

Influence of Amorphous Phase Separation on Crystal Nucleation and Growth in Baria Silica Glasses

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INTRODUCTION

It is well-known that metastable amorphous phase separation is often a precursor to crystal nucleation and growth in the formation of glass ceramics. Amorphous phase separation is thought to have an important role in promoting fine grained crystallization although the precise nature of this role is by no means clear. The picture is further complicated by the effects of certain nucleating agents which promote both phase separation and higher crystal nucleation rates in the same system.

This paper summarizes two independent studies of this problem using the baria-silica system, a 'simple' system which exhibits appreciable volume nucleation without deliberate additions of nucleating agents. In this system (Fig. 1) metastable sub-liquidus immiscibility extends from approximately 100% SiO₂ to the barium disilicate composition at lower temperatures (the boundary is at approximately 31.5 mol% BaO at 700°C. The results show conclusively that phase separation can exert a pronounced influence on crystal nucleation kinetics in this system. The predominant role of phase separation is to produce a progressive shift in the composition of the baria-rich matrix phase with time which in turn causes a marked increase in crystal nucleation rates of barium disilicate.

RESULTS OF FIRST INVESTIGATION

In the first study (1) the nucleation kinetics of the barium disilicate crystal phase ('BS₂') were determined for glass compositions in the range 25 to 34 mol% baria, melted in a gas fired furnace. Let us here briefly consider typical results obtained for one composition containing nominally 26 mol% BaO (chemical analysis gave 25.3 mol%) which will be referred to as Glass 26. This glass had a measured miscibility temperature of 1140°C, i.e. it phase separated at lower temperatures. Three sets of glass specimens were prepared from Glass 26 as follows. Glass 26A was Glass 26 rapidly cooled in air (no additional heat treatment). Glass 26B was Glass 26 heated at 800°C for 1 hour. Glass 26C was Glass 26 heated at 900°C for 10 min. Both 26B and 26C were appreciably phase separated and 26A exhibited the early stages of phase separation on an extremely fine scale. Samples of 26A, 26B and 26C were heated at 700°C (where the maximum in crystal nucleation rate is observed for the stoichiometric barium disilicate glass (2)) for various times and grown at 840°C so that the number density N_v of crystals could be determined by optical microscopy. Some of the results at shorter times are shown in Fig. 2. The effects of the different heat treatments prior to the crystal nucleation treatments at 700°C are particularly striking (any crystal nucleation produced in the prior treatments was negligible in comparison to crystal nucleation at 700°C). The initial strong curvature in the N_v versus time plot for 26A may be attributed to liquid phase separation occurring in the glass at the same time as the crystal nucleation at 700°C. At 700°C phase separation occurred over an extended period during which a silica-rich (droplet) phase was precipitated and the average composition of the baria-rich matrix phase changed gradually, approaching the equilibrium value given by the immiscibility curve. As the composition of the matrix changed and became closer to barium disilicate the crystal nucleation rate increased. However, the nucleation rates were

always significantly less than in the stoichiometric barium disilicate composition. The observed higher crystal nucleation in 26B when compared with 26C (and 26A) was attributed to the much greater degree of phase separation initially present in 26B, and hence to the significant shift in matrix composition that had already occurred in this glass.

The possibility of heterogeneous crystal nucleation at the liquid-liquid interfaces was also considered. Estimations of the interfacial area per unit volume of the phase separated glass using replica electron microscopy showed that this quantity changed only very slowly at 700°C for 26A, 26B and 26C. However, the crystal nucleation rates changed considerably with time at 700°C indicating that the interfacial area was *not* affecting crystal nucleation directly. Also the number of droplets per unit volume in glass 26A was about ten times greater than in glass 26C but initially 26A had a crystal nucleation rate less than (but similar to) 26C. It was concluded that the morphology of the phase separation had little or no influence on crystal nucleation and that the effects observed were due predominantly to the progressive shift in composition of the matrix (barium-rich) phase with time as a result of phase separation. This shift in composition probably caused changes in both the thermodynamic driving force and in atomic mobility which in turn were responsible for the observed marked increase in nucleation rate with time.

RESULTS OF SECOND INVESTIGATION

In the second investigation the work was extended to higher nucleation temperatures than 700°C, and small angle X-ray scattering (SAXS) was used to determine the kinetics of amorphous phase separation.

BaO-SiO₂ glasses with compositions ranging from 27.0 to 33.3 mol% BaO were melted at 1550°C in electric furnaces and quenched by pressing them between two steel plates. Chemical analysis revealed that SrO was the main impurity in the glasses, varying from 0.004 to 0.540 wt%, depending on the type of BaCO₃ used. The total level of other impurities was less than 0.1 wt%. The H₂O content, determined semi-quantitatively by I.R. spectroscopy, was low and, more important, was very similar in all the glasses. SAXS was employed to accurately monitor the development of the amorphous phase separation, which occurred simultaneously with the nucleation of the crystalline phase BaO.2SiO₂ (BS₂), during heat treatment of glasses with less than 28.5 mol% BaO. The integrated SAXS intensity, Q , became constant after approximately 3 h at 760°C and 7 h at 743°C for a glass with 28.2 mol% BaO. For a glass with 27.0 mol% BaO heated at 743°C, Q was constant from $t \leq 2.5$ h. This behaviour implied that the coarsening stage of phase separation was reached after the described periods of heat treatment. The binodal boundary determined by SAXS at 743 and 760°C was 32.0-33.0 mol% BaO and 31.5-32.0 mol% BaO respectively, values which are approximately 1 mol% BaO higher than reported elsewhere (3). Thin foil transmission electron micrographs showed that the development of the amorphous droplets was not affected by the growth of crystalline BS₂ spikes. The diameters of the droplets determined from the micrographs were in reasonable agreement with the diameters obtained from SAXS reinforcing the accuracy of the SAXS technique.

The crystal nucleation density, N_v , versus time curves for glasses heat treated at 718, 743, 745 and 760°C were determined by measuring the size distributions, counting the number of crystals in optical micrographs and applying stereological analysis. Such curves showed that for the quenched glass compositions, in which the amorphous phase separation developed simultaneously

with the nucleation of crystals, the crystal nucleation rate, dN_V/dt , at any given temperature, *increased* with time becoming constant after a time which corresponded to the achievement of the equilibrium composition of the amorphous matrix (shown by a constant value of Q). The crystal nucleation rate of a fully phase separated glass (first heated at a higher temperature) was *constant*, being initially higher than dN_V/dt for a quenched glass of the same chemical composition. The crystal nucleation rates for two glasses that did *not* show amorphous phase separation, having 29.6 and 33.3 mol% BaO, were *constant*. In all cases, dN_V/dt increased with the percentage of BaO (in the matrix for phase separated glasses) and the highest dN_V/dt was observed for the stoichiometric (33.3 mol% BaO) glass. Typical results are shown in Fig. 3 for a glass exhibiting phase separation (containing 28.2 mol% BaO) and for a glass *not* exhibiting phase separation (containing 29.6 mol% BaO). These observations suggest that liquid-liquid immiscibility *increases* the nucleation rate of crystals due to the shift in composition of the BaO-rich matrix with heat treatment, in agreement with the results of the first investigation.

On the other hand, a maximum in dN_V/dt has been observed, and confirmed by duplicate experiments, for a glass with 28.2 mol% BaO heated at 760°C. The maximum coincides with the *beginning* of the coarsening stage of the amorphous phase separation (as revealed by SAXS). The origin of this effect may be some additional preferential nucleation in the diffusion zones around the liquid phase droplets, as suggested for the lithia-silica system (4,5). However, the predominant effect on crystal nucleation arises from the compositional changes brought about by phase separation.

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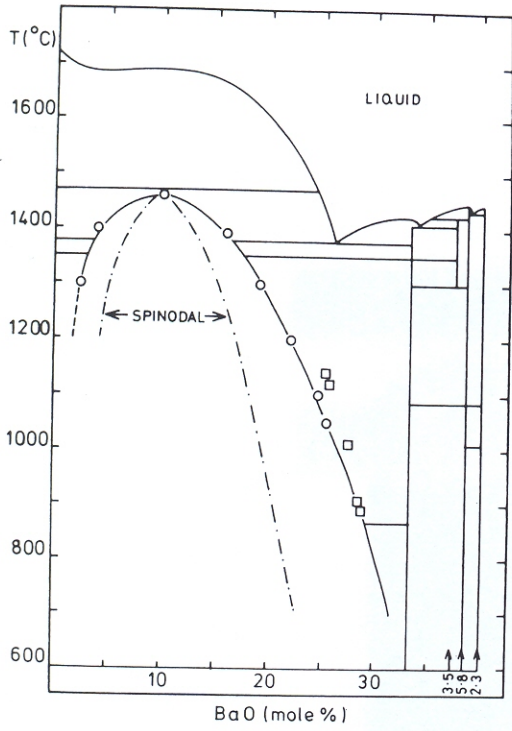


FIG. 1

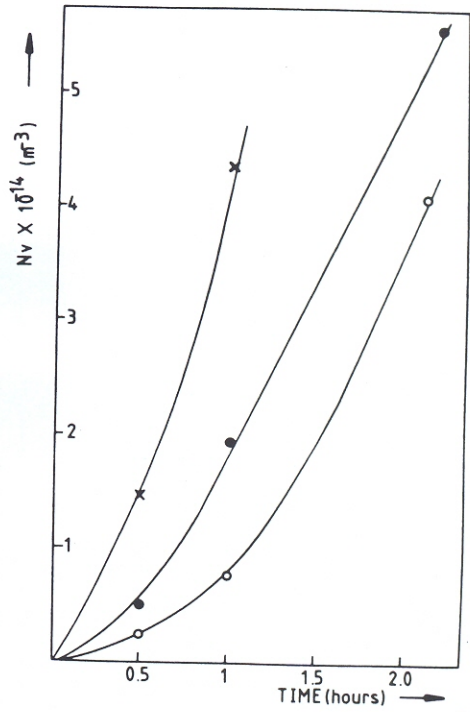


FIG. 2

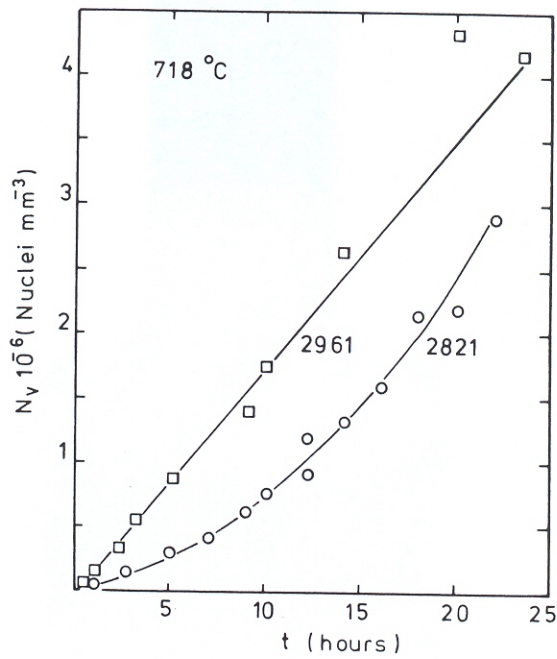


FIG. 3