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INVITED PAPERS

ABSTRACTS FOR POSTER SESSION

OPTOELECTRONICS GLASS IN EUROPE

Giancarlo C. Righini and Fabio Nicoletti*

Istituto di Ricerca sulle Onde Elettromagnetiche, CNR
Via Panciatichi 64, 50127 Firenze, Italy
* Stazione Sperimentale del Vetro, Murano - Venezia, Italy

1. INTRODUCTION

Some milestones of glass technology are certainly represented by the ancient art of Egyptians (more than 3000 years ago), by the development of the first mass production by Romans (some 1800 years ago), which was almost unsurpassed until the 19th Century, and by the advent of the sophisticated glasses and art objects (façon de Venise) by Venetians (almost 500 years ago). A brilliant period for development of glass optics is also constituted by the 17th Century, with the theoretical and experimental investigations by Keplero, Galileo, Descartes (Cartesius) and Fermat: the birth of lens technology as well as the serious concern about the "optical" properties of glass can be dated at that period.

Since then, glass technology has progressed continuously but slowly, at least until Fifties: the last 30 years, in fact, can be said to have really changed the complexion of glass manufacturing, through a surge of technological advances, starting from float glass technology to optical fibers production, sol-gel processing, non-oxide glasses, glassceramics, photosensitive and photochromic glasses production. This "revolution" has been largely stimulated by the contemporary growth of laser and optoelectronics technologies, as well as of biological and environmental researches.

In this paper an attempt is made of reviewing the state of the art of the research on glasses for optoelectronics in Europe: the task is not easy, mainly because the present scenario sees a

relatively large number of small research centers and groups operating independently from each other. For the purpose of this paper it means that it is likely to neglect the contributions of some group; more generally, it means that it is really difficult for Europe to compete with USA or Japan, where larger Companies and/or more efficient cooperation schemes are present.

The European scene in the area of glass research and manufacturing has long been dominated by few industrial Companies: Schott and Jenaer Glass in Germany (Federal Republic of Germany and German Democratic Republic, respectively), Pilkington in Great Britain, Saint Gobain in France. The advent of fiber-optic technology and of photonics has affected only marginally some of these Companies, which have their largest interests in the flat-glass market (see Table 1).

TABLE 1

Flat glass: production capability of major Companies in Europe in 1988.

Saint Gobain (France)	36.5 %
Pilkington-Flachglas (UK-FRG)	26.7 %
P.P.G.-Vernante Pennitalia (Italy)	11.9 %
Asahi-Glaverbel (Belgium)	11.1 %
Societa' Italiana Vetro (Italia)	7.4 %
Guardian (UK)	5.3 %
Others	1.2 %

Note: During 1988 the European market has absorbed more than 1 billion square meters of flat glass; increase of sales in 1989 is estimated around 2%. (Source: *Il Sole-24 Ore*, 28/12/1988)

The area of optoelectronic glasses and, more generally, of new glasses has instead attracted the interest of several research groups in Universities and Research Centers, as well as of Companies already active in electronics and subsequently in optoelectronics: these institutions, often deeply interested in

the application areas of telecommunications, signal processing, optoelectronic integration etc., have been reacting faster and facing the new material challenge with more concern than "classic" glass companies.

A list, surely not exhaustive, of researches on optoelectronic glasses being carried out in European institutions (including some Eastern Countries, but not USSR, where a large activity is obviously present) is reported in Table 2: it turns out that only Schott Glaswerke, among large European glass manufacturers (provided that in this case the "European" label has still some real meaning, due to the international distributions of the share capitals), is significantly involved in this area.

TABLE 2

Research activities on optoelectronic glasses in Europe

Institution	Main research subject
* Central Inst. of Inorganic Chemistry, Acad. of Sciences, Berlin (GDR)	*Glassy dopant deposits on semiconductors*
* Central Inst. of Physics, Hung. Acad. of Sciences, Budapest (H)	*Glass lasers*
* Ecole Polytechnique, Palaiseau (F)	*Nonlinear optics in doped glasses*
* Fraunhofer Inst. for silicate research, Wurzburg (FRG)	*Coatings, ORMOCER films, phototropic glasses, porous and doped glass, structurization of films*
* Institut National du Verre Charleroi (B)	*Technical and scientific support to glass industries*
* Research Inst. on Electromagnetic Waves (IROE), Firenze (I)	*Integrated optical components in glass*
* Stazione Sperimentale del Vetro, Murano Venezia (I)	*Technical and scientific support to glass Industries*
* Technical Research Center of Finland, Espoo (SF)	*Integrated optical components in glass*
* TNO Inst. of Applied Physics (TPD), Delft (NL)	*Technical and scientific support to Industries; IR and active fibers; fluoride glasses*

- University of Clausthal (FRG)	*Ion exchange in glass*
- " " Dortmund (FRG)	*Integrated optics in glass*
- " " Jena (GDR)	*Glasses for integrated optics; nonlinear optics in glasses*
- " " Krakow (Poland)	*Phosphate-glasses fibers*
- " " Lisboa (Portugal)	*Halide-glasses fibers*
- " " Montpellier (F)	*Porous glasses; optical fibers*
- " " Padova (I)	*Sol-gel glasses*
- " " Parma (I)	*Doped glasses*
- " " Rennes (F)	*IR glasses and fibers*
- " " Santiago de Compostela (E)	*Design and analysis of GRIN components*
- " " Sheffield (UK)	*IR glasses; nonlinear glasses, laser glasses*
- " " Utrecht (NL)	*Luminescence in glasses*

* British Telecom Research Laboratories (BRTL), Ipswich (UK)	*Optical fibers; fiber lasers*
* Corning Europe, Avon (F)	*Glasses and processes for ion-exchanged I.O. components*
* CSELT, Torino (I)	*Ion exchange for I.O.*
* CSEM, Neuchatel (CH)	*Integrated optics; glass etching*
* Essilor, (F)	*Optical fibers*
* GEC Hirst Research Center, Wembley (UK)	*High-silica I.O. waveguides*
* Hungarian Optical Works, Budapest (H)	*Glass lasers*
* I.O.T., Waghausel (FRG)	*Special glasses for integrated optics; device fabrication*
* Laboratoires de Marcoussis (CGE), Marcoussis (F)	*Integrated optics in glass*
* Nokia Research Center, Espoo (SF)	*Integrated optics in glass*
* Schott Glaswerke, Mainz (FRG)	*Optical fibers; laser glasses, integrated optics* (see also I.O.T.)
* Siemens Research Laboratory, Munich (FRG)	*Integrated optics in glass*
* York, Southampton (U.K.)	*Special optical fibers; active fibers*

Note: Only those Institutions have been included which have developed a new glass or a dedicated glass process, or are pursuing the goal of a better understanding of these matters. This means, for instance, that, when referring to integrated optics in glass, we have omitted to mention laboratories and industries which are utilizing commercial components to design and/or to produce I.O. devices. Moreover, as this list comes out from the scanning of scientific literature, it is very likely that research projects carried out in industrial laboratories, which have not been subject of publication, do not appear here.

In order to give a better view of the state of the art, some of the researches mentioned in Table 2 will be described in slightly larger detail in the following paragraphs.

2. GLASSES FOR OPTOELECTRONICS

As already mentioned, one of the possible classification areas of new glasses or new applications of already existing glasses is that of glasses for optoelectronics ([1,2]). Due to the promising perspectives of further development of optoelectronic as well as of photonic technologies, the role which new glasses can play appears to be very interesting and should deserve more care from glass industries.

In reporting on the activities in this area, we have assumed that equal interest should be devoted to new materials, new or advanced processes, and new applications. A tentative list of materials and/or applications in this field is shown in Table 3.

2.1. Optical fibers: materials and technology

Technology of glass optical fibers with low losses in the visible to near-infrared portion of the spectrum is already mature. Limited novelties come from the use of plasma technologies for fiber preform fabrication, which have become of great interest in the last few years ([3]). Some additional work in this area is still being done for specific purposes; one example may be represented by the use of phosphate glasses having almost uniform transmission (of the order of 80-85%) in the range

TABLE 3

Materials and/or applications of optoelectronic glasses

* Highly flat and defect-free substrates for optical memories displays, and photomasks.
* Coatings or dopant deposits for semiconductors, optoelectronic devices, and displays.
* Optical fibers for UV-transmission
* Optical fibers for telecommunications, with very low loss at NIR (near infrared) wavelengths
* Optical fibers for IR energy transmission
* Glasses for low-loss integrated optical circuits
* Glasses suitable for photosensitive microstructurization
* Gradient-index components
* Laser glasses
* Faraday rotation glasses
* Acoustooptic glasses, e.g. for delay lines
* Glasses with high nonlinear optical constants

270 to 4200 nm, which are thus convenient for the production of fiberscopes ([4]). Another example is offered by the development of a process which allows to reduce the cost of production of optical fibers by shortening the time required for cladding manufacture: a direct evaporation method is used, which allows to increase significantly the $SiCl_4$ gas flow in different preform-production processes (MCVD, OVD, VAD,.....) ([5]).

Greater attention, however, is being devoted to the development of glasses exhibiting high transmittance in the infrared region of the spectrum. According to a recent survey of Business Communications Company (BCC), IR materials are ranked first among advanced optical materials (AOM), followed by uv-transmitting materials, and cover almost 50% of the totale USA market of AOM. If IR glasses are gaining a wider portion of this market, a relevant position is occupied by IR fibers, both for energy transmission (military, medical, material-processing applications) and for sensors.

In Europe several laboratories are working on this subject: Centro de Fisica Molecular of Lisbon University; Laboratoire de Chimie Minérale, University of Rennes-Beaulieu; Division of Ceramics, Glasses and Polymers - School of Materials, University of Sheffield; Glass Technology Department, TNO Inst. of Applied Physics, Delft. The glasses considered include: heavy metal fluoride glasses based on ZrF_4 or Zn-Cd; bromo-iodide glasses; zinc halide glasses; tellurium halide glasses ([6,7,8]).

2.2 Integrated optical components

Ion-exchange in glass is a promising technique for the low-cost production of optical waveguides and passive I.O. devices which may well find employment in telecommunication, signal processing and sensors applications.

Many research groups, both industrial and academic, are involved in this area, aiming to different targets, which range from the development of special glasses for I.O.applications, to the development of optimized manufacturing processes, and to the fabrication and characterization of waveguides and components. ([9-16])

Researches are also carried out for gaining a better knowledge of the ion-diffusion process, either thermal or assisted by an external electric field ([17,18]). An alternative way of obtaining reproducible fabrication of optical waveguides has been suggested, which uses the exchanged electrical charge as the controlling process parameters ([19]).

This application area has also seen one of the very few national coordinate projects on glass materials in Europe. In fact in 1985 in Germany seven industrial partners and two Research Institutes joined a common Project entitled *Integrated Optics based on glass for sensors, sensor systems and sensor signal transmission*. The total budget of the 5-years Project was about 28 million DM, including 15 million DM provided by the German Ministery for Research and Technology (BMFT). ([20])

In Italy, to mention another initiative, a 5-year Joint Project on *Special Materials for Advanced Technologies* has been just started by the National Research Council (C.N.R.), but glasses for optoelectronics represent a very small activity in the

program. Larger space, and funding, is provided for instance to glasses and composites as structural materials.

2.3 Luminescent and laser glasses

Since many years rare-earth doped glasses have been studied and their luminescence investigated. Recently it has been shown that efficient luminescence is possible even in glasses doped with ions that luminesce under broadband excitation ([21]). Bulk laser devices ([22]) have been made using these glasses; more recently, rare-earth doped fibers have been produced, and fiber lasers demonstrated as well ([23]).

Fiber lasers could represent a possible approach to solve the problem of the thermal load of the active material, which is the limiting factor of the emitted power of solid-state laser systems ([24]). Otherwise suitable geometries of both the active material and of the resonator should be designed; for instance, the use of a cylindrical resonator is efficient in compensating thermal lensing in a Nd-phosphate glass slab laser ([25]).

Another interesting subject is represented by the development of rare-earth-doped integrated optical waveguides ([26]), but so far no results have been published by European research groups, at least at our knowledge.

2.4 Sol-gel glasses and coatings

The sol-gel process is attracting more and more interest because of the very good control of composition, of low processing temperatures, and of the possibilities of processing in the liquid fase as well as of modifying inorganic materials with organic ones.

The full potential of sol-gel glasses in the field of optoelectronics, however, is still to be exploited ([27]). Among aplications already considered, one can mention different kinds of coatings ([28-30]), deposits of zinc-containing silica sols on III-V semiconductor surfaces for the successive doping ([31]), organically modified ceramics (ORMOCER) ([32]), porous glasses ([33])

and SiO_2- TiO_2 waveguides which have been used for fabrication of integrated optic sensors ([34]).

3. CONCLUSIONS

A brief overview of the main research activities in Europe in the field of glasses for optoelectronics has been presented. Among the researches not listed in this paper, but being anyway currently pursued in various laboratories, it is perhaps worthwhile to mention the development and the analysis of metal or semiconductor-doped glasses with high nonlinear optical coefficients ([35-39]), which could represent a viable approach to the realization of photonic components.

In summary, what appears from the previous review is an active scenario where Companies and Research Institutions are pursuing interesting research targets, but where very few cooperations and/or coordinated projects have been established.

This situation, however, may well change, after a meeting held in Murano-Venezia at the end of 1988. The researchers from Universities and Research Institutions who attended that informal European workshop on new-glass research expressed the belief that "the knowledge, the cooperation and the coordination of scientists and technologists are the primary needs for the R&D in the field of new glass applications, the final goal of which is to make European manufacturing industries more competitive in world markets". As a practical consequence, the *European Forum on New Glass Applications* was established, with the aims of coordinating research in Europe, strenghten interdisciplinary cooperation, and improve connections among Research Centers and Industries.

It is our hope that in few years it will be possible to report on the successful actions of this Forum and to underline its active role in the promotion of, among others, the area of optoelectronic glasses in Europe.

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APPLICATION OF NEW GLASS IN JAPAN

Noboru Ichinose

Waseda University, School of Science and Engineering,

3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Abstract

It is known in Japan that new glasses are high technology glasses and consists of the materials such as glasses, amorphous substances, crystallized glasses, and related composite materials. The report of the Association of New Glass Industries in Japan carried out by the corporation of government reveales that the domestic market size of new glass is about 400 billion yen in 1989. The major part is for opto-electronic application. Here, application field of new glasses in Japan was reviewed.

1. Introduction

New glasses in Japan were defined as follows; (1) glasses, (2) amorphous substances, (3) crystalline substances made from glasses and amorphous substances, (4) composite materials based on glass, amorphous substances or crystal obtained from them.

In this case, typical elemental semiconductors (Si and Ge), metal carbons and high polymers are excluded[1)].

Above mentioned, new glasses are completely different from conventional glasses such as container and plate glass, and have been developed in these twenty years. For example, fiber glasses for optical communication, laser glass for nuclear fusion and

bioactive glass-ceramics as artificial bone have an active function in contrast with conventional glasses with passive roles, that is, roles as container; building material or simple path way of light.

The definition of new glasses comes from the basic concept that they are quite a new material and not the extension of glass. They are understood as functional, amorphous material and crystalline material made from them or composite material containing them. Furthermore, many kinds of materials are incorporated into new glasses from the standpoint of new glass industry.

It is understood from above mentioned definition that function is important in new glasses. The following functions are included; (1) optical function, (2) electronic function, (3) thermal function, (4) chemical and biochemical function and (5) biomedical function.

These new glasses are materials required for promoting advanced technologies, such as information and communication technology, electronics, energy technology and biotechnology. The improvement of the their performance will be necessary for contribution to the marked progress of the advanced technology.

2. Application field of new glasses

New glasses are classified by areas of function as shown in Table 1. Many kinds of application field are also shown in this table. New glasses with optical function are mainly consisting of glasses for optical fibers, optical waveguides and micro op-

tics. Photochromic and electrochromic glasses are also included in this category. Among new glasses with electronic function, there are photoconducting chalcogenide glasses, super ionic-conducting glasses and delay line glasses. Glasses for packaging, high purity quartz glasses and low expansion glasses are typical ones with thermal function.

Porous glasses are available for gas molecule separation and supporting enzyme. They are new glasses with chemical and biochemical functions.

Finally, new glasses with biomedical function are bioactive glass-ceramics as artificial bone and glass-ceramics for artificial tooth.

3. Market size of new glasses

The report of the Association of New Glass Industries (abbrivated by New Glass Forum) in 1988[2)] reveals that the annual sale amount of new glasses is as follows; 1983 - 181 billion yen, 1986 - 254 billion yen and 1989(expected) - 397 billion yen. Table 2 shows the details of them. It is found in this table that the major part is coming from optically functional glasses. Its percentage is 61.7%. Second one is 25.2% of thermally functional glasses. The percentage of new glasses with electronic function is only 12.1%. It is very small for new glasses with chemical and biomedical function.

4. Technological development trend in new glasses

In the report of New Glass Forum in 1989[3], we investigated the stage of technological development compared with other materials such as ceramics, metals and polymers. The results are shown in Talbe 3. As expected, it is found from table that the advantage of new glasses is in the field of optical function. In the other field, other materials such as ceramics, metals and polymers are superior to new glasses. However, the character of new glasses is attractive for such field.

Concerned with new glasses with optical function, the scientists and engineers in our country have made considerable contributions to fibers for optical communication and to light guide in glass substrate. The former is already playing an important role in communication. The latter will be important for the future development of optical IC.

5. Conclusion

There are many application fields for new glasses. However, the major part of them is only glasses with optical function. Much effort for developing new glasses with other function except optical one may be important from the standpoint of glass industries.

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Table 1 Classification of New Glasses and their Application Fields

Function	Glass	Composition	Application
optical	optical fiber	SiO_2	optical communication micro-optics
	glass laser	phosphate	fusion
	photochromic glass	Na_2O-Al_2O_3-B_2O_3-SiO_2 (Ag, Cl, Br)	display
	amorphous oxide	Te-O	laser disc
	glass for photomask	SiO_2, Silicate	photomask
electronic	super ionic-conducting glass	AgI-Ag_2O-P_2O_5	solid cell
	delay line glass	R_2O-PbO-SiO_2 (R: alkali metal)	TV, video apparatus
thermal	low expansion glass	TiO_2-SiO_2	microscope
	low expansion crystal glass	Li_2O-Al_2O_3-SiO_2 (ZrO_2-TiO_2)	heat exchanger
chemical	porous glass	SiO_2	bioreactor, catalysis
	boro-silicate glass	B_2O_3-SiO_2	solidification of radio wave waste
biomedical	apatite crystalline glass	K_2O-Na_2O-MgO-CaO-P_2O_5-SiO_2	tooth crown bone

Table 2 Annual Sales Amount of New Glasses

unit (billion yen)

New glasses with different function	1983	1986	1989	Stage
1. Optically functional glasses				
Optical fiber				
(A) Optical fiber for communication	45	67	120	G
(B) Image fiber	1	2	5	E
(C) Light guide for illuminating	2	4	7	E
(D) IR fiber	0	0.1	0.5	L
(E) Fiber for optical measurement	0.3	0.5	3	E
Graded index glass	2	6	10	G
Laser glass	0.2	0.3	1	L
Optical memory glass				
(A) Glass for substrate	0.2	1	3	E
(B) Optical memory glass	0	0	2	L
Glass for photomask	40	60	90	G
Glass with selective transmission and reflection of light	6	10	15	G
Photochromic glass	7	4	4	M
Glass for halogen lamp	0.6	1	2	G
High performance casting glass	0	0.5	3	E
Subtotal	104.3	156.4	265.5	
2. Magnetically functional glass				
Optically controlling glass	0.1	0.1	0.2	L
Amorphous alloy	0	0.2	2	E
Subtotal	0.1	0.3	2.2	

3. Electronically functional glass				
Glass for solar cell	0.1	0.5	2	E
Display	6.5	12	24	G
Glass for substrate of circuit	0	0.1	1	L
Electrical conducting glass	2	2	2	E
Glass for delay line	16	16	16	M
Chalcogenide glass	0	0	0.2	L
Subtotal	24.6	30.6	45.2	
4. Thermally functional glass				
Glass for package	20	30	40	G
High purity quartz	20	20	20	M
Low expansion crystalline glass	11	14	19	G
Subtotal	51	64	79	
5. Mechanically functional glass				
Machinable glass	0.2	0.3	1.5	L
Subtotal	0.2	0.3	1.5	
6. Chemically and biomedically functional glass				
Glass fiber with alkali-resisting	1.5	2	2.5	G
Porous ceramics	0	0	0.2	L
Bio-ceramics	0	0	1	L
Subtotal	1.5	2.0	3.7	
Grand total	181.7	253.6	397.1	

L; Latent, E; Expand, G; Growth, M; Mature, D; Decay

Table 3 Competition of New Glass with other materials

New Glass	Stage of Research and Development	Competition G	C	M	P
Optical fiber	F (Silicate), R (Fluoride)	◎	△	—	○
Glass for photomask	F (Silicate)	◎	—	—	—
Graded index glass	D, Many kinds of production	◎	—	—	△
Photochromic glass	F, O	◎	—	—	○
Nonlinear optical glass	R	○	◎	◎	○
Optical sensing glass	O, D (Application)	○	—	—	◎
Laser glass	D	○	◎	◎	△
Glass substrate for optical disc	D	○	—	—	◎
Glass with transparent electrical conducting film	R	◎	—	—	○
Super ionic-conducting glass	R	○	○	—	○
Chalcogenide glass	R, D (Application)	○	○	○	—
Low firing temperature substrate	F, Partially produced	○	◎	—	◎
Dielectric glass	D	○	◎	—	◎
Amorphous ferrite	R	○	◎	—	—
Glass for package	D	○	—	△	◎
Low expansion glass	D	◎	○	△	—
Glass with thermal resisting	D	○	◎	○	—
Ceramic fiber reinforced glass-ceramics	D	○	○	◎	—
High fracture toughness glass-ceramics	D	○	◎	◎	—
Oxynitride glass	R, Partially developed	○	◎	—	◎
Porous glass	D	○	◎	○	◎
Bio-ceramics	D	○	○	○	—
Artificial tooth	D, Partially produced	○	—	◎	—
Others (Superconducting glass)	R	○	◎	◎	○

G; Glass, C; Ceramic, M; Metal, P; Polymer
R; Research, D; Development, O; Old, F; Finish
◎; Main, ○; Special character, △; Special application, —; No relation

NEW GLASS ACTIVITIES IN GIRIO

Toru Komiyama
Government Industrial Research Institute of Osaka
1-8-31 Midorigaoka, Ikeda, Osaka 563 JAPAN

Government Industrial Research Institute of Osaka (GIRIO) is one of 16 research institutes belonging to the Agency of Industrial Science and Technology (AIST), which belongs to the MITI. It is composed of five departments as shown in **Table 1.** The research on glass is conducted in the Glass and Ceramic Material Department. This department has three sections in glass field and two in ceramics. The number of researchers is 33, and there are 19 members in the glass sections. The annual budget for glass research is about one million dollars except for the personnel expenses.

Table 1 Organization of Government Industrial Research Institute of Osaka

- Inorganic Material Department
- Glass and Ceramic Material Department
  - Glass Technology Section (7)
  - Glass Science Section (5)
  - Advanced Glass Section (7)
  - Engineering Ceramics Section (8)
  - Functional Ceramics Section (5)
- Organic Material Department
- Material Chemistry Department
- Material Physics Department

Table 2 Major Subjects with Glass Science and Technology

(1) Infrared Transmission Halide Glasses
(2) Glass Melting in Microgravity Environment
(3) Lithium Ion Conducting Glasses
(4) Applications of Porous Glasses
(5) Characterization of Nuclear Waste Glasses
(6) Properties and Structure of Glasses

Table 2 shows the main research projects on new glass at GIRIO in 1989. New glasses having optical, electrical, and chemical functions are the main objects.

(1) Infrared transmission halide glasses

Halide glass not including fluorides has long cut-off wavelength in infrared region and is transparent at least at 10.6μm of CO_2 laser as shown in **Fig.1**. Applications to light guide for CO_2 laser, non-contact temperature measurement at low temperature, thermal image guide, etc. are expected.

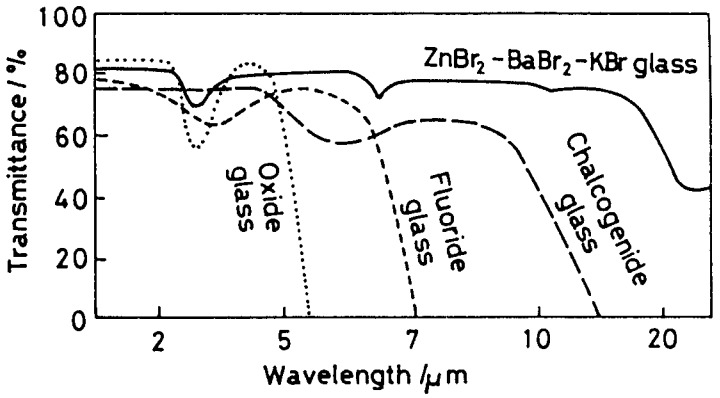

Fig.1 Infrared transmittance of some glasses.

Figure 2 shows the glass forming region in the bromide system having $ZnBr_2$ as the main component. The systems containing $PbBr_2$ and $BaBr_2$ have relatively large glass forming region, which supports that the glass forming region is related to the ionic radius of introduced metal ion[1]. **Figure 3** shows the glass transition temperature in the $ZnBr_2$-$BaBr_2$-KBr glass system. While the glass in the bromide systems has low glass transition temperature, the glass in the

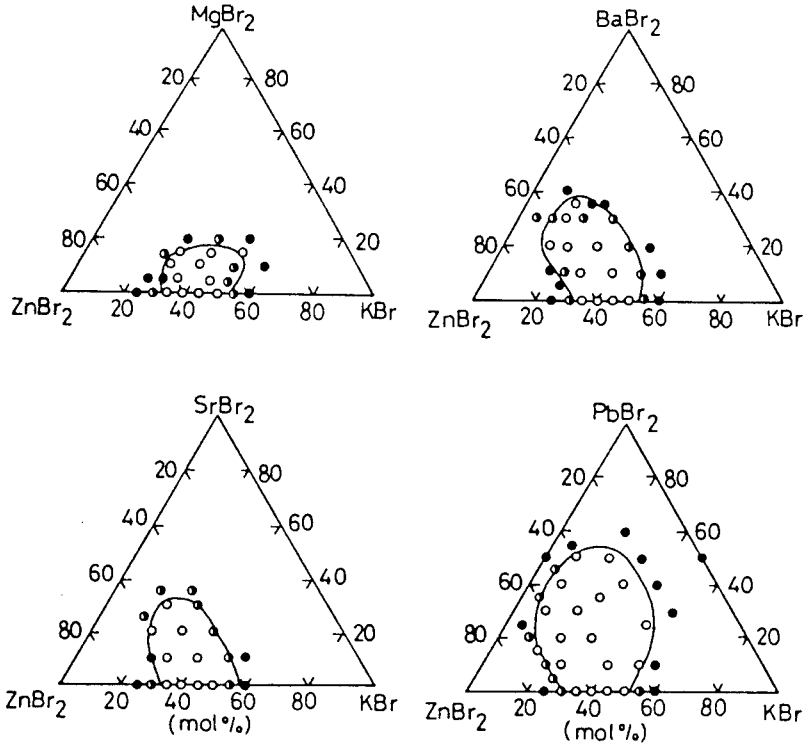

Fig.2 Glass forming regions in $ZnBr_2$-KBr-MBr_2 systems.

$CdCl_2$-$BaCl_2$-KCl system has comparatively high T_g. At present, we are trying to clarify the relation between composition and properties such as thermal stability and chemical durability, to purify the glass composition by eliminating the impurities such as water, and to know the glass structure by Raman spectroscopy[2,3].

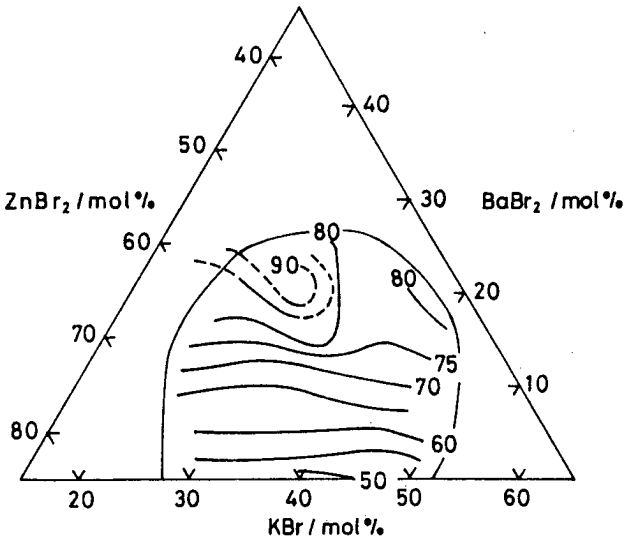

Fig.3 Glass transition temperature of $ZnBr_2$-KBr-$BaBr_2$ system.

(2) Glass preparation under microgravity

Under microgravity condition as in the outer space, containerless melting of glass is possible. Since the containerless melting prevents the contamination from crucible walls and the heterogeneous nucleation at the interface of glass melt and container, it can create the new type of high purity glasses. The GIRIO has a plan to demonstrate the advantage of containerless melting for the CaO-Ga_2O_3-GeO_2 glasses[4] in the US space shuttle in 1991. **Figure 4** shows a schematic diagram of acoustic levitation furnace for containerless melting. The furnace is composed of two halogen lamps of 500W each and ellipsoidal reflector. A loudspeaker is used as a generator of acoustic pressure for the levitation of a sample. At present, we are making preliminary experiments of containerless melting using microgravity of 10^{-2}G for 20sec created by ballistic flight of aircraft[5]. In this situation, there is an advantage that repetition is easy, although a fluctuation of the gravity is sharp and experiment time is short. An example of melting in microgravity is shown in **Fig.5**, in which the glass melt becomes clean sphere by surface tension and is floating in a space[6]. Through these experiments, we found that the heating efficiency in microgravity is higher

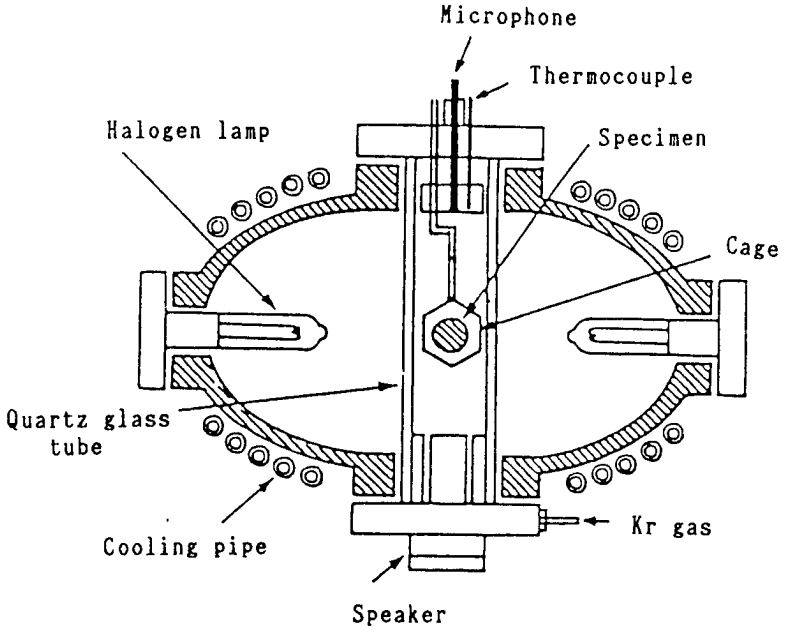

Fig.4 Schematic diagram of the acoustic levitation furnace.

than in common environment because there is no convection and the gas around specimen is kept at high temperature[7]. Now we are investigating the effects of surface tension and interfacial tension on a shape of liquid in microgravity.

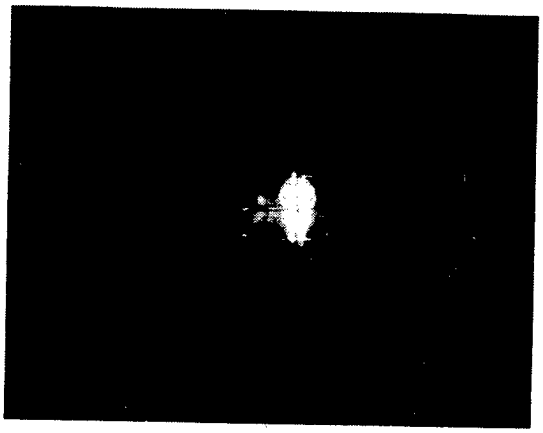

Fig.5 A sample melted in microgravity produced in an aircraft with surrounding cage.

(3) Lithium ion conducting glasses

The Li-ion conducting glass is expected of application to solid state ionic devices such as a solid state secondary battery. **Figure 6** shows the glass forming region, electrical conductivity at room temperature, and its activation energy in the Li_2O-B_2O_3-Li_2SO_4 system[8]. As Li_2SO_4 is introduced in the Li_2O-B_2O_3 system, conductivity of glass increases considerably, and there is a suitable region to obtain high conductivity. Conductivity at room temperature is around 10^{-5}S/cm, while designers of a device demand conductivity of one to two higher order. After

this, we should investigate the mechanism of ionic conduction and enhance a conductivity by enriching Li content using thin film preparation methods such as PVD and CVD.

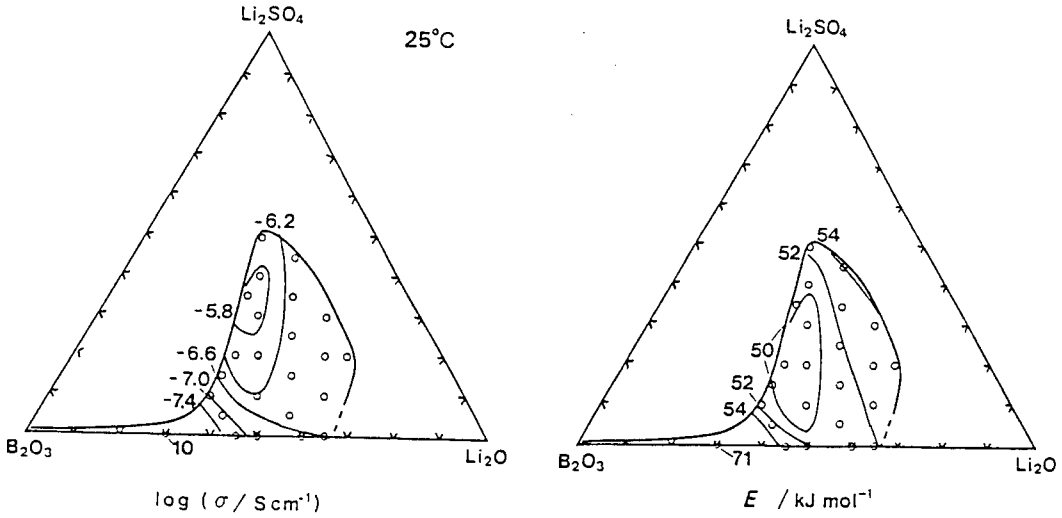

Fig.6 Electrical conductivity and activation energy for conduction of Li_2O-B_2O_3-Li_2SO_4 glasses.

In the meanwhile, we found the good producing method of amorphous iridium oxide film which exhibits pronounced electrochromic characteristic[9]. In this method, Ir-C

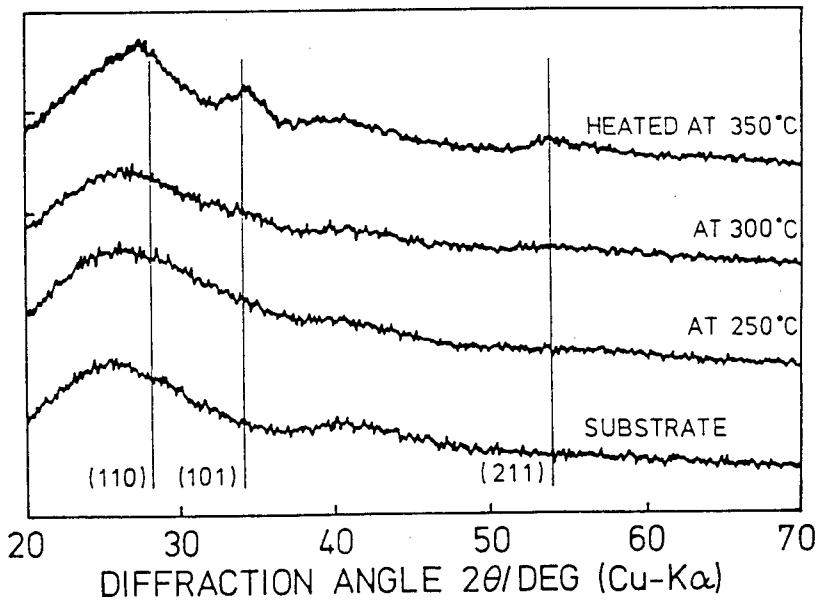

Fig.7 X-ray diffraction patterns of IrO_x films prepared by thermal oxidation of Ir-C composite films.

composite film is prepared by vacuum evaporation, and it is oxidized thermally. We obtain amorphous film at temperatures ranging from 250 to 300°C and crystalline film at 350°C as shown in **Fig.7.** As change in transmittance by applied voltage is small for the crystalline film, amorphous film is better for EC device. This film is confirmed to withstand coloring-bleaching cycle tests of 5×10^5.

(4) Porous glass composite membranes

Pore radius of porous glass can be controlled precisely, the applications of porous glass to separation film of gas-gas or liquid-liquid mixture and reverse osmosis membrane are expected. We now carry out an application research with bases of accumulated knowledge of manufacturing process and characteristics of porous glass.

Porous glass, in general, is highly surface active and then less alkali durable. We introduced ZrO_2 into SiO_2 porous glass and improved its alkali resistance. **Figure 8** shows the weight loss data of porous glasses in NaOH solution. It is easy to know that chemical durability of porous glass in the SiO_2-ZrO_2 system is remarkably improved compared to the SiO_2 system[10].

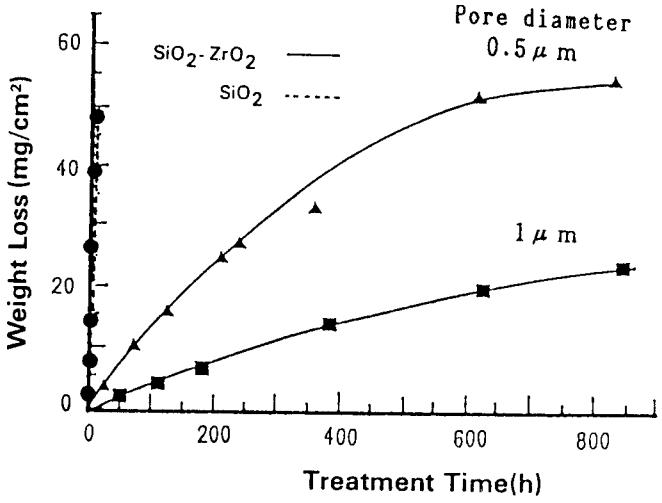

Fig.8 Weight loss of porous glasses in 1N NaOH solution at 30°C.

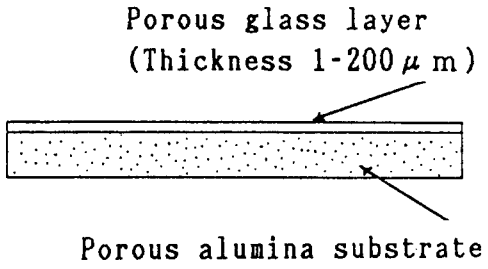

Fig.9 Structure of porous glass composite membrane.

Self-standing glass film needs at least 1mm in thickness from the point of strength, and permeation rate of a medium through porous film decreases with

decreasing pore size. To increase permeability we developed a composite membrane which has thin porous glass film on ceramic substrate having pores of about 1μm (**Fig.9**)[11,12]. To make this kind of membrane, glass thin film is formed on a ceramic film at first, then it is treated to have controlled pores. Another method is a application of the soll-gell process. **Table 3** shows the permeation rate of hydrogen. Permeation velocity increases with decreasing the thickness of porous glass film. Water penetration rate of this composite membrane is about $100l/mm^2 \cdot hr$, and there is a plan of application to the new water treatment system. At present, we are conducting a long-term experiment to evaluate the durability and the clogging process.

Table 3 Permeation rate of H_2

Type of porous glass membrane	Permeation rate ($m^3/m^2 \cdot Pa \cdot s$)
Phase separation method, Single layer	5×10^{-9}
Phase separation method, Composite	68×10^{-9}
Sol-gel method, Composite	230×10^{-9}

(5) Characterization of nuclear waste glasses

The high-level liquid wastes generated at reprocessing of the spent nuclear fuel will be solidified into borosilicate glass. The stainless steel canister containing the glass will be stored until heat-generation by decay diminish, and be disposed of in a geological repository.

We are carrying out safety evaluation of waste glass by investigating the properties such as electrical conductivity, crystallization behavior in transition

temperature range, thermal conductivity, leach rate, and so on. **Figure 10** shows the self-diffusion coefficients of Na and Cs ions in some glasses[13]. Mobility of Na ion in glass is rather large, and it seems to affect on the leachability of the other components. On the other hand, mobility of Cs ion which is dangerous nuclide is very small. Therefore Cs ion leaching is supposed to depend not so much on selective diffusion of Cs ions as on dissolution of glass network. **Figure 11**[14] shows the depth profile of each element in hydrated surface layer formed by Soxhlet type leaching treatment. In surface layer formed by water treatment, concentrations of alkali, alkaline earth, Si, and Al decrease, while rare earth, Zr, and Fe are enriched. The degree of enrichment of each element existing within 100Å from surface is plotted against solubility product of its hydroxide in **Fig.12.** This result expresses that there is a relationship between leach rate and thermodynamic stability. After this we will estimate the long-term stability of nuclear waste glass by natural analogue study.

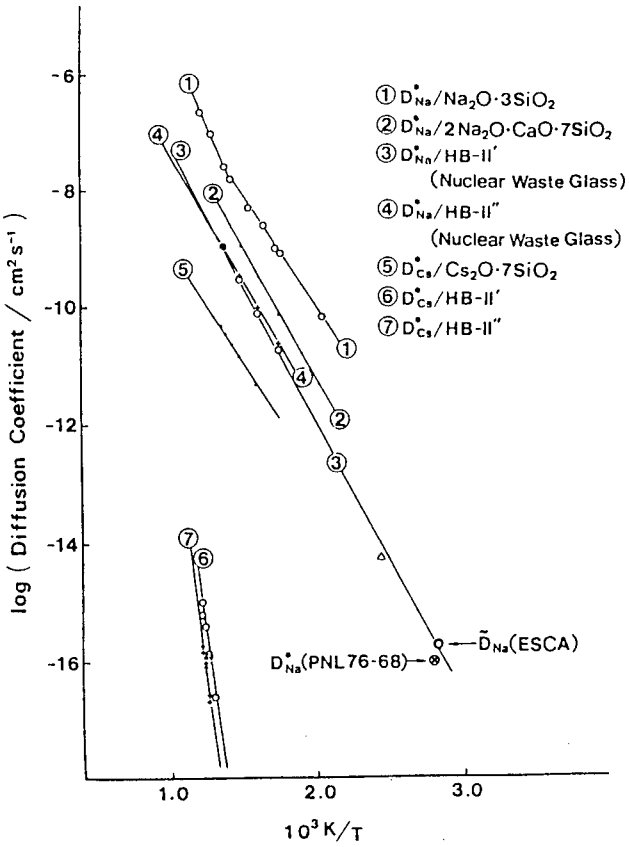

Fig.10 Arrhenius plot of self-diffusion coefficients of sodium and cesium ions in nuclear waste glasses and other glasses.

In addition to the research projects mentioned above, we started researches on non-linear optical glass, precise measurement of refractive indices of various glasses in 10^{-6} order and its temperature dependence, improvement of glass

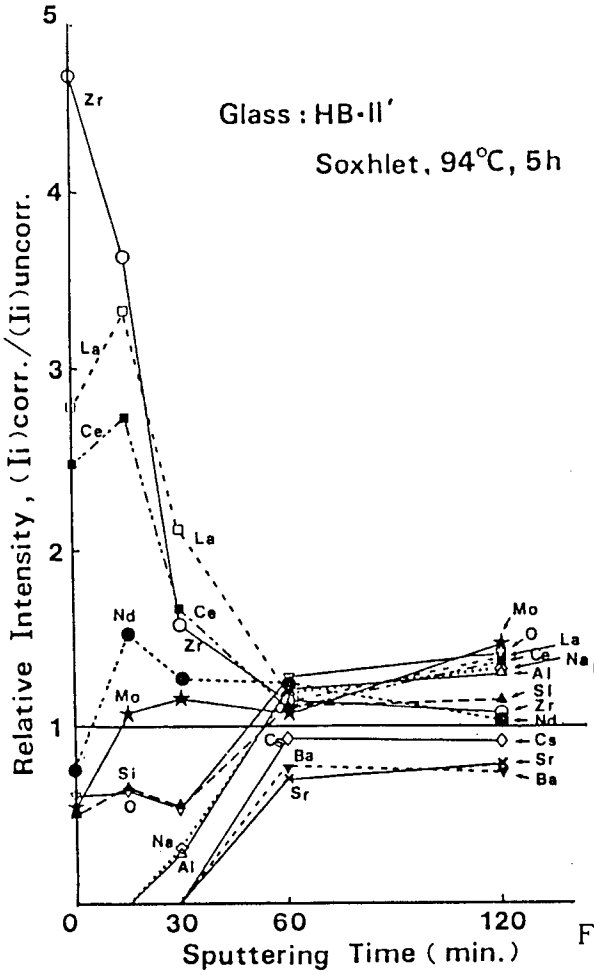

Fig.11 Depth-profile of various elements in glass surface layer determined by ESCA.

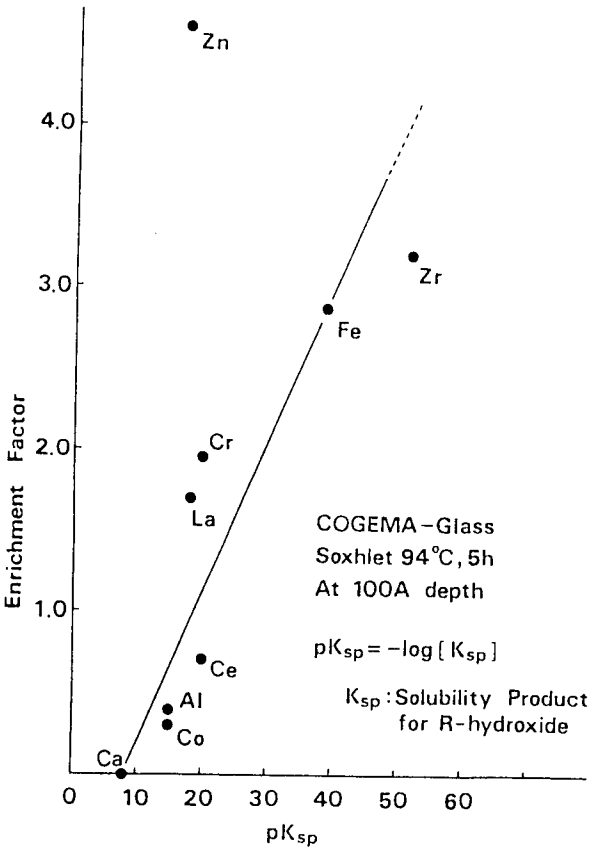

Fig.12 Relationship between enrichment ratio and solubility product of hydroxides.

quality by ion implantation, and so on.

In such a way, having tasks such as investigation of glass structure, development of new processing technique, and establishment of evaluation technique, the GIRIO is supposed to promote basic researches on glass as a national institute as ever.

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Future Outlook for the New Glass Industry

Junichi Inoue
Nomura Research Institute
Technology Management Strategy Dept.
4-7-1 Kajiwara, Kmakura 247, Japan

1.Introduction

The potential of "new glass" featuring high-level functions is rated highly in the aspects of both long-term market growth and the expansibility of the technology. This evaluation is widely supported, and is behind the energetic programs of new glass development. Nevertheless, the prospects are not completely optimistic; as is well known, various limitations and problems can be cited as factors restricting future growth. The small size of the materials market per se and the intense competition with other types of technology are examples as such.

The situation is hardly peculiar to new glass, but is in many respects shared with other so-called "high-tech" fields. Technology development and cultivation of the market must be grown in the needs of prospective customers. Nevertheless, the companies leading such "high-tech" fields are usually gigantic. While the great expenditure of human and financial resources required in such fields certainly calls for the back-up of a large organization, it is also true that gigantism usually impedes close contact with customers. This conflict is the source of numerous problem

saddling development of advanced technology.

This situation forms the background for this report, which presents the macrotrend outlook and considers the environment of and issues facing the new glass industry.

2. The macroenvironment of the new glass industry

The Japanese economy is expected to exhibit a basically favorable trend for the remaining decade of the century. The real GNP is forecast to grow at a rate on the order of 4 percent, and the forecast for other major economic indicators is favorable on the average(as shown below). In addition, the building construction demand, which is of prime concern to the existing glass industry, is expected to expand sharply, and a firm growth is anticipated for the automobile as well.

Fig.1 Major Indicators Related To Glass Industry

(Macroeconomy)	(1990)	(1995)	(2000)	95/90	2000/95
G N P	362.2	440.2	530.7	4.0%	3.8%
Personal Consumption	201.0	250.5	309.2	4.5	4.3
Residential Investment	20.3	24.1	28.2	3.5	3.2
Private Capital Investment	86.6	112.8	145.1	5.4	5.2
Trade Balance ($bil.)	95.6	49.3	10.7	-12.4	-26.3
Exchange Rate (¥/$)	120.6	99.4	90.8		

Note) Real term base. Unit: ¥ tril.
Source) NRI

(Data for Reference)		
Office Demand* (Tokyo, 10^4 m^2)	4000(1985)	6000～6500(2000)
Automotive*(Domestic Production, ¥bil.)	3273(1987)	3716(1992)
Office Automation Equipments**(¥bil.)	387(1987)	873(1998)
Optoelectronics Industry***(¥ tri)	1(1986)	10(1995)
Expenditure for Information & Communication**** (¥ bil.)	9,657(1985)	35,822(2000)

Source) *:NRI
**:JBMA
***:OITDA
****:Ministry of Postal Services

At the same time, qualitative changes are expected to

unfold in numerous respects. For example, the industrial structure is steadily changing, prompting great increases in offshore production in most segments of the manufacturing sector. This is also happening among automakers, which may have given negative influence upon most of Japanese glass makers. It can be added, however, that passenger car assortments are shifting to the larger, more luxurious segments in the transition to economic growth as personal spending picks up. This is acting to stimulate needs for and allow spread of such glass with high values as thermic ray reflective glass and head-up display. Similarly, the spread of the information explosion into the automobile is causing automakers to consider installation of all kinds of information devices and communication media.

There are also such key words presenting features of 1990s as information intensification, aging society, diversifying values, further progress of advanced technology, etc. All of which are likely to exert an impact on business environment. A future agenda item is in-depth examinations of the relationship between these trends and the glass industry, which have generally remained to be analyzed to date.

3. Future prospects for the new glass industry

Obviously, it is no easy task to assess the impact exerted on glass by the aforementioned trends. As such, it is also difficult to assess the future prospects for new glass, especially over the long term. The question of the future

evolution of materials technology in particular harbors numerous elements of uncertainty. This uncertainty stems from factors such as the following:

1) the scheduling uncertainties inherent in materials technology development itself
2) the existence of competing technologies
3) ambiguity about the nature of needs in the market.

And this uncertainty clouding the technology outlook inevitably makes it difficult to conduct accurate forecasts for individual market segments.

Be that as it may, there have thus far been numerous studies of the future prospects of new glass. In Japan, the New Glass Forum has released fairly detailed date concerning the Japanese market for new glass, which provide certain guidelines for those involved with new glass. According to these data, the market will grow at a rate exceeding 15 percent over the next ten years, and reach the scale of 2 trillion yen in terms of potential in the year 2000. The Forum also prepared a breakdown of the future new glass market by type of function. The majority is occupied by optical functions at 65 percent. These are followed by electrical and electronic functions at 12 percent, thermal functions at 9 percent, and mechanical functions at 8 percent, with the remainder occupied by bioadaptive and magnetic functions. This kind of study is vital for shedding light in the macroenvironment of new glass.

4. Issues in the new glass industry

Of course, there is no guarantee that this entire potential market will be captured by new glass. Instead, the data should be interpreted as showing the captured by new functional materials. Based upon this understanding in mind, some issues are shown below by adding certain recommendations for the continuous development of new glass technology and market.

1) Another aspect in technology development

There has already been much examination and discussion of the competition with plastics and fine ceramics in the context of materials development. And there is no denying that the competition with other materials must continue to be carefully monitored. But the point is that such competitive analyses must be joined by analyses of the complementary relationship among materials. In other words, there have not yet been sufficient studies of the domains in which the merits of various types of materials could be effectively utilized.

Possibilities, in concrete, are expected in the combination of the transparency and insulating characteristics of glass with the conductivity of metal or with the light weight and plasticity of plastics. Although both could be used in bulk form, the circle of prospective application fields could widen further through combinations in which one is the base material and the other takes a different form, e.g., a thin film. Thin film, in this sence, will be one of the core technologies in marking glass and another material

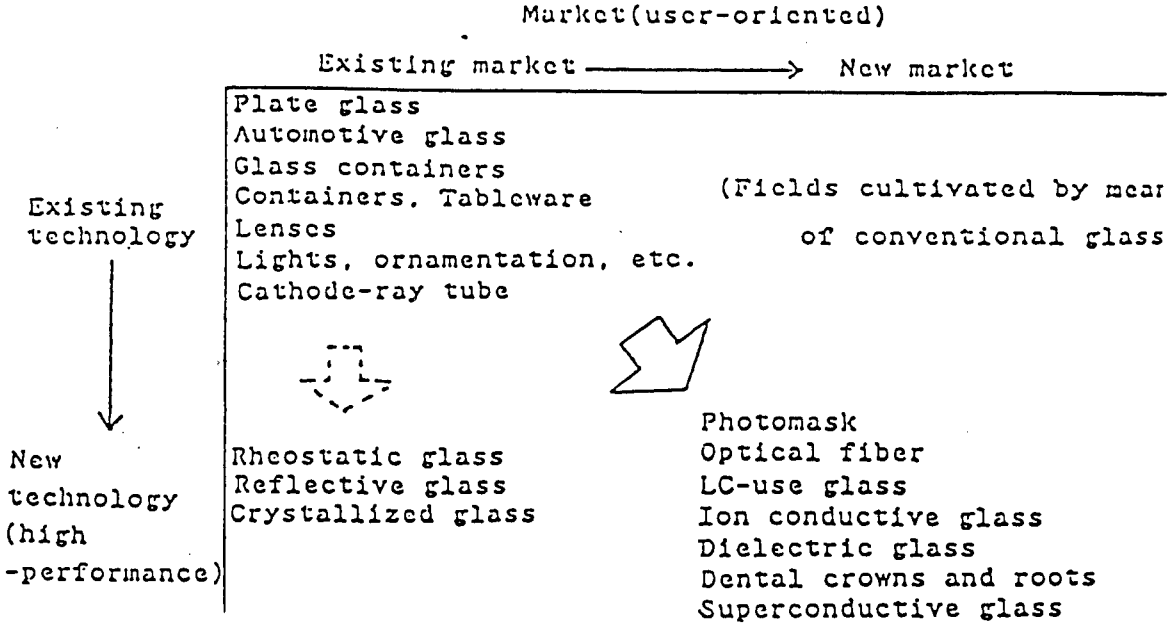
joint each other and will build new functional materials.

Thin film technology is by no means the only "key word" in new glass technology development. Developmental efforts must make more determined approaches to exploit the relationship between glass and the human visual sense, for example. Likewise, such a stance to positively examine the possibilities to adopt other hot technologies is increasing required for another step to make glass technology grow. This kind of approach, in fact, coincides well with long-term macrotrends.

2) Margin for growth in market cultivation

A second issue concerns market cultivation especially over the short and medium terms. As shown below, most varieties of new glass are set apart form the conventional plate glass by not only the newness of the technology, but also the newness of the fields constituting their market. And the cultivation of such fields will require considerable time and funds in most cases.

Glass Materials Technology and Market.



As is well known, the expansion of the scale of the semiconductor production and the market has been driven by the following factors; 1) the expansion of the range of application fields, 2) the expansion of the production and market in the application fields themselves, and 3) a rise in the level of use (input coefficient) in application fields. The expanded scale, in turn, has made it possible to absorb the unit price declines. However, the possibilities of new glass are not analyzed yet from this viewpoint.

Let us consider the possibilities in connection with thermal (infrared) reflective glass. As far as factor 1 is concerned, it has already been applied to the homes, and automobiles. And further growth is likely to be supported by factor 2, i.e., a continued increase in the building demand. But a fullfledged growth would call for the operation of factor 3, i.e, an increase in the level of use will be a key factor. Fortunately, in this case, social environment seems to back up its penetration with emphasis of demand for comfort and luxury in homes, buildings, and automobiles. Other new glasses, in the same way, need to be analyzed.

There also appears, in addition, to be ample margin for marking adding values to glass through the approaches adopting new technology as described in sector 1). This may suggest its possibilities in the area of the market of conventional glass with new technology. Among them, electrolyzed or intelligent glass market has the possibility in connec-

tion with technology trend of information and systematization. It may be interpreted as glass will get closer to electronic device. In such case, the key seems not only materials technology but also process technology including thin film formation and device manufacture.

3) Reassessment of small-scale markets

A third issue concerns evaluation of new glass as a business. Thus far, most companies in the glass industry have developed their business in a highly "monocultural" fashion; even the marketing channels stress automakers and construction related companies. In case of Japan's leading glass manufacturers, which have steadily pursued a greater economy of scale, the new "cultural landscape" in industry calls for "consciousness raising."

On the whole, the needs in advanced technological are becoming more fractionized. This means that the expected each market size cultivated through every possible effort could not be attractive enough for those who have been in the conventional glass industry. This consideration suggests the need for a new stance in assessment of the related market and criteria for the investment.

In this connection, standards for promisingness of the markets need to be devised, apart from its scale. For example, certain market segments, even if its scale is not large enough should be regarded as promising if they are highly specialized or would enable the manufacture to erect formidable barriers to entry by competitors while forging

relationships with customers in them. This kind of approach would also enhance the effectiveness of the effort to cultivate new markets.

5. Summary

There has already been widespread discussion of technology- and market- related issues within the glass industry itself. What is needed for the coming years is perspectives on new glass from the standpoint of glass technology, but from that of interactions with other technologies and other markets. Such a perspective could uncover new possibilities.

International Glass Fact Database -- INTERGLAD

Itaru YASUI

Institute of Industrial Science,
University of Tokyo,
7-22-1, Roppongi, Minato-ku, Tokyo, JAPAN

1. Introduction

Glass has completely different characteristics from crystalline materials with regard to the relation between compositions and properties. First the composition of a certain glass can be changed continuously. The composition of crystalline ceramics, on the other hand, is usually fixed within a limited range. Secondly, the properties of glass are expressed by a linear function of its composition, and are not so much affected by the production process. These two points described above are major reasons why the material design of glass is much easier than that of crystalline ceramics. In the literature, many trials have been made to obtain parameters for each oxide compounds to calculate properties of glasses with known compositions; methods to calculate densities of glasses, thermal expansion coefficients, refractive indices, hardness, Young's modulus are well established. A most recent and extensive trial to make an expert system was made by Makishima et al.[1], in which all such methods were integrated into one computer system. The applicability of the system, however, is limited to the compositions with more than 50% SiO_2, because of the validity of parameters used in the system.

The calculating ability of personal computers have reached the level of a main frame computer of 10 years ago, and the capacity of data to be handled also increased remarkably. Large scale databases can be now constructed on a personal computer system.

The database committee in NGF started to evaluate a possibility to construct "Glass fact database for compositions and properties about 3 years ago. This project was approved by the trustee board of NGF, and now the fact data are being collected by the researchers in the member companies of NGF. INTERGLAD is the name of this database, and it is expected INTERGLAD will be released by the spring of 1991.

In this report, the outline of INTERGLAD is explained.

2. Outline

2.1 Data Source

Glass property-composition data are being collected from five kinds of data sources.

(1) Journals, such as J.Am.Ceram.Soc., J.Ceram.Soc. Jpn., etc.

(2) Preprints for meetings, such as the annual meeting of Ceram.Soc.Jpn., ICG etc.

(3) Data Books published in English, in Japanese.

(4) Catalogs from companies world wide.

(5) Patents USA, Europe and Japan.

Total number of glass compositions to be stored in INTERGLAD of final version will be in the range of 90,000.

Language used to describe the database is English (not Japanese).

2.2 Kinds of Data Fields in INTERGLAD

Data fields are divided into 7 kinds.

(1) Kinds of materials = glass, glass-ceramics, modified glass, composite glass.

(2) Glass composition, mol%, atomic%, weight%, main component, glass system.

(3) Properties of glasses.

(4) Characterization data.

(5) Features, Shapes of glasses.

(6) Usages.

(7) Data sources.

(8) Notes.

Explanations:

(1) The kind of materials, such as glass-ceramics or modified glass, is necessary to determine whether the data can be used for a material design system utilizing the linear relation between properties and glasses.

Modified glasses mean that the glass compositions are changed by means of after treatments, such as ion exchange or ion implantation. Composite glass includes a variety of composite materials with at least 50% of glasses in it.

(2) Glass compositions are described in mol%, weight%, atomic% in the system. Users can select which description they want to use. A term to express glass system, such as silicates, alumino-silicates, alkali-borates are also included in the system.

(3) Almost all kinds of properties appeared in the literature are included in the database. A data field is assigned to one property measured under one condition. For example, thermal expansion coefficients measured for different temperature ranges are expressed with different code numbers, but one common field for a thermal expansion coefficient contains the value described in the fields with specific conditions.

(4) The database describes that there is chracterization data such as IR, Raman, UV, X-ray, etc. for the glass with composition queried. Actual data are not included in the database, because the first version of INTERGLAD is designed without graphic capabilities.

2.3 Database System and Hardwares

Total capacity of INTERGLAD is expected to exceed 100-150MB, which is too large to be handled in a hard disk drive for personal computers. CD-ROM is used as a media for distribution of the database, of which maximum capacity is 540MB.

Data format based on ISO-9660 specification is used for the CD-ROM, and MS-DOS with CD-ROM extensions is chosen as an operation system.

The kind of personal computers supported for the query program now under development are;

(a) NEC PC-9801 series with a CD-ROM drive.
(b) Fujitsu FMR series with a CD-ROM drive.
(c) IBM PC-AT or PS/2 series or true compatibles with a CD-ROM drive.

The access speed to the data on a CD-ROM is not fast. We can expect almost same performance of a floppy drive based system. Internal data handling in the query program is also complicated, so a system with high calculating ability is preferred. As a future problem, we are now considering to allow users to transfer all data to a very large hard disk with the capacity of 300MB or more, or LAN systems.

2.4 Software for the query of INTERGLAD

Three kinds of query softwares to be used by the computer systems described above will be supplied with the CD-ROM. The flowchart of the software is shown in Fig.1. This software is designed to do every kind of query works, but not designed to do a job as a material design system. The software has an interface to down load data to be used by other computer softwares such as

dBASE III or Lotus 1-2-3, so users are expected to construct their own special system for glass composition design.

2.5 Version Up

New data will be added in every two years, and a new version of CD-ROM will be distributed. Softwares will be also rewritten to satisfy new demands from users. Operation system may be changed from MS-DOS to MS-WINDOWS or OS/2 in order to add graphical capability to the query softwares.

3. Summary

Glass database describing the relations between properties and compositions will become a very powerful tool for the designing new glass compositions. INTERGLAD by NGF will be the first and the most comprehensive fact database for glasses. We all the members relating to this project are expecting the day of its release.

4. References

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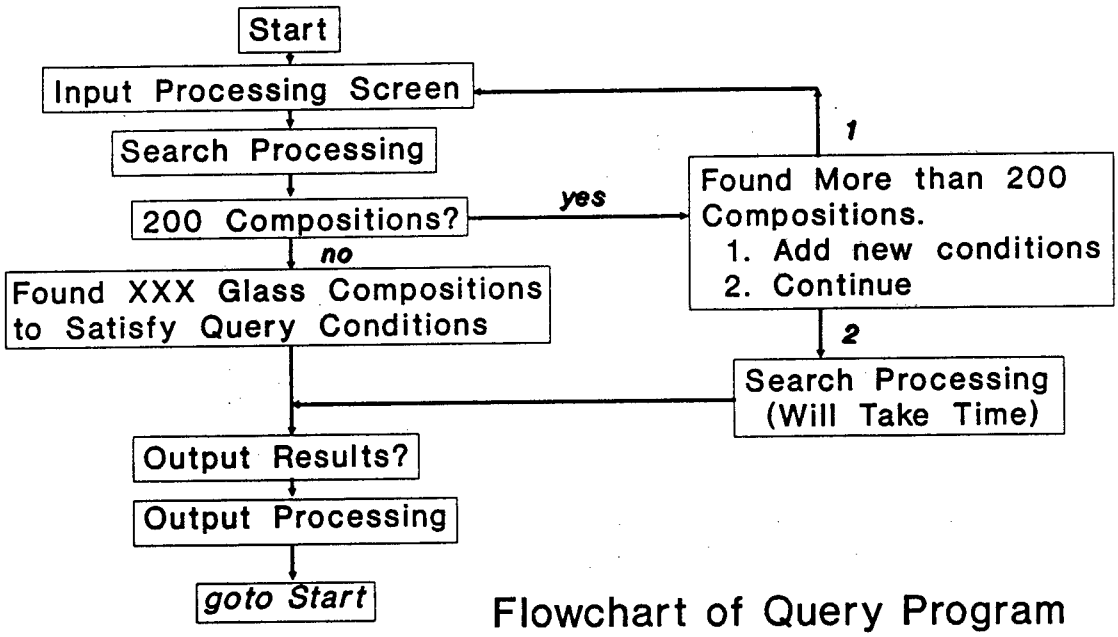
Fig.1 The flowchart of the query program for INTERGLAD



Reliable mechanical splice using precision glass capillary for future single-mode fiber systems

Junji Fujikawa
Nippon Electric Glass Co.,Ltd.
906, Ima, Notogawa, Kanzaki, Shiga. Japan.

In order to deploy high speed single-mode fiber systems for future subscriber loop and LAN applications, it is desirable to implement high performance mechanical splices using simple fiber endface preparation techniques.

This paper describes new splices which use precision capillaries of borosilicate glass as the key elements. The optical and mechanical performance of the splices is also enhanced by using index matched materials; i.e. gel compound and UV curable adhesive.

The concept of this splicing technique is to align cleaved fibers in the capillary hole within a 0.5 microns tolerance, to butt the fibers with gel compound, and then to secure these fibers at the very position of the alignment by UV curable adhesive. The refractive index of both gel compound and adhesive is 1.46 at 1300 nm of wavelength. Figure 1 shows the key elements of the splice.

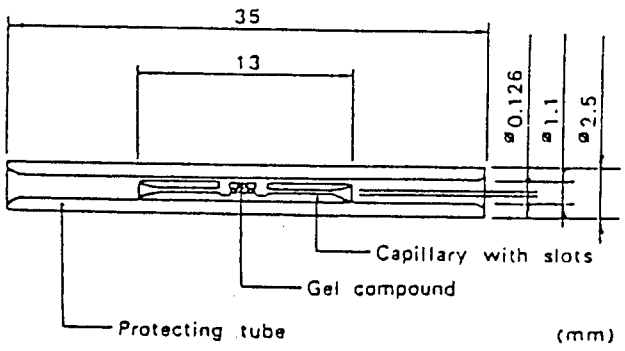


Fig. 1. Physical structure of key elements.

The relationship of splicing loss and capillary hole diameter is shown in Fig.2. The outer diameter and mode field diameter of the fiber used are 125.1 and 10 microns, respectively. The curve reperesents theoretical predictions for the loss due to transverse offset. The result suggests that gel compound and/or adhesive which fills the gap between the inner wall of the capillary and the fiber has self-centering effects on the inserted fibers.

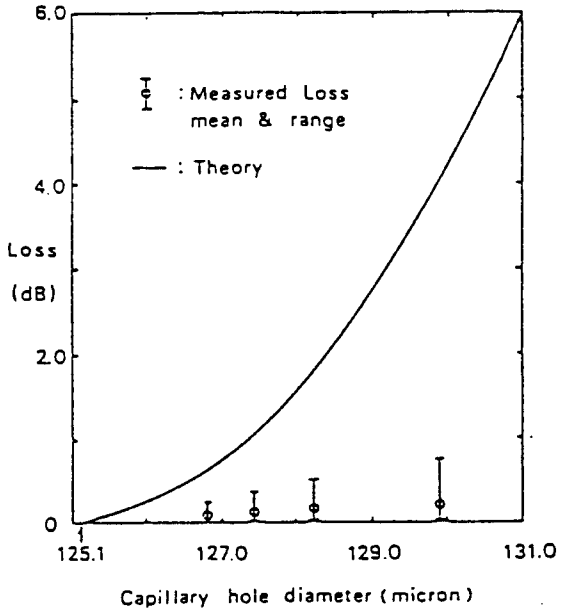


Fig. 2. Splicing loss - Capillary hole diameter.

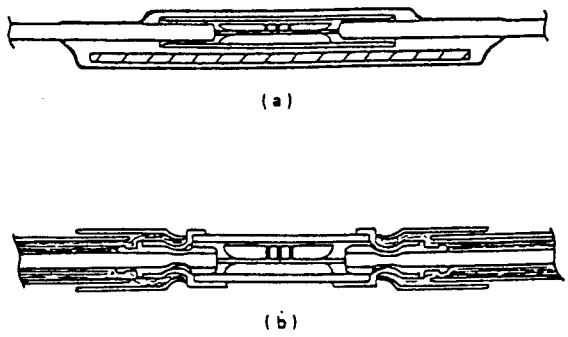


Fig. 3. Configurations of the splices.
(a) Coated fiber splice with thermo - shrinkable reinforcement sleeve. (b) Single fiber cable splice.

Figure 3 shows two different configurations for coated fibers and singlefiber cables. When 125.1 micron outer diameter fibers are spiliced in 126.5 to 127.5 microns hole diameter capillaries, the splices with the configurations shown in Fig.3, achieve optical and mechanical performance listed in Table.

Table. Optical and mechanical performance

Splicing loss	Mean	0.07 dB
	Standard deviation	0.03 dB
Return loss	15 to 50℃	>40 dB
	-40 to 80℃	>35 dB
Fiber pull-out force	for coated fibers	>2 kgf
	for single cables	>5 kgf
Environmental stability in loss variation		
Thermal cycling (-40 to 80℃)		<0.10 dB
80℃ for 720 Hrs holding		<0.10 dB
90% RH at 45℃ for 720 Hrs holding		<0.10 dB
Vibration (10 to 55 Hz with 1.5 mm maximum excursion at 1 oct/min, 24 cycles each for 2 planes)		<0.03 dB

PREPARATION OF LARGE SILICA GLASS FROM ORGANIC POLYMER ADDED SILICON ALKOXIDE SOLUTION

Fusashi Hayashi, Kouichi Takei, Youichi Machii
and Toshikatsu Shimazaki
Tsukuba Research Laboratory
Hitachi Chemical Co.,Ltd.
48 Wadai Tsukuba-city Ibaraki 300-42, JAPAN

I. INTRODUCTION

Sol-gel process has been known to be a method for preparing silica glass at a relatively low sintering temperature and with extermly low concentration of impurities. Such attractive process, however, still has many problems as have been pointed out. The main difficulty through the sol-gel process is in retaining a large gel monolith from which a large silica glass body is to be prepared. In a process of conversion from wet gel to dried gel many cracks are often observed. Recently, we have found that the large silica gel monolith can be obtained when organic polymers are added in the starting sol solution[1]. In this study, sintering behaviors of dried gels prepared with the organic polymers were investigated.

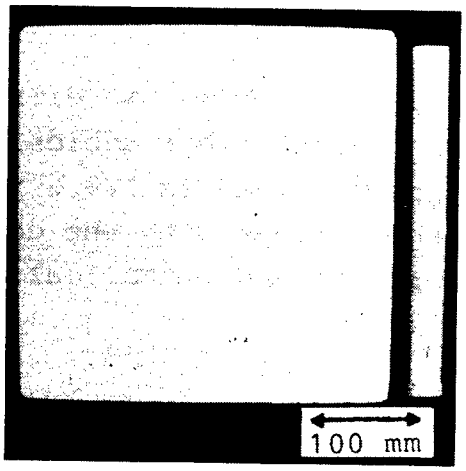


Fig.1 A large dried gel monolith prepared with PVAC.

II. EXPERIMENTAL

The dried gels were prepared by the following procedures. Silicon alkoxide (Condensation product of tetramethoxysilane) was hydrolyzed with 0.01 mol/l choline aqueous solution and various organic polymers. The organic polymers employed in this study were polyethlene glycol monomethyl ether(PEGME), polyvinyl acetate(PVAC) and hydoxypropyl cellulose(HPC). The gels were dried slowly at 60°C for two weeks. A typical dried gel monolith prepared by this process is shown in Fig.1. Thus obtained dried gel was sintered

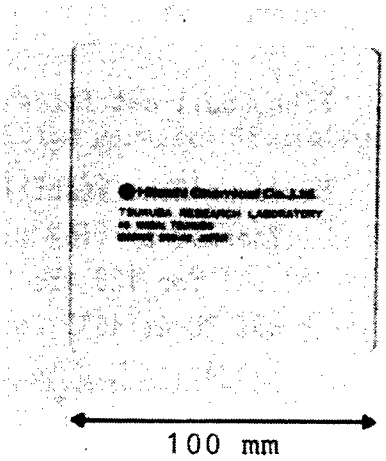


Fig.2 Silica glass sintered from gel monolith prepared with PVAC.

at 1350°C in air to get a clear glass as shown in Fig.2.

III. RESULTS AND DISCUSSION

Figure 3 shows pore size distribution of various dried gels that were measured by Hg penetration porosimetry. The pore in dried gel without polymer are widely distributed with relatively broad peak at about 10 nm. On the other hand, the dried gels with polymers had very large pore in comparison with dried gel without polymers. The remarkable enlargement of the pores seems to be preventing gels from cracking during drying[1].

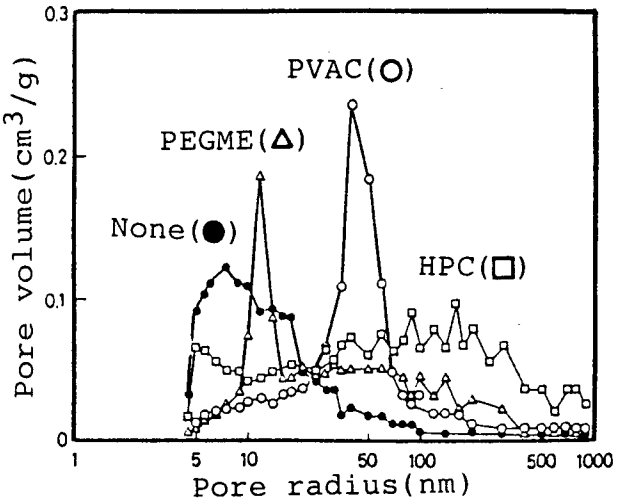


Fig.3 Pore size distribution for various dried gels measured by Hg penetration porosimetry.

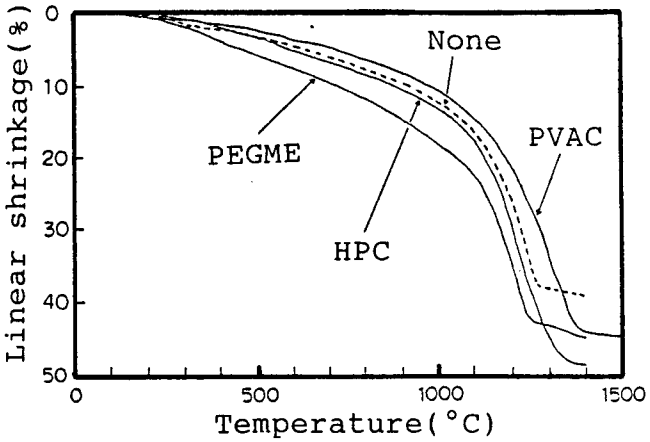


Fig.4 Linear shrinkage of various dried gels heated.

Figure 4 shows linear shrinkages of various dried gels. The shrinkage behaviors in the dried gels are very different from one another. The shrinkage of the gel without polymers begins at about 300°C, and gradually increases up to 1100°C. Above 1100°C, the shrinkage increases very sharply until the gel finally sinters at 1280°C. In the case of HPC, the shrinkage begins at the same temperature as in the gel without polymer, and the sintering temperature is higher than that without polymer. In the case of PVAC, the shrinkage begins at higher temperature than gel without polymer and so is the sintering temperature. These sintering behaviors could be roughly expected from the pore structure of the gels. In the case of PEGME, however, the shrinkage begins at lower temperature than the gel without polymer, the sintering temperature is also lower than that without polymer. The sintering behavior in this case should be attributed some factors besides the pore structure.

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PREPARATION OF HIGH T_c SUPERCONDUCTORS THROUGH GLASS-TO-CERAMICS PROCESS

Hiroshi Hirashima and Akiteru Maruta
Department of Applied Chemistry
Faculty of Science and Technology
Keio University
Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223 Japan

1. INTRODUCTION

Two superconducting phases of the system Bi-Sr-Ca-Cu-O, $T_c \cong 80$ K and 110 K, are known[1]. Glasses of this system can be obtained by melt-quenching. Preparation of these superconducting phases by crystallization of the glasses have been reported[2]. It was also reported that the 110 K phase could be easily obtained with addition of PbO[3]. In this study, crystallization process of Bi-(Pb)- Sr-Ca-Cu-O glasses have been investigated. In order to control size, shape and orientation of crystals deposited from the glasses, glass-forming oxides, such as GeO_2, TeO_2 or B_2O_3, were added. Effects of these additives on the crystallization process and micristructure of the crystallized glasses have been discussed.

2. EXPERIMENTAL PROCEDURES

Reagent grade Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO, $Ca(H_2PO_4)_3 \cdot H_2O$, GeO_2, TeO_2, H_3PO_4 and PbO were mixed and melted in an Al_2O_3 crucible. The mixtures were heated at a heating rate about 300°C/h, and were melted at 1200°C for 1 h in air using an electric furnace. The melts were poured onto a water-cooled Cu plate. The glass formation was determined by X-ray diffraction and optical microscopy. The glass transformation temperatures and the crystallization temperatures were determined by DTA. Crystalline phases deposited after heat treatment were identified by X-ray diffraction. The microstructure of the crystallized glasses was observed by optical microscopy and SEM.

3. RESULTS AND DISCUSSION

Glasses of the compositions $BiSrCaCu_2O_x$ and $Bi_{0.7}Pb_{0.3}SrCaCu_2O_x$ without additives and with addition of 5 and 10 mol% GeO_2, TeO_2 or B_2O_3 were obtained. The glass transformation temperature of the glasses increased with addition of

the glass-forming oxides. The peak height of the first exothermic peak of DTA curves at about 450°C, attributed to the crystallization, decreased with addition of these oxides. These results suggest that thermal stability of the glasses are improved and the rate of crystallization is decreased by addition of these glass-forming oxides. To the contrary, the crystallization temperature was affected little by the additive oxides. The endothermic peak temperature, about 850°C, also changed little with addition of the glass-forming oxides. These results suggest that the deposited crystalline phases in the glasses containing the glass-forming oxides are the same as in the glasses without additives. After the heat treatment at temperatures from 480 to 700°C, $Bi_2Sr_2CuO_6$ was found for all glasses. In the temperature range from 700 to 850°C, the low T_c phase, $Bi_2Sr_2CaCu_2O_8$, deposited in the glasses with and without additives. The X-ray diffraction patterns changed little with addition of the glass-forming oxides. Needle- or plate-like crystals, about 50 μm in length, were observed for the glasses without additives after the heat treatment at 830°C for 3 h. The size of the deposited crystals was decreased by addition of GeO_2 or TeO_2, but changed little with addition of B_2O_3.

The diffraction peaks of the high T_c phase, $Bi_2Sr_2Ca_2Cu_2O_{10}$, were found for $BiSrCaCu_2O_x$ glass after the heat treatment at the temperatures higher than 850°C, and for the glasses containing Pb after the heat treatment at the temperatures higher than 830 °C. Needle-like crystals, about 100 μm in length, were observed for the glasses containing Pb after the heat treatment at 850°C for 3 h. The length and the shape of the deposited crystals varied little with addition of the glass-forming oxides.

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GLASS FOR SPACE

Tokio Kimura, Yoshio Moriguchi, Kazuyuki Komagata,
Kenji Watanabe, Masaki Shiroyama,and Ryo Tamamura
ASAHI GLASS CO LTD.(AGC)
1-1 Suehiro-cho,Tsurumi-ku,Yokohama,230, JAPAN

The glass with various functions is useful for the space material. For example,solar cell coverglass and optical solar reflector(OSR)are used on satellites,and special window is provided for space shuttle. We show an outline of the glass for space ,and the stopping power of glass for proton.

I. GLASSES FOR SPACE

A. Coverglass: Coverglass is attached to the active surface on solar cell to prevent degradation of the cell due to corpuscular irradiation such as proton and electron in space. The upper surface of it is coated with antireflective coating,MgF_2 to minimize reflection losses in the visible range. Light weight is also required for coverglass,so coverglass has thicknesses of from 0.05 to 0.5 mm.

The coverglass must intercept ultraviolet(UV) rays in space,because the adhesive layer between solar cell and coverglass becomes opaque after UV irradiation. To prevent this,small amount of CeO_2 which has UV absorption characteristics,is added to the base glass. Another method to do this is to coat a glass plate with UV reflective film to reduce UV absorption.

B. Optical solar reflecter (OSR): OSR is used as passive thermal control devices on the main body of satellites. OSR needs the functions of both reflecting solar radiation and radiating internal heat,simultaneously. Their functions are acheived by a combination of low solar absorptance(α_s) and high nomal emittance(ε_n). For example, typical OSR has the structure of silver mirror coating protected by Ni-Cr metal film on the rear surface,and has transparent conductive coating,indium tin oxide,on the front surface to prevent of electric charge build up in the satellites' housing.

C. Windows : Almost all windows on outer-space manned flight vehicles are triple-paned assembly. The outer pane

is used for thermal-rejection purposes and as the barrier against micrometeorites. The innermost pane is the primary pressure barrier. The middle pane is required to back up both panes in case either should fail. High purity fused silica is used as the outer and middle pane,and special aluminosilicate glass is used as the innermost pane.[1)]

The windows must also possess functions of reflecting UV and infrared rays,with antireflection for visible light.

Ⅱ.STOPPING POWER OF GLASS FOR PROTON

Component parts for space are space-qualified by means of a rigorous,well designed series of terrestrial test,such as performance test and quality assurance test. As a part of performance test,the stopping power of coverglass for proton, is simply indicated by the ratio of the amount of proton passed through glass to that of proton irradiated.

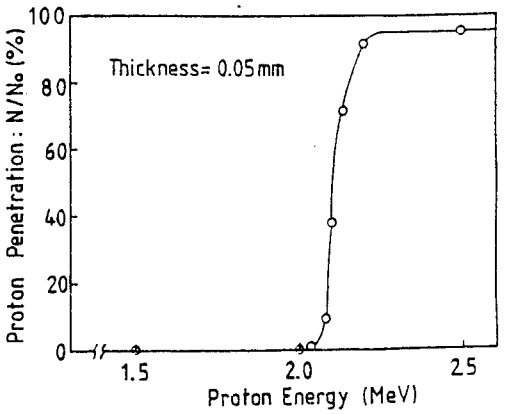

Fig.1. Stopping power of coverglass for proton.

The Tandem accelerator of Government Industrial Research Institute,Osaka,was used as proton implanter. The cover-glass,a soda-lime based glass of 0.05mm in thickness,was used as substrate. Results are shown in Figure.1. It is noted that the coverglass of 0.05mm in thickness is able to intercept proton of 2MeV or less in energy. The stationary satellites are mainly exposed to proton of 1 MeV energy or less, so it is concluded that the coverglass sufficiently possesses the performance of intercepting such proton radiation.

Ⅲ.CONCLUSION

As described above,various glasses,such as coverglass,OSR and window,are shown to be useful under space environment. The space age will come in the near future,and it is expected that the glass will play much important part in space.

Ⅳ.REFERENCE

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AXIAL GRADIENT-INDEX DOUBLET OBJECTIVE FOR OPTICAL DISK SYSTEMS

Shigeo Kittaka, Tsuyoshi Yamane,
Yoshikazu Kaite and Minoru Toyama
Central Res. Lab., Nippon Sheet Glass Co.,Ltd.
1, Kaidoshita, Konoike, Itami, Hyogo pref., Japan

1. Introduction

Gradient-index glass materials have been applied to optical lenses. It is well-known that a plano-convex axial gradient-index(Z-GI) lens is able to correct the spherical aberration. The refractive index profile of the Z-GI lens must be linear to correct the spherical aberration well, while large refractive index change(Δn) is required to make a lens with large numerical aperture(NA). (Approximately $\Delta n = 0.5 \cdot NA^2$) Consequently, the performance of a Z-GI lens depends on "linearity" and "Δn".

2. Refractive Index Profile

Z-GI glass plates(30 × 40 × 1.5mm) were fabricated by the conventional ion-exchange technique. The refractive index profiles were formed in both sides of the plate symmetrically. In order to examine the profile, one of the plates was cut and ground into 15 tips of various thickness. The refractive index of each tip was measured by a Pulfrich refractometer. The result is shown in Figure 1.

The linearity and Δn are satisfactory to attain a diffraction limited Z-GI lens with NA of 0.25.

3. Lens Design of Z-GI Doublet

Objectives for write-once type and re-writable type optical disk systems require large NA of 0.53～0.55. In order to make NA larger, a homogeneous meniscus lens was added to a plano-convex Z-GI lens. The configuration of a Z-GI doublet with NA of 0.55 is given in Figure 2.

4. Fabrication of Z-GI Doublet

The Z-GI glass plates were cut into a number of small disks. The flat surfaces and the convex surfaces of the disks were ground and polished. As far as the flat surface is perpendicular to the gradient-index direction, the optical axis of the both surfaces is also aligned with the gradient-index direction. The homogeneous meniscus lenses were fabricated by the conventional grinding and polishing process. Both lenses were mounted in a plastic holder. The total weight was 76mg. The Z-GI doublet had diffraction limited performance.

5. Conclusions

(1) Z-GI glass plates with linear refractive index profiles were manufactured by the conventional ion-exchange technique.

(2) Several types of Z-GI doublet objectives(NA=0.53～0.60) were designed and fabricated successfully.

6. Reference

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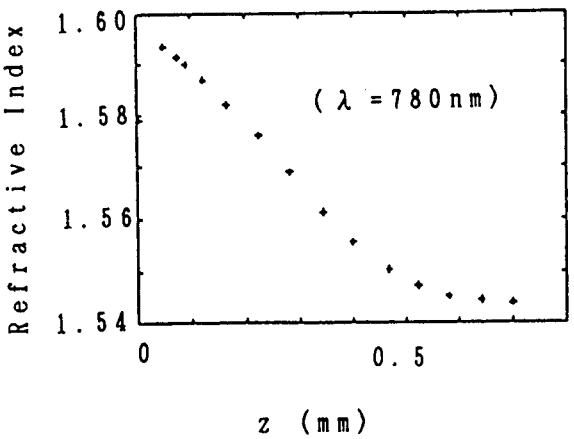

Figure 1

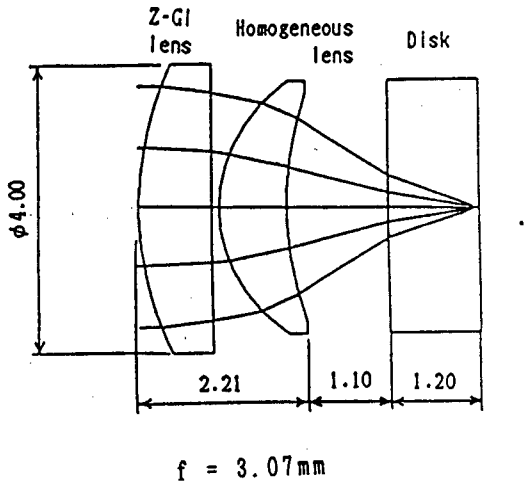

Figure 2

NEW GLASSES FOR I.R. OPTICS

Jacques Lucas, Zhang Xiang-Hua
Université de Rennes, Campus de Beaulieu
Laboratoire de Chimie Minérale D
Avenue du Général Leclerc - 35042 Rennes Cédex (France)

A new family of I.R. glasses based on tellurium halides have been discovered and developed. Depending on their compositions, these so-called TeX glasses are devided in two groups :
a) the light TeX glasses having their I.R. edge in the 13 µm region and containing Cl or S
b) the heavy TeX glasses having their multiphonon cutt-off at 20 µm and containing only heavy elements such as Te-Br-Se, Te-I-Se

Most of these TeX glasses are very stable towards devitrification and water or moisture corrosion. The glass temperature is around 80° C and the viscosity-temperature dependence is very suitable for pressure shaping and optical fibre drawing. The TeX glasses are black with a band gap edge lying from 0.7 to 1.4 eV ; their refractive indices are depending on the chemical composition and vary from about 2.5 to 3.

Examination of the transmission spectra from band gap to multiphonon edge shows almost no parasitic absorption due to impurities.

Optical fibers have been drawn either from preform or melt ; measured attenuations are around 3dB/km and it has been verified that bubbles and fluctuations in diameter are the main reasons of loss. Predicted loss, taking into account band gap edge and multiphonon absorption, is estimated to be lower than 0.1 dB/m in the 8-12 µm region.

In using sputtering technique, thin films of TeX glass belonging to the system Br-Se-Te have been produced. It has been verified that the refractive index of the thin layers was possible to change in modifying the chemical composition of the target. These planar vitreous waveguides represent a new class of materials for low loss integrated optics in the mid I.R.

A STUDY ON AN ALKALINE-FREE MACHINEABLE BIOGLASS-CERAMIC

Luo Lan Li Jiazhi

Shanghai Institute of Ceramics, Academia Sinica

865 Chang-ning Rd., Shanghai 200050, P.R. China

Bioceramics is a kind of ideal prothetic materials, and active study is being carried out on it(1). In this paper, a new machineable bioactive glass-ceramic in CaO-MgO-Al2O3-SiO2- P2O5-F system is reported.

The base glass for making the material has the following composition(wt%) : P2O5 3-20, SiO2 24-45, Al2O3 6-20, CaO 11-20, MgO 10-18, MgF2 6-14. Study shows that the base glass has two phase seperation structure(2). The droplet phase is rich in Ca^{2+}, $Mg^{2+}$and P^{5+}, and the matrix phase rich in Si^{4+} and Al^{3+}. After heat treatment at 700 °C/1h---950°C/3h, the base glass is fully crystallized into a glass-ceramic containing about 22wt% apatite and about 74wt% Ca-phlogopite(3).

Scanning electron microscope image (Fig.1) reveals that the glass-ceramic is full of Ca-phlogopite crystals which show clearly layer structure, and that a great deal of fine short hexa-prismatic apatite crystals are widely dispersed in the Ca-phlogopite. Tests show that the glass-ceramic has very good machineability, which is believed to come from the presence of the large amount of Ca-phlogopite. The material also has a high mechanical strength (table 1)

Acording to cell culture experiments(3), the new material can be considered absolutely biocompatible. In animal experiments(3) we find that the glass-ceramic implants can be directly combined with living bone tissue, and the interface between the material and the bone is closely binded together(see Fig.2).

It's believed that, because of its good machineability and good bioactivity as well as a high strength, the glass-ceramic might be used as an ideal prosthetic material, especially when load-bearing conditions and complex implant shapes are required. Now, animal and clinical experiments are being carried out.

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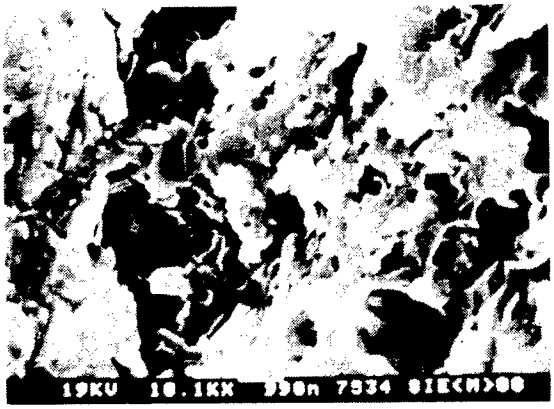

Fig.1 SEM image of the bioglass-ceramic

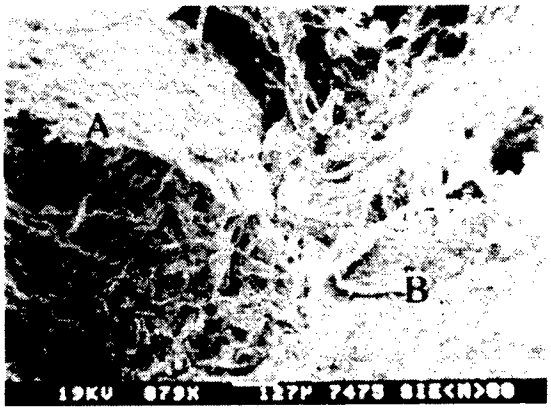

Fig.2 SEM image of the interface between the material(A) and the living bone(B)

Table 1 Mechanical properties

Density (g/cm^3)	2.86
Hardness Hv (kg/mm^2)	673
Bending strength (MPa)	163
Elastic modulus (N/mm^2)	7.49×10^4
Fracture toughness ($MPa\cdot m^{\frac{1}{2}}$)	2.24

FLUOROZIRCO-ALUMINATE GLASS FIBERS

K. Miura, I. Masuda, K. Itoh and T. Yamashita
Materials Research Laboratory
HOYA Corporation
Akishima-shi, Tokyo, 196 Japan

INTRODUCTION

Many applications now appear to be opened for fluoride glasses, for instance, ultra-low-loss fiber for repeaterless communication systems and medium-low-loss fiber for medical, power transmission, infrared emission and temperature sensing. Developmental research for fluoride glasses have been concentrated on fluorozirconate glasses. However fluorozirconate glasses are poor in chemical durability, mechanical strength and thermal stability, hence some improvement of the properties have been needed for a practical use. As a result of the improvement, fluorozirco-aluminate glasses with better chemical durability, mechanical strength and thermal stability have been developed [1,2].

In this study, we prepared fluorozirco-aluminate glass fibers which have numerical aperture of 0.30 and was overclad with oxide or oxyfluoride glass. Potential application of Er:YAG laser power delivery is also discussed for a fiber having large core diameter(500 micron).

GLASS COMPOSITIONS

The glass compositions for base, core and clad glasses and some properties are shown in Table 1. A fluorozirco-aluminate glass was chosen as a base composition which has been previously reported[2]. In order to get a higher refractive index for core glass, AlF_3 and CaF_2 were replaced by other components in the base composition, and chlorine was also added. For a clad glass, both BaF_2 and YF_3 in the base composition were replaced by NaF in order to decrease a refractive index.

Table 1. Compositions and properties of base clad and core glasses

	AlF_3	ZrF_4	YF_3	MgF_2	CaF_2	SrF_2	BaF_2	NaF	Cl
BASE	30.1	10.2	8.3	3.5	20.3	13.2	10.6	3.8	-
CLAD	30.1	10.2	6.3	3.5	20.3	13.2	7.6	8.8	-
CORE	25.1	12.8	11.1	3.7	15.4	13.6	12.6	5.7	1.2

	Nd	Tg(°C)	Ts(°C)	$\alpha(10^{-7})$	NA
BASE	1.44711	383	412	179	-
CLAD	1.43131	369	402	183	0.30
CORE	1.46294	362	395	184	

PREFORMS

A number of methods for preparing a preform of fluoride glass have been investigated in which the preforms are formed by casting at low melt viscosity. However, the preform could not be easily formed by the casting methods without causing crystallites and bubbles under such a low viscosity condition. Therefore the preforms were prepared by extrusion method which is a quite different technique. In this method a preform can be formed at higher viscosity region (10^8 to 10^9 poises) compared with the above casting methods. The preforms were also overclad with oxide or oxyfluoride glass to suppress the surface crystallization during the drawing.

A schematic assembly of extrusion molding was shown in Figure 1. Three optically contacted glass disks(15x35mmϕ) are placed inside of a cylinder and heated up to 415 °C followed by pressurizing at 50 kg/cm^2 with a punch. By this method, three layered preforms of 5 to 10 mm in diameter and less than 1 m in length were able to be obtained.

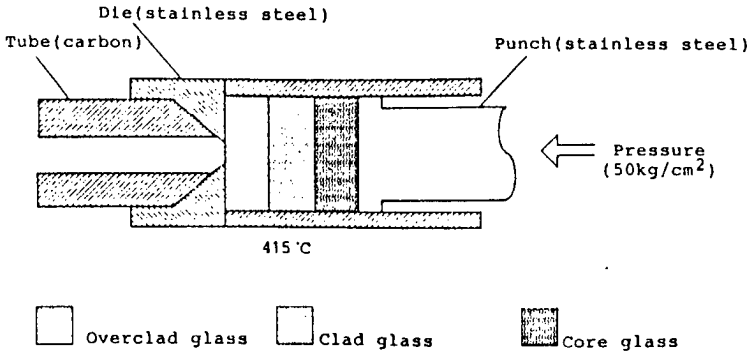

Figure 1. Schematic assembly of extrusion molding

FIBERS

The drawing conditions depend on types of preforms and diameters of fiber. For example, in order to obtain a phosphate glass overclad fiber of 200 micron diameter, the fiber was drawn at 460 °C and a speed of 450 mm/min, and simultaneously coated with UV-curable polymer. At the present stage, the loss spectra of these fibers shows a constant loss of about 1 dB/m between 2 μm and 4 μm. The main cause of loss is due to the scattering at the interface between core and clad glasses and the absorption originated from hydroxyl group.

Er:YAG LASER POWER DELIVERY

A Er:YAG laser(produced by HOYA) emitting high peak power pulses at 2.94 microns (pulse width : about 200 microsecond) was employed for the experiment. The beam was focused on the entrance face of 500 micron core diameter fiber using a 20 mm focal length sapphire lens, and the output power transmitted through the fiber was measured by a power meter. As shown in Figure 3, linear relation between input power and output power indicates that no laser damage occurs up to 600 mJ input which corresponds to a maximum output power of the Er:YAG laser and a power density of 65 kW/mm^2.

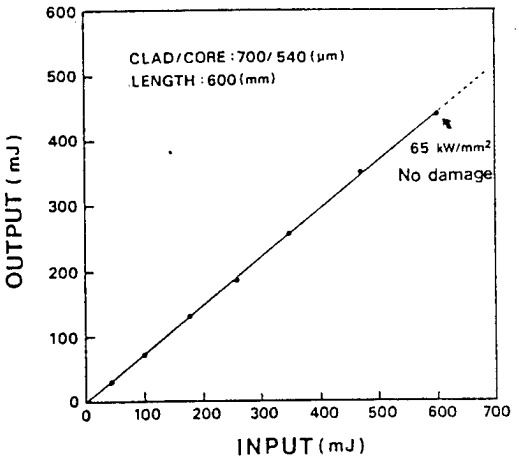

Figure 2. Characteristics of Er:YAG laser power delivery

CONCLUSIONS

Fluoride glass fibers with a high numerical aperture of 0.30 have developed. These fiber have a three layered structure with oxide or oxyfluoride glass overcladding. New extrusion method was successfully applied to make a three layered preform for these fibers. Some preliminary experiment for power delivery of Er:YAG laser confirmed that these fibers have fairly high damage threshold.

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Defects in Pure-Silica Glass for Optical Fibers

K. Nagasawa, Y. Yokomachi*, R. Tohmon*, Y. Ohki* and Y. Hama*

Sagami Institute of Technology, Fujisawa, Kanagawa 251, JAPAN
*Department of Electrical Engineering, Waseda University

Exposure of silica fibers to hydrgen results in the growth of absorption bands in the infrared region, causing optical transmission loss. In this paper, causes of the 1.45 μm [1,2] and broad 1.24 μm bands are discussed.

The samples used are two types of low OH content pure silica core fibers with silicone clad. They differ in manufacturing methods; one is the $Ar+O_2$ plasma method (P6F), the other is the soot method (SFF).

After γ-ray irradiation (20 kGy) and hydrogen treatment (room temperature, 3 atm, 100 hours), the samples were heat treated in air (150°C, 6 hours). In P6F, when the fiber is irradiated by γ-rays and treated with hydrogen at room temperature, peak appeared at 1.52 μm (this absorption band is caused by the following structure: Si-O-O•··· H-H [3]). Figure 1 shows the change in loss specta by the heat treatment in P6F in SFF. The treatment results in a decrease of the 1.52 μm band and a growth of the 1.45 μm band in P6F. On the other hand, in SFF, neither the 1.52 μm nor the 1.45 μm bands appeared after the same treatment. If the heat treatment was done at 90°C, no 1.45 μm band was observed after the heat treatment even in the P6F. So, temperature higher than 150°C seems to be necessary to proceed the reaction making the 1.45 μm band.

After the γ-ray irradiation, peroxy radical was detected in P6F by ESR measurement, while not in SFF. To investigate the relation between the 1.45 μm band and peroxy radical, two sets of P6F were prepared. After the irradiation (2.9 kGy), one set was treated in helium gas at 150°C for 6 hours, while the other in hydrogen gas. The signal intensity of peroxy radicals decreased to 33% after the hydrogen treatment, while to only 83% after the helium treatment. Furthermore, if the treatments were done at 90°C, peroxy radical didn't decrease. It follows that peroxy radicals react with hydrogen molecules at 150°C in the following reaction:

$$\rightarrow Si\text{-}O\text{-}O\bullet + H\text{-}H \longrightarrow \rightarrow Si\text{-}O\text{-}O\text{-}H + H\bullet .$$

This reaction is also necessary higher temperature than 150°C. So, it is clear that the increase of the 1.45 μm band has a close relation to the decrease of peroxy radicals in hydrogen gas. As the first OH-stretching overtone of Si-O-H appears at 1.39 μm, the 1.45 μm band should be due to a similar first OH-stretching overtone of Si-O-O-H.

Figure 2 shows the induced loss spectra of P6F during γ-ray irradiation (dose rate 120 Gy/h). The fiber had been treated with hydrogen (room temperature, 3 atm, 150 hours) prior to irradiation. The figure shows not only the 1.52 μm and 1.39 μm bands but also a band at 1.44 μm. Furthermore, radiation hardening is seen in the 1.52 μm and 1.44 μm bands. The 1.44 μm band is a transient band [2], the cause of which is still being investigated. Careful investigation of Fig. 2 shows a growth of a very broad band

spreading from 1.0 μm to 1.6 μm with a peak around 1.24 μm. The behavior of this broad band is similar to that of the 1.52 μm band. From these results the cause of the broad 1.24 μm band is thought to be the same as the 1.52 μm band (≡Si-O-O•···H-H).

It is known that there is a sharp band caused by hydrogen molecules at 1.24 μm. When hydrogen molecules go out of the fiber, a dip appears at this wavelength in the spectra. (As the curves a, b, c and d in Fig. 2 are the spectra when irradiated for 2, 24, 48 and 72 hours, respectively, the amount of residual hydrogen seems to decrease in this order.) If hydrogen molecules form hydrogen bonds, they would not easily be removed from the fiber. Furthermore, the hydrogen bonds would cause the vibrational absorption band due to hydrogen molecules to broden, and enhance the quantum efficiency of the absorption because polarization in hydrogen molecules is larger. This should result in a large and broad absorption band such as the broad 1.24 μm band in Fig. 2.

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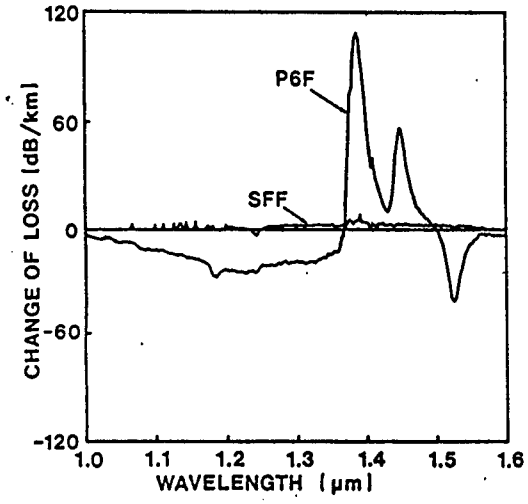

Fig. 1. Change in the loss spectra caused by heat treatment (150 C°) of P6F and SFF fibers which had been irradiated by γ-rays (20 kGy) and treated with hydrogen (room temperature, 3 atm, 100 hours).

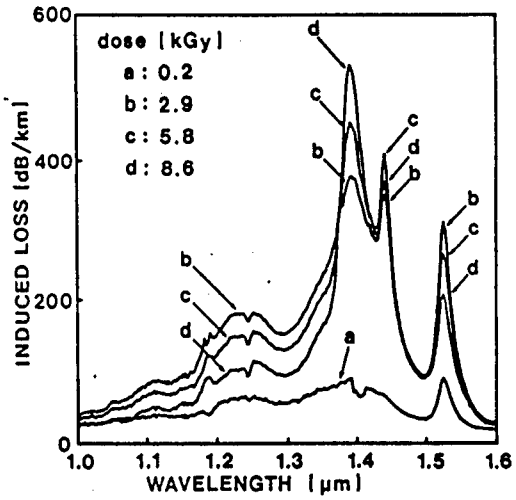

Fig. 2. Change in the induced loss spectra during γ-ray irradiation of hydrogen treated P6F fiber.

A NEW PREPARATION TECHNIQUE FOR SEMICONDUCTOR-DOPED GLASSES(S.D.G.)

Shigeaki Omi, Shuuji Yoshida, Yoshiyuki Asahara,
Akira J. Ikushima
HOYA Corp., Materials Research Laboratory,
Musashino 3-3-1 Akishima-shi Tokyo, 196 Japan

Glasses doped with CdS_xSe_{1-x} microcrystallites (S.D.G.) are interesting composite nonlinear-materials since they have a relatively large third-order optical nonlinearity with fast response time. Quantum confinement effects have been studied by several groups for the enhancement of the nonlinearity. The experimental studies, however, have been plagued with an inability to separate these effects from effects of variation in crystal stoichiometry of CdS_xSe_{1-x} microcrystallites. A wide distribution of crystal stoichiometry and particle size of CdS_xSe_{1-x} microcrystallites are also serious problems for utilizing S.D.G. as nonlinear materials.

In a conventional S.D.G. production, quenched glasses containing Cd, S and Se components are heated up and then kept at a heat-treatment temperature. During this process, CdS_xSe_{1-x} microcrystallites are precipitated in the glass matrix but the difference in precipitation temperature and diffusion rate between S and Se ions causes a wide distribution of crystal stoichiometry and particle size.

We have investigated an alternative heat-treatment technique, which is referred to hereafter as the cool-down technique(C.D.T).

C.D.T. consists of two heat-treatment steps. A glass is initially heated up to about 1100°C and kept for 0.5 h at this temperature. In this step, Cd, S and Se components are ionized and dissolved homogeneously in the glass matrix. The glass is, then, directly cooled down to a heat-treatment temperature and kept at this temperature for extended periods of time. In this step, CdS_xSe_{1-x}

microcrystallites are precipitated from the glass matrix.

The average composition ratio (x) of CdS_xSe_{1-x} microcrystallites gradually decreases with increasing heat-treatment temperature in the conventional process, while in the C.D.T. x decreases with temperature but becomes constant over 680°C. The results indicate that the temperature change beyond 680°C does not affect x in the C.D.T., which should give a narrow distribution of crystal stoichiometry of CdS_xSe_{1-x} microcrystallites.

The average particle diameter (d) of CdS_xSe_{1-x} microcrystallites increases with the heat-treatment time (t) and exhibits a linear relationship of the form log(d)-log(t). On heat-treatment above 680°C, the slope is nearly 0.3 in the conventional process, suggesting microcrystallite recondensation. In the C.D.T., this slope is about 0.5 for an initial 1 h treatment and then saturates to 0. The results indicate that the recondensation process can be ignored in the C.D.T. process, which results in a narrow distribution of crystal size.

In conclusion, these results indicate the possibility of preparing S.D.G. with a narrow distribution of crystal stoichiometry and size of CdS_xSe_{1-x} microcrystallites by the C.D.T.

We would like to acknowledge Hiroyuki Sakai, Toshinobu Miura and Hitoshi Hiraga (HOYA Corp.), Naoshi Uesugi, Junji Yumoto and Hiroyuki Shinojima (NTT Basic Research Laboratories) for their useful discussions.

THE STRUCTURE AND PROPERTIES OF THE HIGH RARE EARTH GLASS WITH NEW OPTICS PROPERTY

Qiu Guan-ming

Materials Engineering Department
Changchun College of Optics and Fine Mechanics
52-4(221) Gong Nong Da Lu Changchun City. P.R.China

I. INTRODUCTION

A new optical property optical glass propel all kinds of the high-grade new type optical glass systems forward. For example, 100 tiems objective lens among making superior quality microscopes, etc.. A lot of the rare earth chemical compound are drawn into glass to improve a lot of the properties of the glasses, but lead glasses to crystellization and chemical stability is poor. In this paper according to the viewpoint that I put forward "glass group structure", 100×100×15mm lanthanum crown glass was tried out with the crystal chemistry parameters for the application, in the same time experiment data and their correctness of the glass structure viewpoint that I put forward metastable immense complex anion groups were proved by the modern time measurement methods.

II. MEASUREMENT AND RESULTS

1. Optical Property

The coarse annealing sample was ground and then polished into 90° right angle. The refractive indexes Nd, Nf, Nc of the sample were measured by v-prism refractometer and $N_f - N_c$, ν_d were calculated. The measurement accuracy is 2.5×10^{-5}. The results are $N_d=1.7677$, $N_f-N_c=0.01536$, $\nu_d=50.0$

2. Chemical Stability Determination

The sample was determined by CS-501 type super constant temperature ware with an acetic acid of PH=2.9 and an acetic acid salt of PH=4.6 . The acid resistance is 1b calss. Moisture resistance is A class.

3. Other Physical Mechanical Properties

Density is 4.42g/cm^3; Micro-hardness is 687 kg/mm^2. Young's modulus is 11725 kg/mm^2; Shear modulus is 4573 kg/mm^2; Bosong ratio is 0.282 etc..

4. X-ray Diffractions Analysis

Dman-ⅢB X-ray diffratometer was used. Scanning speed is 5°/min. Speed range is 5-110°. The crystalline phase is LaB_3O_6 with the method of powder diffraction.

5. Differential Thermal Analysis (DTA)

DTA curve was obtained from Japan differential thermogravimetric analysis instrument at heating rate of 5°/min, 10°/min, 20°/min respectively and paper rate of 5 mm/min . The highest experiment temperature is 1000°C. The result is Tg=670°C, T=864-670=194°C.

6. JMA Equation $Ln(\phi/T_p^2)=E/RT_p+C$

Kissinger method was used to calculate the glass crystallzation activation energy which is E=130 kcal/mol.

7. IR, Raman Spectra Analysis

The IR spectrum was measured by Type FT-IR 5DX spectrophotometer with KBr pellet method. The ratio between the sample and KBr is 1:200 , ware length range is at 400-4000 cm^{-1} The instrument resolving power is 4 cm^{-1}, The sample was polished and the measured by Type JY-T800 laser Raman Spectrum which the resolving power is 0.25 cm^{-1} and wavelength precision is at $\pm 0.02 cm^{-1}$ and spectrum range is at 100-2400 cm^{-1}, slit width may continue to be adjusted at 0-2 mm. The results show that the glass structure consists of $[BO_3]^{3-}$, $[BO_4]^{5-}$, $[SiO_4]^{4-}$, $[AlO_4]^{5-}$ etc. base structure units which form continuance immense metastable complex anion groups composing mainly of four borate at three dimension directions.

8. X-ray Photoelectron spectroscopy (XPS)

ESCALAB MARK II X-ray photoelectron spectrometer of Britain VG company was used. C_{1S} of the pollution carbons in the vacuuty pump was used to make inner-mark of spectrum map. The spectrum curve draft and data treatment were made on computer of the spectrometer supplementary with VGS 5000 software. Oxygen were found to have two kinds states which bridging oxygen are 66% and non-bridging oxygen are 34%.

9. Nuclear Magnetic Resonance(NMR) Study

The NMR experiment in this work was performed on a multi-nucleare pulsed Fourier Transform NMR spectrometer of type SXP4-100(Bruker company of west Germany) at room temperature. The stability of the magnetic field and frequency is in advance of 10^{-7}. The every signal was accumulated 25 times. That three-coordinated boron makes a contribution to NMR spectrum was basically eliminated with narrow band receiving. The error of N_4^B is smaller than 5%. The results are N_4^B=20%, N_3^B=80%, $N_4^B:N_3^B$=1:4, which is by reason that the field strength of complex anion groups outer oxide is big and giving out free oxygen ability is smaller, N_4^B can not be higher. The glass structure mold consist of four borate structure units which is in accordance with the results of IR and Raman spectra analysis.

10. EXAFS Analysis

La-L_{III} absorb EXAFS spectrum experiment was performed at the same step radiation laboratory of Japan Optical Factory with BL-7C Beamline . μx value is about 2. The figures time were written down at 1s /point . X-ray light strength is about 10^{10} photo every second .The standard sample is La_2O_3 powder crystal. The coordinate number of La^{3+} in the glass was obtained to be 8 which higher than 7 coordinate number in La_2O_3. La-O average bond distance is 2.52Å

SINGLE-MODE WAVEGUIDE DEVICES IN MULTICOMPONENT GLASS BY A TWO-STEP PURELY THERMAL ION EXCHANGE PROCESS

Masafumi Seki
Tsukuba Research Laboratory, Nippon Sheet Glass Co., Ltd.
5-4, Tokodai, Tsukuba-city, Ibaraki-Pref. 300-26 Japan

1.INTRODUCTION: Optical fiber communications have reached a new stage where various passive and/or active components are necessary in networking terminals in cost-effective ways. We have developed passive single-mode (SM) waveguide devices made by a two-step purely thermal ion-exchage (I/E) technique[1] in multicomponent glass.

2.WAVEGUIDE FABRICATION: Waveguides are formed in glass substrates of the borosilicate system containing SiO2, B2O3, Al2O3, Na2O,K2O and MO(M:divalent ion). The I/E is carried out two times in different molten salt baths with no assistance of electric field applied. The near field patterns of the waveguides, shown in Fig.1, are ellipselike shapes with major diameter 1.5 to 1.6 times larger than minor diamter[2], which is attributed to ion concentration distribution.

Waveguide propagation loss was less than 0.2 dB/cm at 1.3 um wavelength. The coupling loss to a SM fiber was 0.3 dB/facet which agreed well with the calculation of an over-lapping integral between the linearity-corrected near field profiles of a waveguide and a SM fiber.

3.WAVEGUIDE DEVICES: Y-branches with SM fibers pig-tailed have about 1.6 dB loss for 1.2-1.6 um wavelength region. Both branching ratios for TE and TM mode hold 50 +-2 % over the whole wavelength region[3]. Wavelength-flattened 1xN couplers (N=2xn ; n=1,2,..) were fabricated by connecting Y-branches in a tree sckeme. Fig.2 shows wavelength loss characteristics for a 1x4 branch having 2.2 dB excess loss. WDM (=wavelength division multiplexing) multiplexers were made by incorporating interference filters into branching waveguides[4] or directional couplers. 3 dB (50:50-ratio) directional couplers with less than +-2 % deviation in the branching ratio and a small excess loss of 0.8 dB were realized[5] for a coherent transmission receiver[6].

The I/E process can inherently make complex optical circuits

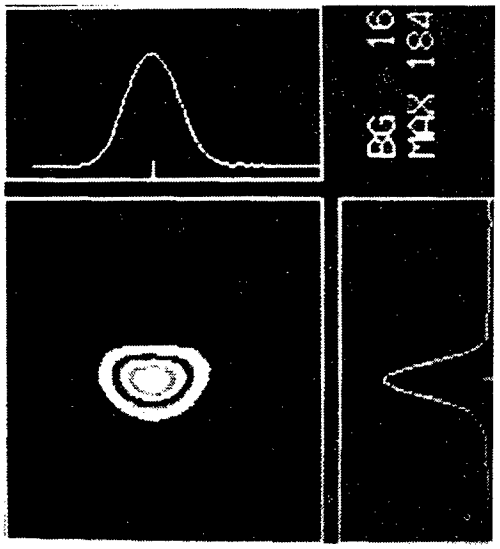

Fig.1 Near field pattern of a singe-mode waveguide

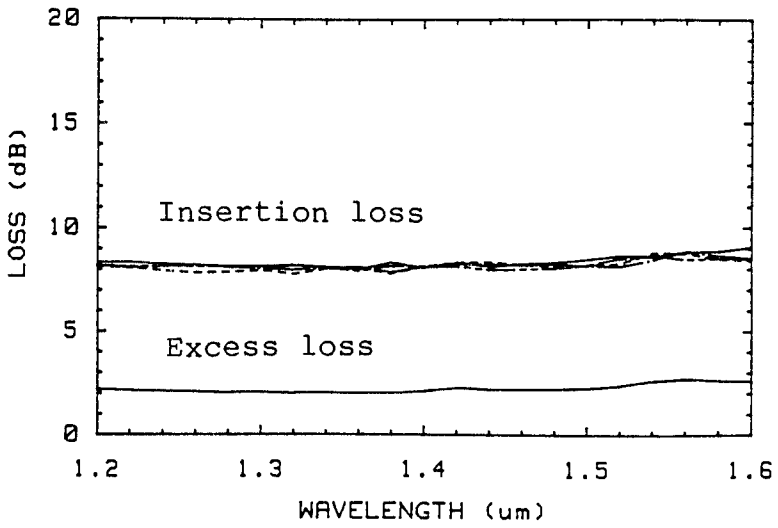

Fig.2 Insertion loss vs wavelength of a 1x4 branch

in a single substrate, such as NxM couplers, tap-and-branches and combiner-and-multiplexers, by just delineating mask pattern onto metal mask for I/E process.

4.RELIABILITY: Telecom-oriented devices are required to meet several severe specifications; dry heat, change of temperature, damp heat, vibration and shock test. To fulfill these, we have studied an assembling technique composed of epoxy resin curing and succesive soldering among waveguide/fiber components[7]. In a 300-cycle heat test of temperature ranging from -40 to +85 deg C with 6 hrs/cycle, devices have been proved to have only a small loss variation of less than +- 0.1 dB. The devices can also pass other tests, such as 95 RH%-60 deg C-100hr damp heat, vibration test of 10-55 Hz with +-1.5 mm amplitude in two directions in 2 hrs and schock test of releasing a sample from 1 m height to concrete floor.

5.CONCLUSION: Low-loss and reliable single-mode waveguide devices in glass have been fabricated by a novel two-step purely thermal I/E process. Such devices should find various applications in today's telecom and sensor needs.

AKNOWLEGDEMENT The author thanks K. Koizumi and K. Sono for their guidance, and his colleague for fruitful discussions.

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GLASS SUBSTRATE FOR MAGNETO-OPTICAL DISK

Tomoyuki Shimizu Hiroshi Arishima
Tohru Momose Takashi Hatano
Advanced Glass R&D Center
ASAHI GLASS Co., Ltd.(AGC)
1-1 Suehiro-cho, Tsurumi-ku
Yokohama-shi, KANAGAWA, 230 JAPAN

1.INTRODUCTION

Magneto-optical(MO) disk system is going to be used as rewritable large-capacity storage. PMMA and PC are widely used as substrate materials for conventional optical disks[1], however, their performances are not sufficient enough for MO disk use. Since MO disk system should detect a slight change in Kerr rotation angle, substrates should be transparent, low in birefringence and dust free. Glass substrates satisfy these requirements and have many advantages because of its excellent optical, mechanical, thermal and chemical properties.

In addition, an optical disk substrate needs grooves as guide track for a laser beam and pits for address information on the surface. We have fabricated the preformatted glass substrates. The grooves and the pits are directly formed on the glass surface by reactive ion etching(RIE).

In this report, the fabrication method of the glass substrates and readout characteristics of preformat signals are described.

2.FABRICATION PROCESS OF GLASS DISK SUBSTRATE

Figure 1 shows the fabrication process of the glass disk substrates. Photoresist is coated by spin method on a glass substrate. The glass substrate is contacted to a photomask fabricated by convetional mastering technique[2] and is exposed by UV light. After being developed and etched by RIE in the CCl_4 gas, the photomask pattern is duplicated to the glass substrate. Finally, residual photoresist on the substrate is removed. In this process, perfect contact between the photomask and the substrate should be required for achieving uniform grooves and pits.

3.READOUT CHARACTERISTICS OF PREFORMAT SIGNAL

A SEM photograph of grooves and pits is shown in Figure 2. Edges of the grooves and the pits are etched clearly. The tracking error signal and the readout signal are shown in Figure 3. Stable tracking operation can be expected from the uniform envelope of tracking error signal and clear waveform of readout signal. For optimum signal modulation, only a certain range of groove and pit dimensions is satisfactory.

4.CONCLUSION

Preformatted glass substrates have been fabricated by using RIE method. It is showed that the glass substrates have sufficient properties for MO disks.

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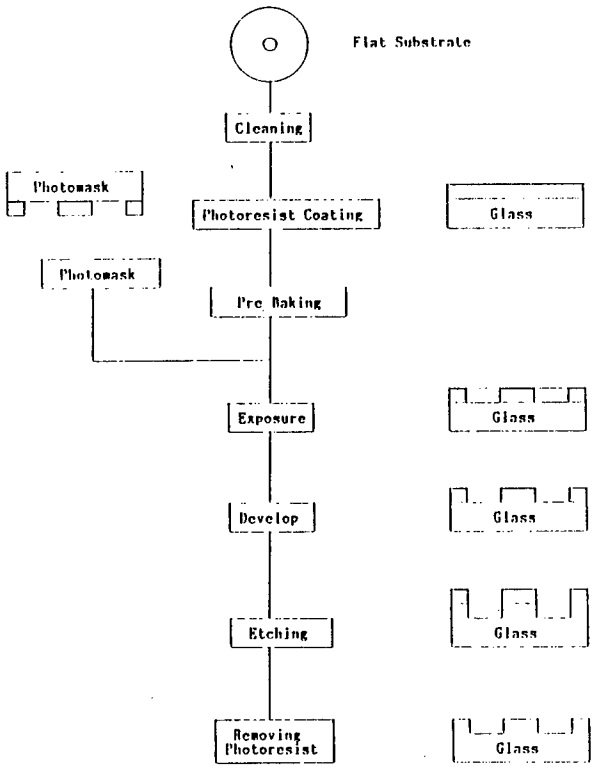

Figure 1 Fabrication process of glass disk substrate.

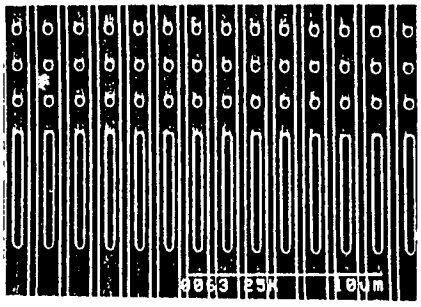

Figure 2 SEM photograph of grooves and pits.

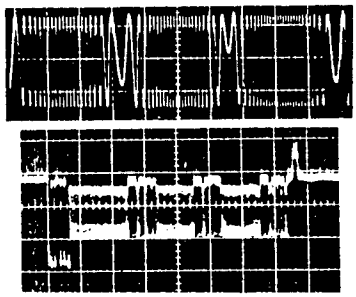

Figure 3 Tracking error signal and readout signal of prepits.

RADIAL GRADED INDEX DOPED-SILICA LENSES PRODUCED BY A SOL-GEL LEACHING TECHNIQUE

Kazuo Shingyouchi, Shirou Konishi
Cable Research Laboratory, Hitachi Cable Ltd.
5-1-1 Hitaka-Cho, Hitachi, Ibaraki, Japan

I. INTRODUCTION

A new technique for producing radial gradient refractive index (r-GRIN) Ti doped-silica rod lenses has been developed employing a sol-gel leaching method. The obtained lenses give good image and show high coupling efficiency with optical fibers. Moreover they have a fairly good resistance to heat, humidity, and radiation.

II. FABRICATION

The fabrication process of r-GRIN lenses consists of three steps: (a) preparation of the wet gels from a mixture of Si and Ti alkoxides, (b) leaching of the Ti component, and (c) heat treatment of the leached wet gels to produce oxide glasses.

III. PROPERTIES

Environmental stability of the lenses was evaluated by their induced absorption as shown in Table 1. The induced absorption was determined from the increment of coupling loss at 0.8 μm between GI fibers with lenses before and after testing under each environment.

(1) Heat resistance

The silica based lenses were heated to 1000℃ in air for 2 h. No melting, deforming, or discoloring were observed. The value of induced loss was nearly 0 dB.

(2) Humidity resistance

The samples were placed in a chamber with a water vapour atmosphere at 121℃ and 2 atm for 10 h. The silica based lenses did not undergo devitrification and no increase in loss was found.

(3) Acid resistance

The samples were put into 1N-HCl at room temperature for 5 h. In the silica based lenses no devitrification or cracking occurred and no change in loss was detected.

(4) Radiation resistance

The irradiations were made with a ^{60}Co source at a dose rate of 1 Gy/min. Exposure of the silica based lenses to radiation doses of about 1000 Gy was found to induce losses of as much as 3.7 dB.

(5) Spread of beam

Spreading of the output beam was verified experimentally using the method illustrated in Fig. 1. The silica based lenses had a good beam collimation.

(6) Coupling efficiency with optical fibers.

The relation between coupling loss and lens spacing was examined using GI fibers. The values of coupling loss were maintained at about 1.7 dB up to the lens spacing of 150 mm.

IV. APPLICATIONS

The r-GRIN lens is a useful component for microoptical systems. With its excellent resistance to heat, humidity, and radiation, it can be deployed in many applications. For example, optical switches can be used in radiation environments such as found in nuclear power stations. Novel optical devices are envisaged which utilize the low coupling losses at longer spacings.

Table 1 Environmental stability of lens

items	condition	stability	
		silica based	multicomponent
heat resistance	1000°C 2h	0 dB	yellow at 600°C melt at 700°C
humidity resistance	121°C 2atm, 2h	0 dB	devitrification
acid resistance	25°C, 5h 1N-HCl	0 dB	devitrification crack
radiation resistance	1000 Gy 25°C	3.7dB	18.4 dB

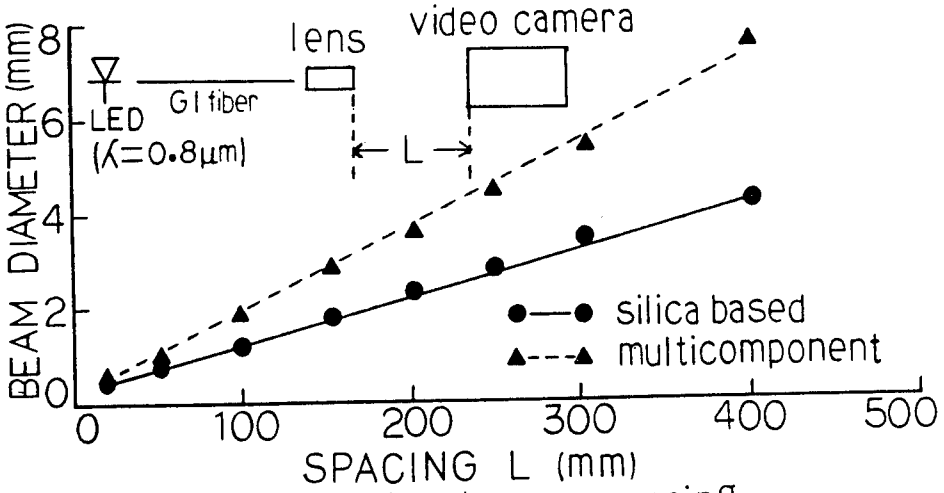

Fig.1 Beam diameter vs. spacing

PHYSICAL PROPERTIES OF SEMICONDUCTOR MICROCRYSTALLITES DOPED IN SiO_2-GLASS THIN FILMS PREPARED BY RF-SPUTTERING

Keiji Tsunetomo, Hiroyuki Nasu[+], Haruyuki Kitayama,
Akira Kawabuchi and Yukio Osaka
Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima, Saijo 724, Japan
[+]Faculty of Engineering, Mie University,
Tsu, Kamihama 514, Japan

I. INTRODUCTION

Recently, Yumoto et al. found optical bistability in semiconductor-doped glasses with the relaxation time of picosecond order, and these results expanded the application of the glasses to a potential candidate as an important device for the optical computer system.

Typical semiconducting microcrystallites in the bulk glasses were spherical and 60-80A in diameter. Thus the microcrystallites can be considered to be "quantum dots". It is well known that the continuous electronic energy levels in bulk bodies are quantized and the energy of the lowest conduction band relative to that of the highest valence band, that is the band gap, increases with the decrease of the microcrystallite size of the quantum dots.

Although these results have been sequentially published, the glasses measured were commercial filter glasses prepared by the conventional melting and quenching technique. In a present paper, we report the successful preparation of CdSe, CdTe and GaAs microcrystallites doped into SiO_2-glass thin films by the magnetron sputtering technique.

II. EXPERIMENTAL PROCEDURE

Thin films of silica glass doped with the semiconducting microcrystallites were prepared by a conventional magnetron rf-sputtering method. The preparation technique was dependent on the semiconductor dopants, except for the sputter gas (pure Ar), the pressure ($5x10^{-3}$Torr), the sputtering time (from 20min to 90min, depending on the sputtering rate), and the SiO_2 target of 10cm in diameter located beneath the semiconductor chips.

The average microcrystallite diameter was determined by two kinds of methods. One was the measurement of the full width at half maximum (FWHM) of the X-ray diffraction (XRD) lines and the other was direct observation by transmission electron microscopy (TEM).

III. RESULTS ON CdSe-DOPED SiO_2-GLASS THIN FILMS

We report only the results on CdSe-doped glass which is the most interesting material for optical functional devices.

The mean diameters of the microcrystallites doped into the films are controllable by changing the relative surface area of the semiconductor chips, the input power and the substrate temperature, and this fact seems to be a great advantage in tailoring microcrystallite size doped into the films.

In this way, CdSe-doped glasses with the average microcrystallite diameter (26Å-15Å) were prepared. The optical absorption edges at room temperature show a blue shift with decreasing diameter. At a liquid nitrogen temperature, the shoulders near the absorption edge were found, which seems to be caused by a quantization of energy levels in a microcrystallite.

IV. ADVANTAGES OF THIS TECHNIQUE

The advantages of this technique can be pointed out as follows. (1) This technique can drastically increase the concentration of the microcrystallite. CdTe microcrystallite-doped films can contain more than 40wt% (15at%) microcrystallites, while the conventional semiconductor-doped glasses contain no more than 2wt% semiconductor microcrystallites. (2) Microcrystallites can be formed in pure silica glass thin films. For the conventional semiconductor-doped glasses, some additives such as Na_2O or B_2O_3 are added to lower the melting point, resulting in the possible defects in semiconductor microcrystalline lattice. These defects contribute to deep-level luminescences in addition to a edge emission. However, our films only reveal a edge emission. This feature shorter the relaxation time of optical switch compared with conventional doped glasses. (3) Thin-film structure is appropriate for application as devices in sophisticated and complicated systems such as integrated circuits and waveguides.

Er^{3+} DOPED FLUOROZIRCO-ALUMINATE GLASSES

H.Yanagita, K.Okada, K.Miura, H.Toratani and T.Yamashita
Materials Research laboratory
HOYA Corporation
Akishima-shi, Tokyo, 196 Japan

INTRODUCTION Lasing at 3 μm region (Er^{3+}:$^4I_{11/2}$ -> $^4I_{13/2}$) is of great interest for surgical application [1]. A fluorozirco-aluminate glass (AZF) was evaluated for 3 μm laser in terms of influence of oxygen impurity, lifetimes of laser levels and effects of codoped deactivator ions.

MEASUREMENTS All measurements were performed at room temperature. Fluorescence spectra were obtained under CW Xe lamp or LD (807nm) excitation with liq. N_2 cooled InAs detector. Fluorescence lifetimes (τ) were measured by selectively exciting initial and terminal levels with proper optical filters. Photomultiplier or Ge-photodiode was used as a detector. Phonon energy of glass network was estimated from IR vibrational spectra.

RESULTS & DISCUSSION In glasses, the laser operation has been demonstrated in ZBLA and ZBLAN with 6-8wt% ErF_3 [2,3]. Higher Er^{3+} content is considered to be preferable for lasing on this transition [4,5]. But it is difficult for these glasses. It was found that AZF (Al-Zr-Y-Mg-Ca-Sr-Ba-Na,F+Cl) can be incorporated with ErF_3 up to 20mol% (30wt%). This is a strong advantage of AZF. Moreover, AZF has good mechanical and chemical properties which are important in practical applications [6].

Emission properties of AZF were compared with those of other fluoride glasses (ZBLAN and fluoroaluminate glass AYF), fluorophosphate glass (FCD10), tellurite glass (AOT5) and phosphate glass (LHG8) [Table 1]. Spontaneous emission probabilities for 2.7 μm [A(->$^4I_{13/2}$)] and branching ratios (β) are nearly the same for all of these glasses (except for AOT5). However only ZBLAN and AZF have reasonably high quantum efficiencies (η x β, $\eta=\tau/\tau_R$:radiative quantum efficiency, β:branching ratio) for this transition. It was indicated that multiphonon decay had a great role on this transition with such a small energy gap. It was also found that this 2.7 μm emission was significantly degraded by adding only several thousand ppm oxygen [$(PO_3)^-$] into 10% Er^{3+}:AZF (Fig.1-), but that oxygen impurity less than several hundred ppm incorporated under normal melting conditions has no influence on the emission intensity (Fig.1-).

In most materials, τ(initial level $^4I_{11/2}$) <τ(terminal level $^4I_{13/2}$) has been reported (self-terminating). In AZF, that is also the case. To get a lifetime inversion, codoping with Ho^{3+} or Tm^{3+} in 10 mol% Er^{3+}:AZF was investigated. In the case of Ho^{3+}, inversion was observed beyond 1% codoping.

CONCLUSIONS AZF will be a good host for 3 μm glass laser because of high quantum efficiency of emission comparable with ZBLAN, high doping of Er^{3+} and good mechanical and chemical properties. It was found that oxygen impurity has no effect on emission properties if it is less than 1000 ppm though the

transition is greatly affected by multiphonon decay process. Ho^{3+} is a suitable ion to solve the self-terminating problem in AZF.

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Table 1. Intensity parameters Ω, spontaneous emission probabilities A, branching ratio β at 2.7 μm, radiative lifetimes τ_R, measured lifetimes τ, quantum efficiencies η for $^4I_{11/2}$ level and peak wavenumbers ω in IR transmittance spectra in 6 glass systems at 300 K (<MD> means magnetic-dipole induced A).

Matrix	Ω_2 Ω_4 Ω_6 ($\times10^{-20}cm^2$)	$A(\rightarrow{}^4I_{13/2})$ (s^{-1}) <MD>	$A(\rightarrow{}^4I_{15/2})$ (s^{-1})	β (%)	τ_R (ms)	τ (ms)	η	$\beta\eta$ (%)	ω (cm^{-1})
ZBLAN	2.97 1.23 1.17	20.5 <7.4>	105.7	16	7.9	8.4	~1	16	500
AZF	2.08 1.29 1.15	18.7 <6.8>	92.0	17	9.0	7.3	0.8	14	620
AYF	1.28 1.35 1.01	16.8 <6.4>	79.7	16	10.3	3.1	0.3	5	620
FCD10	2.88 1.40 1.27	20.1 <6.8>	105.2	16	8.0	×	~0	-	1120
AOT5	6.05 1.78 1.07	53.0<17.6>	319.1	14	2.7	×	~0	-	660~920
LHG8	4.76 1.14 0.86	19.3 <8.0>	97.9	17	8.5	×	~0	-	1270

ZBLAN : 53Zr-20Ba-4Er-3Al-20Na (mol%)
AZF : 25Al-13Zr-6Y-5Er-46R-3Na-2NaCl <R=Mg+Ca+Sr+Ba> (mol%)
AYF : 36Al-7.5Y-2La-50R-4.5Er <R=Mg+Ca+Sr+Ba> (mol%)
FCD10 : Fluorophosphate glass (HOYA)
AOT5 : Tellurite glass (HOYA)
LHG8 : Phosphate glass (HOYA)

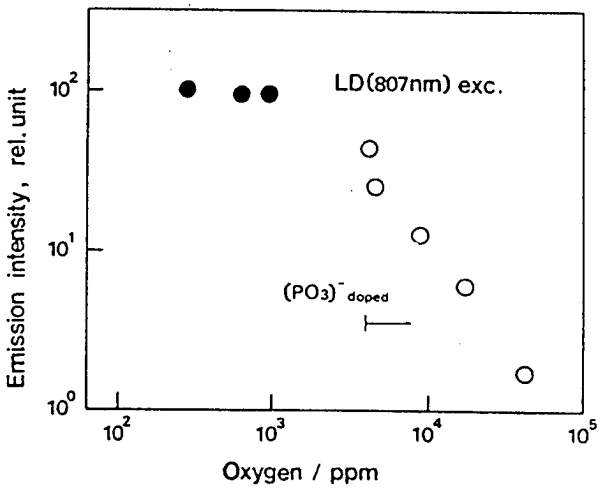

Fig. 1 Relative intensities of 2.7 μm emission of AZF (10mol% ErF_3) as a function of oxygen content

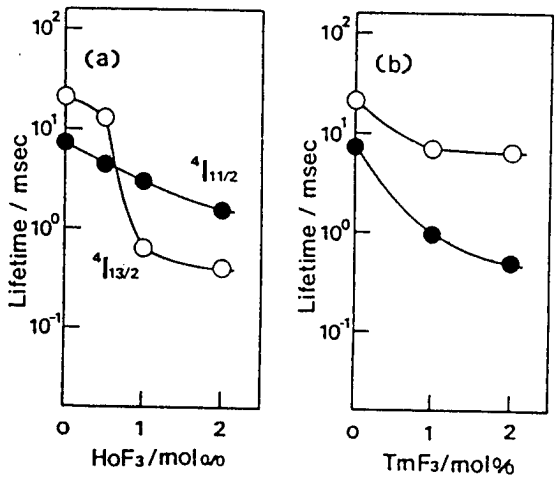

Fig. 2 Lifetimes of Er^{3+} laser levels as a function of (a) HoF_3 and (b) TmF_3 concentrations

POROUS GLASS CAPILLARY FOR SEPARATION

Tetsuo YAZAWA, Hiroshi TANAKA and Kiyohisa EGUCHI
Glass and Ceramic Department
Government Industrial Research Institute, Osaka
Ikeda, Osaka 563 Japan

Recently, active researches on membrane material have been carried out. Of all the polymers used in membrane processes, porous glass has a unique place[1].

1. Sharp pore size
2. Pressure stability
3. Temperature stability
4. Stability against organic solvents

Borosilicate glass having appropriate composition can be separable into two phases. One phase is silica rich phase and the other phase is alkali borate rich phase. Impregnating this phase separated glass in acid solution, alkali borate phase into acid solution, so we can obtaine porous glass.

Depending on the form of the membrane used the type of modules are flat-plate, spiral wound, tubular and capillary (including hollow fiber) modules. Capillary modules allow the highest packing density (that is the density of membrane area per module volume). Here, capillaries are thin tubes with an outer diameter 500μm and inner diameter 300μm. The pore radii of capillaries range from 20nm to about 1.5μm. Fig.1 shows the shape of porous glass capillary and its EM-micrographs. Fig.2 shows the pore distribution of capillaries. The composition of mother glass of porous glass capillary is 62 SiO_2· 16 B_2O_3· 12 ZnO· 5 Na_2O ·5 ZrO_2· 1 Al_2O_3 (wt%). A porous glass obtained from the mother glass makes a rapid increase in alkali durability[2], so we can obtaine a porous glass capillary easily.

Emulsion separation is one of the attractive example of the application of porous glass capillary. The Porous glass capillary membrane cannot permeate oil emulsions, but modified hydrophobic membrane can permeate only oil emulsions.

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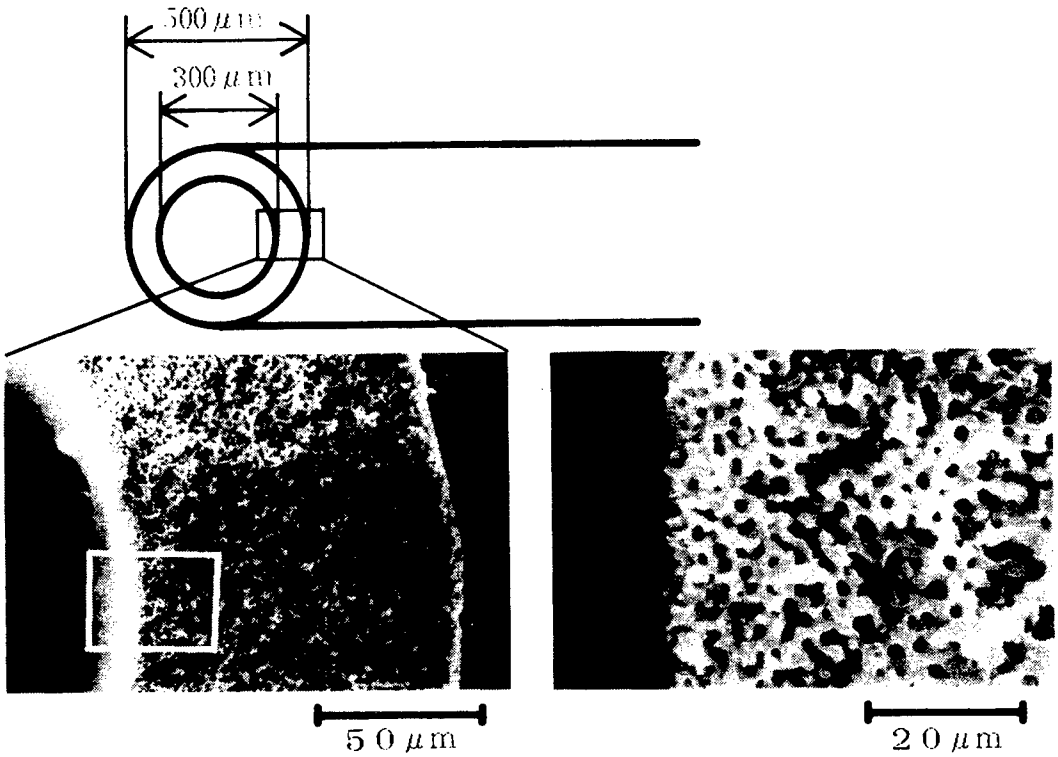

Fig.1. Shape of porous glass capillary and its EM-micrographs.

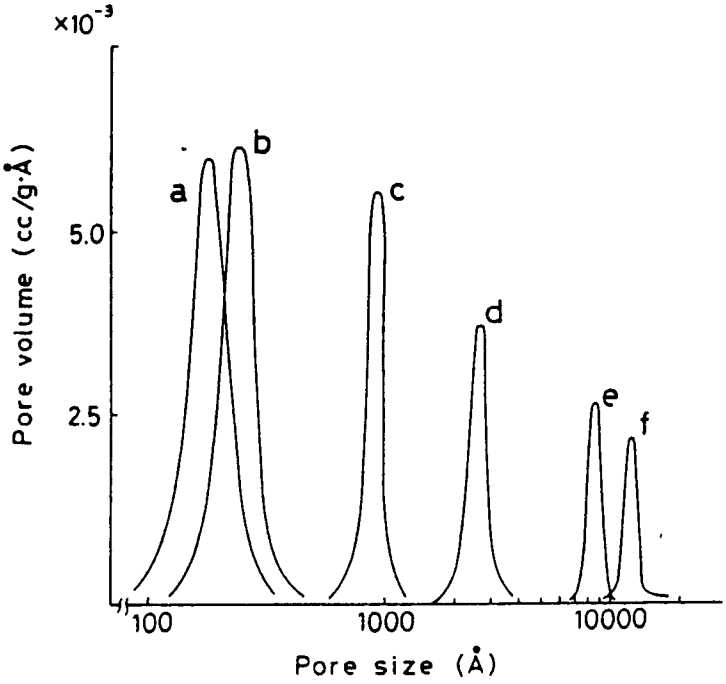

Fig.2. Pore distribution of cappillaries

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