

## SAXS AND TEM STUDIES OF PHASE SEPARATION IN BaO-SiO<sub>2</sub> GLASSES

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**Résumé** - La séparation de phases amorphes des verres de BaO-SiO<sub>2</sub> a été étudiée par diffusion de rayons X aux petits angles et microscopie électronique de transmission, dans la région de germination et croissance de la lacune de miscibilité. Les diamètres des particules sphéroïdales précipitées, déterminés avec la loi de Guinier et par microscopie électronique, sont en accord. La cinétique de croissance des particules est bien décrite par la théorie classique de "coarsening". Les intégrales des courbes de diffusion de rayons X ont permis de déterminer la frontière de la lacune de miscibilité et le temps nécessaire pour que la matrice atteigne sa composition d'équilibre. La germination se produit pendant le refroidissement du liquide ou dans les tous premiers stades du traitement thermique. La processus de "coarsening" commence avant que la matrice atteigne la composition d'équilibre.

**Abstract** - Amorphous phase separation was studied in the nucleation and growth region of the BaO-SiO<sub>2</sub> miscibility gap. Nearly spherical droplets were precipitated, the diameters obtained from SAXS and TEM being in reasonable agreement. The growth kinetics of the droplets were well described by the classical theory of coarsening. From the integrated SAXS intensities the times to reach the equilibrium matrix compositions at 743 and 760°C were determined, and the binodal boundary located. Nucleation occurred during quenching from the melt or within a very short time of heat treatment. Coarsening began well before the attainment of the equilibrium matrix composition.

1. **Introduction.**- The kinetics of amorphous phase separation (APS) in glasses can be studied by small-angle X-ray scattering (SAXS) or by transmission electron microscopy (TEM). Apart from the intrinsic scientific interest, the determination of the APS kinetics in glasses which crystallize internally may lead to a better understanding of the influence of APS on the nucleation and growth of crystals in glass ceramics. We report here a study of the kinetics of APS in BaO-SiO<sub>2</sub> glasses with 27.0 and 28.3 mol% BaO (glasses '27.0' and '28.3B').

2. **Experimental.**- Well mixed batches of silquartz SiO<sub>2</sub> and Fisons BaCO<sub>3</sub> (AR grade) were sintered at 1300°C for 24 hours and melted in electric furnaces at 1550°C. The crushing/remelting technique was used for homogenization. The melts were pressed between two steel plates yielding clear glasses about 1 mm thick. Chemical analysis indicated 0.3 wt% SrO as the main impurity, and less than 0.1 wt% total of other impurities. Samples of about 20 x 6 x 1 mm were heated at 743°C or 760°C (T<sub>g</sub> ≈ 700°C) for various times, air quenched, annealed at 650°C (or below) and ground and polished to 0.03-0.05 mm for the SAXS experiments. Ion beam thinned foils and carbon replicas were studied in a Hitachi HU 11A electron microscope. For the SAXS a Rigaku small angle goniometer was used with slit collimation. A graphite monochromator in the scattered beam isolated the CuK radiation. A scintillation detector and a step scanning device were used to determine the intensities. The cross-section of the beam had negligible width and was taken as 'infinitely high' [1]. This condition was satisfied for most specimens. The experimental SAXS curves were corrected for parasitic scattering and normalized to a constant sample thickness and to a constant beam intensity.

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3. Results.— Part of the BaO-SiO<sub>2</sub> phase diagram including the miscibility gap is shown in Fig.1. For the temperatures used (743,760°C) the two glasses studied here were situated in the 'nucleation and growth' region of the gap.

No phase separation was detected by TEM in the as-prepared glass 28.3B but after heat treatment at 760°C for 8.25h nearly spherical droplets were clearly observed (Fig.2). Glasses 27.0 and 28.3B, heat treated at 743°C for times up to 17h, gave similar micrographs, only the number and size of droplets varying. Crystallization of the matrix phase was observed for samples heated for longer times, the amorphous particles remaining undisturbed.

A mean diameter  $D$  of the droplets was determined using the Guinier equation [2]

$$J(q) = J(0)\exp(-D^2q^2/20)$$

where  $J(q)$  is the SAXS intensity for a 'dilute' system of spherical particles of constant electronic density in an homogeneous matrix,  $q$  is the modulus of the scattering vector and  $J(0)$  is the SAXS intensity for  $q = 0$ . At small angles  $q \approx 2\pi/\lambda$  where  $\epsilon$  is the scattering angle and  $\lambda$  the X-ray wavelength (0.154 nm). Typical Guinier plots ( $\log J$  vs  $\epsilon^2$ , Fig.3) were linear over a wide range, indicating narrow size distributions. The mean diameters obtained from the slopes of these plots are shown in Fig.4 for glass 27.0 heated at 743°C and glass 28.3B at 743 and 760°C. The mean diameters from thin foil TEM are also shown for glass 28.3B at 760°C. The diameters from SAXS and TEM are in reasonable agreement. The small discrepancy in values from SAXS and TEM at early times of phase separation may be explained by (a) errors in the measurement of small droplets using TEM and/or (b) errors in the values from the Guinier plots due, for example, to the high particle concentration [2]. The good agreement at longer times suggests that the assumptions of Guinier's law are better satisfied in the later stages of separation.

The diameters measured in replica micrographs were about 2.5 times larger than those obtained from SAXS or thin foil micrographs, indicating that the replica values were subject to large errors. This point is fully discussed elsewhere [3].

For glass 28.3B heated at 760°C the slope of the straight line plot of  $\log D$  vs.  $\log(\text{time})$  in Fig.4 is  $0.32 \pm 0.02$ . At 743°C, the slope is  $0.34 \pm 0.03$  whereas for short periods of heat treatment the slope is about 0.5. For diffusion controlled growth, the slope should be 0.50 in the initial stage of APS [4] and 0.33 in the final stage [5] (when the equilibrium composition of the matrix is reached). Therefore, the results for glass 28.3B agree well with the theories [4,5]. For glass 27.0 at 743°C the slope is  $0.43 \pm 0.03$ . In this case the agreement with the theories is not as good. It should be stressed, however, that these theories were derived for a small volume fraction of the second phase, and this condition is more closely obeyed in glass 28.3B.

For 'infinitely' high beam cross-section the integrated SAXS intensity in reciprocal space is given by

$$Q = \text{const.} \int J(q)q \, dq$$

For a 'two electronic densities' system

$$Q \propto \phi_1(1 - \phi_1)(\Delta\rho)^2$$

where  $\phi_1$  is the volume fraction of scattering particles and  $\Delta\rho$  the electron density difference between particles and matrix [2]. Thus when the matrix reaches its equilibrium composition in the final stage of phase separation  $Q$  is constant. Here  $Q$  was determined by a method described in [6]. For glass 28.3B a constant value of  $Q$  is approached (Fig.5) after 3-4h at 760°C and after 7h at 743°C. For glass 27.0 at 743°C,  $Q$  is constant from  $t < 2.5$ h of heat treatment. The increase in  $Q$  for glass 28.3B, after 30.2h at 743°C, is probably associated with the onset of crystallization in this specimen. A similar effect was observed in Li<sub>2</sub>O-SiO<sub>2</sub> glasses [7].

From the SAXS curves, (even when in relative units) it is possible to obtain the relative number of particles per unit volume of glass,  $N$ , the interfacial area per unit volume  $S_v$ , and the position of the binodal boundary. For a beam of linear and 'infinite' cross-section the SAXS intensity extrapolated to  $q = 0$  in the Guinier plot,  $J(0)$ , is given approximately by [8,9]



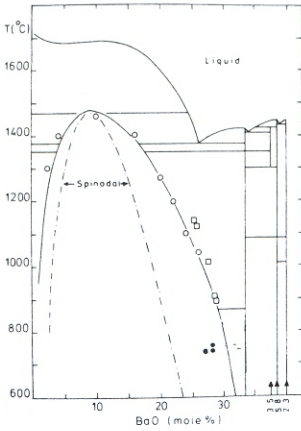


Fig.1. BaO-SiO<sub>2</sub> system. Calculated binodal (solid curve) and spinodal (dashed curve) are shown [13]. Experimental points O [14], □ [15], - (this work). Heat treatments used here (●).

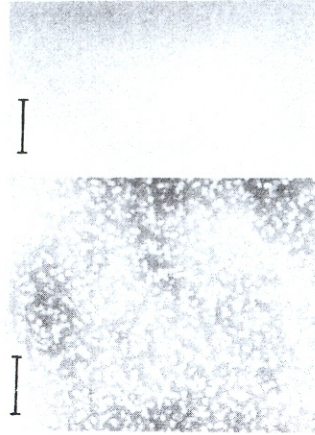


Fig.2. TEM micrographs of glass 28.3B; as prepared (top), and heated 8.25h at 760°C (bottom). The bars denote 0.2μm.

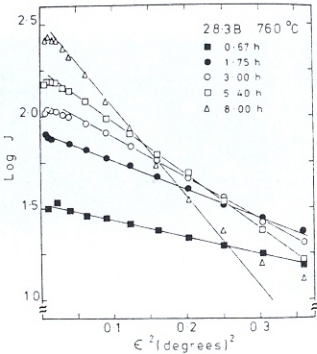


Fig.3. Guinier plots for glass 28.3B heat treated at 760°C. J in arbitrary units (a.u.).

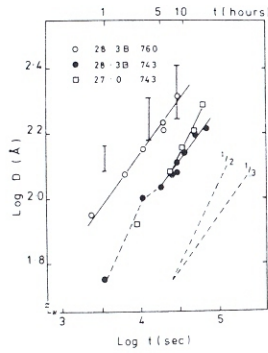


Fig.4. Log<sub>10</sub>D vs. Log<sub>10</sub>(time) plots for glass 27.0 at 743°C and glass 28.3B at 743°C and 760°C. Vertical bars indicate values from TEM for glass 28.3 at 760°C.

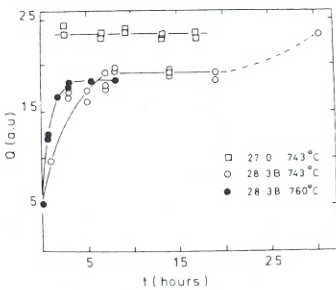


Fig.5. Integrated SAXS intensity for glasses heat treated at 743°C and 760°C. Q in arbitrary units (a.u.).

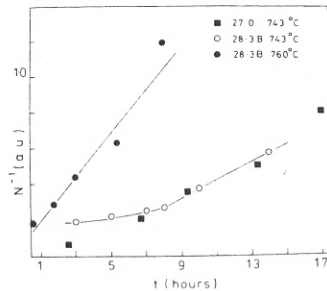


Fig.6. Inverse of the number of amorphous droplets versus time of heat treatment in BaO-SiO<sub>2</sub> glasses.

$$J(0) = \text{const.} (\Delta\rho)^2 N D^5.$$

Therefore, if  $\Delta\rho$  is assumed constant the variation of  $N$  with time of isothermal treatment may be followed. Fig.6 shows the inverse of the relative number of droplets (from SAXS) versus time of heat treatment. Straight lines fit the experimental data reasonably well for glass 27.0 heated at 743°C and glass 28.3B at 760°C. For glass 28.3B at 743°C, there is a change in the slope after 8h when  $N$  begins to decrease more rapidly. Of particular interest is the observation that the number of droplets decreases from the first heat treatment time given, suggesting that most of the nucleation of amorphous particles occurs either during cooling from the melt or within a very short time of heat treatment. The highest rate of dissolution of particles, however, occurs when the matrix composition reaches equilibrium. This is clear from Figs.5 and 6 for glass 28.3B heated at 743°C. Also it should be noted that the early period of slower decrease in  $N$  for this glass at 743°C coincides with the  $t^{\frac{1}{2}}$  variation of droplet diameter (Fig.4). It should be stressed that the  $N^{-1}$  values for different glasses, or the same glass heated at different temperatures, are not directly comparable because  $(\Delta\rho)^2$  is not the same in each case. Also, the  $N^{-1}$  values would be smaller for glasses in which the phase separation was in the early stages, as in this case  $(\Delta\rho)^2$  would be smaller. This reinforces the conclusion that  $N$  begins to decrease well before the attainment of the equilibrium matrix composition. These results contradict a classical study [3] which showed that coarsening started when the matrix phase reached equilibrium. However, in agreement with the present results, Kirkwood [10] found that coarsening of precipitates in metallic alloys began well before the attainment of the equilibrium matrix composition.

According to Porod's law [11], the asymptotic value of  $J(q)q^3$  at large angles ( $q \rightarrow \infty$ ) for a 'two electronic densities' system and a linear and 'infinite' X-ray beam cross-section, is proportional to the surface area of the interface between the particles and the matrix. The absolute values of the surface area per unit volume,  $S_v$ , determined from

$$\{J(q)q^3\}_{q \rightarrow \infty} / Q = S_v / 8\pi\phi_1(1-\phi_1)$$

were 1.2 to 2.0 times smaller than those obtained by the method of Debye et al [12]. However, the values from both methods decreased with time of heat treatment for both glasses, as expected for the coarsening stage.

From the ratio of the constant values of  $Q$  for the two glasses the equilibrium composition of the matrix phase was determined at 743°C as described in [7,9]. Similarly, by comparing the values of  $Q$  at 743°C and 760°C for glass 28.3B, the matrix composition was determined at 760°C. The compositions (in mole% BaO) were 32.0-33.0 at 743°C and 31.5-32.0 at 760°C (Fig.1). These values are 1-2 mole% BaO outside the binodal calculated by Haller et al. [13] which was based on data [14] accurate to within  $\pm 1$  mole% BaO and  $\pm 50$ -100°C. Differences in the levels of SrO, the main impurity, could also explain the discrepancy.

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