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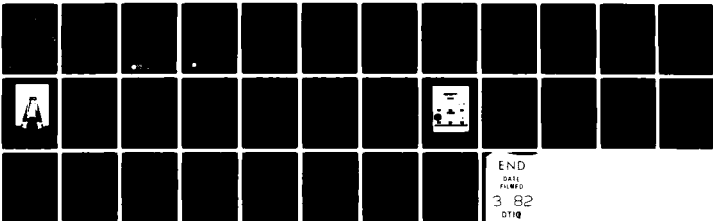
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FORMATION OF MONOLITHIC OXIDE MATERIALS BY CHEMICAL POLYMERIZAT--ETC(U)
JAN 82 B E YOLDAS, D P PARTLOW DAAG29-80-C-0055

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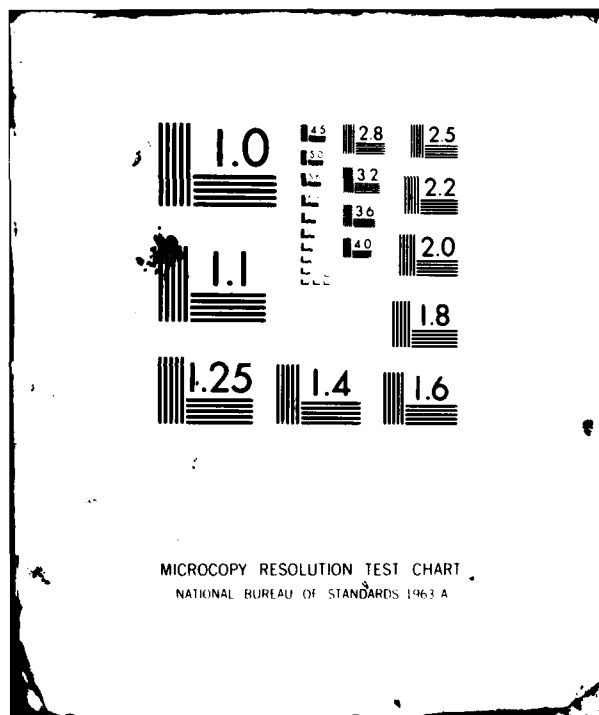
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20. ABSTRACT CONTINUED

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**FORMATION OF MONOLITHIC OXIDE MATERIALS
BY CHEMICAL POLYMERIZATION**

**B. E. Yoldas, D. P. Partlow
Ceramics and Glasses**

**Final Report
Contract No. DAAG 29-80-C-0055
January 1, 1979 to December 30, 1981**

January 14, 1982

**U.S. Army Research Office
Research Triangle Park, NC 27009**

**Westinghouse R&D Center
1370 Dutch Road
Pittsburgh, Pennsylvania 15235**

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PROBLEM STATEMENT

This project was designed to investigate the formation of oxide networks by chemical polymerization from metal organic compounds and the chemical and structural parameters involved in the process.

ABSTRACT

Hydrolysis of metal alkoxides results in the formation of polymer molecules with oxide main chains framed by hydroxyl and organic groups. The skeleton of the main structural chains in these polymer molecules is generally analogous to the skeleton of fused silica and quartz. However the method of hydrolysis affects the nature and extent of the oxide network. Thus changes in the hydrolysis process alter many of the fundamental properties of the gel which are reflected in its general behavior, as well as the oxide materials derived from the gel. One of the critical factors affected by the method of hydrolysis is the capability of the gel to remain monolithic through pyrolysis.

This report presents an investigation of various parameters involved in the formation of inorganic polymers from metal alkoxides and the structures of these oxide materials.

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1. INTRODUCTION

Preparation of oxide materials from metal-organic compounds, particularly from metal alkoxides, is well known. Alkoxides of almost any metal can be synthesized, and their various physical and chemical properties have been extensively studied¹⁻⁵. Thermal degradation or hydrolysis of these compounds leads to the formation of submicron-sized oxide and hydroxide powders, typically less than 50Å in diameter. Much of the early interest in these materials centered around their submicron particle size, which provided for high reactivity and lower processing temperatures, as well as the high purity and homogeneity attainable in multi-component systems^(6,7). These properties have been used advantageously in making materials for phase stabilization⁽⁸⁾, hydrothermal experimentation⁽⁹⁾, and for the preparation of high density electronic and nuclear materials⁽¹⁰⁾.

Recently, the feasibility of forming monolithic glass and ceramic materials through chemical polymerization at low temperatures has been demonstrated⁽¹¹⁻¹⁷⁾. This development in glass formation largely owes its success to preparation of soluble intermediate species capable of polymerizing into an oxide network without thermal fusion, using metal organic compounds as starting materials. The polymerization of glass-forming species takes place at or near room temperature in a liquid medium and leads to gelation during the process. These gels, however, must not be confused with classical colloidal gels formed from metallic salts and colloidal sols⁽¹⁸⁾. With the exception of thin films coated on substrates, the inorganic materials obtained from the latter gels are particulate and must be subsequently melted or sintered into bulk form. This has historically been characteristic of all ceramic and glass forming processes; that is, the precursor material was always particulate at some stage of the process, and heat had to be applied to

cause fusion and coherency. Only the polymerized system transcends this historical limitation and thus represents a fundamental deviation from traditional processes.

Furthermore, glasses and oxide powders prepared from metal organic compounds under various hydrolysis and polymerization conditions show significant differences in their properties and behavior. A closer analysis shows that chemical polymerization, unlike melting or sintering, permits the introduction of structural variations into the inorganic network. These variations, in turn, significantly alter the behavior of materials and affect some of their basic properties such as melting point, crystallization, structural transformations, and viscosity^(19,20). Thus the technique is of considerable scientific and technological importance, since it may provide a tool of modifying behavior and properties of an important class of materials. In this work various aspects of preparation of oxide materials from metal-alkoxides are investigated.

2. CONCLUSIONS

1. Hydrolysis of metal alkoxides produces polymeric molecules having an oxide skeleton framed by hydroxyl and organic groups. The molar ratio of hydrolysis water to alkoxide affects the nature of this network, its chemical and its structural make-up.

2. The oxide content of these polymers increases with increasing amount of hydrolysis water, indicating an increasing oxide network formation and polymeric connectivity.

3. Investigations using photoacoustic and infrared spectroscopy, also show an increased concentration of bridging oxygen, long range order, and lower tetrahedral distortion with increasing amount of hydrolysis water in the silica system.

4. An increase in the average network connectivity induced by high-water hydrolysis enhances the strength and capability of the gel network to remain monolithic during pyrolysis.

5. Silica gels produced by low water hydrolysis, i.e., less than 1.5 moles per mole alkoxide remain elastic and retain their shape at temperatures below 150°C due to the presence of ester, (OR), groups in the structure. Removal of these organic groups during pyrolysis, however, results in extensive breakdown of these low-water hydrolyzed gels.

6. Structural studies indicate that the oxide network formed by this chemical polymerization method, in the case of high water hydrolysis, is essentially similar to that of fused silica.

3. RECOMMENDATION

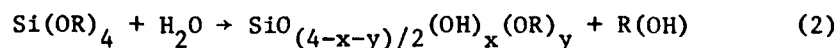
1. It has been established that molecular-structural variations can be introduced into oxide systems, including Al_2O_3 , ZrO_2 , TiO_2 , and SiO_2 by controlled hydrolysis and polymerization reactions during the formation of oxides from metal-alkoxides. A detailed study should be done to investigate the exact nature of these variations and their effect on sintering, crystallization, and crystalline transformations. Such an investigation may provide a way of producing modified materials without having to make compositional changes.

4. HYDROLYSIS OF METAL ALKOXIDES AND RESULTANT MATERIAL

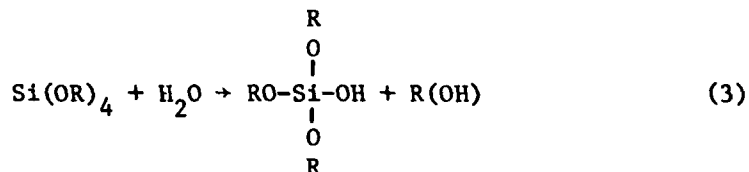
Metal-alkoxides generally react with water vigorously; this reaction, which is called hydrolysis, is often described using the simple equation:



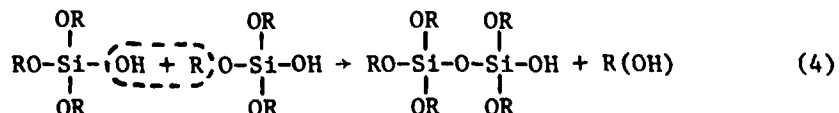
where M is metal with valence n, and R is an alkyl group, i.e., $R = C_{x-1}H_{2x-1}$. However, the hydrolysis product is rarely, if ever, the pure hydroxide shown in equation (1). It may contain in its structure a significant amount of ester groups, (OR), in addition to nonhydroxyl oxygens, i.e., bridging oxygens. For example, silicon alkoxides, even in excess water, do not completely hydrolyse to an "OR"-free complex, e.g., $Si(OH)_4$. Not only can "OR" and "OH" radicals coexist in the hydrolysed product, but substantial amounts of bridging oxygens are also formed⁽¹¹⁾:



This may be represented schematically:

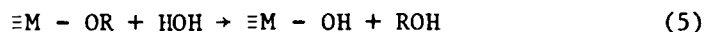


These soluble ethoxysilanol species self-polymerize upon aging, creating numerous less active secondary species, e.g.:

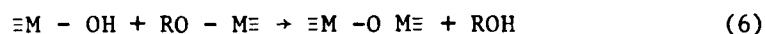


Hydrolysis of metal-alkoxides therefore results in the formation of polymer molecules with oxide main chains framed by hydroxyl, (OH), and ester, (OR), groups. These polymers are formed through the occurrence of two simultaneous reactions:

Hydrolysis:



Polymerization:



The hydrolysis reaction occurs between the alkoxide and water, converting some of the "OR" bonds into "OH" bonds. The polymerization reaction, triggered by the first, occurs concurrently between remaining OR species and freshly formed hydroxyl groups of the surrounding species. Both reactions release alcohol, but only the latter reaction forms bridging oxygens and eventually leads to either continuous network formation, e.g. gel, or condensation of hydroxide or oxide particles by limited network formation. The extent of network formation is determined by the kinetics of both reactions.

4.1 Gelling

Gelling in polymer solutions is basically due to chemical reactions leading to higher network connectivity, as shown in equation 4. This contrasts with colloidal sols, where the gelling occurs as a result of electrolytic interaction and does not involve a chemical change⁽¹⁸⁾. Furthermore, there are differences among various polymer systems which provide the basis for a breakdown of these gels into 2 types, as shown in figure 1.

In the first type, polymer species may be formed by the initial polymerization, and the system may be gelled by evaporating the excess liquid. In the second type, the chemical reactions leading to polymerization and network formation continue in the liquid. Active species

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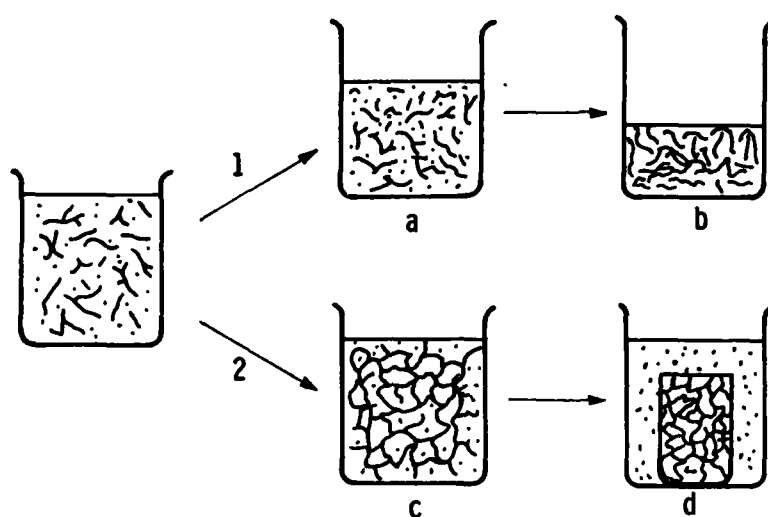


Figure 1 - Polymer solutions exhibit two methods of gellation

slowly build up an inorganic network by expelling organic groups from the structure by chemical reaction. If the reaction rate and nature are such that continuity is maintained, we found that the gel continued to shrink within the liquid. This behavior was in clear contrast with that of colloidal systems, where the volume of the gel could not be smaller than its liquor, and the organics had to be driven out thermally. An example of this type of polymer gel was found in the titania system (figure 2). Whether a polymer solution would gel or not depended upon numerous parameters, e.g., type of solvent, temperature, etc., but there were two predominant factors:

- Water/alkoxide ratio
- Dilution of reacting species in the carrier solvent

The first parameter affected the nature of the initial species formed and the degree of overall hydrolysis. The second one affected the reaction rates, uniformity and equilibrium of the process.

In our investigation of silica systems, silanol solutions of ten weight percent equivalent SiO_2 were prepared by hydrolyzing silicon tetraethoxide, $\text{Si}(\text{OC}_2\text{H}_5)_4$, in ethanol, with hydrolysis water varying from 1 to 15 moles per mole of alkoxide. After a 24-hr. stand at 60°C in closed containers, these solutions were boiled to gels. The gelling volume of the solutions showed a substantial increase with increasing hydrolysis water, from about 100 cc per mole alkoxide at 1 mole of hydrolysis water to about 600 cc at 15 moles. A sharp increase occurred above 3 moles of water (Figure 3). In polymer systems gelling volume has a different significance than in colloidal systems. Here it is not an indication of electrolyte interaction between individual particles, but instead reflects the degree and type of polymerization. Low-water hydrolysis produced a gel of low volume because of a lack of extended polymerization. Also in contrast to colloidal systems, addition of electrolyte had a relatively small effect on the gelling volume. Gelling in polymer systems also occurred by aging, without a need for concentrating, provided that the initial equivalent oxide concentration

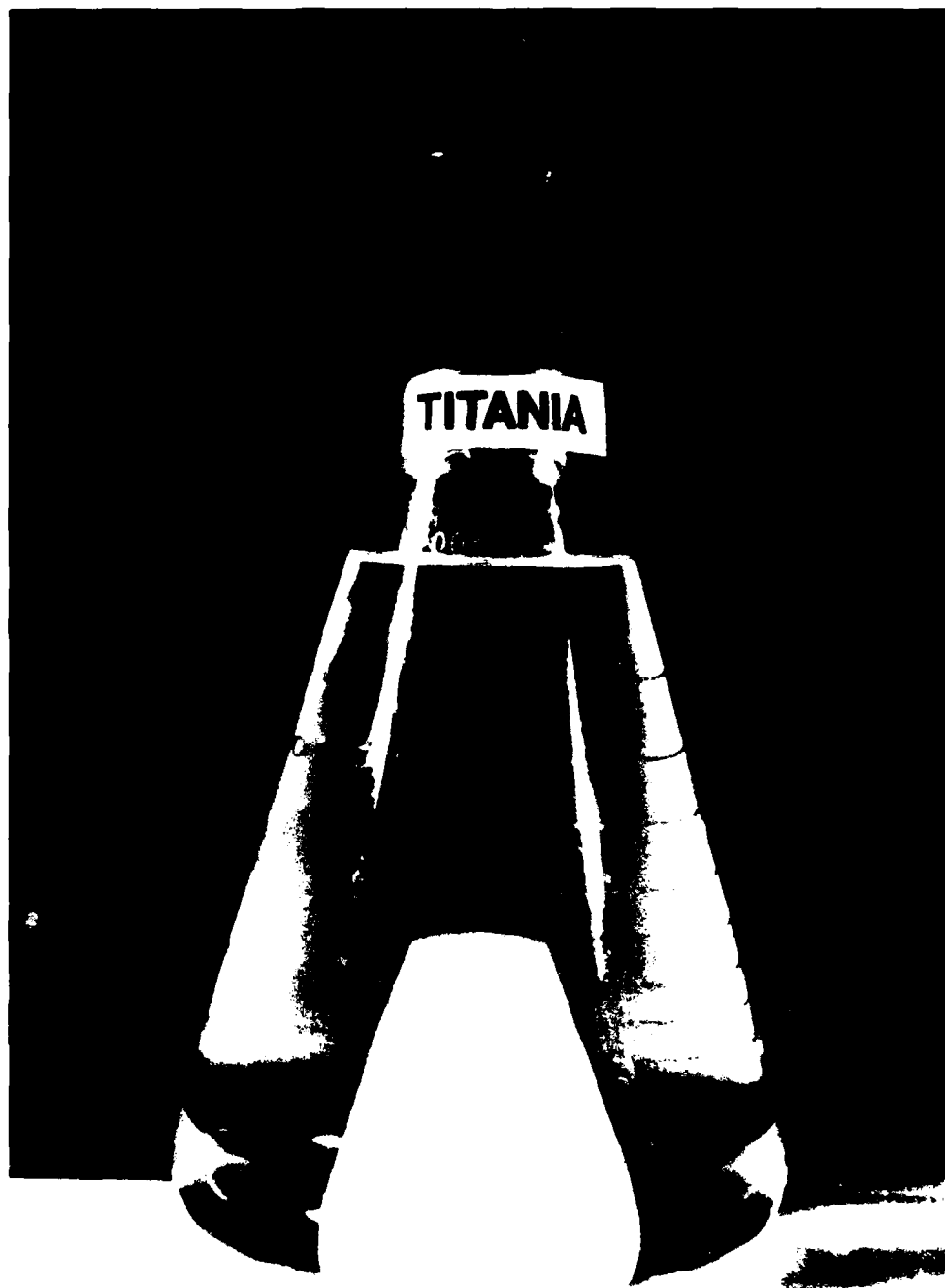


Figure 2 - Titania is a type 2 polymer system. Organics are expelled during continuous buildup of the inorganic network by chemical reaction, allowing the gel to form and shrink within the liquid

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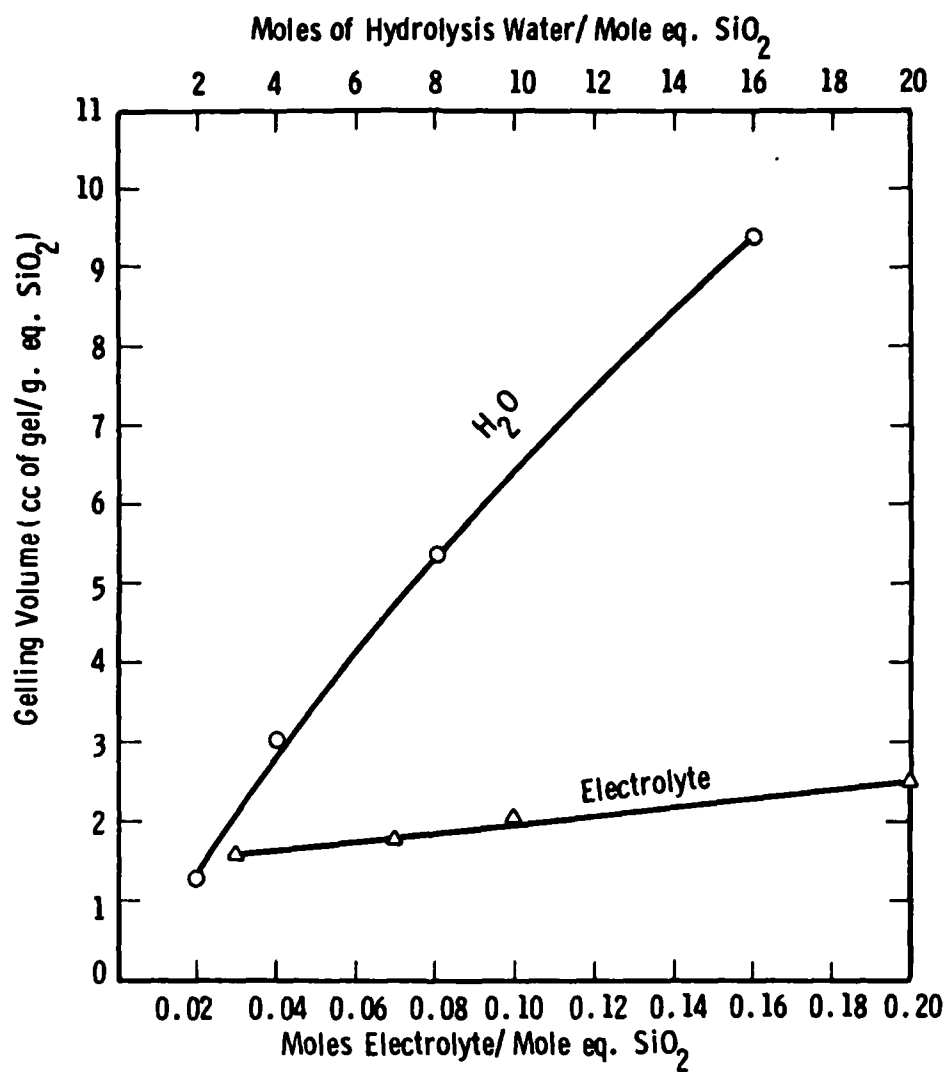


Figure 3 - Comparison of the effect of electrolyte concentration and the effect of hydrolysis water concentration on gelling volume in the silica system

of the solution was sufficiently high. In these instances the amount of hydrolysis water played a dominant role. Table 1 shows how the amount of hydrolysis water affected the gelling time when the solution concentration was fixed at 10% equivalent oxide in silica systems.

TABLE 1
EFFECT OF THE AMOUNT OF HYDROLYSIS WATER ON THE TIME
REQUIRED FOR GELLING OF 10% EQUIVALENT SiO_2 SOLUTIONS

<u>HYDROLYSIS WATER</u> <u>(moles/mole alkoxide)</u>	<u>GELLING TIME</u> <u>(hours)</u>
1	does not gel*
2	does not gel*
5	235
10	47
20	23

*observation extended over 100 days.

It was possible to produce highly concentrated solutions with long stability of shelf life in the silica system. Stable solutions having as high as 35-40% wt % SiO_2 were produced in this system. This required keeping the amount of hydrolysis water below 2 moles per mole of alkoxide, e.g., 1.0-1.5 mole. However, even with a hydrolysis water content as high as 3-4 moles, a relatively stable solution was produced containing more than 10% equivalent SiO_2 .

In oxide systems other than silica, gelling occurred at much lower concentrations and/or hydrolysis water content. For example, in the titania system, it was scarcely possible to provide non-gelling solutions above 5-6% e.g., TiO_2 with hydrolysis water above 2 moles. Table 2 shows the strong effect of the amount of hydrolysis water and concentration on gelling time in the TiO_2 system.

TABLE 2
EFFECT OF HYDROLYSIS WATER AND CONCENTRATION
ON GELLING TIME IN THE TITANIA SYSTEM*

<u>TiO₂ Concentration</u> <u>(% wt)</u>	<u>Hydrolysis Water</u> <u>(mole/mole alk)</u>	<u>Gelling Time†</u>
1	5	Does not gel
2	5	~24 hrs.
2	2.5	Does not gel
4	2.5	4-5 days
5	2.5	3 days
7	2.5	Immediate Gelling

*Ti(OC₂H₅)₄ hydrolyzed in ethyl alcohol.

†Observed after a 1-month stay at room temperature

As one can see, gellation is determined by the interaction of two factors. There is, however, a minimum concentration below which the solutions will not gel regardless of the amount of hydrolysis water. We found this concentration to be between 1 and 2% in most oxide systems e.g., TiO₂, ZrO₂, Al₂O₃, etc.; but it was significantly higher for SiO₂, e.g., 3-5%.

The viscosity changes in these solutions were gradual at first, but, after a certain time, a relatively rapid change in viscosity occurred, leading to gellation. This time corresponds to growth of the polymer molecules until a size is reached where close interactions between them occur. Figures 4 and 5 show viscosity changes in the SiO₂ and TiO₂ system as a function of time.

4.2 Variability of Chemical Make Up of Inorganic Polymers

It has been mentioned that the hydrolysis-polymerization reactions of metal alkoxides lead to formation of inorganic polymers with oxide main chain framed by hydroxyl groups. This suggests the very interesting and significant observation that the chemical composition

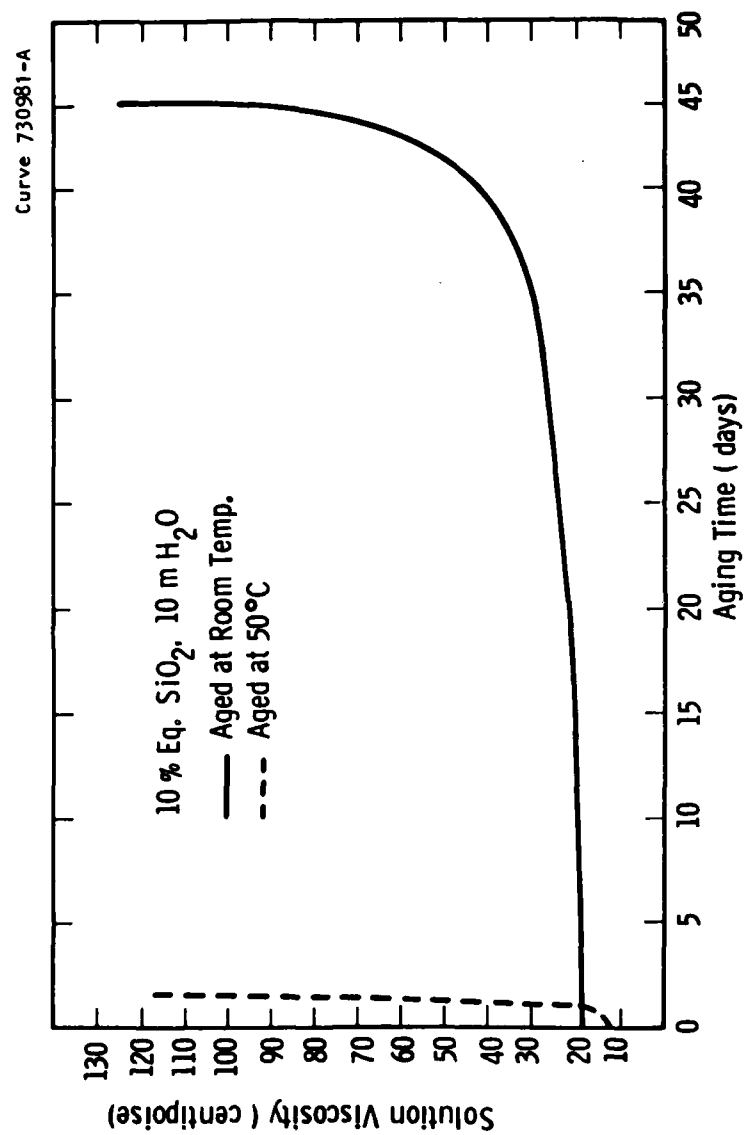


Figure 4 - Change in the viscosity of silica solutions upon aging

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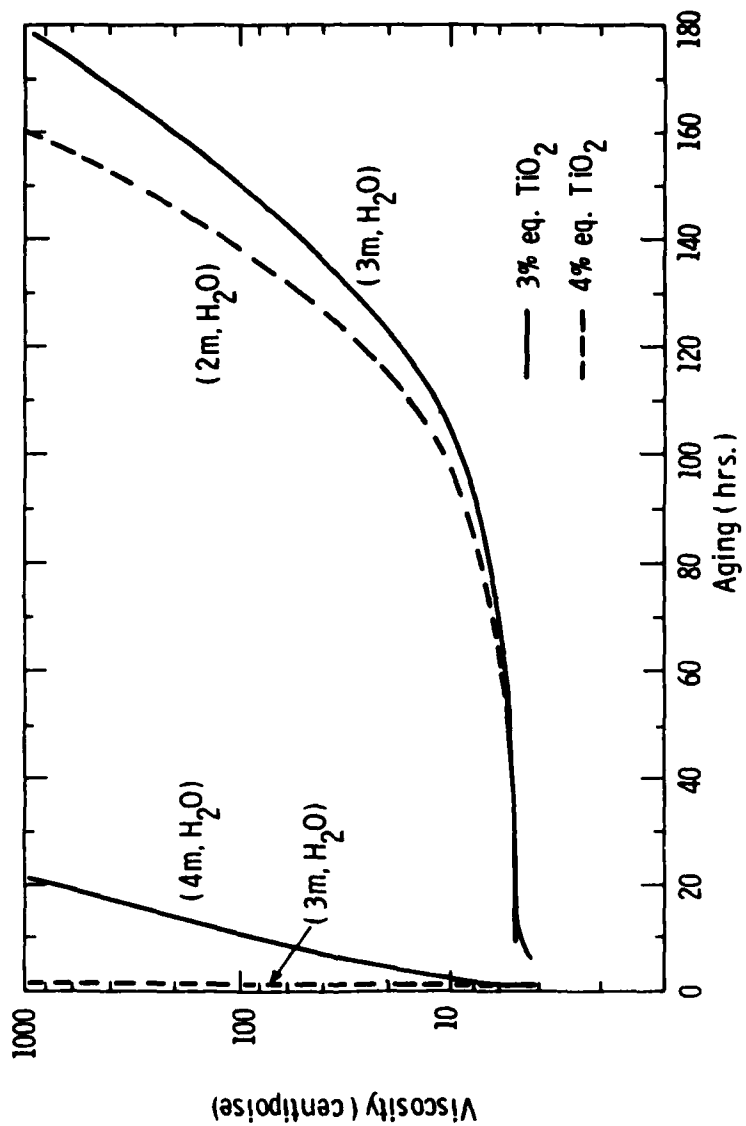


Figure 5 - Changes in the viscosity of various TiO_2 solutions upon aging

of the hydrolysis products should depend on, among other things, the extent of polymerization. This was indeed the case. It was shown that the chemical composition and overall network connectivity in these inorganic polymers depends strongly on the extent of polymerization, which is reflected by the overall oxide content. Equations were derived for various relationships between chemical composition, network connectivity, and extent of polymerization^(19,20). These relationships are summarized for the silica system in Table 3. The experimental curve in Figure 6 clearly shows that the oxide content of the hydrolysis products is not constant and depends on the hydrolysis conditions. Concentration of hydrolysis water affects the degree of polymerization and determines the particle size which in turn determines the oxide content, as predicted by the equations in Table 3.

In these experiments, hydrolysis was performed in alcohol, varying amount of water. The amount of alkoxide used was such that the equivalent oxide concentration of the final mixture was fixed at 5% by weight. The oxide contents of the resultant materials were determined by calcining the material to 600°C after drying at 120°C for 24 hr.

Zirconium presented a rather unique situation, since it does not form hydroxide at all. The zirconium atom does not give up electrons; instead, electrons may either be bound to its ligands covalently or accepted by the zirconium, producing a negative charge⁽²¹⁾ which repels hydroxyl groups. This condition leads to preferential formation of oxo and aquo groups rather than true hydroxides⁽²²⁾.

4.3 Properties of Gels and Pyrolysis

As the amount of hydrolysis water is increased an increase in the overall network connectivity occurs and the molecular size increases, as discussed in the previous section (see Table 4). An increase in the connectivity, in turn, produces a tighter network and affects those properties that are related to the distribution of network bonds. These include physical characteristics such as melting point and viscosity,

Silica Gels

120°C

1 H₂O

2 H₂O

15 H₂O

500°C

1 H₂O

2 H₂O

15 H₂O

METRIC 1 2 3 4 5 6 7 8 9 10

Figure 6 - Polymerized silica gels produced by various degree of hydrolysis before and after the pyrolysis

Table 3
Chemical Makeup, Oxide Content, And Connectivity Of
Silica Polymers As A Function Of Molecular Size (n)

Polymer Type	Polymers Formula	Connectivity (C_n)	Polymers Oxide Content	Maximum Oxide Content (%) ($n \rightarrow \infty$)	Critical Size* (n_c)
Linear	$\text{Si}_n\text{O}_{n-1}(\text{OH})_{2n+2}$	$2 - \frac{2}{n}$ ($C_\infty - 2$)	$\frac{60}{78 + \frac{18}{n}}$	76.92	18
Planar**	$\text{Si}_n\text{O}_{1.5n - (\frac{1}{2}\pi n)^{\frac{1}{2}}(\text{OH})_{n+2(\pi n)^{\frac{1}{2}}}$	$3 - \left(\frac{4\pi}{n}\right)^{\frac{1}{2}}$ ($C_\infty - 3$)	$\frac{60}{69 + 18\left(\frac{\pi}{n}\right)^{\frac{1}{2}}}$	86.96	$\sim 2 \times 10^3$
3 Dimen.†	$\text{Si}_n\text{O}_{2n - (\frac{9}{2}\pi n^2)^{\frac{1}{3}}(\text{OH})_{(36\pi n^2)^{\frac{1}{3}}}$	$4 - \left(\frac{36\pi}{n}\right)^{\frac{1}{3}}$ ($C_\infty - 4$)	$\frac{60}{60 + 9\left(\frac{36\pi}{n}\right)^{\frac{1}{3}}}$	100.	4×10^5

* Size, Above Which Oxide Content Is Stable Within 1%

** Circular Expansion

† Spherical Expansion

TABLE 4

RELATIONSHIP BETWEEN OXIDE CONTENT AND VARIOUS PARAMETERS
OF SPHERICALLY EXPANDING INORGANIC POLYMERS IN SILICA SYSTEM

<u>Oxide Content (% Wt.)</u>	<u>Molecular[†] Size (n)</u>	<u>Relative* Particle Diameter (Si)</u>	<u>Network** Connectivity</u>
70	~5	~2	1.1
80	~24	~3.6	2.32
85	70	5	2.83
90	280	8	3.26
93	900	12	3.49
95	2620	17	3.65
98	4.5×10^4	44	3.86

[†]Number of silicon atoms in the molecule

*Expressed in number of silicon-silicon separation distances

**Average number of bridging oxygens per silicon

and mechanical properties such as strength and capability of the gel network to remain monolithic.

The silica gels shown in figure 6 were produced from 1, 2 and 15 moles of H_2O hydrolysis of $Si(OC_2H_5)_4$, these gels had equivalent oxide contents of about 70%, 78%, and 93%, respectively. Accordingly, their average network connectivities would be 1.1, 2.2 and 3.5 (from equation (19) in ref. 19). Gels produced by low water hydrolysis, i.e., less than 1.5 moles, remained elastic and retained their shape better at low temperatures due to the presence of ester groups in the structure which change the properties in the direction of carbon polymers. Removal of organic groups during pyrolysis, however, resulted in extensive breakdown of these gels. High-water hydrolyzed gels, on the other hand, tended to remain monolithic during pyrolysis as a consequence of higher network connectivity (Figure 6). However the former gels are more suitable for the spinning or drawing of fibers due to elasticity and suitable viscosity if the diameter of the fibers is small, e.g., below 0.5 mm.

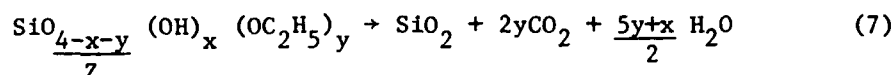
The non-oxide components of the gels can be classified in two groups:

- Chemically unbound components
- Chemically bound components

Unbound components usually exist in liquid form and generally consist of alcohol, water, and dissolved matter, e.g., electrolytes, etc. This liquid component constituted 80-99% of the system and was removed by evaporation during drying at room temperature. As the liquid portion diminished the viscosity usually increased gradually. This was followed by a pronounced increase in the viscosity, and finally gelation occurred. Even at this point the gel contained 50-70% of the chemically unbound liquid component, which required further drying. We observed that most of the cracking occurred at these later stages of drying.

Chemically bound components are generally alkyl, i.e.,

$C_n H_{2n+1}$, and hydroxyl groups that are bound to the main skeleton of polymer chains. These groups had to be removed by pyrolysis. For example,



The above reaction requires external oxygen in amounts proportional to the number of alkyl groups in the network. If enough oxygen was not available, carbon was deposited within the polymer. Most of the organic, "OR", groups were released within a very narrow temperature range corresponding to 200-250°C. The dried gel lost 80-90% of its non-oxide component at this stage. This required that extreme care be taken at this stage if the monolithic nature was to be retained. A gradual and smaller weight loss occurred throughout the heat treatment, extending to 400-600°C. This latter reaction is related to "OH" release. This heat treatment resulted in an essentially organic-free oxide material.

4.4 Structure

Electron micrographs showed that hydrolysis of alkoxides produces spherical polymeric units with diameters varying from 30Å-300Å, depending on the alkoxides and hydrolysis conditions (Figure 7). Polymerization appears to maximize the oxide content of the molecule. This driving force, however, diminishes rapidly as polymerization proceeds and eventually limits the particle size to within 3-10% of the optimum. Overall connectivity increases with increasing molecular size and with oxide content.

Hydroxide polymers of Al, Ti or Si, can be formed such that they may contain from 65 to over 90% equivalent oxide by weight when calcined. It is important to note that the hydroxyl content was inversely related to the amount of water used during hydrolysis, indicating that these groups were not merely absorbed species but were part of the structural makeup. Increasing network connectivity, i.e.

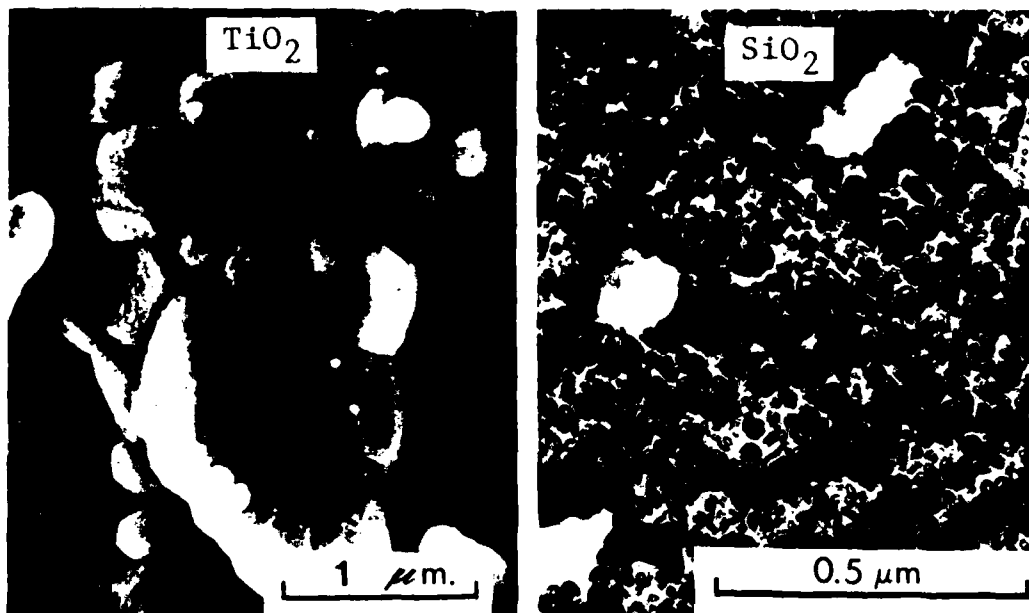


Figure 7 - Electron micrographs of TiO_2 and SiO_2 formed via hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$, and $\text{Ti}(\text{OC}_2\text{H}_5)_4$.

bridging oxygens, with increasing amount of hydrolysis water was indicated not only by the chemical composition but also by direct evidence obtained by IR investigations of these gels.

Silica gels were formed by hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ with 1, 2, 5, 10 and 15 moles of water per mole of alkoxide. These gels were dried and pyrolyzed at 500°C . The resultant gels were extremely porous. However, porosity and surface area varied as functions of hydrolysis water (Figure 8).

IR spectra of these gels were obtained with a Nicolet Model 7199 Fourier Transform infrared spectrophotometer using a liquid-nitrogen-cooled TGS detector and 4 cm^{-1} resolution. The spectra in figure 9 are representative of the samples studied. The three principle bands were centered near 1130 , 790 and 470 cm^{-1} . Previous studies⁽²³⁾ of silicates identify these bands as resulting from three vibrations: the assymetrical Si-O-Si stretch, the symmetrical Si-O-Si stretch (active infrared-forbidden but due to tetrahedral distortion) and an Si-O-Si bending mode. These one-component silica samples resulted in a doublet split of the 1100 cm^{-1} band, indicating that at least two major Si-O-Si geometries were formed.

To discern the small intensity variations in the spectra required band integrations. The integrations listed in Table 5 were normalized to 100% of the 470 cm^{-1} band. Differences between samples in overall intensity were due to surface scattering in reflection, and variations of pellet thickness and ground powder size in absorption. For both modes, intensity was proportional to concentration at each band as discussed previously. The normalized values permitted direct comparison among the samples.

Normalized values of the 800 cm^{-1} band in both absorbance and reflectance were relatively constant within the sample series, but the values of the 1100 cm^{-1} band increased with the quantity of hydrolysis water in solution as shown in Figure 10. Sample #5 most closely approximated the structure of the classical SiO_2 glasses. The preferential

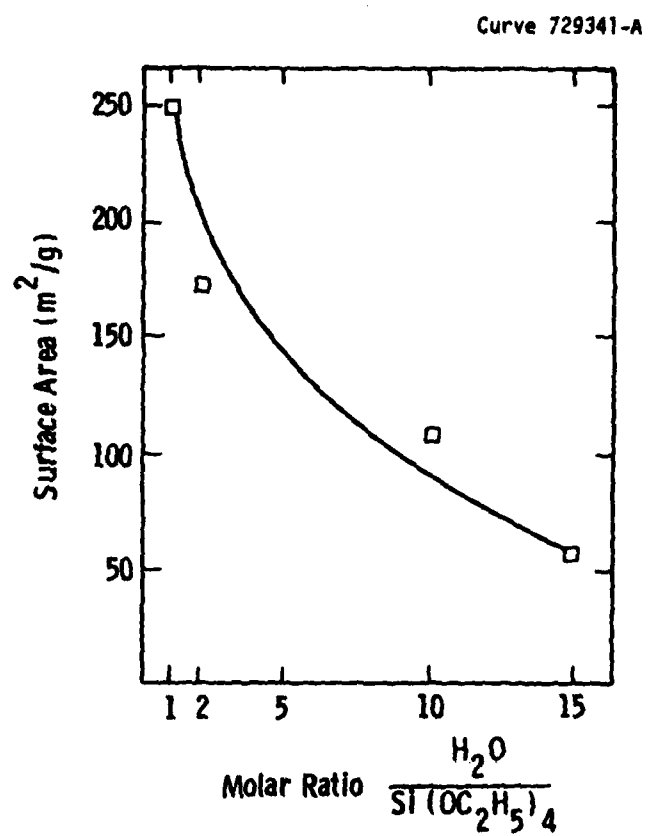


Figure 8 - Variation in surface area with concentration of hydrolysis water as determined by the BET liquid nitrogen absorption method

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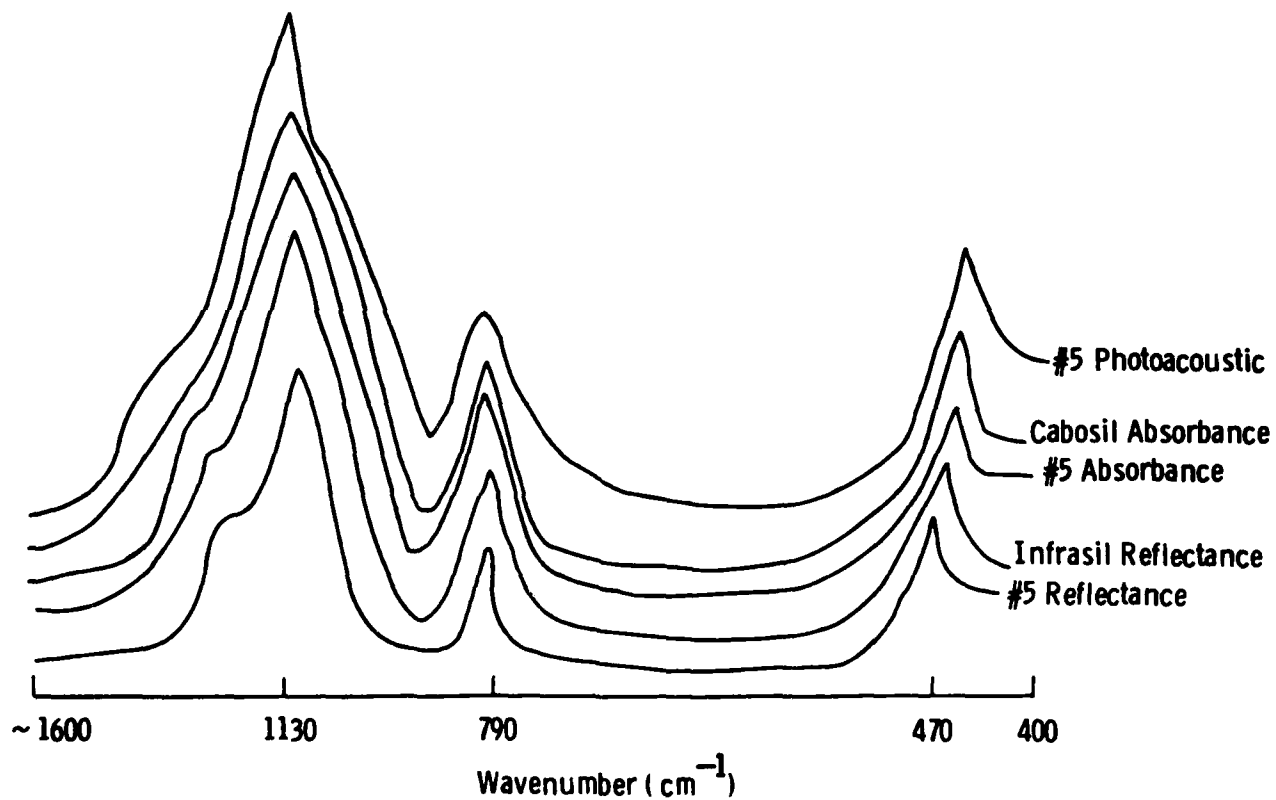


Figure 9 - Spectra of sample #5 in photoacoustic, absorbance, and reflectance modes compared to those of classical silicas in absorbance and reflectance modes

TABLE 5

BAND INTEGRATIONS

<u>Range (cm⁻¹)</u>	<u>525-400</u>	<u>845-700</u>	<u>1365-845</u>	<u>1790-1590</u>	<u>3800-3000</u>
<u>Reflectance</u>					
#1	4.084-1	.4851-.118	22.01-5.39		
#2	5.285-1	.6916-.131	31.52-5.96		
#3	5.318-1	.7020-.132	30.07-5.65		
#4	5.219-1	.7156-.137	33.82-6.48		
#5	3.642-1	.5060-.139	24.67-6.77		
Infrasil	5.610-1	.8234-.147	39.61-7.06		
<u>Absorbance</u>					
#1	96.30-1	26.75-.278	367.7-3.82	7.995-.083	134.7-1.40
#2	50.03-1	18.80-.375	199.5-3.98	.9891-.019	28.26-.564
#3	69.75-1	25.93-.372	268.4-3.85	2.677-.038	56.91-.816
#4	36.29-1	13.13-.362	166.9-4.56	2.524-.070	49.54-1.37
#5	18.59-1	7.095-.381	178.0-9.58	1.803-.097	55.36-2.98
Cabosil	10.26-1	4.874-.475	145.8-14.21	1.912-.186	37.85-3.69

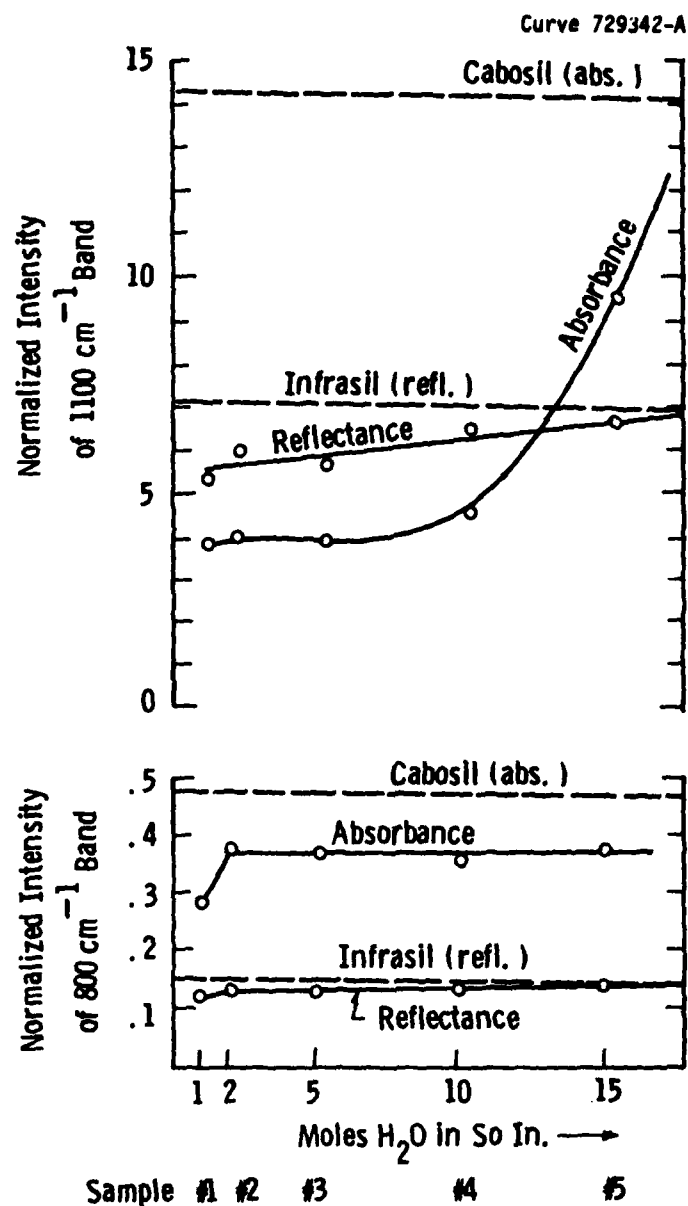


Figure 10 - The increasing concentration of bridging oxygens from sample #1 to #5 is shown by the increased intensity of the 1100 cm^{-1} band, while slight increases in the 800 cm^{-1} band intensity point toward an increase in long range order and lower tetrahedral distortion with higher water of hydrolysis concentrations. Band intensities for classical silicas are dashed in for comparison

increase in intensity of the 1100 cm^{-1} band points toward an increased concentration of bridging oxygen and long range order with lower tetrahedral distortion. Thus, it may be concluded that the concentration of bridging oxygen increased through the series, in direct correlation with increased ratio of hydrolysis water. At high water hydrolysis, e.g. 15 moles, the structure very much resembled that of traditional SiO_2 glasses with low hydroxyl content.

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