Lawrence Berkeley National Laboratory
Recent Work

Title
THE FORMATION AND MICROSTRUCTURE OF Mg-Si-O-N GLASSES

Permalink
https://escholarship.org/uc/item/4jh7c0sf

Authors
Shaw, T.M.
Thomas, G.
Loehman, R.E.

Publication Date
1984-04-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

THE FORMATION AND MICROSTRUCTURE OF Mg-Si-O-N GLASSES

T.M. Shaw, G. Thomas, and R.E. Loehman

April 1984

DISCLAIMER

THE FORMATION AND MICROSTRUCTURE OF Mg-Si-O-N GLASSES

T.M. Shaw, G. Thomas and R.E. Loehman

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

April 1984

THE FORMATION AND MICROSTRUCTURE OF Mg-Si-O-N GLASSES

T.M.Shaw,[*] G. Thomas[†] and R.E. Loehman[§]

ABSTRACT

Bulk oxynitride glasses in the Mg-Si-O-N system have been prepared by melting mixtures of SiO_2, MgO and Si_3N_4 powders and the microstructures and compositions of the glasses were analyzed using electron microscopy, energy and wavelength dispersive x-ray analysis and energy loss spectrometry. The melting experiments indicate the presence of a limited glass forming region in the system. For the melting conditions used, nitrogen was found to be a necessary constituent of the melts to prevent crystallization on cooling. Extension of the miscibility gap in the binary $MgO-SiO_2$ system into the Mg-Si-O-N system results in phase separation in most of the glasses. A partial plot of the miscibility gap in the Mg-Si-O-N system is established from analysis of the composition of the phases formed during phase separation of the glasses.

* Rockwell International Science Center, Thousand Oaks, CA 91360.
† Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720.
§ Sandia National Labs, Albuquerque, NM 87185.

INTRODUCTION

Oxynitride glasses were originally discovered when it was found that oxide glasses after nitriding with nitrogen or ammonia contained small amounts of nitrogen.[1-3] More recently, interest in oxynitride glasses has been stimulated by the discovery that they form the bonding layer between silicon nitride grains in silicon nitride ceramics hot pressed or sintered with additives. This discovery has prompted attempts to prepare oxynitride glasses by melting mixtures of oxides and nitrides in a nitrogen atmosphere. By this method oxynitride glasses containing up to 18 at% nitrogen have been produced in a variety of different systems.[4-11]

The Mg-Si-O-N system is one of the most important compositional systems in the fabrication of silicon nitride ceramics. Magnesium oxide is commonly used as a sintering aid in the fabrication of silicon nitride ceramics. The oxide reacts with SiO_2 on the surface of silicon nitride particles and with the silicon nitride grains themselves to form an Mg-Si-O-N liquid. On cooling the liquid solidifies to form an oxynitride glass at grain boundaries. The present investigation examines bulk glass formation in the Mg-Si-O-N system by determining the extent of the glass forming region using melting experiments. The microstructures of the as-cooled glasses are then characterized using transmission electron microscopy. The results of the investigation are related to known phase equilibria in the Mg-Si-O-N system.

EXPERIMENTAL

Glass Preparation

Starting compositions for melting experiments were prepard by thoroughly mixing weighed amounts of Baker reagent grade SiO_2 and MgO powders and amorphous Si_3N_4 powders.* Ten grain batches of each composition were melted in

---

*GTE Sylvania SN402

shallow molybdenum dishes for 1 - 4.5 hrs at temperatures of 1600°C to 1700°C using a graphite element furnace. A static nitrogen atmosphere at one atmosphere pressure was maintained in the furnace during melting in an effort to suppress the loss of nitrogen from the melt. The melts were cooled by turning off the furnace at the end of the run. Exact cooling rates were not measured, but generally the melts cooled to below 1000°C in less than ten minutes. To supplement these experiments some additional compositions were melted using a tungsten element furnace. The appearance of quenched melts were noted and inhomogeneous melts were remelted to improve mixing. Each melt was checked for crystallinity by x-ray diffraction analysis using a standard diffractometer and CuK_α radiation. Compositions prepared in this investigation are given in Table 1.

Composition Analysis

Two independent methods were used to analyze the bulk compositions of glasses after melting. First, nitrogen contents of each glass were measured by an inert gas fusion technique. Second, to obtain specific compositional data, several glasses were also analyzed using a JEOL 773 microprobe equipped with a wavelength dispersive spectrometer to detect light elements (oxygen and nitrogen) in the glasses. The spectrometer was calibrated using samples of quartz for Si/O ratios, CVD Si_3N_4 for Si/N ratios and MgO for Mg/O ratios. Bulk compositional data were obtained by scanning the probe over an area of about 3 μm × 5 μm on a highly polished carbon coated surface of the sample. For greater accuracy, an analysis was performed on several areas of each sample.

To check the local compositions of phases formed in the glasses, carbon coated ion milled samples were examined using a Philips 400 transmission electron microscope equipped with energy dispersive x-ray and electron energy loss spectrometer attachments. The energy dispersive x-ray spectrometer was calibrated for measurement of Mg/Si ratios in the samples using powdered samples of high purity forsterite and enstatite dispersed on carbon grids. The energy loss spectrometer was used for qualitatitve comparison of the relative amounts

of nitrogen in phases formed in the glasses. Thin areas of the specimens were selected for the analysis so as to reduce the effects of multiple inelastic scattering. Generally, areas that gave a first plasmon loss peak that was about a quarter of the height of the zero loss peak were found to be suitable for analysis. Spectra were acquired over the 0 - 1 KeV energy loss range. Comparisons of the nitrogen contents of the different phases were made by comparing the areas under energy loss edges after background stripping.

EXPERIMENTAL RESULTS AND DISCUSSION

Melting Experiments

Figure 1 shows the extent of the glass forming region found in the Mg-Si-O-N system for the furance conditions and cooling rates used in the present melting experiments. The starting compositions, melting temperatures and time at temperature for each melt are given in Table 1 along with a description of each melt on cooling. The region of glass formation lies predominantly in the $SiO_2-Si_2N_2O-MgSiO_3$ compatibility triangle of the $SiO_2-MgO-Si_3N_4$ phase diagram and is centered around the composition A.

The extent of the glass forming region was limited by crystallization of the melt on cooling and frothing of the melt during melting. Partly crystalline specimens were obtained from resulted in compositions containing less Si_3N_4 (Melts I and J) or more MgO (Melts K and L) than composition A. The binary SiO_2-MgO phase diagram[12] indicated that compositions I was completely molten at the melting temperatures used and therefore crystallized on cooling. The rapid increase in liquidus temperature with increasing MgO content in the $MgO-SiO_2$ system suggests that the crystallinity in compositions J, K and L is in part due to incomplete melting. In compositions richer in SiO_2 or Si_3N_4 than A (Melts G and H) copious frothing occurred on melting. This resulted in glassy materials which contained a larger number of bubbles on cooling. Melts A to F all produced glassy materials which are largely bubble free. However, some bubbling was initially observed in all these compositions, particularly in the more SiO_2

rich composition (B and C). In this respect, the glass forming region indicated by the dotted line in Fig. 1 is somewhat arbitrary. Glass formation occurs over a different range of compositions than those initially determined to be glass formers by Jack.[4] Later work on the Mg-Si-O-N system, however, is in good agreement with the compositions shown in Fig. 1.[13,14] An important observation regarding glass formation is that melt I that contained no Si_3N_4 readily crystallized on cooling. In fact in the $MgO-SiO_2$ system it has been found that melts containing MgO crystallize even when rapidly quenched.[13] This clearly indicates that nitrogen plays an essential part in promoting glass formation in the Mg-Si-O-N system. The most successful glass forming composition was A, which produced a completely bubble-free glass after melting for one hour.

Measurement of the nitrogen contents of the glasses by the fusion technique indicated that about 30% of the nitrogen initially added was lost on melting. In contrast, electron microprobe analysis indicated that only about 5% of the nitrogen was lost during melting along with small amounts of MgO. Results obtained using the microprobe were reproducible to within ±1 wt% of Si_3N_4, and microprobe analysis of samples of known composition (for example Si_2N_2O) were accurate to within 1 wt% of Si_3N_4. Also, a recent analytical study[15] that compared inert gas fusion with ion chromatography for nitrogen determinations of oxynitride glasses showed that the former technique considerably underestimates actual nitrogen contents. In view of these observations, it is felt that the microprobe analysis provided a more accurate measurement of the compositions of the glasses. The compositions for glasses A - F, after melting, are marked on the phase diagram in Fig. 1. The results indicate that only small composition shifts occurred during melting.

Characterization of the Glasses

On cooling melts, A, B, C and D produced opaque glasses. Microstructural examination revealed that the opacity was caused by phase separation in the glasses. For example, a low magnification view of the microstructure of glass A is shown in Fig. 2. The microstructure consists of groups of droplets

of a minor phase (appearing in light contrast in Fig. 2), dispersed in a continuous matrix of a second glassy phase. EDS spectra from the two phases (Fig. 2b) indicated that the discontinuous phase contained mainly silicon and virtually no magnesium, whereas the matrix phase contained significant amounts of both elements (Fig. 2c). Similar spectra obtained from the matrix and minor phases in glasses B, C and D indicated that in each glass the discontinuous phase consisted mainly of SiO_2 while the matrix phase contained both SiO_2 and MgO. The only other element detected (nitrogen and oxygen being undetectable by EDS due to x-ray absorption by the beryllium detector window) was a trace amount of chlorine in the magnesia-rich matrix phase of the glasses. This probably came from the amorphous Si_3N_4 powders used to prepare the glasses.

Preferential etching of the SiO_2 phase occurred during the ion milling of thin foils of glasses A - D. This hindered the preparation of uniformly thinned specimens of the glass for TEM observations. In most cases the SiO_2-rich phase was almost completely etched from the microstructure, leaving holes in the foils. However, from the size and shape of the holes, an estimate of the amount and morphology of the SiO_2-rich phase in the glasses could be obtained. For comparison, low magnification views of the microstructures of glasses A, B, and C are shown in Figs. 3a, b, and c, respectively. From the size of the holes in the foils it can be seen that glasses B and C contain considerably more SiO_2-rich phase than glass A and that the amount of the SiO_2-rich phase increases with the SiO_2 content of the glasses. The scale of the phase separation in all three glasses is unusually coarse. However, it is quite distinct from the macroscopic liquid unmixing observed at melting temperatures in immiscible silicate liquids.[16,17] This suggests that at the melting temperatures used in the present experiments, glasses A, B and C, were all homogeneous liquids and that phase separation occurred as the melts were cooled. It is possible that a combination of the moderate cooling rates used in the present experiments and high miscibility temperatures contributed to produce the coarse phase-separation observed.

In order to obtain more precise information about the extent and shape of the miscibility gap in the Mg-Si-O-N system, quantitative microanalysis was used to examine the compositions of the SiO_2- and MgO-rich phases in glasses A - D. Each glass was annealed at 850°C (just above the glass transition temperature) for 2 hrs to equilibrate the glasses at the same temperature. The ratio of magnesium to silicon in each phase was then determined in the TEM using energy dispersive x-ray analysis.

A problem encountered in this analysis was the sensitivity of the MgO-rich phase to radiation damage. When a high intensity electron probe was focused on areas of the matrix phase, extensive bubble formation occurred in the exposed region after only a short time. Similar behavior has been observed in glassy pockets in Si_3N_4 ceramics,[18,19] and it has been suggested that damage is caused by ionization of atoms in the glass under the influence of the electron beam.[18] EDS analysis showed that accompanying the damage in the MgO-rich phase, there was a loss in magnesium from the exposed region. This loss resulted in considerable errors in the analysis of Mg/Si ratios in the glasses when long counting times were used. To avoid this problem a low intensity beam was used to record all spectra and, for each phase, spectra were first recorded at 60 second intervals to check for changes in composition with exposure. Counting times were selected for which no change in composition could be detected and were then used to record subsequent spectra.

To further improve the analysis, spectra were recorded from 10 different regions of phases in each glass, typically using 250 second counting times and a low intensity beam. Using this technique, values of Mg/Si count ratios, that were reproducible to within ± 2% for each phase could be obtained.

The Mg/Si ratio fixes a line in the phase diagram along which the composition of a phase must lie. To further fix the composition of the phases in a glass it is necessary to know how the nitrogen is partitioned between the two phases in a given composition. The composition of both phases in a glass may be calculated if the average composition of the glass, the Mg/Si ratios for each phase and the relative amounts of nitrogen in the phases are known.

J5125A/jbs

To determine the relative nitrogen contents of the Mg- and SiO_2-rich phases in glass A energy loss spectra were recorded from the two phases; typical spectra are shown in Figs. 2d and 2e. Both spectra contain prominent oxygen K edges; the nitrogen edges, however, are only clearly seen after background stripping and magnification of the spectra. The relative areas of the nitrogen edges after stripping indicate that there is approximately twice the weight fraction of nitrogen in the continuous Mg rich phase that there is in the SiO_2-rich phase.

The results of the energy loss analysis, combined with the EDX measurements of Mg/Si ratios in each phase and miocroprobe analysis of the average composition the glasses, allow the composition of both phases in glass A to be determined. By assuming that the nitrogen content of the Mg-rich phase in the other glass compositions is, similary twice that in the SiO_2-rich phase, the compositions of the phases in glasses B, C and D can also be estimated. A summary of the estimated compositions and measured Mg/Si ratios for the phases in glasses A, B, C and D is given in Table II. As the miscibility gap in the Mg-Si-O-N system undoubtedly results from extension of the binary $MgO-SiO_2$ miscibility gap into this system an additional point on the miscibility surface at 850°C can be obtained by extrapolating the miscibility gap in the $MgO-SiO_2$ system to 850°C. The extrapolation indicates that the binary MgO-rich phase has a composition close to that of enstatite. The experimental data in Table II and the extrapolated composition for binary MgO-rich phase allow the partial plot of the miscibility gap shown in Fig. 1 to be constructed.

Although the position of the miscibility gap is only approximate the results show that at 850°C glasses A - D separate into a minor phase with a composition close to the $SiO_2-Si_2N_2O$ tie line and a matrix phase whose composition lies close to the $MgSiO_3-Si_2N_2O$ tie line. Both phases contain nitrogen but more is segregated to the MgO-rich phase. The shape of the miscibility gap suggests that additions of Si_3N_4 tend to restrict the extent of the miscibility gap in the Mg-Si-O-N system.

As a further test for the position of the miscibility gap, compositions E and F were prepared and examined for phase separation (see Fig. 1 for the com-

positions of glasses E and F). Electron microscopy showed that glass E, whose composition after melting lies within the experimentally determined miscibility gap, phase separated on a fine scale during cooling. Glass F, with a composition outside the miscibility gap, was completely clear and, even after annealing for 2 hrs at 850°C, showed no evidence of phase separation. The consistency of these results with the experimentally determined miscibility gap suggests that miscibility boundary shown in Fig. 1 may be used with some confidence to predict immiscibility in Mg-Si-O-N glasses. It is interesting to note that in an investigation of an MgO hot pressed silicon nitride , Clarke et al. observed phase separation in the glassy intergranular phase.[20] The compositional analyses of those phases agree very well with those predicted by the experimentally determined miscibility gap[20,21] presented here. The results of the present experiments, therefore, further support the conclusions that the intergranular phase in the compositions prepared by Clarke et al, lie in the SiO_2-$MgSiO_3$-Si_2N_2O compatibility triangle of the Mg-Si-O-N system.

In addition to the phase separation just discussed, a few crystalline particles were found in some of the glasses. The particles were most common in glasses B and C and a typical example from glass B is shown in Fig. 4a. The corresponding electron diffraction patterns indicated that the particles were twinned crystals of elemental silicon. This observation was further confirmed by the finding that EDS spectra from the particles contained only a peak corresponding to silicon (Fig. 4b). Small dark particles were frequently associated with the silicon crystals (arrowed in Fig. 4a). EDS spectra from the small particles showed that they contained Si, Ti, Cr and Fe (Fig. 4c). These were thought to come from impurities in the starting powders used to prepare the glasses.

The origin of the Si particles is less clear. The silicon nitride powder used to prepare the glasses contains no free silicon, as it is prepared by the vapour phase reaction of $SiCl_4$ and NH_3. The most likely explanation is that silicon is produced by the decomposition of silcon nitride during melting according to the reaction

$$Si_3N_4 \rightarrow Si(\ell) + N_2 \uparrow \quad .$$
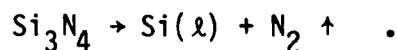
This reaction is consistent with the frothing observed in the glasses. (A more complete analysis of reactions that lead to frothing in oxynitride glasses suggests that this is not the only reaction possible.[22]) If the above reaction is responsible for the silicon particles, the occurrence of crystalline silicon in oxynitride glases may be quite general and could account for the gray color of many oxynitride glasses.

Summary

Oxynitride glasses can be synthesized over a narrow range of compositions in the Mg-Si-O-N system by melting mixtures of oxides and silicon nitride. The glass forming region is limited by frothing of the melt towards SiO_2- and Si_3N_4-rich compositions and by crystallization of the melt on cooling in MgO rich or nitrogen poor melts. For the moderate cooling rates used in this investigation silicon nitride was found to be a necessary constituent of the melts for glass formation. Microstructural examination showed that most of the compositions in the glass forming region undergo phase separation on cooling. The resulting microstructure consists of coarse droplets of a SiO_2 rich phase dispersed in a matrix of MgO-rich glass. Both phases contain nitrogen but more nitrogen separates to the MgO-rich phase on cooling. The phase separation results from extension of the miscibility gap in the binary MgO - SiO_2 system into the Mg-Si-O-N system. In addition to phase separation the microstructures of the glasses contained small crystalline particles of elemental silicon. These are throught to come from decomposition of the silicon nitride powder during melting.

Acknowledgments

REFERENCES

1. Elmer, T.H., and Nordberg, M.E., "Nitrided Glasses," Paper No. 30, Proc. VIII International Congress on Glass, Brussels, Belgium, 1965, Instuit National du Verre Charleroi, Belgium, (1965).

2. Elmer, T.H., and Nordberg, M.E., "The Effect of Nitriding on Electrolysis and Devitrification of High Silica Glasses," J. Amer. Ceram. Soc., 50, 275-279.

3. Mulfinger, H.O., "The Physical and Chemical Solubility of Nitrogen in Glass Melts," J. Amer. Ceram. Soc., 49, 462-467 (1966).

4. Jack, K.H., "Sialon Glasses," in Nitrogen Ceramics, Proc. NATO Advanced Study Institute, ed. F.L. Riley, 257-261, Noordhoff (1977).

5. Loehman, R.E., "Preparation and Properties of Yttrium-Silicon-Aluminum Oxynitride Glasses," J. Amer. Ceram. Soc., 62 (9-10), 491-494 (1979).

6. Loehman, R.E., "Oxynitride Glasses," J. Non-Cryst. Solids 42 (1-3) 433-46 (1980).

7. Jankowski, P.E. and Risbud, S.H., "Synthesis and Characterization of an Si-Na-B-O-N Glass," J. Am. Ceram. Soc. 63 (5-6) 350-52 (1980).

8. Wusirika, R.R. and Chyung, C.K., "Oxynitride Glasses and Glass-Ceramics," J. Non-Cryst. Solids, 38-39 (Pt. 1) 39-44 (1980).

9. Frischat, G.H. and Schrimpf, C., "Preparation of Nitrogen-Containing Na_2O-CaO-SiO_2 Glasses," J. Am. Ceram. Soc. 63 (11-12) 714-715 (1980).

10. G. Thomas, C. Ahn and J. Weiss, "Characterization and Crystallization of Y-Si-Al-O-N Glasses," J. Amer. Ceram. Soc. 65, (11) C-185, 1982.

11. Drew, R.A.L., Hampshire, S. and Jack, K.H., "Nitrogen Glasses," Proc. Brit. Ceram. Soc., 31 (6) (Special Ceram. 7) 119-132 (1981).

12. Levin, E.M., Robbins, C.R., and McMurdie, H.F., "Phase Diagrams for Ceramists," ed. M.K. Reser, The American Ceramic Society, Inc., Columbus, Ohio (1964).

13. R.A.L. Drew, S. Hampshire and K.H. Jack, "The Preparation and Properties of Oxynitride Glasses," in Progress in Nitrogen Ceramics Proc. NATO Advanced Study Institute, ed. F.L. Riley, 323-330 Martinus Nijhoff (1983).

14. R.L. Tsai "Studies on High Temperature mechanical Behavior and Phase Change Kinetics of Magnesium-Silicon-Oxynitride Glass Ceramics," PhD thesis, Cornell University (1981).

15. R.W. Merrill and R.E. Loehman, to be published.

16. Greig, J.W., "Immiscibility in Silicate Melts," Amer. J. of Science, XIII, 1-44 and 132-154 (1927).

17. Tewhey, J.D., and Hess, P.C., "The Two Phase Region in the $CaO-SiO_2$ System Experimental Data and Thermodynamic Analysis," Phys. and Chem. Glasses, 20 (3), 41-53 (1979).

18. Drew, P., and Lewis, M.H., "The Microstructures of Silicon Nitride Ceramics During Hot-Pressing Transformations," J. of Mat. Sci., 9, 261-269 (1974).

19. Lavel, J.Y., and Westmacott, K.H., "The Mechanism of Ionization Damage in Glassy Ceramics," to be published in J. Amer. Ceram. Soc.

20. D.R. Clarke, N.J. Zaluzec and R.W. Carpenter, "The Intergranular Phase in Hot-Pressed Silicon Nitride: II, Evidence for Phase Separation and

Crystallization," J. Amer. Ceram. Soc. 64, (10) 608-611 (1981).

21. D.R. Clarke and N.J. Zaluzec, "The Intergranular Phase in Hot-Pressed
     Silicon Nitride: III, A Refinement of the Elemental Composition," J. Amer.
     Ceram. Soc. 65, (8) C-132-C133 (1982).

22. Shaw, T.M., "The Crystallization of Glasses in the Mg-Si-O-N System," Ph.D
     Thesis, University of California, Berkeley (1980)

Table I

Melts Prepared in the Mg-Si-O-N System

| Melt | Composition Wt% | | | Melting Conditions | | Appearance of Melt on Cooling |
	SiO_2	MgO	Si_3N_4	Temperature (°C)	Time Hours	
A	59.1	31.81	9.09	1700	4-1/2	Gray opaque glass
B	65.0	26.0	9.0	1650	1	Gray opaque glass, some bubbles
C	67.0	24.0	9.0	1650	1	Gray opaque glass, some bubbles
D	61.91	33.33	4.76	1650	1	Gray opaque glass
E	55.0	35.0	10.0	1650	1	Clear blueish colored glass
F*	52.5	37.5	10.0	1600	1	Clear glass
G	70.0	21.0	10.0	1650	1	Frothy glass
H	54.2	29.0	16.8	1600	1	Frothy glass
I	65.0	35.0	0	1700	1	Crystalline opaque
J*	55.0	40.0	5.00	1600	1	Partly crystalline
K	50.0	40.0	10.0	1650	1	Crystalline opaque
L	45.0	45.0	10.0	1600	1	Crystalline opaque

*Melted using tungsten element furnace.

Table II

Mg/Si Ratios and Compositions of SiO_2 and MgO-Rich Phases in
Phase-Separated Mg-Si-O-N Glasses

| | Mg/Si Ratios | | Composition (Equivalent %) | | | |
| | | | SiO_2-Rich Phase | | MgO-Rich Phase | |
Glass	SiO_2-Rich Phase	MgO-Rich Phase	Mg	N	Mg	N
A	1.6×10^{-2}	0.80	0.01	5.8	28.5	12.6
B	*	0.79	0.0	5.6	28.2	12.1
C	*	0.76	0.0	6.0	27.6	13.0
D	*	0.91	0.0	2.4	31.2	5.3

*Mg not detectable.

FIGURE CAPTIONS

Fig. 1   Partial plot of the phase diagram of the Mg-Si-O-N system showing the
          glass forming region identified from melting experiments, melt compo-
          sitions and the experimentally determined boundary of the miscibility
          gap in the Mg-Si-O-N system.

Fig. 2   TEM micrograph of phase separation in a glass of composition A. EDS
          and EELS spectra from matrix and minor phases are shown in (b), (c),
          and (d), (e) respectively.

Fig. 3   Low magnification views of phase separation in glasses A, B and C.

Fig. 4   TEM micrograph of silicon and impurity particles observed in glass B.

EQUIVALENT % MAGNESIUM

o CLEAR GLASS
◑ PHASE SEPARATED
    GLASS
⊕ FROTHY GLASS
⊗ CRYSTALLINITY
× COMPOSTION AFTER MELTING
--- EXTENT OF GLASS FORMING REGION
— ESTIMATED BOUNDARY OF THE
    MISCIBILITY GAP

FIG. 1   SC83-23385

17

FIG. 2 a-e

XBB 802-1977
XBB 806-7159

18

a glass A

5μm

b glass B

5μm

c glass C

5μm

FIG. 3 a-c   XBB 809-10369

0·3 μm

FIG. 4 a-c