERIVED ORMOSILS
BASED ON COMBINATIONS OF TETRAMETHOXYSILANE AND
METHYLTRIMETHOXYSILANE.**

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Ormosils have been prepared in the series TMOS_x . MTMS_{100-x} (where TMOS is tetramethoxysilane; MTMS is methyltrimethoxysilane; x is mol% silane with respect to total silane for $0 \leq x \leq 100$) by means of acid catalysed, sol-gel processing. After drying at 60°C , small bulk samples were obtained of excellent optical clarity. Powder X-ray diffraction patterns, in the range 5 to $60^\circ 2\theta$, were compared with that of fused silica. All of the prepared samples were amorphous. Fused silica exhibits one broad peak, d^1 , centred at the d-spacing $4.12\text{\AA}$. For the TMOS_{100} silica xerogel, the analogous broad peak had shifted slightly, to be centred at $3.88\text{\AA}$; and remained in about the same position as x was decreased for the series TMOS_x . MTMS_{100-x} . In addition, a second, broad diffraction peak, d^2 , was observed for the ormosil series centred at the d-spacing $8.7\text{\AA}$ for MTMS_{100} (i.e. at $x=0$) and increasing smoothly as x was increased, reaching $11.3\text{\AA}$ for $x=70$, and $>11.3\text{\AA}$ for $x>70$. The intensity of d^2 was found to have trebled, relative to the intensity of d^1 , on increasing the organic character of the matrix from TMOS_{70} . MTMS_{30} to MTMS_{100} .

The d^1 peak appearing at about $4\text{\AA}$ for both fused silica and the ormosils is associated with the spacing between silicon atoms connected by means of an oxygen bridge. The Si-O-Si angle for silica xerogels is known to depend upon the nature of the sol-gel processing and is bigger than that of fused silica. We suggest that the d^2 peak is associated with the spacing between silicon atoms attached to methyl groups and may be indicative of channels of methyl groups in the structure.

THIN ORMOSILS FILMS WITH DIFFERENT ORGANICS

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The present work deals with the study of structure, optical and electrical properties of silicate films modified by structure fragments containing different organic groups, as well as with the properties of film-semiconductor interface. The building up of ORMOSILS structure was performed by a cohydrolysis of tetraethoxysilane with different types of alkyl (aryl) substituted alkoxy silanes: methyltriethoxysilane, trimethylethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, allyltriethoxysilane, hexyltriethoxysilane, phenyltriethoxysilane, and diphenyl diethylhexyloxy diethoxy disiloxane. The films were deposited on silicon substrates by spin-on technique. Film structure and its evolution during heat treatment were studied by ellipsometry and IR spectroscopy. Only for methyl- and phenyl-modified silicate films the shrinkage is lower than for silicate ones in the range of annealing temperature from 200 to 500°C. The shrinkage of phenyl-modified silicate film is therewith more than three times lower than of methyl- and trimethyl-modified ones. The presence of single or double C-C bonds in organic chain leads to an increase in the film shrinkage due to its thermodestruction, as it is confirmed by IR data. In the case of phenyl- and methyl-modified silica films this process starts from 500°C and it is accompanied by abrupt film shrinkage. The dielectric constant and the loss tangent of methyl and phenyl groups decrease due to reduction of hydroxyl content and film density. Other groups are not effective due to thermodestruction at low temperatures. The film/semiconductor interface was studied by CV-techniques. Some questions of electronic application of these films are discussed as well. In addition to chemical ways of changing film structures and properties, there exists a physical one performed by deposition conditions. An effect of substrate temperature during the spin-on process on the properties and planarisation characteristics of ORMOSILS layers is discussed as well.

LEACHING OF DYES INCORPORATED INTO ORGANICALLY MODIFIED SILICA XEROGELS

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The leaching behaviour of dyes incorporated into silica based xerogels has been studied. The effects of preparation method, precursor composition and type of dye on the leaching behaviour of dye incorporated were investigated. Xerogels were prepared under acidic conditions with mixtures made of 20 mol% of organically modified silicon alkoxides, $R'-Si(OR)_3$, in $Si(OR)_4$, R = methyl or ethyl, R' = methyl, vinyl, phenyl. The dyes (Solvent Blue 59, Methylene Blue, Thymol Blue sodium salt and Rhodamine 6G) were added at the beginning of the sol-gel reaction. The reaction was carried out using either hydrolysis or acidolysis by formic acid. Dyes incorporated were leached with refluxing ethanol using a Soxhlet extraction procedure to simulate the long term stability of the samples prepared. The amount of dye in the extract was measured with UV/Vis spectroscopy. In addition, selected samples were characterised by N_2 and CO_2 adsorption experiments.

With the exception of a few samples, the amount of dye leached from the xerogels prepared using acidic hydrolysis is smaller when compared to the corresponding samples prepared by acidolysis with formic acid. In addition, with increasing size of organic substituent (methyl < vinyl < phenyl), the amount of dye leached decreases. Comparing the dyes used in this study, it was found that xerogels doped with Thymol Blue sodium salt were most stable against leaching. The relative amount of dye leached is less than 2% for all samples prepared with this dye. This is in contrast with the behaviour of Solvent Blue 59, where the fraction of dye leached out varies between 12 and 95%. These results reflect the influence of dye structure.

Results from nitrogen adsorption experiments show that all samples characterised have about the same average pore diameter, but they differ in total pore volume and BET surface area. With increasing size of the organic residue, the pore volume decreases by an order of magnitude. Therefore, it is concluded that the microstructure of the xerogels prepared can determine the retention behaviour of dyes incorporated during the sol-gel reaction.

HYBRID PIGMENTS VIA SOL-GEL PROCESSING

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The incorporation of organic dyes into inorganic and hybrid sol-gel derived materials is a valuable method for the fabrication of coloured layers for optical applications like filters, recording media, solar energy conversion and non-linear optically active devices. There have been clear hints for a photochemical stabilisation of the organic dyes within glass-like matrices. But so far the underlying mechanisms of degradation or stabilisation have not been fully elaborated. Therefore, our aim was to design and to investigate new techniques to prove the light stability of organic dyes within amorphous solids.

Besides the traditional way of doping sol-gel coatings with dyestuffs, they were also covalently attached to the hybrid matrix and pigments were produced by spray drying sols via conventional techniques. The resulting spherical powders were dried and investigated with respect to their morphological, structural and photochemical properties. Scanning electron microscopy, vibrational spectroscopy, multinuclear NMR experiments and light stability testing were used as characterisation tools.

The results show that uniformly shaped and coloured hybrid pigments can be synthesised by cohydrolysis and condensation of an epoxy functional silane and aluminium-sec-butoxide together with silylated azo and perylene dyes. The spectroscopic results demonstrate the fixation of the dye to the matrix and show the high degree of crosslinking achieved in the nanocomposite. It is anticipated that the rigidity and the residual free volume of the matrix have great influence on the translational, rotational and vibrational degree of freedom of the dye molecule and consequently its reactivity with oxygen. Therefore a higher photochemical stability of the dye is observed within the hybrid matrix compared with solution, organic or inorganic hosts. Additionally the hybrid pigments drastically improve the resistance of the dye against bleeding from thermoplastic polymers.

**LIGNIN-SILICA-TITANIA HYBRIDS AS PRECURSORS OF
Si-Ti-C-O FIBRES**

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We have so far reported the synthesis of hybrid fibres consisting of phenolic resin, silica (SiO_2), and/or titania (TiO_2) components by sol-gel processing, and their conversion into SiC, TiC, or Si-Ti-C fibres by carbothermal reduction under Ar atmosphere. This process is cost effective for fabricating these carbide fibres.

Lignin is one of main components of wood, which is a high-molecular compound consisting of the phenylpropane unit as the building block. A large amount of lignin is present in waste liquor formed on production of pulp. Many efforts have been made to utilise lignin. Its use, however, has not been exploited enough except production of vanillin. Recently, synthesis of carbon fibres from lignin has been demonstrated.

Then, we attempted to hybridise lignin with SiO_2 and TiO_2 components by sol-gel processing with a view to investigating on availability of lignin as a carbon source of Si-Ti-C-O ceramics as well as phenolic resins.

We used lignin prepared by digestion of cedar with acetic acid. Starting solutions with a Si-to-Ti atomic ratio of 1.0 were prepared by dissolving tetraethoxysilane, titanium tetrakis(2,4-pentanedionate), and the lignin in 2,4-pentanedione, followed by the addition of distilled water and sulphuric acid. The solutions were stirred for 20 min at room temperature, and then held at 65°C. The viscosity of the solutions increased with time, giving viscous sols. After 5–5.5 h, they were held at room temperature, from which fibres could be drawn.

In this presentation, characterisation of the obtained fibres and their conversion to Si-Ti-C-O fibres will be discussed.

**ORMOCER COATINGS BASED ON TITANIUM AND
POLY(TETRAETHYLENE GLYCOL MALONATE).**

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Organically modified ceramic oxide coatings based on titanium and poly(tetraethylene glycol malonate) (PTEGM) have been prepared by sol-gel methods. FT-IR spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy were combined to study the composition and structure of the coatings and their variation during subsequent drying and after heat treatments at various temperatures. Results indicate that malonate units (TEGM) in poly(tetraethylene glycol malonate) form a coordination bond with titanium, enabling titania to be distributed homogeneously in the polymer matrix, as evidenced by transmission electron microscopy observations of coatings. Heat treatment promotes the reaction between titanium and dicarbonyl groups. The effects of processing conditions, including concentration of titanium isopropoxide and poly(tetraethylene glycol malonate) in solutions and withdrawal speed, on the structure and thickness of the coatings were investigated. Maximum thicknesses of *ca* 1.2 μm for crack-free coatings prepared by a single dip using solutions with a molar ratio of $[\text{TEGM}]:[\text{Ti}] = 1:1$ were achieved. Conductivity measurements were performed on coatings having molar ratios $[\text{TEGM}]:[\text{Ti}]:[\text{Li}^+] = 5:5:1$, with lithium perchlorate as the electrolyte, giving an ionic conductivity of *ca* $10^{-7} \text{ S.cm}^{-1}$. This coating is of interest as the counter-electrode of electrochromic devices.

ORGANIC-INORGANIC HYBRID MATERIALS BASED ON VANADIUM PREPARED BY A SOL-GEL METHOD

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Poly(tetramethylene oxide), PTMO(Mw~650) and poly(tetraethylene glycol), PEG(Mw~600) were reacted with ethyl acetoacetate, EACAC, by an ester-interchange reaction. The resulting polymers having diketo groups were characterised by FT-IR and GPC techniques. Organic- Inorganic nanocomposites built on vanadium oxide were made by reacting the functionalised polymers and vanadium i-propoxide. Rubbery to brittle gels were obtained by hydrolysis of sols depending on the ratio of alkoxide to the diketo groups, the structures of which were analysed by FT-IR, TGA, DSC, TMA and TEM. The FT-IR spectra of gels showed that the functionalised polymers are reacted with diketo groups built on a V-O-V network. Single dip-coating gave rise to amorphous and crack-free films up to 20 microns in thickness. The coatings based on PEG polymer showed electrochromic behaviour with a colour change upon applying +2 volts in an all solid window : glass/ITO/HYBRID COATING/PEO-LiClO₄/ITO/glass. The ac conductivities of films were found to be 10⁻⁶ S. cm⁻¹ at room temperature by dissolving LiN(SO₂CF₃)₂ salt in the sols.

**SAXS AND TEM INVESTIGATIONS ON THERMOPLASTIC
NANOCOMPOSITES CONTAINING FUNCTIONALISED SILICA
NANOPARTICLES**

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Transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) were used to characterise the morphology of thermoplastic nanocomposites. These nanocomposites were based on a copolymer of methylmethacrylate (MMA) and 2-hydroxyethylmethacrylate (HEMA) as thermoplastic matrix spherical 10 nm silica particles as fillers (2, 5 and 10 vol.%). Depending on the surface modification of the particles, it was possible to control the aggregation tendency of the primary filler particles. In the case of uncoated filler particles large aggregates of about 100 nm in size could be observed by TEM, which show a mass fractal character. For the nanocomposites containing filler particles coated with methacryloxypropyltrimethoxysilane (MPTS), the TEM analysis showed a better dispersion of the filler particles in the polymer matrix. The MPTS-coated particles formed only mean size aggregates consisting of two or three primary particles. In comparison to TEM, the volume weighted particle size distribution calculated from SAXS for the systems with uncoated particles is monomodal and shows particle sizes in the range of primary particles. SAXS analysis on the systems with MPTS coated particles revealed a bimodal size distribution with particle sizes comparable to TEM. For complete information about the morphology of nanocomposites TEM and SAXS analysis have to be combined. Above the critical upper limit of detectable scattering vectors corresponding to particle sizes of about 50 nm SAXS has to be complemented by TEM, whereas in the nanosize range below the critical limit both methods exhibit an excellent correspondence.

EP20

SIZE DISTRIBUTION AND EPR OF SILVER NANOPARTICLES IN SiO₂ MATRIX

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Metallic silver nanoparticles were prepared by the Sol-Gel method in a SiO₂ matrix. The process includes complexation of silicon alkoxides with metal salts, hydrolysis, polycondensation, formation of powder, and subsequent thermal treatment first in oxidising and second in reducing atmosphere. The metal particle sizes were determined both by X-ray diffraction and transmission electron microscopy. These measurements revealed the existence of metallic nanoparticles with diameters between 1 and 20 nm, depending upon the processing conditions. The magnetic properties were investigated with both CW and pulsed electron paramagnetic resonance (EPR) spectroscopy in a temperature range between 4K and 300K. The variation of the CW-EPR signal intensity with temperature can be approximated by the Curie law indicative for the quantum size effect. The temperature dependence of the spin lattice relaxation time (T_1) can give valuable information about the energy spectrum of the particles. The results are discussed taking into account the predictions of Gor'kov and Eliashberg.

CONTROL OF DOPANT ADSORPTION FROM AQUEOUS SOLUTION INTO NANOPOROUS SOL-GEL FILMS

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The adsorption of cations onto silica from aqueous solutions has long been known. In this work such a process is used as a method to dope porous silica-based films, to fabricate multicomponent glasses for applications in integrated optics. The porous films are fabricated using the sol-gel method, as this is particularly adaptable for making glasses with a finely controlled microstructure. The nanometer scale of the pore network gives high surface area and a homogeneous structure on the scale of the optical wavelength. After coating and initial heat treatment, films are soaked in a solution of the desired dopant, with or without a masking layer being first applied, and then given a further heat treatment to consolidate the structure. We have shown that patterned doping with high spatial resolution can be obtained using this method.

We have investigated various dopants, including lead, aluminium and calcium, and have studied in detail the mechanisms controlling the amount of dopant adsorbed. The main methods investigated were: changing the sol-gel chemistry, varying the film processing parameters, and varying the conditions of the doping solutions. The amount and distribution of dopant was determined by several techniques, including ellipsometry, energy dispersion spectroscopy (EDS), and secondary ion mass spectroscopy (SIMS).

FACTORS CONTROLLING OPTICAL LOSS IN SOL-GEL FILMS

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For applications such as integrated optic devices, thin films prepared by the sol-gel process may be used as planar waveguides, which usually have propagation losses considerably higher than optical fibres. Scattering mechanisms (both surface and bulk) appear to predominate.

In order to investigate the influence of thin film roughness on the optical loss, SiO_2 - TiO_2 films of different compositions were deposited by spin-coating onto single crystal Si substrates (previously covered with a SiO_2 buffer layer) by two different sol-gel techniques: the conventional spincoating, which leads to the occurrence of surface striations on the multilayer films (high roughness) and spin-coating under a saturated ethanol atmosphere, which leads to a silica-titania film surface without striations (low roughness). Some of the SiO_2 - TiO_2 waveguides were also covered with a SiO_2 cladding layer prepared by sol-gel and its influence on the optical loss was investigated as well.

The planar waveguide optical loss was measured using a prism coupling technique and collecting the scattered light (632.8 nm from a He-Ne laser) with a CCD camera, in a direction perpendicular to the surface of the films. Occasionally, different lines of an argon-ion laser were also employed. Loss measurements were performed for those waveguides as a function of surface roughness, sol ageing time and film storage period in the lab atmosphere. Most loss values found are below 1 db/cm.

The present results indicate no significant difference in loss between waveguides prepared by spin-coating without or with ethanol atmosphere, but the presence of a cladding layer on top of the waveguides leads to some decrease in the optical loss values. After a few months of storage in the lab, the waveguides did not change their optical quality.

SILICATE XEROGELS WITH DOPANT-INDUCED CHIRALITY

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Sol-gel technology allows preparation of low-temperature transparent xerogels from liquid precursors. This enables doping of the xerogels with chemical molecules varying from simple inorganic salts to proteins. Doping procedure is relatively straightforward since solutions or suspensions of dopants can be admixed to the liquid hydrolysates. After gelation the added dopant molecules are effectively immobilised within the solid matrix. In this way the sol-gel glass acquires the physical and chemical properties of the entrapped substances.

We have prepared a series of xerogels with entrapped chiral aminoacids. The obtained transparent, glassy xerogels exhibit chirality in the bulk due to the presence of the entrapped molecules. Measurements of the optical activity of the xerogel samples reveal that the entrapment does not influence significantly the optical activity observed for liquid solutions of the aminoacids. Thus, the sol-gel method allows preparation of amorphous optical materials exhibiting properties of strictly spatially defined molecular systems.

OPTICAL AND SPECTROSCOPIC PROPERTIES OF Pr^{3+} DOPED SILICA XEROGELS

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Monolithic $\text{SiO}_2:\text{Pr}^{3+}$ xerogels, obtained by acid catalysis, have been prepared with different Pr^{3+} content ranging from 200 to 105 ppm Pr/Si. The samples were treated at the same temperature in order to compare the effect of the Pr^{3+} concentration on the densification. Physico-chemical properties such as refractive indices and densities have been measured. Samples have been investigated using different spectroscopic techniques: CW and pulsed luminescence, Raman, UV-Vis-Nir absorption and FTIR. The OH content is estimated from the FTIR spectra. Similar changes in the OH content is observed in Raman spectra. Moreover the position of the 'Boson peak' is found to shift for the different samples. Our results show that there is a correlation amongst porosity, OH content, Pr^{3+} concentration and the position of the Boson peak. For high Pr^{3+} content Raman and luminescence spectra indicate that nanocrystals containing Pr^{3+} are present.

Luminescence spectra, obtained by exciting into the $^3\text{P}_1$ state, show an important emission from the $^3\text{P}_0$ state in comparison to the one from the lower lying $^1\text{D}_2$ state. This indicates that the population of the $^1\text{D}_2$ state by multiphonon process from the $^3\text{P}_0$ is not very efficient. Comparison of site selection spectroscopy and lifetime measurements obtained by exciting in $^3\text{P}_0$ and in $^1\text{D}_2$ states allows us to describe the different non-radiative relaxation mechanism as a function of Pr^{3+} concentration, OH content and densification degree.

PREPARATION OF Ce^{3+} ION DOPED INORGANIC-ORGANIC HYBRID MATERIALS USING FUNCTIONALISED SILANES

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The transparent inorganic-organic monoliths doped with cerium (III) ions, which are of interest for laser materials, have been prepared below 100°C by sol-gel process. The functional groups of silane coupling agents was coordinated with Ce^{3+} ions within the inorganic-organic materials, and the optical properties such as absorption spectra, emission spectra and quantum efficiencies, for the Ce^{3+} ion doped materials were strongly influenced by the surroundings around Ce^{3+} ions.

Ce^{3+} doped inorganic-organic materials were prepared from $\text{Si}(\text{OCH}_3)_4$, $\text{CH}_3\text{Si}(\text{OCH}_3)_3$, CeCl_3 and various functionalised silanes (FS) such as amino (APT), gricidexy:- (GPT), mercapto- (MPT), trifluoro- (TFT) and chloro- (CPT) containing silanes.

Transparency of Ce^{3+} doped materials was depend on FS and the ratio of FS to Ce^{3+} . In cases of APT, MPT and GPT, transparent materials were obtained at FS/ Ce^{3+} ratio of 50 when the cerium concentration in the materials was lower than $1.0 \times 10^{-4} \text{ mol/cm}^3$. On the other hand, the inorganic-organic materials, whose Ce^{3+} concentration was between 1.0×10^{-5} and $1.0 \times 10^{-4} \text{ mol/cm}^3$, prepared from TFIM and CPIM were transparent at the FS/ Ce^{3+} ratio of 100 and 150

The emission spectra were observed for all Ce^{3+} doped materials below 400 nm in wavelength. The emission intensities of the materials prepared - from TFT, CPT and without FS were approximately 100 times higher than that prepared from APT, GPT and MPT.

The quantum efficiency of the fluorescence around 350 nm excited at 300 nm was highest (11%) for the material prepared from TFT among the three which had high emission intensity.

QUANTITATIVE SPECTROSCOPIC STUDIES OF METAL ION DOPED SOL-GEL SILICAS.

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Porous sol-gel materials provide an excellent vehicle for the incorporation of secondary phases including metal ions, organic molecules, macromolecules e.g. enzymes and intact organisms such as yeast. These species may be doped into the gel-matrix as it is being formed (pre-doped) or incorporated after the glass has been prepared (post-doping). Both the qualitative and quantitative spectroscopic behaviour of inorganic, organic and macromolecular species in solution is generally well established, but this is not the case if they are incorporated into a porous sol-gel matrix. Our current research is directed at understanding the extent of molecular interactions between the secondary, dopant phase and the gel matrix and the effect of these interactions on the spectroscopic behaviour of all components in the gel-glass composite. Samples containing Ce, Nd, Cr and Co (together with a range of counter ions) were prepared by pre-doping and post-doping methods and allowed to dry at different temperatures and with varying rates of solvent removal. Samples were studied by FTIR, NIR and UV/VIS spectroscopy in the transmittance and reflectance modes. The presence of the dopants (even at concentrations as low as 10^{-7}M) has an effect on the development of the gel matrix and the removal of solvent from the sample. At these low concentrations it has not been possible to investigate the coordination chemistry of the metal ions. At higher concentrations, it has been possible to identify the effect of the gel-network on metal-ion coordination chemistry. The relationship between metal ion concentration (in the glass) and observed absorbance has been investigated. It is clear that metal ions can have an important role to play in the development of the gel network and that the silanol groups in the gel affect qualitative and quantitative aspects of the metal ion chemistry.

OPTICAL PROPERTIES OF Pr DOPED SILICA GLASS OBTAINED BY SOL-GEL METHOD

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The thermally densified silica glasses doped with Pr ions were prepared by sol-gel method. The procedure of preparation is described. Absorption, emission and excitation spectra of Pr doped silica glasses obtained by sol-gel method are reported. We have found that the intensities of absorption bands of Pr(III) changed with concentration, in particular a strong increase of $^3P_2$ term intensity was observed.

The luminescence spectra were dependent on excitation wavelength. The spectra excited in high UV range exhibited besides an emission in the red range corresponding to the $^1D_2 \rightarrow ^3H_4$ transition a broad band emission with the characteristic holes at the envelope corresponding to the $^3P_2, (^3P_1 \ ^1I_6)$ and $^3P_0$ terms. The nature of broad band emission is discussed. The observed holes are resulting from a reabsorption processes however their mechanism is unknown. No emission from $^3P_0$ level was observed. The emission processes were strongly temperature and concentration quenched.

FP9

UNHYDROUS SILICA GEL-GLASSES DOPED WITH Nd-IONS

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Significant interest in preparation and investigation of optical properties of Nd-doped silica glasses has been recently noticed. Such glasses are important in communication systems as materials for construction of signal amplifiers and fibre lasers.

The glasses were obtained by the sol-gel technology which allows to produce high optical quality silica glasses at low temperatures. The most essential limitation of the sol-gel glass is a high concentration of OH-groups which are the principal technological factor decreasing the luminescence quantum yield of Nd-doped silica glasses. A significant decrease in the hydroxyl ions concentration was realised by thermal treatment of xerogels in a freon ($C_2Cl_3F_3$)/oxygen atmosphere at 1000°C. The content of OH-groups in Nd-doped gel-glass was 10–30ppm. The xerogels were consolidated into monolithic silica glass in air atmosphere at 1200°C.

In the present work we report the influence of freon heat treatment on optical characteristics of Nd-doped silica glasses obtained by the sol-gel method.

PREPARATION AND CHARACTERISATION OF ORGANOEUROPIUM-DOPED SILICA GLASSES

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Gels have been investigated as potential matrices for rare earth luminescence. The use of complexing ligands in the sol-gel synthesis of the rare-earth doped glasses has been suggested to improve the rare earth ion luminescence properties in these matrices due to the changes in the local environment experienced by the rare earth ion.

In this work, transparent Eu^{3+} -doped gels were prepared from $\text{Si}(\text{OCH}_3)_4$ and fluorinated and/or complex-forming Eu^{3+} precursors ($\text{Eu}(\text{fod})_3$, $(\text{CF}_3\text{SO}_3)_3\text{Eu}$, $(\text{CF}_3\text{CO}_2)\text{Eu}\cdot 3\text{H}_2\text{O}$, $\text{Eu}(\text{thd})_3$ and $\text{Eu}(\text{acac})_3$). The synthesised Eu^{3+} -doped gels were characterised by means of differential thermal analysis (DTA), thermogravimetry (TG) and IR spectroscopy. Measurements of the emission spectra and fluorescence lifetime of Eu^{3+} were obtained. Analysis of the fluorescence decays of the $^5\text{D}_0$ state suggest that the use of the fluorinated Eu^{3+} precursors reduces the hydrophobic content in the silica gels matrices.

FP11

LUMINESCENCE OF Eu^{3+} ION IN DIOPSIDE PREPARED BY SOL-GEL PROCESS

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The thermal evolution and crystallisation of the $\text{MgCaSr}_2\text{O}_6$ gels and luminescence of Eu^{3+} ions in diopside prepared by sol-gel process have been investigated. The residual solvents were vaporised between room temperature and 200°C . The organic compounds chemical bound to Mg and Si were eliminated between 350°C and 420°C , and the organic compounds chemical bound to Ca and Si were eliminated between 500°C and 550°C . When gels were heat treated between 750°C and 1050°C , the crystalline phase was the diopside. The emission band corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu^{3+} ion was split by the crystal field into three bands, and the band corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition was split into two bands in the diopside. With the increase of heat treatment temperature, the position of the maximum of the broad excitation band corresponding to the charge transfer transition shifted towards long wavelength and the intensity of the emission band at 583 nm that corresponds to transition from $^5\text{D}_0$ to lower level of $^7\text{F}_1$ gradually decreased.

**Eu³⁺-DOPED SiO₂, TiO₂-SiO₂, Al₂O₃-SiO₂ COATINGS ON GLASSES BY
THE SOL-GEL TECHNIQUE**

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Eu³⁺-doped SiO₂, TiO₂-SiO₂, Al₂O₃-SiO₂ thin films have been prepared on microscope slides of soda-lime silica glass by the sol-gel process using the dip coating technique. The several kinds of starting solutions were prepared by varying the ratio of tetraethoxysilane, titanium propoxide, aluminium isopropoxide, water and ethanol. EuCl₃·6H₂O was used as the Eu³⁺ precursor. The influence of dip coating parameters such as the ratio of metal alkoxide/water/ethanol, baking temperature, acid catalysis was investigated. The classification of the gel was examined by Fourier transform infrared spectroscopy at different stages of drying and baking up to 450°C. The optical coatings were characterised using the following techniques: coating thickness measurement, surface morphology, elemental analysis, excitation/emission spectroscopy. The fluorescence spectra of Eu³⁺ in the different matrix (SiO₂, TiO₂-SiO₂, Al₂O₃-SiO₂) were measured, and their similarities and differences are discussed.

FP13

**FLUORESCENCE AND ABSORPTION PROBE OF METAL ION
CENTRE IN SILICATES OBTAINED BY SOL-GEL TECHNIQUE**

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An optical probe of structure of metal ion centre in sol-gel systems based on the Eu^{3+} and Nd^{3+} emission and absorption measurements have been developed. It was tested how the structure and composition of organic complexes of Eu^{3+} affects the clustering processes and retention of water molecules in the gel and glasses. Mechanical properties of the system after adding of triton was also investigated. The studies were performed for two types of lanthanide phosphoro-azo betha-diketones and mixed benzoylophenylo acetylaceton as a precursor lanthanide salts. The emission, excitation and absorption spectra of the precursor salts, gels and glasses heated to 1100 K were measured. Splitting of the levels and electronic transitions probabilities were analysed. The IR spectra were used for the OH^- mode detection in the glasses. The results presented now will be confronted with those obtained for somewhat different systems in which precursor salts form the polymeric chains.

RARE EARTHS CONTAINING OPTICALLY ACTIVE BULK XEROGELS AND THIN LAYERS

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Despite the huge number of papers dealing with rare earths containing bulk materials or waveguides processed by sol-gel methods, only few papers deal with the details in the rare earth neighbourhood and its evolution with the materials preparation. Nowadays main efforts have been directed to the control of the precipitation of nanophases in the amorphous media and the subsequent optimisation of optical properties. For example, concentration and multiphonon quenching of emission are some of the problems one has to deal when designing a new rare earth based optical material.

With these questions in mind we have systematically studied ZrO_2 , SiO_2 and $\text{SiO}_2\text{-TiO}_2$ bulk xerogels and thin films (deposited on glass substrates). In this work we present some results on $\text{Eu}^{3+/2+}$ and $\text{Sm}^{3+/2+}$ spectroscopic properties.

Samples have been prepared by the well known sol-gel method of hydrolysis of metal alkoxides. Controlled heat treatments have been performed under partially containing H_2 or H_2S atmospheres.

Spectroscopic properties as a function of temperature, heating time and the furnace atmosphere composition are stressed with the aim of monitoring and controlling the relative quantities of different metal oxidation states and oxide/sulphide contents.

SPECTROSCOPIC STUDIES OF RARE EARTH IONS IN MgSiO_3 GEL-DERIVED CRYSTALS

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The spectroscopic properties of Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} and Er^{3+} ions in the MgSiO_3 gel and the MgSiO_3 gel-derived crystals have been investigated. The main excitation band of Eu^{3+} ions and Tb^{3+} ions in the gel-derived crystal can be attributed to a charge transfer transition and 4f-5d transition, respectively. The emission bands of Tb^{3+} ions in the gel appear at the same positions as in the gel-derived crystal and the relative intensities of the groups of the bands are approximately the same. Similar to Eu^{3+} ions, however, the intensities of emission bands of Tb^{3+} ions in the gel-derived crystal are orders of magnitude greater than that in the gel since multiphonon relaxation can effectively compete with radiative transitions due to the higher phonon energy in the gel. The energy level splitting caused by crystal field can be observed clearly in the emission spectra of Eu^{3+} and Sm^{3+} ion activated gel-derived crystals. The excitation and emission spectra of Sm^{3+} and Dy^{3+} ions in the gel-derived crystal are predominantly from that in the gel. In contrast, the excitation and emission spectra of Er^{3+} ions in the gel-derived crystal are approximately the same as that in the gel with respect to the positions, number and intensities of excitation and emission bands.

SOL-GEL FABRICATION AND PROPERTIES OF SILICA CORES OF OPTICAL FIBRES DOPED WITH Yb^{3+} , Er^{3+} , Al_2O_3 OR TiO_2

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Optical cores of preforms for drawing optical fibres doped with Er^{3+} and Yb^{3+} have been fabricated by the sol-gel method with the aim of increasing the thickness of glass layers coated in one coating cycle and to determine the relation between the core composition and the refractive index, attenuation and the amplified stimulated emission (ASE) of Er^{3+} in the fibres. Al_2O_3 - P_2O_5 - SiO_2 and TiO_2 -(P_2O_5)- SiO_2 glasses have been studied as matrices for entrapping the rare-earth elements. Input sols with low contents of solvents have been prepared by mixing alkoxides and chlorides of Si and Ti together with AlCl_3 , ErCl_3 , YbCl_3 , POCl_3 , and with water and a modifier under acidic catalysis of HCl. The sols were coated on the inner wall of a silica substrate tube by a modified dip-coating method. After sintering of the coated film at temperatures up to 1500°C the glass layer was collapsed into a circular core of the preform.

Continuous and homogenous glass films have been fabricated with thicknesses depending on the composition of the input sols. A maximum layer thickness of about $5\text{ }\mu\text{m}$ has been achieved with sols containing silica and alumina. In the case of sols composed of silica and titania a thickness of about $1\text{ }\mu\text{m}$ has been measured. A relation between pH, contents of water, solvent, rare-earth chlorides and AlCl_3 used during the preparation of alumina stock sols and the contents of Al_2O_3 and the rare-earth ions in the layers has been observed. On this basis, glass layers with TiO_2 , Al_2O_3 , Yb^{3+} and Er^{3+} contents up to 10, 8, 2 and 0.5 mol.%, respectively, have been prepared. The fibres with a base line attenuation of up to 50 dB/km have been drawn from preforms fabricated under optimised oxygen content during the layer sintering. The data on ASE and lasing of Er^{3+} around $1.55\text{ }\mu\text{m}$ are shown for the both studied glass matrices which were measured under excitation of the fibres by a Nd:YAG laser at $1.064\text{ }\mu\text{m}$. These data imply better suitability of matrices doped with Al_2O_3 and P_2O_5 for the development of fibre lasers.

CADMIUM SELENIDE DOPED ORMOSILS

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Materials which exhibit third order optical nonlinearity are of interest for all-optical switching devices, for instance for telecommunications. A candidate material is based on microcrystallites of CdSe ('quantum dots') dispersed in an amorphous, dielectric host. Such materials can exhibit a high nonlinear refractive coefficient and picosecond relaxation time. Optimisation of materials synthesis has made some progress, but melted glass routes suffer from a lack of uniformity of CdSe microcrystallite size and sol-gel methods have so far proved complicated. Here we present a new sol-gel approach.

Phenyl capped CdSe quantum dots have been synthesised independently via a reverse micellar route which allows control over the dot size. These dots were successfully dispersed in amine-functionalised ormosil hosts. Visible absorption spectra clearly show the blue shift of the optical absorption edge and the first exciton absorption peak. The CdSe doped ormosil can be easily processed into small monoliths or films at room temperature.

The phenyl capped CdSe quantum dots were not dispersible in most solvents and sol-gel hosts; the amine functionalised ormosils proved an exception. In order to understand why, structural studies of the host aminoormosils were carried out using ^{29}Si and ^{13}C solid state nuclear magnetic resonance spectroscopy, mid- and near-infrared spectroscopy

SANS STUDY OF QUANTUM DOTS CRYSTAL GROWTH IN SILICA GEL MATRIX

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Semiconductor nanocrystals, acting as quantum dots, embedded in a dielectric matrix are interesting materials to produce the quantum confinement of the photoexcited species (excitons and biexcitons), as a consequence the composite gives rise a non-linear optical behavior. The size and size distribution of the crystals play the most important role for the line broadening and their optical behaviour. In this way Small Angle Scattering techniques (X-ray or neutrons) allow to study the crystal growth process and their size on the 1-100 nm length scale.

Liquid samples for SANS experiments were prepared in quartz cells 1 mm pathway by means a mixture of TMOS:D₂O:Formamide in a molar ratio of 1:4:7. Before reaction, in the aqueous solution acCd (Cadmium acetate) and TAA (Thioacetamide) were diluted as a source of the Cd⁺² and S⁻² ions, or SeCl₄ for the Se⁻² ions, in order to promote the nucleation. Crystal concentration was fixed to 5 wt% of total silica. SANS measurements were carried out in the V4 experimental station at the Berlin Neutron Scattering Center facility. The kinetic process of silica aggregates and crystal growth were monitored at intervals of 30 min for each sample, taking into account that gelation time is around 5 h. Using 0.6 nm as neutron wavelength, the sample-detector distance was selected at 8 m to cover a q-range from 0.05 to 0.3 nm⁻¹.

The results show new aspects of the CdS and CdSe crystal growth as quantum dots. One of them is the change produced by the aggregation process of the silica matrix. Under the assumption that total scattered intensity would be the contribution of the silica matrix and the nanocrystals, the difference of these intensities would account for the crystal size and their distribution, as well as for the crystal growth kinetics. CdS crystals grow faster and bigger than CdSe ones.

OPTICAL AND STRUCTURAL PROPERTIES OF DOPED ZnS NANOPARTICLES PRODUCED BY THE SOL-GEL METHOD

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Optical and structural properties of Mn^{2+} -doped ZnS nanoparticles in an organic matrix are experimentally and theoretically studied. The nanoparticles, which were produced by the sol-gel method, are nearly monodisperse with a diameter of approximately 3 nm and show the characteristic orange luminescence of Mn centres in a ZnS matrix.

The absorption spectra of the embedded ZnS nanoparticles is slightly blue shifted and broadened compared to the reference bulk material. This blue shift is caused by quantum size effects. Whereas the broadening is due to defects such as lattice distortions, vacancies etc., which are probably located close to the surface for small particles. These defects produce enlarged fluctuations in the absorption spectra due to the higher possibility of the electrons and holes to 'see' disorder, generating an enhanced broadening of the absorption spectra for small nanoparticles.

In contrast to that result, the spectral feature of the emission spectra via the Mn^{2+} centre is nearly unchanged compared to the bulk material, showing that the Mn atoms are mainly located in the crystalline core of the particles. Furthermore, the quantum efficiency is increased and the decay time of the electron-hole pairs is shortened to the nanosecond regime because of the enhanced possibility of the electron-hole pairs to see the Mn^{2+} centre. Therefore, the only effect of doping of ZnS nanoparticles with Mn^{2+} centre is the suppression of the relaxation of the electron-hole pairs via surface defects and generating an highly efficient and fast relaxation of the electron-hole pairs via Mn^{2+} centre.

Consequently, it is postulated that these effects are not produced by the change of the electronic coupling of the Mn^{2+} centre on the ZnS host lattice for small particles as usually assumed. It is only an effect of the linear reduced dimension of the particles, increasing the possibility of the excited electron-hole pairs to 'see' the Mn^{2+} centre.

**SYNTHESIS AND ISOLATION OF PbS NANOPARTICLES AND
THEIR INCORPORATION IN A SOL-GEL MATRIX.**

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Semiconductor nanoparticles have received particular attention because of their interesting size-dependent properties, such as third-order optical nonlinearity and their physicochemical characteristics.

The goal of this work is to study the behaviour of amino functional groups triethoxysilanes as both stabilising agents and surface modifiers in the reverse micelles synthesis of PbS nanoparticles.

We present an interesting method to allow the separation of the particles avoiding the agglomeration prior their incorporation in the sol-gel matrix.

Through the presence of -NH and -Si-OR functional groups found on the triethoxysilanes, the reaction at the surface of PbS nanoparticles and the formation of a gel network by the hydrolysis-condensation process is allowed.

Using UV-Visible spectra of the particles samples, we have determined the band gap values as a function of the surface modifiers and other parameters inducing the size of the nanoparticles.

These nanoparticles have been used to dope $\text{SiO}_2\text{-ZrO}_2$ films with closed porosity by spin-coating method using metal alkoxides in a wet atmosphere without addition of water.

In this way we have obtained doped organic-inorganic hybrid matrices on which the non-linear optical properties by DWFM method have been studied.

OPTIMISATION OF ORMOSIL FILMS FOR OPTICAL SENSOR APPLICATIONS

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Sol-gel-derived films are becoming increasingly important for optical sensor applications. Analyte-sensitive dyes are easily entrapped in the porous film while remaining accessible to the analyte, and the nature of the sol-gel process lends flexibility to film fabrication, in particular enabling tailoring of films properties for specific sensor applications.

Recent work has indicated that ormosil films, fabricated from organically-modified precursors, produce better sensor performance for some specific applications, compared to films from conventional sol-gel precursors such as TEOS or TMOS. This paper aims to compare film properties and sensor behaviour for films fabricated from both methyltrimethoxysilane (MTMOS) and methyltriethoxysilane (MTEOS) organically modified precursors. Microstructural differences, for example porosity changes due to the different precursor backbone structures, are interrogated by monitoring sensor response. Sol-gel fabrication parameters such as sol pH and R-value (molar ratio of water to precursor) were varied for the two film types. Resulting film properties such as thickness, thickness stabilisation time and sensor response are discussed in terms of relative hydrolysis and condensation behaviour for the two different precursors as a function of pH and R-value. Issues which have been identified as being of crucial importance for optimum sensor response, such as dye leaching, film surface hydrophobicity and humidity response, are discussed for both film types. The main motivation for this work is film optimisation for a number of optical sensors including pH, ammonia, oxygen and biosensors.

SOL-GEL BASED AMMONIA OPTICAL SENSOR

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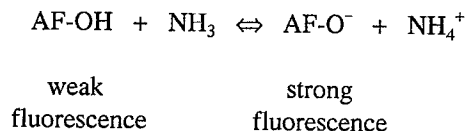
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The sol-gel technology enables the production of glasses at room temperature. In contrast to conventional glass sintering at high temperature, a great variety of novel glasses containing both organic and inorganic additives can be made.

Conventional sol-gels are rather hydrophilic and well suited for sensing ions (including the proton). A more hydrophobic material is obtained by preparing organically modified siloxanes (ormosils). Ormosils have more dense structures and therefor more suitable in gas sensing.

Ormosils were prepared in different ratios of phenyltrimethoxysilane (Ph-TriMOS) and tetramethoxysilane (TMOS). A pH indicator such as aminofluorescein has been incorporated into ormosils and the resulting materials were tested for its relative response to pH as well as to ammonia (dissolved ammonia at constant pH). In case of totally hydrophobic matrices only ammonia response has been observed. Ammonia reacts with the immobilised aminofluorescein (AF-OH) in giving its strongly fluorescent anion (AF-O⁻) according to the following equation:



FP24

**SOL-GEL PREPARATION AND SECOND-ORDER NONLINEAR
OPTICAL PROPERTIES OF SILICA SOL-GEL THIN FILMS**

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Sol-Gel derived inorganic materials have been of interest as hosts instead of organic nonlinear optic polymer molecules. This paper deals with a new sol-gel system has been produced by the interaction between Tetramethoxy Silane (TMOS) with Methyltrimethoxy Silane (MTMS) under specific chemical conditions so as to produce a sol-gel silica polymer which was used as a host for Disperse Red 1 Chromophore. Investigations of this inorganic-organic combination of second-harmonic nonlinearity show a quasi permanent second-harmonic nonlinearity. Birefringence and Dichroism have been studied and they show that this new system has nonlinear optical quality.

A comparison between this sol-gel system/DSR1 and PMMA/DSR1 system is discussed as well.

**AGGREGATION PROPERTIES OF METALLIC
TETRASULPHOPHTALOCYANINES ENCAPSULATED IN SOL-GEL
MATERIALS**

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Metallic phthalocyanines exhibit, among many useful properties, the ability to protect sensors against short, intense optical pulses deleterious to efficient sensor operation. It is possible by means of low temperature sol-gel techniques to obtain porous monolithic materials encapsulating metallic ions, and all sorts of complex organic molecules.

We report here the study of water-soluble metallic tetrasulphophtalocyanines (MTSPc) encapsulated in silica obtained by sol-gel techniques. These materials are transparent and stable and exhibit interesting optical properties. Absorption in the visible region of the spectrum reveals aggregation of the MTSPc species to form dimers which modify the optical absorption of excited states and the resulting optical properties. We investigate the relative importance of the various physicochemical parameters affecting dimer formation (dye concentration, pH, presence of species such as dimethyl formamide, pyridine, etc.), in order to control and inhibit dimer formation.

FP26

**PHOTODEGRADATION OF LUMINESCENCE IN SiO_2 :Rh B GELS
EXPOSED TO YAG:Nd LASER PULSES⁺**

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In the last years silicate gels doped with organic dyes have been proposed as solid state tuneable lasers. In this kind of application it is important to know the photostability under intense photoexcitation. Usually this has been estimated by measuring the laser output as a function of the number of excitation pulses. In this work we followed the optical absorption and luminescence of SiO_2 silica gels doped with Rhodamine B exposed to second harmonic pulses of a YAG:Nd laser. In addition to the characteristic exponential decay with the number of pulses, overlapped intensity oscillations were observed. This behaviour can be explained in terms of a long lived metastable electronic excited state of the dye molecules.

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**THE ENTRAPPING PROCESS OF RHODAMINE 6G IN SILICA
SOL-GEL FILMS**

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The entrapping process of rhodamine 6G in silica sol-gel films has been studied by absorption spectroscopy.

The dimer-monomer changes in the matrix have been followed as a function of the water-alkoxide ratio, r , in the precursor sol and drying temperature.

The dimerisation process has been found to be strongly affected by the presence of residual water molecules that promotes the dye aggregation and screens the electrostatic interaction with the pores surface. Evaporation of the water with drying, on the contrary, causes a deaggregation of the dimers that are reduced to monomers.

The dimer-monomer process during drying has been modelled by deconvolution of the absorption spectra.

The amount of dimers was found to decrease from as deposited to 150°C dried samples.

A lower amount of water and a higher drying temperature have been found to be effective in changing the dimers to monomers.

MOLECULAR ENTRAPMENT WITHIN SURFACTANT ENVIRONMENTS IN SOL-GEL MATERIALS. THE SYSTEM SiO_2 /CTAB/pH-INDICATORS

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Direct entrapment of organic and bio-organic molecules within oxide sol-gel materials exposes the dopants to a cage environment which is dictated by the interfacial moieties of the ceramic material. Since the immediate environment of the dopant affects and modifies its optical properties, its chemical performance and the stability, it has been of interest to tailor cage properties which are different than the properties of the bulk matrix. One convenient route has been to polymerise or co-polymerise monomers which carry a non-hydrolysisable residue. Another route, which we have explored in detail and report here, is the co-entrapment of the dopant with surface active agents.

The particular systems we report on are TMOS ($\text{Si}(\text{OCH}_3)_4$) - derived silica sol-gel materials in which the cationic surfactant CTAB (cetyltrimethyl ammonium bromide) is co-entrapped with the following pH indicators: alizarin red, bromocresol green, bromocresol purple, bromophenol blue, bromophenol red, bromothymol blue, bromoxylene blue, Congo red, chlorophenol red, methyl orange (MO), methyl red, methyl red amidopropyltrimethoxysilane, a-naphtholphthalein, nitrazine yellow, phenolphthalein, p-(p-dimethylamino-phenylazo)benzoic acid, phenol red, thymolphthalein, thymol blue and 3,4,5,6-tetrabromophenolsulphonaphthalein.

It was found that the indicating ranges of the entrapped azo dyes and the sulphonaphthaleins are shifted to more acidic values, while those of the phthaleins are shifted to more basic values. *Very large pK_i shifts of 3 and 4 orders of magnitude* were obtained for some indicators, such as MO. Marked effects of changing the concentration of CTAB on λ_{max} of MO at neutral pH were also found. Determination of isosbestic behaviour within the porous glasses revealed sharp points, indicative of homogeneous environment within the glass. The general shape of the titration curve is likewise preserved in the glass, but shifted. Depending on the structure of the indicator, the shifts may be in opposite directions. It was found that co-entrapment with CTAB reduces leaching dramatically to half life values of months and years.

The various aspects of behaviour and the special properties are rationalised in detail in terms of the specific interactions between the indicators and the surfactant on one hand, and the surfactant with the silica surface on the other hand.

THERMOCHROMIC PROPERTIES OF SILVER-DOPED SILICA GELS

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Using sol-gel methods we have been able to obtain colloids of good transparency and consisting of small particles of metallic silver, by the spontaneous reduction of Ag(I) salts through an autocatalytic reaction involving acidic alcohol-water solutions.

The thermochromic properties of the small particles or thin films thus obtained were determined by measuring the shift towards the red of the cut-off in the transmittance spectrum in the visible region. The rate of change as a function of time of this shift has been measured.

Gels of silica doped with silver ions were prepared either in the presence of ethanol or in its absence. In the temperature range 20–150°C the observed shifts in the cut-off were rather large, specially in the samples prepared without ethanol, with shifts going from 300 to 700 nm. The absorption band at 300 nm, a well known band assigned to silver clusters, increases with temperature and at the same time a band at 425 nm appears, which is commonly assigned to plasmons in the surface of the colloids. The former are responsible for the observed colours.

**APPLICATION OF SOL-GEL FILMS FROM
TEOS-FLUOROALKYLSILANE-CARBOXYLIC ACID**

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Sol-gel films with low refractive index were prepared by polycondensation reactions of TEOS-fluoroalkylsilane-carboxylic acid systems without addition of water. On the other hand, hydrolysis of their materials gave higher refractive index films. For example, refractive index value of film without hydrolysis was 1.38 at curing temperature of 100°C, and that of film from hydrolysis was 1.45. It was considered that the difference of refractive index property was caused by polymer conformation i.e., the former were linear-like polymer, the latter were cross-linked polymer. In this investigation, we have developed the low refractive index films. These films are very useful to anti-reflection films for LCD's etc.

SOL-GEL PREPARATION OF α -Fe₂O₃ THIN FILMS: STRUCTURAL CHARACTERISATION BY XAFS AND RAMAN

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Thin films of α -Fe₂O₃ are interesting due to their large non-linear optical susceptibility $\chi^{(3)}$. In this work we report on the characterisation by Raman and XAFS spectroscopy of films of α -Fe₂O₃ obtained by two different sol-gel precursors: 1) Fe(NO₃)₃·9H₂O in a mixture of 2-methoxyethanol and 2,4 pentanedione (CH₃COCH₂COCH₃); 2) FeCl₃·6H₂O, hydrolysed at pH=9. The films were obtained by single and multiple (5–15) dip coatings on silica and glass substrates.

The Raman spectra on the films in the Brewster configuration show all phonon peaks of rhombohedral α -Fe₂O₃, when heated at 500°C. Confinement effects due to the presence of nanocrystals both in the powders and in the films are discussed on the basis of frequency shifts and peak broadening. XAFS (X-ray Absorption Spectroscopy) measurements, taken at the Fe K-edge in fluorescence mode, confirm the α -Fe₂O₃ local structure also in the films obtained by a single dipping, which are hardly investigated by other techniques. Both XANES and EXAFS regions were investigated and the local coordination of iron is followed from the gel to the heat treated films. The morphology of the films was studied by AFM and some differences between the two preparations are reported.

GP1

SYNTHESIS AND CHARACTERISATION OF ORGANICALLY MODIFIED CERAMICS AS SCRATCH RESISTANT COATINGS

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Organically modified silicates (ORMOSILS) have become one of the most interesting materials made by the sol-gel method. They are synthesised by chemically incorporating organic polymers into an inorganic silicon based network and have unique properties since they are essentially a composite with nano-dispersion of polymers and ceramic phases.

Organic-inorganic hybrid materials have been synthesised from poly(silicic acid ester) precursors in sequential reaction steps. The overall properties of the low shrinkage composite materials was varied by the control of the reaction conditions during the chemical synthesis. ^1H NMR, ^{29}Si NMR Spectroscopy, Infrared Spectroscopy (IR), Near Infrared Spectroscopy (NIR) and Gel Permeation Chromatography (GPC) techniques were applied to study the structure of the precursors.

Thermal behaviour of the resulting composite materials was studied using Dynamic Mechanical Thermal Analysis (DMA) and Differential Scanning Calorimetry (DSC). The microstructure was characterised using Small Angle X-ray Scattering (SAXS). Also, dielectric behaviour showing the interrelation between morphology, composite miscibility and polymer relaxation will be described.

Some of the results on the resistance of coated thin films on ophthalmic lenses will be described and discussed.

**MICROSTRUCTURE AND CORROSION RESISTANCE OF
INORGANIC-ORGANIC (ZrO₂-PMMA) HYBRIDS COATING ON
STAINLESS STEEL**

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Inorganic-organic (ZrO₂-PMMA) hybrids prepared by sol-gel were dip-coated on stainless steel (SS 316L) in order to improve etching protection. The sol was prepared by hydrolysing the alcoholic solution of zirconium propoxide in presence of polymethylmetacrylate (PMMA) under ultrasound irradiation. The films were heat-treated at 200°C during different periods of time and their structural and microstructural characteristics analysed by IRFT, SEM, X-ray reflectometry and adhesion measurements. The results show that films are homogeneous, adherent to the substrate and present low roughness ($\cong 2\text{nm}$). The electrochemical behaviour was analysed in H₂SO₄ (0.5M) aqueous solution through potentiodynamic polarisation curves at room temperature. Comparative tests performed on samples prepared with one, two or three ZrO₂-PMMA layers and with the uncoated substrate have shown that hybrids are more efficient against etching than ZrO₂ inorganic films.

GP3

**INVESTIGATION OF GLASS-LIKE SOL-GEL COATINGS FOR
CORROSION PROTECTION OF STAINLESS STEEL AGAINST LIQUID
AND GASEOUS ATTACK**

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Glass-like sol-gel coatings have been investigated as corrosion protective coatings on stainless steel. Boron-, magnesium-, phosphorous and sodium silicate coatings with thickness of about 100..300 nm and CH₃ modified SiO₂ coatings with a thickness of about 2 µm were deposited on stainless steel plates by dipcoating. The coatings were densified at 500°C in different atmospheres (N₂, air) for 1 h. The corrosion protection against gaseous attack was investigated by accelerated corrosion tests at 500°C and 800°C in air for 1 h. A corrosion protection factor was calculated from the relation between Fe and Fe₂O₃, determined by XRD on the surface of coated and uncoated samples. CH₃ modified SiO₂ coatings showed a protection factor, which was 2 orders of magnitude higher than for the other coatings. Electrochemical investigations were performed on samples submerged in a sea water solution for 200 h. The corrosion propagation, polarisation resistance and impedance vector were measured. For accelerated corrosion tests, polarisation intensity curves were determined for high potentials of up to 1 V. Again excellent results were only obtained for the 2 µm thick CH₃ modified SiO₂ coatings, which remained passive for 200 h. Furthermore the behaviour of sodium silicate and SiO₂ coatings against attack of different food stuff and household cleaners at different temperatures up to 400°C was investigated. After 45 min. of exposure and cooling, the coatings were washed with water and the corrosive attack was evaluated visually. With SiO₂ coatings a very good corrosion protection was obtained against food stuff (acid attack) for temperatures up to 350°C and against cleaners (basic attack) up to 250°C. Similar results were obtained with sodium silicate coatings after leaching the coating surface by phosphoric acid.

SOL-GEL COATINGS ON 316L STEEL FOR CLINICAL APPLICATIONS

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Metallic implant materials such as 316 L stainless steel, Co-Cr alloys and Ti are widely used for prosthetic applications due to their excellent mechanical properties. These implants show two severe shortcomings: a limited corrosion resistance in the human body (specially critical in the case of stainless steel), and the lack of bioactivity, ie., they are not able to bond to living tissue without cementation or external fixation devices. On the contrary, certain glasses and ceramics are bioactive, but show poor mechanical properties. Thus, coating metallic prosthesis with bioactive glasses could be a route to combine both mechanical resistance and bioactivity in one material.

The sol-gel method has shown to be adequate to produce good and adherent coatings on metals in a wide range of compositions at temperatures around 500°C. This temperature looks low enough to strongly reduce Fe diffusion to the coating surface, an element that inhibits bioactivity. In this work, SiO_2 and $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ coatings have been prepared on electropolished stainless steel 316 L with the aim of providing a first barrier, able to reduce the corrosion attack and avoid the iron diffusion, and a final bioactive layer to be in contact with living tissue. SiO_2 starting solutions were prepared from TEOS and TEOS + methyltriethoxysilane (MTES) to obtain coatings from 400 nm to 2 μm . $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ coatings and self-supported films with a composition similar to previously reported bioactive glass powders, have been prepared by using solutions obtained from TEOS, triethylphosphate (POEt3) and calcium methoxyethoxide.

The corrosion behaviour of silica coated steel samples in simulated physiological conditions (SBF solution) was analysed through electrochemical tests consisting on measuring the corrosion potential, polarisation curves and impedance vector. SiO_2 coatings obtained from TEOS and MTES showed an excellent corrosion behaviour, remaining passive after 200h of electrochemical attack.

The Fe present in the surface was analysed by XPS spectroscopy, showing that the thicker the coating the lower is the surface Fe content, the ratio Fe/Si being as low as 0.01 for a layer of 1.8 μm .

Finally, in vitro tests of the different composition coatings have been also performed. After soaking the samples in SBF solution, their surfaces were analysed by SEM microscopy and FTIR spectroscopy. SiO_2 coatings did not show any bioactive response after 30 days of immersion. $\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ coatings with composition similar to bioactive glass powders should be able to provide bioactivity to the protective SiO_2 coating. In vitro tests of this coatings are now under evaluation.

GP5

ORGANOPOLYSILOXANES AS PROTECTIVE AND CHEMICALLY SENSITIVE COATINGS FOR OPTICAL FIBRES

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Various types of organically modified siloxanes (ORMOCERs) with a polysiloxane backbone and UV curable acrylate side groups have been synthesised with the aim of fabricating protective and/or chemically sensitive coatings for silica optical fibres. The polysiloxane network was prepared by the sol-gel method, UV crosslinking and curing was carried out during the drawing of the silica fibres.

The refractive index of the coating material can be tailored in the range from 1.57 to 1.46 by special chemical modifications. The coating hardness depends mainly on the chain length of the spacer group connecting the siloxane backbone and the organic network.

ORMOCER coatings with thickness from 5 to 60 μm were continuously processed on silica fibres. The average strength of these fibres was about 3.5 GPa.

The interaction of ORMOCER coatings with water, hydrocarbons and petrol and CO_2 has been studied in immersing experiments by measuring the output light intensity from the fibre in the wavelength range from 500 nm to 1800 nm. The observed chemical sensitivity of the coatings can be attributed to the reaction with special incorporated groups or immobilised chemical transducers. These effects induce changes of the light absorption coefficient and the refractive index of the coatings and they have been employed in the development of fibre-optical chemical sensors.

PREPARATION AND PROPERTIES OF SOL-GEL DERIVED THERMOCHROMIC AND PHOTOCHROMIC COATINGS

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As a versatile preparation method, the sol-gel process provides a good opportunity to the production of functional coatings. Its unique advantages, especially the low processing temperature and the solution chemical reaction allow the introduction of both inorganic ions and organic molecules into the coatings which are targeted to possess certain optical, electrical or magnetical properties. In the present work, we report on the preparation and properties of sol-gel derived thermochromic (TC) and photochromic (PC) coatings.

Vanadium dioxide TC coatings were successfully prepared using tri-isopropoxyvanadyl as the starting material on silica and slide glass substrates. These coatings exhibit significant thermochromic effect, i.e. reversible change in both optical and electrical properties due to the reversible phase change between the metal and semiconductor states. Doping of $\text{Cu}^{(2+)}$ ions into the vanadium oxide coatings leads to lower thermochromic transition temperature compared with the undoped ones.

PC coatings prepared by doping spirooxazine into organic-inorganic hybrid matrices possess attracting performances: the photochromic response and the thermal decolouration rate of the coatings are similar to those of the dye-ethanol solution, while the photostability of the dyes has been improved by a factor of >50 compared with the dye solution by optimising the composition of the coating sols and introducing appropriate additives.

GP7

ORGANIC-INORGANIC NANOCOMPOSITE COATINGS WITH ANTI-GRAFFITI-EFFECT

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The concept for the preparation of controlled gradient layers by a thermodynamically driven self alignment of side chain fluorinated silanes in sol-gel derived lacquer systems is used for the fabrication of low surface free energy coatings for anti-graffiti applications.

The coating is composed of organoalkoxysilanes (3-glycidyloxypropyl-trimethoxysilane (OPTS) and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (FTS)) to form an inorganic polysiloxane backbone and organic crosslinking agents (1-methylimidazole, bisphenole-A) to obtain a sufficient flexibility.

The nanocomposite (Nanomer) is applied e.g. on steel substrates with polyurethane coating and after curing at 70–130°C results a transparent coating with very good adhesion (O in cross-cut test DIN 53151, 5A in tape test ASTM D3359). Due to the high degree of crosslinking in the inorganic network the coating shows a good abrasion resistance (>600 cycles taber abrader test CS10F wheels and 5 N load). Contact angles of 96° with water and 52° with hexadecane show, that low surface free energies (21 mJ/m²) are achieved with FTS concentrations as low as 1.3 mol% FTS, indicating that the main fraction of FTS is located at the coating/air interface and not in the bulk. Therefore water and organic solvent based spray paints show a poor wetting on the nanocomposite and closed paint films are not achieved. The coating is chemically resistant against organic solvents (for example alcohols, lactones) typically used as graffiti cleaners. The material was optimised to be used as a spray coating lacquer on large areas and shows excellent properties for an application as anti-graffiti protection on various painted substrates and is presently tested on three carriages of the German Railway.

SOL-GEL PROCESSING OF ORGANIC-INORGANIC NANO-COMPOSITE FILMS

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Sol-gel chemistry makes easy the design of molecular hybrid materials from modified silicon alkoxides. The chemical flexibility of tailoring inorganic and organic structures in combination with the concept of incorporating nanosized metal oxide particles opens the possibility of achieving new multifunctional materials.

This communication will describe our attempts to incorporate homogeneously the oxide particles (AlOOH , Al_2O_3 , ZrO_2 , with particle sizes <50 nm) into molecular inorganic-organic composite matrices in the films processing by spin technique. The alumina and zirconia particles are first surface modified with Si-OH and its distribution/interface in the matrices has been characterised. The hybrid matrices are derived from TEOS, modified silicon alkoxides such as epoxysilanes, diols and/or $\text{Ti}(\text{OC}_4\text{H}_9)_4$ et al., surfactants having been involved in some cases. The sol-gel processing factors like the hydrolysis conditions, the hybrid matrices composition as well as the nature of surfactants are evaluated in view of the film properties. The characterisation techniques used are IR, DTA, SEM, Surface profiler, TEM ...

Works in this direction lead us to prepare high scratch resistance, corrosion-inhibitant and hydrophobic coatings on metals and glass.

GP10

SYNTHESIS OF TRANSPARENT MESOPOROUS AND MESOSTRUCTURED THIN SILICA FILMS

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Transparent periodic mesoporous thin films have been successfully synthesised by a simple sol-gel method.

Since the synthesis of the ordered mesoporous silica materials MCM41, the use of surfactants as templates to prepare mesostructured materials has been widely developed. The synthesis of thin mesoporous films by such a way is one of the current aspects of the problem. Several studies have recently reported the preparation of surfactant nanocomposite films but one of the major problems to obtain transparent films is the removal of the template. Thermal treatments indeed introduce defects in the sample by delamination mechanism for instance.

We describe here a novel method to obtain crack-free mesoporous structured films. Such films are prepared by a sol-gel process with a pretreatment of the glass substrate. The silicate precursor (tetraethoxysilane) is pre-hydrolysed under acidic conditions before dissolving directly cetyltrimethylammonium bromide (CTAB). The solution is then spincoated on pretreated glass substrate. After the film has been deposited, it is calcined in air.

X-ray Diffraction has been used to characterise the film before and after thermal treatment. The film consists in a nanocomposite material with periodic structure. The XRD pattern is characterised before calcination by a sharp peak at $d=3.8$ nm which is broadened and shifted at about 3.0 nm after calcination. Infrared transmission spectra have been performed on the films which indicate the removal of the surfactant after calcination in addition to an enhancement of the specific area estimated by the analysis of the stretching vibration of the free OH groups.

**ELABORATION AT 80°C OF SCRATCH RESISTANT SiO₂ LAYERS
DEPOSITED BY AEROSOL-GEL PROCESS**

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Aerosol-gel process is a thin film deposition technique based on the sol-gel polymerisation of a liquid film deposited from an ultrasonically sprayed aerosol. Diluted TEOS solutions have been prepared using an original two-step procedure including an hydrolysis step at pH=2 and a dilution step at pH=4. This procedure leads to a very slow polymerisation rate of the diluted solution. The slow polymerisation allows a flexible control of the aerosol transport and a good spreading and coalescence of the ultrasonically thick liquid film.

After solvent evaporation, the polymerisation reaction takes place fully at a very low temperature and leads to scratch resistant layers for a post-deposition treatment temperature as low as 80°C. In this paper, the chemical mechanisms involved in the formation of mechanically resistant layers are studied by FTIR spectroscopy and discussed with respect to the solution composition and preparation and to the thin film deposition and post-deposition conditions.

GP14

**THE ROLE OF HF IN THE WET-CHEMICAL PREPARATION OF
SiO₂ LAYERS**

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The addition of HF to a silica sol-gel system has an enormous effect on the condensation reactions. To get more insight in this effect we recorded hydrolysis time versus gelation time curves of TEOS systems with varying amounts of HF. By comparing the results with previous obtained curves for systems to which no HF was added we could elucidate the mechanism of fluoride on the condensation reactions. The condensation rate of the silanols increases drastically after a small addition of fluoride ions. Attenuated total reflection Infrared spectroscopy was used to get an extra verification of this mechanism.

The main interest of sol-gel systems is in the field of the preparation of wet-chemical layers. Therefore we also investigated the effect of the addition of HF to a coating solution. By the determination of the etch rate of the SiO₂ coatings as a function of the HF concentration in the coating solution the effect of the fluoride could be visualised.

LOW-TEMPERATURE MODIFICATION METHODS FOR SOL-GEL THIN FILMS

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Various new techniques have been investigated to modify sol-gel derived thin films at low temperatures. Irradiation by energetic photons and exposure to water vapour were applied to densify and/or crystallise of sol-gel films. Silica and titania films derived from alkoxide precursors were densified by irradiation with ultraviolet (UV) light. Particularly, vacuum UV light which had a higher energy than the bandgap induced a significant compaction of silica gel films with dehydration. The increase in temperature of the films during the irradiation was less than 50°C. Changes in the infrared absorption spectra indicated that the irradiated films had a different structure from conventionally annealed ones. Implantation of He⁺ ions promoted a similar structural change in the films. These results suggest that the densification can be attributed to rearrangement of the network by electronic excitation. Using ultraviolet lasers instead of incoherent light, crystallisation of titania and indium oxide gel films was observed. Water vapour was also effective in the modification of sol-gel films. Densification of silica gel films was induced by exposure to water vapour even at temperatures below 100°C; however, the vapour-exposed silica films were not stable to post annealing. On the other hand, sol-gel titania films was crystallised by exposure to water vapour. Cleavage of the network with water vapour is presumed to promote the changes in the film structure. The difference in the structures of the UV-irradiated, the vapour-exposed and the conventionally annealed films is discussed.

GP16

INHIBITION OF Pb-LEACHING FROM LEAD CRYSTAL GLASS BY COATING WITH FILMS PREPARED BY THE SOL-GEL ROUTE

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The corrosion resistance of lead crystal glass ware intended for use in contact with food and drinks to different aqueous solutions has become recently of particular concern because of the toxic nature of lead ions released from the glass ware to the aqueous solution. This concern has increased because of the chronic toxicity of Pb as it accumulates in the body.

The chemical resistance of lead crystal glass (24% PbO) toward the attack of organic acids, alcoholic solutions, water and acetic acid has recently been reported previously by Ahmed et al. The quantities of Pb leached out of the glass were found to be a function of the type of corroding solution. Water releases the least quantities of Pb whereas acidic or alcoholic solutions increase the rate of extraction of Pb. Although the levels of Pb released by these solutions are low, it is necessary to inhibit it to avoid the risk of health hazards.

In this work, a study of the chemical resistance of a commercially available lead crystal glass tumblers (24% PbO) before and after coating with sol-gel derived glass films was carried out. The results obtained are evaluated and related to the chemical composition of the deposited films.

**COMPARISON OF DIFFERENT HIGH AND LOW INDEX
MATERIALS IN THE MANUFACTURE OF HIGH LASER DAMAGE
THRESHOLD MIRRORS AT THE 351 nm WAVELENGTH.**

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Sol-gel material based mirrors have been produced by forming alternate layers of high refractive index and low refractive index thin films. These mirrors have proven to have a high laser induced damage threshold (LIDT). Using nitric acid stabilised Zirconia derived from Zirconium-n-propoxide and base catalysed Silica, a 16 layer mirror with a reflectivity of better than 94% at 351 nm and 45° angle of incidence was fabricated. This had a LIDT of 7.7 J/cm² at 351nm with a 0.7 ns pulse width. Cracking prevented further layers being deposited. Both spin and dip coating were attempted with dip coating yielding the best results.

The coating structure has been analysed using Scanning electron microscopy, XPS depth profiling, and Atomic force microscopy. The bulk materials have been investigated using Transmission electron microscopy, X-ray diffraction, BET analysis, and Thermal gravimetric analysis.

High refractive index layers using Hafnia and Yttria with nitric or acetic acid and methoxyethanol have also been investigated as prospective high refractive index candidates for high LIDT mirrors.

Alternative acidic routes to silica have been studied as a possible low index material and a route to preventing cracking.

GP18

**ATOMIC FORCE MICROSCOPY STUDY OF NaOH CORRODED
Al₂O₃-TiO₂-SiO₂ COATINGS ON GLASS**

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Atomic force microscopy (AFM) was used to study the topography of Al₂O₃-TiO₂-SiO₂ sol-gel coatings on glass substrates following corrosion in 1 M NaOH solutions at 60°C. The coatings prepared were about 80 nm thick, were homogeneous on a nanoscale and displayed the 'glass pattern' before corrosion. Differently composed layers behaved differently during the corrosion process. Thus a 5Al₂O₃-40TiO₂-55SiO₂ layer was corroded away stepwise with increasing time up to 24 h. On the other hand a 20Al₂O₃-40TiO₂-40SiO₂ layer showed a pseudo-hexagonal surface morphology. A similar topography with hexagonals on the surface was found for the composition 20Al₂O₃-50TiO₂-30SiO₂. This possibly is caused by the formation of crystals with nephelin (Na₂O·Al₂O₃·2SiO₂) composition. However, layer compositions like 30Al₂O₃-40TiO₂-30SiO₂ or 20Al₂O₃-60TiO₂-20SiO₂ displayed tetragonal-like crystals on their surfaces following the corrosion process. These nanocrystals are similar to those formed after an NaOH corrosion of TiO₂ coatings and display the habit of anatase crystals. It is tried to explain the differently proceeding corrosion process.

ATOMIC FORCE MICROSCOPY STUDY OF TiO₂ FILM OBTAINED BY SOL-GEL METHOD.

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Among the transition metal alkoxides, those of titanium have been systematically studied from both experimental and theoretical point view. However, further information about the influence of different experimental parameters on the properties of the resulted materials can be still addressed.

In the present work Atomic Force Microscopy (AFM) was used to study the influence of the thermal treatment on the structural and textural properties of the sol-gel TiO₂ films obtained starting with Ti(OC₃H₇)₄.

The surface was imaged by Nanoscope III Atomic Force Microscope operating in the contact mode. Si₃N₄ cantilevers with a tip radius of 10 nm were used in the experiments. The normal force of the AFM tip was reduced to 10-10N by imaging the surface in the presence of a liquid. The resolution of the images was 512 × 512 points, and a typical image acquisition time was 1-2 minutes at a scanning rate of several lines per second.

Supplementary information have been obtained by XRD, ellipsometric and porosity measurements.

The TiO₂ films obtained by sol-gel method were homogeneous, transparent and amorphous. By thermal treatment in 400-600°C range, the strong crystallisation tendency of the films has been established. The high initial homogeneity of the TiO₂ films was preserved during the crystallisation process, too.

The thermally treated films exhibit uniform, monodispersed crystals as determined by AFM.

GP20

VANADIUM DOPED SOL-GEL TiO₂ COATINGS

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TiO₂ sol-gel films have found wide applications for venous optical coatings, porous coatings, photocatalysts, photoelectrochemical coatings and sensors. During the last decade, TiO₂ films doped with transition metal ions have been suggested as electrochromic materials for display devices. In the case of vanadium doped TiO₂ films these exhibit high electrochemical conductivity and have been suggested for potential application as antistatic coatings or switchings.

In the present work a study of the experimental conditions of the obtaining of vanadium doped sol-gel TiO₂ coatings has been carried out. Tetraethyl orthotitanate was employed as TiO₂ source and VCl₃, VOSO₄ H₂O and VOSO₄ solution in H₂SO₄ where employed as vanadium sources.

Supported materials have been obtained by dip coating method on silicon wafers, carbon spectral electrodes and titanium electrodes. The presence of vanadium ion in different valency state has been evidenced by UV-VIS absorption spectra, IR spectroscopy and X-ray diffraction, both on supported and unsupported coatings. The measurements have been made on initial and thermally treated samples at temperatures ranged between 100–300°C. The thermal treatment temperatures have been established according to the DTA/TGA results.

The vanadium doped sol-gel TiO₂ coatings have been tested as sensors in electrochemical processes (redox potential). The influence of both the thickness of films and the nature of substrate has been investigated.

TiO₂ PHOTOCATALYSIS ANTIBACTERIAL FILMS BY SOL-GEL

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Illuminated by ultraviolet ray, photo semiconductor TiO₂ is excited and has very strong oxidation. Combining such effect with the antibacterial effect of some metal ions (Ag⁺, Cu⁺), TiO₂ photocatalytic antibacterial film (ABF) was made by sol-gel spraying and dipping techniques. Plating ABF on matrixes glaze tile and glass, antibacterial tile (ABT), antibacterial glass (ABG) and some other products were fabricated, which can make our living environment cleaner and more comfortable.

Referring to some medical assessment standards, we put forward a assessment method to evaluate the antibacterial effect of glaze tiles and glasses. By this assessment, ABF showed different antibacterial effect under different illumination conditions (dark, fluorescent lamp, UV lamp).

The doping method of dopants (Ag⁺, Cu⁺) was studied. In order to enhance the photocatalysis activity and efficiency of TiO₂ film, some factors, such as processing method, precursor, heat treatment, specific area, crystal type, chemical component and light source, were discussed.

GP24

ANALYSIS OF SOL-GEL ALUMINA COATINGS ON STEEL SUBSTRATES

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Alumina coatings may improve the chemical resistance of steel substrates. Among the major applications of coated steels it can be cited uses in the chemical industry and automotive industry.

In this work, sol-gel alumina coatings were obtained using aluminium isopropoxide. Structural characteristics of the coatings were evaluated using ESCA.

It was observed the homogeneity of the film and the nature of chemical bonds.

**DEVELOPMENT OF HETEROPOLYSILOXANE COATINGS ON
ELECTROGALVANISED STEEL**

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The development of heteropolysiloxane coatings on electrogalvanised steel by the sol-gel process has been studied from the sol state to the solid state using techniques such as ^{29}Si NMR, SIMS, XPS, and the mechanical three point flexure test.

It was possible, from the overall results obtained, to propose a simplified modelisation for the coatings which brings into play two layers of differing molecular structure: an extremely thin internal layer and an outer layer, respectively called the 'anchoring' and 'volume' layers.

MULTI-LAYER SiO_2 - B_2O_3 - Na_2O FILMS ON Si FOR OPTICAL APPLICATIONS

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The fabrication of glass films by the sol-gel technique has attracted considerable attention in microelectronics, optics and other fields. In particular, we are interested in silica and multicomponent-based glass films for applications in integrated optics on silicon substrates, where sol-gel offers the possibility of a great variety of compositions and structures. For example, the porosity may allow the insertion of a dopant species, such as nano-crystals for third-order optical nonlinearity, into the host glass. The goal of this work was to prepare buffer layers on silicon of several microns thickness, using SiO_2 - B_2O_3 - Na_2O compositions to obtain low process temperatures, and to prepare SiO_2 guiding layers with a porosity control using the technique for the preparation and compositions of Vycor type glasses.

Films of several μm thickness were prepared, in many compositions of the SiO_2 - B_2O_3 - Na_2O system. The process included a two-step method to introduce water while inhibiting crystal formation, a repetitive spin-coating technique with a chamber to control the atmospheric humidity, and rapid thermal annealing. The results show good quality in terms of homogeneity, thickness, absence of cracks, and versatility in the studied compositions, and so suggest a good approach to the objectives. However, the results also show a high carbon concentration in the prepared films. This causes strong optical absorption, and inhibits the phase separation and the leaching processes associated with the Vycor technique. Reduction of carbon content has been investigated through the application of an adapted heat treatment.

**SYNTHESIS OF NANOCRYSTALLINE, REDISPERSABLE
ANTIMONY-DOPED SnO_2 PARTICLES FOR THE PREPARATION
OF CONDUCTIVE, TRANSPARENT COATINGS**

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Nanocrystalline, redispersable Sb-doped SnO_2 with Sb contents from 0.1–10 mol% (with respect to Sn) and a primary particle size of about 5 nm was prepared from SnCl_4 and SbCl_3 in solution by a growth reaction. The aggregation of the particles was avoided by in-situ surface modification with bifunctional organic molecules. The stabilising effect of the surface modification could be maintained during the following hydrothermal crystallisation step (150°C, 10 bar). The resulting nanocrystalline particles are fully redispersable in aqueous suspensions at $\text{pH} \geq 11$, solid contents up to 40 wt. % can be achieved.

Such aqueous dispersions were used to prepare transparent, conductive coatings on glass by spin-coating. After thermal densification (1 h at 550°C) transparent coatings of 220 nm thickness were obtained. A minimum specific electrical resistance of $2.5 \cdot 10^{-2}$ for Sb contents between 4 and 5 mole % was measured, the transparency in the visible range against air was 90 %.

GP28

HIGH CONDUCTIVITY INDUCED BY PHOTODESORPTION IN SnO_2 THIN FILMS GROWN BY SOL-GEL DIP COATING TECHNIQUE

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Optical transparency and high electrical conductivity of SnO_2 thin films are very attractive properties for using this oxide semiconductor as transparent electrodes for many kinds of optoelectronic devices. We have investigated pure, Sb-doped and Nb-doped films obtained by sol-gel dip coating technique. Although the heavy doping (2%) should yield degenerate e-type conduction, we have obtained highly resistive samples and moreover, they present thermally activated electron trapping in two levels of about 30 meV and 70 meV. Monochromatic light excitation (305 nm) in the range 77 K–300 K induces an increase in the sample conductivity, which depends on exposure time and the number of cooling cycles. Conductivity also increases with heating under vacuum to about 473 K. Both phenomena indicate a possible oxygen desorption and contribute to the elimination of electron trapping, which suggests that adsorbed gas atoms have participation in the electron capture in the dark. We have evaporated three different metals to make contact to SnO_2 samples: Cu, Au and In and although the resistivity shifts slightly, the same conductivity effect is obtained. We present results of optical absorption, complex impedance, resistance as a function of temperature in the dark and under influence of monochromatic light. The most important feature is the improvement in the sample quality by heating under vacuum and by thermally stimulated photodesorption, since the sample conductivity increases about 4 orders of magnitude.

PHASE DEVELOPMENT IN SOL DERIVED NANOPOROUS MEMBRANES FOR GAS PERMSELECTIVITY

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A sol-gel route has been used to produce a nanoporous membrane for the separation of 'greenhouse' gases from power plants at elevated temperatures (673–873 K). The membrane has a controlled pore size distribution and is multiphasic, in order to prevent grain growth and pore coarsening.

The alumina/titania diphasic ceramic was obtained from alkoxide precursors with additional magnesium or lanthanum doping to stabilise low temperature phases and to provide possible chemisorption of CO₂.

Thermal analysis (DTA and TG) was used to obtain information on crystallisation and transformation temperatures. X-ray diffraction and transmission electron microscopy, together with ²⁷Al magic angle spinning nuclear magnetic resonance, have been used to examine the phase development and the microstructure in these materials.

The xerogels of the La and Mg doped and undoped materials contained pseudo-boehmite and anatase. However, the boehmite XRD line widths were greater for the La doped material and increased with La content, indicating either smaller crystallites or a disordered solid solution.

Below 1120 K the undoped material gave a diphasic nanocrystalline microstructure of anatase and γ -alumina and both phases had fully transformed to their high temperature forms (rutile and α -alumina) by 1173 K. The Mg doped material additionally produced spinel, at levels determined by the extent of doping and the γ -alumina phase was stable to higher temperature.

At lower levels of La doping α -alumina had formed by 1170 K and at 1270 K a second phase, identified to be LaTi₂Al₉O₁₉, appeared. At higher doping levels a solid solution between LaAlO₃ and LaTiO₃ was seen with α -alumina appearing at a higher temperature (1373 K). At 1750 K the α -alumina was replaced by a lanthanum containing β -alumina phase (LaAl₁₁O₁₈).

GP31

**STUDY OF THE SELECTIVITY OF SnO_2 SUPPORTED MEMBRANES
PREPARED BY SOL-GEL ROUTE**

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During the last years the interest in inorganic materials to be used as filter in separation processes has been improved and the preparation of ceramic membranes by means of the sol-gel route has been widely investigated. In this work the sol-gel process was used to prepare SnO_2 supported membrane presenting average pore size of 3 nm. The effect of salt concentration (NaCl or CaCl_2) and of the pH of aqueous solution on the permeate flux and selectivity through the SnO_2 membrane were analysed by permeation experiments and the results interpreted taking account of the zeta potential values determined from electrophoretic mobility and potentiometric titration. The results show that the increase of salt concentration in the solution leads to the decrease in the permeate flux values. Moreover, this effect is more intense as the charge of the cation increases, indicating that the selectivity of the membrane is affected by the intensity of electrostatic interaction.

**CHEMISTRY-CRYSTALLISATION-MICROSTRUCTURE
RELATIONS OF SOL-GEL DERIVED LANTHANUM MODIFIED
LEAD TITANATE THIN FILMS**

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Lanthanum modified lead titanate thin films with a composition of $\text{Pb}_{0.88}\text{La}_{0.08}\text{TiO}_3$ have been obtained by the deposition by spin-coating of sol-gel synthesised solutions on $\text{Pt/TiO}_2/(100)\text{Si}$ substrates.

Solutions with the nominal composition and containing a 5, 10, 15 and 20 mol% excess of PbO were tested. The physico-chemical characteristics of these solutions were studied by means of infrared analysis (IR) and thermogravimetry and differential thermal analysis (TGA and DTA).

As-deposited amorphous layers were crystallised by firing at 650°C for 12 minutes with slow ($10^\circ\text{C}/\text{min}$) and rapid ($500^\circ\text{C}/\text{min}$) heatings.

Stoichiometry of the precursor solution and the type of thermal treatment used for the crystallisation of the films have shown to have a large effect on the composition, structure, texture and microstructure of the resulting films. These characteristics have been studied by Energy Dispersive X-ray Spectroscopy (EDXS), Grazing Incidence X-ray Diffraction (GIXRD) and Scanning Electron Microscopy (SEM).

Ferroelectric parameters of $P_r \sim 25 \mu\text{C}/\text{cm}^2$ and $E_c \sim 90\text{kV}/\text{cm}$, and pyroelectric coefficients of $p \sim 3 \cdot 10^{-8} \text{C}/\text{cm}^2 \cdot \text{K}$ have been measured in films deposited from solutions with a 20 mole excess of PbO and crystallised with rapid thermal annealings.

HP2

**STUDY BY RBS OF THE HETEROSTRUCTURE OF LEAD
TITANATE THIN FILMS**

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The depth profile analysis of modified lead titanate thin films is studied by means of Rutherford Backscattering Spectroscopy (RBS).

These films were deposited from sol-gel synthesised solutions onto platinised silicon substrates and crystallised by thermal treatments at temperatures of about 650°C with rapid heatings.

The chemistry of the solutions and the thermal treatment of crystallisation affect the heterostructure of the resulting films. This heterostructure is formed by a bottom interface produced by the reaction between the underlaying substrate and the film, an intermediate ceramic layer with a perovskite structure and a top surface with different lead content than the bulk film.

The ferroelectric response of these films is related to the composition, crystallinity and thickness of the former layers.

A RAMAN SCATTERING STUDY OF PbTiO_3 AND TiO_2 OBTAINED BY SOL-GEL

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PbTiO_3 and TiO_2 are parent compounds for a large variety of materials of widespread applications. PbTiO_3 and TiO_2 powders, obtained by the sol-gel method have been investigated by Raman and micro-Raman spectroscopy in order to assess the nature of the crystallisation phases, the stoichiometry and the degree of the segregation of phases, after the appropriate heat treatment. The nanocrystalline nature of the sol-gel products has been verified and confinement effects, pressure effects and non-stoichiometry of the grains have been discussed on the basis of the vibrational spectrum.

In lead titanate, a residual stress due to the ferroelectric transition gives a frequency shift of the Raman peaks. In titanium dioxide, confinement and non-stoichiometry effects produce large Raman peak broadening. The confinement has been observed in the anatase phase in 10–12 nm sized nanocrystals and has been explained by the non-conservation of the phonon momentum selection rule. The effect of the oxygen vacancies has also been discussed. The results give important suggestions on the optimisation of the physico-chemical parameters involved in the sol-gel process.

THE EFFECT OF BARRIER LAYER COMPOSITION AND STRUCTURE ON THE CRYSTALLISATION OF PZT COATINGS ON Si

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Lead-zirconate-titanate (PZT) is an interesting and promising ferroelectric phase. For some microelectronics applications it is particularly interesting to find ways for optimising the structure of the PZT when fired in close proximity to either silicon or to silicon dioxide surfaces. Usually, these surfaces poison the PZT crystallisation process and thus the ferroelectric or piezoelectric behaviour is prevented. Two key effects are important for these processes: (1) nucleation of the PZT into the perovskite phase, and (2) prevention of Pb loss by diffusion or reaction with the substrate material.

The present work reports on extensive studies to optimise the crystallisation of PZT with a variety of very thin barrier layers. Acetate based Pb-Zr-Ti sol-gel solutions (Zr:Ti = 50:50 with 10%Pb excess) were used throughout the studies. Fired coatings were 200-250 nm in thickness after normal heat treatment at 550-600°C. Barrier layer compositions which displayed beneficial effects included: SrTiO₃, BaTiO₃, BaZrO₃, LaAlO₃, and NdAlO₃. Other layers, including PbTiO₃, were not as useful. The thicknesses of these layers ranged from 20 to 100 nm, depending on processing conditions. X-ray diffraction of thin films was performed to monitor the phase transformation with temperature and barrier layer combination. High Resolution Transmission Electron Microscopy (HRTEM) was used to characterise selected samples. Energy Dispersive X-ray Spectroscopy (EDX) was applied for microchemical analysis and with a step scanning method the lead distribution could be determined through the depth of the thin film. Barrier layers which were nanocrystalline and relatively dense were better at promoting PZT microstructure development, because of increased nucleation density as well as preventing the loss of lead by diffusion.

STUDY OF THE LEAD ENVIRONMENT IN LIQUID AND AS-DRIED PRECURSORS OF PZ, PT AND PZT THIN FILMS

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Alkoxide based sol-gel processing of multicomponent materials is recognized to yield more homogeneous products at lower processing temperatures as compared to solid state synthesis due to the formation of heterometallic compounds in solution. However in the field of PZT sol-gel derived materials, such as thin films, only scarce data on homogeneity in the liquid state exist. X-ray absorption spectroscopy (EXAFS) was found to be a useful tool for local structure determination in liquid and amorphous state. The aim of this work was to analyse local environments of lead atoms in liquid and amorphous precursors for PZ (PbZrO_3), PT (PbTiO_3) and PZT ($\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$) based thin films.

Sols for thin film deposition were prepared via 2-methoxyethanol route with lead oxide and lead anhydrous acetate as lead sources. Lead L-edge EXAFS spectra of the sols and as-dried amorphous gels were measured at HASYLAB ROEMO beamline.

EXAFS analysis of PZ sols prepared from lead oxide reveals oxygen atoms in the first shell (2.2–2.3 Å) of lead neighbours and zirconium atoms in the second shell (3.9–4.0 Å). Similar results in terms of interatomic distances are obtained also with lead acetate. It is found that drying of the sol has no influence on the local structure of lead atoms. The EXAFS results therefore prove the existence of Pb–O–Zr bonding in liquid and amorphous states. Preliminary results on PT and PZT based sols similarly suggest the existence of Pb–O–M bonding (M=Ti and Zr, respectively).

HP6

**PREPARATION OF PZT FILM AND POWDER BY SOL-GEL
TECHNIQUE USING Ti- AND Zr- ALKOXIDES AND A NOVEL
Pb-PRECURSOR PREPARED FROM $\text{Pb}(\text{NO}_3)_2$ AND 1.5 EO_3
(EO_3 =TRIETHYLENEGLYCOL)**

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We are studying new precursors for the preparation of thick PZT films with the composition $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$, for applications in micro-engines. The films should be in the order 10 μm thick. We will describe the synthesis of a new precursor for lead, prepared from $\text{Pb}(\text{NO}_3)_2$ and EO_3 , and how it can be used together with $\text{Zr}(\text{OR})_4$ and $\text{Ti}(\text{OR})_4$ for the preparation of films of up to 0.4 μm , in a single layer. Repeated depositions were used to obtain thicker films. The decomposition pattern of the precursors and structural development has been evaluated by TGA, Thermo-Mass Spectroscopy, SEM-EDS, powder-XRD and FT-IR spectroscopy.

HP7

**DETERMINATION OF PARTICLE SIZE AND SHAPE IN THE SOL-
GEL TRANSITION OF PZT PRECURSOR SOLUTIONS**

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The formation and growth of polymeric particles in the hydrolysis and condensation of PZT sol-gel precursor solutions have been investigated by using photon correlation spectroscopy (PCS), small angle X-ray scattering (SAXS) and by measuring their rheological properties. The measurements indicated that the growth rates of the particles were largely dependent on the stages of hydrolysis. The average particle size in a newly prepared PZT solution was about 4-5 nm in diameter. Hydrolysis leads to an increase of the size up to 12-16 nm in diameter in about the first eight days. Sizes measured by SAXS were systematically smaller than those measured by PCS. Particles with linear or rod shape were found in the hydrolysed solutions.

SYNTHESIS AND CHARACTERISATION OF HIGHLY ORIENTED SOL-GEL (Pb,La)TiO₃ THIN FILM OPTICAL WAVEGUIDES

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Lanthanum-modified lead zirconate titanate (PLZT) system is a powerful candidate material for electro-optic application since it is transparent in the visible and the near infrared region and has excellent electro-optic properties. We have prepared the highly oriented crystalline, transparent, and crack-free PLT thin films on MgO and sapphire single crystal substrates by sol-gel method. For the preparation of the solution and thin films, lead acetate [Pb(CH₃COO)₂·3H₂O], lanthanum nitrate [La(NO₃)₃·6H₂O], and titanium isopropoxide [Ti[(CH₃)₂CHO]₄] were used as precursors. The PLT films fabricated on MgO(100) and c-plane sapphire substrates grow highly preferentially to (100) and (111) orientations, respectively. As La content increases, the PLT films have good orientation due to small misfit between the substrate and the PLT film by the structural change of PLT film from tetragonal to near cubic. PLT thin films with high La content have the low refractive index due to the decrease of the anisotropy of refractive indices. The propagation losses of the PLT films decrease as La content increases by the complex effect of reducing the surface scattering and the non-surface scattering. And though the surface roughness of the films having same composition is not affected by the film thickness, the propagation losses increase exponentially with growing the film thickness. Thus, the main mechanisms of the propagation loss with increasing the thickness are the internal scattering by the unavoidable defects and interface scattering by the multi-coating in sol-gel film rather than the surface scattering. Also, the highly oriented PLT films show high electro-optic coefficients. Thus, the PLT thin film can be a good candidate for the modulator application for integrated optics.

**PREPARATION AND DIELECTRIC PROPERTIES OF DENSE, FINE-
GRAINED BaTiO₃ CERAMICS FROM SOL-GEL-DERIVED
TRANSPARENT, PARTIALLY-CRYSTALLISED XEROGELS**

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Transparent, partially-crystallised nanostructured barium titanate (BaTiO₃) monolithic gels have been successfully synthesised via hydrolysis of a Ba,Ti-alkoxide precursor solution of 1.0 mol/L using water vapour. The gels had a density of around 2.7g/cm³ and consisted of pseudo-cubic BaTiO₃ particles in a region of 10 nm with a sharp size distribution. The crystallinity of the gels, which was defined by the ratio of the (110) peak area of the gels to that of a gel fired at 600°C (assumed to be 100%) by X-ray diffractometry, reached a value of 60%, and no crystalline phase other than BaTiO₃ was confirmed to exist in the materials. Organic compounds of <16% (in wt.%) were found to remain in the transparent gel monoliths as-dried at 90°C, which could be entirely removed by heat-treatment at 600°C for 2h in oxygen. The gels were still transparent even after firing them at 500°C in oxygen, though the degree of their transparency was significantly degraded. Firing at elevated temperatures above 500°C yielded translucent ceramics with translucency decreasing rapidly with increasing sintering temperature, and usual opaque ceramic bodies were finally produced at 600°C. Dense BaTiO₃ ceramics with a relative sintered density of about 94% and an average grain size of $\approx 1 \mu\text{m}$ were obtained from the gel monoliths by sintering at 1100°C for 2h in oxygen. Dielectric properties of the ceramic showed a normal ferroelectric dielectric response, but considerably diffused, with $\epsilon_r = 1800$ and $\tan\delta = 1\%$ (100kHz) at room temperature.

**SOL-GEL BARIUM-STRONTIUM TITANATE FILMS:
PREPARATION, PROPERTIES, AND APPLICATIONS IN
INTEGRATED CIRCUITS**

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Barium-strontium titanate (BST) films have been intensively investigated during the last years as a high-dielectric constant material for high density dynamic random access memory (256 Mbit/1 Gbit), as well as for millimetre microwave integrated circuits.

We discuss the sol-gel techniques for the BST films preparation. We have studied two ways of BST films preparation: from alkoxides solutions and from alkoxides solutions modified by 2-ethylhexanoic acid. The main attention is paid to the study of correlation between film microstructure and electrical properties. The effects of solution chemistry (in particular the degree of precursors modification by 2-ethylhexanoic acid), crystallisation procedure, film thickness, and Ba/Sr composition on microstructure and physical properties of sol-gel derived films are discussed.

The film structure and morphology, as well as their transformations during heat treatment of the films were characterised by X-ray diffraction, SEM, and ellipsometry. Capacitance-voltage and current-voltage characteristics, as well as frequency and temperature dispersion of dielectric constant and losses are used for characterisation of electrical properties of the films.

In addition, some issues of BST films integration are reported: a new system for multilayer spin-on deposition, a dry etching process of BST films, as well as sequence of processing steps during production of BST capacitors.

**SrBi₂Nb₂O₉ FERROELECTRIC POWDERS AND THIN FILMS
PREPARED BY SOL-GEL**

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Bismuth oxide layer ferroelectric thin films have attracted considerable attention for applications to non volatile memories and capacitors of dynamic-random-access memories due to their reversible spontaneous polarisation and their high dielectric constant. So far, Bi₄Ti₃O₁₂ and SrBi₂Ta₂O₉ are practically the only compounds used for thin film studies of bismuth oxide layered materials. Such thin films have high ferroelectricity comparable with PZT films and good electrical properties such as high fatigue resistance.

Stable sols or gels with SrBi₂Nb₂O₉ composition were obtained from mixtures of niobium ethoxide, bismuth and strontium 2-ethylhexanoates. XRD line broadening analysis was used to characterise the size and shape of powders of SrBi₂Nb₂O₉ crystallised during 2 hours at 700°C.

SrBi₂Nb₂O₉ thin films were prepared by spin-coating stable precursor solution on Si/SiO₂/TiO₂/Pt substrates. An acceleration of 7 rpm/s, a rotation speed of 4000 rpm and a rotation time of 30 s were retained as the most appropriate deposition conditions. Thin films were characterised using temperature-programmed XRD, SEM, AFM and hysteresis loops measurements. Randomly oriented 0.3 µm-thick crack-free films were obtained after 10 successive depositions and an heat-treatment of 2 hours at 700°C. Pure SrBi₂Nb₂O₉ crystallises at about 550°C. An increase of the average grain-size related to an augmentation of the roughness of the films is observed with increasing coatings number. P-E hysteresis loops have confirmed the ferroelectric behaviour of the films: such thin films show a remanent polarisation of 2.5 µC/cm² (measured for a voltage of 5V and a pulse of 8 ms). No fatigue are observed up to 10⁹ full switching.

FERROELECTRIC THIN FILMS OF BISMUTH STRONTIUM TANTALATE PREPARED BY ALKOXIDE ROUTE

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The study of interaction in $\text{Bi}(\text{OR})_3\text{-Ta}(\text{OR})_5\text{-ROH}$ system, where $\text{R} = \text{Me, Et}$ or ^iPr by the method of phase diagrams permitted to establish that metal ethoxides are the best of investigated precursors of bismuth tantalates via alkoxide route. In the methoxide system the solutions, where $\text{Bi/Ta} = 1$ cannot be prepared because of insolubility of polymeric $\text{Bi}(\text{OMe})_3$ in $\text{Ta}(\text{OMe})_5$ solutions. Bimetallic alkoxide $\text{BiTa}_2(\text{O}^i\text{Pr})_{13}$ crystallises from isopropoxide solutions and therefore only solutions of mass concentration less than 10% can be prepared.

Only in the ethoxide system solutions of various concentrations. where $\text{Bi/Ta} \leq 1.5$ can be prepared. Vacuum evaporation of the solvent from these solutions results in formation of viscous pastes, which can be stored without noticeable decomposition as long as several months. These pastes were used as precursors in the synthesis of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films which are considered as promising materials for ferroelectric memory devices.

The synthesis of bismuth strontium tantalate thin films by alkoxide route and their ferroelectric properties were studied. It was found that single phase ferroelectric films of thickness $0.4\text{--}0.5\text{ }\mu\text{m}$ could be formed by four repeating cycles of deposition of 2-ethylhexanoic acid solutions on $\text{Si-SiO}_2\text{-Ti-Pt}$ wafers followed by annealing in the temperature range of $700\text{--}750^\circ\text{C}$ for 30 min. after each deposition. The films demonstrated good ferroelectric properties: remanent polarisation ranged from 3.5 to $4.0\text{ }\mu\text{C/cm}^2$ and coercive voltage $1.5\text{--}2.0\text{ v}$.

PREPARATION AND CHARACTERISATION OF SOL-GEL DERIVED Y_2O_3 THIN FILMS

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The increasing demand for higher memory density in DRAMs necessitates dielectrics with high values of dielectric constant. SiO_2 is the standard dielectric material in microelectronics but yield a dielectric constant of only 3.8. The materials studied so far include ferroelectrics, rare earth oxide, Y_2O_3 and Ta_2O_5 films. In this study, sol-gel derived Y_2O_3 thin films have been prepared on platinised Si wafers and fired to temperatures ranging from 400°C to 750°C. Multiple spincoating was performed to obtain films up to 0.5 μm thick with an intermediate firing of 400°C between coatings. Top Pt electrodes were sputtered to form monolithic capacitors. These films exhibit dielectric constants as high as 16 and leakage currents of $2.5 \times 10^{-10} \text{ A/cm}^2$ at 3V, making them attractive candidates for high dielectric constant dielectric films in ultrahigh density DRAMs.

HP15

**DIELECTRIC AND FERROELECTRIC PROPERTIES OF SOL-GEL
DERIVED YMnO_3 FILMS**

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As part of the growing interest in ferroelectric films, reports have appeared on sputtered YMnO_3 films which exhibit a single polarisation axis and do not contain volatile species such as Pb or Bi. Single crystal YMnO_3 exhibits satisfactory polarisation ($<6 \mu\text{C}/\text{cm}^2$) and low coercive field ($<20 \text{ kV}/\text{cm}$). Additionally, the dielectric constant of YMnO_3 is quite low (<30) which should facilitate ferroelectric switching. In this study, sol-gel derived YMnO_3 films were prepared on platinised Si wafers and their dielectric and ferroelectric properties were characterised. Their electrical properties will be discussed with respect to development of the hexagonal phase and processing conditions. The potential of YMnO_3 as a candidate material for non-volatile memory applications will be evaluated.

**PREPARATION AND DIELECTRIC PROPERTIES OF YMnO_3
FERROELECTRIC THIN FILMS BY THE SOL-GEL METHOD**

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Thin films of ReMnO_3 (Re: rare earth) are proposed as a new candidate for non-volatile ferroelectric memory devices since they have one polarisation axis, contain heavy and hardly deoxidising elements, and do not contain Bi and Pb. We have prepared YMnO_3 thin films by the sol-gel method on Pt and Si substrates with two different processes; thermal decomposition and reflux processes. In both processes, tetrahydrated yttrium acetate ($\text{Y}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$) and tetrahydrated manganese acetate ($\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) were used as starting materials. In the thermal decomposition process, the solution containing $\text{Y}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ dissolved in ethanol containing diethanolamine (DEA) was used for coating. X-ray diffraction pattern of the coating films prepared from this solution showed that the YMnO_3 single phase was obtained with heat treatment at 900°C . In the reflux process, the $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ dissolved in 2-ethoxyethanol was dehydrated and refluxed at 125°C . Then, $\text{Y}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ dissolved in 2EE containing DEA was added, and the solution was again refluxed at 125°C . In the films prepared from this solution, the YMnO_3 single phase was obtained with heat-treatment at 800°C . Scanning electron microscopic observation showed that the thin films prepared with the composition of stoichiometric Y/Mn ratio had many pinholes, and dielectric properties could not be measured due to large leak current. It was found that 5–10% excess of Y in the coating solution was effective to grow dense structure and improve the dielectric properties. The dielectric constant and loss tangent of the thin films with Y/Mn ratio of 1.00/0.90 were about 20 and 0.05 at 100 kHz, respectively.

HP18

INVESTIGATION OF NEW-ION CONDUCTING ORMOLYTES SILICA-POLYPROPYLENEGLYCOL

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Two families of hybrid organic-inorganic composites exhibiting ionic conduction properties, so called ORMOLYTES (organically modified electrolytes), have been prepared by the sol-gel process. The first family has been prepared from mixture of 3-isocyanatopropyltriethoxysilane (IsoTrEOS), O,O'Bis(2-aminopropyl)polypropyleneglycol and lithium salt. These materials present chemical bonds between the organic (polymer) and the inorganic (silica) phases. The second family has been prepared by ultrasonic method from a mixture of tetraethoxysilane (TEOS), polypropyleneglycol and lithium salt. The organic and inorganic phases are not chemically bonded in these samples.

The Li^+ ionic conductivity σ of all these materials has been studied by AC impedance spectroscopy up to 100°C. Values of a up to $10^{-4} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ have been found at room temperature. A systematic study has been done changing the lithium concentration, the polymer chain length and the polymer to silica weight ratio and shows the strong dependence of σ with the preparation conditions. The properties of the Ormolytes have been related to their structure using linewidth and relaxation times NMR measurements of ^7Li between -100°C and 90°C.

At least, a rheological study of the sol-gel transition of the first family samples has been done, which show that these materials have mainly a viscous behaviour, even if a weak permanent elasticity appears at gel stage.

The structures and the ionic conduction properties of both families were compared with emphasis on the nature of the bonds between the organic and inorganic components.

OPTICAL AND ELECTRICAL SWITCHING IN VO₂ THIN FILMS

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Vanadium dioxide thin films have been deposited from vanadium oxoalkoxides VO(OR)₃ onto various substrates (SiO₂, Si, Ge...). An amorphous film is formed that has to be heat treated around 500°C under a reducing atmosphere in order to form the crystalline VO₂ phase. Optically transparent thin films are obtained that exhibit both electrical and optical switching around 70°C. The switching temperature together with the shape of the hysteresis cycle can be modified by doping VO₂ films with foreign cations. Doped M_xVO₂ (M = W⁶⁺, Nb⁵⁺, Ti⁴⁺ or Al³⁺) thin films are prepared under the same conditions by mixing the vanadium all oxide and a metal salt in an alcoholic solution. The switching temperature decreases when the film is doped with high-valent cations (W⁶⁺) and increases with low-valent cations (Al³⁺). TiO₂ doped VO₂ thin films do not exhibit the same behaviour as other doped VO₂ films. The width of the hysteresis curve first decreases and then increases when Ti is added to the VO₂ film. Best switching characteristics are obtained around Ti=5%. Devices based on VO₂ thin films are presented. They can be used for the protection of electronic circuits against over voltage or laser aggression

HP21

SOL-GEL METHOD TO PREPARE $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) THIN FILMS ON $\text{SrTi}(\text{Nb})\text{O}_3$ CERAMICS: PART 1 - THIN FILMS BY DIPPING

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Superconductor films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO or 1:2:3) were formed by dip-coating, on SrTiO_3 (STO) and Nb-doped STO ceramic substrates. The coating solution (M27) was based on Y-acetate, Ba alcoholate in 2-methoxy ethanol and Cu-butyrate, in an alcoholic matrix.

For ten (N) and twenty (NO) layers [multiple dippings on STO] systems and for heat treatment (HT) times of 8h (N) and 2h (NO) at 870°C under oxygen flow, there were obtained T_c (onset of superconducting transition temperature) of 90 and 91, 7K respectively. For HT under N_2 flow up to 625°C and then continued under O_2 up to 870°C (2h), the 20 layer system (NN) gave a T_c of 82.2K; whereas for the 10 (S) layers, heated under N_2 similarly and then heated in O_2 till 870°C for 8h, the T_c was 88.7K.

To explain these observations, the coatings (N,S), as well as the dried powder obtained from solution M27 [subjected to heatings HT1 (869°C, O_2 , 10h) or HT2=HT1+(942°C, O_2 , 10h)], were examined in an X-ray (XRD) diffractometer and in a SEM/EDX microscope. It was obtained powders HT1 and HT2 to correspond respectively to the orthorhombic and tetragonal phases, and that materials HT1&2 showed crystals in plate form, very similar in morphology to the crystals obtained in coatings N and NN. The XRD patterns for N and S coatings differed in S having more 2:1:1 and 0:1:1 impurities and perhaps (within the experimental error) a slightly higher c-axis, than for coating N, suggesting the former S coating might have lower oxygen content.

Finally, it was noted the nominal composition for M27 appeared to differ significantly from the stoichiometric 1:2:3, as judged from the DTA/TGA traces for M27, indicating (run under flowing O_2) a lower peritectic temperature for M27 than 1020–1040°C valid for 1:2:3 (run under oxygen flow). Also, M27 showed an unusually large DTA endothermic peak at 900–930°C, which could be assigned to a Y-deficient and Cu-rich composition as compared to nominal 1:2:3 composition.

ELECTROCHEMICAL PROPERTIES OF TUNGSTEN OXIDES SYNTHESISED FROM AQUEOUS SOLUTIONS

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Tungsten oxides are known to exhibit interesting electrochemical properties. Ion insertion (Li^+ , H^+) within the oxide network is highly reversible and thin or thick WO_3 films could be used as reversible cathode in lithium batteries or electrochromic layers in display devices.

We have shown that tungsten oxide can be conveniently synthesised via the condensation of tungstic acid in aqueous solutions. Molecular polytungstic acids are first obtained that further condense into hydrated tungsten oxide $\text{WO}_3 \cdot 2\text{H}_2\text{O}$. The nature of the polytungstic species formed upon condensation can be controlled by adding foreign ions in the solution. Precipitation for instance is no more observed in the presence of H_2O_2 . Peroxopolytungstic acids are then formed in which chelating $[\text{O}_2]^{2-}$ ligands prevent the formation of an oxide network. Such solutions are specially convenient for the deposition of optically transparent thin films. Mixed oxides $\text{WO}_3\text{-MO}_x$ are obtained when condensation is performed in the presence of foreign cations ($\text{M} = \text{Mo}^{6+}$, V^{5+} , Ti^{4+} ...). This paper addresses the solution chemistry of polytungstic acids and describes the electrochemical properties the resulting products.

HP23

**METAL (Fe, Co, Ni) NANOPARTICLES IN SILICA GELS,
PREPARATION AND MAGNETIC PROPERTIES**

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Metal containing silica gels are prepared from a mixture of tetraethyl orthosilicate, ethanol, 0.1 N nitric acid and formamide in the proportion 1:4:4.5:1 in which the metal is added in the form of a nitrate, in order to obtain M/Si molar ratios from 0.01 to 0.3. After drying, the xerogels are submitted to thermal treatments under hydrogen within the temperature range 600 to 1000°C. The changes occurring during these treatments are followed by X-ray diffraction, transmission electron microscopy, Mössbauer spectroscopy and magnetisation measurements.

During these treatments, nickel is nearly totally reduced to the metallic state in the form of particles the mean size of which increases from 3 to 10 nm with increasing temperature. Increasing the nickel concentration does not modify this size, but induces a broadening of the size distribution width. At room temperature, they exhibit a superparamagnetic behaviour. They are stable towards reoxidation when reexposed to air at room temperature.

Iron and cobalt behave in a notably different manner. First, in both cases, within a certain temperature range (700 to 850°C), silicates are formed during the thermal treatment and the metal is only partially reduced. Secondly, particularly for iron, the small metallic particles formed at low temperature (<700°C), reoxidise when the samples are reexposed to air. A nearly total reduction of the metal is obtained only at high temperatures (1000°C and above). The particles formed are then large enough to prevent reoxidation. The resulting evolution of the magnetic behaviour is much more complex than in the case of nickel.

IRON-OXIDE SILICA COMPOSITES. SYNTHESIS AND PROPERTIES

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Composites containing ferrimagnetic oxide nanoparticles dispersed in silica are required for the studies of magnetic interactions between particles and surface effects. The sol-gel process allows the control of the size and dispersion state of the particles in the matrix.

Spinel iron oxide particles with adjusted mean size were prepared by coprecipitation of ferric and ferrous ions in alkaline medium. A sol of non aggregated maghaemite particles was obtained by dispersion in acidic water (pH~2). The polymerisation of silica precursors (triethoxysilane or silicic acid) inside this aqueous sol leads to nanocomposite materials. The observations of composites by electron microscopy showed a homogenous dispersion without noticeable aggregation of particles in both matrices.

The interactions at the iron oxide-silica interface were studied by thermal analysis, IR, NIR and Mossbauer spectroscopies. No Si-O-Fe bonds are formed in the xerogels and only hydrogen bond interactions between hydration layers of particles and remaining silanol groups are observed.

The thermal properties of these nanocomposites suggest new applications. Under oxygen flux, the matrix prevents sintering of particles and allows the stabilisation of maghaemite up to at least 1000°C. Under limited agglomeration the particles transform into ϵ -Fe₂O₃ which transforms into haematite under extended agglomeration. Under inert gas, the cleavage of Si-H bond in triethoxysilane-based composites allows the reduction of the iron oxide. This yields a new process for the synthesis of metallic ceramics.

JP1

AGGREGATION, AGEING AND DRYING OF SiO_2 SOLS IN AQUEOUS SOLUTION

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The aggregation of SiO_2 sols in aqueous solution and the behaviour of the resulting gels during ageing and drying processes are investigated by small angle X-ray scattering experiments.

In a sodium-water glass solution an ion exchange results in an aggregation of the previously existing colloids. The aggregation clusters can be characterised by their size, fractal dimension describing the mass distribution of the clusters and the size of the primary units.

When the pH of the gel preparation varies between 2 and 5.8, the gelation time changes strongly. The value of the fractal dimension of the aggregation clusters remains constant at about 2.2. However, if the pH exceeds 5.8, the gelation time increases again and the fractal dimension decreases to a value of nearly 1.7. This process is attributable to the increase of the surface charge of the aggregating particles as the pH increases and to the resulting Coulomb repulsion. These facts are in contrast to results of computer simulations described in the literature.

The ageing of the wet gels can be interpreted by means of a classical Oswald ripening. The pH value only influences the velocity of the particle growth because the solubility of SiO_2 in H_2O depends on the pH. The comparison of the experimental and theoretical results shows that the ripening is a diffusion limited process.

During drying, an evaporation of the solvent of up to 70% does not cause a change in the structure of the clusters in a size range up to 30nm (the visual field of the experiment). The solvent leaves the large pores first.

STRUCTURAL EFFICIENCY AND MICROSTRUCTURAL MODELING OF WET GELS AND AEROGELS

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Structural efficiency for this work is defined as the ratio of apparent density of the porous gel network to the density necessary to produce an ideal foam of the same elastic modulus. The ideal structure is assumed to be fully connected and to exhibit a scaling relationship between modulus E and density ρ of the form $E \propto \rho^\alpha$ with the scaling exponent $\alpha = 2$. Using the measured moduli published for a variety of aerogels and wet gels, the structural efficiency is discussed as a function of porosity, skeleton material (silica [SiO_2], Resorcinol Formaldehyde [RF], Melamine Formaldehyde [MF] and amorphous Carbon [C]) and heat treatment. Typical values range from >50% for high density and heat treated aerogels to <10% for low density wet gels.

Microstructural modelling is based on an ideal cubic cell that has been used to model sintering behaviour of aerogels. Realistic features typical for nonfractal gel structures are then added: the cylinders are replaced by spherical particles joined together by necks of relative radius a ; mass is added to the system that does not contribute to the stiffness of the structure ('dangling ends'); and the connection between adjacent nodes is taken to be curved instead of straight (tortuosity). The evolution of the elastic modulus as well as the density is then calculated as a result of these modifications and its influence on the scaling behaviour quantified. It is shown that the elastic modulus scales with the square of the relative neck radius and linearly with the inverse tortuosity, whereas the density is hardly influenced by the first and increases linearly with the latter. The influence of necks can be demonstrated for RF aerogels produced with various monomer: catalyst (RC) ratios and for silica aerogels in the first stages of sintering. Relative neck radii for these systems range from 0.4 to 1.0. The tortuosity can be estimated from thermal measurements to be 1.5–2. Especially for low density networks, the main reason for the low structural efficiency is concluded to be mass in the dangling ends.

LASER SINTERING OF $\text{SnO}_2\text{:Sb}$ SOL-GEL COATINGS

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Sb doped sol-gel SnO_2 films were prepared from alcoholic solution and deposited via a dip coating process on fused silica substrates. The coatings have been sintered by CO_2 laser irradiation by means of a 700 W cw CO_2 instrument using a *fast scan* mode in which the laser beam is scanned by a high speed rotating polygon scanner ($\omega_{\text{max}} = 8800$ rpm) in one direction and the sample is moved perpendiculary at a speed up to 250 mm/s. The temperature of the substrate was monitored by a fast pyrometer with a time resolution of 5 μs . The coatings have been characterised by several methods. Their electrical resistivity, ρ , has been measured using the Van der Pauw technique and the corresponding carrier density, n , and mobility, μ , by Hall effect in the temperature range $200 < T < 580$ K. The structure of the coatings has been determined by X-ray diffraction at grazing incidence and their thickness by a surface profiler. The mesoscopic morphology was analysed by scanning electronic microscopy and the micromorphology by transmission electronic microscopy. The density profile and roughness of the layers were measured by X-ray total reflection. The densification and sintering process by CO_2 laser radiation is mainly a thermal driven process, as size of the particles, layer thickness and electrical properties (up to 500°C) scale with the temperature generated by the irradiation. However, the morphology of the coatings and the electrical properties (for $T > 500^\circ\text{C}$) are affected by the laser power and energy density. The technique allows to produce coatings with $\rho \approx 6 \times 10^{-3} \Omega \text{ cm}$, $\mu \approx 12 \text{ cm}^2/\text{Vs}$ and $n \approx 2.5 \times 10^{20} \text{ cm}^{-3}$ at a rate of $10\text{--}15 \text{ cm}^2/\text{s}$. These coatings have a high optical transmission in the visible range and can substitute advantageously TEC coatings prepared by other deposition techniques when a sheet resistance higher than $80 \Omega_{\square}$ is sufficient (antistatic, heating application).

EFFECT OF PRASEODYMIUM DOPING ON THE PROPERTIES OF Y-FSZ OBTAINED BY SOL-GEL METHODS

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Stabilisation of cubic zirconia by addition of yttria, magnesia, ceria or calcia allows to toughen ceramics. The mechanical properties of these materials depend on several parameters like the doping concentration, zirconia particle size as well as microstructural characteristics like shape, grain size, densification. In this communication, the effect of adding praseodymium and the synthesis route, in a molar composition $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}(\text{Pr}_2\text{O}_3)_{0.05}$ prepared by several gels methods has been studied.

Ceramic process (CE), coprecipitation route (CG), citrates polymerisation (CI), gelatine protected gels (GE) and polymeric gels obtained by hydrolysis-condensation of alkoxides (PG) has been used and compared for the synthesis of the material.

Powder fired at 500°C has been sieved at 60 µm, uniaxially pressed and fired at 1550°C. The obtained tablets were tested by DRX, SEM-EDX, density measurements and Vickers hardness. Pt electrodated tablets has been tested by Impedancy Spectroscopy.

Results indicate that praseodymium addition improves the mechanical and microstructural shape of the material.

**THERMAL EVOLUTION OF DENSITY AND CRYSTALLINE
TRANSFORMATIONS OF SILICA OBTAINED FROM ALKOXIDE**

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The possibility of controlling the properties of the amorphous oxides of silica at the stage of hydrolysis of their alkoxide precursor (tetraethoxysilane) by varying the nature of the reaction medium and water-alkoxide molar ratios (η) was studied.

The processes were simulated for the main temperature points of the physico-chemical transformations in the products of hydrolysis of tetraethoxysilane on heating.

The organic solvents were selected for their differences in chemical nature, dielectric constant and capacity to participate in protolytic substitutional reactions of organic groups attached to silica (ketones, alcohols and cellosolves).

We related the density response to the initial content of the precursors in the xerogels. The precursors govern the pore-structure relaxation as well as the intramolecular and intermolecular condensation. The microstructure is clearly related to the hydrolysis conditions.

The possibility of controlling the processes of crystallisation the amorphous silica by varying the nature of organic solvent was also established. This is clear because the η at which one gets silica with the highest crystallisation activity are distinctive for each medium. The specific conditions for obtaining the thermal-metastable and thermal-stable silica were determined for each of the organic solvents.

SILICA GELS AND GEL-GLASSES CONTAINING SILVER AND PLATINUM METAL PARTICLES

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Silica gels containing Ag_2O from 0.05 to 20 mol % and PtO_2 from 0.1 to 1 mol% have been synthesised using TEOS, $\text{C}_2\text{H}_5\text{OH}$, H_2O , HNO_3 , HCl , AgNO_3 and PtCl_4 as precursors. The obtained gels with Ag_2O are colourless, while the gels containing PtO_2 are yellow. The gels have been heat treated in the 25–1000°C temperature range. The processes of structural evolution of the gels have been studied by means of IR-spectroscopy, X-ray diffraction, transmission electron microscopy (TEM) and transmission electron microdiffraction (TEMd). It has been established that the temperature of gel to gel-glass transition decreases, when the Ag_2O content in the glass increases.

Special attention is paid to the formation of silver and platinum metallic particles in amorphous materials. The microstructure of the gels has been observed and the sizes of the metal particles are determined to be from 3 to 25 nm.

The crystallisation processes in the gels heat treated at 1000–1200°C are carried out and besides the silver and platinum particles the crystalline phase of α -cristoballite is separated.

It has been shown that nanocomposite materials containing ultrafine silver and platinum particles in SiO_2 amorphous or polycrystalline matrixes can be obtained.

CRYSTALLISATION BEHAVIOUR OF TITANOSILOXANES ON PYROLYSIS

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The preparation of titanasiloxanes and their ceramisation process were investigated. Titanasiloxane compounds, which have a well-defined sequence and silicon and titanium formula, were synthesised by the reaction of silanol with titanium chelate compound or titanium alkoxide followed by the pyrolysis in air.

Cyclic titanasiloxanes, $[R_2SiOTi(acac)_2O]_2$ ($R=Bu^iO$ (CTS) and Ph (Ph-CTS)), were prepared by the reaction of silanediols with bisacetylacetonatodisopropoxidotitanium in methanol in 1/1 molar ratio. CTS and Ph-CTS provided yellow crystals, which proved to be consisted of $[Si-O-Ti-O]_2$ eight membered ring in the center of the molecule.

On the other hand, $[(Bu^iO)_3SiO]_nTi(OPr^i)_{4-n}$ ($n=2$ (TS2) and 3 (TS3)) were synthesised by the reaction of tri-*t*-butoxysilanol with titanium tetraisopropoxide in THF followed by distillation and recrystallisation.

CTS, Ph-CTS, TS2 and TS3 were subjected to the pyrolysis under air condition to give $nSiO_2-TiO_2$ oxide. On the pyrolysis, titanium component crystallised in anatase to provide a phase separated ceramic material, which consists of a sea (SiO_2) and islands (TiO_2). The crystallisation temperature of TiO_2 component decreased with the increase of the titanium component. The crystallisation of TiO_2 was supposed to be controlled by the silica component surrounding the titania. The mean crystalline size of anatase increased with the increase of the pyrolysis temperature. In addition, the crystalline size increased with the increase of the titanium component in the sample.

As a result, we suppose the possibility in the control of the crystallisation temperature and crystalline size by regulating the sequence of the precursor polymers.

**SOL-GEL COMPOSITE CERAMIC MATERIALS IN THE SYSTEM
 $\text{ZrO}_2\text{--Al}_2\text{TiO}_5$**

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The ceramic composite materials on the basis of ZrO_2 are very promising today for the science and technology. Investigations on the sol-gel synthesis of composite materials in the system $\text{ZrO}_2\text{--Al}_2\text{TiO}_5$ are made. The purpose is an obtaining of ceramics with improved thermal stability. By the sol-gel method the processes of stabilisation of ZrO_2 and the synthesis of tialite occur simultaneously.

The studies are carried out with different ratio between ZrO_2 and tialite. The most perspective ratio are found to be 80:20 and 70:30. Using X-ray diffraction and IR-spectroscopy the phase formation in composites with participation of Y_2O_3 and CeO_2 as additives in amounts 5, 8, 10 and 12 weight % is followed in the temperature range 200–1380°C.

It is established that the introducing of Y_2O_3 stabilises the tetragonal modification of ZrO_2 up to 1200°C and after that the monoclinic modification appears. This modification could be obtained at lower temperatures if the ZrO_2 content is higher and the Y_2O_3 content reaches 10–12%. The most intensive is the tialite synthesis at 1100 and 1200°C. At 1380°C a new phase, probably ZrTiO_4 , appears in Y_2O_3 and ZrO_2 rich compositions. In whole temperature range monoclinic ZrO_2 presents always in compositions with CeO_2 . The presence of the monoclinic ZrO_2 in the composite materials will improve their thermal properties.

β -EUCRYPTITE LAS VIA SOL-GEL ROUTE

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β -eucryptite solid solution LAS $\text{Li}_2\text{O}:\text{Al}_2\text{O}_3:3\text{SiO}_2$ was processed via sol-gel route. This was intended for future development of humidity sensor. Stoichiometric sols were prepared using lithium chloride monohydrate, aluminium nitrate ninehydrate and tetraethoxysilane precursor as sources of Li_2O , Al_2O_3 and SiO_2 respectively. Complex solutions of lithia and alumina in ethanol/water mixtures were catalysed by inorganic acids in ratios of 0.01, 0.05 or 1.0 based on TEOS. Solutions were refluxed at 85°C , cooled and TEOS was hydrolysed. Drying control agent was added. After ageing for one week, the stable sols gave clear gels. TGA and IR were used to determine the minimum burn out temperatures. XRD and TEM were used to characterise the structural parameters of the gels, powered gels (110°C) and calcined ones at 900°C .

Results proved that the maximum % yield of LAS could be obtained in presence of H_2SO_4 , catalyst with a ratio of 0.10 to TEOS in preference to hydrochloric and nitric acids. The minimum calcination temperature was proved to be at least 400°C . Low crystallinity resulted even on heating up to 900°C .

SOLVENT EFFECT ON THE SOL-GEL SYNTHESIS OF LITHIUM ALUMINATE

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Lithium aluminate provides the required thermophysical, chemical, mechanical stability and favorable irradiation behaviour to be used as a tritium-breeding blanket in fusion reactors. γ -LiAlO₂ can be prepared by solid-state fusion, coprecipitation or by sol-gel procedures. This last method could assure a high purity product obtained at low temperature.

In this work, lithium aluminate was prepared using different alcohols as solvents. Aluminum sec-butoxide was dissolved with ethyl, isopropyl or n-butyl alcohol and hydrolyzed simultaneously with LiOH. The resulting solids were characterised by XRD, DTA, TGA and SEM. Lithium aluminates were also prepared by fusion and peroxide methods as comparison.

It was found that the precursors are semi-crystalline Al-Li mixed carbonates using ethyl or isopropyl alcohol whereas a high crystalline Li-Al hydroxyl is obtained with the n-butyl alcohol. In the calcined samples, the carbonates were partially eliminated in the ethyl and isopropyl preparations (800°C), while in the n-butyl sample the highest yield and a perfect γ -LiAlO₂ phase was obtained at 600°C.

JP15

**ROLE OF MnO ON MULLITISATION BEHAVIOUR OF Al_2O_3 - SiO_2
GELS**

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Gels were synthesised from tetraethylorthosilicate (TEOS) and aluminium nitrate. The structural evolution of the gels as a function of its MnO amount and heat-treatment temperature was studied by differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and visible spectrophotometry (VIS). The obtained results prove that the presence of MnO can induce mullitisation at lower temperatures. However, the effect of MnO depends of its contents and in the way how it enter into mullite structure.

**ULTRAVIOLET-LASERS-INDUCED CRYSTALLISATION OF SOL-
GEL DERIVED INDIUM OXIDE FILMS**

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Modification of sol-gel derived indium oxide thin films by ultraviolet lasers was investigated. Irradiation by an ArF excimer (6.4 eV) and the fourth harmonic generation of a Nd:YAG laser (4.7 eV) was found to be effective in the crystallisation of the sol-gel films. On the other hand, no changes were observed in the films irradiated by a 2.3-eV laser. The induced crystallisation was accompanied with a decrease in the sheet resistance and a loss of OH groups. Transparent crystalline indium oxide films were obtained by a low fluence ($<20\text{mJ/cm}^2$) laser irradiation although degradation of the film surface was promoted with a high fluence laser pulse. Since the sheet resistance of the irradiated films was lower than that of conventionally heated films, displacement of oxygen atoms is suggested to be induced by the irradiation.

JP17

SOL-GEL-DERIVED LEAD TUNGSTATE FILMS

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Sol-gel lead tungstate thin films were prepared from the precursor including peroxytungstic ester, lead acetate trihydrate. The heat-treatment process was determined by TG and DTA measurement. Structural changes undergone by samples heated under different temperatures were investigated using X-ray diffraction, IR and SEM.

SOL-GEL SYNTHESIS AND MICROSTRUCTURAL CHARACTERISATION OF SILICON OXYCARBIDE GLASS SHEETS WITH HIGH FRACTURE STRENGTH AND HIGH MODULUS

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A synthesis route to silicon oxycarbide glass sheets with thickness in the range from 50 to 1000 μm and area up to 20 cm $\times$ 35 cm has been developed for the first time. Methyl modified nano particulate SiO_2 sol (solid content ~70 wt%) obtained by basic catalysis of methyltriethoxysilane, tetraethoxysilane and colloidal silica precursors was casted by doctors blade method, dried at 50°C for 15h and sintered in nitrogen atmosphere at various temperatures between 850°C and 1600°C for 30 minutes.

The influence of the SiO_2 particles content on sheet formation was investigated. Sheets prepared without colloidal silica sol, were completely cracked after sintering, whereas crack free sheets were obtained from sols containing 0.10 to 0.35 moles of colloidal silica sol per mole alkoxide. The addition of colloidal silica increases the specific surface area of the dried gel from 0.55 to 4.48 m^2/g and the pore volume from 0.003 to 0.026 cm^3/g , which allows the crack free removal of organics under heating rates of up to 150 K/h.

The sheets show a high level of fracture strength (three point bending) between 200 MPa (95% level of confidence range 180–220) and 300 MPa (272–352) (depending upon colloidal silica content) for sintering temperatures between 900 and 1200°C. For higher sintering temperatures the fracture strength decreases significantly down to about 114 MPa (102–133). The Young's modulus (impulse echo method) increases monotonously with increasing sintering temperature from 80 GPa at 850°C to 128 GPa at 1200°C and decreases to 102 GPa at 1450°C. High resolution TEM, NMR, XRD and elemental analysis show a homogeneous amorphous matrix of $\text{SiC}_x\text{O}_{2-2x}$ units and around 4–5wt % of free carbon for temperatures up to 1200°C. At sintering temperatures of 1450°C and 1600°C about 20 wt. % β -SiC crystals (3–5 nm) and 1–2 volume % of lamellar graphite (25–30 nm long) are formed. Simultaneously the fraction of Q^4 units (SiO_4) increases from 56% (900°C) to 75% (1450 °C). This phase separation process is assumed to be responsible for the observed behaviour of strength and modulus. Such oxycarbide glass sheets could have an application potential as substrates for microelectronic packaging and for laminates.

JP20

**SOL-GEL SYNTHESIS, STRUCTURE AND PROPERTIES OF
MULTICOMPONENT OXYCARBIDE GLASSES**

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Existing sol-gel polymerisation/pyrolysis routes employing two separate metal alkoxide precursors have been applied to form multi-component silicon oxycarbide glasses based on a borosilicon oxycarbide (B-Si-O-C) system. These materials have been characterised at the gel, glass and glass ceramic stage by ^{29}Si and ^{11}B magic angle spinning nuclear magnetic resonance (MAS NMR), X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

The sol-gel process has been adapted to form a pyrolysed, micrometre thickness borosilicon oxycarbide layer on suitable substrate materials. The layer system provides the basis for quantifying mechanical properties of these borosilicon oxycarbide materials.

**MORPHOLOGY AND MICROSTRUCTURE REARRANGEMENT
INSIDE ZnO PARTICLES PROCESSED BY THE SPRAY PYROLYSIS
METHOD**

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The research in the field of advanced materials synthesis efforts emphasise the ultrafine powder synthesis control ability. Spray pyrolysis, as a dispersion phase powder processing method, is applied in zinc oxide submicrometer to nanosized powder synthesis. The process involves aerosol formation from the precursor salt solutions and control over aerosol decomposition in a high temperature tubular flow reactor in the temperature range from 873 to 1173K. In order to estimate the influence of the initial droplet size on resulting particle size and morphology, the aerosol was proceeded by means of twin-fluid as well as ultrasonic mist generator. X-ray diffraction (XRD), differential scanning calorimetry (DSC), infrared spectroscopy (IR) and scanning electron microscopy (SEM) were used in particle characterisation. It was shown that twin-fluid derived ZnO particles are hollow spheres ranged from 1 to 4 μm with the crust thickness 0.2–0.3 μm , composed of ZnO microcrystals the size of 200–500nm. For 0.004 mol/l precursor solution, spherical, smooth, 100–200nm dia ZnO particles are obtained. The model of evaporation from droplets containing dissolved solids is applied and correlated with the empirical results. It was shown that good agreement between the experimental results and numerical predictions for variety of evaporation regimes is achieved.

KP3

PREPARATION OF Ti-Nb-O NANO-POWDERS AND PHASE DEVELOPMENT STUDIES DURING HEAT TREATMENT

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Nano-porous film electrodes of TiO_2 has become a very active area of research, which aims to improve the properties of Grätzel type solar cells, displays and batteries based on this types of electrodes. We are investigating various ways of improving the electrical properties of the TiO_2 nano particles and to finding ways of understanding the conduction process in the nano-porous films.

In this study, we investigate the preparation of Nb_2O_5 - TiO_2 nanoparticles, in the whole range of compositions from pure TiO_2 to pure Nb_2O_5 , and their phase and microstructural development on heat-treatment. The preparation of nano particles was made by rapid hydrolysis of $\text{Ti}(\text{OPr})_4$ and $\text{Nb}(\text{OEt})_5$, under basic conditions, in ethanol. The characterisation of the precipitates and the phase and microstructural studies during heat-treatment were monitored by means of TGA, DSC, TEM-EDS, powder-XRD and FTIR.

GRAIN GROWTH AND PHASE TRANSFORMATION IN GELS DERIVED ZIRCONIA NANOCRYSTALLINE POWDERS

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The hydrolysis of zirconium alkoxide is certainly one of the most employed route to synthesise zirconia nanocrystals. Three different materials were prepared, precipitate was obtained by step hydrolysis of the zirconium n-propoxide while xerogel and aerogel were synthesised with controlled amount of acetylacetone as chelating agent.

The crystallisation processes of the three products were studied and presented previously in the '8th International Workshop on glasses and Ceramics from Gels'. Summarily, these three materials were shown to be composed of similar elementary particles whose size, as established by Small Angle X-rays Scattering (SAXS), was close to 2 nanometers. However, their interparticle arrangement were different from one to the other giving rise to striking differences in the crystallisation scheme.

The present work states upon the role of the elementary particles organisation elementary particles within aggregates, as well on zirconia grain growth as on phase transformation. The grain size and lattice microstrains were established by Rietveld refinement of XRD patterns. The influence of such parameters on the transformation processes are discussed together with HRTEM analysis of structural defects.

It is shown that precipitates display classical martensitic transformation while aerogel and xerogel reveal more progressive evolution (massive transformation) assisted by diffusion processes.

KP6

PREPARATION OF Li_6SiO_5 COMPOUND BY THE SOL GEL ROUTE AND ITS CHARACTERISTICS

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A pressable and sinterable powder was obtained after drying the gel formed by mixing an alcoholic suspension containing appropriate amounts of LiOH and SiO_2 (Aerosil). The dried powder is then calcined at 420°C . Sintering of the pellets formed by pressing the calcined powder at temperatures below 700°C results in the formation of the compound hexalithium monosilicate, Li_6SiO_5 . Scanning electron microscope showed one phase for this new compound in the lithium silicate family which is characterised by six-edges plate crystals. X-ray studies showed that these crystals have main X-ray diffraction lines with d-values at 4.407, 3.548, 3.339, 2.419, 2.360, 2.010, 1.421 and 1.418. The compound Li_6SiO_5 decomposes at temperatures above 700°C to Li_4SiO_4 and Li_2O as indicated by X-ray analysis. The high lithium content of Li_6SiO_5 permits its usage as blanket material for breeding tritium, consequently the energy, in fusion reactors.

**PREPARATION OF HYDRATED ANTIMONY PENTOXIDE
MICROSPHERES (DIAMETER $<40\ \mu\text{m}$) BY WATER EXTRACTION
VARIANT OF SOL-GEL PROCESS AND ITS APPLICATIONS TO
SORPTION OF SODIUM**

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Hydrated Antimony Pentoxide (HAP) microspheres (diameter $<40\ \mu\text{m}$) were obtained in the following steps: (1) hydrolysis of SbCl_5 with water, at temperatures $3\text{--}30^\circ\text{C}$, (2) peptisation of the resulting precipitate (sometimes with addition of small quantities of water) at $70\text{--}90^\circ\text{C}$ to the sols of concentration $0.1\text{--}0.5\ \text{M}$ and of Cl/Sb molar ratio $0.04\text{--}0.24$ respectively, (3) formation of sol emulsion in 2-ethylhexanol-1 (EH)³, (4), gelation of emulsion drops by extraction of water with partially dehydrated EH ³. The obtained gels were then leached with water, concentrated NH_4OH or 3M HNO_3 , washed from NH_4 , NO_3 ions and dried at ambient conditions. The XRD patterns have shown that all the samples have similar crystalline structure of $\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. However thermal analysis has shown that the prepared sorbents have initially the composition $\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$. Upon heating one molecule of H_2O is lost with endothermic effect with a maximum at 125°C and the remaining 3 molecules are lost with a similar effect at 285°C . Retention of ^{24}Na on all non calcined samples has been studied under static and dynamic conditions. The untreated gel had a maximum capacity of $13\ \text{mg Na/g}$. After the treatment the capacity increased to approx. $18\ \text{mg Na/g}$ and even to $21\ \text{mg Na/g}$ (as determined in dynamic conditions). All samples showed good activity and stability, high sedimentation rate and low hydraulic resistance. The poor retention of untreated samples can be due to absorption of the solvent used in the sol-gel process.

KP8

PREPARATION OF MULLITE FIBRES BY THE SOL-GEL METHOD

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Mullite fibres were synthesised from an aqueous solution of aluminium nitrate, aluminium isopropoxide and tetraethoxysilane by the Sol-Gel method. The starting solution was prepared by hydrolysing tetraethoxysilane into an aqueous solution of aluminium nitrate and aluminium isopropoxide. The spinnability of the starting solution was investigated by varying the molar ratio of the aluminium isopropoxide/aluminium nitrate in the solution. The difference of chemical structure between spinnable solution and unspinnable solution was investigated by viscosity and NMR analysis. Fibre drawing from viscous solution yielded gel fibres of about several metres long. Thermal changes of gel fibres to mullite fibres were also studied as a function of heat treatment temperature by DTA/TGA, XRD, IR spectroscopy and SEM.

SYNTHESIS AND CHARACTERISATION OF PZT FIBRES VIA SOL-GEL PROCESS

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A new trend in the field of ceramic fibre synthesis are fibres which can play an active role in composites. One of these are the piezoelectric lead zirconate titanate (PZT) fibres which can be used for producing sensors and actuators composites. Spinnable PZT-gels were produced via sol gel process, using zircon-n-propylate, titan-iso-propylate and leadacetate in butoxyethanol. It can be seen from the investigations of the spinnability that the best drawing conditions can be achieved at a water content of $W=6$ ($W=[H_2O]/[Ti^{4+}+Zr^{4+}+Pb^{2+}]$) and a pH=3: the length of the drawn fibre was about 90 cm and the diameter of the gel fibre was 20–60 μm . Rheological investigations (dynamic and intrinsic viscosity) show a direct connection between the spinnability and the morphology of the sol particles: only chain-like particles lead to good spinning conditions of the PZT-sol. A water content of $W=3$ (pH=3) lead to more particularly gel structures, whereas a network-like structure could be observed at a water content of $W=9$ (pH=3). The one hour sintered (700°C) fibre shows a porous structure with a 250 nm thick and dense layer at the fibre surface. Further investigations were made in order to achieve a dense and crack-free microstructure by using nucleation particles. The incorporation of the PZT seeds (diameter ranges about 300 nm) changes the drawing conditions of the PZT gel. It was necessary to produce the fibres via a new spinning process. The seeded PZT gels was produced by extrusion by using small nozzles ($\varnothing=50, 100, 200, 500 \mu m$). Another advantage of the extrusion of the PZT fibres was the possibility to produce fibres continuously. The length of the gel fibre ranges between 7 and 15 m ($\varnothing=20-60 \mu m$). 2 wt% seeds are necessary to obtain a dense and crack free microstructure after sintering the gel fibre for one hour at 700°C. The pure perovskite phase crystallises at 600°C.

KP10

SOL-GEL PRODUCTION OF MgO, YBCO AND BSCCO-2212 FIBRES

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MgO, YBCO and BSCCO-2212 fibres were synthesised using the sol-gel method following two alternative routes, the organometallic polymeric gel route and the alkoxide route.

In the first method, excellent MgO fibres were produced using magnesium acetate solution mixed with PAA. In the second method, ethylene glycol was added to a magnesium methoxide solution. Fibres were extruded from the resulting gel. The precursor fibres were fired between 1400°C and 1600°C.

YBCO fibres were produced using polyacrylic acid (PAA) for metal chelating or polymethylmethacrylate (PMMA) as a binder. BSSCO-2212 fibres were produced using PMMA as a binder. In the case of PAA, the precursor gel was produced by mixing an aqueous solution of the acetate salts of the corresponding metals with a hot (50°C) solution of polyacrylic acid which was alkalified using NH_4OH to pH 8 and evaporating the solution. In the case of PMMA an acetic solution of the corresponding metals was added to an acetic solution of PMMA. From the resulting gel precursor fibres of excellent rheologic properties were drawn.

The fibres were characterised by SEM, XRD and SQUID measurements. It was found that the produced YBCO fibres consisted of pure 123 phase and the BSSCO-2212 fibres consisted of 2212 phase with some traces of impurities and 2223 phase. The fibres produced using PAA were of higher quality than the fibres produced using PMMA. They were more compact and presented some degree of orientation. The results show that both polymers PAA and PMMA are suitable for producing very good precursor fibres. But after the burning of the binder, the fibres from PMMA showed porosity. In the other hand, the thin (ca 20 μm in diameter) fibres from PAA showed almost no porosity.

CATALYTIC BEHAVIOUR OF SOL-GEL Pt/SiO₂ GLASSESS. Castillo*⁺ and M. Moran-Pineda*Instituto Mexicano del Petróleo, Eje Central L. C. 152, Box 14-805, 07730
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Platinum supported on silica was synthesised by the sol-gel method using tetraethoxysilane (TEOS) and trans-[Pt(NH₃)₂Cl₂] as precursors. Pt/SiO₂ sol-gel catalysts acid (HCl, pH3) and base (NH₄OH, pH9), with 0.5 % to 2 % of metal loading were obtained.

The study of catalytic activity of CO oxidation over sol-gel Pt/SiO₂ catalysts at low (450°C) and high (800°C) thermal pretreatment is presented. The behaviour of catalytic activity of sol-gel preparations and reference catalysts under same conditions were compared.

The sol-gel samples showed higher activity than reference catalysts mainly the acid sol-gel preparation. In acid and base sol-gel catalysts a redispersion of the metal phase and higher resistance to sinterisation was observed.

With regard to the metallic load of sol-gel catalysts Pt/SiO₂, a little effect was observed, since at lower load of Pt, the sol-gel catalysts showed better activity. In accordance with the obtained results, the sol-gel Pt/SiO₂ catalysts could be a good choice for its applications in environmental catalysts.

We acknowledge the support given to us by FIES-IMP.

KP12

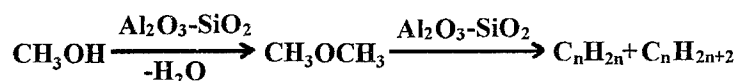
EFFECT OF SOLVENT DIOLS AND LIGANDS ON THE PROPERTIES OF SOL-GEL ALUMINA-SILICAS

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Amorphous alumina-silicas were prepared from a tetraalkoxysilane and anhydrous aluminium trichloride or an aluminium alkoxide by sol-gel process using 2-methyl-2,4-pentanediol, pinacol, 1,2-propanediol, 2,3-butanediol or ethylene glycol as the solvent or complexing agent, and the effect of diols and alkoxy groups on the physical and chemical properties of the alumina-silicas were examined. The pore size and pore volume of the alumina-silicas varied with diols employed and alkoxy groups, or roughly speaking, when the diol used or the alkoxy group is bulky, the alumina-silica with relatively bigger mesopores, bigger pore volume and higher surface area was obtained. In the conversion of methanol catalysed by the alumina-silicas, bulkier diols and alkoxides gave the catalysts producing dimethyl ether in higher yield and hydrocarbons in lower yield. Thus, when ethylene glycol was used as the diol, the best catalyst for the production of hydrocarbons, especially the production of olefins such as ethylene, propylene and butene was obtained. Furthermore, the sol-gel alumina-silicas were compared in the methanol conversion performance with that prepared by a traditional kneading process. It was found that the sol-gel ones can well convert methanol to dimethyl ether and hydrocarbons, but the kneading one can not almost convert methanol to other compounds.

Reaction Scheme of Methanol Conversion



APPLICATION OF $\text{ZrO}_2\text{-Al}_2\text{O}_3$ AEROGELS TO CATALYSTS

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Catalyst is a potential application of aerogels with high porosity and large surface area. We have reported the high catalyst activity of Al_2O_3 aerogel for selective reduction of NO using C_3H_6 under an oxidising atmosphere. However, its activity rapidly decreases with decreasing temperature when $<500^\circ\text{C}$. On the other hand, ZrO_2 has higher activity at low temperatures. In this study, $\text{ZrO}_2\text{-Al}_2\text{O}_3$ aerogels have been prepared in order to obtain better de- NO_x catalyst with high activity in wide temperature range. $\text{ZrO}_2\text{-Al}_2\text{O}_3$ wet gels have been prepared by hydrolysis of metal alkoxides in alcoholic solutions. The wet gels were supercritically dried in an autoclave or dried at 90°C in air to obtain aerogels or the xerogels, respectively. The aerogels have about 20–50% higher activity for NO reduction than the xerogels in the temperature range $300\text{--}600^\circ\text{C}$. The higher activity of aerogels may be attributed to the higher effective gas diffusivity of the aerogels, estimated to be about 10^3 times higher than that of the xerogels, because of their high porosity and large pore size. The catalyst activity of aerogels containing 4–10 mol% ZrO_2 is more than 20% higher than that of Al_2O_3 aerogels at temperatures $<450^\circ\text{C}$. The effects of ZrO_2 -addition on the microstructure and catalyst activity of the aerogels were discussed.

PREPARATION OF LAYER STRUCTURE-CONTROLLED Ru-Sn-Al₂O₃ CATALYSTS AND THEIR REACTIVITY

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It is known that the surface structure of catalyst has great influences on catalytic activities and selectivities. So, the controlling of the layer structure is very important in realizing functional group selective reaction.

We have reported that the development of new sol-gel Ru-Sn-Al₂O₃ catalysts prepared by a complexing agent-assisted sol-gel method, which selectively hydrogenate unsaturated or aromatic carboxylic acid and ester to corresponding unsaturated or aromatic alcohol. In this work, we tried to control the layer structure of Ru-Sn-Al₂O₃ catalysts by using the sol-gel, impregnation and their combination methods, and examined their properties and hydrogenation of dimethyl terephthalate.

Ru-Sn-Al₂O₃ catalysts were prepared by the sol-gel, impregnation and their combination methods. Ru(NO)(NO₃)₃, Sn(OnBu)₄ and aluminum isopropoxide were used as raw materials. The catalysts which were activated in a hydrogen atmosphere at 673 K were characterised by X-ray fluorescence, X-ray photoelectron spectra (XPS) and hydrogen and carbon monoxide adsorption. The hydrogenation of dimethyl terephthalate was carried out at 513 K and 523 K in a batch reactor at 8MPa.

Observed bulk Ru Sn and alumina compositions of all catalysts characterised by X-ray fluorescence analyses are almost same. The surface Sn contents of catalysts characterised by XPS depended on the preparation method, that is, the surface on the Ru (sol-gel) → Sn (impregnation) and Ru (impregnation) → Sn (impregnation) catalysts had a higher content of tin than that of the Sn (sol-gel) → Ru (impregnation) and Sn (impregnation) → Ru (impregnation) ones. surface tin content of Ru-Sn (sol-gel) showed middle value between the other catalysts.

TPR and CO adsorption depended on catalyst preparation methods.

With regard to the conversion rate of dimethyl terephthalate and the rate of product conversion from methyl 4-hydroxymethylbenzoate to p-xylene via methyl p-toluate, Ru impregnation catalysts were higher than the other catalysts.

CHARACTERISATION OF CuO/ZrO_2 CATALYSTS SOL GEL DERIVED

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CuO/ZrO_2 catalysts were obtained by impregnation of copper oxide, with different contents, on Zirconia Sol-Gel derived. The samples were characterised by IR spectroscopy, CO_2 Temperature Programmed Desorption (TPD), TPR and BET surface area. Catalytic activity was determined using the test reaction of 2-propanol conversion. As for the nature of catalytic sites in the supported catalysts, the results of the CO_2 adsorption, analysed by IR spectroscopy, show the formation of a great quantity of carbonates with different structure. However, the intensity of these signals decrease with the content of CuO, particularly the signal of the bidentate carbonate structure placed at 1600 cm^{-1} which corresponds to a stretching vibration. The basic nature of the samples also appears clearly from the results of CO_2 -TPD as well as from the catalytic activity: in the first case, the maximum of CO_2 desorption occurs when the content of copper oxide is about 5 wt % and in the second case selectivity of the catalyst is close to 100 % acetone. The results for surface area of the samples show that this does not change significantly in spite of the content of CuO. That is, the controlled Zirconia surface area, by means of Sol-Gel method, let us obtain a high dispersion of copper oxide in the sample as well as tiny crystals. This last result was corroborated from the TPR studies which show highly dispersed Cu (II) for values less than 10 wt % of CuO and segregated copper oxide for larger contents. The importance of the system as well as the analysis of above and other results vis a vis the Sol-Gel method are discussed in the extended work.

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**EVIDENCE FOR LEWIS AND BRØNSTED ACID SITES ON MgO
OBTAINED BY SOL-GEL**

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Traditionally, magnesium oxide, MgO, has been considered a typical basic catalyst, catalyst support and/or adsorbent. In this study MgO was prepared using Mg-ethoxide dissolved in ethanol and hydrolysed with various aqueous inorganic acids and bases. The hydrolysis catalysts are crucial to control the textural, acid-base and catalytic properties of the final solids. We have found recently that it is possible to induce Brønsted and Lewis acid sites depending on the method of preparation and, more specifically, on the type of inorganic acids used in the hydrolysis stage of MgO prepared by Sol-Gel. For instance, by means FTIR of adsorbed pyridine on MgO obtained using aqueous HCl (pH=3), the bands corresponding to Lewis (1603, 1496 and 1445 cm^{-1}) and Brønsted (1550 cm^{-1}) acid sites are observed. Important to mention is the fact that upon vacuum high temperature treatment, i.e. at 773 K, the above mentioned bands are clearly distinguishable indicating that the acid sites are very strong. On the other hand, the MgO materials obtained using aqueous acetic acid as a hydrolysis catalyst (pH=5), and that without any catalyst (pH=7) showed only Lewis acid sites. In this case the intensity of the bands ascribed to adsorbed pyridine on Lewis sites decreases markedly upon higher temperature treatment. These results indicate that the acid strength in these materials is comparatively lower than that in MgO obtained using HCl. When aqueous NH_4OH (pH9) is used as the hydrolysis catalyst, the obtained MgO showed both Lewis and Brønsted acid sites, however the number of Brønsted acid sites is smaller than that of MgO obtained with HCl and decrease with increasing treatment temperatures. In all cases the number of Lewis acid sites is greater than that of Brønsted ones.

CHEMICAL MICROENGINEERING IN SOL-GEL DERIVED FLUORIDE AND LANTHANIDE MODIFIED CERIA MATERIALS

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Although lanthanide oxides including ceria have been shown to be active catalysts for a number of processes, the activity of the pure oxide materials can be improved by the incorporation of other ions in the lattice. In addition, the conductivity of ceria can be enhanced by doping with trivalent lanthanides, and these materials have applications in solid oxide fuel cells. The preparation of these materials is usually effected by sol-gel methods followed by a calcination procedure before use. Both the presence of fluoride and the particular rare earth cation influence profoundly the constitutional and microstructural nature of the materials obtained, which will inevitably lead to changes in their performance. Here we examine the nature of ternary Ln-Ce-O (Ln = La, Pr, Nd) oxide materials with and without added fluoride ion using powder XRD and TEM coupled with electron diffraction and EDX analysis.

Every variable appears to have an effect upon both the chemical constitution and the physical nature, including particle size and morphology, of the materials. For example, in the absence of fluoride incorporation of Ln results in the formation of Ln/CeO₂ solid solutions at low Ln levels, but a microscopic mixture of two cubic phases, one pure ceria and the others a Ln-Ce-O phase of composition Ce_{0.35}La_{0.65}O_{1.67}, at a Ln:Ce ratio of 1:1. TEM of this material shows it to appear homogeneous, both phases appearing as small (*ca.* 20nm) cubes and are indistinguishable from one another. In contrast incorporation of fluoride in the materials obtained from solutions containing both La and Ce cations increases linearly with the La content. XRD shows that for all La:Ce ratios pure CeO₂ and LaF₃ are the only phases present showing that, in the presence of lanthanum, all the fluoride is segregated as LaF₃ and no mixed Ln-Ce-O phase is formed. TEM shows that the microstructure of this material is complex. Individual particles of both ceria, which are now much larger than in the absence of fluoride, and LaF₃ are seen. In addition to these are particles of ceria on the surface of which are 'seaweed' type growths of LnF₃ and other aggregates of ceria particles adhered together by LnF₃. The nature of analogous Pr- and Nd-substituted ceria materials will also be described.

STRUCTURAL AND CHEMICAL MODIFICATION OF POLYDIENE LATEXES BY GEL DERIVED SILICA

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The incorporation of colloidal silica into polydiene elastomers is a well-known method to improve their mechanical and thermal properties. The sol-gel technology allows to create the silica and silicate networks directly in a latex using various watersoluble precursors. In comparison with the incorporation of the silica flow, this approach is not accompanied by the agglomeration of silica particles and guarantees a more homogeneous distribution of the filler.

The objective of the present work is to prepare interpenetrating polydiene-silica networks starting from the liquid systems: polydiene latex - water-soluble silicate. Natural Qualitex or synthetic butadiene-styrene latexes were used as the organic components. Aqueous solutions of methylamine silicate, acidified sodium silicate and sodium -tetraamminezinc silicate were used as the silica and silicate precursors. The latex films were prepared by ageing and drying the liquid compositions for 5–10 days at room temperature. The efficiency of modification was controlled by the rotational viscometry of latex-silicate mixtures and the standard mechanical tests of the obtained films. The structures of interpenetrating networks were studied by IR spectroscopy.

The dependence of rheological properties of the binary gels on the silica - diene ratio and pH, was investigated. In most systems, yield stress values were found to increase at the silica concentrations increased up to 4 wt.%. The latex films obtained from the silica-containing systems, are characterised by the improved elastic and strength properties, in comparison with those of pure polydiene films. The features of inorganic networks depending on the types of modifying ions and the gelation mechanism, are discussed. The advantage of the ternary $\text{Na}_2\text{O-SiO}_2\text{-ZnO}$ precursor is the possibility of the dilution-caused gelation and its additional function as a vulcanisation activator.

**PREPARATION OF A WHISKER REINFORCED CERAMIC BY
APPLICATION OF THE SOL-GEL PROCESS**

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A composite ceramic consisting of tielite (Al_2TiO_5) and potassium hollandite ($\text{K}_2\text{Al}_2\text{Ti}_6\text{O}_{16}$) has been prepared by internal precipitation from an amorphous bulk obtained via the sol-gel process. The crystallisations of the two phases, tielite and potassium hollandite, have been studied by X-ray diffraction, ^{27}Al -NMR-MAS-spectroscopy, DTA/TG and SEM/EDX. It has been shown, that the hollandite phase crystallises whisker shaped within the tielite matrix.

This approach could be an interesting alternative for the conventional preparation of whisker reinforced ceramics.

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 W. Huang *F1*
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 N. Husing *D4*
- I**
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