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Phase separation behaviour of a metal-organic derived sodium silicate glass

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The phase separation behaviour of an 18.56 mol % Na_2O–SiO_2 glass prepared via the standard glass preparation technique and the metallic–organic derived (MOD) method have been studied and contrasted. Our results suggest that at this composition the miscibility temperature is significantly elevated when a MOD preparation procedure is used. The origin of this effect appears to be related to the enhanced water content in the glass prepared by the MOD procedure.

1. Introduction

The process of phase separation in glasses has received intensive study in recent years [1]. Interest in this topic has been stimulated, in part, due to the observed relationship between glass-ceramic formation and the prior appearance of phase separation in glasses used for the fabrication of glass-ceramic materials [2]. In addition, it is well known that phase separation can effect the physical and electrical properties of glass [3, 4]. Also, since it has been suggested that the occurrence of very fine scale phase separation may alter the chemical durability of glass [5], it is clear that a detailed understanding of the phase separation process in glass is of practical as well as of scientific interest.

Here the influence of phase separation upon the properties of glass will not be considered. On the contrary, an example of the effect of glass processing procedure upon the tendency towards phase separation will be discussed. It has been recognized that the phase separation process, and in particular miscibility temperatures, are quite sensitive to even trace amounts of impurities [6]. Such impurities are typically metallic oxide compounds.

Along a somewhat different vein, Kreidl and Maklad [7] have studied the effect of water content on the phase separation in soda–silica glass. They observed that kinetics of the phase separation process in this glass could be substantially hastened by an increase in its water content. Kreidl and Maklad produced soda–silica glasses with enhanced water content by melting the batch under pressurized steam atmosphere.

Recently, in a comparitive study of the behaviour of "gels" and oxide mixtures for glass production, Mukherjee *et al.* [8] noted differences in the phase separation of gel and oxide SiO_2–La_2O_3 glasses. Their primary observation was that phase separation in the gel glasses produced a quite uniform microstructure with small droplets while the microstructure of the phase separated oxide glasses exhibited a non-uniform distribution of larger, somewhat irregularly shaped, particles. Mukherjee *et al.* attributed this difference to the presence of -OH groups incorporated into the structure of the gel glasses.

Mukherjee *et al.* could only study the differences in the phase separation behaviour of gel and oxide glasses in the La_2O_3–SiO_2 in a cursory manner for several reasons. First of all, the focused heating procedure employed caused a degree of vaporization of the samples, thus making it difficult to insure that gel and oxide glasses produced would be of the same composition. In addition, due to the rapidity of the phase separation process, unmixing occurred during the quench in all cases.

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Thus, as mentioned by the authors, the thermal histories of each sample would have to be known in order to make detailed comparisons between the phase separation in oxide and gel glasses. Furthermore, the rapidity of the phase separation precluded the study of this process under isothermal conditions.

Since the observations of Mukherjee *et al.* are of interest, we undertook to contrast the phase separation of "gel" or MOD glass with batch glass in a system in which phase separation may be more conveniently studied, and thus in which any such difference in phase separation behaviour may be more accurately and reliably described. Here we present the preliminary investigation of the phase separation of a MOD and batch Na_2O-SiO_2 glass of identical composition. As we shall discuss, phase separation occurs sufficiently slowly in this composition such that careful isothermal heat treatments may be used sequentially to increase the degree of phase separation in the glass. In addition, in the case of the batch glass, phase separation during quench may be completely obviated.

For the particular composition Na_2O-SiO_2 glass investigated, we found several notable differences between the phase separation behaviour of the MOD and batch glass. Perhaps of most interest, was our observation that the equilibrium miscibility temperature is raised substantially in the MOD glass. Also, we believe that there is strong evidence to indicate that at the particular temperature at which isothermal heat treatments were performed, the MOD and oxide glasses phase separate by means of different mechanisms. Furthermore, we have obtained experimental evidence which suggests that the MOD glass does, indeed, possess an enhanced -OH content as postulated by Mukherjee *et al.*

In Section 2 we briefly discuss the experimental procedures which were employed. The preparation of MOD and batch glasses, water analysis, small angle X-ray scattering (SAXS) and replication electron micrograph (REM) techniques will be considered. In Section 3 we present the results of this study. The microstructure of the annealed and isothermally heat treated glasses will be displayed and discussed.

Our results will be analysed in terms of existing theoretical knowledge of the phase separation in Na_2O-SiO_2 glasses in Section 4. Our discussion will close by mentioning future experimental work which our conclusions suggest.

2. Experimental

2.1. Preparation of batch glass

A 5 kg melt of 18.56 mol % Na_2O-SiO_2 glass was made using Q–P quartz processed from Brazilian quartz and Baker reagent Na_2CO_3. The raw materials were blended and heated electrically in a platinum crucible at 1565° C for 74 h. The melt was stirred continuously with a platinum stirrer. The melt was poured into stainless steel moulds to produce glass bars of various dimensions. As needed, small quantities (of the order of a couple of hundred grams) of this glass was crushed into coarse fragments and remelted at 1565° C for 3 h and recast into glass bars of about 1 cm thickness. Wet chemical analysis was employed to verify the glass composition.

2.2. Preparation of MOD glass

The procedure used to produce the MOD glass closely followed the technique devised by Levene and Thomas [9]. Tetraethyl silicate (682 g) was added to water (200 g) and 1 N nitric acid solution (40 g) and stirred until a clear single solution resulted. A solution of sodium nitrate (122 g) in water (200 g) was added to the above and the resulting clear solution was evaporated by boiling until gellation occurred. The remaining gel was dried at 110° C overnight. The next day it was heated slowly to 700° C and held at this temperature for 8 h. A white granular solid product was obtained, which we refer to as the MOD precursor material. Wet chemical analysis was made of the product to ensure that the composition corresponded to that of the batch mixture.

Glass was formed from the MOD precursor material by melting this solid electrically at 1565° C for 3 h and casting thin bars (~ 1 cm thickness) of glass in stainless steel moulds.

2.3. Microstructure studies and H_2O analysis

Replicas were obtained from freshly fractured glass surfaces etched with 2% HF in H_2O for 15 sec. The etched glasses were shadowed with a platinum film after which a thin film of carbon was deposited. The micrographs were produced employing an RCA electron microscope operating at 50 or 100 keV with a resolution of approximately 100 Å.

The SAXS intensity was measured utilizing a Kratky camera. The sample to detector slit distance was 210 mm, and the entrance slit width was 0.04 mm. A high powered Seimens X-ray tube with copper anode, operating at 38 mA and 35 kV, served as the X-ray source. A nickel filter was used in the direct beam, and the scattered Kα radiation was detected with a scintillation counter in conjunction with a pulse height analyser.

The relative water content of glass samples were obtained by means of infra-red spectroscopy. Glass samples of approximately 1 cm × 2 cm × 0.19 cm were heated for 90 min at 130° C in a vacuum oven and then stored in a desiccator. I.r. spectra from 2.5 to 5 μm were obtained with a Perkin-Elmer 467 Grating Infra-red Spectrophotometer from these vacuum-baked samples.

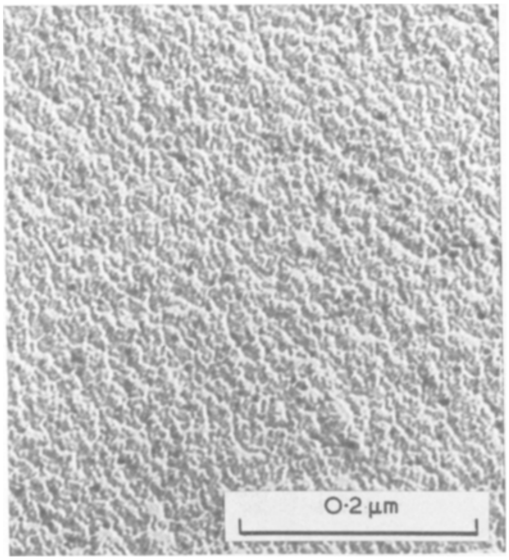


Figure 1 Electron micrograph of 18.56 mol % Na_2O-SiO_2 glass prepared from batch Na_2CO_3 and quartz, annealed for 1 h at 500° C.

3. Results

3.1. Annealed glass

Figs. 1 and 2 are micrographs of the annealed glass prepared from batch and MOD materials, respectively. The grainy structure appearing in these figures, which is on a scale of roughly 75 to 100 Å, is an artifact of the platinum film shadowing technique employed. Similar topographical features have been observed in the micrographs of vitreous silica. Thus although these micrographs do not reveal any apparent signs of phase separation, a fine-grained phase separating on a scale of less than about 100 Å would not be visible in these figures. Thus, while the REM seem to preclude the possibility of large scale particle formation during the preparation of the glass, the formation of a secondary phase on a very fine scale may not be excluded solely on the basis of these REM.

Fig. 3 shows the experimental SAXS intensities, in counts per minute (after correction for background and parasitic scattering), from the batch and MOD glasses plotted as a function of the scattering angle. Several features concerning these traces should be noted. First of all, the scattering intensities are extremely low for the annealed glasses. For example, in a previous study [10] it was found that a 13.2 mol Na_2O-SiO_2 glass which was air quenched and not annealed showed 5–10 times the scattering intensities of those exhibited in Fig. 3 at all angles. Also, one observes that the scattering intensity of the annealed MOD glass is distinctly larger than that of the batch glass, notably at larger angles. Such scattering from the MOD glass sample could be indicative of a small degree of formation of a fine scale secondary phase. In order to further elucidate the nature of the larger angle scattering from the MOD glass, Guinier plots were constructed (see Fig. 4). If one assumes that the scattering intensity of larger angles reflects the formation of roughly spherical particles, then the average particle diameter may be obtained from the linear portion of the Guinier curve. Using the line shown in Fig. 4 for the annealed MOD glass, we calculate an average particle diameter of 106 Å. The existence of particles of this size in the annealed MOD glass is

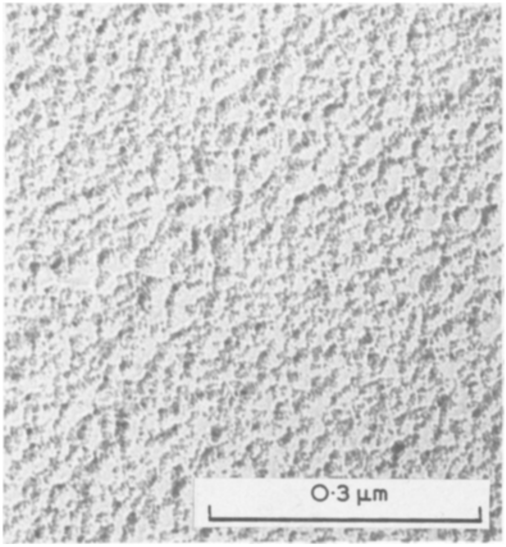


Figure 2 Electron micrograph of 18.56 mol % Na_2O-SiO_2 glass prepared from MOD precursor, annealed for 1 h at 500° C.

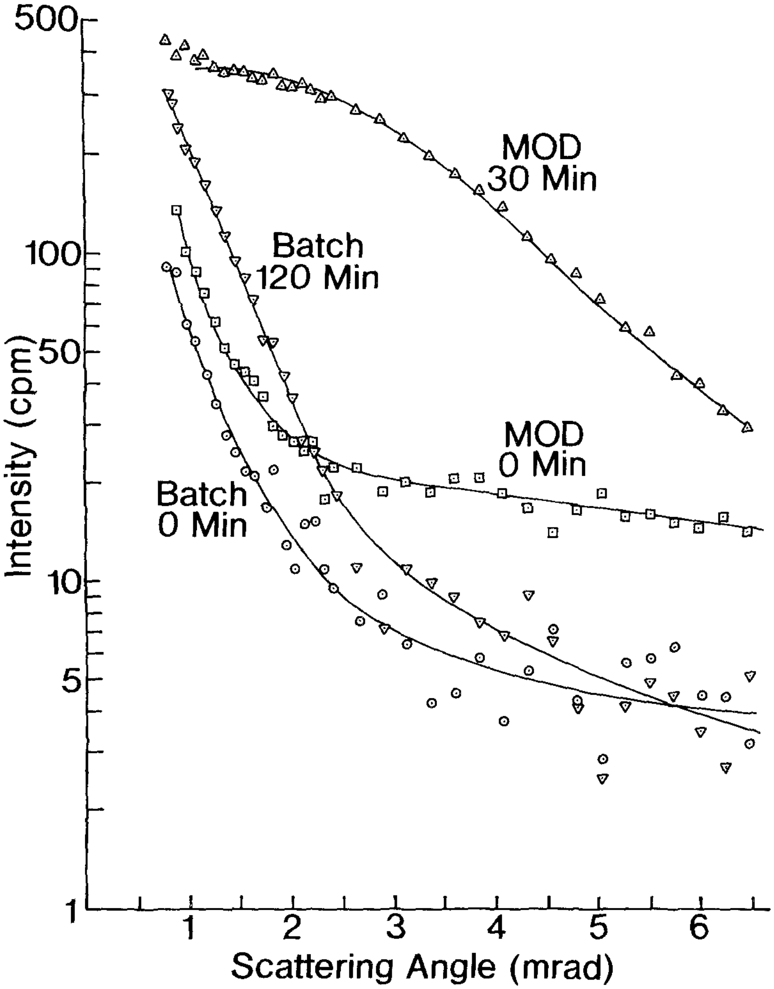


Figure 3 Experimental SAXS curves of the annealed batch and MOD Na_2O-SiO_2 glasses shown in Figs. 1 and 2, as well as the SAXS curves for these glasses after an additional heat treatment of 630° C for the times indicated.

not inconsistent with the findings of our micrographic studies. The larger angle scattering could also be due to the formation of a fine-grained, interspersed secondary phase. In this case the Guinier analysis presented above would be inapplicable.

The batch glass exhibits significantly lower scattering intensity at large scattering angles, both before and after heat treatment, than do the MOD glasses. In Fig. 4 the line drawn for the batch glass, as well as those batch samples heat least-squares fit to the intensity data in the angular range from 3.1 to 8.4 mrad. This level of scattered intensity is also typical for the annealed and other heat treated batch glasses in this angular range, and it is regarded as the essentially constant background scattering. However, even the annealed batch glass, as well as those batch samples heat treated for short times at 630° C, exhibit weak, though experimentally significant, scattering in the angular range below 3 mrad, as seen in Figs. 3 and 4. Guinier anlysis of these low angle SAXS data indicates a particle size of about 1100 Å diameter, assuming the scattering centres to be spherical in shape. Particles in this size range do not appear to be present in the unheated batch glass (see Fig. 1). Thus, the small angle scattering in both batch and MOD glasses may be attributed to some large scale fluctuations (perhaps frozen in density fluctuations) present in these glasses.

3.2. Heat treated glasses at 630° C

Samples of the annealed batch glass were heated at 630° C for periods of 30, 60, and 120 min, and MOD glass samples for periods of 30 and 120 min at the same temperature. SAXS data and micrographs were obtained of all heat treated samples. (However, SAXS data was not obtained from the MOD sample which was heated for 120 min).

Figs. 5 and 6 are the micrographs of the batch

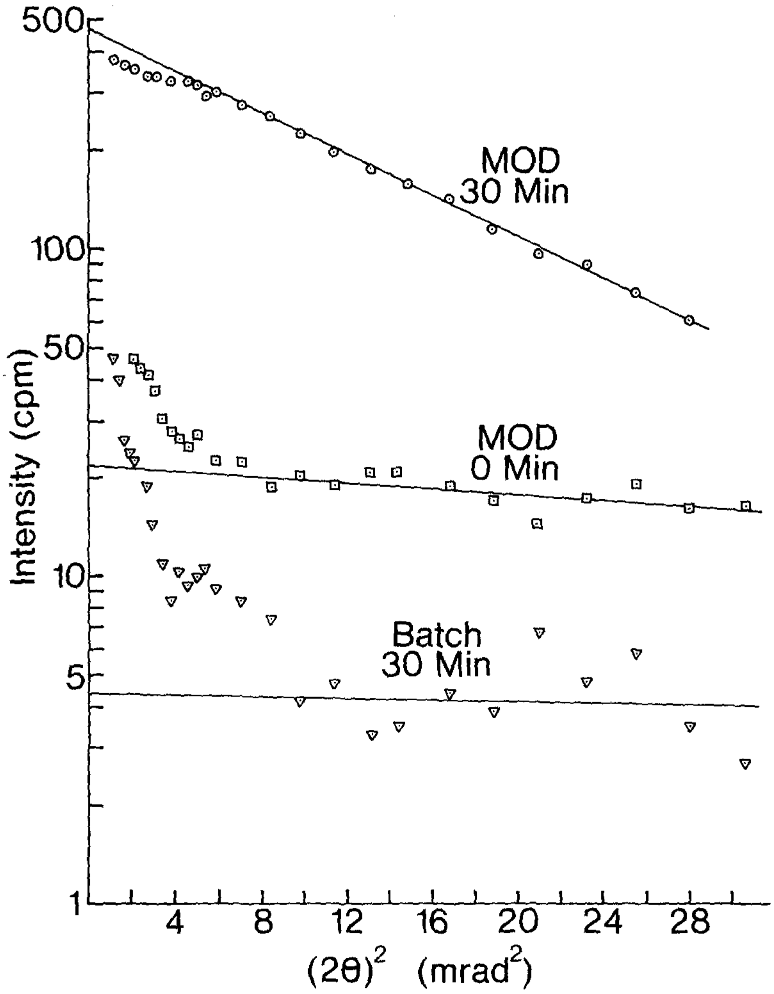
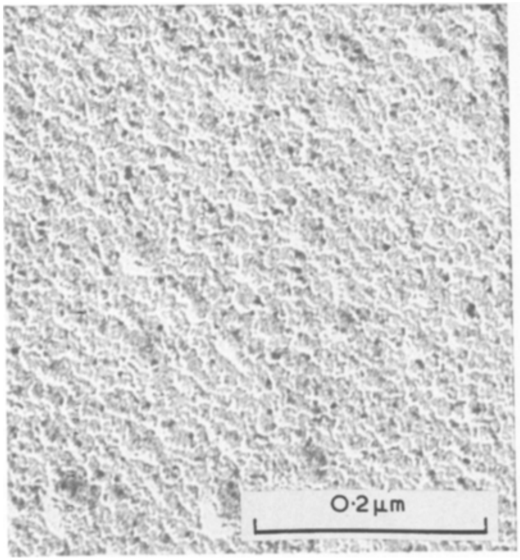


Figure 4 High angle Guinier plots of the SAXS data of the annealed MOD glass, and of the MOD and batch glasses after heat treatment at 630° C for 30 min.



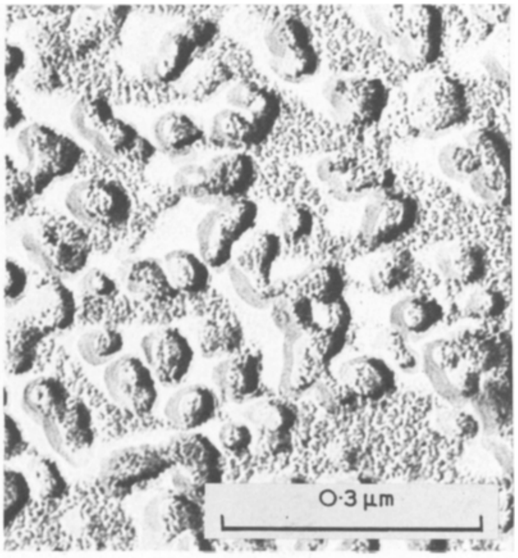


Figure 5 Electron micrograph of batch Na_2O-SiO_2 glass after heat treatment at 630° C for 30 min.

Figure 6 Electron micrograph of MOD Na_2O-SiO_2 glass after heat treatment at 630° C for 30 min.

and MOD glasses, respectively, which were heat treated at 630° C for 30 min. The contrast between these REM is striking. The batch glass appears to have undergone a small degree of phase separation with the formation of particles with an average diameter of 400 Å. On the other hand, the MOD glass exhibits a large scale phase separation. Furthermore, the MOD glass yields a micrograph which appears characteristic of phase separation via a spinodal or non-classical mechanism. Figs. 3 and 4 show the large increase in SAXS intensity in the MOD glass observed after heat treatment at 630° C for 30 min. The deviation from linearity of the SAXS intensity at small angles in the Guinier plot of Fig. 4, and the extended range of linearity exhibited in this figure at intermediate and large angles, is indicative of diffuse boundaries between phases and is characteristic of phase separation via a non-classical mechanism [11]. The SAXS data obtained from the batch glass sample heat treated for 30 min shows no apparent signs of particles of the sizes observed in Fig. 5. However, making use of the size and number density of particles which are shown in Fig. 5, we have computed that the scattering from such a small particle density would be undetectable and certainly obscured by the low angle fluctuation scattering. From the scattering data shown in Fig. 4, and assuming a spinodal mechanism of phase separation, one can estimate Λ, the interparticle spacing (periodicity) [10]; we find $\Lambda \approx 800$ Å, which is in very good agreement with the average spacing exhibited in Fig. 6.

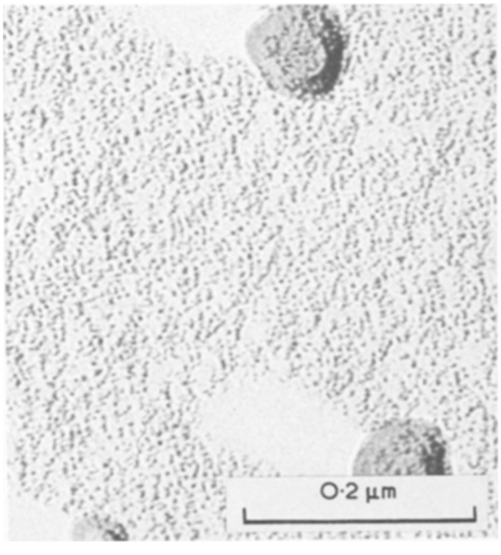


Figure 7 Electron micrograph of batch $Na_2O–SiO_2$ glass after heat treatment at 630° C for 120 min.

Micrographs of both the MOD and batch glasses heat treated at 630° C for times longer than 30 min show characteristics of a coarsening behaviour. Figs. 7 and 8 are the micrographs of the batch and MOD glasses, respectively, which were heat treated for 120 min at 630° C. In Fig. 9 are shown Guiner plots of batch glass samples which were heat treated for 60 and 120 min at this temperature. The progressive particles size increase is evident, and the spherical diameters of 840 and 905 Å determined for the 60 and 120 min samples, respectively, by Guinier analysis are in excellent agreement with the mean particle diameters observed in the corresponding micrographs.

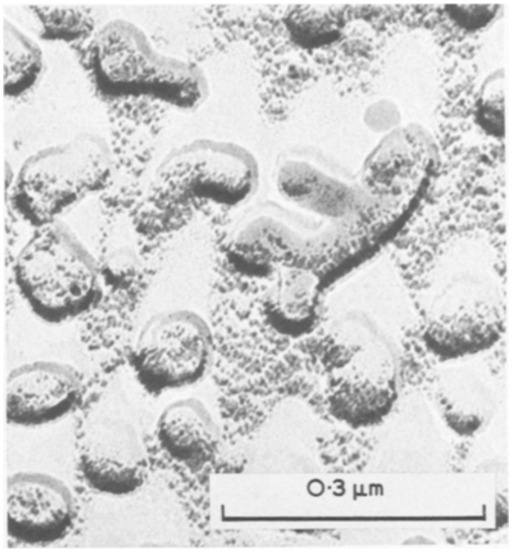


Figure 8 Electron micrograph of MOD $Na_2O–SiO_2$ glass after heat treatment at 630° C for 120 min.

3.3. Miscibility temperature

Experimental measurements indicate that the miscibility temperature at 18.56 mol % soda should be between 630 and 655° C [6, 12]. Haller *et al.* predict a coexistence temperature of 643° C at this temperature.

Fig. 10 is an REM taken from a sample prepared from batch materials and heat treated for 4 h at 640° C. Clearly there is no sign of phase separation in this glass, and thus we observe that the coexistence temperature will fall somewhere between 630 and 640° C.

On the other hand, at this composition, the binodal is raised significantly for the MOD prepared glasses. Figs. 11 to 14 show REM prepared from MOD glass samples heat treated at 690° C for 1 h, 710° C for 1 h, 755° C for 10 min, and 755° C for 20 min, respectively. Evidence of phase separation is found at all these temperatures indicating that the miscibility temperature has been raised by at least 100° C with respect to the batch prepared glass. Furthermore, the micrographs shown in Figs. 11 to 14 suggest that a change in the mechanism of the phase separation process has taken place at elevated temperatures. In the immiscibility region near the binodal, phase separation should proceed by a classical nucleation mechanism, and REM will exhibit a well-defined nearly spherical droplet structure as observed in these latter figures. Near or below the spinodal, however, phase separation will advance via a non-classical path and the REM show a more "worm-like" interconnected morphology such as shown in Fig. 8. Finally, it is worthwhile noting that Figs. 13 and 14 indicate that growth or coarsening occurred during the ten minute heating interval between 10 and 20 min at 755° C. This observation indicates that we are truly observing phase separation occurring at this temperature, and are not merely observing any possible phase separation which may have taken place at a lower temperature.

3.4. Water analysis

I.r. spectroscopy is a standard technique employed to measure the water content of glasses. The precise location of the absorption peaks due to water in a glass is a function of both the glass composition and the "condition and location of the water." For example, Scholze [13] has discussed how the relative intensity of the two prominent water peaks in soda–silica glass shift as the soda content of the glass is increased. At very low soda content the absorption at 2.73 μm is quite large compared to the peak at 3.6 μm. However, at 15 mol % soda the 3.6 μm peak is far more pronounced that the 2.73 μm peak. Water

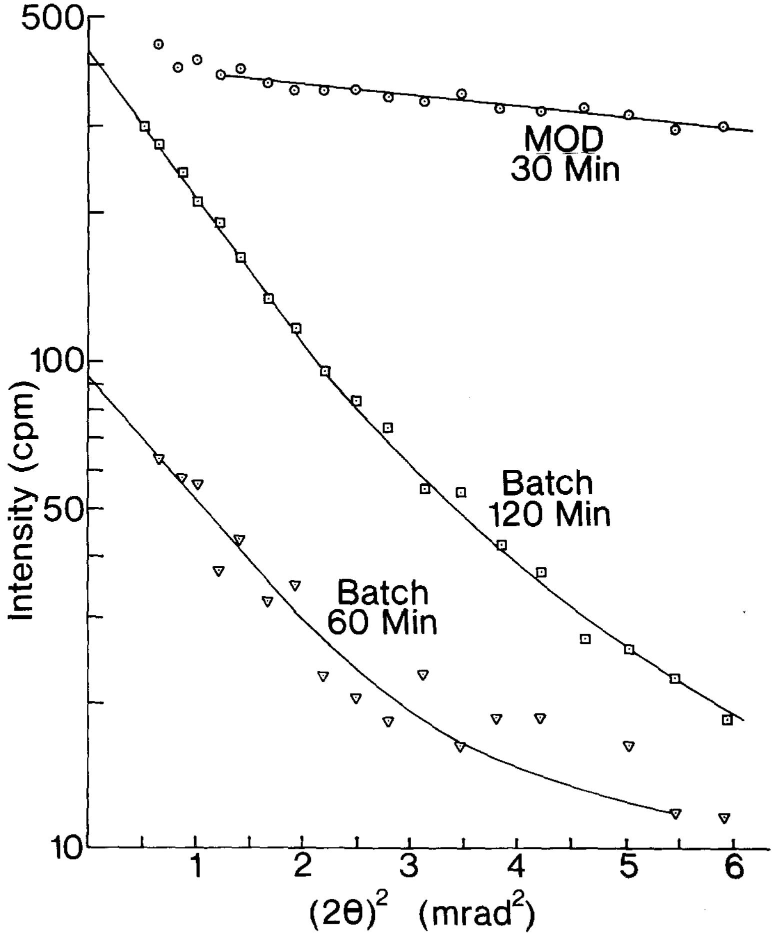


Figure 9 Low angle Guinier plots of the SAXS data of the batch glass after heat treatments at 630° C for 60 and 120 min.

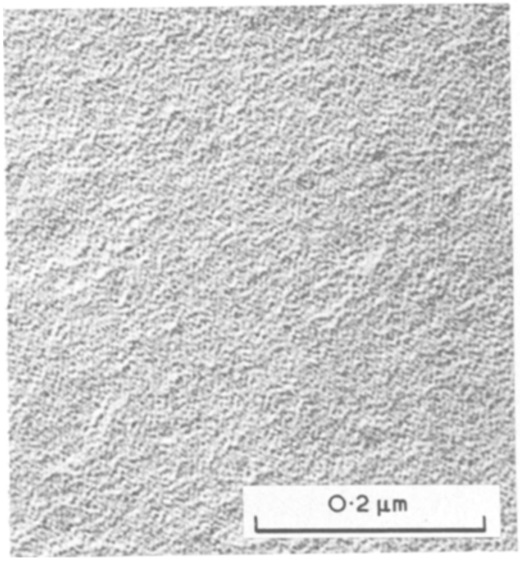


Figure 10 Electron micrograph of batch glass after heat treatment at 640° C for 4 h.

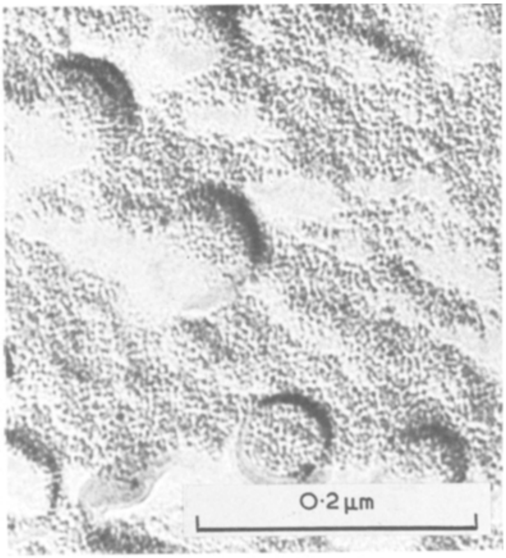


Figure 12 Electron micrograph of MOD glass after heat treatment at 710° C for 1 h.

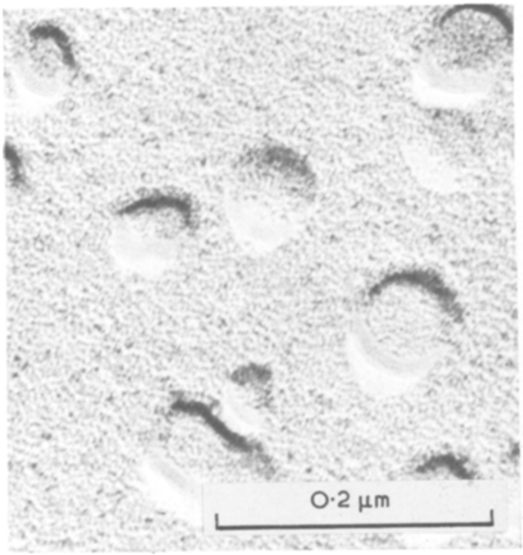


Figure 11 Electron micrograph of MOD glass after heat treatment at 690° C for 1 h.

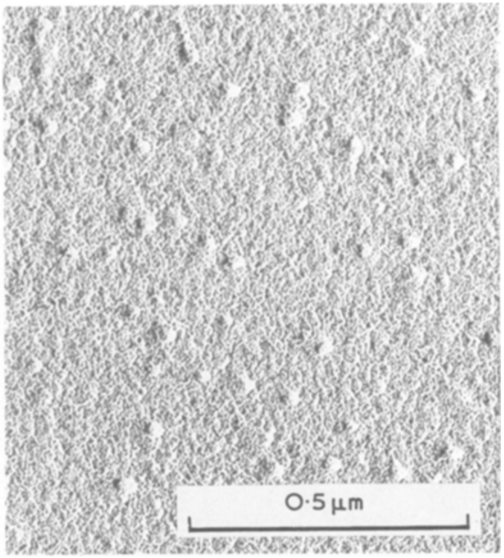


Figure 13 Electron micrograph of MOD glass after heat treatment at 755° C for 10 min.

may be present in the glass as free water molecules located in interstitial cavities or as OH groups bound to the lattice. Scholze has argued that both free water and bound water groups contribute to the absorption peaks in the $3\,\mu m$ region. Adams [14] has pointed out that the spectrum of pure silica only contains the $2.73\,\mu m$ peak while soda–silica glass may contain peaks at $2.73\,\mu m$ and $3.6\,\mu m$. He attributes the latter peak to OH groups hydrogen bonded to non-bridging O^- ions in the network structure. Such non-bridging sites are absent in SiO_2 (and B_2O_3) resulting in the absence of the $3.6\,\mu m$ absorption.

Scholze [15] has illustrated that in most instances it is extremely difficult to obtain precise values for the total water content of a given glass. For example, one would have to know the molar absorptivities for each band (quantities which vary as a function of the glass composition), and one would have to deconvolute the absorption bands since in general they overlap. Hence, Scholze has suggested an approximate method for the investigation of the H_2O content in a series of glasses of similar composition. Since for glasses of nearly indentical composition, the ratios of the intensities of the various absorption peaks will be nearly constant (since these ratios are independent of the total water content of the glass), one may obtain a good estimate of the water concentration in the glass from one characteristic water band. Scholze has defined an effective extinction coefficient which can be used for this purpose. In addition, he has tabulated a number of these coefficients for several simple silicate glasses.

Fig. 15 shows the i.r. spectra of samples of 18.56% sodium silicate glasses, of approximately 2 mm thickness, prepared from batch and MOD precursor material, respectively. Employing a value of 68 for the effective extinction coefficient of the 2.73 μm band, we find the wt% of H_2O in the MOD glass to be 0.0048, while the batch glass contains 0.0014 wt % water. Although the total water content quoted above is quite approximate, the ratio of the water content in these two glasses, which is 3.4:1, can be estimated with much greater confidence.

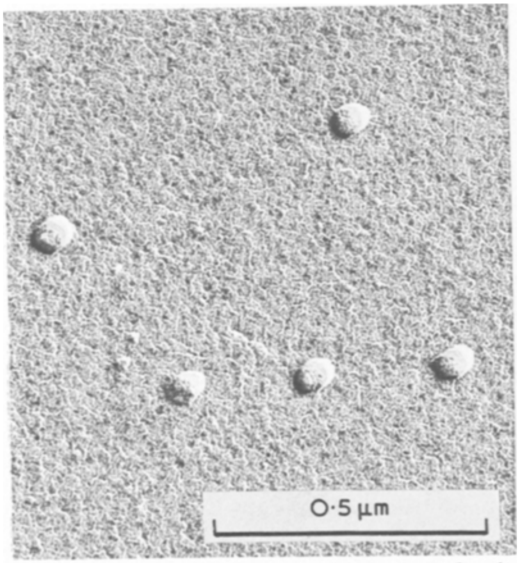


Figure 14 Electron micrograph of MOD glass after heat treatment at 755° C for 20 min.

Finally, it should be noted that the lengthy heating time used for the preparation of the batch glass has no bearing upon the above results. Batch glass which was made using a 3 h heating period also exhibited roughly the same relatively low water content.

4. Discussion

4.1. Thermodynamic considerations of immiscibility in silicate glasses

The binodal (two phase boundary) curve may be calculated if one is able to compute the enthalpy and entropy of mixing of the glass components as a function of concentration. Since the entropy of mixing makes an exothermic contribution to the free energy of mixing, the enthalpy of mixing must be endothermic, and of greater absolute value, for phase separation to occur. For mixtures of simple liquids one may rely upon the use of an uncomplicated model such as the regular solution model [16] to compute these quantities. For a two component system the latter model predicts a symmetric binodal curve about the one-to-one mixture of components. However, in a number of glassy systems (including the Na_2O-SiO_2 system) it is experimentally observed that the binodal is asymmetric. Furthermore, since the common inorganic oxide glasses and glass melts usually consist of complex network (or partial network) type structures, it would be surprising if the regular solution model would be applicable to such systems in an unmodified form.

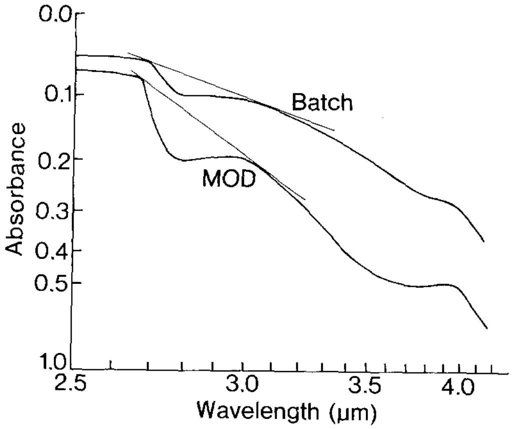


Figure 15 Infra-red spectra in the water band region of 2 mm slices of batch and MOD Na_2O-SiO_2 glasses.

Thus, a number of authors [17–20] have attempted to explain the origins of immiscibility in a number of silicate systems. Charles [20] recapitulates the work of Ramberg [21] concerning enthalpy effects in crystalline silicates. Ramberg decomposes the heat of mixing of silica with a metal oxide into two terms. One term involves the heat associated with conversion of a bridging oxygen in the network structure to a non-bridging oxygen. This term is always exothermic. The second term is associated with the enthalpy difference between the metal–network oxygen bond and the metal–oxygen bond in the pure solid metal. The latter term can be endothermic. However, Charles has demonstrated that for alkali silicate systems this term is exothermic too, thus invalidating the above description as an explanation of the origin of immiscibility of alkali silicates.

Charles ascribed the endothermic contribution to the enthalpy as arising from the partial molar heat of solution of silica. Furthermore, he interpreted the origin of this heat on a structural basis as arising from strains induced in the Si–O network bond angle upon solution. Thus, the formation of a chain or polymer-like structure by SiO_2 in solution during phase separation is held responsible for the origin of the separation.

Haller *et al.* [6] have adopted a similar point of view. They found that by considering $[N(SiO_2)m]$ and $[N(R_2O \cdot nSiO_2)]$ as the components to be used in the regular mixing equations (where m, n and N are integers), they could quite accurately reproduce the experimental binodal curves for the $Li_2O–SiO_2$ and $Na_2O–SiO_2$ systems. The integer n was chosen from inspection of the experimental binodal and m was chosen in such a manner to produce a symmetric binodal. The index m explicitly accounts for the chain-like structure of silica in solution discussed by Charles. Haller *et al.* related the mole fractions of pure SiO_2 and R_2O, x and y, respectively, to the mole fractions of $(SiO_2)m$ and $R_2O \cdot nSiO_2$, denoted by $\bar{x}$ and $\bar{y}$ via

$$\bar{y} = y\{y + [1-(n+1)y]m^{-1}\}^{-1} \qquad (1)$$

$$\bar{x} = 1 - \bar{y} \qquad (2)$$

Using the regular mixing equations in conjunction with the variables $\bar{x}$ and $\bar{y}$, they obtained the following expression for the reduced coexistence temperature

$$T_{\text{coex}}/T_c = (2 + \Delta S/R) \times \left\{\frac{(1-2\bar{y})}{\ln[(1-\bar{y})/\bar{y}] + (1-2\bar{y})\Delta S/R}\right\} \qquad (3)$$

In Equation 3 T_c is the critical temperature and ΔS is an entropy term related to the change in internal degrees of freedom upon mixing. ΔS was chosen to fit the experimental data. However, as one may see from an inspection of Equation 3, and as was pointed out by Haller and co-workers, the value of ΔS does not affect the symmetry of the binodal curve, but solely its shape.

4.2. Interpretation of experimental results

The contrast between the phase separation behaviour of the MOD and batch soda–silica glasses will now be discussed within the framework of the descriptions given by Charles and Haller *et al.* described above. A cautionary remark, however, is appropriate at the outset. Here, we merely suggest that an interpretation of our results consistent with the ideas expressed above is possible. A complete verification of the hypotheses which we suggest would detail a broader experimental programme, which we outline at the end of this section.

A sketch of the arguments which we present to explain the higher binodal temperature and non-classical phase separation behaviour of the MOD glass at the particular sodium silicate composition studied are as follows. The MOD material contains additional water in the form OH^- which are incoporated into the glass structure. This residual water tends to break up the network structure resulting in a lower degree of polymerization of SiO_2 units. This has the same effect, at a given temperature, as shifting the composition in the direction of smaller $\bar{y}$. Since the composition under investigation is on the high soda side of the critical composition, this effective shift in composition could, in essence, translate the MOD material into the spinodal region. Below we present a more detailed exposition of these postulates.

The i.r. spectra shown in Section 3.4 clearly illustrate the enhanced water content of the MOD glass. A number of authors [13, 14] have indicated that the overall mechanism describing the solubility of water in a typical silicate glass is given by $\equiv Si–O–Si \equiv H_2O \rightarrow 2 \equiv Si – OH$. In addition, Mukherjee *et al.* [8] have discussed the network breaking effects of OH^-. Referencing Buerger [22], they allude to the effectiveness of OH^- and F^- in the conversion of bridging to non-bridging oxygens and the resultant alteration of the network silicate structure into small silicate islands. Thus, we would anticipate that the structural coherency of the MOD melt would be smaller than that of the batch melt.

Thus, in terms of the Haller desciption we would expect the structural units of the silica complex to be somewhat smaller in the MOD melt. Although Haller and co-workers indicate that the $[SiO_2]_m$ complex does not necessarily represent an observable structural unit, since the quantities $[N(SiO_2)_m]$ and $[N(R_2O \cdot nSiO_2)]$ are given as possible structural units, it is very plausible to postulate that the m value for MOD melt is somewhat smaller than the value of $m = 8$ used by Haller. We will discuss this assumption further subsequently. Following the consequences of this assumption, we see from Equation 1 that for a given composition y, a reduction in the value of m will produce a reduction in the value of $\bar{y}$. Thus, we anticipate that the MOD melt of identical compostion, y, to the batch melt would have an effectively lower $\bar{y}$ value. On the high silica side ($\bar{y} > 0.5$) of the critical composition we see that this shift would effectively raise the coexistence temperature for this composition. If the effective shift is large enough, then the effective $\bar{y}$ may be located in or near the spinodal region. Thus, we have varied the value of m, at $y = 0.1856$ and calculated effective values of $\bar{y}$, T_{coex} and T_{sp}. If $m = 4$, we find that $T_{\text{coex}} = 755°$ C and $T_{\text{sp}} = 603°$ C. We recall that we observed that for MOD glass $T_{\text{coex}} > 755°$ C. Thus, by choosing m so that the binodal data is approximately fitted, we predict a $T_{\text{sp}} > 603°$ C. This is qualitiatively in agreement with our observation of a non-classical phase separation mechanism occurring at 630° C. It is of interest to note that a reduction in m for a composition on the high silica side of the critical temperature would imply an effective lowering of the coexistence temperature. This result does not appear to be inconsistent with the qualitative structural interpretation of phase separation in alkali silicate presented by Charles.

It is clear that more experimental data is required to see if the Haller scheme will be capable of quantitatively fitting the phase separation thermodynamics of the MOD $Na_2O–SiO_2$ system. Thus, a miscibility gap study for MOD $Na_2O–SiO_2$, similar to the one performed by Haller and co-workers, would be highly desirable. Such a study would not only provide a test of the validity of the hypothesis concerning phase separation in the MOD glass proposed in this paper, but would also be of importance in evaluating the ideas proposed by Charles and Haller and co-workers regarding phase separation in binary alkali silicate melts.

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