Part I

Chemistry and Phase Transformations

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Multicomponent Glasses from the Sol-Gel Process

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HISTORICAL INTRODUCTION

The preparation of multicomponent glasses by the sol-gel process dates from 1950; at that time Della and Rustum Roy[1] prepared a number of compositions from silicon tetraethoxide and metal nitrate salts primarily for phase equilibrium studies where homogeneous samples are essential. This new method gave products which, when melted just once, gave a glass more homogeneous than the best glasses obtained after three successive melting and crushing operations of samples prepared in the conventional manner from individual oxides. Hamilton and Mackenzie in 1960,[2] Luth and Ingamells in 1965,[3] Hamilton and Henderson in 1968[4] and Biggar and O'Hara in 1969[5] all described variations of the same process primarily directed towards the preparation of silicate mixtures for phase equilibrium studies.

An investigation of bulk glass systems by the sol-gel process was started at Owens-Illinois, Inc. in 1967 by Levene and Thomas.[6] This work resulted in the commercialization of several four component sputtering glass target discs in 1969 and six component planar dopant discs a few years later. The process involved a combination of metal alkoxides and metal acetates as oxide sources and was used because of the high purity requirements not specifically for homogeneity. Dried gel products were melted and fabricated by conventional means.

Sol-gel coating systems were extensively studied at Schott Glass starting in the 1950's. Although the initial emphasis appeared to have been on the preparation of single oxide optical coatings, mainly TiO_2 and SiO_2, mixed oxide materials were also investigated and this led to commercial products. The work is described by Schroeder first in 1962[7] and in more detail in 1969;[8] a summary is also given by Dislich.[9] Later both Schroeder and Dislich investigated bulk gel preparation by an all alkoxide route described by Dislich in 1971[10] and resulting in a number of patents.[11,12]

The increasing interest of many investigators in the sol-gel process became apparent in the mid-1970's and the amount of published work has blossomed since that time. In the following sections various aspects of multicomponent glass preparation, properties and uses will be described. The review is restricted to multicomponent glass systems and so the emphasis will naturally be on silicate materials. It is of note, however, that a lot of work has been reported on silica alone and on both single oxide and multicomponent oxide ceramic systems. The ceramic systems have shown some impressive advantages, especially with respect to processing, over their conventional equivalents.

PREPARATION

General

The prime objective in all preparations of multicomponent oxide compositions is to obtain initially a solution of all components in the form of soluble precursor compounds; mixing can then be considered to be at the molecular level and if this level can be retained in the subsequent conversion to oxides a very homogeneous product should result. In most cases it does appear that oxide products prepared in this manner at low temperature are indistinguishable from those obtained in the conventional manner by fusing the relevant oxide mixtures at high temperature. This will be discussed in more detail later.

There are a number of different types of precursor materials that can be used. All should be soluble in organic solvents and easily converted to the relevant oxide preferably by hydrolysis but alternatively by chemical reaction or thermal or oxidative decomposition. Several preparative methods are available dependent on the nature of the starting materials and these are described below.

All-Alkoxide Method

Probably the best starting materials for sol-gel preparations are the class of materials known as metal alkoxides. All metals form alkoxides and they have the following general formula:

$$M(OR)_x$$

where M is the metal, R is an alkyl group, and x is the valence state of the metal.

All metal alkoxides, with two notable exceptions, are rapidly hydrolyzed to the corresponding hydroxide or oxide. The method of hydrolysis can be varied and many times depends on the final use of the product. This will become apparent later but the overall reaction can be represented as follows:

$$H(OR)_X + XH_2O \rightarrow M(OH)_X + xROH$$

$$2M(OH)_X \rightarrow M_2O_X + {}_XH_2O$$

The by-product, ROH, is an aliphatic alcohol and readily removed by volatilization.

The two notable exceptions are the alkoxides of silicon and phosphorus. Silicon alkoxides require an acid or basic catalyst for hydrolysis and even with these the reaction rate is slow. Trialkylphosphates are very difficult to hydrolyze and this precludes their use as a source of phosphorus in sol-gel preparations.

There is also a limited class of compounds known as double alkoxides. These contain two different metals in the same compound and have the general formula:

$$M'_x M''_y (OR)_z$$

where M′ and M″ are metals, R is an alkyl group and x, y and z are integers.

The physical properties of metal alkoxides can be varied by changing the alkyl group and for most metals soluble, and in some cases even liquid, products can be obtained. In addition, many alkoxides are volatile and can readily be purified by distillation; this can lead to very pure oxide products. Double alkoxides have the added advantage of not only being volatile but retaining exact molecular stoichiometry between the metals. An excellent source of information on metal alkoxides is the book by Bradley et al[13] which is highly recommended reading for anyone starting in the sol-gel field.

The simplest method of preparation of multicomponent systems involves making a solution of all the components as alkoxide precursors in a suitable organic solvent and then reacting the solution with water to form the oxide mix. The reaction can be represented for a three component system as follows:

$$M(OR)_a + M'(OR)_b + M''(OR)_c + xH_2O \rightarrow MO_{a/2} + M'O_{b/2} + M''O_{c/2} + yROH$$

This was the method first used by Schroeder[11] and Dislich[10] and has since been used by many other investigators. The reaction is far more complex than the simple hydrolysis shown in the equation above. It involves first hydrolysis of metal alkoxide groups to metal hydroxide groups and subsequent condensation of these groups with each other or with unhydrolyzed alkoxide groups to give products containing M-O-M linkages (metallometalloxane polymers).

$$M–OR + H_2O \rightarrow M–OH + ROH.$$

$$M–OR + M–OH \rightarrow M–O–M + ROH.$$

$$M–OH + M–OH \rightarrow M–O–M + H_2O$$

The products can contain one or more metal atoms in the same molecule depending on the relative hydrolysis and condensation reaction rates of the component metal alkoxides. The more alkoxides present in the original mixture the more complex can the polymerization become. Ultimately, the polymeric products become insoluble due to cross-linking and gellation or precipitation results. The complexity of a multicomponent system makes investigation of the reaction mechanisms extremely difficult. Brinker and Scherer[14] give an excellent summary of research in this field and describe their own extensive investigations on polymer growth and gel formation.

The variation in reaction rates especially in the initial hydrolysis can give rise to inhomogeneities in the final product. This is particularly the case for those materials containing silicon which of course includes all silicate glasses. When hydrolysis is rapid, as is the case with the addition of an excess of liquid water, the hydrolysis rate of silicon alkoxides is so slow that they can remain substantially unreacted when all other components in the mixture have already precipitated as oxides. Gross inhomogeneities then result.

One way of avoiding this problem is to carry out the hydrolysis very slowly. The alkoxide mixture can be made up in a suitable solvent then exposed in bulk to atmospheric moisture, or wet alcohol, sometimes containing acidic or basic catalysts, can be slowly added. In both cases, soluble polymerized products are initially formed and this is followed by a viscosity increase and eventual gelation; this process combined with concurrent solvent evaporation can take from days to weeks. The exact method of hydrolysis depends on the final use of the product; at the viscous, but still soluble, stage fibers have been spun from certain compositions; monolithic dried gels have been obtained when the process is taken to the gel stage. Both of these topics are covered in much greater detail in other sections of this book.

Another method for avoiding the variable hydrolysis rate problem was devised by Levene and Thomas[6] in 1972. This involved a partial hydrolysis of the silicon alkoxide (usually the ethoxide) with an equimolar quantity of water using an acid catalyst to give a trialkoxysilanol which remained in solution:

$$(RO)_4Si + H_2O \rightarrow (RO)_3SiOH + ROH.$$

The addition of other alkoxides then followed and this resulted in reaction between them and the silanol derivative to form soluble metallosiloxane derivatives:

$$(RO)_3SiOH + M(OR')_x \rightarrow (RO)_3Si\text{–}O\text{–}M(OR')_{x-1} + R'OH.$$

This reaction is well known and has been used in the preparation of many siloxy-metal monomers[15] and polymers[16] in non sol-gel applications, e.g.:

$$Ti(OC_3H_7)_4 + 4(CH_3)_3SiOH \rightarrow Ti[OSi(CH_3)_3]_4 + 4C_3H_7OH.$$

All metal alkoxides so far investigated react with silanol derivatives to give metallosiloxane products, so all alkoxides subsequently added to the partially hydrolyzed silicate mixture will react provided that there are sufficient silanol groups available for reaction. This is usually no problem in silicate glass compositions which normally contain a major portion of silica. While the formation of these metallosiloxanes is a complex reaction, especially if more than one additional alkoxide is added, it was found that these derivatives were susceptible to further hydrolysis and can be considered to be similar to single alkoxides except that they contain two or more metals in the same compound. Addition of more water ultimately gave homogeneous oxide products.

A similar method for titanium silicate systems was later used by Yoldas[17] in which he prehydrolyzed a titanium alkoxide and then reacted this with silicon tetraethoxide monomer to give a soluble titanosiloxane polymer:

$$\mathrm{Ti(OR)_4 + H_2O \rightarrow (RO)_3TiOH + ROH.}$$

$$\mathrm{(RO)_3TiOH + Si(OC_2H_5)_4 \rightarrow (RO)_3Ti{-}O{-}Si(OC_2H_5)_3 + C_2H_5OH.}$$

Further hydrolysis of the product ultimately gave a homogeneous oxide mixture.

It is fairly obvious that this method can be extended to cover the use of any metal alkoxide that can give soluble partially hydrolyzed materials containing reactive hydroxyl groups. The latter can then be reacted with the silicate to form a metallosiloxane polymer.

Alkoxide-Salt Method

For some metals it is inconvenient to use alkoxides because of preparation problems or unavailability and alternative starting materials must be found. This is particularly the case with Group I and Group II elements whose alkoxides are solid, non-volatile and in many cases of low solubility; consequently, they are sometimes difficult to obtain pure. Metal salts provide a viable alternative provided that they are readily converted to the oxide by thermal or oxidative decomposition and are preferably soluble in organic solvents. They also usually can be obtained as a high purity analytical grade. Salts of organic acids, in particular acetates but also formates, citrates, tartrates, etc. are potential candidates. Nitrates are really the only suitable inorganic salts because others, such as chlorides or sulfates, are more thermally stable and the anion may be difficult to remove.

The normal method of sol-gel preparation using salts is first to form a solution of all components which are to be added as alkoxides, as described in the preceding section, and then add one or more salts as solutions in alcohol or, if this is not possible, in the water that is to be used for further hydrolysis. All components are then uniformly dispersed and subsequent gelation should then freeze all elements in a gel network.

The first sol-gel preparations carried out by the Roys[18] used silicon tetraethoxide and solutions of the nitrates of Group I and Group II elements as well as those of aluminum, lead, iron, lanthanum, titanium, zirconium, thorium, nickel and gallium. A major drawback to the preparation of ultrahomogeneous glass using nitrates was pointed out by Roy and McCarthy[19] and this was the tendency for one or more nitrates to crystallize during dehydration thereby destroying homogeneity; this effect was especially bad with sodium, lead and barium nitrates. The solution to the problem was to evaporate a large portion of the water before the solution gelled which was possible if the pH was kept low.

A word of warning should be given on the use of nitrates in preparations involving more than a few hundred grams of material. Nitrates are strong oxidizing agents and there are initially large quantities of oxidizable material present in the system, this can lead to uncontrollable exotherms and even explosions during drying.

The use of acetate salts was first described by Levene and Thomas[6] and these were used in much the same way as nitrates. In some cases acetates are more soluble than the corresponding nitrates for example, those of sodium, potassium and barium, and their use therefore reduces the crystallization tendency described above. Also the explosion hazard is eliminated in large scale preparations. Disadvantages are that they do not thermally degrade as cleanly as nitrates and can be a source of carbonaceous residues; also solutions of many acetates are basic and therefore their use leads to rapid gelation in silicate systems due to the high pH but this can be partly negated by buffering with acetic acid.

Thomas[20] has found that the use of sodium acid tartrate as a sodium source in silicate systems led to stable solutions especially useful for coating applications where gelation must be avoided. This salt is acid and also contains alcohol groups which are potential reactants for alkoxides in the system. No doubt other acid tartrates could be used in like manner.

Nitrates and acetates continue to be the most commonly used salts in preparations described in the recent literature, their use, however, is much less frequent than the all alkoxide method. Some recent examples are Brinker and Mukherjee[21] who used sodium and barium acetates with aluminum, boron and silicon alkoxides; Holand, Plumat and Duvigneaud[22] used magnesium acetate with aluminum and silicon alkoxides; Phalippou, Prassas and Zarzycki[23] prepared lithium aluminosilicates from lithium and aluminum nitrates and ethyl silicate; and some calcium silicates were prepared from calcium nitrate and ethyl silicate by Hayashi and Saito.[24]

Sol-gel preparations involving salts are usually more complex than those with only alkoxides because the hydrolysis of the latter is more readily accomplished than the thermal or oxidative degradation required for the former. A novel use of certain acetates was developed by

Thomas[20] mainly to reduce the amount of acetate groups that had to be removed by thermal degradation during oxide conversion. It was found that certain acetates react with some alkoxides to form metallometalloxane derivatives with the liberation of alkyl acetate, the first step in the reaction is as follows:

$$M(OR)_n + M'(OAc)_n, \rightarrow (RO)_{n-1}\, M\text{–}O\text{–}M'(OAc)_{n'-1} + ROAc$$

where Ac represents the group –$COCH_3$.

The reaction then continues with further reaction of acetate and alkoxide groups to increase molecular weight. The reaction is carried out by heating the reagents together in the absence of solvent and in most cases about 60–80% of the theoretical ester can be distilled out. It is preferable for the mol ratio of alkoxide to acetate to be greater than one and this leads to a soluble and hydrolyzable product that can subsequently be used in sol-gel preparations in a similar manner to a double alkoxide.

Some acetate-alkoxide pairs that can be reacted in this manner are as follows:

Calcium acetate–aluminum alkoxide
Magnesium acetate–aluminum alkoxide
Zinc acetate–aluminum alkoxide
Lead acetate–silicon alkoxide
Lead acetate–titanium alkoxide

Thomas[20] prepared $CaO–MgO–Al_2O_3–SiO_2$ and $PbO–B_2O_3–SiO_2$ glass compositions using this method and the reaction was also used by Gurkovich and Blum[25] to prepare monolithic lead titanate.

The acetate-alkoxide reaction is particularly useful for lead silicate containing compositions because lead acetate is particularly prone to leaving carbonaceous residues in the oxide product.

Other Methods

As an alternative to alkoxides or salts there are a few other materials that can be used for certain specific elements. Some metal oxides and hydroxides are soluble in alcohols because of reaction to form partial alkoxides; these solutions can then be used in sol-gel preparations in the same manner as alkoxides. The reactions with alcohols are reversible and solubility can sometimes be increased if the water is removed:

$$MO_x + 2nROH \rightleftharpoons MO_{x-n}(OR)_{2n} + nH_2O$$

$$M(OH)_x + nROH \rightleftharpoons M(OH)_{x-n}(OR)_n + n/2H_2O$$

Ultimately, of course, the fully substituted alkoxide will be formed when all the water is removed.

Examples of compounds that can be used in this manner are the oxides and hydroxides of all Group I metals, boric acid and oxide, phosphoric acid and oxide, lead monoxide and vanadium pentoxide. Perhaps the most commonly used material is boric acid which can be obtained in a high state of purity and is quite soluble in methanol (10%) because of partial alkoxide formation. Many workers have incorporated boron into sol-gel preparations in this manner though it is difficult to avoid loss of boron from the system during the drying process because of the high volatility of trimethylborate. It is better to dissolve the acid in a higher alcohol and remove the water if necessary to increase solubility. Dislich[26] reports that even using ethanol with boric acid there is considerable boron loss because of the volatility of triethylborate.

Phosphoric acid is the only good source of phosphorus as the phosphorus alkoxides are precluded because of stability; it reacts readily with silicon alkoxides in particular to give useful phosphorosiloxane intermediates.[27]

In cases where suitable oxide precursors are not available preparations can be carried out in which all components except one are made up in solution by any of the standard methods and the odd one then added as a solid oxide. The particle size of the latter oxide should be as small as possible and mixing then carried out vigorously enough to coat each particle with the solution of the other components. While the homogeneity is obviously not as good as a true sol-gel material it can be considerably better than a conventional oxide mix. Thomas[28] prepared lead and zinc aluminoborosilicates and borosilicates by suspending the relevant lead or zinc oxide in a solution of the other components then gelling and drying in the normal manner. It was then possible to obtain these low melting glasses free of carbonaceous residues an objective not possible when lead or zinc acetates were used as precursor materials.

Perhaps the ultimate in hybrid systems is the use of colloidal suspensions as precursor materials. These are the ultimate in particle size and dispersion and silica sols in particular have been investigated. These are commercially available in aqueous suspension, acid or base stabilized, with particle size down to 8 nm. The early investigators of sol-gel systems mentioned in the introduction such as Luth and Ingamells[3] and Hamilton and Henderson[4] used aqueous colloidal silica as an alternative to silicon tetraethoxide in aqueous systems with nitrate salts. More recently Rabinovich et al[29] prepared SiO_2–B_2O_3 compositions from aqueous colloidal silica and an aqueous solution of boric acid. It was possible to cast this mixture into molds and prepare large solid sinterable bodies on drying. The system obviously is limited to water soluble precursor reagents for the other components but these mixtures can be gelled by pH control and processed in much the same way as alkoxide derived products.

There is now considerable interest in aqueous metal oxide sols and mixtures in ceramic processing but this is beyond the scope of this article.

PROPERTIES

Homogeneity

The methods used for sol-gel preparations should in theory give very homogeneous products. If one assumes that a typical sol-gel solution prior to conversion contains all the components mixed at or near the molecular level and if this level can be maintained during the subsequent conversion, then the product should be very good. With silicate systems for example one might expect the product after drying at relatively low temperatures to be equivalent to or better than glass “cullet” which is normally prepared from an oxide melt. The first sol-gel preparations were carried out with the sole objective of obtaining homogeneous products and the results were very successful; later work has usually indicated that the homogeneity of the product was excellent although this was rarely the prime objective of the particular study.

A simple analysis of dried gel particles from a sodium aluminosilicate glass batch was carried out by Levene and Thomas.[6] Three samples approximately 10 mg each were removed at random from a 200 g batch which had been heated to 400°C and which was prepared from sodium acetate and aluminum and silicon alkoxides; these were analyzed for SiO_2 and Al_2O_3 with the following results:

SiO_2	63.9%	64.0%	64.5%
Al_2O_3	24.1%	24.3%	24.0%

Later Thomas[19] did the same thing with samples taken from a SiO_2–Al_2O_3–B_2O_3–MgO batch prepared from all alkoxide reagents with the following results:

SiO_2	56.2%	54.3%	55.0%	58.6%	56.1%	57.0%
Al_2O_3	21.8%	21.2%	21.4%	22.6%	21.8%	22.4%
MgO	7.3%	7.5%	7.4%	7.4%	7.2%	7.7%

Even allowing for analytical error these results show good but certainly not excellent homogeneity.

Mukherjee and Mohr[30] measured homogeneity using light scattering. They found that samples of a Na_2O–B_2O_3–SiO_2 composition prepared by two different sol-gel methods, all alkoxide and nitrate-alkoxide, when melted without stirring had a scattering intensity of only 1% of that of the best regions in a similar composition prepared in the conventional manner but also without stirring. The gel glasses were also striae-free and of optical quality.

Another study was carried out by Yamane et al.[31] They compared the homogeneity of a TiO_2–SiO_2 gel prepared by various methods with physical mixtures of the individual oxide gels. The method used involved glass formation by the addition of sodium nitrate and measurement of refractive index deviation and transmission of melted crushed samples. No samples were found to be of optical quality but the gel glasses were found to be superior to the physical gel mixture. It was also claimed that base hydrolysis of a physical alkoxide mixture gave better homogeneity than either acid hydrolysis of a physical alkoxide mixture or acid hydrolysis of a titanosiloxane polymer; the latter material is erroneously referred to in the paper as being prepared by the Yoldas method rather than the Levene and Thomas method.[6]

Comparison with Conventional Glass

Perhaps a more significant factor than homogeneity is whether there is any basic difference between sol-gel products and the same products prepared conventionally each under the best conditions. There have been several studies of this type. Vergano[32] concluded that there was little or no difference in the physical properties of $CaO–MgO–Al_2O_3–SiO_2$ and $CaO–Li_2O–Al_2O_3–SiO_3$ compositions prepared from conventional or sol-gel starting materials and melted in the usual manner. Slight differences in viscosity were attributed to the high hydroxyl content of the sol-gel glass due to its method of preparation. Minimal differences were also found in the physical properties of melted $TiO_2–SiO_2$ glasses by Kamiya and Sakka[33] and in $Na_2O–K_2O–Al_2O_3–B_2O_3–SiO_2$ compositions by Dislich.[10]

However, slight differences in properties such as liquidus temperature, crystallization behavior and phase separation were found by Weinberg and Neilson[34,35] who did an extensive study of the sodium silicate system and by Mukherjee et al[36] with $La_2O_3–SiO_2$, $La_2O_3–Al_2O_3–SiO_2$ and $La_2O_3–ZrO_2–SiO_2$ compositions. Both investigations attributed the differences to sharply different structural factors and high hydroxyl content.

Purity

The purity of sol-gel compositions obviously depends on the purity of the relevant starting materials and the degree of care taken in the conversion to oxide. Metal alkoxides are particularly good reagents for high purity products because many of them are volatile and hence readily purified by distillation. This is especially the case for the alkoxides of boron and silicon which can be fractionally distilled under nitrogen at atmospheric pressure to give extremely high purity materials. Other alkoxides normally require vacuum distillation which, while not as efficient as atmospheric pressure distillation, can give excellent material. In the absence of a suitable alkoxide it is now possible to obtain commercially many metal salts or metal oxides, which can be converted to salts, in super-pure grade. The use of these materials in clean apparatus in a clean room can give excellent high purity material with most common compositions.

Some purity studies have been carried out. Gossink et al[37] prepared SiO_2 and Al_2O_3 from distilled samples of silicon tetraethoxide and aluminum isopropoxide respectively and obtained products in which the major impurity was iron at the 30–50 ppb range. These oxides were to be used for the preparation of fiber optic waveguides where transition metal impurities were particularly detrimental. For a similar use Thomas[38] prepared a Al_2O_3–SiO_2 sol-gel glass from the alkoxides which had an iron content of 90 ppb.

FABRICATION AND USE

General

The fabrication and use of materials prepared by the sol-gel process can be divided into three main categories, bulk glass, coatings and fibers. The latter two are well covered in other chapters of this book and will not be considered here. The bulk glass category can be further divided into products that are prepared from dried gel by conventional melting at high temperatures and products that are fabricated at lower temperatures without melting. Each of these will be considered.

Bulk Glass by Melting

One of the first uses of the sol-gel process was in the fabrication of bulk glass by the conventional melting of dried gel. This was described in the introduction for the phase equilibrium studies by Roy and others and for the first commercial products from Owens-Illinois, Inc. While this method gives glass of excellent quality there are disadvantages as well as the obvious advantages of the gel being homogeneous and amorphous leading to lower melting temperatures and no stirring requirement.

The disadvantages are that the gel must be heated very slowly to the melting temperature to ensure that all carbonaceous residues, water and hydroxyl groups are removed. A very seedy and foamy melt can be obtained if this process is not carried out correctly. Another disadvantage is that the raw material cost is very high compared to the cost of the individual oxides and the end result must therefore justify this charge. In Roy's case cost was of little consequence in view of the quality of the product and the quantity prepared. With the sputtering target discs manufactured at Owens-Illinois the improved purity justified the cost, however such would not be the case nowadays because of the ready availability of high purity oxides not available at that time.

Much of the justification of fabrication in this manner will depend on the composition under consideration. High melting, high viscosity glasses are very difficult to melt conventionally but quite readily fabricated using sol-gel starting materials. A good example is the zero expansion composition 92% SiO_2 –8% TiO_2. When this was prepared by the sol-gel process and melted at 1590°C a seedy but otherwise homogeneous glass was obtained within 6 hours. A standard batch from the individual oxides was only partially melted after 89 hours at 1590°C.[6]

An interesting potential use of unmelted gel was proposed by Neilson and Weinberg[39] who suggested that gel precursors would probably be the preferred starting materials for preparing glasses in space because of their microhomogeneity and amorphous properties.

Bulk Glass Without Melting

Many attempts have been made to prepare bulk materials directly from gels without going through the melting process. There are a number of potential methods and some have been quite successful. The simplest is the preparation of monolithic pieces by the slow drying of alcogels which have been molded directly from sol-gel solutions. This subject is covered in detail in another chapter of this book but briefly some difficulty arises from the extremely large surface tension forces in effect during drying due to the very small pore sizes in the gel. This makes the preparation of a large crack-free body difficult; more success has been obtained with gels prepared from colloidal solutions in which pore sizes are much larger and surface tension effects much reduced. The difficulties of the system are well summarized by Zarzycki et al[40] who concluded that the method which gives the most consistent results in regard to crack-free samples is that of supercritical drying of the alcogel. This eliminates surface tension effects and gives a product known as an aerogel.[41] Large monolithic dense pieces have been obtained by heating aerogels to high temperatures.[40]

An alternative use for aerogels was described by Thomas.[42] Aerogels of several glass-ceramic compositions were prepared in the normal manner and then crushed to give a very fine powder. This powder was then cold pressed in a steel mold and the green body sintered by heating in the conventional manner. Dense transparent glass samples were obtained at temperatures as low as 800°C, further heating allowed crystallization to take place to give a final molded glass ceramic body. This process avoided the necessity of obtaining completely crack-free aerogels, very much reduced the shrinkage of going from gel to dense product and allowed a number of different shapes to be fabricated by ceramic techniques.

Ceramic techniques were also used by Decottignies et al[43] who hot pressed gels to obtain dense bodies. The compositions investigated were SiO_2, La_2O_3–SiO_2 and B_2O_3–SiO_2 and it was found that careful drying and calcining of the gels prior to pressing was required to ensure removal of carbonaceous residues and water. These were high melting compositions and pressing temperatures of 1400°C were used to obtain dense samples.

Bulk glass can also be of use in a porous granular form rather than as a dense shaped body especially in the catalyst field. The high surface area of aerogels is particularly advantageous and Teichner et al[44] describe a NiO–Al_2O_3–SiO_2 aerogel prepared from nickel acetate and alkoxides which was found to be a very selective catalyst for the partial oxidation of isobutylene.

Commercial Products

Commercialization of multicomponent sol-gel products has been slow. The bulk glass products produced at Owens-Illinois, Inc. in 1970 were discontinued because of cost and it may be that no large quantities of sol-gel glass will ever be produced simply because the raw material and processing costs are very high. Coatings are much more promising because on a square foot basis raw material and processing costs are low. Schott Glass continues to produce coated products for architectural and other uses and these are presumably profitable. More recently Owens-Illinois and several other suppliers have produced a series of metal silicate solutions used to dope silicon wafers with arsenic, antimony, boron or phosphorus for semi-conductor use.[45]

There may also be commercial internal uses in which sol-gel processing precedes the final manufacturing step for products whose association with the sol-gel process is not immediately apparent.

One particularly promising aspect of sol-gel coatings that appears to be close to commercialization is in the field of optical coatings. The ease with which high purity oxide materials can be laid down from solution is particularly useful. One specific example is the development of a cheap SiO_2–TiO_2 antireflective coating for silicon solar cells by Yoldas and O'Keeffe.[46]

One assumes in view of the wide variety of potential uses that other commercial products will be forthcoming in the near future.

CONCLUSIONS

The variety of preparative methods and ready availability of a large number of starting materials means that almost any glass composition can now be prepared by the sol-gel method. Bulk glass, both porous and dense, coatings and fibers have all been obtained and some have been shown to have superior performance to their conventional equivalents in a number of applications. As is often the case however, theory lags behind application. The chemistry of the polymerization of even silicon tetraethoxide alone has not yet been fully determined; the tetrafunctionality of this material results in early branching and crosslinking to three dimensional structures during polymerization which is also affected by the type of catalyst, acidic or basic, used. Whether the far more complex multicomponent systems will ever be understood remains to be seen.

The potential applications have obviously not yet been fully realized as indicated for example by the disappointing lack of commercialization. However, there appears to be no reason to expect interest in this field to wane. This is a new method for preparing a very old product, a product having a broad variety of uses; research interest should therefore remain high and the field should be fruitful for many years to come.

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