Preparation and Properties of New Inorganic Glasses and Gel-Derived Solids

J. D. Mackenzie

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Research has been carried out on two families of solids. This first one involves solids made by the sol-gel process and includes composites. The second one involves non-oxide glasses based on fluorides, chalcogenides and chalcohalides. The structures of oxide gels were studied by X-ray photoelectron spectroscopy, and the gelation of gels investigated as a function of temperature and catalyst. A new theory was developed on gel transformations. A number of new composites made by the sol-gel route were examined including the use of SiC and diamond powder as fillers and some triphasic solids. The viscosity and viscoelasticity of fluorozirconate glasses and glass fibers have been studied. New chalcohalide glasses were prepared and their optical properties evaluated. Structural information was derived from Raman spectra.
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Preparation and Properties of New
Inorganic Glasses and Gel-Derived Solids

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ABSTRACT

Research has been carried out on two families of solids. This first one involves solids made by the sol-gel process and includes composites. The second one involves non-oxide glasses based on fluorides, chalcogenides and chalcohalides. The structures of oxide gels were studied by X-ray photoelectron spectroscopy, and the gelation of gels investigated as a function of temperature and catalyst. A new theory was developed on gel transformations. A number of new composites made by the sol-gel route were examined including the use of SiC and diamond powder as fillers and some triphasic solids. The viscosity and viscoelasticity of fluorozirconate glasses and glass fibers have been studied. New chalcohalide glasses were prepared and their optical properties evaluated. Structural information was derived from Raman spectra.
1. INTRODUCTION

This research program, under Contract No. AFOSR-84-0022 was studied in October 1983. It is concerned with two relatively new families of solids of importance to the Air Force. The first family consists of porous oxides derived from gels and composites prepared from such porous gels. The second family is concerned with non-oxide glasses which are infrared transmitting. The broad objectives of this program are to learn how to prepare these solids, measure some important properties and understand how these properties are controlled by chemical composition, structure and microstructure.

This final technical report covers the period from 1 October 1986 to 30 September 1987.

2. Progress in Sol-Gel and Composites Research

a. Fundamental Understanding of the Sol-Gel Process

The sol-gel process for the preparation of glasses and ceramics has received a great deal of attention in the past few years.\(^{(1,2)}\) Although this new processing route does hold promise for new materials and enhanced properties, truly successful applications are relatively few.\(^{(3)}\) The main barrier to progress is the lack of sufficient knowledge on the process of gelation. The UCLA group has performed systematic studies on the effects of solvent, catalyst, raw materials and temperature on the rates of gelation, and the microstructure of the resulting gel. Silica was selected for the studies because of its relative simplicity. The very significant effects of all these factors were clearly demonstrated.\(^{(4)}\)
During gelation, the viscosity of the solutions increases as a function of time. Throughout this process the molecular weight is also increasing. We have developed two theoretical models to elucidate this structural evolution utilizing data. The first one, applicable to linear gels such as SiO$_2$ with HCl as a catalyst is represented by the equation:

$$\ln(\eta) = \left[\ln(A) + m\ln(\Omega) \right] + m\ln(\alpha/1-\alpha)$$

(1)

where $\eta$ = viscosity,

$A = \nu_o/M_o$ = initial viscosity/initial molecular weight.

$m$ = slope

$\Omega = 2M_o/(F-2)$ and

$F$ = functionality

$\alpha = $ reduced time of gelation $= t/t_{gel}$

The second model, applicable to fractal growth such as HF-catalyzed SiO$_2$ gel, is represented by:

$$\ln(\eta_s) = \ln(QL/p_o) + (3 - D)qr t$$

(2)

where $\eta_s = $ reduced viscosity $= (\eta/\eta_0 - 1)$,

$Q = $ mass conc. of hydrolyzed monomer in solution

$L = $ Einstein geometrical constant

$D = $ fractal dimension

$qr = $ exponential constant for radius growth
\( \rho_0 \)  = fractal core density, and

\( t \)  = time

The first model, linear growth, appears to be applicable to silica gels catalyzed by HCl as seen in Fig. 1. The complexities involving HF catalyst are illustrated by the three growth regions for a silica gel in Fig. 2. The two models developed will serve to differentiate the various growth mechanisms under different conditions. They have contributed to the understanding of gelation in the silica system. The application of these models to other gel systems will be attempted in the near future. For this purpose, research has commenced on the measurement of viscosity for the \( \text{Al}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3-\text{SiO}_2 \) system as for the \( \text{SiO}_2 \) system.

After gelation has occurred and the gel has been dried, two types of dense oxides can be prepared, namely, glasses and polycrystalline ceramics. The porous gel will have to be heated, of course. The difference between a melt-formed glass and a gel-derived amorphous solid is shown in Fig. 3. During this period, significant progress has been made in the understanding of what controls the ultimate structure of a gel-derived amorphous solid. The theory we have developed is based on the application of a topology concept similar to Zachariasen's rules for oxide glasses. Based on such an approach, some gel systems are more likely to give a polycrystalline ceramic (e.g., \( \text{Al}_2\text{O}_3, \text{TiO}_2, \text{BaTiO}_3 \)) and some are more likely to give glasses (e.g., \( \text{SiO}_2, \text{GeO}_2 \)). These two groups of oxides are shown in Tables 1 and 2, respectively. This fundamental understanding of the gel transformation process will be very useful for the preparation of all types of oxides via the sol-gel process in the future.
b. New Inorganic Composites Based on Gels

By the addition of inorganic or organic particles to sol-gel solutions and allowing the mixture to gel, a porous composite can be made. The preparation of silicon carbide-silica porous composites was successful. The porous composites were subsequently fired to give dense composites. The porous composite, however, can also be impregnated with organic polymers. We thus have a triphasic composite. In Fig. 4, it is seen that a triphasic composite consisting of SiO₂, SiC and PMMA exhibits yield behavior similar to that of a metal. A tentative theory has been formulated to explain this very interesting property of this new composite.

By stirring dye molecules into a sol-gel solution and allowing the solution to gel, it has been shown that the dye molecules are encased in an oxide gel. The dyes can no longer be leached out from the oxide matrix. Such composites are potentially useful for many optical applications especially if the dye molecules are non-linear in their optical properties. These types of composites, however, are very porous and have low mechanical strengths. Further, the interconnective fine pores permit the passage of impurities which can degrade the mechanical, chemical and optical properties of the composite. We have successfully filled up the pores with PMMA, thus giving a dense composite which is still optically transparent.

Work is continuing on diamond-oxide, cubic boron nitride-oxide composites. Such new composites have unique properties and will be useful as coatings or substrate materials because of their high hardness, high electrical resistivity and low dielectric constant.
c. Ferroelectrics and Ferromagnetics by the Sol-Gel Technique

The sol-gel method for the preparation of glasses and ceramics has a number of advantages over conventional methods. One is the ability to achieve homogeneity at the molecular level since liquid molecules are mixed instead of micron-size powders. Another one is the ability to obtain dense polycrystalline ceramics because of the ease of sintering ultrafine particles. A third one is the ease of fabricating thick films from the liquid solutions. These advantages were exploited in the present research. Lead zirconium titanate (PZT) thick films have been successfully prepared from sol-gel solutions. Recently, by carefully control of viscosity and from an understanding of the gel transformation process, we have succeeded in the preparation of PZT ceramic fibers. Our group has pioneered research on the amorphous oxide to crystal transformations in gel systems and have obtained the first T-T-T curves. Such a plot is shown in Fig. 5.

3. Progress in Non-Oxide Glass Research

a. Chalcohalide Glasses

We have maintained a world-wide leadership position in the study of chalcohalide glasses such as Ge-S-I and Ge-Se-I. The structures of these glasses are not known. We have succeeded in elucidating the structures of glasses in these systems by the use of Raman and IR studies. Recently, we have prepared new glasses based on the Ge-S-Br system. Typically Raman spectra are shown in Fig. 6. As for the iodine-containing systems, complex groups such as GeBrₓS₄₋ₓ are formed when Br is added to GeS₂. Simultaneously, S is removed from the Ge atom to form S₈ rings. The structure of the resultant glass is shown in Fig. 7. Similar
results have been obtained for glasses containing Se in place of S.

b. Chalcogenide Glasses

We have continued to use the National Science Foundation Surface Analytical Facility at Montana to examine the X-ray photoelectron emission spectra (XPS) of chalcogenide and other glasses. For chalcogenides, when Ti is added to GeSe, for instance, two types of Se atoms can be formed as shown in Fig. 8. The XPS spectra are shown in Fig. 9. Both peak positions and peak shapes are altered. Figure 10 shows the results of a best-fit curve which gave quantitative information of the concentrations of non-bridging and bridging Se atoms.

c. Viscoelasticity of Glass Fibers

Recently, a study of the viscoelastic behavior of fluorozirconate glass fibers has been initiated. It has revealed that such fibers can undergo permanent deformation at temperatures some 150°C below T_g under relatively low levels of applied stress. This result is of great importance to the future application of halide glass fibers. We have therefore performed accurate annealing temperatures on ZBLA and ZBLAN glass fibers. Figure 11 shows the length changes of a 20 cm long, 130 μm diameter fibers with T_G= 300°C. It is seen that even at 100°C, the fiber can contract appreciably and after stabilizing in 72 hrs, would contract again at 150°C. From results such as those shown in Fig. 11, the activation energy for deformation is of the order of 10 Kcal/mole. This is about one-fifth of the value for viscosity at elevated temperatures. The phenomenon of low temperature deformation is thus not related to normal viscous flow. It is most likely the result of excess free volume in the fiber because of rapid cooling.
e. Volumetric Changes

Because of the unexpectedly large deformations found for halide glass fibers and because of the unusually large changes in viscosity over a relatively short temperature range, it was considered essential to obtain more information on volumetric changes between the solid glass and the melt. Figure 12 shows the variation of molar volume with temperature for two fluorozirconate systems. The difference in molar volume between the melting (liquidus) temperature, \( T_M \) and \( T_g \) is large and is likely to be the cause of the large viscosity differences between \( T_M \) and \( T_g \). Direct observations of structural changes via Raman spectroscopy of the melt are now planned.


5. Presentation of Research Based on this Project


6. Personnel

During this period the following people had participated and made contributions to the progress reported.

Dr. J.D. Mackenzie                  Principal Investigator
Dr. R. Almeida                    Visiting Research Fellow
Dr. J.S. Sanghera                 Postdoctoral Scholar
Dr. K. Chemseddine                Postdoctoral Scholar
Dr. Florence Babonneau            Postdoctoral Scholar
Ms. Mary Colby                    Research Assistant
Ms. Azar Nezeri-Eshghi            Research Assistant
Mr. Edward Pope                   Research Assistant
Mr. Jong Heo                      Research Assistant
Mr. Joseph Yuen                   Research Assistant
Mr. K.C. Chen                     Research Assistant
Mr. S.Y. Ryou                     Research Assistant
Mr. H.X. Zheng                    Research Assistant

In addition, a number of undergraduate laboratory assistants were employed to assist in this research program.
7. References


HCl Catalyzed Silica Gel
4:4:1 Formula (0.05HCl)
50°C Closed System

Fig. 1  Viscosity of silica gel illustrating nearly linear growth model.
III. Fractal Network Growth

\[ r_{11}/r_0 = 26.2 = 40 \text{ } (\text{assuming } D=2, r_0=1.1\text{A}) \]

II. Fractal Growth Regime

\[ r_{1}/r_0 = 2.43 = 3.7 \text{A} \]

I. Early Chain-Like Polymerization

Fig. 2 Viscosity data for HF-catalyzed silica gel.
Fig 3  Comparison of preparation processes of melt-formed glass and gel-derived amorphous solid.
Fig. 4  Yield behavior of a triphasic composite.
Fig. 5 T-T-T plots for PZT from gels
Fig. 6 Raman spectra of chalcohalide glasses.
Structural Model $\text{Ge}_{20}\text{S}_{60}\text{Br}_{20}$

Fig. 7 Structure of chalcohalide glasses showing $S_8$ rings.
Fig. 8    Formation of non-bridging Se atoms in GeSe glass
Fig. 9 XPS spectra of GeSe₂ and GeSe₅ containing Tl₂Se (b and c).
**Fig. 10** Selenium 3d XPS spectra of 70GeSe$_2$-30Tl$_2$Se: (---) raw spectrum after smoothing;

(---) convoluted spectrum; (---) 4-peak gaussian fit. 1, 2, 3, and 4 refer to the Se$_b$ 3d$_{5/2}$, Se$_{nb}$ 3d$_{5/2}$, and Se$_{nb}$ 3d$_{3/2}$ peaks, respectively.
CONTRACTION OF FIBER

(N1FQ)

Fig. 11 Low temperature deformation of halide glass fibers.
Variation of molar volume with temperature for two fluorohexoniates.

Fig. 12
Table 1

Vitrifiable Oxides from Gels

<table>
<thead>
<tr>
<th>System</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_L$ (°C)</th>
<th>Ref.</th>
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<tr>
<td>$SiO_2$</td>
<td>1070</td>
<td>1400</td>
<td>1728</td>
<td>26</td>
</tr>
<tr>
<td>20$B_2O_3$–80$SiO_2$</td>
<td>490</td>
<td>1000</td>
<td>1050</td>
<td>27</td>
</tr>
<tr>
<td>15$P_2O_5$–85$SiO_2$</td>
<td>510</td>
<td>980</td>
<td>1030</td>
<td>28</td>
</tr>
<tr>
<td>20$Na_2O$–80$SiO_2$</td>
<td>460</td>
<td>620</td>
<td>1100</td>
<td>29</td>
</tr>
<tr>
<td>34$Li_2O$–66$B_2O_3$</td>
<td>280</td>
<td>550</td>
<td>920</td>
<td>30</td>
</tr>
<tr>
<td>$GeO_2$</td>
<td>600</td>
<td>695</td>
<td>1116</td>
<td>31</td>
</tr>
<tr>
<td>10$PbO$–90$GeO_2$</td>
<td>462</td>
<td>540</td>
<td>1040</td>
<td>32</td>
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<tr>
<td>25$CaO$–25$Al_2O_3$–50$SiO_2$</td>
<td>875</td>
<td>1060</td>
<td>1550</td>
<td>33</td>
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Table 2

Easily Crystallized Oxides from Gels

<table>
<thead>
<tr>
<th>System</th>
<th>$T_c$ (°K)</th>
<th>0.5 $T_L$ (°K)</th>
<th>$T_L$ (°K)</th>
<th>Ref.</th>
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<td>$Al_2O_3$</td>
<td>748</td>
<td>1162</td>
<td>2323</td>
<td>34</td>
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<td>$4Y_2O_3\cdot 6Al_2O_3$</td>
<td>1083</td>
<td>1087</td>
<td>2173</td>
<td>35</td>
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<tr>
<td>$TiO_2$</td>
<td>473</td>
<td>1072</td>
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<td>36</td>
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<td>$BaTiO_3$</td>
<td>873</td>
<td>943</td>
<td>1885</td>
<td>37</td>
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<td>$SrTiO_3$</td>
<td>773</td>
<td>1157</td>
<td>2313</td>
<td>38</td>
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<tr>
<td>$PbTiO_3$</td>
<td>723</td>
<td>722</td>
<td>1443</td>
<td>37</td>
</tr>
<tr>
<td>$PbZr_0.5Ti_0.5O_3$</td>
<td>803</td>
<td>847</td>
<td>1693</td>
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<td>$ZrO_2$</td>
<td>773</td>
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<td>$ZrO_2\cdot 2SiO_2$</td>
<td>673</td>
<td>1350</td>
<td>2700</td>
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<tr>
<td>$CoFeO_4$</td>
<td>880</td>
<td>950</td>
<td>1900</td>
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<td>$Li_2O\cdot Fe_2O_3$</td>
<td>573</td>
<td>950</td>
<td>1900</td>
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<td>$KTa_0.6Nb_0.4O_3$</td>
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<td>772</td>
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<td>963</td>
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<td>2123</td>
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<td>($film$)</td>
<td>908</td>
<td>1062</td>
<td>2123</td>
<td></td>
</tr>
<tr>
<td>$2TiO_2\cdot 5Nb_2O_5$</td>
<td>1083</td>
<td>874</td>
<td>1748</td>
<td>47</td>
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