

International Conference on  
**SOL-GEL**  
**MATERIALS**

Research, Technology, Applications

13 - 16 June 2001

Wrocław-Rokosowo, Poland

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SOL- GEL MATERIALS 2001

## International Conference on



# Sol-Gel Materials

13-16 June 2001

Wrocław - Rokosowo, Poland

**Organized by**

**Institute of Material Sciences and Applied Mechanics, Wrocław University of Technology**  
**Institute for Low Temperature and Structure Research, Polish Academy of Sciences**

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## Schedule

Wednesday 13.06.2001	Thursday 14.06.2001	Friday 15.06.2001	Saturday 16.06.2001
<p>12.00 <b>Registration begins</b></p>	<p>9.00 - 10.00 <i>breakfast</i></p> <p><b>session: Syntheses - Materials -Applications</b> chair: R. Reisfeld</p> <p>10.00 - 10.40 L. Klein (IL3) 40 min 10.40 - 11.00 M. Łączka (O8) 20 min 11.00 - 11.40 J. Phalippou (IL5) 40 min</p> <p><i>coffee break</i> 20 min</p> <p>12.00 - 12.30 G.H. Frischat (IL2) 30 min 12.30 - 13.00 H.C. Zeng (IL7) 30 min 13.00 - 13.40 K.-H. Haas (O4) 40 min</p> <p>14.00 - 15.00 <i>lunch</i></p> <p><b>session: Rare Earth Systems</b> chair: J. Phalippou</p> <p>15.00 - 15.40 R. Reisfeld (IL6) 40 min 15.40 - 16.00 J. Legendziewicz (O7) 20 min 16.00 - 16.20 G.E. Malashkevich (O9) 20 min</p> <p><i>coffee break</i> 20 min</p> <p>19.00 dinner</p> <p>20.30 <b>Get together party</b></p>	<p>9.00 - 10.00 <i>breakfast</i></p> <p><b>session: Nanomaterials / Doped Matrices</b> chair: L. Klein</p> <p>10.00 - 10.40 M.A. Aegreter (IL1) 40 min 10.40 - 11.00 V. Gurin (O3) 20 min 11.00 - 11.20 D. Kovalenko (O6) 20 min</p> <p><i>coffee break</i> 20 min</p> <p>11.40 - 12.20 A.M. Klonkowski (IL4) 40 min 12.20 - 12.50 O.A. Serra (O12) 30 min 12.50 - 13.10 K. Kledzik (O5) 20 min 13.10 - 13.30 K.V. Yumashev (O14) 20 min</p> <p>14.00 - 15.00 <i>lunch</i></p> <p><b>session: Electrochemical Properties</b> chair: M.A. Aegreter</p> <p>15.00 - 15.30 M. Opałto (O11) 30 min 15.30 - 15.50 H. Sodolski (O13) 30 min 15.50 - 16.10 Z. Ziembik (O15) 20 min</p> <p><i>coffee break</i> 20 min</p> <p>16.30 - 18.30 poster session</p> <p>20.30 <b>Conference dinner</b></p>	<p>9.00 - 10.00 <i>breakfast</i></p> <p>10.30 <b>Excursion</b></p> <p>14.00 - 15.00 <i>lunch</i></p> <p><b>Conference closes</b></p>
	<p>16.40 - 17.00 W. Stręk (O13) 20 min 17.00 - 17.20 N.V. Gaponienko (O1) 20min 17.20 - 17.40 B. Grobelna (O2) 20 min</p> <p>18.15 - <b>Grill party</b></p>		

Times scheduled for lectures include a few minutes for short questions.

## Conference Programme

**Thursday 14.06.2001**

9.00 - 10.00 *breakfast*

session: **Syntheses - Materials -Applications**

chair: Renata Reisfeld

10.00 - 10.40 Lisa Klein (IL3); *Opportunities for Sol-Gel Materials in Fuel Cells*

10.40 - 11.00 Maria Łączka (O8); *Application of Sol-Gel Method to Obtain Various Types of Materials*

11.00 - 11.40 Jean Phalippou (IL5); *Highly Porous Aerogels with Very Low Permeability*

*coffee break 20 min*

12.00 - 12.30 Guenter Heinz Frischat (IL2); *Innovative Sol-Gel Coatings on Glass*

12.30 - 13.00 Hua Chun Zeng (IL7); *Gel-Matrixes as Confined Space for Synthesis of Nano-Structured Materials*

13.00 - 13.40 Karl-Heinz Haas (O4); *ORMOCER's: Properties and Applications of Hybrid Inorganic-Organic Polymers*

14.00 - 15.00 *lunch*

session: **Rare Earth Systems**

chair: Jean Phalippou

15.00 - 15.40 Renata Reisfeld (IL6); *Rare Earth Complexes in Sol-Gel Matrices*

15.40 - 16.00 Janina Legendziewicz (O7); *Spectroscopy of nanometer – range media and mixed lanthanide  $Ln\beta_3L$  compounds. Their application perspectives.*

16.00 - 16.20 Georgii E. Malashkevich (O9); *Influence of Activators Concentration and Preparation Redox Conditions of Tb- and Ce-Tb-Containing Silica Gel-Glasses on their Spectral-Luminescent Properties*

*coffee break 20 min*

16.40 – 17.00 Wiesław Stręk (O13); *Rare Earth Doped Silica Glasses and Ceramics*

17.00 – 17.20 Nikolai V. Gaponienko (O1); *Enhanced Luminescence of Lanthanides from Xerogel Solids Embedded in Porous Anodic Alumina*

17.20 – 17.40 Beata Grobelna (O2); *Improvement of Emission Intensity of Eu(III) Complexes with Heteropolyanions in Oxide Xerogels*

18.15 - **Grill party**

## Friday 15.06.2001

9.00 - 10.00 *breakfast*

session: **Nanomaterials / Doped Matrices**

chair: Lisa Klein

10.00 - 10.40 Michel A. Aegreter (IL1); *Use of Redispersable Crystalline Nanopowder to Coat Substrates at Low Temperature: Application to Transparent Conducting Coatings*

10.40 - 11.00 Valerii Gurin (O3); *Optical Features of the Silica Sol-Gel Matrices with Nanoparticles of a Series of Cu-Containing Semiconductors*

11.00 - 11.20 Dmitry Kovalenko (O6); *Porous Silica Films as a Support of Ultrafine Metal Particles and Clusters*

*coffee break 20 min*

11.40 - 12.20 Andrzej M. Klonkowski (IL4); *Optical Materials Prepared by the Sol-Gel Procedure*

12.20 - 12.50 Osvaldo A. Serra (O12); *Spectroscopic Studies on the Inclusion Complexes of Tetrakis(2-Hydroxy-5-Nitrophenyl)Porphyrin with alpha-Cyclodextrin in Sol-Gel Matrix*

12.50 - 13.10 Krzysztof Kledzik (O5); *Sol-Gel Materials Doped with Chemosensors*

13.10 - 13.30 Konstantin V. Yumashev (O14); *Sol-Gel Glasses Doped with Copper Selenide Nanoparticles: Non-Linear Optical Properties and Laser Passive Shutters Applications*

14.00 - 15.00 *lunch*

session: **Electrochemical Properties**

chair: Michel A. Aegreter

15.00 - 15.30 Marcin Opałto (O11); *Electrochemical Redox Reaction in Silica Sol-Gel Glass Monoliths and Films*

15.30 - 15.50 Henryk Sodolski (O13); *Ions Transport in Nanoporous Xerogel Structure*

15.50 - 16.10 Zbigniew Ziembik (O15); *Air Humidity Influence on Electrical Properties of Silica Gel Glass*

*coffee break 20 min*

16.30 - 18.30 **poster session**

20.30 **Conference dinner**

## Participant list

1. Michel A.	Aegreter	Germany	27. Maria	Łączka	Poland
2. Alexander	Alexeenko	Belarus	28. Edward	Łukowiak	Poland
3. Tran Kim	Anh	Vietnam	29. Georgii E.	Malashkevich	Belarus
4. Sergey M.	Arabei	Belarus	30. Krzysztof	Maruszewski	Poland
5. Andrei	Boiko	Belarus	31. Ewa	Miller	Poland
6. Katarzyna	Cholewa-Kowalska	Poland	32. Marcin	Opalło	Poland
7. Jan	Czyżewski	Poland	33. Phillip	Parrish	USA
8. Guenther H.	Frischat	Germany	34. Tatiana A.	Pavich	Belarus
9. Vladimir E.	Gaishun	Belarus	35. Jean	Phalippou	France
10. Nikolai V.	Gaponienko	Belarus	36. Marek	Pietraszkiewicz	Poland
11. Beata	Gobelna	Poland	37. Evgueny	Poddenezhny	Belarus
12. Valerii	Gurin	Belarus	38. Yanina	Potapenok	Belarus
13. Karl-Heinz	Haas	Germany	39. Małgorzata	Przebyt	Poland
14. Dariusz	Hreniak	Poland	40. Renata	Reisfeld	Israel
15. Agnieszka	Hreniak	Poland	41. Ewa	Rysiakiewicz-Pasek	Poland
16. Marek	Jasiorski	Poland	42. Monika	Sączek-Maj	Poland
17. Donata	Jóźwik	Poland	43. Galina I.	Semkova	Belarus
18. Krzysztof	Kledzik	Poland	44. Svetlana V.	Sereshkina	Belarus
19. Lisa	Klein	USA	45. Osvaldo A.	Serra	Brasil
20. Anna	Klukowska	Germany	46. Henryk	Sodolski	Poland
21. Andrzej M.	Klonkowski	Poland	47. Wiesław	Stręk	Poland
22. Małgorzata	Kogut	Poland	48. Krystyna	Szaniawska	Poland
23. Łukasz	Korach	Poland	49. Konstantin V.	Yumashev	Belarus
24. Dmitry	Kovalenko	Belarus	50. Hua Chun	Zeng	Singapore
25. Joanna	Kukułka-Walkiewicz	Poland	51. Zbigniew	Ziembik	Poland
26. Janina	Legendziewicz	Poland			

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L.C. Klein (IL3)

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# ABSTRACTS

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**USE OF REDISPERSABLE CRYSTALLINE NANOPOWDER TO COAT  
SUBSTRATES AT LOW TEMPERATURE: APPLICATION TO TRANSPARENT  
CONDUCTING COATING**

**N. Al-Dahoudi and M.A. Aegerter**

Institut fuer Neue Materialien - INM, Department of Coating Technology, Im Stadtwald, Gebaeude 43,  
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A concept has been developed at INM for the deposition of large coatings by wet chemical processes using crystalline nanoscale powders fully redispersable in a solvent down to their primary scale (5 to 20 nm). It will be exemplified for the case of transparent and antiglare conducting oxide coating (TCO) made of  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO). The coating sols are obtained by dissolving in an environmentally friendly solvent a highly stable (> 1 year) paste containing surface modified crystalline ITO nanoparticles. Thick single layers (< 500 nm) were deposited on plastic or glass substrates by spin and dip coating techniques and then polymerized at temperature as low as 130°C by UV irradiation. A sheet resistance as low as 2 k $\Omega$ , a photopic transparency > 85%, a roughness < 1 nm and excellent mechanical properties have been so far obtained. Antiglare-antistatic coatings with a gloss of 60–70 GU, an optical resolution > 8 lines/mm and similar electrical property have been produced by a spraying process.

## INNOVATIVE SOL-GEL COATINGS ON GLASS

G.H. Frischat

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Glass is a material with a very long history. It is increasingly used in every-day life, and both privacy and industry would be impossible without glass. However, there are many demands today where ordinary glass would fail. This is the reason why coatings with specific properties are needed, and the sol-gel technology is getting increasing importance in this respect.

In recent years we studied the preparation and performance of different innovative sol-gel coatings on glass substrates. Thus, for example, BaO-TiO<sub>2</sub>-SiO<sub>2</sub> coatings of 60 to 200 nm thickness, prepared by dip-coating, strongly protect glass surfaces (fibers, bulk glasses) against alkaline attack [1]. Sol-gel prepared Al<sub>2</sub>O<sub>3</sub> (corundum) coatings on float glass strongly enhance the scratch resistance without decreasing the optical transmission in the visible wavelength range [2]. Indium tin oxide (ITO) coatings show high transmission in the visible range, high infrared reflection and low electrical resistivity. Because of these properties ITO films are widely used as transparent electrodes in displays, solar cells and in many other electronic and optoelectronic applications. It has been shown that the sol-gel technique is a powerful means to develop such coatings [3]. On the other hand, broad-band and low-cost anti-reflection coatings are necessary for solar collector covers. Porous SiO<sub>2</sub> coatings of ≈100 nm thickness, prepared by the dip-coating process with silica sol as a precursor, can increase the transmittance of float glass up to 99% [4].

Several examples are discussed which show the applicability of the sol-gel technology to tailor such innovative coatings on glass substrates.

*References*

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- [3] Jian Liu, E. Rädlein, G.H. Frischat, *Phys. Chem. Glasses* **40** (1999), 277-281; 282-286.
- [4] G. Hensch, E. Rädlein, G.H. Frischat, *J. Non-Cryst. Solids* **265** (2000), 193-197.

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**OPPORTUNITIES FOR SOL-GEL MATERIALS IN FUEL CELLS****L.C. Klein***Rutgers-the State University of New Jersey, Piscataway, NJ 08854-8065*

Fuel cells are electrochemical devices that convert the chemical energy of a fuel and oxidant directly to electrical energy. Three types of fuel cells are (a) proton-exchange membrane fuel cells (PEMFC), (b) molten carbonate fuel cells (MCFC) and (c) solid oxide fuel cells (SOFC). In each case, there is a role for sol-gel processing. In the case of PEMFC, sol-gel modifications to the membrane are designed to increase the operating temperature. In the case of MCFC, sol-gel corrosion barriers extend the lifetime of the current collector. Finally, sol-gel processing is being used to assemble the electrolyte and electrode layers in SOFC. Examples are given for the application of sol-gel processing in each system, pointing out the derived benefits and areas for further development.

## OPTICAL MATERIALS PREPARED BY THE SOL-GEL PROCEDURE

**A.M. Klonkowski<sup>1</sup>, S. Lis<sup>2</sup>, M. Pietraszkiewicz<sup>3</sup>, Z. Hnatejko<sup>2</sup>, I. Szałkowska<sup>1</sup>  
and M. Elbanowski<sup>2</sup>**

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e-mail: aklonk@chemik.chem.univ.gda.pl

<sup>2</sup> Faculty of Chemistry, A. Mickiewicz University, Poznan, Poland

<sup>3</sup> Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland

Our studies are focused on luminescent materials based on the antenna effect and prepared by the sol-gel method. These materials are composed of Eu(III) complex (luminescence centre) entrapped in xerogel matrix. Luminescence intensity and lifetime depend on efficiency of energy transfer from the absorption centre (ligand) to the emission centre (central ion) and on concentration of O-H oscillators (quenchers) surrounding the central ion. In this study such luminescence properties as emission intensity and lifetime were improved by modifying the coordination environment of the central ion, changing anion group and matrix. Results of the experiments concerning the coordination sphere show that a cryptand ligand with aromatic groups and a second aromatic ligand, settle efficient action the antenna effect and isolate the central ion from each efficient quenchers as e.g. water molecules. Luminescence properties depend also on anion in the Eu(III) complex salt and a type of matrix material as well as concentration of water and OH groups in the matrix. The prepared luminescent materials have been tested for their photochemical stability under conditions of continuous UV irradiation.

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**HIGHLY POROUS AEROGELS WITH VERY LOW PERMEABILITY****J. Phalippou, T. Woignier, R. Sempere**

*Laboratoire des Verres – UMR 5587, Université de Montpellier 2  
Place E. Bataillon, 34095 MONTPELLIER Cedex 5, e-mail: phalippo@crit.univ-montp2.fr*

In this paper we firstly investigate the way the porosity is built up in silica gel during the gelation step. Then we show the solid particle sticking acts on the geometrical pore characteristics [pore volume and pore size distribution]. According to pore size value the permeability of gels is quite low even in the case where the gel porosity value is higher than 95% porous. Analogous properties can be extended to silica aerogels for which now the solvent is replaced for air. Here we report peculiar experiments allowing to estimate the mechanical properties of aerogels thank to the low value of the average pore size. Moreover we demonstrate that aerogels may be densified at room temperature using an external isostatic pressure. In that the pore size may be tailored with respect to the nature and the characteristics of the starting aerogel. The evolution of the textural properties such as the mean pore size and the specific surface area of these tailored aerogels is investigated as a function of pressure.

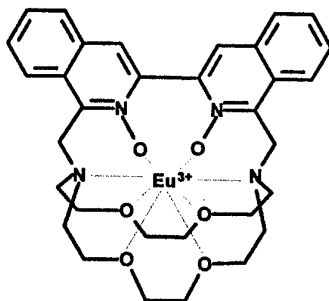
Consequently and according to their low permeability light weight aerogels exhibit very striking response to mechanical.

## RARE EARTH COMPLEXES IN SOL GEL GLASSES

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The origin of the spectra of rare earth ions arising from  $f \rightarrow f$  and  $f \rightarrow d$  transitions will be surveyed. The parity forbidden luminescence of lanthanide ions can be strongly intensified by excitation via molecules characterized by high transition probabilities. Such behavior opens a route for creation of a class of new sophisticated materials. Luminescent materials based on heteroaromatic lanthanide cryptates are attractive as labels for advanced time-resolved fluoroimmunoassays, molecular markers and their potential use is conceivable in the field of luminescent displays, molecular photonics and highly luminescent materials in hybrid organic/inorganic glasses. The recent findings of lanthanide complexes trapped in sol-gel inorganic glasses based on silica, titania and zirconia networks [1] will be discussed and theoretical basis of their spectroscopy presented. One example of europium cryptate is given below.



This compound displays remarkable stability and an excellent quantum yield of emission upon UV irradiation as a result of intramolecular energy transfer.

The incorporation of the cryptate complexes into silica, titania and especially zirconia films results in dramatic increase of the emission intensity as well as in the increase of the absorption intensity of Eu. The high quantum efficiency results from the shielding of OH-vibrations responsible for the non-radiative relaxation. The covalent bond between Eu and the organic ligands is much stronger than the bond between Eu and oxygen in the oxides, and the site symmetry lower, relaxing the parity rule.

The later phenomena of increase of transition probabilities are reflected by higher absorption of the complex. The lecture is based on my discussions with Prof. J.-M. Lehn and part of the experiments performed with the Polish group of Prof. M. Pietraszkiewicz [2].

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**GEL-MATRIXES AS CONFINED SPACE FOR SYNTHESIS OF NANO-STRUCTURED MATERIALS****H.C. Zeng**

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The recent advance in sol-gel science and technology has allowed us to tailor-make a gel matrix with great flexibility in terms of compositional, structural, and textural properties at low-temperatures. The sol-gel derived solid matrices, which can be deliberately anchored with both organic compounds and metal additives, could be possibly utilized as a reaction space that contains prefilled reactants for solid-state reactions. Using gel matrices as a confined reaction space, we describe here a novel solid-state route for carbon nanotube synthesis. Carbon nanotubes have been synthesized at 300°C for the first time in a gel matrix prepared by sol-gel method. Acetylacetone ( $C_5H_8O_2$ ) was used as a solid-state carbon source and was pre-introduced into a gel matrix of Co-doped  $Al_2O_3$  via metal-chelating. Upon heating, acetylacetonate groups ( $C_5H_7O_2$ ) anchored in the matrix were converted into carbon nanotubes while nanometer size  $Co_3O_4$  and  $CoAl_2O_4$  were formed. As the synthetic growth is confined within the gel space, the present method can be further developed to make 1D, 2D and 3D carbon nanotubes by controlling the shape and dimension of a gel matrix. It is suggested the present method can also be extended to the synthesis of other nanostructured materials.

## ENHANCED LUMINESCENCE OF LANTHANIDES FROM XEROGEL SOLIDS EMBEDDED IN POROUS ANODIC ALUMINA

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Fabrication of silica, titania or alumina xerogel films doped with Er, Tb or Eu onto porous anodic alumina 1-30 microns thick reveals strong enhancement of lanthanides photoluminescence (PL) in comparison with xerogels fabricated onto flat surface of silicon wafers [1-5]. The total integral intensity of lanthanides PL increases with the increase of the porous anodic alumina thickness and number of xerogel layers, mesoscopically confined in porous anodic alumina. For example, terbium luminescence from porous anodic alumina 30 microns thick spin-on coated with Tb-doped xerogel in a single step is 15-20 times greater than that from terbium-implanted thin films. The results are compared with experimental data obtained for erbium and terbium doped microporous silica globules. It was found that exploiting of porous anodic alumina as a template for xerogel host materials reduces significantly the temperature quenching of lanthanides. Possible mechanisms driving the enhancement of lanthanides PL in the structure microporous xerogel/mesoporous anodic alumina are discussed.

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## IMPROVEMENT OF EMISSION INTENSITY OF Eu(III) COMPLEXES WITH HETEROPOLYANIONS IN OXIDE XEROGELS

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Polyoxometalates (POM) have attracted attention in the past years because of their wide applications in catalysis, photochemistry and oxidation chemistry [1]. They are purely inorganic compounds which offer attractive properties as Ln(III) ligands. POMs can form complexes with Ln(III) ions e.g. Ln(POM)<sub>2</sub>, in which lanthanide is sandwiched between the defect sites of two ligands or can be encapsulated by ligands and act as inorganic cryptands [2]. The most important advantage of complexes with rare-earth ions e.g. Eu<sup>3+</sup>, is the fact that they emit narrow band, almost monochromatic light and they have long emission lifetimes. It creates the possibility of their usage as effective luminescent centers and their wide use in the industry [3].

Rare-earth ion emission is easily quenched in aqueous solution because water molecules present very high vibrational frequencies [4]. Therefore, in order to increase inertness and minimize the solvent interaction, we used a system consisting of complex Eu(III) with heteropolyanions, which is entrapped in porous silica matrix. The matrix is prepared by the sol-gel process [5]. One of the major advantages of the sol-gel method is the possibility of preparing multicomponent systems at low temperatures. In this process, silicon alkoxides were allowed to undergo hydrolysis and condensation. Thus, complexes Eu(III) with POM ligands can be immobilized by the sol-gel method in silica xerogel.

Point of our interest is photoconversion *via* an absorption energy transfer-emission sequence carried out in Eu(III) complexes with POM. Energy of UV radiation absorbed by ligand groups are efficiently transferred to the central cation, which finally emits visible light [6].

Presently we study the luminescence behaviour of these complexes in the rigid matrix by means of luminescence techniques.

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**OPTICAL FEATURES OF THE SILICA SOL-GEL MATRICES WITH NANOPARTICLES OF A SERIES OF CU-CONTAINING SEMICONDUCTORS****V.S. Gurin<sup>1</sup>, A.A. Alexeenko<sup>2</sup>, V.B. Prokopenko<sup>3</sup>, K.V. Yumashev<sup>4</sup>,  
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Semiconductor nanoparticles are of great interest last years in different fields of physics, chemistry, material science, etc. due to their unique properties provided by size effects, formation of new chemical species and peculiar electronic structure. A successful study of the nanoparticles aimed at possible applications requires building up a solid material which incorporates and stabilizes them. The sol-gel technique has been shown to be one of useful methods for fabrication of materials with nanoparticles. In contrast with other techniques of nanoparticles incorporation (e.g., ion implantation, melting and recrystallization) in the case of sol-gel-derived matrices there are much more routes to control chemical composition and tune particle characteristics. Meanwhile, nanoparticles of transition metal compounds have more complicated chemistry than the traditional II-VI compounds, and sol-gel-based methods are more appropriate for their directed synthesis within dielectric matrices. The present report concerns a review of the recent results on optical features of the semiconductor-doped sol-gel materials with nanoparticles of copper compounds: oxides, sulfides and selenides. Binary semiconductors with the VIa group elements are most frequently studied with respect to quantum size effects, linear and non-linear optics, luminescence and electrooptics.

This series of copper compounds in the form of nanoparticles (<100 nm) has been produced by means of the modified silica-based sol-gel sequence, and the main optical features are presented here in Fig. 1 as absorption spectra in the visible/near IR. The two types of matrices were investigated: amorphous silica films (right plot) and monolithic glasses (left plot). The main features observed include (i) a fundamental absorption edge which is most pronounced in the case of copper selenide nanoparticles, but accompanied with the smoothed excitonic maxima for oxide and sulfide in monoliths; and (ii) the intense additional absorption band peaked in the red part of the visible (films) or near-IR (monoliths). These features admit a tuning of the position by stoichiometry of the compounds, size of particles, their concentration, etc. The quantum confinement and a partial surface chemical modification of the nanoparticles are considered as possible reasons of appearance of these features specific for the copper multivalent compounds. The materials developed are promising for non-linear applications.

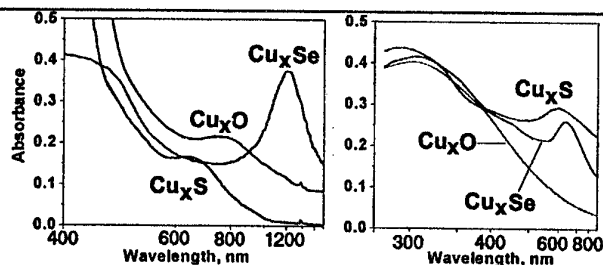


Fig. 1. Typical absorption spectra of the sol-gel derived silica monolithic glasses (right plot) and films deposited onto a fused quartz substrate (left plot) doped with nanoparticles of the copper compounds indicated.

## ORMOCER<sup>®</sup>s: PROPERTIES AND APPLICATIONS OF HYBRID INORGANIC-ORGANIC POLYMERS

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ORMOCER<sup>®</sup>s are molecular composites of inorganic and organic structures based on organically modified silicon and other metal alkoxides as molecular precursors. The modified heteropolysiloxane network is synthesized via sol-gel-processing in a two step process. After the formation of the inorganic network by polycondensation reactions leading to clusters/sols the organic crosslinking takes place.

Since curing of ORMOCER<sup>®</sup>s is accomplished well below 200 °C – in some cases even with UV-radiation – a wealth of organic functionalities can be incorporated in the hybrid networks and used for tailoring materials properties. Optical transparency and hardness with ease of functionalization are some of the main advantages of ORMOCER<sup>®</sup>s.

The presentation focuses on the structures of the precursors, the processing technology of ORMOCER<sup>®</sup>s and their applications as coatings, resins, fibers etc.

Some property/composition relationships are shown for mechanical, electrical, optical and barrier properties.

Examples for industrial implementation of ORMOCER<sup>®</sup> technology are given.

## SOL-GEL MATERIALS DOPED WITH CHEMOSENSORS

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During recent decades a very important aim is to prepare the sensors for many kinds of molecules. Our work is focused on synthesis and applications of fluorescent chemosensors. Chemosensor is a molecule that reacts reversibly with a chemical analyte and gives a measurable signal in response. The simplest fluorescent chemosensors are based on aromatic groups such as anthryl ones linked to amino groups. They are considered as chemosensors for transition metal ions. Changing the intensity of fluorescence is caused by photoinduced electron transfer. Fluorescent chemosensors are high sensitive, and this properties allow the researchers to use small concentration of them.

Another kind of sensors are chromogenic azacrown ethers, that react with alkali metal ions. They are not so sensitive as fluorescent ones, but gives the possibility to determine these important cations by spectrophotometric method. Complexation of alkali metal ions by azacrown ethers changes the UV-Vis spectra of ligand. It causes the deference between colour of free and complexed chemosensor.

Using chemosensors as solution has many disadvantages. The better way is to encapsulate them into the micropores of amorphous solids. It gives the possibility to reduce dimensions of obtained bulk.

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## POROUS SILICA FILMS AS A SUPPORT OF ULTRAFINE METAL PARTICLES AND CLUSTERS

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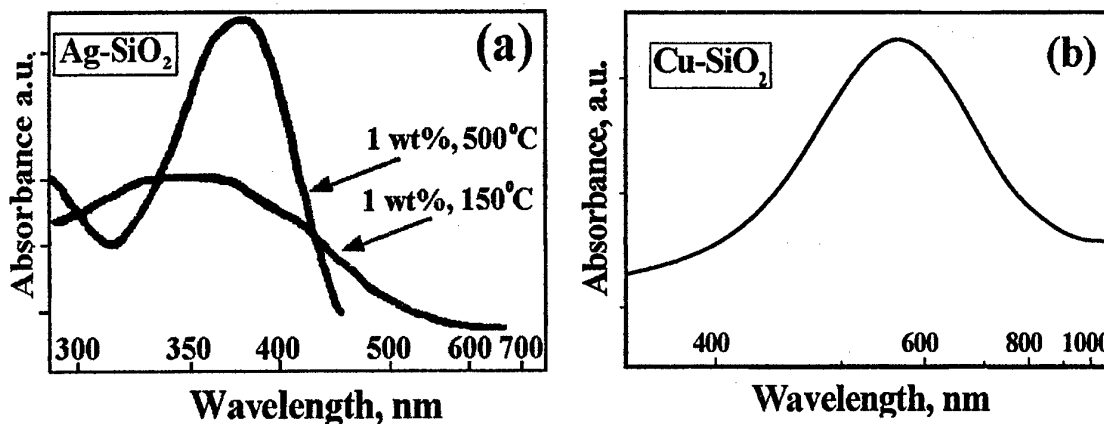
Composite solid materials like glasses and films with complicated structure of pores are of great significance for fabrication of optical device components with controlled features and for study of low-dimensional structures due to active and/or passive contribution from pores and incorporation into them clusters, small aggregates and nanoparticles. In this respect the sol-gel technique is of interest since different sol-gel derived materials can possess a developed porous structure which is easily variable by preparation condition of sols and subsequent heat treatment of solid matrices. The latter can be combined with metal and semiconductor nanoparticles in the size range when their optical features are very sensitive with respect not only to size but also to porous structure of matrices. Besides, the matrix incorporation stabilizes the nanoparticles that makes them applicable for practical purposes as sensors, catalysts, optical elements, etc.

The present work is devoted to the studies of incorporation of small metal particles (Ag and Cu) into silica sol-gel derived films. Within the conventional sol-gel process with the TEOS hydrolysis, metal salts were introduced into precursor sols, and the subsequent heating in oxidized and reduced atmospheres resulted in formation of silver or copper nanoparticles. An appearance of the particles was recorded by optical absorption spectroscopy (Fig. a, b) as the plasmon resonances and other absorption features prescribed to aggregations of less size. Usually, the short-wavelength maxima ( $\lambda < 350$  nm) attributable to the few-atomic clusters are not observable for silver reduced in similar systems, however, in our case the tuning of the preparation method can provide the participation of the lower-size pores like those in zeolites with regular cavities.

The absorption spectra of Ag-SiO<sub>2</sub> films (~1 wt.% of Ag) (Fig. a) reveal the remarkable effect of the hydrogen reduction temperature: its variation from 150 to 500°C shows change of the absorption peak position which may be interpreted as transition from clusters (Ag<sub>n</sub>, n < 30) those grow further to the particles with size > 100 nm (according to the plasmon resonance).

An incorporation of copper in the sol-gel films results also in production of nanoparticles with intense plasmon resonance peak (Fig. b), however, reduction conditions required are more hard, and any cluster-like absorption was not detected up to date in these films.

These data indicate feasibility of the sol-gel materials in the size regulation of metal nanoparticles, however, the physical and chemical nature of this phenomenon is not clear yet and requires more detailed studies of nanoporous structure of the matrix and doped materials.



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**SPECTROSCOPY OF NANOMETER – RANGE MEDIA AND MIXED LANTHANIDE LN $\beta_3$ L COMPOUNDS. THEIR APPLICATION PERSPECTIVES****J. Legendziewicz**

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To obtain cathode-ray pumped powder lasers for high resolution monochromatic displays, important is to produce low density scattering media for optically pumped lasers with sufficiently low generation threshold and relatively small volume of the excited medium involved in generation of light. The aim of this presentation is focused on the physical properties and the methods of synthesis of nanosized systems incorporated in silica gel and glasses [1]. Comparison of spectroscopic properties and types of species created in gels and silica glasses will be presented and discussed.

On the other hand, the basically similar compounds to those used as a precursor in creation of nanometer systems can be used in organic layered electroluminescent diodes (OLEDs). The important characteristics of these materials can be correlated with donor-acceptor properties of the substituents in the ligands.

Moreover, these donor-acceptor properties are responsible for location of energy levels, efficiency of energy transfer, electron-phonon coupling and finally quantum yield of luminescence.

Two types of lanthanide mixed  $\beta$ -diketones will be characterized and their applicability in OLEDs basing on spectroscopic data will be analyzed [2, 3].

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## APPLICATION OF SOL-GEL METHOD TO OBTAIN VARIOUS TYPES OF MATERIALS

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Chemical method of material synthesis defined as the sol-gel method represents the low-temperature way of the production of glasses, ceramic and composed materials. This method bases on the possibility of the obtaining of continuous structure of the solid body as the result of the reactions occurring in the solution. In this method the different organic and inorganic chemical compounds may be used as the precursors of final components of the material.

Our research concerns two kind of materials, obtaining by the sol-gel method, with different properties: – bioactive materials, – organic-inorganic hybrid glasses with special optical properties.

Bioactive materials are amorphous materials from the  $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$  system, as well as glass-ceramics with hydroxyapatite and wollastonite as crystalline phases. These materials are produced at the temperature not exceeding  $1000^\circ\text{C}$  are obtained in the form of powders, granules, coatings and dense sinters. The materials were characterised with respect to surface development and behaviour in simulated body fluid SBF. It has been found that in SBF the materials become covered with a surface hydroxyapatite layer, which is evidence of their bioactive properties. In order to estimate the biocompatibility of the obtained materials they have been subjected to selected tests *in vitro* (cultures of macrophages, fibroblasts and bone marrow cells) and *in vivo* (implantation to the rats bone defect). From our results it follows that these gel-derived materials have a higher bioactivity than melting materials and show excellent biocompatibility.

Organic-inorganic hybrid glasses (HG) represent a very interesting material of special optical and other physical or chemical properties. These glasses are formed from various combinations of metal alkoxides and polymers to create a nanoscale admixtures of inorganic oxide and organic polymers. Organically modified silica gels are obtained by the sol-gel method using as the starting materials tetraethoxysilane (TEOS) and the gel modifier, diethoxydimethylsilane (DEDMS). From our investigation it follows, that using DEDMS as an organic modifier of TEOS it is possible to obtain transparent gels of good quality at the molar ratio  $\text{DEDMS} : \text{TEOS} \leq 1$ . An addition of DEDMS affects the structure and microstructure of gel derived from TEOS. DEDMS accelerates the polycondensation reactions of gel at low temperature and causes the reduction of the specific gel surface. Introducing the organic dye 2',7'-dichlorofluorescein into TEOS gel, as well as to TEOS gel modified by DEDMS, develops the intensive yellow colour, stable up to  $100^\circ\text{C}$ . Heating the gels to  $200^\circ\text{C}$  reduced the colour intensity of the gels, which might be connected either with the dye decomposition or with its removal from the gel. Establishing the factors determining the colour stability in gels will be the object of further research.

**INFLUENCE OF ACTIVATORS CONCENTRATION AND PREPARATION REDOX CONDITIONS OF Tb- AND Ce-Tb-CONTAINING SILICA GEL-GLASSES ON THEIR SPECTRAL-LUMINESCENT PROPERTIES**

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It is shown that for Tb-containing glass with low concentration of the activator ions the shares of photons emitted from  $^5D_3$  and  $^5D_4$  states at excitation in inter-configuration transition are close. An increase of the  $Tb^{3+}$  ions concentration is accompanied by essential reducing of intensity of their  $^5D_3 \rightarrow ^7F_1$  transitions as a result of cross-relaxation quenching of luminescence. A change of redox conditions of vitrification and annealing the Tb-containing glass occurs a weak influence on its spectral-luminescent properties. A co-doping with Ce of this glass vitrified in oxygen or in air leads to formation of complex  $Ce^{4+}-Tb^{3+}$ -centers. At high concentration of the co-activators, the two types of the complex centers are discovered. Such centers are characterized with intra-centers sensitizing their  $Tb^{3+}$  ions luminescence by metastable photo-reduced  $(Ce^{4+})^-$  ions. It is noted that the sensitizing occurs to  $^5D_4$  state. A quantum yield of the sensitized luminescence depends to a considerable extent on efficiency of the luminescence extinguishing which stipulated by Ce-containing clusters and, perhaps, by  $Tb^{4+}$  ions. The redox conditions of obtaining the co-doped glass with quantum yield of the sensitized luminescence closing to 1 is found. It is established that the transfer of energy between the complex centers and simple  $Tb^{3+}$ -centers is insignificant.

## THE ELECTROCHEMICAL REDOX REACTIONS IN SILICA SOL-GEL GLASS MONOLITHS AND FILMS

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The electrochemical redox reaction of ferrocene and Co(II)tris(bipyridine) has been studied in silica sol-gel glass with embedded organic electrolyte. This material has been prepared by acid catalysed hydrolysis of the tetraalkylorthosilicate sol mixed with salt solution in organic polar solvent. Tetramethyl- or tetraethylorthosilicate was used as precursor. Lithium or tetraalkylammonium perchlorate solution in propylene carbonate or sulpholane was used as modifier. Sol-gel glass has been prepared in a form of monolith or film. The electrochemical behaviour of the redox probe was studied by cyclic voltammetry and chronoamperometry on ultramicroelectrodes in the absence of macroscopically liquid phase.

The accessible potential window in solid material is more narrow than in analogous liquid organic electrolyte. The shape of the cyclic voltammograms corresponding to electrochemical redox reaction in sol-gel monolith is similar to obtained in liquid electrolyte and it does not depend on gel aging. On the other hand, the current substantially decreases during the first few days after gelation and later it becomes weakly dependent on aging. The precursor, salt, solvent and the type of the redox probe affect the motion rate of the latter. The latter is five times slower in electrolyte made of tetraethylorthosilicate in comparison to that obtained using of tetramethyl derivative. The diffusion coefficient of ferrocene is larger in the gel obtained in the presence of the large tetraalkylammonium cations.

The electrooxidation of ferrocene was also studied in sol-gel films casted on the surface of the electrode assembly. For the electrolyte obtained from tetraethylorthosilicate the magnitude of the current is similar to that obtained in glass monolith made of the same material whereas for matrix obtained from tetramethylorthosilicate it is considerably smaller.

## SPECTROSCOPIC STUDIES ON THE INCLUSION COMPLEXES OF TETRAKIS(2-HIDROXY-5-NITROPHENYL)PORPHYRIN WITH $\alpha$ -CYCLODEXTRIN IN SOL-GEL MATRIX

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Cyclodextrins (CD) are naturally occurring cyclic oligosaccharides. Because their water solubility and hydrophobic cavity, organic compounds can be incorporated to form inclusion complexes in aqueous solution. The central importance of porphyrins in heme proteins has stimulated much interest in their water-soluble compounds. Porphyrins are investigated and employed as catalysts of oxidation processes, in supramolecular devices and as contrast agents for magnetic resonance imaging, to cite a few fields [1, 2].

In this work we study the inclusion complexes of tetrakis(2-hydroxy-5-nitrophenyl)-porphyrin (T2H5NPPH<sub>2</sub>) with  $\alpha$ -cyclodextrin in water solution, in a solid state and in a sol-gel matrix. Firstly, the porphyrin solution (in dichloroethane-DCE) was added into  $\alpha$ -cyclodextrin aqueous solution (molar ration 1:100). The two phases system was stirred and heated until all DCE was evaporated and the porphyrin was transferred to the aqueous solution. The solution was dried and to the solid inclusion complex were added ethanol, tetraethoxysilane, water and 1Mol/L HCl. The resulting solution was stirred for 30 minutes and then allowed to stand at 25°C. A xerogel with glassy appearance was obtained after 3 days of aging.

The excitation and the emission spectrum showed peaks presented in the Table.

As we observe in the Table and Figure, the T2H5NPPH<sub>2</sub> maintained its luminescent properties in all environments that indicate a structural stability under the experimental procedures. It is also observed an enhancement in the emission of the porphyrin in the  $\alpha$ -CD sol-gel matrix leading to the conclusion that the use of  $\alpha$ -CD is a valid methodology to solubilize organic molecules in order to produce designed materials by sol-gel technology.

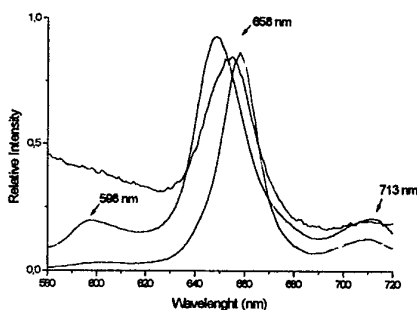


Table. Excitation and emission maxima of the luminescence spectra of the T2H5NPPH<sub>2</sub> in different media.

	Excitation $\lambda_{\max}$ (nm)	Emission $\lambda_{\max}$ (nm)
T2H5NPPH <sub>2</sub> in DCE (—)	422	658, 713
T2H5NPPH <sub>2</sub> / $\alpha$ -CD aqueous (---)	427	658, 713 (w)
T2H5NPPH <sub>2</sub> / $\alpha$ -CD solid (···)	425	654, 713 (w)
T2H5NPPH <sub>2</sub> / $\alpha$ -CD sol-gel matrix (-·-·)	424	598, 648, 713

w = weak;

*Acknowledgements:* CAPES, CNPq, FAPESP.

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**TRANSPORT OF IONS IN NANOPOROUS XEROGEL STRUCTURES****H. Sodolski**

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Recent developments in the sol-gel technology have led to new possibilities of obtaining a whole group of innovative nanoporous materials. The unique physical properties of these materials, modifications readily allowed by their structure and the possibility of doping them on the molecular level make them very interesting both from the scientific and the practical points of view.

The object of presented investigations has been the electrical properties of doped and undoped silica xerogels with highly developed internal surface. The ionic character of electrical conductivity in the investigated xerogels has been confirmed experimentally by the discovery of a step-reversible high-pressure-stimulated change in SiO<sub>2</sub> gel conductivity. Mechanisms responsible for charge carrier generation and transport in nanoporous silica xerogel structures have been investigated in detail. Both are strongly determined by the state of the gel pores' internal surface. This state may be modified by the sorption/desorption processes of water vapour and thermal treatment of gel in vacuum. Our analysis of the current-field characteristics suggests the presence of polarization effects in the nanopores, which can essentially modify the effective electric field responsible for the transport of ions in silica gel structures. The connection between electric conductivity and polarization phenomena in SiO<sub>2</sub> xerogels has been investigated by applying the thermally stimulated polarization (TSP) and depolarization (TSD) methods. Due to great temperature gradients which accompany the TSP and TSD measurements of silica xerogels in vacuum, the methods have been applied in their new, modified form.

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**RARE EARTH DOPED SILICA GLASSES AND CERAMICS****W. Stręk**

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A review of various sol-gel technologies leading to rare-earth ions doped silicate matrices will be given. The matrices can be obtained in forms of bulks, films and powders with mezo and nanostructures. Doping with lanthanides yields materials promising a variety of possible applications. For example, cathodo-ray and X-ray scintillators, optics and lasing materials and sensor can be manufactured via this approach.

## SOL-GEL GLASSES DOPED WITH COPPER SELENIDE NANOPARTICLES: NON-LINEAR OPTICAL PROPERTIES AND LASER PASSIVE SHUTTERS APPLICATIONS

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Copper chalcogenides quantum dots (QD's) are of great interest since the presence of multivalence transition metal (Cu) and variable stoichiometry open many pathways to change their optical properties. In this report, we study transient absorption changes, intensity-dependent transmission, and passive Q-switch operation of sol-gel glasses containing copper selenide ( $\text{Cu}_x\text{Se}$ ) QDs. The mean radius of the QDs studied was about 25 nm with size distribution of 30%. The overall concentration of particles was  $10^{13}$ - $10^{14}$   $\text{cm}^{-3}$ . Figure 1 shows the absorption spectra of different  $\text{Cu}_x\text{Se}$  QD's glass samples. Oxidation of the  $\text{Cu}_x\text{Se}$  QD's results in the appearance of the additional absorption band peaked at 1.0-2.2  $\mu\text{m}$ . Its position depends on stoichiometry coefficient  $x$  of the  $\text{Cu}_x\text{Se}$  compound. The broad absorption bands are attributed to transitions from deep energy levels within the band gap to the quantum-confined electron levels. Transient absorption changes of the  $\text{Cu}_x\text{Se}$  QDs have been measured with picosecond pump-probe technique. The bleaching recovery time was found to depend on coefficient of stoichiometry  $x$  and vary from 130 ps to 1.4 ns (Fig. 2).

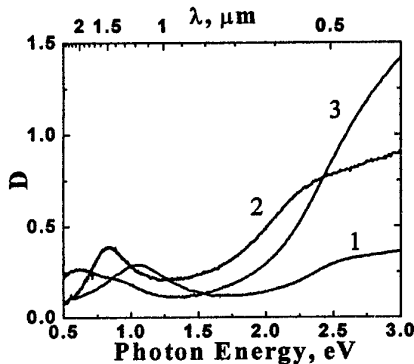


Fig. 1. Absorption spectra of  $\text{Cu}_2\text{Se}$  (1) and  $\text{Cu}_{2+x}\text{Se}$  (2, 3) nanocrystals in the sol-gel silica glasses.

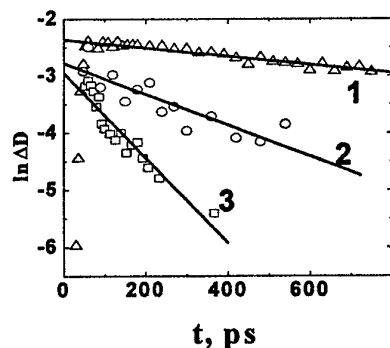


Fig. 2. Bleaching decay for various stoichiometry  $x$  of  $\text{Cu}_x\text{Se}$ .

Transmission  $T(I_0)$  of the  $\text{Cu}_x\text{Se}$  QDs glass samples in dependence on intensity  $I_0$  of incident nanosecond laser pulses was measured at the wavelengths of 1.06, 1.34 and 1.54  $\mu\text{m}$ . The noticeable bleaching was observed. The best fits to the experimental data were obtained for  $I_S=2.2$   $\text{MW}/\text{cm}^2$  and  $\sigma_E/\sigma_G=0.35$  at 1.06  $\mu\text{m}$  (sample 1) and  $I_S=7$   $\text{MW}/\text{cm}^2$  and  $\sigma_E/\sigma_G=0.05$  at 1.54  $\mu\text{m}$  (sample 2).

The above described bleaching effect with low absorption saturation intensity makes the  $\text{Cu}_2\text{Se}$ - and  $\text{Cu}_{2+x}\text{Se}$ -doped glasses suitable for application in Q-switched solid state lasers. Passive Q-switching of neodymium laser emitting at wavelengths of 1.06 and 1.34  $\mu\text{m}$  and erbium glass laser at 1.54  $\mu\text{m}$  were obtained. Pulse duration was 100, 90 and 60 ns, respectively.

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## INFLUENCE OF AIR HUMIDITY ON SILICA GEL GLASS ELECTRICAL PROPERTIES

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In some earlier works the silica gel based materials utilisation as sensors of many substances was shown. While gel glass preparation the indicating material could be mixed into substrate chemicals. After hardening the glass material containing indicator molecules could be utilised as chemical sensor. If the material was placed in the gas ambient some physico-chemical processes occur. The porous structure of gel glass allowed the substances molecules to move in the material depth and, if possible, to react with the immobilised indicator. If the ambient mixture contained the indicator reacting substance, the chemical process would occur. Changes in optical properties of the embedded indicator could be taken as a measure of the determined substance concentration.

Porous gel glass could be described as two-phase system. One of the phases may represent solid glass components i.e.  $\equiv\text{Si-O-Si}\equiv$  chains, immobilised water and other substances that can not be removed from glass in experimental conditions. The effective properties of this phase remain unchanged. The second phase represents channels in the material. Liquid medium filling pores causes changes in this phase effective properties. For any two-component system the electrical properties are determined by its composition, the components features and preparation conditions. For a certain sample of gel glass the constant amounts and unchanged structure of both phases could be supposed. If the sample's ambient atmosphere was changed only the effective properties of the second phase are expected to vary. As the result changes in the sample's electrical properties could be observed.

The DC and AC electrical properties of porous xerogel were investigated. For the constant voltage applied the electrical conductivity of the sample decreased in time. For AC measurements the circuit of parallelly connected conductance  $G$  and capacity  $C$  was considered. The electrical parameters dependences on time and water vapour concentration were investigated. After a change of vapour amount in sample's ambient variations in  $C$  and  $G$  values appeared after not more than a few dozen of seconds. Influence of benzene and acetone vapours on sample's electrical parameters was also investigated.

## AN INCORPORATION OF TRANSITION METALS AND THEIR COMPOUNDS INTO SILICA SOL-GEL MATERIALS

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Silicate glasses doped with different inorganic compounds are widely used in laser technologies and optoelectronics. We consider the possibility of fabrication of the sol-gel derived glasses containing nanosize particles of transition metals and their compounds. On the example of a series of copper compounds (CuO, Cu<sub>x</sub>S, Cu<sub>x</sub>Se) we illustrate the fabrication methods for some "particles-matrix" systems with controlled composition in the form of both thin films and monolithic glasses.

The beginning step of the preparation sequence (see the scheme below) was the hydrolysis of TEOS followed by addition of aerosil (SiO<sub>2</sub> with sizes of particles ~ 20 nm) to avoid a strong volume change under gelation and further operations. High temperature treatment of the gel leads to the formation of porous silicate xerogels with density 0.8-0.9 g/cm<sup>3</sup> and pore size 10-200 nm (adjusted by the sintering temperature). The open porous system allowed easy incorporation of dopants from liquid and gaseous phases remaining inside. A subsequent chemical transformation under heating in different atmospheres (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, Se) resulted in formation of corresponding nanoparticles, and the finishing annealing did the transparent monolithic glasses. The particles appear in the size range of 10-150 nm with comparatively low concentration (from 10<sup>12</sup>-10<sup>13</sup> cm<sup>-3</sup>). The film materials (the thickness of the films up to 1 μm) were got under milder heat treatment on substrates with optical characteristics similar with the glasses, however, the nanoparticle concentration was on 2-3 orders higher. XRD and XPS studies allowed us to establish the chemical composition and its relationship with optical features.

### **The scheme of preparation of the doped glasses and films**

#### **1. Gels**

The preparation of water-alcohol solution of an polysilicate acid: Si(C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub> + H<sub>2</sub>O + acid catalyst →

The preparation of aqueous emulsion of SiO<sub>2</sub> (with ultrasonication)

Mixing of the above followed by centrifugation

pH upgrade (5.5-6) by aqueous NH<sub>3</sub>

Gelation in a forming volume

#### **2. Doped xerogel**

Drying of gels and heat treatment at 600-800°C

The impregnation of xerogels in a doping solution with metal compounds

#### **3a. Glass doped with nanoparticles**

Heating and annealing of xerogels (about 1200°C) in air - **metal oxides in glass**

Heating and annealing of xerogels (about 1200°C) in H<sub>2</sub> - **metal particles in glass**

Heating in air followed by H<sub>2</sub>S (400 °C) and annealing in closed volume (1200°C) - **metal sulfide particles in glass**

Heating in H<sub>2</sub> (600°C) followed by annealing in Se vapour in closed volume (1200°C) - **metal selenide particles in glass**

#### **2b. Films doped with nanoparticles**

An incorporation of the metal salts in sols

Spin-coating of the sol onto a solid substrate with simultaneous gelation

Heating of the films (500-900°C) in air - **metal oxides in films**

Heating of the films in H<sub>2</sub> (500-900°C) - **metal particles in films**

Heating in air followed by H<sub>2</sub>S (400°C) - **metal sulfides in films**

Heating in H<sub>2</sub> (600°C) followed by Se vapour (300°C) - **metal selenide particles in films**

**SOL-GEL MATERIALS  $\text{SiO}_2\text{-TiO}_2\text{:Eu,Er}$  FOR PLANAR WAVEGUIDE****L.Q. Minh<sup>a</sup>, N.T. Huong<sup>a</sup>, Ch. Barthou<sup>b</sup>, P. Benalloul<sup>b</sup>, W. Streck<sup>c</sup> and T.K. Anh<sup>a\*</sup>**

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Sol-gel thin films  $\text{SiO}_2\text{-TiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$  doped Eu or Er were prepared in the clean room by spin-coating with a variety of the molar concentration ratio of Tetrathoxysilane (TEOS) and Titanium isopropoxide (TPOT). The different ratio of  $\text{SiO}_2\text{-TiO}_2$  are 90/10, 85/15, 80/20, 75/25 and different concentration of Eu and Er of  $10^{-3}$  to  $5 \cdot 10^{-2}$  mol%. Refractive index and thickness of silica-titania thin films after heat treatment from 150, 300, 500, 700, 800, 900°C were determined from 1.49 to 1.62 and 150 to 300 nm respectively. The multilayer (6–8 layers) silica-titania thin films with thickness of about 1.2 to 1.6  $\mu\text{m}$  have been developed in order to make highly doped Eu or Er planar wave guides on silica substrate. Luminescent spectra, life times as well as FTIR and Micro Raman results have been presented and discussed. The influence of the concentration of Eu, Er on luminescent spectra, life times and the strong influence of annealing temperature on the structure of thin films were detailed and studied.

## PROTONATION-DEPROTONATION OF THE FREE-BASE PORPHIN MOLECULES EMBEDDED IN SILICATE GEL MATRICES

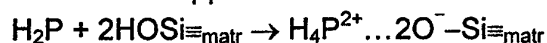
**S.M. Arabei, T.A. Pavich, K.N. Solovyov**

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Interactions between a silicate gel matrix and organic impurity molecules may essentially change the physical and chemical properties of impurity centres. The understanding of the nature of these interactions, of the mechanisms of various reactions both in pores and on the surface of the silicate skeleton as well as the possibility to control these processes are necessary for targeted chemical synthesis of doped sol-gel materials with redesigned properties.

In this work we have carried out a detailed investigation of the influence of the nature of silicate inorganic TEOS and hybrid organic-inorganic VTEOS gel matrices, the chemical composition of the initial reaction sol-gel mixture and the gel matrix drying process on the spectral properties of the free-base porphin ( $H_2P$ ) molecules embedded in the nanodimension pores.

It has been established that, as the solid TEOS gel matrix is being formed, the visible four-band absorption spectrum of  $H_2P$  is transformed into single-band spectrum. On the contrary, in solid hybrid VTEOS gel matrix no spectral changes are observed. Based on the totality of the experimental data obtained a conclusion is drawn that the neutral  $H_2P$  molecules interact with the surface of the TEOS pores by means of the formation of hydrogen bonds between the central nitrogen atoms and the hydrogen atoms of the surface silanole groups. As a result, the centre of the  $H_2P$  molecules is protonated, i.e. the dicationic form appears



to which the transformed absorption spectrum belongs. Evidently, in the case of VTEOS gel matrices the surface vinyl groups are not capable of protonating the  $H_2P$  molecules. Subsequent prolonged drying process of doped TEOS matrices leads to the reverse process of  $H_4P^{2+}$  deprotonations of, the result of which is the formation of the monocationic species  $H_3P^+$  with the corresponding absorption spectrum.

The fluorescence and absorption spectra of all protonated forms of  $H_2P$  have been studied in detail at 300 and 77 K. At 4.2 K the fluorescence line-narrowing spectrum of  $H_4P^{2+}$  in the TEOS gel matrix has been obtained. The causes of the changes in the frequencies and activity of the  $H_4P^{2+}$  vibrations in the excited  $S_1$  state are discussed. It has been inferred that the structural rearrangement (increase in non-planarity) of the dication takes place in the  $S_1$  state.

This work was performed with financial support from the Belarusian Republican Foundation for Fundamental Research (Grant No. F99-207).

## SOL-GEL SYNTHESIS OF Fe-CONTAINING SILICA SPHERICAL POWDERS

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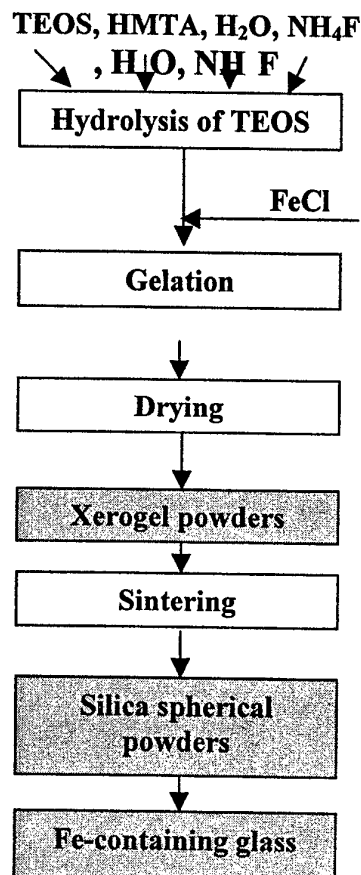
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Iron-containing silica glasses and nanocomposites can be used as ferromagnetic materials and color filters [1, 2]. Utilization of the sol-gel process for synthesis of silica glass is preferable because its low sintering temperature and high efficiency. Incorporation of fluorine into xerogel simultaneously with Fe-ions reduces bubble formation upon consolidation by sintering and result in the formation of Fe-containing clusters in the network of silica-gel glass.

The Fe-doped spherical powders for a formation of glasses and composites were prepared by sol-gel process, modified in the part of TEOS hydrolysis technique. The flowchart of novel sol-gel process shows in figure.

The process of monolithic silica spherical powders incorporates the hydrolysis of tetraethylorthosilicate in the system  $\text{Si}(\text{C}_2\text{H}_5\text{O})_4 - \text{H}_2\text{O} - \text{NH}_4\text{F} - (\text{CH}_2)_6\text{N}_4$ , addition of ferric sel into sol, gelation. After gelation the wet gel was dried slowly from room temperature up to  $100^\circ\text{C}$  in the period 1–2 days. The following thermo-treatment of Fe-containing xerogel in air at the temperature  $600^\circ\text{C}$  lead to formation of silica glass-like powders of spherical form. The following thermo-treatment of Fe-containing xerogels in air at the temperatures  $1200^\circ\text{C}$  lead to formation of silica glass-like powders containing ~200–250 ppm of  $\text{OH}^-$  groups.

REM investigation demonsttraite spherical formes of particles sized up to 1.0–1.5 mkm of diameter. The models of  $(\text{MeF}_x)_n$  nanosized clusters in the structure of silica gel-matrixes were proposed after studying of morphology and optical parameters silica spherical powders. The cold izostatic pressing (CIP) procedure for preparation of  $\text{Fe}^{3+}$ -containing silica powders results in light-scattered materials of brown colour.



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**BIOACTIVE GEL-DERIVED MATERIALS****M. Łączka, K. Cholewa-Kowalska**

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Materials which are introduced in medical practice for reconstruction and replacement of the diseased and damaged human bones are called „biomaterials”. According to the character of tissue response at the implant interface, biomaterials has been divided into: almost inert, resorbable and bioactive.

Bioactive materials are amorphous materials from the  $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$  system, as well as glass-ceramics with hydroxyapatite and wollastonite as crystalline phases. Bioactive materials induce specific tissue response, which results in the formation of a bonding interface between the implant and the natural host tissue.

In our laboratory, these materials, with different chemical composition, are obtained by the sol-gel method, using TEOS, triethylphosphate ( $\text{OP}(\text{OC}_2\text{H}_5)_3$ ), calcium nitrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  as the starting compounds.

The maximum temperature of thermal treatment is  $800\text{--}1200^\circ\text{C}$ , it is about  $300\text{--}500^\circ\text{C}$  lower than in case of conventional methods like melting and controlled crystallisation. These materials are obtained in the form of powders, granules, coatings and dense sinters.

The materials were characterised with respect to phase composition and behaviour in simulated body fluid SBF to estimate their bioactivity *in vitro* conditions, which can be seen as ability to form on its surface a layer of hydroxyapatite as a result of its contact with SBF.

From our studies it follows that all pellets become covered with a layer enriched with calcium, and phosphorus, which may be evidence of surface crystallisation of calcium phosphate, but in the case of sinters only on the A material's surface crystallisation of calcium phosphate was observed. However the material A in the form of granules behaves like resorbable material while the granules of S show high bioactivity. These facts indicate that the form of materials, in case of gel-derived materials determines their chemical properties.

In order to estimate the biocompatibility of the obtained materials they have been subjected to selected tests *in vitro* (cultures of macrophages, fibroblasts and bone marrow cells) and *in vivo* (implantation to the rabbits bone defect and in skeleton muscle of rats).

Considering the results of the performed experiments, it can be assumed that none of the tested materials deteriorates the vital function of the cells, and the process of bone reconstruction stimulated by obtained materials is satisfactory.

## SOL-GEL METHOD PREPARATION AND PROPERTIES OF COLLOIDAL NANOSIZE SILICA DIOXIDE FOR POLISHING OF MONOCRYSTALLINE SILICON WAFERS

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Colloidal silica can be used for final general metallographic polishing. It is used to polish single crystal silicon for electronic applications and, subsequently, polycrystalline silicon for solar cells, gallium arsenide, indium phosphide, titanium, gadolinium gallium garnet and sapphire [1-3].

Colloidal silica, also referred to as a sol, contains very fine particles (1 to 300 nm in diameter) that remain in suspension over a long period of time. In colloidal silica, the particles are amorphous rather than crystalline, and they have a negative electrical charge. The particles are nearly insoluble in the dispersing medium (distilled water). pH is the main factor influencing the stability of colloidal silica and, in addition, pH is the electrochemical factor, which plays a significant role in polishing semiconducting material slices.

Following chemical agents are used for synthesis of colloidal silica: powder of silica dioxide, alkaline compound distilled water and surface-active substances. The silica dioxide are dispersed in water with alkaline compound added to obtain the desired pH.

Therefore, we have established that density and viscosity of the obtained colloidal silica dioxide decrease with increase of specific surface of particles  $\text{SiO}_2$ . Thus, the viscosity of synthesized suspensions is increased with reduction of specific surface of particles silica dioxide and increase in their size.

The aim of the present work is to prepare and to investigate the physical-chemical properties of colloidal nanosize silica dioxide used for final polishing of silicon wafers.

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**PHOSPHOSILICATE COMPOSITE MEMBRANES FOR PROTON EXCHANGE  
MEMBRANE FUEL CELLS (PEMFC)**

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A limitation of current proton-exchange membrane fuel cells (PEMFC) is the maximum operating temperature, the boiling point of water, where the membranes lose conductivity because of drying. The incorporation of phosphosilicate gels into the membranes can improve the proton conductivity and thermal stability above 100°C. Composite membranes were prepared by soaking commercial NAFION in phosphosilicate sols. The composite membrane has an oxide content up to 10% by weight. Performance in an operating fuel cell was compared between the NAFION with and without gel to determine the ability of the modified membrane to retain conductivity above the boiling temperature.

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**PHOTOCHROMIC, HYBRID SOL-GEL COATINGS: PREPARATION,  
PROPERTIES, AND APPLICATIONS****A. Klukowska<sup>1</sup>, U. Posset<sup>2</sup>, G. Schottner, J. Kron***Fraunhofer-Institut für Silicatforschung (ISC), Neunerplatz 2, D-97082 Würzburg, Germany;  
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Inorganic-organic hybrid polymer (ORMOCER<sup>®3</sup>) coatings with a fast photochromic response and high photochromic activity were prepared by incorporation of organic photochromes into hydrolysates of organofunctional alkoxy silanes and metal alkoxides, with subsequent thermal curing. The resulting materials were characterized by means of Raman spectroscopy. Matrix rigidity and mechanical stiffness were assessed via micro hardness measurements. Adhesion properties were determined on different substrates such as hard resin, polycarbonate and glass. The coating approach for photochromic materials provides benefits like a more general applicability to different substrates, in particular to those that cannot be tinted by state-of-the-art mass or thermal transfer dyeing techniques. High dye concentrations, being a prerequisite for high colourability of thin films, were achieved by means of silylated photochromic species equipped with hydrolytically condensable groups (photochromic silanes), that can be grafted to the hybrid matrix. The resulting thin films showed high photochromic activity and mechanical properties comparable to the pure host material. Photochemical degradation was studied by means of artificial weathering (suntest) on selected systems. The influence of the matrix and radical or excited state quenchers was examined. Matrix-dye-stabilizer interactions were found to be complex, rendering it difficult to find appropriate stabilizer compositions for mixtures of different dye classes. The most effective fatigue protection resulted, when the photochromic layers were not accessible for ambient oxygen. The developed coatings may be preferably employed in the preparation of optical ophthalmic and non-ophthalmic articles such like prescription lenses or sunglasses. Besides, the coatings have potential for utilization for radiation protection devices, filter devices, printing/publishing applications, reversible switching markings, and in the textiles/clothing sector.

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<sup>3</sup> Trademark of Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V.

**ORGANICALLY MODIFIED SILICA XEROGELS – TEXTURE AND STRUCTURE CHARACTERISTICS****M. Łączka, K. Cholewa-Kowalska, M. Kogut**

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Organic-inorganic hybrid glasses (HG) represent a very interesting material of special optical and other physical or chemical properties. These glasses are formed from various combinations of metal alkoxides and polymers to create a nanoscale admixtures of inorganic oxide and organic polymers. The goal for this work was to produce a family of materials with properties intermediate between those of polymers and glasses.

Organically modified silica gels were obtained by the sol-gel method using as the starting materials tetraethoxysilane (TEOS) and the gel modifiers, diethoxydimethylsilane (DEDMS), diethoxymethylvinylsilane (DEMVS). The effect of various molar ratios ( $4 \div 0,8$ ) of TEOS and DEDMS or DEMVS on the quality of gels was investigated. Next, the porous structure as well as the surface development of gels were determined (using a multi-functional apparatus ASAP 2000). Spectroscopic examinations (FTIR) were carried out in order to explain the character of hydrolysis-polycondensation reactions in gels and bonds forming between the organic and inorganic nano-structures in the obtained materials. It can be seen that the addition of DEDMS (or DEMVS) causes reduction of surface area in comparison with pure TEOS gel. According to FTIR and examination organically modified gels have spatial, stable structure already after drying at 40°C.

Because these copolymers have potential application as a matrix for organic dyes species, optically active organic dye (2',7'-dichlorofluorescein) has been incorporated into the gel matrix. Preliminary studies of coloured gels concerning evaluation of the thermal, chemical and mechanical stability of organic dye in the silica structure were carried out.

Immersion methods were used in order to determine the effect of addition of organic gel modifiers on the effective refractive index of gels.

The investigations realized within this work extend the basic knowledge of the preparation processes and internal structure of unconventional hybrid glasses. The results also provided a basis for the preparation of other organic-inorganic hybrids with modified optical properties.

## SOL-GEL MATERIAL AS A SUPPORT OF METALLOCENE CATALYSTS FOR ETHYLENE POLYMERIZATION

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Homogeneous metallocene catalysts for olefin polymerization are heterogenized using various supports, mainly oxides (silica) and  $MgCl_2$  as well. However products obtained over magnesium dichloride supported catalysts contain unprofitable chloride quantity, and in spite of their high activity it seems proper to replace  $MgCl_2$  with other, non chloride carrier.

Our earlier studies on titanium- and vanadium-based catalysts, supported on modified oxides (silica and alumina) showed that such catalytic systems are less active than similar ones obtained with magnesium dichloride. Searching for other, non-chloride support, we applied a new silica-type material, obtained in sol-gel process under conditions that allow receiving a silica powder. Resulting product, after drying and chemical modification was successfully used as a carrier for both: Ziegler-Natta and metallocene catalysts [1–4].

The influence of the conditions of the sol-gel powder preparation on supported catalytic system activity in ethylene polymerization process was investigated. As a catalyst zirconocene ( $Cp_2ZrCl_2$ ) was applied and activated with methylaluminoxane (MAO). Received catalytic system dependently on its composition and preparation conditions gives yield of polyethylene in range  $4 \cdot 10^6 - 16 \cdot 10^6 g_{PE} \cdot mol_{Zr}^{-1} \cdot h^{-1}$ .

Besides catalysts supported on mentioned sol-gel product give polyethylene with good morphology particularly in comparison to product received with  $MgCl_2(thf)_2$  supported system. Molecular weight of polymers is about 300 000 and the molecular weight distribution is relatively narrow ( $MWD < 3$ ).

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**THE MOTION OF REDOX ACTIVE PROBES IN SILICA SOL-GEL GLASS WITH EMBEDDED ORGANIC ELECTROLYTE****J. Kukulka-Walkiewicz and M. Opałło**

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The transport of the redox active probes (ferrocene and Co(II)tris(bipyridine)) in silica sol-gel glass with embedded organic electrolyte has been studied. The material has been prepared by acid catalyzed hydrolysis of the tetramethylorthosilicate sol mixed with lithium or tetraethylammonium perchlorate solution in polar organic solvent. Sol-gel glass has been prepared in a form of monolith with immersed electrodes. The shape of obtained voltammograms indicates that ferrocene molecules and Co(II)tris(bipyridine) ions are mobile within the matrix.

The rate of transport of the redox probes has been estimated by means of apparent diffusion coefficients by cyclic voltammetry and chronoamperometry on ultramicro-electrodes. They substantially decreases during the first few days after gelation and later it becomes weakly dependent on aging. The difference between apparent diffusion coefficients of ferrocene and Co(II)tris(bipyridine) as well similar temperature dependence to that in liquid electrolyte indicates that silicate matrix acts as porous reservoir for the organic electrolyte. The high temperature treatment of gel monolith increases the mobility of the redox probes.

**SPECTRAL-LUMINESCENT PROPERTIES OF Dy-CONTAINING GLASSES  
OBTAINED BY DIRECT AND NON-DIRECT SOL-GEL METHODS****G.E. Malashkevich, V.A. Boiko<sup>1</sup>, V.E. Gaishun<sup>1</sup>, I.M. Mel'nichenko<sup>1</sup>,  
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In this paper, the results of spectral-luminescent investigation of silica glass and glass of system  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Dy}_2\text{O}_3\text{-Na}_2\text{O}$  obtained by above methods are reported. It is established that for  $\text{Dy}^{3+}$  ions in both glasses the luminescence transitions from  $^4\text{F}_{9/2}$  state to all sublevels of  $^6\text{F}_j$  and  $^6\text{H}_j$  states are observed. In doing so, the silica glass is characterized by significant larger splitting of the activator energy states and high relative intensity of  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ ,  $^6\text{F}_{5/2}$  transitions. For the many-components glass, a high intensity of  $^4\text{F}_{9/2} \rightarrow ^6\text{F}_{7/2}$  transition takes additionally place. The activator luminescence decay kinetics for both glasses are characterized by slightly non-exponential curves with average duration 500–600  $\mu\text{s}$ . It is noted that for the glass obtained by the direct methods and activated by impregnation of the xerogel with spirits solution of  $\text{DyCl}_3$  the appearance of the luminescence at excitation with diode laser at  $\lambda=808$  nm takes place. That permits us to consider similar glasses as possible materials for up-conversion fiber laser.

## STUDY ON THE SOL-GEL-XEROGEL TRANSITION BY FLUORESCENCE SPECTROSCOPY

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The sol-gel process enables the preparation of room-temperature oxide glasses. By utilising this method it is possible to encapsulate organic dyes in an inorganic matrix. Thanks to their unique properties, the dye-doped sol-gel glasses are applied as laser media, non-linear optical materials, membranes in optical sensors, support in photocatalysis, etc.

The great advantage of this process relies on the possibility to influence the structure of the formed gel by changing the concentrations of the substrates, the pH of starting sol, the type of hydrolysis of the silane monomers, the temperature of the process and finally the conditions of drying gel to xerogel.

The silane gel, used in our investigation, was prepared by acidic hydrolysis followed by polycondensation. The starting solution contained triethoxysilane, ethanol and water in molar ratio 1:6:6, respectively. Pyrene was used as a luminescent probe sensitive to the trapped surroundings. Its concentration in the sol ranged from  $1 \times 10^{-6}$  to  $4 \times 10^{-3}$  M. The pH of the sol was changed from 1.8 to 5.9. The gelation and following vacuum drying was carried out at room temperature.

The steady state (Fluoromax-2) and the time resolved (FL 900 CDT Analytical Edinburgh Instrument) fluorescence spectra of pyrene were collected for deaerated samples at various stages of sol-gel-xerogel transition. The fluorescence anisotropy was also measured.

The changes of polarity in the reaction medium during gelation and drying processes were observed by variation of the intensity ratio of the third peak to the first peak of the pyrene monomer fluorescence. The increase of the viscosity of the system was determined by measuring pyrene fluorescence anisotropy in the wavelength region 350 to 500 nm. The differences in the structure during gel and xerogel formation were observed by changes in the intensity of the pyrene excimer emission at 470 nm. The phenomena observed during the sol-gel-xerogel transition were also correlated with the determined life times of excited pyrene.

### Acknowledgement

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## EFFECT OF THE NATURE OF SILICATE GEL MATRIX ON THE SPECTRAL AND LUMINESCENT PROPERTIES OF METALLOPORPHYRINS

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Unique properties and vast diversity of metalloporphyrins enable their wide practical use. The stability of the metal complexes towards destruction in certain matrix environment or under various external attacks is one of the most important conditions of their specific applications. Of interest is the preparation of silicate sol-gel metalloporphyrin-activated matrices which, having certain spectral and photochemical properties, may find promising applications in creation of materials for optics, spectroscopy, and laser technics.

In this communication we report on the results of the investigation of the influence of the nature of silicate sol-gel matrices on the spectral-luminescent and photochemical properties of embedded in them metal complexes of tetrabenzoporphin and its tetraaza derivatives. Zn tetrakis(4-*tert*-butylbenzo)porphin (ZnTBP<sup>tBu</sup>), YbCl phthalocyanine (YbPc), and YbCl 1,2-naphthalocyanine (YbNc) were incorporated in tetraethoxysilane (TEOS) or vinyltriethoxysilane (VTEOS) sol-gel mixtures of various chemical composition at the stage of their condensation with varying the reaction medium acidity. Hard sol-gel matrices colored this way were obtained as solid monoliths.

It has been established that all metal complexes are embedded into the VTEOS gel matrix without essential changes in their initial spectral-luminescent properties. On the incorporation of YbPc in the neutral TEOS sol-gel mixture rapid bleaching of the starting solution is observed, contrary to ZnTBP<sup>tBu</sup> and YbNc. The very unstable YbPc easily dissociates in the TEOS sol-gel medium under the action of proton-donating silanole HO-Si≡ groups and then undergoes hydrolytic splitting to colourless products. Under similar conditions YbNc is stable. However, for its spectra considerable bathochromic shift (~20 nm) is observed in passing from the liquid sol to the hard gel matrix. This indicates that YbNc suffers protonation at the macrocycle periphery due to the formation of hydrogen bonds between the aza-bridge nitrogen atoms with the surface HO- groups and the appearance of the H<sub>n</sub>(YbNc)<sup>n+</sup> cation:



The results of the temperature dependence investigations for the spectroscopic properties of the ytterbium complexes are presented. For the zinc complex the observed highly-efficiency reaction of its photodestruction is discussed in detail.

This work was performed with financial support from the Belarusian Republican Foundation for Fundamental Research (Grant No. F99-207).

## THE ROLE OF FLUORINE IONS IN THE FORMATION SILICA GEL AND GLASS STRUCTURE

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Fluorine-containing silica gels can be used as precursors of anhydrous glasses for radiation hard fiber optics. The silica gels were prepared by the sol-gel process including following stages: hydrolysis of tetraethylorthosilicate (TEOS) in a four-component system  $\text{Si}(\text{OC}_2\text{H}_5)_4 - \text{C}_2\text{H}_5\text{OH} - \text{H}_2\text{O} - \text{HCl}$ , adding the fumed silica (aerosil) into the sol, sonoactivation, centrifugal separation, neutralization by the ammonia solution, gelation, washing the gels in distilled water, drying and fluorination the xerogels by the procedure of heating in the freon/oxygen atmosphere. Fluorinated gels were consolidated into transparent silica glass in the atmosphere of helium gas at the temperature 1200-1300°C. SEM and AFM analysis BET surface area investigations were used for characterization of the xerogels and glasses morphology.

The pore volume increases until heating up to 800 °C and when the temperature rises up to 1100 °C the process of pore collapse is began, resulting in 1.6% porosity. At the temperature 1200 °C the pores are eliminated and the density becomes equivalent to fused silica.

There is a little change in the pore distribution of the hybrid silica gels until heating to the interval 800-1100 °C. Densification primarily is due to only the number of pore decreasing.

The pore-size distribution of fluorinated gels has a trimodal character: the network contains micropores (3.0 nm), mezo- and macropores (5.0-25.0 nm). The pore size can be largely by chemical attack of silica network with fluorine ions in vapor phase until heating and dissociation of ammonium fluoride.

Some fluorine-containing compounds ( $\text{HF}$ ,  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{HF}_2$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{C}_2\text{F}_3\text{Cl}_3$  etc.) can react with surface hydroxyl groups and gel silica network at elevated temperature, replacing OH-ions and forming the fluorine-containing volatile substances ( $\text{SiF}_4$ ,  $\text{SiF}_3$ ).

The process of gas-phase fluorine doping reduces hydroxyl level in the dense silica glass to below 3-5 ppm. The contents of fluorine determined by the MXRSA is 0.4-0.45% by weight. Such glasses have about 90% transmission at  $3671 \text{ cm}^{-1}$  (hydroxyl group absorption) region. The gas-phase doped sample contains also the chlorine contamination in the level of 0.17% by weight.

**SPECTRAL-LUMINESCENT PROPERTIES OF SILICA GEL-GLASSES, DOPED  
Sm-IONS RECEIVED BY SOL-GEL METHOD**

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There is currently a great deal of interest in the development of active glass devices that derive their important optical properties from organic or inorganic species doped into the glass.

Optical materials prepared by the sol-gel process are of current technological interest. Sol-gel silica glasses doped with rare-earth ( $RE^{3+}$ ) ions are an important class of optical materials with applications including solid-state lasers, optical waveguides, fiber amplifiers and devices for optical communications. In this paper, we describe the preparation of  $Sm^{3+}$ -doped silica gel glasses and discuss the spectral-luminescent properties of silica glasses. The samples were prepared from tetraethoxysilane (TEOS), water, ethanol, fumed silica and soluble in a water or ethanol the salt of the  $Sm^{3+}$  element.

The process of synthesis samples of silica gel-glasses included hydrolysis tetraethyl-orthosilicate in a water solution of an acid before reception sol, preparation colloid by addition in received sol of  $SiO_2$ , neutralization of sol-colloid system up to  $pH=6,5-7$  by introduction of a solution of ammonia and drying. Received xerogels were impregnated with solution  $SmCl_3$ . The sintering received xerogels was carried out on air or in atmosphere of He at  $T=1250^\circ C$ .

## ENZYME ELECTRODES WITH ENZYME IMMOBILISED BY SOL-GEL TECHNIQUE

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The method of sol-gel entrapment of biomolecules is a very promising technique of immobilisation for biosensors construction, because of its simplicity, low temperature of the process, large amount and low leakage of entrapped material. In this work the preliminary results of immobilisation of enzymes in silica gel on oxygen electrode are reported.

The stock solutions of sol was prepared as follows: **SOL I** – 4,5 ml of tetraethylorthosilicate, 1,4 ml H<sub>2</sub>O and 0,1 ml 0,1 M HCl; **SOL II** – 5 ml of tetramethylortosilicate, 1,0 H<sub>2</sub>O and 0,05 ml 0,1 M HCl were stirred vigorously at room temperature (**SOL I** – 3 hours, **SOL II** – 15 minutes) and stored in refrigerator. As the model enzyme glucose oxidase was used. A casting solution was prepared by mixing 200 µl of the sol solution with enzyme solution with volume ranging from 200 to 800 µl. 20 µl of this mixture was dropped immediately after mixing on the surface of oxygen electrode covered with nylon mesh. The rigid gel was formed in few minutes and the resulted enzyme electrode was dipped in 100 ml of phosphate buffer, pH=7. The response of the electrode to glucose was measured using microcomputer oxygen meter CO-551.

The influence of the composition of the casting solution (gel precursor, pH of the enzyme solution, sol-water ratio) on the electrode response was investigated. Also the addition of  $\gamma$ -aminopropyltriethoxy silane to the casting solution was checked. The best electrode with stable signal was obtained when the formed gel was not very rigid (buffer pH=6 and high water-sol ratio). For the optimal composition of the casting solution some properties of the glucose electrode were investigated (stability, influence of pH and temperature).

The method of sol-gel entrapment was also used to obtain the electrodes for disaccharides by coimmobilisation of invertase, lactase and maltase with glucose oxidase. Also other oxidases were immobilised with this method.

### *Acknowledgement*

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## SPECTROSCOPY, STRUCTURE AND FERROELECTRIC PROPERTIES OF $\text{BaTiO}_3:\text{Eu}^{3+}$ NANOCRYSTALLITES PREPARED BY THE SOL-GEL ROUTE

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Preparation by the sol-gel method of  $\text{BaTiO}_3:\text{Eu}^{3+}$  nanocrystallites and optical properties of  $\text{Eu}^{3+}$  are reported. Its perovskite-like crystallographic structures of the samples which underwent various thermal treatments were studied by XRD measurements (Fig.1). Existence of ferroelectric hysteresis loop for the nanocrystallites was confirmed. Emission spectra (Fig.2) and luminescence decays were measured at room temperature and at 77K for the successive stages of thermal treatment.

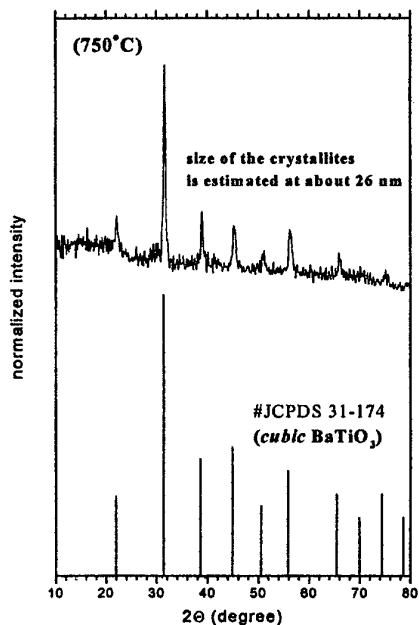


Fig. 1

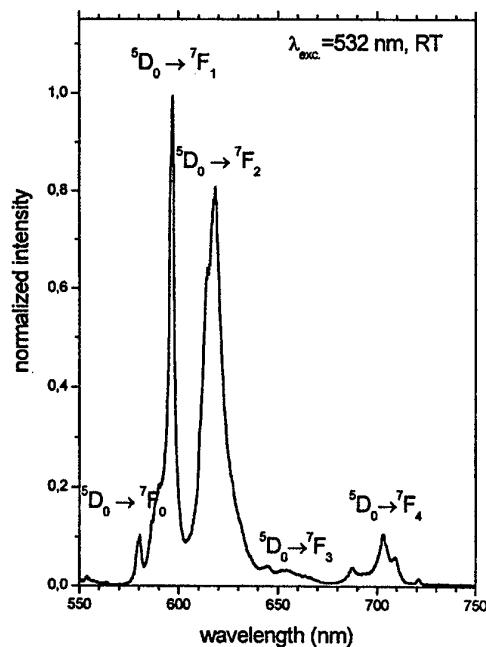


Fig. 2

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**COMPARISON OF THE POROUS SOL-GEL AND SILICA GLASSES'  
LINEAR DIMENSION DEPENDENCIES ON HUMIDITY**

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Permanent interest to porous sol-gel glasses is explained by the possibility of their broad application in electronics, sensors, pharmacology, prosthetic appliance, etc. As for their chemical content, sol-gel glasses are rather close to silica porous glasses that allows to employ techniques probated for silica porous glasses for the aims of their investigation.

In this work we have studied the influence of the humidity of the surrounding atmosphere on the linear dimensions of porous sol-gel and silica glasses. The measurements were performed using the interferometric measuring technique.

Pore size distribution spectra have similar shape for both types of glasses but for the sol-gel glass there are only two peaks in contrary to several ones with decreasing amplitudes in the silica glass. The difference in the sensitivity to moisture for both types of porous materials is explained by the presence of secondary silica gel in the pores of silica porous glasses while in sol-gel glasses this phase is absent because of the fabrication conditions. Thus the capillary effects prevail in sol-gel glasses. The revealed peculiarities of sol-gel glasses make possible to produce the new type of threshold humidity sensors.

## HYDROPHOBIC CARBON DOPED SILICA MATRIX AS A SUPPORT FOR LIQUID-LIQUID INTERFACE

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The hydrophobic carbon doped silica matrix was obtained by sol-gel process using methyltrimethoxysilane as a precursor. The graphite powder was added directly to the sol and the resulting mixture was placed into glass tube. After gelation and drying the solid matrix was filled with organic liquid: hydrophobic organic solvent (toluene, hexadecane, nitrobenzene) containing redox probe (decamethylferrocene). The modified matrix was connected to the potentiostat as a working electrode and immersed into aqueous salt solution.

Approximately symmetric cyclic voltammograms were obtained corresponding to the electrooxidation of decamethylferrocene. The current magnitude indicates, that electrode process occurs only close to the sol-gel matrix/aqueous electrolyte interface. The shape of voltammogram and current magnitude depends on the organic solvent. They also depend on the salt concentration in aqueous phase and the type of the anion. For the sol-gel matrix modified with nitrobenzene the position of the voltammogram on the potential scale correlates with Gibbs energy of anion transfer from aqueous to organic phase. It has been concluded that the mechanism of the electrode process involves electron transfer between graphite particle and the redox probe in organic phase. The formation of the decamethylferrocene cation is followed by anion transfer through the liquid-liquid interface.

**SPECTRAL-LUMINESCENT PROPERTIES OF SILICATE SOL-GEL FILMS  
DOPED WITH XYLENOL ORANGE AND YTTERBIUM****G.E. Malashkevich, T.A. Pavich, G.I. Semkova, P.P. Pershukevich and W. Strek<sup>1</sup>**

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Xylenol orange is a widely known reagent for photometric determination of some elements and metal-chromatic indicator at compleximetric titration. However, the investigations of complexing the reagent with rare earth metals and spectral-luminescent properties of obtaining complexes in sol-gel matrixes are absent. In the present paper, we attempt to make up for the deficiency with respect to complexes of xylenol orange with ytterbium in silicate sol-gel films.

It is established that the xylenol orange incorporated to above films is characterized in visible region of spectrum with a broad absorption band at 440 nm and intensive luminescence band at 600 nm. At co-doping the film with ytterbium, a considerable deformation and displacement of the absorption band up to 580 nm take place. In doing so, the changes of the xylenol orange luminescence band is lesser displayed, however, on its long-wavelength side is appeared a band connected with Yb<sup>3+</sup> ions. The share of photons emitted by these latter at excitation in absorption band of formed complex can exceed 20%. A thermal stability and influence of variation of H<sub>2</sub>O : Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> molar ratio as well as of co-doped components concentration on spectral-luminescent properties of the films is examined.

## THERMOSTIMULATED PROCESSES OF PRODUCTION OF METAL NANOPARTICLES IN OXIDE FILMS FORMED BY SOL-GEL METHOD

Yu.V. Bokshits, L.T. Potapenko, S.V. Serezhkina, G.P. Shevchenko

Since the discovery of nonlinear optical characteristics of glasses doped with ultradisperse noble metals (Ag, Au), the thin film "metal-oxide" systems formed by sol-gel method have been of considerably growing interest. This paper presents the results of the investigation on the sol-gel formation of the "metal-oxide" film systems from the composite sols consisting of Ag or Au nanoparticles produced by chemical reduction of appropriate soluble salts in SiO<sub>2</sub> sol, as well as on that of the films of ultradisperse germanium in SiO<sub>2</sub> matrix, which were formed either from codeposited or from mixed SiO<sub>2</sub>-GeO<sub>2</sub> sols.

Thin Me-SiO<sub>2</sub> film systems (Me is for Ag, Au, Ge) were formed by centrifugal casting from the respective composite sols, and the as-deposited layers were subsequently heated in air and/or in hydrogen. The films produced were characterized by electron microscopy and optical spectroscopy methods.

The Ag-SiO<sub>2</sub> films formed from composite sols containing silver particles 7-35 nm in size, were shown to be discolored on heating them in air at 500°C, the discoloration temperature being only slightly affected by a particular way of the sol preparation. Silver particles are formed again on heating discolored samples in hydrogen (500°C, 40 min), thus imparting a color to the nanocomposite. The nanoparticles formed are 1.5-2 times smaller in size than the initial ones, and they become encapsulated, thus no longer being susceptible to oxidation, and the composite remains colored on further oxidative heat treatment. Heating the as-prepared Ag-SiO<sub>2</sub> layers in hydrogen results in an about twofold growth of the silver particles in the films formed, and in a red shift of the silver plasmon absorption band. Au-SiO<sub>2</sub> films produced from the composite sols with 5-10 nm gold particles do not lose their colour when heated in air, while the size of the particles therein remains the same or grows by a factor of two and more, depending on the nature of the precursor sol from which they were formed.

The Ag(Au)-SiO<sub>2</sub> film layers are of different colors, from light-pink to dark-purple for Au and from light-yellow to dark-gray for Ag. The results obtained are of importance in producing a new type of pigments based on "nanodisperse noble metal-oxide matrix" composites.

Different approaches to the formation of SiO<sub>2</sub>-GeO<sub>2</sub> sols were studied, and SiO<sub>2</sub> films containing ultrafine germanium particles were formed by the reduction thereof in hydrogen (650°C, 2 hours). The Ge particles size was from several to 20-25 nm, depending on the method of the initial sol production. The film colour varies from yellow-brown to red-brown, and a blue shift of the absorption band edge is observed in the optical spectrum compared to that of the bulk germanium. The conditions were found under which germanium particles are uniformly distributed in the silicon dioxide matrix. GeO<sub>2</sub> reduction with hydrogen in the SiO<sub>2</sub>-GeO<sub>2</sub> films was shown to proceed at temperatures higher than the individual GeO<sub>2</sub> films (600-650°C and 450-500°C, respectively), which may be due to the mixed Si-O-Ge bonds present in such films and hindering the reduction process.

Thus, it has been found that the particle size in the "metal-oxide" film systems formed by sol-gel route from the composite sols produced by a variety of methods, and the optical characteristics of the films are largely governed by the way of the oxide matrix production and by the heat treatment conditions (temperature and atmosphere).

**SOL-GEL METHODOLOGY IN THE SYNTHESIS OF  
Zn-TETRA-*p*-UREAPHENYLPORPHYRINOSILICA:  
ABSORPTION AND LUMINESCENT PROPERTIES****J.C. Biazzotto, Y. Iamamoto and O.A. Serra**

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Utilizing the sol-gel matrix to incorporate and study luminescent molecules has formed an important area of research, both using the luminescent dyes to monitor the sol-gel process [1] and also the sol-gel glass as an environment in which to study the photophysics of dye molecules as well their interaction with the matrix [2]. In this way, the immobilization of luminescent porphyrins and metalloporphyrins in sol-gel matrices has been considered for applications as probes and sensors [3].

In the present work we describe the synthesis, absorption and luminescent properties of a material, named zincporphyrinosilica, containing a zincporphyrin incorporated to a silica network. The Zn-tetra-*p*-ureaporphyrinosilica (ZnTUPPS) was prepared using the sol-gel process, through the reaction between the Zn-tetra-*p*-aminophenylporphyrin and 3-isocyanatopropyltriethoxysilane, generating the monomeric specie, which is added to a pre-polymerized solution of TEOS, ethanol, water and ammonia. The UV/Vis spectrum of the ZnTUPPS presents the zincporphyrin Soret band at 430 nm indicating that its structure and spectroscopic properties were preserved. The material presents emission bands at 610 and 660 nm, blue-shifted 12 nm compared to the zincporphyrin due to interaction with the matrix. An interesting observation is that after addition of polar solvent, as acetone, to the ZnTUPPS the maxim emission band shift to 622 nm and its intensity increased. This fact can be due to loss of the interaction between the porphyrin and silica promoted by the polar solvent.

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**AEROGELS AND THEIR MODIFICATIONS****K. Szaniawska, L. Murawski, R. Pastuszak\*, M. Walewski\***

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The modification of silica aerogel can be achieved by ammonia treatment at the range of temperatures from 700°C to 1300°C. During this process ammonia reacts with silica aerogels to form Si-N bonds. We have found that the ammonolysis of porous silica gels is an effective way to introduce a large amount of nitrogen in silica network. A different kind of aerogels which have different porosity were nitrided. The best results were obtained for aerogels of the surface area smaller than 600 m<sup>2</sup>/g. It can be estimated that 90% of the pore volume is in pores with diameters between 10 and 120 nm. The amount of nitrogen that was incorporated in the silica aerogel depends on the final temperature of ammonolysis and on the time of heat treatment. The maximum amount of nitrogen which we introduced into an aerogel after 36 hours heating in ammonia at 1300°C was 33.1 wt%. The specific surface area of nitrided aerogels remains high and decreases with the temperature of ammonolysis and with nitrogen content. Nitrided aerogels can be converted into dense homogeneous oxynitride glasses containing 8.4 wt%–13.0 wt% of nitrogen by heat treatment at 1600°C in vacuum or in nitrogen atmosphere. FTIR spectra reveal that Si-N bonds exist in nitrided aerogels as well as in oxynitride glasses.

## NANOMETER-RANGE MEDIA FOR POWDER LASERS

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To obtain a cathode-ray pumped powder laser for high resolution monochromatic displays one should solve the problem of producing low density scattering media for optically pumped lasers with sufficiently low generation threshold and with relatively small volume of excited medium involved in the generation of light.

In this communication we present the methods of synthesis and physical properties of nanosized systems for optically pumped powder lasers. The samples consist of neodymium and/or europium doped nanometer-sized seeds. The silica ceramics heavily doped with Nd<sup>3+</sup> and/or Eu<sup>3+</sup> were obtained by two different sol-gel based methods. Additionally, Eu-doped nanometer-range oxysulfide was synthesized for comparison of their spectroscopic properties with those shown by europium oxysulfides spread within silica glasses and gels obtained by homogenous sedimentation and hydrolyses of TEOS. Comparison of spectroscopic properties is presented and different type of species created in gels and silica glasses will be discussed. A low temperature (4K) absorption spectrum of Nd<sup>3+</sup>-doped silica sol-gel glasses revealed two sites of the dopant ion.

The neodymium doped lanthanum oxide powders were synthesized combusting lanthanum nitrate with urea. Subsequently, these oxides were used as precursors to made Nd/Eu-activated oxisulfide powders. Optical properties of these materials were investigated. The role of photonic crystal band-gap effects on the generation threshold of powdered luminophors will be discussed.

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