©*Proc. Indian natn. Sci. Acad.*, 52, A, No. 1, 1986, pp. 159–175.
Printed in India.

SOL-GEL ROUTE TO INORGANIC MATERIAL SYNTHESIS*

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(*Received 4 December 1985*)

The sol-gel process has added a new degree of freedom to the synthesis of various materials e.g., glasses, glass-ceramics and oxides of practical importance. This paper reviews the present state of understanding with regard to the mechanisms involved in the gel formation and densification on specific heat-treatments. The wide range of materials prepared by this technique are delineated and some of its future possibilities are discussed.

Key Words : Sol-Gel Process; Inorganic Material Synthesis; Glass Ceramiics; Glasses.

INTRODUCTION

SOL-GEL method of preparing materials has emerged as a powerful technique in recent years.[1] Initially, the interest in classical gel-derived materials arose from some of their special characteristics viz., submicron particle size leading to high reactivity and low processing temperatures, high purity and homogeneity attainable in multi-component systems.[2–5] Lately, the advantages of sol-gel process have been exploited in making a wide range of materials especially, glasses, glass-ceramics and oxides of practical importance.[6–8] In this paper, we give an overview of the subject emphasizing on the current understanding of the mechanisms of gel formation and their subsequent conversion to the desired products by suitable heat treatment.

SOL-GEL MECHANISM

A sol represents a suspension or dispersion of discrete colloidal particles, while gels are colloidal solids usually containing also a fluid component and having a network internal structure so that both the solid and the fluid components are in a highly dispersed state. Gel is a broad term[9] covering both liquid-rich and liquid-free systems. The term xerogel is used to designate dry gels, e.g. a sheet of gelatin, a foil of cellophane etc.

Gelation

Gelation, the setting of colloidal solutions, can proceed by different routes[9] to produce either colloidal or polymeric gels.[10] In colloidal gels, electrolytic or steric effects in the precursor solution or sol dominate gel formation, while for polymeric gels, the relative rates and extents of chemical reactions (including polymerization) are critical. In organic systems, the gel consists of polymers or long chain molecules crosslinked to create a tangled network which extends through

*Presented at the INSA Colden Jubilee Symposium on Solid State Chemistry held at INSA, New Delhi during December 4–6, 1985.

a liquid, whereas, the so-called colloidal gels consist of discrete colloidal particles which are linked together into branched chains which form extensive networks throughout the liquid medium by a mechanism similar to flocculation (hydrogen bond, electrostatic attraction).[11] By controlling the *p*H, dilution, and water content of the solutions, polymeric or colloidal gels can be obtained.[10] At low *p*H (< 2.5) in alkoxide solutions with low water to alkoxide molar ratios, relatively linear polymeric species are produced, which can crosslink to yield a polymeric gel. At higher *p*H values (> 2.5), regardless of the water content, alkoxides and polysilicic acids polymerize to form colloidal silica or weakly crosslinked clusters.

Polymeric Gels—The most widely used starting materials for making polymeric oxide gels are metal alkoxides. These compounds have the general formula $M(OR)_n$, where M is a metal ion and R is an alkyl group. There are essentially four steps involved in the process of formation of a polymeric gel. These are as follows;

(*a*) Reaction of several metal or nonmetal alkoxides

(*b*) Hydrolysis : $M(OR)_n + xH_2O \rightarrow M(OH)_x(OR)_{n-x} + xROH$ ...(1)

(*c*) Polycondensation :

$$-M-OH + OH-M- \rightarrow -M-O-M- + H_2O \text{ (Dehydration)} \quad ...(2)$$

$$-M-OH + RO-M- \rightarrow -M-O-M- + ROH \text{ (Dealcoholation)} \quad ...(3)$$

It is to be noted that all the above reactions take place simultaneously.[12] Gel state can be achieved in two ways.[1] In the first case, removal of the solvent forms

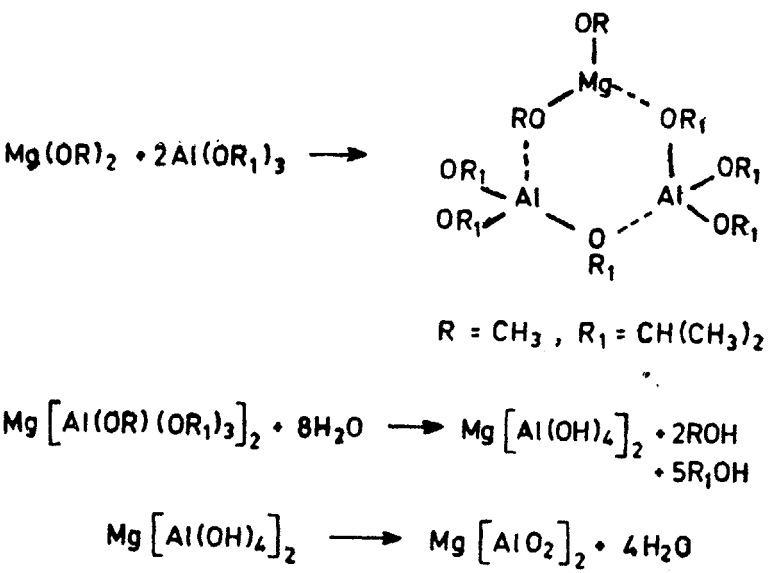

FIG 1 Spinel synthesis *via* alkoxide route.[7]

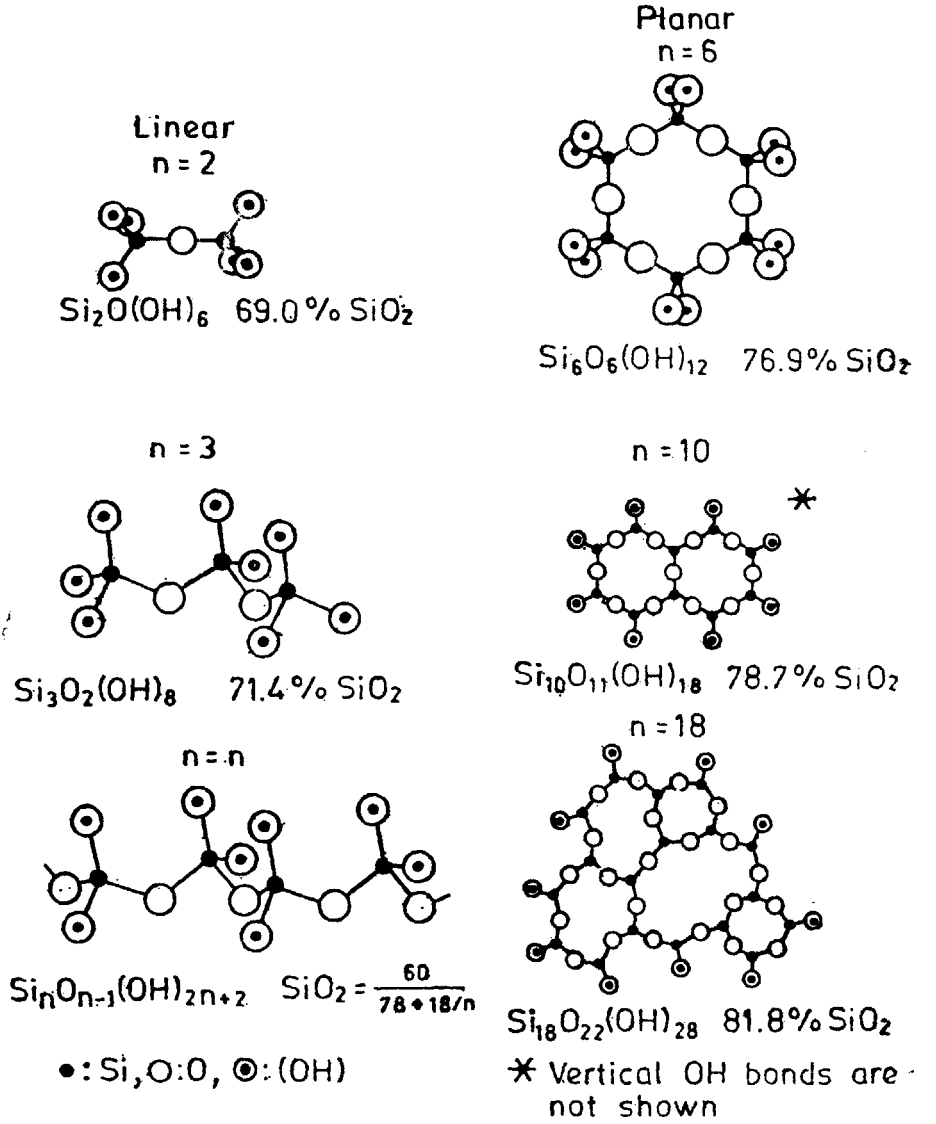

FIG 2 Example of how molecular size and polymerization type affect chemical make-up of silanol polymers.[14]

the polymer species into closer proximity, thereby increasing the probability of crosslinking between them. When sufficient crosslinking is achieved, the viscosity of the solution increases rapidly and the solution gels. In the second case, aging of the solution allows the dehydration and hydrolysis reaction to proceed whenever polymer species randomly collide in solution. Continued polymerization leads to network formation, expulsion of organic groups, and gelation. Several solution parameters must be considered to ensure success in obtaining polymeric gels. The

important parameters are molar ratio of water to alkoxide, *p*H of the solution (Acid or base can act as a catalyst)[13] and temperature. Fig. 1 gives a typical example of spinel synthesis by the alkoxide route[7] and Fig. 2 depicts the chemical make up of Silanol (—SiOH) polymers of different sizes made by a similar reaction.[14]

Colloidal Gels—Colloidal gels are typically formed from metallic salt solution (Chlorides, nitrates, sulfates etc.) and oxide or hydroxide sols. The presence of potential determining ions (H^+ or OH^- for oxide/hydroxide systems) as well as nonpotential determining ions affect the stability of the colloids through their effect on double layer.[15] According to Dell,[16] there are three principal methods to form a gel from concentrated sols; (*a*) removal of water; (*b*) neutralization of the stabilizing anion; and (*c*) removal of acid by solvent extraction. Yoldas[17] used both dehydration and neutralization (using ammonia) to gel boehmite (hydrous aluminium oxide) sols. Gelation by extraction of acid has been discussed by Dell,[16] who noted that the technique had been applied to many ceramic systems including calcia stabilized zirconia, manganese zinc ferrite, strontium ferrite, yttrium iron granet and lead zirconium titanate. Marboe and Bentur[18] have discussed the effects of precipitation and aging conditions on the formation of gels (aluminium hydroxide gels). When this material is precipitated from cold acidic solutions by rapid addition of base, an amorphous gelatinous solid is formed upon dehydration, the solid often forms aluminium trihydrate $Al_2O_3.3H_2O$, but under suitable aging conditions bayerite $Al(OH)_3$ is formed. If aluminium hydroxide is formed by very slow addition of base to a hot aqeuous solution of an aluminium salt, the resulting amorphous gel ages to form boehmite AlO(OH). The *p*H of the solution also plays an important role here. When $Al(NO_3)_3$ is decomposed to the hydroxide by base addition at *p*H = 10, aging for 6.00hr develops microcrystalline $Al(OH)_3$, but precipitation at *p*H = 5 yields gels which retain their amorphous character even after 6 days. The effects of temperature in case of aluminium hydroxides system have been studied by Yoldas.[19] For gels formed by hydrolysis of aluminium sec-butoxide and aluminium isopropoxide at 20 °C, the precipitate consists largely of amorphous monohydroxide, while the same process performed at 80 °C produces boehmite.

Aging and Desiccation

The effect of volume changes on stresses produced during drying has been discussed by Cooper.[20] The permissible drying rates, consistent with the avoidance of fracture, were evaluated and found to vary inversely with the thickness of the body being dried. Changes in gel structure during aging and desiccation were studied by Zarzycki *et al.*[21] During the initial stages of drying, the volume change of the gel is equal to the volume of evaporated liquid. The gel network is still flexible and can rearrange to accommodate the decreasing volume. All pores are filled with solvent and liquid-air interfaces are not present. As drying proceeds, the gel network becomes more restricted, and the removal of liquid leads to the formation of such interfaces and the development of capillary stresses. The tendency toward fragmentation due to capillary stress is determined by both the average pore size and the pore size distribution. The larger the diameter of the pores, the lower

is the capillary pressure and at the same time minimum in pore size variations gives rise to minimum pressure differences between the capillaries with consequent lowering of stresses. An example is provided by the work of Yoldas[17] on Al_2O_3 gels. It was found that the tendency to form monoliths is maximum at an acid/hydroxide ratio equal to 0.07. Interestingly, this ratio corresponds to the maximum in pore size and minimum in pore size variation.

Zarzycki[21] compared three different drying procedures : slow drying, addition of surfactants during gelation, and hypercritical evacuation. The gels were prepared by hydrolysing tetramethylsilane in methanol with $H_2O/TMS = 4.65$. The most effective method for producing monolithic dried gels was found to be hypercritical drying. Such drying was effected by heating the gel with methanol in an autoclave to temperatures and pressures exceeding the critical point of methanol. In general, hypercritical drying produces dried gels with much larger pore volumes than that obtained by conventional evaporative drying. Because of the absence of liquid-vapour interfaces in case of hyper-critical drying no capillary forces arise to cause network collapse and the net shrinkage during drying is very low.

Wang and Hench[22] studied the principal mechanisms of sol-gel process which uses a drying control chemical additive (DCCA) in the sol to prevent fracture during drying. The system investigated was $20Na_2O.80SiO_2$ and the properties of gels made from this system with and without formamide as a DCCA were compared. A primary advantage of the DCCA in the gel is that the critical shrinkage rate is substantially higher. Consequently, the evaporation rate can be higher and drying times reduced several fold. The increase in critical shrinkage rate has been attributed to the formamide increasing the gel strength by amine group bonding of the gel particles.

In order to avoid crack during drying, double process of dispersion, drying and redispersion has been employed by Rabinovich *et al.*[23] for fumed silica (colloidal silica formed by flame decomposition of $SiCl_4$) sol-gel system. The material was dispersed using a blender in twice deionized water to form a sol. The *p*H of the sol was adjusted. Gelation was done by drying the sol at 150 °C. The dried material crumbled and this material was redispersed to get a sol aging. After casting and gelation crackfree monolith was obtained. This effect of double process has been ascribed to the formation of an interconnected structure of pores in the 1–10μm size range allowing water evaporation without significant shrinkage.

Wall adhesion of the gel is another problem which needs thorough studies. Klein and Garvey[24] have proposed an idea of "floating" a gel on mercury in order to avoid stresses during shrinkage. Further research is needed in this area.

The drying behaviour of polymeric gels, such as those obtained by the acid catalysis of silicon alkoxide at low water contents can be considerably different with respect to those of colloidal gels. In these gels, the polymeric species are weakly crosslinked and as solvent is removed, they can deform readily and form a dense gel structure while the polymer itself shrinks and forms more crosslinks. The overall

result can be a dense dried gel with no large voids. Schaefer and Keefer[25] recently postulated that phase separation should be observed in such inorganic systems. However, the resulting phase separated structure may bear no relation to the structure of the gel originally formed in solution.

The *p*H of the initial solution has also an important role in the structure of dried polymeric gel. Fig. 3 gives a schematic representation of gel desiccation[26] in acid and base conditions for polymeric gels, and the desiccation of colloidal gels under two particular conditions have also been shown.

Sintering

Depending upon the nature of the gel and the conditions of its formation, any of the following reactions may occur during firing : (*i*) decomposition of salts; (*ii*) carbonization or combustion of residual organic groups; (*iii*) desorption of absorbed solvent from the walls of micropores; (*iv*) dehydration (polymerization); (*v*) formation of micropores or even foams from gas generation; (*vi*) collapse of micropores; (*vii*) sintering and densification.

Yamane *et al.*[27] have recognized several temperature ranges of importance in the firing of silica gels prepared by alkoxide route. These are (*a*) 100–200 °C, desorption from the micropore walls of physically absorbed water; (*b*) 300–500 °C decomposition of organic compounds into CO_2; (*c*) 400–500 °C, collapse of small pores (*d*) 700–900 °C, collapse of larger pores. With non-optimized firing schedules, residual organic groups and H_2O can lead to blackening and fragmentation, as well as to the formation of bloated and foamed samples.

The densification of gel is a complex process.[28] At least four mechanisms contribute to gel shrinkage : (*a*) capillary contraction; (*b*) condensation; (*c*) structural relaxation; and (*d*) viscous sintering. In case of borosilicate compositions, the above authors identified three temperature regions having different shrinkage rates. These are : (*i*) 25–150 °C, weight loss with negligible shrinkage; (*ii*) 150–250 °C, shrinkage and weight loss; (*c*) 525–700 °C, dramatic shrinkage with little weight loss. Shrinkage in region (*i*) has been attributed to capillary contraction. Shrinkage in region (*ii*) is due to skeletal densification which occurs primarily by condensation reactions accompanying the loss of water and organic residue. According to these authors some amount of shrinkage in the temperature range 400–525 °C is due to structural relaxation. The rapid shrinkage in region (*iii*) is the result of viscous flow which permits the tiny pores in the gel to collapse. It should be noted that the processing variables during gelation may affect the shrinkage to some extent. Brinker and Scherer[29] found that gels prepared with low *p*H and low water of hydrolysis, which should be only modestly crosslinked, exihibit much greater densification at low temperatures than the more highly crosslinked gels prepared at high *p*H and high water of hydrolysis. Brinker and Scherrer[26] also observed that the amount of water and its distribution as well as heating rate are important to the kinetics of gel densification.

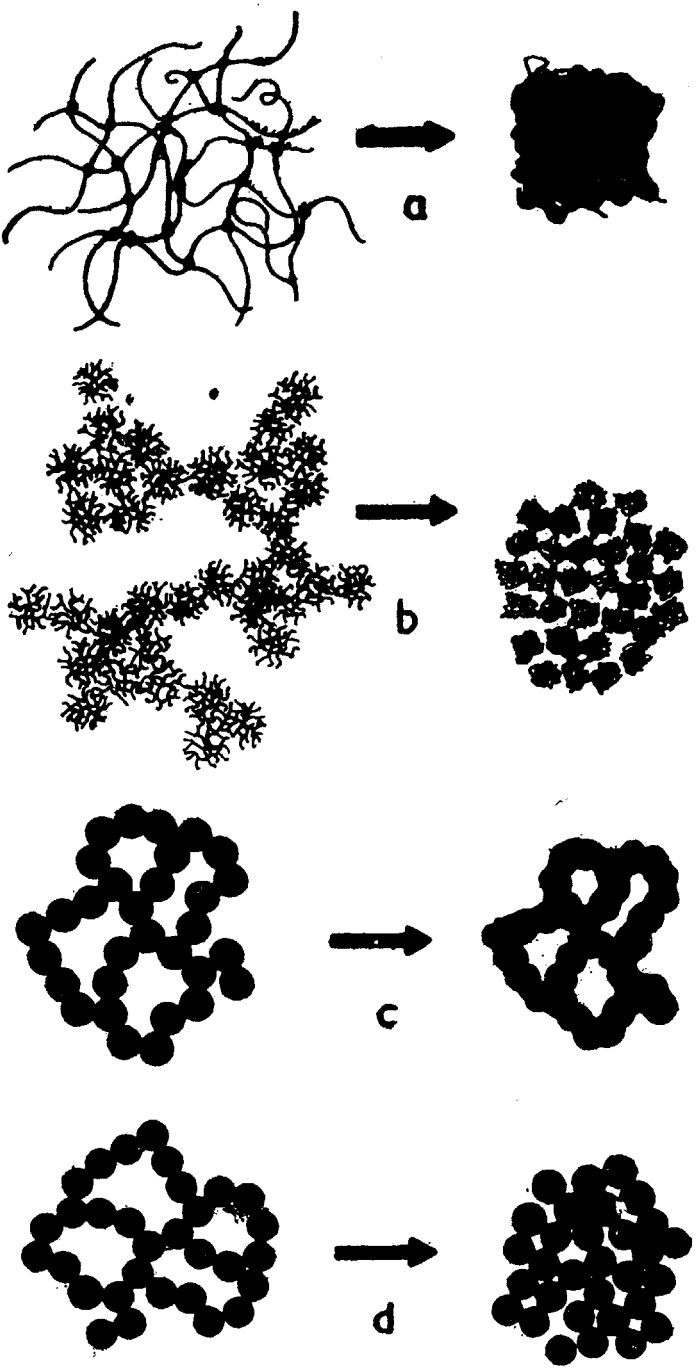

FIG 3 Schematic representation of gel desiccation for (*a*) acid-catalyzed gels, (*b*) base-catalyzed gels, (*c*) colloidal gel aged under conditions of high silica solubility, (*d*) colloidal gel composed of weakly bonded particles.[26]

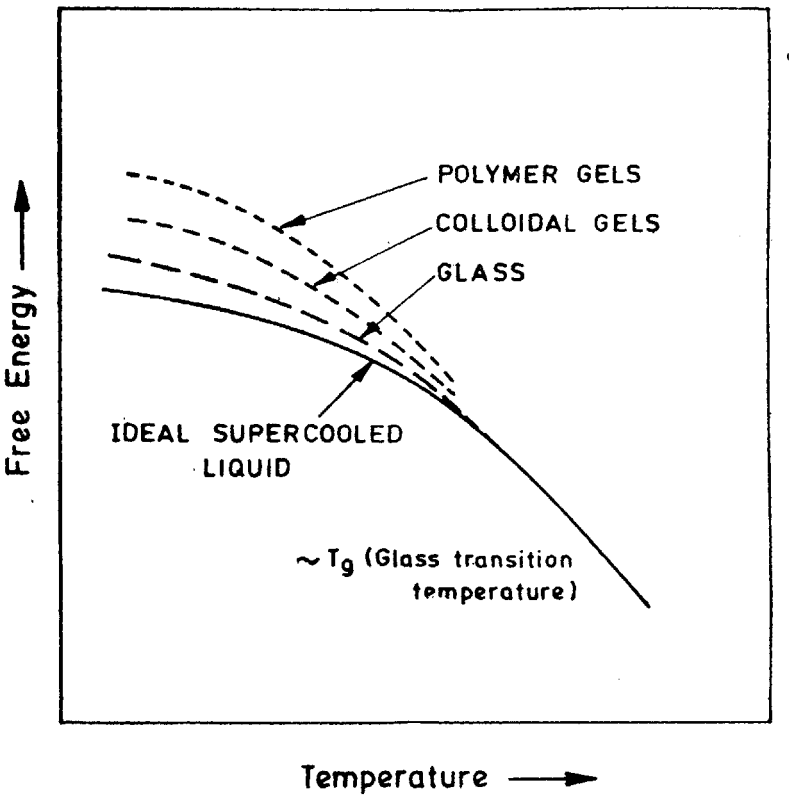

FIG 4 Schematic representation of free energy-temp. relations between various desiccated gels, glass, and an ideal supercooled liquid of the same oxide composition.[26]

Thermodynamically, xerogels (dried gels) may be considered high free energy materials compared to their dense oxide conunterparts prepared by melting/ sintering. The structural characteristics of the gel contribute to this high free energy. Surface area created by the formation of pores during desiccation makes the largest contribution toward this surface energy. Fig. 4 gives a schematic representation of free energy *vs* temperature relations between various desiccated gels, glass, and an ideal supercooled liquid of the same composition.

SOL-GEL DERIVED MATERIALS

In the following sections, we discuss the preparation of different types of materials undertaken to date using the sol-gel technique.

Ceramics and Minerals

Since stoichiometry is controlled by the first step of the reaction between alkoxide partners the sol-gel technique is increasingly being applied to the synthesis of minerals and ceramics. The other favourable reason for this technique is the

possibility of low temperature densification of the solid due to the initial high surface energy of the gel particles.

Using $Al(OR)_3$ and $Ti(OR)_4$ as raw materials, Duerksen *et al.*[30] prepared sintered titanate powder. This material is of interest to space and nuclear engineering due to its high temperature shock resistance and high negative temperature coefficient of electrical conductivity. Komarneni and Roy[31] have reported a new sol-gel process for the preparation of TiO_2 gel spheres. The gel sphere preparation process involves the dispersal of the polymerized titanium ethoxide solution into a two phase liquid suspension in kerosene followed by heating in a microwave oven. The xerogel spheres obtained by this process were in the range of tens of micrometers in diameter. Spherical Na–Li aluminate particles have been successfully prepared[32] by using sol-gel technique. ThO_2 and $(U, Pu)O_2$ microspheres have also been prepared by the sol-gel route.[33–35] Suzuki *et al.*[36] synthesized mullite powder by calcination of the products of hydrothermal treatment of mixed alkoxide or mixed sol.

By co-precipitation of $Al(OH)_3$, and $Mg(OH)_2$ Bratton[37] was able to form $MgAl_2O_4$ (spinel). Dislich[38] prepared the same spinel *via* alkoxide route. Gels in the system Cr_2O_3–Fe_2O_3 have been studied by Bhattacharya *et al.*[39] SiO_2–Al_2O_3 catalyst has been prepared by Barrett *et al.*[40] by using sol-solution technique. Serpentines and related layer silicate minerals have been synthesized by Roy and Roy.[41] Strictly stoichiometric mullite ($3Al_2O_3.2SiO_2$) has been prepared by Mazdiyasni and Brown[42] through alkoxide route. Dense conductive β″-alumina has been synthesized by Chen *et al.*[43] $BaTiO_3$, $KTaO_3$, $KNbO_3$, $K(Ta, Nb)O_3$, $SrZrO_3$ and PLZT, YIG ceramics have been prepared too.[44–46] ZrO_2–Y_2O_3 ceramics have been fabricated by Van De Graaf *et al.*[8] by using metal alkoxide as precursors. Haaker and Ewing[47] have synthesized polycrystalline $ZrSiO_4$, and are envisaging the synthesis of huttonite $ThSiO_4$, Yttrialite $Y_2Si_2O_7$, Olivine Mg_2SiO_4, and silicate oxyapatite $CaLa_4(SiO_4)_3O$. Pentinghous used $Si(OR)_4$ (and other alkoxides)[82] for the synthesis of $NaBSi_3O_8$, which cannot be prepared in any other way since it melts incongruently. Likewise he prepared Mg_2GeO_4, $CsAlSiO_4$, $CsAlSi_2O_6$, $CsAlSi_5O_{12}$. SiO_2-Fe_2O_3 system has been studied by Guglielmi and Prinicipi.[48] Sol-gel method has also been employed to fabricate high-field ZnO varistors[49] and improved ferrite memory-cores.[50]

For materials whose alkoxides are either difficult to make or use, or are too expensive, the method of McCarthy and Roy[51] may be employed to incorporate them into a gel. These workers added the materials to a solution of alkoxides in the form of chlorides, nitrates, sulphates or acetates. This approach was adopted by Hayashi and Saito[52] who produced gels in the CaO-SiO_2 system by mixing TEOS (tetraethyl-orthosilicate) and $Ca(NO_3)_2$ in ethanol.

Glasses

Gel-derived powders are used as batch ingredients for glass melting primarily because of the high degree of chemical homogeneity which they offer. This leads to shorter melting times and lower melting temperatures as well as compositional

uniformity. In sintering or hot pressing amorphous gel derived powders, the key to glass formation is the development of an appropriate heat treatment schedule to remove the residual organic groups and achieve pore collapse without inducing crystallization. These often indicate an upper limit to temperature for processing, above which crystallization precludes the achievement of complete densification as a glass.[53,54]

The physical properties of gel derived glasses are very similar to those of glasses obtained from a melt.[27] But there are notable differences in kinetic behaviour between gel-glasses and melted glasses. Mukherjee *et al.*[5] found that gel derived glasses exhibit a much more uniform microstructure and finer scale of phase separation than corresponding melted glasses. In addition, the rates of crystallization of the gel-derived glasses were much higher than those of melted glasses. The differences in kinetic behaviour were associated with higher OH content of the gel-derived glasses.[5] Weinberg and Nelson[55] reported a marked difference in liquidus temperature between gel-derived and melted glasses. Hench *et al.*[53,54] noted that the aqueous corrosion resistance of gel-derived glasses was considerably less than that of melted glass. Gottardi *et al.*[56] found a sharper glass transition in gel-derived glasses, reflecting a narrower distribution of relaxation times, compared with melted glasses.

Apart from the conventional glasses like SiO_2, SiO_2–Al_2O_3, SiO_2–P_2O_5, SiO_2–P_2O_5, B_2O_3–P_2O_5–Na_2O, SiO_2-Al_2O_3–B_2O_3-K_2O-Na_2O etc.,[10] many novel glasses have been developed by the sol-gel technique. Glasses in the system BeO–CeO_2–ZrO_2 have been reported.[57] Hayashi and Saito[52] have prepared glasses in the system CaO–SiO_2. In this case, transparent glasses were obtained of compositions in the field of the liquid-liquid immiscibility gap, which require very high melting temperatures (2000 °C) and even then are obtainable only as a grossly two-phase or partly crystallized glasses. Glasses in the system Na_2O–ZrO_2–SiO_2 containing high ZrO_2 (upto 33 wt per cent) have been fabricated by Kamiya *et al.*[58,59] Makashima *et al.*[60] studied glasses in the system SiO_2–Al_2O_3–ZrO_2.

Superionic glasses have been prepared by Boilot *et al.*[59b] *via* sol-gel process using alkoxides as raw materials. The systems studied were M_2O–M^1O_2–SiO_2 -P_2O_5 (M = Li, Na, K; M_1 = Zr, Ti) and Li_2O–Al_2O_3–SiO_2–P_2O_5. These glasses were made by heating gels above 400 °C and they generally remain stable upto 700 °C.

Chi[61] was able to synthesize carbon containing glasses by inert atmospheric pyrolysis of glass precursors (dry gels) made from methyltrimethoxysilane and colloidal silica. Brinker *et al.*[62,62a] obtained oxynitride glass when porous, multicomponent silicate gels were heated in flowing and pressurized NH_3. These treatments resulted in dense, homogeneous oxynitride glasses which were synthesized at low temperature ($\leqslant$ 1000 °C) without melting.

Transparent microporous silica has been fabricated by Klein *et al.*[63] These porous glasses can be used as supports for catalysts. The sol-gel procedure also offers the possibility to encase radioactive waste material in glass.[64]

Ohno *et al.*[65] fabricated micron order relief patterned SiO_2 glass using a sol-gel process. The relief pattern was clearly replicated from a master pattern onto the SiO_2 glass surface.

Another kind of sol-gel technique is the fabrication of thin-walled glass hollow spheres. Such spheres (diameter 80–100μm, wall thickness 1μm) are inflated and formed by gases originating from the gel.[7] Dueterium-tritium fuels can be stored within such hollow spheres for thermonuclear fusion.[66] Also hollow glass supports for growing cell cultures have been made by using sol-gel technology.[67]

Glass-Ceramics

In 1971, the first glass-ceramic synthesis by sol-gel route was reported by Dislich;[7] meanwhile numerous syntheses have been reported. For example, partially ceramized glasses were described by Gottardi *et al.*[68] in the system Na_2O–Cr_2O_3–Al_2O_3–SiO_2–ZrO_2. In addition to glass phase, tetragonal and monoclinic ZrO_2, $ZrSiO_4$, Al_2O_3/Cr_2O_3 are obtained as crystalline phase, depending on the composition and heat treatment temperature. As a result of the higher homogeneity and reactivity possible in the sol-gel procedure, these phases are formed at relatively lower temperature.

Glass-ceramics in the system SiO_2–Al_2O_3–MgO, containing high quartz, low quartz and spinels as crystalline phases (small amount of TiO_2 and Li_2O were added to the glass compositions) have been studied by Holand *et al.*[69]

Coatings and Thin Films

Since drying stresses can readily be accommodated for thin gel layers, the use of gel techniques to produce coatings has acquired much importance. Using gel techniques, antireflection films with attractive properties have been prepared by a number of workers. These include single layer TiO_2–SiO_2 films,[70] SiO_2–Na_2O–B_2O_3 films.[71] Multilayer TiO_2–SiO_2 films[72,73] and BaO–Al_2O_3–B_2O_3–SiO_2 films of Brinker *et al.*[73,74]

Gel technology has also been exploited to make protective coatings. Interesting exambles are β-Al_2O_3 coating[74a] on substrates to enhance mechanical and chemical properties, CeO_2 coating to gas cooled reactor materials for environmental protection,[10] coatings of Al_2O_3 on silicon carbide and silicate glass fibres,[75–77] Si_3N_4 coatings on quartz and sapphire,[78] expansion adjusted SiO_2–GeO_2 coatings (for protecting nonoxide ceramics against oxidation at high temperature.[79]

Sol-gel process has been employed to form siliceous membranes at the surface of filter media to improve their filtration properties.[80] Similar technique has been used by Carturan *et al.*[81] to coat glass microspheres with thin layers of porous oxide, and such materials can be used as supports for catalysis.

Gel derived coatings have also been studied to modify the optical and electrical properties of materials. Some interesting examples are colloidal palladium embeded TiO_2 coatings on float glass (to have desired absorbance of visible light), IR reflecting ITO (Indium Tin Oxide) coatings,[82,82a] Optoelectronic PLZT films,[83] transparent, electrically conductive cadmium stannate,[84] tin dioxide[85] coatings.

Sol-gel method can also be employed for coating glass fibres. Guglielmi and Maddalena exploited the sol-gel technology to coat E-glass fibres with a SiO_2–ZrO_2 film. These fibres can be used for cement composites.

The use of sol-gel techniques on the production of free standing films has been surveyed by Sakka.[87] Several techniques for making such films have been developed, including (*a*) pouring alkoxide solutions onto liquids which do not mix with the solution and allowing the film to hydrolyze; (*b*) pouring the solution onto non-wetting surfaces such as Teflon; and (*c*) forming films using wire rings with solutions of appropriate viscosity.

Fibres

Both polycrystalline as well as glass fibres have been prepared by sol-gel method. Using appropriate conditions, continuous fibres may be drawn from solutions of metal alkoxides. Fibrous gels are converted to glass fibres by heating. In many cases, heating of the gels produces a blackening of the fibres, very likely associated with fine carbon particles. Their formation can, however, be suppressed by heating the gels immediately after fibre drawing before further polymerization can occur.[58,58a]

Glass fibres have been fabricated in the systems SiO_2,[88,89] SiO_2–Al_2O_3, SiO_2–TiO_2,[89,89a] SiO_2–ZrO_2, SiO_2–ZrO_2–Na_2O.[58,58a]

Kokubo *et al.*[90] have developed a method for preparation of amorphous ZrO_2. Zirconia hydrogel was made from $ZrOCl_2$ solution. The gel was placed in a plastic cylinder and unidirectionally frozen by lowering the cylinder into a $-$ 78 °C cold bath at 4–6cm/hr. A bundle of parallel fibres longer than 8cm and 10–60μm in diameter was obtained after thawing. The fibres were amorphous and porous as dried at 25 °C. Their pores were greatly eliminated by heat treatment in vacuum at 290 °C for 2 days. The chemical composition of the heat treated fibres was approximately $ZrO_2.H_2O$.

As extreme purity is needed for telecommunication glass fibres, there is a strong tendency to produce performs by the sol-gel process, from which the fibre is drawn subsequently by melting.[7,91]

Polycrystalline α-Al_2O_3 fibres have been prepared by Blakelock *et al.*[92] by extruding gelled solutions through dies of appropriate diameter and sintering the resulting fibres at 1750 °C. Polycrystalline fibres in the systems Al_2O_3–Cr_2O_3–SiO_2[93] as well as mullite $3Al_2O_3.2SiO_2$, and aluminoborosilicate $3Al_2O_3.B_2O_3.3SiO_2$ have been reported. Fibres in the systems Al_2O_3–Cr_2O_3–ZrO_2, Al_2O_3–Cr_2O_3–TiO_2 and Al_2O_3–Cr_2O_3–SnO have also been investigated by Sowman.[94]

Fine grained metastable tetragonal ZrO_2 fibres have been drawn by Leroy *et al.*[95] Such fibres were obtained by extrusion and air-jet drawing of an aged (polymerized) concentrated solution of zirconium acetate.

Mahler and Bechtold[96] obtained silica fibres by directional crystallization of silicic acid solutions. The polysilicic acid-rich material is rejected at the ice-water

interface, and undergoes accelerated concentration-dependent polymerization. As a result, it becomes insoluble, and after thawing, it retains the structural forms developed during crystallisation.

Composites

Fibre-reinforced sol-gel derived aluminium oxide composites have been fabricated by Lannutti *et al.*[75–77] In case of short ceramic fibres and whiskers (ZrO_2, SiC, graphite), they were uniformly dispersed in a low viscosity sol and then frozen into the matrix via geletion. For long fibres, preforms were placed in trays and subsequently liquid alumina sol was added and gelled.

Roy and Roy[97] prepared ceramic-metal composites from diphasic xerogels. The final microstructure consisted of noncrystalline (in a few cases, microcrystalline) ceramic matrix with small metallic islands (5–50nm) and micro (and macro) pores. Such "nanocomposites" have been obtained in SiO_2, Al_2O_3, ZrO_2 systems containing metallic Cu, Pt, Sn and Ni.

Datta *et al.*[98] have prepared glass-metal microcomposites containing nickel islands (5–30nm) dispersed in a silica matrix.

Abrasives

Leitheiser and Sowman[97a] employed sol-gel techniques to produce non-fused alumina based abrasives with a microcrystalline structure of randomly oriented crystallites. After gelation and drying, the material was crushed and sized. The sized powders were then fired, typically in the range of 1250–1300 °C. In this way, Al_2O_3 abrasive particles with uniformly dispersed ZrO_2 particles were obtained. Such abrasive particles showed superior grinding performance compared with fused or sintered Al_2O_3-based abrasives.

Breval *et al.*[99] prepared single phase Al_2O_3 and 2-phase Ni—, NiO—, and $NiAl_2O_4Al_2O_3$, and AgCl—SiO_2 abrasive grains through sol-gel process.

Newer Applications

In the field of refractories, sol-gel process may be employed to get better results. One such attempt was made by Selyanko *et al.*[100] They used sol-gel process for the manufacture of binders from $AlCl_3$ solutions by hydrolysis with MgO or NH_4OH in high Al_2O_3 grog.

In order to get ultrapure homogeneous glasses, the recent trend is to exploit containerless melting in space. Because of the absence of gravity induced convection currents, the homogenization of glass using conventional raw materials is difficult in the space environment. Multicomponent, homogeneous, noncrystalline oxide gels can be prepared by the sol-gel process and these gels are promising starting materials for melting glasses in space environments (Batt. Col. Lab.)[101]

Sol-gel method seems to open a new way in the field of biomaterials technology. The lower temperature range of gel glass synthesis makes it possible to get inorganic-

organic glasses. Recently, Philipp *et al.*[102] fabricated such glasses (e.g., epoxysilane-titanium orthoester) for hard contact lenses.

Other prospective products[103] are nonoxide communication fibres, controlled release medications, photo and electrochromics, electrical and magnetic devices from transition element gels etc.

Concluding Remarks

Though sol-gel process has made an impact on materials technology as well as on novel materials exploration. the high cost of alkoxides seems to be an hindrance for its large scale use in preparing conventional materials. It will be worthwhile to find out whether alkoxide route can be substituted by a more economic one.

The sol-gel process should also be tried in nonaqueous media to explore the possibilities of preparing novel materials. Such experiments have been tried in a few cases. Bonner *et al.*[104] prepared fumed silica gels with a wide variety of nonaqueous liquids like methanol, ethanol, propanol, ethyl glycol etc. Brinker[13] replaced water by ammonia (hence ammonolysis in place of hydrolysis of sol-gel process) and in the process got nitrides and oxynitrides. This area should be explored in a systematic way.

Since many of the intresting ceramic materials which can be obtained from gels consist of several chemical components, it is imperative that advantage be taken of complex precursor formation. Hence, detailed studies should be done on formation of complexes and characterization of reaction products in multi-component systems.

References

1. D P Partlow and B E Yoldas *J Non-cryst Solid* **46** (1981) 153
2. R Roy *J Am ceram Soc* **39** (1956) 145
3. K S Mazdiyasni C T Lynch and J S Smith *J Am ceram Soc* **50** (1967) 532
4. R Roy *J Am ceram Soc* **52** (1969) 344
5. S P Mukherjee J Zarzycki and J P Traverse *J Mater Sci* **11** (1976) 341
6. J D Mackenzie *J non-cryst Solids* **48** (1982) 1
7. H Dislich *J non-cryst Solids* **57** (1983) 371
8. M A C G Van de Graaf J H H Termaat and A J Burggraaf *J Mater Sci* **20** (1985) 1407
9. B Jirgensons and M E Straumanis *A Short Textbook of Colloid Chemistry* Pergamon Press Oxford (1962) p 377
10. B J J Zelinski and D R Uhlmann *J Phys Chem Solid* **45** (10) (1984) 1069
11. R L Iler *The Chemistry of Silica* Wiley New York (1979)
12. E M Rabinovich *J non-cryst Solids* **71** (1–3) (1985) 187
13. C J Brinker *Commun Am ceram Soc* **C-4** (1982)
14. B E Yoldas *J non-cryst Solids* **51** (1982) 105
15. E J W Verwey and J Th G Overbeek *Theory of the Stability of Lyophobic Colloids* Elsevier Amsterdam (1948)
16. R M Dell In: *Proc 7th int Symp Reactivity of Solids* (*Ed* J S Anderson) Chapman and Hall London (1972)

17. B E Yoldas *J Mater Sci* **10** (1975) 1856
18. E C Marboe and S Bentur *Silic Ind* **26** (1961) 389
19. B E Yoldas *J appl Chem Biotechnol* **23** (1973) 803
20. A R Cooper In : *Ceramic Processing Before Firing* (*Ed* G Y Onoda Jr and L L Hench) Wiley New York (1978)
21. J Zarzycki M Prassas and J Phalippou *J Mater Sci* **17** (1982) 3371
22. S H Wang and L L Hench In : *Better Ceramics Through Chemistry* (*Ed* C J Brinker D E Clark and D A Ulrich) North-Holland New York (1984)
23. E M Rabinovich D W Johnson Jr J B MacChesney and E M Vogel *J Am ceram Soc* **66** (10) (1983) 683
24. L C Klein and G J Garvey *J non-cryst Solids* **45** (1980) 30
25. D W Schaefer and K D Keefer In : *Better Ceramics Through Chemistry* (*Ed* C J Brinker D E Clark and D A Ulrich) North-Holland New York (1984)
26. C J Brinker and G W Scherer *J non-cryst Solids* **70** (1985) 301
27. M Yamane S Aso S Okano and T Sakaino *J Mater Sci* **14** (1979) 607
28. G W Scherer C J Brinker and E P Roth *J non-cryst Solids* **72** (1985) 379
29. C J Brinker and G W Scherer In : *Ultrastructures Processing of Carmamics Glasses and Composites* (*Ed* L L Hanchand and D R Ulrich) Wiley New York (1984)
30. W K Duerksen C E Holcombe and M K Morrow *United States Atomic Energy Commission* DOS 2 345 778 Washington D C USA (1972)
31. S Komarneni and R Roy *Mater Lett* **3** (4) (1985) 165
32. O Sbaizero *Thermochim Acta* **85** (1985) 227
33. V N Vaidya R V Kamat J K Joshi V S Iyer S Suryanarayan N L Srinivasan K T Pillai and D D Sood *Proc nucl Chem Radiochem Symp* (1981) 549
34. H D Ringel and E Zimmer *Nucl Tech* **45** (3) (1979) 287
35. P A Haas *ORNL/Th*-3978 (1972) Oak Ridge National Laboratory
36. M Suzuki S Hiraishi M Yoshimura and S Y Somiya *Yogyo Kyokaishi* **92** (6) (1984) 320
37. R J Bratton *Am ceram Soc Bull* **48** (8) (1969) 759
38. H Dislich *Angew Chem int Edn* (*Engl*) **10** (1971) 363
39. S K Bhattacharya V S Ramachandran and J C Ghosh In : *Proc int Congr Catal* (*Ed* A Farakas) Academic Press New York (1957)
40. W T Barrett M G Sanchez and G W Smith In : *Proc int Confr Catal* (*Ed* A Farakas) Academic Press New York (1957)
41. D M Roy and R Roy In : *Experimental Study of the Formation and Miner* **39** (11 12) (1954) 957
42. K S Mazdiyasni and L M Brown *J Am ceram Soc* **55** (1972) 548
43. K Chen S Tian and Z Lin *Mater Sci Congr* **16** (1983) 587
44. K S Mazdiyasni and L M Brown *J Am ceram Soc* **54** (1971) 539
45. L M Brown and K S Mazdiyasni *J Am ceram Soc* **55** (11) (1972) 541
46. E Wu K C Chen and J D Mackenzie In : *Better Ceramics Through Chemistry* (*Ed* C J Brinker D E Clark and D A Ulrich) North-Holland New York (1984)
47. R F Haaker and R C Ewing *Commun Am ceram Soc* (1981) C-149
48. M Guglielmi and G Principi *J non-cryst Solids* **48** (1982) 161
49. R J Lauf and W D Bond *Am ceram Soc Bull* **63** (2) (1984) 278
50. L J Koppens *IEEE Trans Magn* **8** (9) (1972) 303
51. G J McCarthy and R Roy *J Am ceram Soc* **54** (1971) 39
52. T Hayashi and H Saito *J Mater Sci* **15** (1980) 1971
53. L L Hench M Prassas and J Phalippou *J non-cryst Solids* **53** (1982) 183
54. L L Hench M Prassas and J Phallippou *Ceram Engng Sci Proc* **3** (1982) 477

55. M C Weinberg and G F Neilson *J Mater Sci* **13** (1978) 1206
56. V Gottardi G Scarinci G Carturan A Marchetti and V Frosini In : *Thermal Analysis* (*Ed* H Wiedemann) Birkaurer Verlog Basel (1980)
57. S Meriani V Longo D R Festa and M Guglielmi *Trans Br ceram Soc* **80** (1981) 87
58. K Kamiya S Sakka and Y Tatemichi *J Mater Sci* **15** (1980) 1765
59. K Kamiya and S Sakka *J Mater Sci* **15** (1980) 2937
59*a*. J P Boilot Ph Colomban and N Blanchard *Solid St Ion* 9 **10** (1) (1983) 639
60. A Makashima H Ooohashi M Wakakuwa K Kotani and T Shimohira *J non-cryst Solids* **42** (1980) 545
61. F K Chi *Ceram Engng Sci Proc* **4** (9–10) (1983) 704
62. C J Brinker K D Keefer D W Schaefer and C S Ashley *J non-cryst Solids* **48** (1982) 47
62*a*. C J Brinker *Commun Am ceram Soc* (1982) C-4
63. L C Klein T A Gallo and G J Garvey *Proc SPEI-int Soc Opt Engng* 70
64. W D Arnold W D Bond and S M Robinson *Radioact Waste Manage nucl Fuel Cycle* **3** (1982) 57
65. M Ohno J Yamada and T Kurokawa *J appl Phys* **57** (8) (1985) 2951
66. C D Hendricks A Rosencwaig R L Woerner J C Koo and J L Dressler *Lawrence Livermore Lab Rep* **UCRL-81415** (1979) 18
67. R L Downs and R L Noleu *Fr Demande* **FR** (1983) **2** 518, 569
68. V Gottardi M Guglielmi A Tiziani and G Carturan *J non-cryst Solids* **43** (1981) 105
69. W Holand E R Plumat and J Duvigneaud *J non-cryst Solids* **48** (1982) 205
70. C J Brinker and M S Harrington *Solar Energy Mater* **5** (1981) 159
71. S P Mukherjee and W H Lowdermilk *Appl Opt* **21** (1982) 293
72. B E Yoldas and O T W Keeffe *Appl Opt* (1979) 3133
73. C J Brinker and D M Haaland *J Am ceram Soc* **66** (11) (1983) 758
74. C J Brinker and R B Pettit *Ann Meet Am ceram Soc* Chicago Illinois (1983)
74*a*. B E Yoldas and D P Partlow *Bull Am ceram Soc* **59** (1980) 640
75. J J Lannutti and D E Clarke *Mater Res Soc Symp Proc* (1984) 375
76. J J Lannutti and D E Clarke *Mater Res Soc Symp Proc* (1984) 369
77. J J Lannutti and D E Clarke *Ceram Engng Sci Proc* **5** (7–8) (1984*b*) 574
78. J Martinsen R A Figat and M W Shafer *Mater Res Soc Symp Proc* (1984) 145
79. J Schlichting and S Neumann *J non-cryst Solids* **48** (1982) 185
80. A Kaiser and H Schimdth *J non-cryst Solids* **63** (1984) 261
81. G Carturan G Facchin V Gottardi and G Navazio *J non-cryst Solids* **63** (1984) 273
82. H Dislich *J non-cryst Solids* **57** (1983) 371
82*a*. H Dislich and P Hinz *J non-cryst Solids* **48** (6982) 11
83. A V Novoselvoa N Ya Turova E P Turevskaya M J Yanovskaya A Kozunova and N J Koznova *Neorg Mater* **15** (6) (1979) 1055
84. H Dislich P Hinz and G Wolf *Belg* (1979) 872 697
85. H Dislich P Hinz and G Weber *Ger* (1980) 2 847, 453
86. M Guglielmi and A Maddalena *J Mater Sci Lett* **4** (1) (1985) 123
87. S Sakka In : *Treatise on Materials Science and Technology* **22** (1982) *Glass III* (*Ed* R Doremus and M Tomozawa) Academic Press New York
88. S Sakka and K Kamiya *J non-cryst Solids* **48** (1982) 31
89. K Kamiya S Sakka and M Mizutani *Yogyo Kyokaishi* **86** (1978) 552
89*a*. K Kamiya S Sakka and N Tashiro *Yogyo Kyokaishi* **84** (1976) 614
90. T Kokubo Y Teranishi and T Maki *J non-cryst Solids* **56** (1-3) (1983) 411
91. K Susa I Matsuyama S Satoh and T Suganuma *Electron Lett* **18** (12) (1982) 499
92. M D Blakelock N A Hill S A Lee and E Goatcher *Proc Br ceram Soc* **15** (1970) 69

93. H G Sowman *US Pat* (1978) **4** 125 406
94. H G Sowman *Ger Offen* (1975) **2** 432 434
95. E Leroy C Robin-Brosse and J P Torae In : *Ultrastruct Proc ceram Glasses and compos* (*Ed* L L Hench and D R Ulrich) Wiley New York (1984)
96. W Mahler and M F Bechtold *Nature* **285** (1980) 27
97. R A Roy and R Roy *Mater Res Bull* **19** (2) (1984) 169
97*a*. M A Leitheiser and H G Sowman *US Pat* (1982) **4** 314 827
98. S Datta S S Mitra D Chakravorty S Ram and D Bahadur *J Mater Sci Lett* (1985) (*In Print*)
99. E Breval G C Dodds and N H Macmillan *Mater Res Bull* **20** (4) (1985) 413
100. V T Selyanko and G M Shigaleva *Zh Prikl Khim* **57** (9) (1984) 1987
101. Battelle Columbus Laboratories *NASA Contract Rep* **CR-169939** (1982)
102. G Philipp and H Schmidt *J non-cryst Solids* **63** (1-2) (1984) 283
103. N Kreidl *Am Ceram Soc Bull* **63** (11) (1984) 1394
104. F J Bonner G Kordas and D L Kinser *J non-cryst Solids* **71** (1-3) (1985) 361