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Preparation of glasses and ceramics from metal-organic compounds

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The preparation of glass and ceramic systems from metal–organic compounds permits the mixing of the constituents at the molecular level. These mixes form clear glasses or sinter to dense bodies at temperatures considerably lower than the equivalent compositions prepared by classical methods. A significant recent development in this field has been the preparation of monolithic glass and ceramic material without the need of melting or high temperature sintering. Glass-forming reactions, previously achievable only by thermal means, can take place by chemical polymerization at room temperatures. Structural studies indicate that these materials are indeed amorphous or glassy in nature. Thus, the often used description of glass as a "supercooled liquid" is, in the literal sense, inapplicable for these materials.

1. Introduction

The preparation of glass and ceramic materials from metal–organic compounds, such as the metal alkoxides, permits the mixing of constituents at the molecular level. Owing to this intimate mixing, these materials melt to clear glasses or sinter to dense bodies at temperatures considerably lower than the equivalent compositions prepared by classical methods. Doping and stabilizing ceramic materials via the metal–organic and sol–gel process have proven extremely effective [1–4].

The attractive properties of materials derived from metal–organic precursors generally include: high purity; molecular level homogeneity in multicompetent materials; submicron particle size (typically 20 to 50 Å); high reactivity and surface area; lower processing temperatures. Because of these characteristics, sol–gel material preparation processes have been applied in hydrothermal experimentation for phase studies [5], coating technology [6, 7], and in the preparation of high density nuclear materials [8–10]. With the exception of thin films coated on substrates, the inorganic materials obtained previously from these sols have been in particulate form. The powders were subsequently melted or sintered into bulk form.

Further advances in ceramic processing can be made in the area of forming monolithic glass and ceramic materials through chemical polymerization at low temperatures as discussed in this work. Such a development would allow, for example, glass formation without melting. The scientific and technological significance of forming bulk glasses and ceramics below their melting, crystallization, or phase separation temperature is obvious. The potential also exists to form numerous new materials which are structurally unstable at high temperature and, therefore, could not have been prepared by thermal reactions.

2. Metal–organic compounds as glass ceramic precursor

The term "metal–organic" rather than "organometallic" has been used in this paper to include those compounds in which organic groups are bound to a metal via oxygen, etc. The classical definition of the term "organometallic" would exclude all compounds except those in which at least one organic group is bound directly to a metal atom. Here the term "metal–organic" includes all compounds having organic groups along with a metal (or metals). Compounds of special interest to material scientists are metal alkoxides, $M(OR)_n$, formates, $M(HCOO)_n$, acetylacetonates, $M(CH_3COCHCOCH_3)_n$ and alkyl MR_n, where M is a metal having a valence n, and R is an alkyl C_xH_{2x+1}. The chemical properties of these compounds are discussed in detail in the literature and textbooks. Here we will only make general remarks which are pertinent to their use as ceramic and glass percursors.

Metal alkoxides, $M(OR)_n$, are by far the most useful compounds for the ceramic forming processes reviewed here. Alkoxides of group III and IV metals, which constitutes a large portion of glass and ceramic compositions, are often volatile liquids that can readily be purified by distillation. High purity alkoxides of silicon, titanium, aluminium, and boron are commercially available at relatively low costs. Alkoxides of almost any metal can be synthesized [11–14] and all metal alkoxides can be converted to metal oxides either by thermal degradation or by hydrolization followed by dehydration, as shown in Equations 1 to 3.

Thermal degradation:

$$M(OR)_n \rightarrow MO_{n/2} + \frac{n}{2}R(OH) + \text{olefins}. \quad (1)$$

Hydrolysis and degradation:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nR(OH) \quad (2)$$

$$M(OH)_n \rightarrow MO_{n/2} + \frac{n}{2}H_2O. \quad (3)$$

These reactions take place below 500° C. The oxide products of the first method consist of unusually small particles, i.e. 20 to 50 Å [15]. The routine product of the second method is again in the form of particulate material. However, the hydrolysis reaction of alkoxides can be controlled to proceed in an orderly manner to cause polymerisation. This is especially true for those alkoxides where the reaction is relatively slow, thus permitting a large degree of control, e.g. $Si(OC_2H_5)_4$.

Metal carboxylates, $M(OCOR)_n$, become particularly important when M is a metal of group I or II and R is methyl, CH_3, in the carboxylate. These are water soluble acetates of group I and II metals which do not form suitable alkoxides. These compounds are non-volatile; nevertheless, they can be purified by crystallization from solutions. Acetates thermally decompose to give oxides:

$$M(OCOCH_3)_n + 2nO_2 \rightarrow MO_{n/2} + 2nCO_2 + (3n/2)H_2O. \quad (4)$$

Pyrolysis of these materials generally takes place gradually between the temperatures of 150 to 450° C. Their particular usefulness arises because of their water solubility and compatibility with alkoxides as will be evident. The metal alkyls, MR_n, are generally pyrophoric and require special handling. Their reaction with water gives hydroxides. They can also be converted to corresponding alkoxides. Some of these are volatile liquids and can be distilled to a high degree of purity.

There are numerous other classes of metal–organic compounds with lesser use in the ceramic forming process described which will not be discussed.

3. Preparation of oxides and other ceramics

As mentioned earlier, metal alkoxides may be converted to metal oxides either by thermal degradation or by hydrolysis followed by dehydration. Zirconium tetra-tertiary butoxide and aluminium sec-butoxide illustrate these reactions:

$$Zr(OC_4H_9)_4 \xrightarrow{325-500^\circ C} \underline{ZrO_2} + 2C_4H_9OH + 2C_4H_8 \quad (5)$$

$$Al(OC_4H_9)_3 + 3H_2O \rightarrow Al(OH)_3 + 3C_4H_9OH \quad (6)$$

$$2Al(OH)_3 \xrightarrow{150-450^\circ C} \underline{Al_2O_3} + 3H_2O. \quad (7)$$

These are simplified reactions. The actual reactions are much more complex and take place in steps [16]. Of great interest is the unusually small particle size of the resultant oxide. Average particle size of the ZrO_2 obtained by Reaction 5 was found to be 30 to 50 Å; electron microscope studies indicate that larger particles were agglomerates of particles having sizes of 20 Å or less [15].

The importance of high purity submicron-sized particles in preparation of high density special ceramics, films for electronic components, absorbents, and filters are well known. In addition, these powders are extremely reactive due to their high surface area, and sinter to dense bodies at much lower temperatures than classical oxides.

High purity submicron-sized oxides of almost any element, e.g. Hf, Y, Ce, Th, Ti, Sn, Ge, V, Nb, Ta and Fe, can also be obtained from their alkoxides in a similar manner.

The simultaneous degradation of metal–organic compounds may be employed to prepare submicron-sized ultra-high purity mixed or doped oxides. Obviously, the compounds used must have similar volatility and decomposition characteristics in order for the resultant mixed-oxide phase to be homogeneous.

Another method involves dissolving one or more alkoxides in a mutual solvent, e.g. benzene C_6H_6. Distilled water is then added dropwise to the solution, while vigorously stirring. Mixed oxides will precipitate from the solution. Yttrium doped zirconia, "Zyttrite*", has been prepared by this method from $Zr(OC_3H_7)_4$ and $Y(OC_3H_7)_3$. Titanates can also be prepared in this matter. $BaTiO_3$ and $HfTiO_4$ have been prepared with purities better than 99.9% and particle size less than 50 Å. There has been evidence that some of the titanates are formed even before the solid state reaction of the two individual oxides [17]:

$$Hf(OR)_4 + Ti(OR)_4 + 4H_2O \rightarrow HfTiO_4 + 8ROH. \quad (8)$$

The governing factor in this method is that the alkoxides involved must have relatively compatible reaction rates. Silicon alkoxides, for example, are much slower to hydrolyse than the aluminium alkoxides. A mixture of these alkoxides will result in preferential precipitation of the aluminium hydroxide. However, in the case of silica-based oxides, this problem is easily solved by forming a single compound of metallo-siloxane between the silicon alkoxides and other alkoxides, so that it is the single compound that reacts. Details of this important technique are given later.

Practical and commercial importance of metal–organic precursors in ceramic preparation has been demonstrated by the stabilization of zirconia and active alumina [4, 1]. ZrO_2 and HfO_2 need to be stabilized in the cubic form to avoid the destructive shock of the monoclinic–tetragonal phase transformation. Mazdiyasni and other workers have demonstrated that, by mixing classical oxides, it required at least 12% Y_2O_3 and a heat-treatment of 24 h at 1800° C to stabilize the zirconia in the cubic phase; whereas 6% Y_2O_3 and $\frac{1}{2}$ h heat-treatment at 800° C is all that is required to obtain a 100% stabilized cubic phase zirconia via the metal–organic route [1].

Metal–organic compounds can also be employed advantageously in preparation of ceramics other than oxides. For example, a common method of producing boron carbide is to react a boron halide and a hydrocarbon under a hydrogen atmosphere [18]:

$$4BCl_3 + CH_4 + 4H_2 \rightarrow B_4C + 12HC_1. \quad (9)$$

Similarly, boron alkyls can be decomposed in the vapour phase to yield extremely fine boron carbide powder.

Metal–organic compounds also lend themselves to the preparation of free metal–oxide dispersions by decomposing suitable metal compounds to free metal along with one of the alkoxides to produce metallic dispersion in the oxide phase.

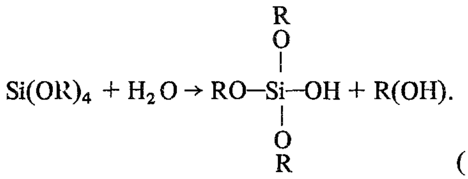
4. Chemical formation of monolithic glass and ceramic materials

The most important advantages of using metal–organic compounds are brought to bear in the formation of multicomponent glasses and ceramic materials. When a glass composition is prepared from metal–organic compounds under proper conditions, initially a clear liquid results, indicating a homogeneous mixture at the molecular level. However, during the hydrolysis, drying, etc., inhomogeneities often occur unless the initial phase is structurally frozen. In classical glass formation, the liquid structure is preserved by supercooling of the melt from elevated temperatures; here the preservation of the liquid structure is accomplished by the gelling process.

A great majority of technical and commercial glasses contain the glass former silicon. For this reason, we will describe preparation of silica-containing glasses. The preparation of other glasses follows similar lines.

Silicon alkoxides are slow to hydrolyse compared to most other alkoxides. This means that, if a solution of silicon and other alkoxides is prepared by physical mixing, a differential precipitation will occur during hydrolysis. This is circumvented by a technique, where initially a single compound is formed by silicon alkoxide and other precursors, which then reacts as a unit. This technique also illustrates formation of a glass network at room temperature by chemical polymerization.

For example, silicon alkoxide and alkyls may be partially hydrolysed with insufficient water to form a soluble silanols [19], e.g.:



$$Si(OR)_4 + H_2O \rightarrow RO\text{—}\overset{\overset{\displaystyle R}{\displaystyle O}}{\underset{\underset{\displaystyle R}{\displaystyle O}}{Si}}\text{—}OH + R(OH). \quad (10)$$

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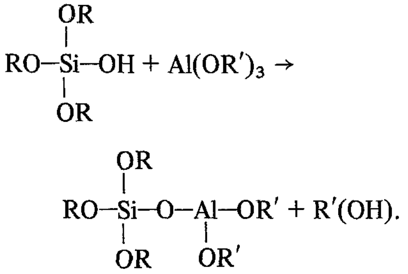
* Cherrybrook Company, Fairborn, Ohio, USA.

In the case of silicon tetraethoxide, $Si(OC_2H_5)_4$, the resultant ethyoxysilanol, $(C_2H_5.O)_3Si{-}OH$, is soluble in ethanol, $C_2H_5(OH)$, and readily reacts with other metal alkoxides, e.g. $Al(OR')_3$, as follows:



$$\mathrm{RO{-}\underset{OR}{\overset{OR}{Si}}{-}OH + Al(OR')_3 \rightarrow}$$

$$\mathrm{RO{-}\underset{OR}{\overset{OR}{Si}}{-}O{-}\underset{OR'}{Al}{-}OR' + R'(OH).} \tag{11}$$

The alumino–siloxane derivative formed by the above reaction contains glass network formers, Si and Al, connected by oxygen. Furthermore, since metallo–siloxane derivative is also soluble, it does not precipitate. The addition of more water and other alkoxides, as the glass composition may dictate, causes further polymerization and cross-linking until the entire solution gels into a clear stiff single phase.

Some glass constituents (elements of Groups I and II) do not form suitable alkoxides. Water soluble salts such as acetates and nitrates can be used for these constituents. When the acetates of these elements yield a basic solution which cause premature gelation, the solution must be made acidic by acetic acid.

The gel thus formed must be dried gradually. Heating of the dryed gels to 400 to 500° C causes pyrolysis to an essentially pure oxide system. In some cases, it may be necessary to heat the material to somewhat higher temperatures in order to remove the last traces of organic matter. At this point, either powder or clear but porous glass granules result. The material may have as much as 200 to 500 $m^2 g^{-1}$ surface area and extremely high reactivity. It was found that this material can be sintered to dense clear glass pieces well below the melting temperature. This fact can be used for preparing high temperature glasses, e.g. titanate glasses, at significantly lower temperatures. It should also be noted that no stirring would be required. However, the material must not be heated rapidly, for this may cause extensive foaming and trapping of carbonaceous residues. In the case of some glass constituents, such as lead or zinc oxide, the use of metal–organic compounds may cause free metal formation during the degradation. Fine oxide powder suspension of these elements can directly be introduced into the solution. Alkoxide batches other than silicon may also be prepared similarly; these latter systems generally give fine particulate reactive powders, rather than coherent bodies.

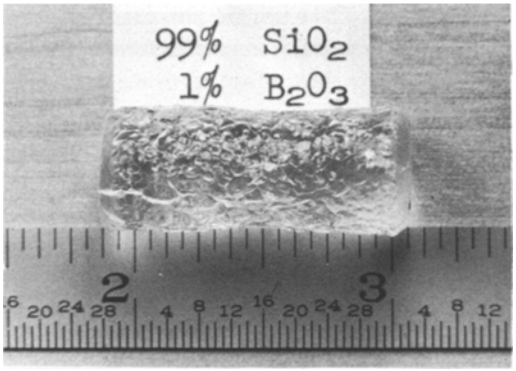


Figure 1 Monolithic glass sample obtained from a gel prepared from silicon and boron alkoxides. The gel was dried and fired to 500° C, remaining monolithic during the pyrolyses.

A significant development in this field has been the preparation of non-particulate materials from organo-metallics at low temperatures. Formation of a transparent monolithic Al_2O_3 produced from aluminium alkoxides at 500° C has been reported [20]. This alumina material is 64% porous, yet due to the very small pore size, ~30 to 50 Å, it is transparent. It can also be incorporated with other constituents to give various alumina-based ceramic materials.

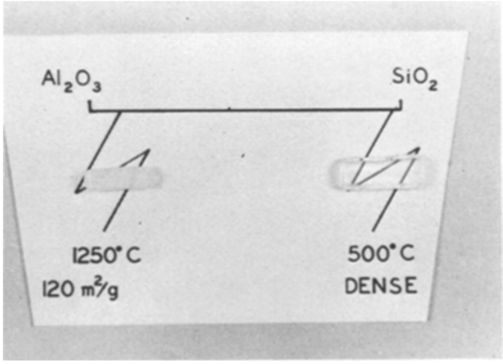


Figure 2 Two monolithic samples obtained from gels in the Al_2O_3–SiO_2 binary system by using silicon tetraethoxide and aluminum sec-butoxide as precursors. (The sample on the left having composition 94% Al_2O_3, 6% SiO_2 is fired to 1250° C and the one on the right having composition 98% SiO_2, 2% Al_2O_3 is fired to 500° C, both for 15 min.) Percentages given are wt %.

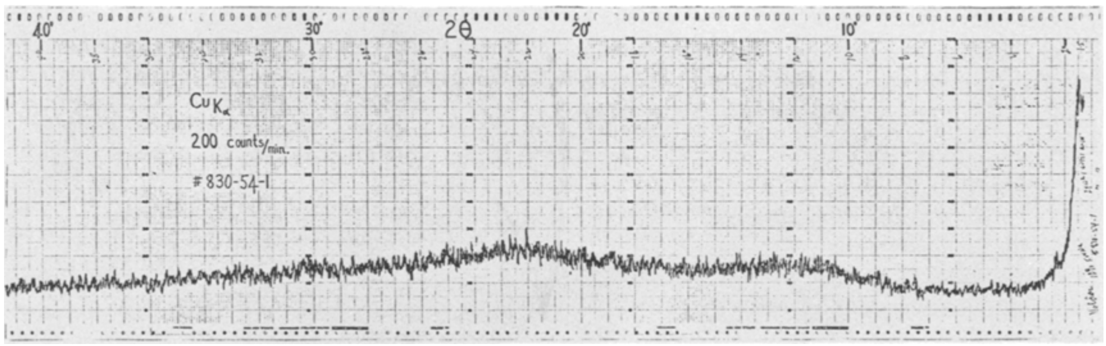


Figure 3 The X-ray diffraction pattern of composition 90% SiO_2–10% Na_2O. (The material is produced from $Si(OC_2H_5)_4$ and $Na(OCH_3)$ and fired to 500° C for 15 min.) Percentages given are wt%.

In the laboratory, several cm large monolithic glass samples of a wide variety of compositions were prepared by gel processes at low temperatures from silanol solutions, metal alkoxides, and hydroxide sols. Under controlled conditions, the constituents of the mixtures were reacted and gelled to a clear state, the gels were dryed and heated to 400 to 500° C to drive off the water and organic groups; transparent monolithic pieces of glass and ceramic materials resulted (Fig. 1).

The versatility of these processes in controlling and producing special properties in ceramic and glass materials is evident in Fig. 2. The composition, 6 wt% SiO_2–94 wt% Al_2O_3 is porous (pore diameters ~100 Å) and has a surface area of 120 $m^2 g^{-1}$ after a heat-treatment at 1250° C, whereas the composition 98% SiO_2–2% Al_2O_3, similarly produced is practically dense at 500° C.

X-ray diffraction of these materials often shows the complete absence of crystalline peaks, indicating the amorphous nature of their structure (Fig. 3). The noncrystalline nature of the structure is also confirmed with other methods of investigation, e.g. Infra-red, electron microscopy, etc. The details and analysis of these studies will be presented in a future publication. The infra-red spectrum, in addition to indicating absence of crystallinity, shows that there is no significant concentration of hydroxyl ions in the lattice (Fig. 4). (However, there may be considerable amount of surface water due to the high surface area, 100 to 500 $m^2 g^{-1}$.) It appears that enhanced melting and sintering of these materials is largely due to the chemical bond formation between the constituents rather than presence of hydroxyls in the lattice. In classical glass melting processes, large amounts of thermal energy must be spent to cause reaction and diffusion between separate batch particles.

5. Discussion

The gels prepared by classical methods eventually break down to produce oxide powders, whereas the gels prepared from metal–organic compounds under certain conditions tend to retain their integrity producing relatively large pieces of transparent glass and ceramic materials. Unfortunately, very little is known about the structural requirements for the gel to remain monolithic during the drying and pyrolysis. In the case of monolithic alumina, it was observed that only when the electrolyte concentration was in the range of 0.03 to 0.1 mole/mole of alkoxide, where the gelling volume goes through a minimum, the gel retains its integ-

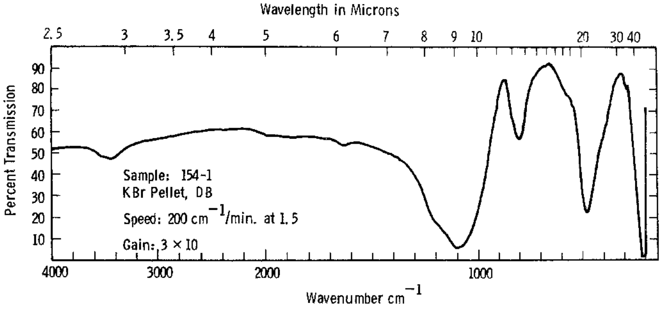


Figure 4 The infra-red spectrum of composition 90% SiO_2–10% Na_2O. (The same material as in Fig. 3.) Percentages given are wt%.

rity during drying and pyrolysis [21]. The reason the gel retains its integrity only in a narrow electrolyte concentration range, in this case, may be due to a requirement for the average interparticle distance which must not be exceeded if the gel is to remain monolithic [22].

The reason certain other gels, such as silanol gels, retain their integrity may be due to the degree and nature of polymerization, e.g. linear or cross-linked, concentration of remaining alkyl and hydroxyl groups, and certainly the distribution and location of such groups in the structure. For example, it would be desirable for the organic components to be located largely at the terminating points in the structural chains, rather than being bridging components. In the latter case, the structure will break up by the removal of the organic component. The amount of organic bridging component that can be tolerated before the gel loses its monolithic character is an unknown but certainly an important parameter.

The amount of a second oxide that can be incorporated in monolithic material forming systems, such as in the alumina and silanol sols, appears to be determined in part by the electrolytic effect of the added compound, and subject to the same considerations mentioned above. Therefore, it is possible to introduce more of the same oxide into these systems from a weak electrolyte source, e.g. acetates, than from a strong electrolyte source such as nitrates or chlorides [22]. For example, one can only introduce 3 to 5% Na_2O from $NaNO_3$ into these sols before the resultant materials start to lose its monolithic and transparent nature; whereas, the entire range of the compositions in the Al_2O_3–SiO_2 binary system can be produced in monolithic form from the silanol and alumina sols previously described [23] (Fig. 2).

Results to date, nevertheless, are empirical and there is a need for basic research to establish and explain the underlying forces which determine the capability of a sol/gel system to retain its integrity during the heat-treatment.

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