11-9-90
E5740

NASA Contractor Report 185293

Low Temperature Synthesis of CaO-SiO_2 Glasses Having Stable Liquid-Liquid Immiscibility by Sol-Gel Process

Narottam P. Bansal
Case Western Reserve University
Cleveland, Ohio

October 1990

Prepared for
Lewis Research Center
Under Cooperative Agreement NCC3-133

National Aeronautics and
Space Administration

LOW TEMPERATURE SYNTHESIS OF $CaO-SiO_2$ GLASSES HAVING STABLE LIQUID-LIQUID IMMISCIBILITY BY SOL-GEL PROCESS

Narottam P. Bansal*
Case Western Reserve University
Cleveland, Ohio 44106

E-5740

ABSTRACT

Calcium silicate glass compositions lying within the liquid-liquid immiscibilty dome of the phase diagram, which could not have been prepared by the conventional melting method, have been synthesized by the sol-gel process. Hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS) solutions containing up to 20 mole % calcium nitrate resulted in the formation of clear and transparent gels. The gel formation time decreased with increase in water:TEOS mole ratio, calcium content and the reaction temperature. Smaller values of gel times in the presence of calcium nitrate are probably caused by lowering of the ionic charge on the sol particles by the salt present. The gelation activation energy, E_{gel}, was evaluated from temperature dependence of the gel time. Presence of Ca^{2+} ions or the water:TEOS mole ratio did not have an appreciable effect on the value of E_{gel}. Presence of glycerol in the solution helped in the formation of crack-free monolithic gel specimens. Chemical and structural changes occurring in the gels, as a function of the heat treatments, have been monitored using DTA, TGA, IR-spectroscopy, x-ray diffraction, surface area and pore size distribution measurements.

---

*NASA Resident Research Associate at Lewis Research Center.

1. INTRODUCTION

Low temperature synthesis of glass compositions lying within the liquid-liquid immiscibility region has been reported by a number of researchers[1-5]. Relatively, only a few such glasses containing alkaline earth metal oxides have been prepared by the sol gel procedure; $CaO-SiO_2$ by Hayashi and Saito[2], $SrO-SiO_2$ by Yamane and Kojima[3], and $MgO-SiO_2$ by Bansal[1]. Preparation of gels in the $CaO-Al_2O_3-SiO_2$ system using tetraethoxysilane (TEOS), aluminum sec-butoxide, and calcium nitrate has been investigated by Pancrazi et al[6]. Tredway and Risbud[7] made use of TEOS, aluminum sec-butoxide and barium acetate for the synthesis of $BaO-Al_2O_3-SiO_2$ gel. Earlier attempts[2] to prepare $CaO-SiO_2$ glasses by the gel method using calcium nitrate as the source of calcium oxide resulted in white powders containing crystalline $Ca(NO_3)_2.nH_2O$ (n = 0,1,2). The possibility of introducing the modifier cation as an alcoholic solution of calcium nitrate into silicon tetraethoxide has been examined in the present investigation.

The objective of the present study was to synthesize $CaO-SiO_2$ glass compositions having liquid-liquid immiscibility, which cannot be prepared by the conventional melting technique, using the sol-gel process. These compositionally homogeneous precursor materials were also needed to study the effects of microgravity on liquid-liquid phase separation in glasses.

Gels of various compositions lying within the liquid-liquid immiscibility dome of the $CaO-SiO_2$ system were synthesized under different experimental conditions using TEOS and calcium nitrate as the starting materials. Structural developments in the gels as a function of the thermal treatment were monitored using several techniques. The results of these investigations are presented in this paper.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Tetraethyl orthosilicate (TEOS) from Alfa Products, calcium nitrate tetrahydrate (Analytical Reagent) from Mallinckrodt, and 200 proof absolute ethyl alcohol were used as received. Calcium alkoxides are only slightly soluble in common solvents. The solubilities[8] of calcium methoxide and calcium ethoxide in their parent alcohol are only 2.3 mMol/l and 75 mMol/l, respectively. When suitable alkoxide is not available, acetate or nitrate salt of the metal is used. Calcium acetate is soluble in water but almost insoluble in alcohol. Calcium nitrate is soluble both in water and alcohol. An alcoholic solution of calcium nitrate was consequently used as the source of calcium.

2.2. Gel Synthesis

The method of gel synthesis was similar to that described earlier [1,9]. A flow diagram of the procedure used for glass preparation by the sol-gel process is shown in Fig. 1. An alcoholic solution of calcium nitrate tetrahydrate was mixed under continuous stirring with TEOS which had been diluted with ethanol. The calculated amount of water was then slowly added dropwise under vigorous stirring resulting in a homogeneous clear solution. The container was sealed with parafilm and left to stand for gelation under ambient conditions or in a constant temperature bath. The pH of some solutions was monitored as a function of time using a Fisher Accumet (Model 815 MP) pH meter. The gel formation was complete, as tested by tilting the container, in less than an hour to several days depending upon the reaction temperature, water concentration, and the calcium content. Clear and transparent bulk gels were obtained which cracked into smaller pieces on slow drying under ambient conditions. To prepare monolithic gel samples, ~2 weight % of glycerol was added to the solution as the drying control agent. The gels were stored at room temperature for several days followed by drying and calcination at higher temperatures.

2.3. Characterization of Gels

Chemical and structural evolution of gels as a function of the heat treatment was followed using a number of techniques. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using Perkin-Elmer DTA-1700 and TGS-2 systems, respectively, which were interfaced with computerized data acquisition and analysis systems. A Netzsch thermal analyzer STA-429 with a super kanthal heating element furnace was also used for simultaneous recording of DTA and TGA on the same specimen. Infrared transmission spectra were recorded from 400 to 4000 cm^{-1} using the KBr pellet method with a Perkin-Elmer 1750 Fourier Transform Infrared Spectrometer interfaced with a Perkin-Elmer 7300 professional computer. X-ray powder diffraction patterns were recorded at room temperature using a step scan procedure ($0.03^{o}/2\theta$ step, count time 0.4s) on a Phillips ADP-3600 automated powder diffractometer equipped with a crystal monochromator employing copper $K\alpha$ radiation. BET surface area and pore volume measurements were made from the nitrogen adsorption isotherms at 77K using Micromeritics Digisorb 2500 system. Krypton gas adsorption was used for some specimens having low surface area. Fractured surfaces of the sintered gel samples were examined using a Cambridge Stereoscan 200 scanning electron microscope (SEM). A thin layer of gold was evaporated onto the sample surface before viewing in the SEM.

3. EXPERIMENTAL RESULTS

3.1. Gel Formation

Chemical compositions of the glasses synthesized and their acronyms are given in Table I. All the compositions lie within the liquid-liquid immiscibility region of the $CaO-SiO_2$ phase diagram as shown in Fig. 2.

Monolithic gel specimens of 10CS composition were prepared in the presence of glycerol as the drying control agent. On slow drying for several weeks under ambient conditions, the gel samples typically reduced to about one-tenth of the original volume as shown in Fig. 3. A typical crack free monolithic body is shown in the foreground of Fig. 3.

The gelation times and gel appearance under ambient conditions for solutions of various compositions are given in Table II. All the gels were clear and gel formation time decreased with increase in calcium concentration. However, the value of water:TEOS mole ratio, r, was not the same for different solutions.

Typical values of solution pH as a function of time for four different compositions for r = 6 at room temperature are given in Table III. There is a systematic decrease in pH with increase in Ca^{2+} concentration. The pH of the solution with no calcium drops from 5.8 to 5.06 after 24h. In contrast, the solutions containing Ca^{2+} show hardly any change in pH after ~24h.

Figure 4 shows the influence of water:TEOS mole ratio on time of gel formation for the $10CaO-90SiO_2$ composition at room temperature. The values of gelation time for $10CaO-90SiO_2$ composition for r = 4, 6, and 7.5 at various temperatures are listed in Table IV. For comparison the data for TEOS for r = 6 are also given. The value of t_{gel} decreases with increase in r or temperature. Also, the presence of Ca^{2+} greatly lowers the time taken for gel formation in comparison to TEOS.

Table V shows the effect of Ca^{2+} ion concentration in the solution on gelation times at various temperatures for r = 6. By the addition of just 2 mol% of Ca^{2+}, gelation time is greatly reduced. At any temperature, the time of gelation decreases with increase in Ca^{2+} ion concentration. The effect is more pronounced at low concentration and seems to level off at higher concentrations of the metal ion. The reduction in gelling time in the presence of Ca^{2+} ions may be due to the lowering of ionic charge on sol particles by the salt.

3.2. Thermal Analysis

DTA thermograms of gels of different compositions, which had been dried for several weeks at room temperature, were recorded at a heating rate of $5^{o}C$/min in air. Typical DTA curves for the 2CS and 20CS compositions are shown in Fig. 5. The broad endothermic peak at $120^{o}C$ for 2CS and at $130^{o}C$ for 20CS gel may be attributed to the evaporation of physically adsorbed water and alcohol. The sharp endothermic peak for 2CS at $215^{o}C$ and two sharp endotherms for 20CS at 188 and $237^{o}C$ may be assigned to the volatilization of organic species such as ethers and esters which might have formed as a result of the reactions taking place during the sol-gel process. The broad exothermic peak at $398^{o}C$ for 2CS and at $387^{o}C$ for 20CS may be ascribed to the pyrolysis of the residual organic groups and the decomposition of nitrate. Brown fumes, probably of NO_2, were observed during pyrolysis of the gels at ~400 - $500^{o}C$.

TGA and DTGA curves of various room temperature dried gels were also recorded under air flow at a heating rate of $5^{o}C$/min. Typical curves for the 2CS and 20CS gels are presented in Fig. 6. The temperatures corresponding to various weight losses in the TGA are in excellent agreement with the DTA results. Gradual weight loss above ~$600^{o}C$ may be assigned to the network condensation. Total weight loss from the 20CS gel sample (38.3%)

is much higher than from 2CS (~22.1%) due to the higher nitrate content in the former.

3.3. Pyrolysis of Gels

Gels of various compositions were allowed to stand under ambient conditions for several months followed by drying for a week at ~66°C in air. The resulting gels were transparent, colorless, and amorphous. These were then calcined under dynamic air flow at a heating rate of ~2°C/min to different temperatures (2CS, 5CS, and 10CS to 800°C, 15CS to 780°C, and 20CS to 740°C) and furnace cooled. After this heat treatment all the samples remained colorless, glassy, and transparent except for the 15CS and 20CS which had turned white. The 10CS composition was further treated in air for 23h at 800°C when it turned white and opaque, at 900°C for 8h, and at 1000°C for 5h.

Another part of the 10CS gel was subjected to isothermal heat treatments for 24h each at 100, 300, 500, 600, and 700°C, followed by 17h at 780°C and 16h at 860°C in air. A part of the sample was saved for characterization after pyrolysis at each temperature. The gel became light yellow in color after the 100°C heat treatment. The yellow color disappeared when the gel was fired at 300°C. The sample had turned into white powder after the 700°C calcination and remained so following the subsequent heat treatments at higher temperatures.

3.4. Infrared Spectroscopy

IR absorption spectra in the 400- to 4000-cm^{-1} range for the 10CS gel dried for several weeks under ambient conditions is shown in Fig. 7. Figure 8 compares the IR spectra of 10CS gel calcined in air at various temperatures. The heat treatments are cumulative at subsequent temperatures. IR spectra of gels of different compositions heated to 740 - 800°C in flowing air at ~2°C/min and furnace cooled are presented in Fig. 9. Positions of various IR absorption peaks observed and their assignments[10-19] are shown in Fig. 7 and also listed in Table VI. The absorption peak around 950 cm^{-1}, attributed to the Si-O terminal non-bridging vibration, decreased in intensity with increasing firing temperature indicating the decrease of non-bridging oxygens. It is present only as a shoulder in the 300°C heated sample and has completely disappeared in the 500°C heated specimen indicating slow polymerization of residual Si-OH bonds at these temperatures. The strongest absorption peak at ~1080 cm^{-1}, ascribed to Si-O-Si streching vibration in SiO_4 tetrahedra, shows a slight shift to higher frequencies with increase in calcination temperature suggesting the strengthening of the Si-O bonds in the tetrahedra. A similar shift in this peak was also reported by Varshneya and Suh[20], and by Kamiya et al.[19] However, no such shift was observed in the $MgO-SiO_2$ gels in an earlier study by the present author[1]. The bands around 460 and 800 cm^{-1} are assigned to bending modes of Si-O-Si and O-Si-O bonds, respectively. The intensity of the peak around 1385 cm^{-1}, attributed[17] to the $-NO_3$ group, increased with the calcium nitrate concentration in the gel, decreased with increase in heat treatment temperature, and is completely absent in the

$700^{o}C$ heated sample. A very weak 1385 cm^{-1} peak in the specimens fired for 24h at 500 or $600^{o}C$ implies a very slow rate of nitrate decomposition at these temperatures. The broad absorption bands around 1640 and 3450 cm^{-1}, attributed to water absorption, decreased in intensity with increase in heat treatment temperature. The broad high-frequency peak at ~3450 cm^{-1} is assigned to the superposition of physically absorbed water, hydrogen-bonded hydroxyl groups, and, at higher temperature, isolated -OH. Gel samples heat treated at temperatures as high as 800 to $860^{o}C$ still showed the presence of traces of water, but no absorption peaks attributable to organic groups were present. This may be due to the absorption of atmospheric moisture during the IR samples preparation by mixing with undried KBr. The double peak around 2340 and 2360 cm^{-1}, attributed to absorption by the atmospheric CO_2, is present in some of the spectra.

3.5. X-ray Diffraction

Structural changes occurring in the gels as a function of the thermal treatments were monitored by XRD. All the $CaO-SiO_2$ gels dried at ~$66^{o}C$ for 7 days were amorphous to x-rays as shown in Fig. 10. These gels when further calcined in air at ~$2^{o}C/min$ to various temperatures and furnace cooled were found to be amorphous by XRD (Fig. 11) except for the 2CS composition which showed the precipitation of small amounts of α-quartz. The 10CS composition was subjected to further isothermal heat treatments and the XRD spectra are given in Fig. 12. It was amorphous to x-rays after heat treatment at 800°C for 23h. However, low intensity peaks of α-cristobalite were detected after firing for 8h at 900°C. On further calcination at 1000°C for 5h, α-cristobalite and the strongest peak of wollastonite ($CaSiO_3$) at $2\theta = 29.9^{\circ}$ were present in the XRD. Hayashi and Saito[2] reported the precipitation of wollastonite ($CaSiO_3$) in $CaO-SiO_2$ gels when heated above 800°C. Yamane and Kojima[3] attributed the decrease in transparency of $SrO-SiO_2$ gels, when heated to high temperatures, to the crystallization of α-quartz. The precipitation of α-quartz has also been observed by the present author[1] in $MgO-SiO_2$ gels when heated to ~950°C. Precipitation of β-quartz has been reported[5] in gels of composition $4Na_2O-10.5B_2O3-85.5SiO_2$ (mol%) when heated to 750°C for 0.5h. However α-cristobalite was the crystalline phase when calcined at 750°C for a longer time or for only 15 minutes at 800°C or above.

The 10CS gel was also isothermally calcined at various temperatures starting from 102°C for different times and the XRD patterns of the resulting specimens are shown in Fig. 13. The gel samples heat treated at 780°C or above showed the presence of weak diffraction peaks in the XRD which could not be assigned to any known phase.

3.6. Surface Area and Pore Size Distribution

The pore volume and BET surface area calculated from the adsorption isotherms for the 10CS gel with r = 4.95 are shown in Fig. 14 as a function of the calcination temperature. Thermal treatments at subsequent temperatures are cumulative. The surface area sharply decreases from room temperature to 300 - 500°C, increases at 600°C, and gradually decreases with further increase in firing temperature. The pore volume shows a small increase between 300 and 500°C and a sharp jump at higher temperature, its value becoming maximun at 700°C. Gel treated at higher temperatures shows a sharp reduction in pore volume. Values of both the surface area and the pore volume probably become maximum at ~650°C as shown by the broken lines in Fig. 14. The increase in surface area and pore volume at intermediate temperatures may be ascribed to the decomposition of nitrate and the loss of solvents trapped within the micropores of the dried gel. These results are consistent with the DTA, TGA, and IR analyses as described above. The rapid reduction in both pore volume and surface area at higher temperatures may be attributed to densification due to sintering.

Scanning electron microscopy of the $10CaO-90SiO_2$ gel calcined to 800°C at 2°C/min followed by isothermal heat treatments at 800°C for 23h and at 900°C for 8h in air showed the material to be dense. However, pores were present in certain regions of the sample as shown in the SEM micrograph (Fig. 15). Similar behavior has been recently observed by Woignier et al.[21] when silica glasses prepared by densification of the aerogels were heated at temperatures above 1200°C. This porosity is caused by foaming due to the high OH content in the interior of the dense material. During thermal treatment, the surface of the specimen is densified before the interior which makes it difficult to remove the OH species present within the interior pores. The water vapors formed from decomposition of the OH groups get trapped in the micropores. At higher temperatures, the increased water vapor pressure in the closed micropores results in bloating.

4. DISCUSSION

Gelation of TEOS occurs in two stages, the hydrolysis and the condensation steps, as represented by the following reactions:

$$Si(OEt)_4 + nH_2O \longrightarrow Si(OEt)_{4-n}(OH)_n + nEtOH \quad (1)$$

$$-\overset{|}{\underset{|}{Si}}-OH + EtO-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + EtOH \quad (2A)$$

$$-\overset{|}{\underset{|}{Si}}-OH + OH-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O \quad (2B)$$

where Et represents C_2H_5 group and n varies from 1 to 4. The condensation process, occurring via dealcoholation(2A) or dehydration(2B) steps, results in the formation of $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ bonds.

In the absence of a catalyst, as is the case in the present study, hydrolysis of TEOS is rather slow so that condensation of the partially hydrolyzed monomers occurs simultaneously with the hydrolysis step. It is difficult to separate hydrolysis from condensation. However, in the presence of an acid catalyst, hydrolysis is considered to be complete[22] just after the addition of water, as long as a large excess of water is present, and condensation is the rate controlling process[10]. The rate of hydrolysis is known to increase monotonically[23] as the pH decreases from 7, but the condensation reaction rate shows a local minimum at around pH 2. In this region, hydrolysis may well go to completion before any significant condensation occurs and polymerization will have the normal pattern. Higher water content also promotes hydrolysis and tends to inhibit condensation. It is also known[23] that the time of gelling of silica sols is lowered in the presence of sodium salts at all pH. The presence of sodium salts has little effect on gel time at low pH (~1-3) but in the neutral region, the pH of minimum sol stability is increased from ~5.5 to 7. Presence of the salts probably helps in lowering the ionic charge on the sol particles. The lowered values of gel times in the presence of Ca^{2+} ions, as observed in the present study, may also be caused by a similar mechanism.

The temperature dependence of the rate of gel formation may be expressed as:

$$k = A \exp[-E^*/RT] \qquad (3)$$

where k is the reaction rate constant, A the frequency factor, E^* the apparent activation energy, R the gas constant, and T the reaction temperature in Kelvin. The time of gel formation, t_{gel}, may be taken as the average rate of gelation and Eq.(3) may be written as:

$$1/t_{gel} = A' \exp[-E^{*}/RT] \qquad (4)$$

Taking the logarithm of Eq.(4) gives:

$$\log(t_{gel}) = -\log A' + E^{*}/(2.3026RT) \qquad (5)$$

according to which a plot of $\log(t_{gel})$ vs. 1/T should be linear with a slope of $(E^{*}/2.3026R)$. The values of E^{*} and A' can be evaluated from the slope and the intercept, respectively.

Plots of $\log(t_{gel})$ vs. 1/T for the gelation of $10CaO-90SiO_2$ composition at three water:TEOS mole ratios are presented in Fig. 16. The solid lines in this and the next figure are from linear least-squares fitting of the experimental data to Eq.(5). In all cases the value of the correlation coefficient exceeded 0.99. Values of the parameters E^{*} and A', evaluated from linear least-squares curve fitting of the experimental data, are listed in Table IV. The presence of Ca^{2+} ions or the water:TEOS mole ratio have no appreciable effect on E^{*}. Similar results in the presence of many other metal ions (Li^{+}, Na^{+}, Mg^{2+}, Sr^{2+}) have been reported recently by the present author[9]. However, a sharp increase in gel formation time and the gelation activation energy was observed[9] in the presence of other cations (Al^{3+}, La^{3+}, Y^{3+}) which undergo hydrolysis in the solution.

Figure 17 shows the plots of $\log(t_{gel})$ vs. $1/T$ for three concentrations of Ca^{2+} ions at the same value of $r = 6$. Also shown for comparison is the plot for SiO_2. All the plots are linear indicating applicability of Eq.(5). Values of the Arrhenius parameters evaluated from linear least-squares curve fitting of the experimental data are given in Table V. The Ca^{2+} ion concentration has virtually no influence on the value of E^*. The gelation activation energy is probably related[24,25] to the transport of the condensing species during the polymerization process and not to the Si-O bond energies.

Aelion et al.[22] and Vekhov et al.[26,27] reported values of 26.4 and 28.4 kJ/mol, respectively, for the hydrolysis activation energy of TEOS. Colby et al. attributed[24] a value of 19.4 kJ/mol to the activation energy of hydrolysis rather than polycondensation for the TEOS system at $r = 4$ in the absence of a catalyst. These values are much lower than those obtained in the present work (54.5 kJ/mol) at $r = 6$ in the absence of a catalyst. Values of 61.1 and 55.2 kJ/mol have been reported[24,25] for gelation activation energy of TEOS at $r = 4$ in the presence of HF and HCl catalysts, respectively. For the HCl-catalyzed TEOS system, Bechtold et al.[28,29] reported values of 40 to 70 kJ/mol depending on water concentration.

According to Colby et al.[24], if hydrolysis is the rate determining step, the gelation time should decrease with increase in r even after sufficient water for hydrolysis is present. Also, the activation energy should decrease with increase in r, if the hydrolysis was not complete. For the acid-catalyzed TEOS system, Colby et al.[24] showed that the gelation time did not decrease with increase in water concentration when enough water was present. But in the absence of sufficient water to complete hydrolysis, the activation energy systematically decreased when r was increased from 3 to 3.5 to 4. The higher activation energy at low r was attributed[24] to the steric hinderance offered by the non-hydrolyzed alkoxy groups still attached to silicon. For the 10CS system, t_{gel} systematically decreased when r was increased from 4 to 7.5 but the activation energy was more or less independent of the water concentration. This probably indicates that hydrolysis is the rate determining step and the calculated activation energy is for this process. However, these values are much higher than a value of 19.4 kJ/mol reported by Colby et al.[24] for the hydrolysis activation energy for TEOS at r = 4 in the absence of a catalyst.

From XRD no crystalline phase was detected in the dried gels indicating incorporation of the Ca^{2+} ions into the silica gel network possibly by a cation exchange reaction[30] between the Ca^{2+} ions and the weakly acidic silanol group:

$$\mathrm{Ca^{2+}} + 2(-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-OH}) \dashrightarrow \mathrm{Ca}--(--\mathrm{O}\overset{|}{\underset{|}{\mathrm{Si}}}-)_2 + 2\mathrm{H^+} \qquad (6)$$

Probably the Ca^{2+} ions are only loosely bonded in the gel. In acidic solutions, reaction (6) is reversible[30] and is the sum of the following two reactions:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-OH} \rightleftharpoons -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O^-} + \mathrm{H^+} \qquad (7)$$

$$\mathrm{Ca^{2+}} + 2(-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-O^-}) \rightleftharpoons \mathrm{Ca(O}\overset{|}{\underset{|}{\mathrm{Si}}}-)_2 \qquad (8)$$

However, crystallization of other metal salts has been reported during drying of various metal silicate gels. Yamane and Kojima[3] observed precipitation of strontium nitrate during the synthesis of $12.7SrO-87.3SiO_2$ (mol%) gels from $Sr(NO_3)_2$ and tetramethoxy silane. Sodium nitrate crystallized out on desiccating $Na_2O-B_2O_3-SiO_2$ gels.[5] Crystallization of $Mg(NO_3)_2.6H_2O$ was observed by the present author[1] during drying of $20MgO.80SiO_2$ (mol%) gels prepared from magnesium nitrate and TEOS.

5. SUMMARY OF RESULTS

$CaO-SiO_2$ glass compositions having stable liquid-liquid immiscibility have been prepared at low temperatures by the sol-gel method using calcium nitrate and TEOS. Gels containing up to 20 mole % calcium nitrate were clear and transparent. The time of gelation decreased with increase in calcium or water concentration and temperature. The value of E_{gel}, determined from temperature dependence of the gel time using the Arrhenius equation, was more or less unaffected by the Ca^{2+} as well as the water contents. Chemical and structural evolutions in the gels, after various thermal treatments, were followed using TGA, DTA, IR-spectroscopy, x-ray diffraction, surface area and pore size distribution measurements. Glycerol was effective as a drying control agent to form crack-free monolithic gel bodies.

6. CONCLUSION

Calcium silicate glass compositions lying within the liquid-liquid immiscibility region, which cannot be prepared by the conventional glass melting method, can be synthesized at low temperatures by the sol-gel process using tetraethoxy silane and calcium nitrate.

ACKNOWLEDGMENTS

The technical assistance of Anna Palczer, Ralph Garlick, and Beth Hyatt during the course of this research is very much appreciated.

REFERENCES

1. N.P.Bansal, "Sol-Gel Synthesis of Magnesium Oxide-Silicon Dioxide Glass Compositions," J. Am. Ceram. Soc.,**71**[8] 666-672 (1988).

2. T.Hayashi and H.Saito, "Preparation of CaO-SiO_2 Glasses by the Gel Method," J. Mater. Sc., **15**[8] 1971-1977 (1980).

3. M.Yamane and T.Kojima, "Low Temperature Synthesis of Non-Crystalline Solids of the System SrO-SiO_2," J. Non-Cryst. Solids, **44**[2] 181-190 (1981).

4. M.A.Villegas, J.M.Fernandez Navarro, "Characterization and Study of of Na_2O-B_2O_3-SiO_2 Glasses Prepared by the Sol-Gel Method," J. Mater. Sc., **23**[6] 2142-2152 (1988).

5. S.P.Mukherjee, "Gels and Gel-Derived Glasses in the Na_2O-B_2O_3-SiO_2 System," in "Materials Processing in the Reduced Gravity Environment of Space" (G.E.Rindone, Editor), North-Holland, New York, 1982; pp. 321-330.

6. F.Pancrazi, J.Phalippou, F.Sorrentino, and J.Zarzycki, "Preparation of Gels in the CaO-Al_2O_3-SiO_2 System from Metal Alkoxides," J. Non-Cryst. Solids, **63**[1-2] 81-93 (1984).

7. W.K.Tredway and S.H.Risbud, "Gel Synthesis of Glass Powders in the BaO-Al_2O_3-SiO_2 System," J. Non-Cryst. Solids, **100**[1-3] 278-283 (1988).

8. H.D.Luth, Z. Anorg. Allg. Chem., **353**, 207 (1967).

9. N.P.Bansal, "Influence of Several Metal Ions on the Gelation Activation Energy of Silicon Tetraethoxide," NASA Technical Memorandum 101380 (1988); J. Am. Ceram. Soc., **73**[ ] (1990).

10. S.Sakka, "Gel Method for Making Glass", pp 129-167 in Treatise on Materials Science and Technology, Vol 22, Glass III. Edited by M.Tomozawa and R.H.Doremus, Academic Press, New York, 1982.

11. I.Matsuyama, K.Susa, S.Satoh, and T.Suganuma, "Synthesis of High-Purity Silica by the Sol-Gel Method," Am. Ceram. Soc. Bull., **63**[11] 1408-1411 (1984).

12. M.Decottignies, J.Phalippou, and J.Zarzycki, "Synthesis of Glasses by Hot Pressing of Gels," J. Mater. Sci., **13**[12] 2605-2618 (1978).

13. G.H.Sigel, "Optical Absorption of Glasses" pp. 5-89 in Treatise on Materials Science and Technology, Vol. 12, Glass I: Interaction with Electromagnetic Radiation. Edited by M.Tomozawa and R.H.Doremus, Academic Press, New York, 1977.

14. J.Wong and C.A.Angell, "Application of Spectroscopy in the Study of Glassy Solids, Part II. Infrared, Raman, EPR, and NMR Spectral Studies," Appl. Spectrosc. Rev., **4**[2] 155-232 (1971).

15. I.Simon, "Infrared Studies of Glass"; pp. 120-151 in Modern Aspects of the Vitreous State, Vol 1. Edited by J.D.Mackenzie. Butterworths, London, UK, 1960.

16. R.Hanna, "Infrared Absorption Spectrum of Silicon Dioxide," J. Am. Ceram. Soc., **48**[11] 595-599 (1965).

17. I.Nakagawa and J.L.Walter, "Optically Active Crystal Vibration of the Alkali-Metal Nitrates," J. Chem. Phys., **51**[4]1389-1397 (1969).

18. M.L.Hair, "Hydroxyl Groups on Silica Surface," J. Non-Cryst. Solids, **19**[2] 299-309 (1975).

19. K.Kamiya, S.Sakka, and M.Mizutani, "Preparation of Silica Glass Fibers and Transparent Silica Glass from Silicon Tetraethoxide," Yogyo Kyokaishi, **86**[11] 552-559 (1978).

20. A.K.Varshneya and N.Suh, "Sol-Gel Derived Soda-Lime-High Silica Glass," J. Am. Ceram. Soc., **70**[1] C-21 - C-22 (1987).

21. T.Woignier, J.Phalippou, and M.Prassas, "Glasses from Aerogels. Part 2. The Aerogel-Glass Transformation," J. Mater. Sc., **25**[7] 3118-3126 (1990).

22. R.Aelion, A.Loebel, and F.Eirich, "Hydrolysis of Ethyl Silicate," J. Am. Chem. Soc., **72**[12] 5705-5712 (1950).

23. R.K.Iler, "The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry," Wiley Interscience, New York, 1979.

24. M.W.Colby, A.Osaka, and J.D.Mackenzie, "Temperature Dependence of the Gelation of Silicon Alkoxides," J. Non-Cryst. Solids, **99**[1] 129-139 (1988).

25. M.W.Colby, A.Osaka, and J.D.Mackenzie, "Effects of Temperature on Formation of Silica Gel," J. Non-Cryst. Solids, **82**[1-3] 37-41 (1986).

26. V.A.Vekhov, E.P.Dudnik, and K.G.Marin, "Preparation of Silicon Dioxide by Hydrolysis of Tetraethoxysilane," Russ. J. Inorg. Chem., **9**[3] 294-296 (1964).

27. V.A.Vekhov, E.P.Dudnik, and E.I.Rumyantseva, "Hydrolysis of Tetraethoxysilane," Russ. J. Inorg. Chem., **10**[10] 1281-1283 (1965).

28. M.F.Bechtold, W.Mahler, and R.A.Schunn, "Polymerization and Polymers of Silicic Acid," J. Polymer Sc.:Polymer Chem. Ed., **18**[9] 2823-2855 (1980).

29. M.F.Bechtold, R.D.Vest, and L.Plambeck, Jr., "Silicic Acid From Tetraethyl Silicate Hydrolysis. Polymerization and Properties," J. Am. Chem. Soc., **90**[17] 4590-4598 (1968).

30. D.L.Dugger, J.H.Stanton, B.N.Irby, B.L.McConnell, W.W.Cummings, and R.W.Maatman, "The Exchange of Twenty Metal Ions with the Weakly Acidic Silanol Group of Silica Gel," J. Phys. Chem., **68**[4] 757-760 (1964).

Table I. Acronyms for the Glass Compositions Studied

Acronym	Mole %		Weight %	
	CaO	SiO_2	CaO	SiO_2
2CS	2	98	1.87	98.13
5CS	5	95	4.68	95.32
10CS	10	90	9.38	90.62
15CS	15	85	14.12	85.88
20CS	20	80	18.89	81.11

Table II. Batch Compositions, Gelation Time, and Gel Appearance at Ambient Temperature for CaO-SiO$_2$ System*

System	$Ca(NO_3)_2 \cdot 4H_2O$ (g)	$H_2O:Si(OC_2H_5)_4$ (Mole ratio)	Gelation time (h)	Gel Appearance
2CS	1.16	4.59	73	Clear
5CS	2.99	4.72	55	Clear
10CS	6.31	4.96	43.5	Clear
15CS	10.02	5.22	36	Clear
20CS	14.19	5.52	31	Clear

*50 g of $Si(OC_2H_5)_4$, and 80 ml of C_2H_5OH.

Table III. pH of Various Solutions as a Function of Time at Room Temperature; Water:TEOS Mole Ratio = 6, TEOS = 50g, C_2H_5OH = 80 ml.

Reaction time	pH	Reaction time	pH	Reaction time	pH	Reaction time	pH
SiO_2		$2CaO-98SiO_2$*		$5CaO-95SiO_2$		$10CaO-90SiO_2$	
3 min	5.80	5 min	4.26	5 min	4.18	5 min	4.00
5 min	5.43	15min	4.30	15min	4.18	15min	4.00
10min	5.38	30min	4.30	30min	4.19	30min	3.98
35min	5.26	40min	4.30	2 h	4.14	1 h	3.96
50min	5.26	1.5 h	4.25	5 h	4.12	3 h	3.96
1.5 h	5.29	3 h	4.26	6 h	4.12	20h	3.95
2.5 h	4.51	21 h	4.23	24 h	4.14		
5.0 h	4.77						
7.0 h	4.92						
24 h	5.06						

*All compositions in mole %

Table IV. Influence of Water:TEOS Mole Ratio on Gelation of SiO_2 and $10CaO-90SiO_2$ Systems at Various Temperatures

System	H_2O:TEOS mole ratio	Gelling time (h) at temp. (°C)					Arrhenius parameters	
		2	23	40.5	58	68	E*, kJ/mol	A', s^{-1}
SiO_2	6	-	156	38.5	15.3	7.9	54.5	7.8×10^3
10CS	4	-	40[a]	12	4.3[c]	2.4	52.9	1.5×10^4
	6	-	23[b]	7.5	2.5	1.3	55.8	7.4×10^4
	7.5	130	23.5	6	2.1	1.1[d]	56.9	1.3×10^5

[a] At 23.5°C.
[b] At 25°C.
[c] At 57.5°C.
[d] At 67°C.

Table V. Influence of Ca^{2+} Concentration on Gelation of TEOS at Various Temperatures; Water:TEOS Mole Ratio = 6

System, mole %	Gelling time (h) at temperature (°C)					Arrhenius parameters	
	1	23	40.5	58	68	E*, kJ/mol	A', s^{-1}
SiO_2	-	156	38.5	15.3	7.9	54.5	$7.8x10^3$
$2CaO-98SiO_2$	260	44	10.3	4	2.6[b]	54.7	$3.0x10^4$
$5CaO-95SiO_2$	-	27[a]	8.5	3	1.6	55.2	$4.9x10^4$
$10CaO-90SiO_2$	-	23[a]	7.5	2.5	1.3	55.8	$7.3x10^4$

[a] At 25°C.
[b] At 67°C.

Table VI. Infrared Absorption Peaks Observed in $CaO-SiO_2$ Gels and Glasses and Their Assignments

Frequencies of IR absorption bands	**Functional group**
460 cm^{-1}	Bending modes of Si-O-Si bonds
800 cm^{-1}	Bending modes of O-Si-O bonds
950 cm^{-1}	Si-OH bonds containing nonbridging oxygen
1080 cm^{-1}	Stretching vibration of Si-O-Si bonds
1385 cm^{-1}	$-NO_3$ group
1640 cm^{-1}	H_2O
3450 cm^{-1}	H_2O

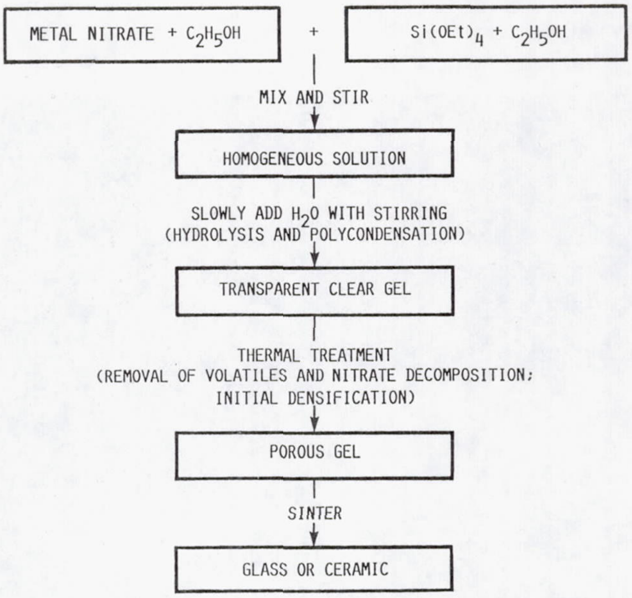

FIGURE 1. - FLOW CHART OF GLASS SYNTHESIS BY THE SOL-GEL METHOD.

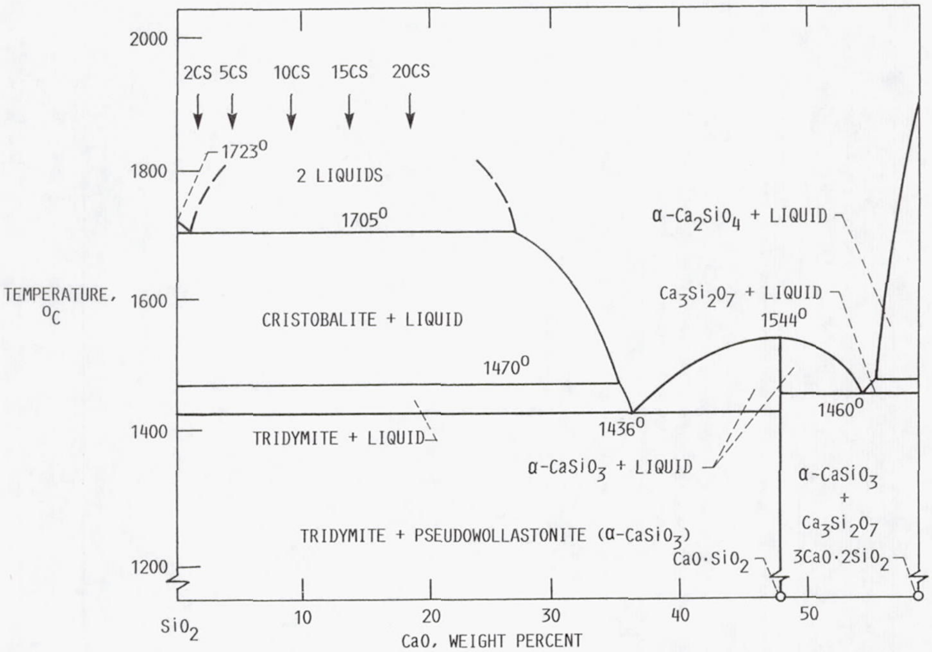

FIGURE 2. - PARTIAL PHASE DIAGRAM OF CaO-SiO_2 SYSTEM SHOWING POSITIONS OF THE VARIOUS GLASS COMPOSITIONS INVESTIGATED.

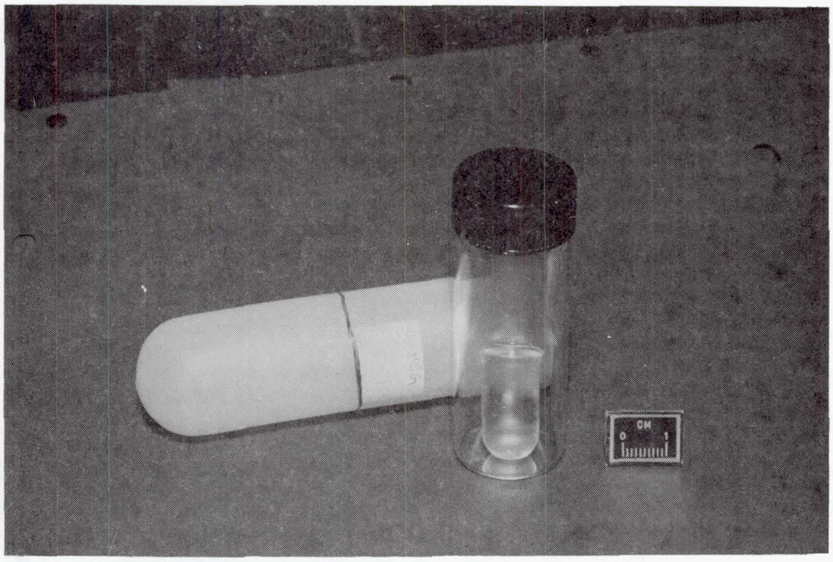

FIGURE 3. - MONOLITHIC 10CaO-90SiO$_2$ (MOL %) GEL SPECIMEN, PREPARED USING GLYCEROL AS THE DRYING CONTROL CHEMICAL ADDITIVE, AFTER DRYING FOR SEVERAL WEEKS UNDER AMBIENT CONDITIONS (FOREGROUND).

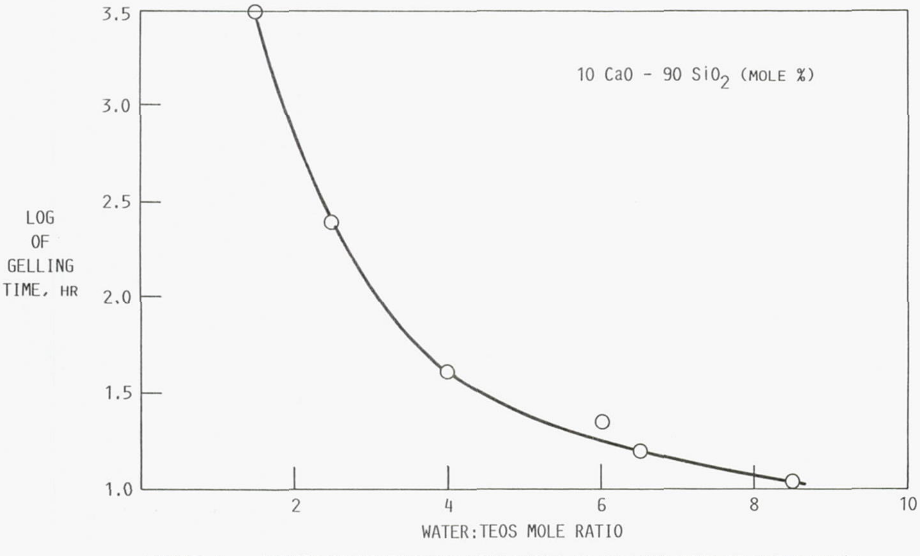

FIGURE 4. - EFFECT OF WATER:TEOS MOLE RATIO ON GELLING TIME OF 10CaO-90SiO$_2$ (MOL %) COMPOSITION AT ROOM TEMPERATURE. $Si(OC_2H_5)_4$ = 50 g, C_2H_5OH = 80 ml, AND $Ca(NO_3)_2 \cdot 4H_2O$ = 6.31 g.

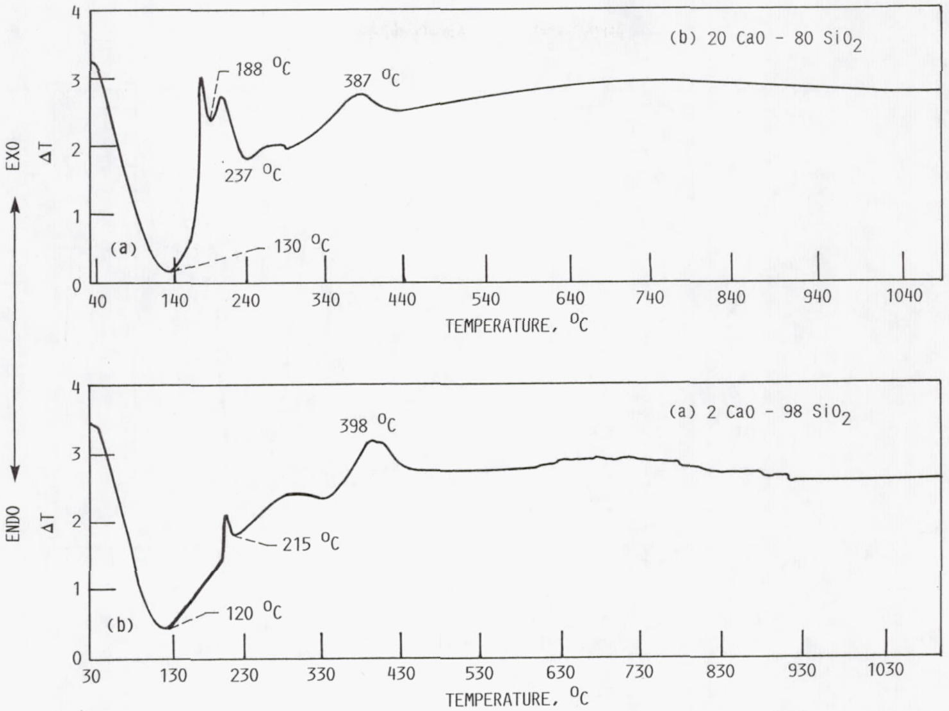

FIGURE 5. - DTA SCANS OF (a) 2CS AND (b) 20 CS GELS AFTER DRYING FOR SEVERAL WEEKS UNDER AMBIENT CONDITIONS; HEATING RATE OF 5 °C/MIN IN FLOWING AIR.

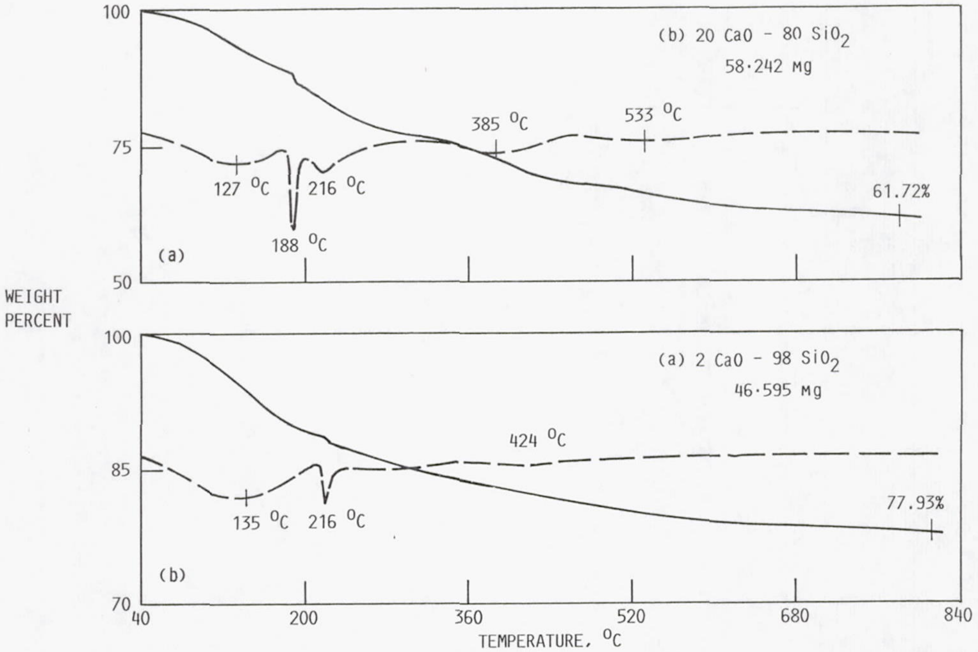

FIGURE 6. - TGA AND DTGA CURVES FOR (a) 2CS AND (b) 20CS GELS AFTER DRYING FOR SEVERAL WEEKS UNDER AMBIENT CONDITIONS; SCAN RATE OF 5 °C/MIN IN FLOWING AIR.

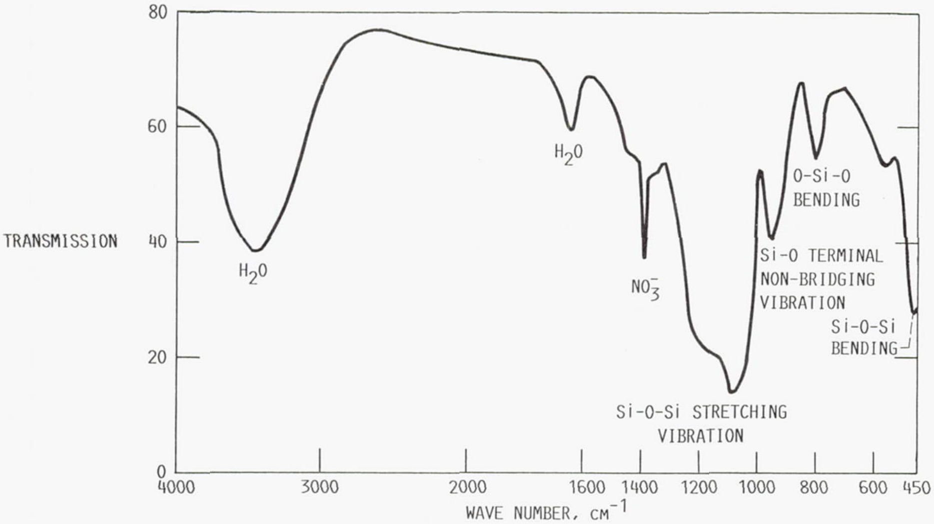

FIGURE 7. - INFRARED SPECTRA OF $10CaO-90SiO_2$ (MOL %) GEL AFTER DRYING FOR SEVERAL WEEKS UNDER AMBIENT CONDITIONS; WATER:TEOS MOLE RATIO = 4.95.

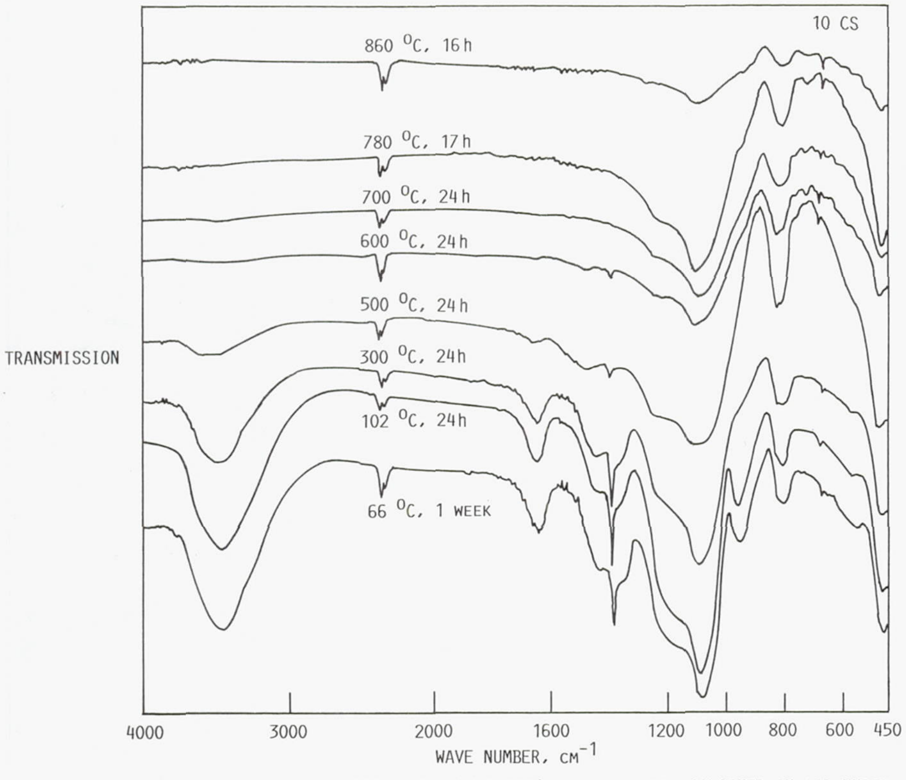

FIGURE 8. - INFRARED SPECTRA OF $10CaO-90SiO_2$ (MOL %) GEL CALCINED IN AIR UNDER DIFFERENT CONDITIONS. THE HEAT TREATMENTS ARE CUMULATIVE AT SUBSEQUENT TEMPERATURES.

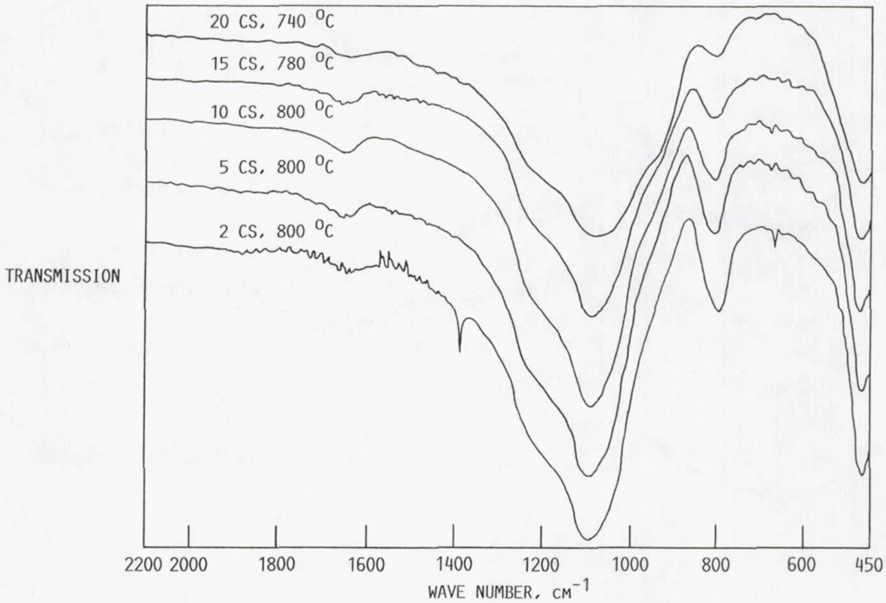

FIGURE 9. - INFRARED SPECTRA OF CaO-SiO$_2$ GELS OF VARIOUS COMPOSITIONS HEATED TO VARIOUS TEMPERATURES AT ~2 °C/MIN IN AIR AND FURNACE COOLED.

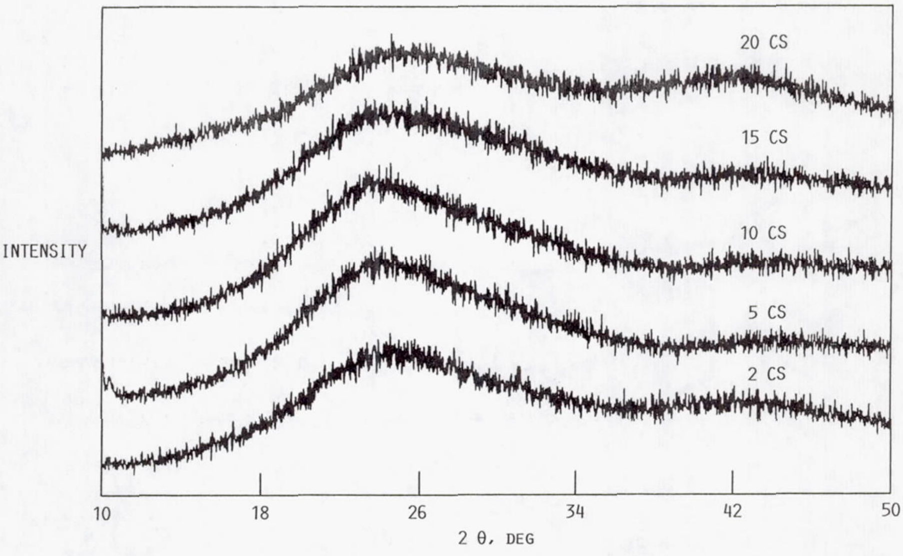

FIGURE 10. - X-RAY DIFFRACTION SPECTRA OF CaO-SiO$_2$ GELS OF VARIOUS COMPOSITIONS AFTER DRYING AT 66 °C FOR 7 DAYS IN AIR.

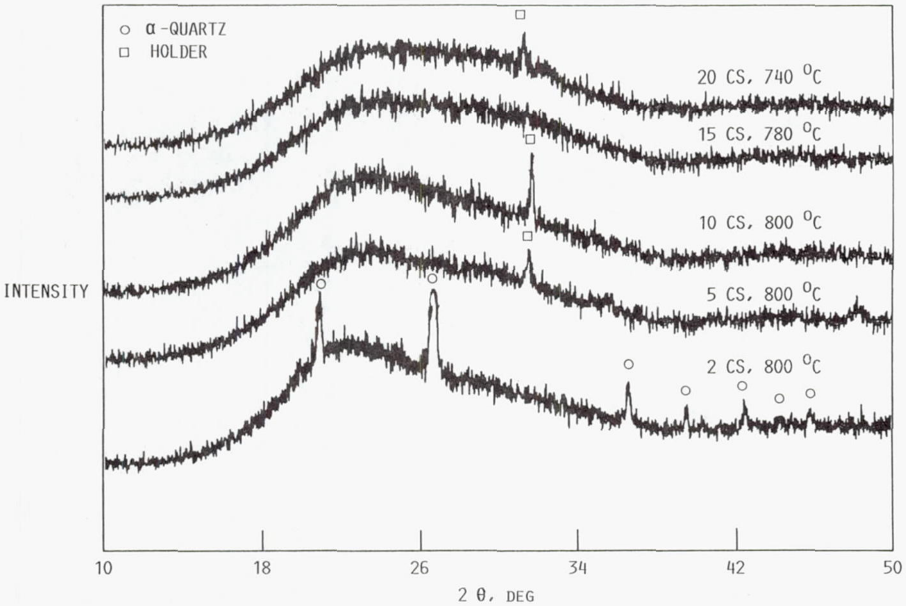

FIGURE 11. - X-RAY DIFFRACTION PATTERNS OF $CaO-SiO_2$ GELS OF VARIOUS COMPOSITIONS HEATED IN FLOWING AIR UP TO THE TEMPERATURES INDICATED AT ~2 °C/MIN AND FURNACE COOLED.

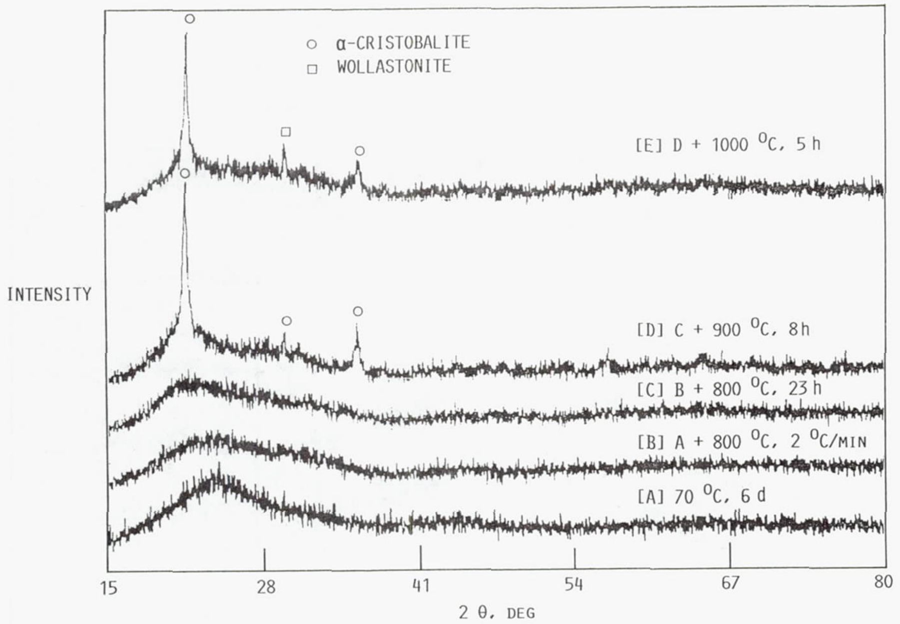

FIGURE 12. - X-RAY DIFFRACTION SPECTRA OF $10CaO-90SiO_2$ (MOL %) GEL CALCINED IN AIR AT VARIOUS TEMPERATURES.

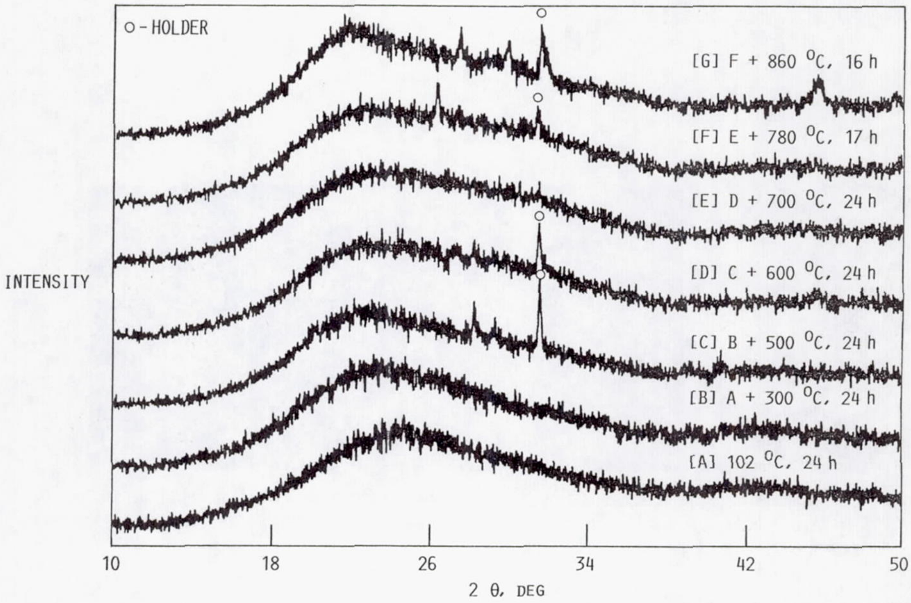

FIGURE 13. - X-RAY DIFFRACTION PATTERNS OF $10CaO-90SiO_2$ (MOL %) GEL HEAT TREATED IN AIR AT VARIOUS TEMPERATURES FOR DIFFERENT TIMES.

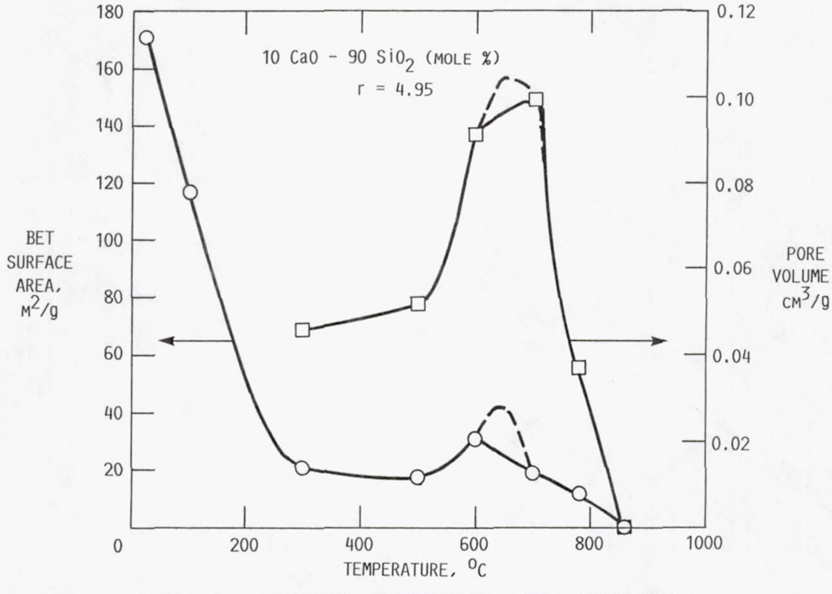

FIGURE 14. - VARIATIONS IN BET SURFACE AREA AND CUMULATIVE PORE VOLUME VERSUS CALCINATION TEMPERATURE OF $10CaO-90SiO_2$ (MOL %) GEL; WATER:$Si(OC_2H_5)_4$ MOLE RATIO = 4.95; HEAT TREATMENTS ARE CUMULATIVE AT SUBSEQUENT TEMPERATURES. GEL DRIED UNDER AMBIENT CONDITIONS FOR ~2 MONTHS, FOR 24 h EACH AT 102, 300, 500, 600 AND 700 °C, FOR 17 h AT 780 °C, AND FOR 16 h AT 860 °C.

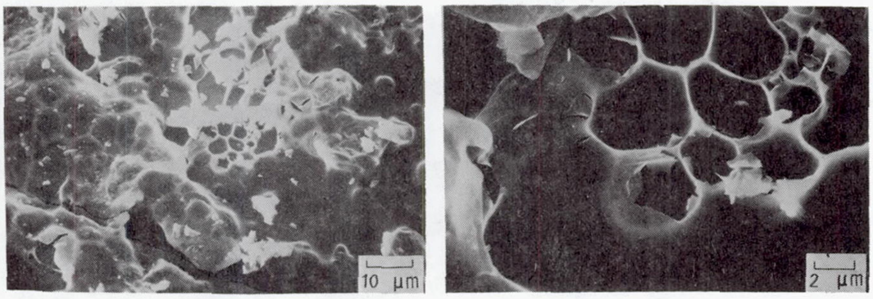

FIGURE 15. - SCANNING ELECTRON MICROGRAPHS OF THE 10CaO-90SiO$_2$ (MOL %) GEL HEAT TREATED TO 800 $^{\circ}$C AT 2 $^{\circ}$C/MIN FOLLOWED BY ISOTHERMAL HEAT TREATMENTS AT 800 $^{\circ}$C FOR 23 h AND AT 900 $^{\circ}$C FOR 8 h IN AIR.

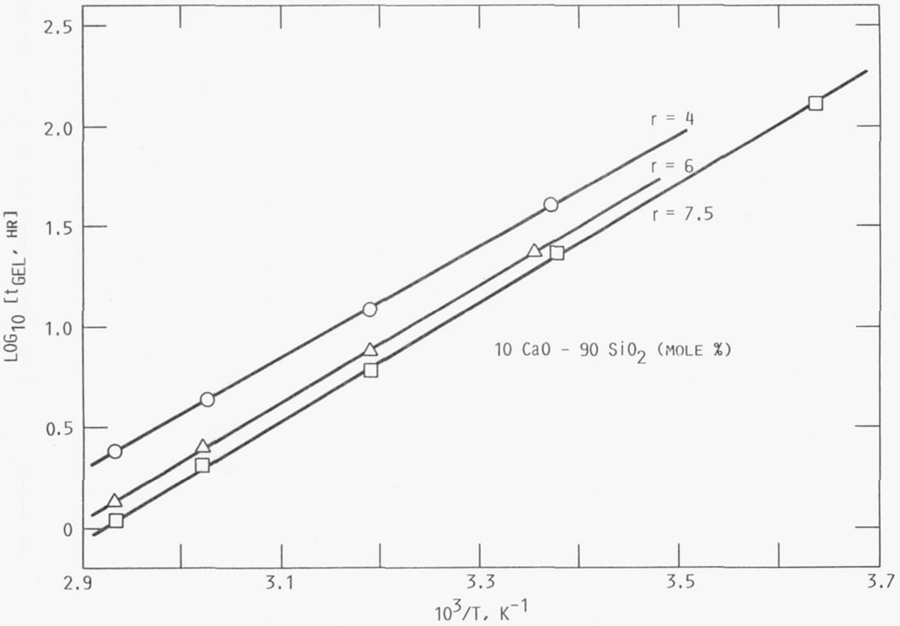

FIGURE 16. - TEMPERATURE DEPENDENCE OF GEL FORMATION TIME FOR 10CaO-90SiO$_2$ (MOL %) COMPOSITION AT VARIOUS WATER:Si(OC$_2$H$_5$)$_4$ MOLE RATIOS (r).

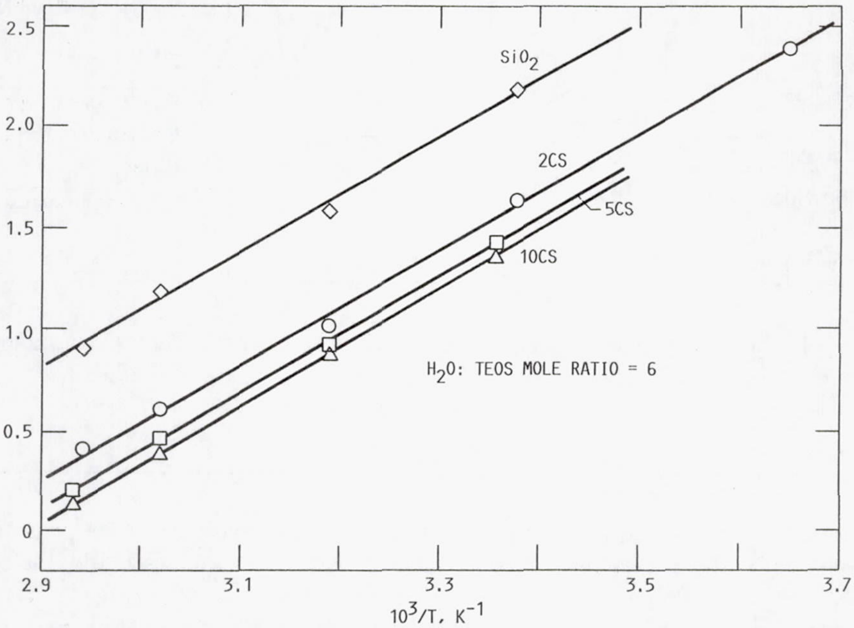

FIGURE 17. - TEMPERATURE DEPENDENCE OF GELLING TIME FOR VARIOUS $CaO-SiO_2$ COMPOSITIONS; WATER:$Si(OC_2H_5)_4$ MOLE RATIO = 6.

NASA
National Aeronautics and
Space Administration

Report Documentation Page

1. Report No. NASA CR-185293	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Low Temperature Synthesis of CaO-SiO_2 Glasses Having Stable Liquid-Liquid Immiscibility by Sol-Gel Process

5. Report Date

October 1990

6. Performing Organization Code

7. Author(s)

Narottam P. Bansal

8. Performing Organization Report No.

None (E-5740)

10. Work Unit No.

510-01-01

9. Performing Organization Name and Address

Case Western Reserve University
Cleveland, Ohio 44106

11. Contract or Grant No.

NCC3-133

13. Type of Report and Period Covered

Contractor Report
Final

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

14. Sponsoring Agency Code

15. Supplementary Notes

Project Manager, Stanley R. Levine, Materials Division, NASA Lewis Research Center. Narottam P. Bansal, NASA Resident Research Associate at Lewis Research Center.

16. Abstract

Calcium silicate glass compositions lying within the liquid-liquid immiscibility dome of the phase diagram, which could not have been prepared by the conventional melting method, have been synthesized by the sol-gel process. Hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS) solutions containing up to 20 mol % calcium nitrate resulted in the formation of clear and transparent gels. The gel formation time decreased with increase in water:TEOS mole ratio, calcium content and the reaction temperature. Smaller values of gel times in the presence of calcium nitrate are probably caused by lowering of the ionic charge on the sol particles by the salt present. The gelation activation energy, E_{gel}, was evaluated from temperature dependence of the gel time. Presence of Ca^{2+} ions or the water:TEOS mole ratio did not have an appreciable effect on the value of E_{gel}. Presence of glycerol in the solution helped in the formation of crack-free monolithic gel specimens. Chemical and structural changes occurring in the gels, as a function of the heat treatments, have been monitored using DTA, TGA, IR-spectroscopy, x-ray diffraction, surface area and pore size distribution measurements.

17. Key Words (Suggested by Author(s)) Sol-gel; Glasses; Immiscibility; Phase separation; Silicates	18. Distribution Statement Unclassified – Unlimited Subject Category 23

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 38	22. Price* A03

NASA FORM 1626 OCT 86

*For sale by the National Technical Information Service, Springfield, Virginia 22161

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio 44135

Official Business
Penalty for Private Use $300

FOURTH CLASS MAIL

ADDRESS CORRECTION REQUESTED

NASA