

Preparation of CaO-SiO₂ glasses by the gel method

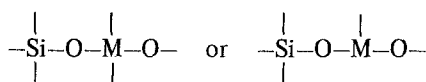
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The formation of CaO-SiO₂ glasses, which could not have been prepared with the conventional glass-melting technique because of the presence of the stable liquid-liquid immiscibility zone, was investigated by the gel method. The monolithic transparent glasses of CaO·9SiO₂ and CaO·4SiO₂ composition were obtained by slowly heating to 800° C the transparent gels formed by hydrolysis with atmospheric moisture. In this binary system, the promotion of hydrolysis by the addition of water was not so favourable, because it caused the precipitation of the hydrolysed product, i.e. Ca(OH)₂, and therefore the gels obtained were translucent or opaque. The values of true density and refractive index measured for the transparent glasses were comparable with those calculated from the corresponding compositions. Crystallization occurred during heat-treatment above 800° C and wollastonite was precipitated.

1. Introduction

The preparation of monolithic glasses, glass fibres, pure fine powders and ceramic materials from metal alcoholates or metal salts by the gel method has recently been investigated by several researchers [1-8]. Roy [9] has suggested that because of the excess free energy of a gel compared to a glass of the same composition, a gel may be converted to a glass below the normal melting temperature of that composition. Thus, it should be possible, in principle, to convert dried gels into glasses at a temperature substantially below the liquidus temperature. This method is mainly based on the polymerization reaction (i.e. hydrolysis and polycondensation) of silicon alcoholate with other metal alcoholates or suitable metal salts in the presence of a limited amount of water to produce multi-component inorganic gels probably with networks like the following:



where M is a metal atom, e.g. Ti, Zr, Al, B, etc. The glasses obtained by this new method have the same physical and chemical properties as the analogous materials obtained by the conventional

melting method, but have the advantage of a higher homogeneity and the disadvantage of a higher hydroxyl group content. This gel method is particularly suitable for the preparation of glasses having a very high melting temperature and glasses of the compositions within the stable of metastable liquid-liquid immiscibility region. Indeed, relatively few glasses containing alkali or alkali earth oxides were obtained by the gel method. This study was undertaken for the purpose of preparing CaO-SiO₂ glasses which have not been obtained by the conventional glass-melting technique, because of the presence of the stable liquid-liquid immiscibility region in this system.

2. Experimental details

2.1. Materials

Silicon ethylate, Si(OEt)₄, a commercially available reagent, was used as-received. Calcium ethylate, Ca(OEt)₂, was obtained by reacting the appropriate amount of high-purity calcium metal with ethanol. Calcium nitrate was also used as a source of CaO. Solvent was dried with molecular sieves 4A.

2.2. Preparation of CaO-SiO₂ glasses

The compositions of glasses in the binary system is

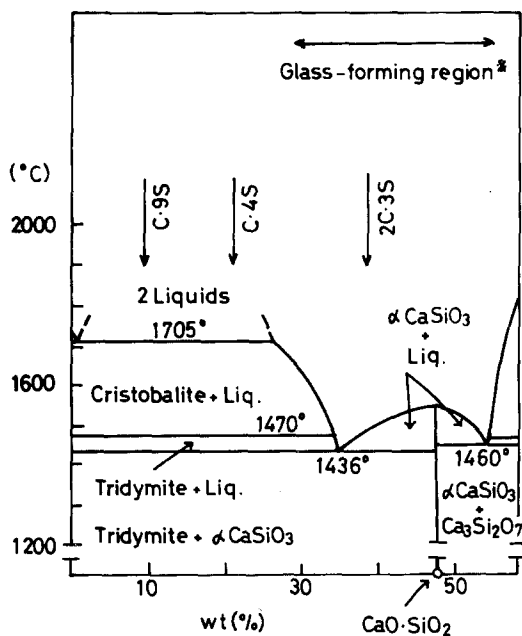


Figure 1 Phase diagram of CaO-SiO₂ system showing the positions of the compositions investigated. C and S denote CaO and SiO₂, respectively. * [10].

shown in Fig. 1, Tables I and II. Si(OEt)₄ was added to a stirred solution of Ca(OEt)₂ in 100 ml dried ethanol under Ar gas. The mixture was allowed to react under reflux for 4 h with constant stirring. The colour of the solution changed from light yellow to red-brown. The solution obtained was gelatinized using the following two methods: the first is based on gelation with the addition of water and the other is based on gelation with atmospheric moisture. In the former method, the mixture solution was quickly hydrolysed and polymerized by the addition of a small amount of water dissolved in ethanol. A translucent or opaque gel was formed in several hours. In the latter method, the mixture solution was slowly hydrolysed by atmospheric moisture at room temperature. A transparent or translucent gel was then formed in a

few days. The dehydration of the gels obtained by both methods was accomplished by stepwise heating in the following sequence: initially drying at 100°C, then the gel was heated very slowly to 400°C and was kept at 400°C for 1 day for the removal of residual alkoxy groups and then at 500, 600 and 700°C for 1 day respectively, and finally at 800°C for 12 h.

On the other hand, the reaction using Ca(NO₃)₂ as a source of CaO was carried out as follows: the mixture of Si(OEt)₄ and Ca(NO₃)₂ in ethanol was reacted at 70°C for 3 h and then the necessary amount of water was added to the mixture under stirring. A translucent or opaque gel was formed in approximately a week. The heat treatment of gels was carried out in a similar manner as above.

2.3. Measurement of the properties of gels and glasses

Each product was characterized with X-ray diffraction for crystallinity, with the oil immersion technique for refractive index, with optical microscopy and electron microscopy using double carbon replicas for microstructure, with the Archimedes method for true density, with TGA and DTA techniques for thermal characteristics, and with the infra-red technique.

2.4. Elemental analysis

Analysis for SiO₂ and CaO was performed by the standard gravimetric method and the chelate method, respectively.

3. Results and discussion

3.1. The gelation process

The hydrolysis of metal alcoholates diluted with ethanol was carried out using either the moisture in the ambient atmosphere or water. Only a translucent or opaque gel was formed by the addition of water, whereas a transparent or translucent stiff gel was formed by using the atmospheric moisture.

TABLE I Batch composition and appearance of glasses obtained from the mixture of Si(OEt)₄ and Ca(OEt)₂

Composition (mol %)	Metal Ca (g)	Si(OEt) ₄ (g)	H ₂ O/Si(OEt) ₄ (molar ratio)	Appearance
CaO·9SiO ₂	0.352	16.46	0	transparent bulk
	0.352	16.46	2	transparent bulk
	0.352	16.46	4	white, opaque bulk
CaO-4SiO ₂	0.685	14.27	0	transparent bulk
	0.685	14.27	2	translucent bulk
	0.685	14.27	4	opaque bulk
2CaO-3SiO ₂	1.318	11.21	0	carbonized, grey bulk
	1.318	11.21	2	translucent bulk

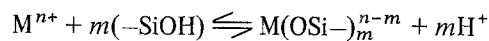
TABLE II Batch composition and appearance of glasses obtained from the mixture of $\text{Si}(\text{OEt})_4$ and $\text{Ca}(\text{NO}_3)_2$

Composition	$\text{Ca}(\text{NO}_3)_2$ (g)	$\text{Si}(\text{OEt})_4$ (g)	$\text{H}_2\text{O}/\text{Si}(\text{OEt})_4$ (molar ratio)	Appearance
$\text{CaO} \cdot 5\text{SiO}_2$	3.18	20.01	6	translucent, powder
$\text{CaO} \cdot 4\text{SiO}_2$	3.25	16.01	6	white opaque, powder
$\text{CaO} \cdot 3\text{SiO}_2$	3.15	12.01	6	white opaque, powder

The degree of transparency of the resulting gels was appreciably dependent on the humidity in the atmosphere under hydrolysis, and therefore, in very high humidity the gel became translucent. The structure and properties of dry gels are substantially determined by the rate of dehydration polymerization which occurs after the hydrolysis of metal alcoholate. The greater the rate of dehydration polymerization, the more unreacted ethoxy groups and water will be left in the dry gel. The presence of bulky ethoxy groups in the resultant product also appears to be related to the structural disorder. Therefore, the larger porosity in the bulk form of the gel was produced as a result of the higher rate of dehydration polymerization, which is due to the catalytic action of the hydroxyl ions in the high calcium hydroxide content. If the rate of dehydration polymerization is large, compared to that of the hydrolysis reaction, the polymerization occurs as soon as the resultant ethoxy silanol groups, $\text{Si}(\text{OH})_x(\text{OEt})_{4-x}$ approach each other. When the dehydration polymerization proceeds to some extent, the gels will become too rigid for further contraction due to either the development of strong $\text{Si}-\text{O}-\text{Si}$ bonds or contact of the polymers at their non-reactive sites. But in the case of the presence of alkali or alkali earth metal ion, the contact of SiO_4 networks is interfered with by the metal ions, and consequently the shrinkage of the gel containing the metal ions is much less, compared with the SiO_2 gel, and therefore this open structure containing many small pores results in the gel. The gelation of the solution started from the surface and gradually developed into the bulk. The gel attains its final volume while a certain amount of water, ethoxy groups and solvent are still left within it. The monolithic gels obtained by both methods usually cracked into a few pieces in a week at room temperature. In this binary system, the promotion of the hydrolysis with the addition of water to the mixture of alcoholates was not so favourable, because as calcium ethylate is much faster to hydrolyse than silicon ethylate, it resulted in more preferential precipitation of the hydrolysed product, i.e.

$\text{Ca}(\text{OH})_2$, during hydrolysis and, therefore, inhomogeneities occurred. But the tendency toward the preferential precipitation of the calcium hydroxide was mostly avoided by the hydrolysis using atmospheric moisture and the homogeneity of the structure seemed to be preserved in the glass from the optical microscope observations. In general, it is desirable that the alcoholates used have a relatively compatible reaction rate in order to obtain a homogeneous gel. In contrast with the case of $\text{Ca}(\text{OEt})_2$, only a fluffy, low-density gel powder was obtained from the solution containing calcium nitrate. In the gels dried at 100°C , which were formed from the mixture of $\text{Si}(\text{OEt})_4/\text{Ca}(\text{NO}_3)_2$ molar ratio < 4 , a small amount of $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 2$) was detected by X-ray diffraction. A major drawback in the use of these dried gels obtained from the metal nitrate is that the nitrate is usually crystallized during dehydration, thereby destroying the homogeneity achieved by stirring. It seems that the ions are very mobile in the gel during dehydration because of its large H_2O content.

It is well known [11, 12] that the silanol group ($-\text{SiOH}$) of the hydrated silica gel surface is weakly acidic, and therefore when the gel is mixed with an aqueous electrolyte there is some cation exchange as follows:



where M is the metal. The reaction is reversible in an acidic solution [12], but in the alkaline solution the reaction appeared to proceed to some extent.

3.2. Effects of heating on the gels

The reddish brown, transparent gels obtained by the hydrolysis with atmospheric moisture became bright yellow at 300°C , and then light grey at 500°C , but the greyish white colour disappeared on heating above 500°C and changed to colourless, transparent glasses at 800°C . On heat treatment from 300 to 500°C , the gels cracked more extensively into small pieces (5 to 10 mm rectangular). The maximum size of glasses obtained by the heat treatment to 800°C is approximately 10 mm \times

TABLE III Density and refractive index of the glasses prepared from alcoholates by the heat treatment at 800° C

Composition	Analysis (wt %)				Density (10 ³ kg m ⁻³)		Refractive index	
	SiO ₂		CaO		Found	Calc	Found	Calc
	Found	Calc	Found	Calc				
CaO·9SiO ₂	87.4	90.6	12.4	9.4	2.44	2.33 (2.39)*	1.504	1.489 (1.502)*
CaO·4SiO ₂	78.8	81.1	21.1	18.9	2.51	2.48 (2.52)*	1.527	1.524 (1.533)*

* The values in parentheses were calculated from analytical composition.

calculated from the analytical compositions, although the latter were slightly different from the batch compositions because of the evaporation of Si(OEt)₄ during the gelation. The small-angle X-ray scattering was observed in the materials obtained by heat treatment below 600° C, but was hardly observed above 700° C. The gels were found to vitrify into transparent or translucent glasses at 800° C. A typical transmission electron micrograph of the CaO–SiO₂ glasses is shown in Fig. 4. The microstructure of the glass showed that small pores ($\approx 60 \text{ \AA}$) and large circular depressions ($\approx 500 \text{ \AA}$), in which small droplets existed, were observed in the glass. It appears that the large circular depressions represented cross-sections of the calcium-rich phase that are less resistant to etching. It is considered that this observation may probably be due to the glass phase separation. A systematic experimental and theoretical investigation has been undertaken of the two-phase region that is known to exist at high temperatures in the silica-rich portion of the CaO–SiO₂ system, and it has been found by Tewhey and Hess [14] that immiscible CaO–SiO₂ melts that have been quenched from 1700° C or above, consisted of a

clear siliceous phase and a white opaque calcium-rich phase containing droplets partially composed of cristobalite. It appears that the results obtained in this work are somewhat different from those reported for glasses produced by the melting method. Therefore, further results on the phase separation of glasses obtained by the gel method will be presented later in detail.

3.4. Infra-red spectra

Infra-red spectra gave some important information on the structural and compositional change in the heating process. The spectra of the samples corresponding to 20 wt% Ca–80 wt% SiO₂ glasses are shown in Fig. 5. The absorption peak around 870 cm⁻¹, attributed to the Si–OH vibration, decreased in intensity with increasing temperature and disappeared above 500° C. No absorption attributable to the alkoxy groups was found. The absorption band around 1100 cm⁻¹, attributed to the Si–O vibration in the SiO₄ tetrahedron, shifted slightly to lower frequencies as the temperature increased to around 400° C, but shifted to higher frequencies as the temperature was raised above 400° C, suggesting that the Si–O bonds in tetrahedra were strengthened.

3.5. Thermal properties

DTA and TGA curves of the dried gel corresponding to CaO·4SiO₂ glass are shown in Fig. 6. In the DTA curve of the gel obtained from the alcoholates, an endothermic peak was observed, in the range 100 to 150° C, which could be attributed to an oxidation involving the solvent or to the oxidation of residual organic groups in the gel, was observed in the range 220 to 300° C. The higher contents of CaO in the composition of the gel caused the greater exothermic peak in DTA curves because of the oxidation of residual organic groups. In addition, in the TGA curve a weight loss was observed in the range of room temperature to

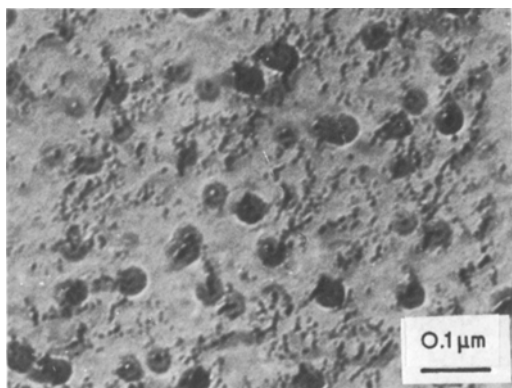


Figure 4 Electron micrograph of the replicated surface of the CaO·4SiO₂ glass.

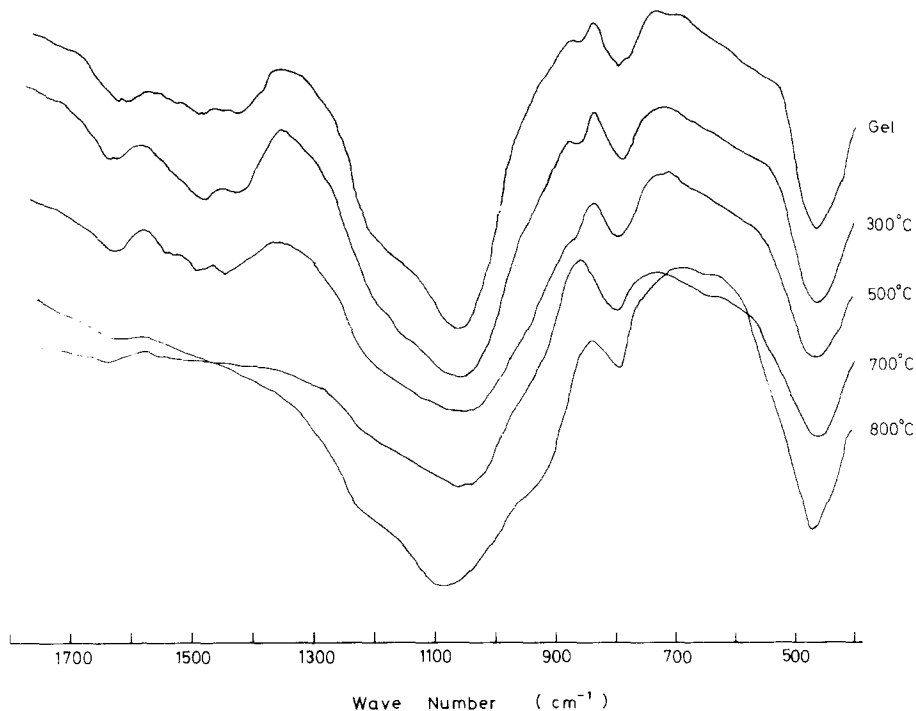


Figure 5 Infra-red spectra of the specimens obtained by heating the $\text{CaO}\cdot 4\text{SiO}_2$ gel at various temperatures.

400° C. This is probably due to the evaporation of the adsorbed water and solvent, by-products and unpolymerized or small chain-length polymers of silicon ethylate. In the DTA curve (Fig. 6) of the $\text{CaO}\cdot 4\text{SiO}_2$ glass obtained by very slowly heating the corresponding gel to 800° C, only an exothermic peak was observed near 900° C, which could be attributed to the crystallization of wollastonite. On the other hand, in the DTA curve

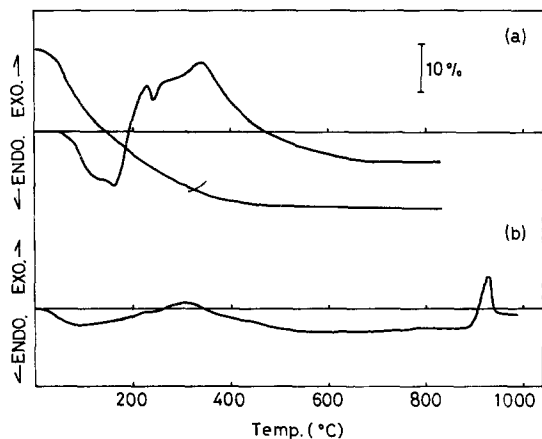


Figure 6 DTA and TGA curves of the dried gel corresponding to the $\text{CaO}\cdot 4\text{SiO}_2$ glass, and DTA curve of the $\text{CaO}\cdot 4\text{SiO}_2$ glass obtained by very slowly heating the gel to 800° C: (a) gel; (b) glass.

of the gel, corresponding to the $\text{CaO}\cdot 4\text{SiO}_2$ glass, obtained from calcium nitrate and silicon ethylate, two endothermic peaks were observed in the ranges 100 to 200° C and 570 to 700° C as shown in Fig. 7. The former peak resulted mainly from the evaporation of the adsorbed water and the removal of the water contained in $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ compounds whereas the latter peak resulted probably from the loss of H_2O incorporated into the gel structure and from the melting and decomposition of nitrate (pure $\text{Ca}(\text{NO}_3)_2$ melts at 561° C and the absorption peak of the NO_3^- group around

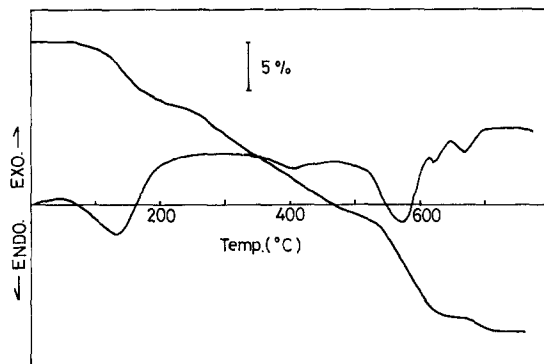


Figure 7 DTA and TGA curves of the dried gel ($\text{CaO}\cdot 4\text{SiO}_2$) obtained from a mixture of $\text{Si}(\text{OEt})_4$ and $\text{Ca}(\text{NO}_3)_2$.

1370 cm⁻¹ disappeared above 700°C). The thermal expansion coefficient of the CaO·4SiO₂ glass obtained from alcoholates has been measured on a bar 5 mm long. The expansion, α , is almost linear up to 600°C, averaging $1.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.

4. Conclusions

The formation of CaO–SiO₂ glasses of compositions within the stable liquid–liquid immiscibility region was investigated by the gel method.

(1) The mixture of calcium ethylate and silicon ethylate was hydrolysed either by the addition of water or by atmospheric moisture. In the former method, a translucent or opaque gel was formed in several hours, whereas in the latter method a transparent or translucent gel was formed in a few days. The degree of transparency of the resulting gel was dependent on the humidity in the ambient atmosphere. In this binary system, the promotion of the hydrolysis by the addition of water was not so favourable, because it caused the precipitation of the hydrolysed product.

(2) The monolithic transparent glasses of CaO·9SiO₂ and CaO·4SiO₂ composition were obtained by slowly heating the clear gel formed by the hydrolysis with atmospheric moisture to 800°C. Only porous opaque or translucent glasses were obtained from the gel formed by the addition of water. The gel of the composition containing more than 40% CaO was changed into black powder when heated above 500°C.

(3) The values of true density and refractive index for the glasses were comparable with those calculated from the corresponding compositions. In transmission electron microscopy, many small pores ($\approx 60 \text{ \AA}$ diameter) were observed. But small-angle X-ray scattering was hardly observed in the specimens heat-treated above 700°C.

(4) In general, crystallization occurred on heat treatment above 800°C and wollastonite was precipitated.

(5) In contrast with the alcoholate mixture, only a fluffy low-density oxide powder was obtained from the mixture of calcium nitrate and silicon alcoholate.

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