22.3-02 X-RAY DIFFRACTION STUDIES OF GLASSES IN THE SYSTEM CaO-B2O3-Al2O3-SiO2. By J. W. Whittaker, Department of Geology and Mineralogy, Parks Road, Oxford.

An investigation was made of five glasses in the quaternary system CaO-B2O3-Al2O3-SiO2 from the glass-forming region 10-30% CaO, 20% MgO, 9-15% Al2O3, 50-60% SiO2, and also of a pure SiO2 glass. Intensity data were obtained with a specially designed monochromator which permitted measurements using incident beam crystal monochromatised CuKα and AgKα radiations without moving the goniometer. Incoherently scattered radiation was eliminated by the fluorescence excitation technique (B.E. Warren and G. Mavel, Rev. Sci. Instrum. (1966) 36, 196).

The two sets of experimental intensities were corrected for background, polarisation, absorption and multiple scattering before being independently normalised. Difficulties in merging the data were attributed to uncertainty in the polarization factor for the monochromator and to some incoherent radiation in the Ag data. As a result, despite careful data collection and reduction up to k max = 21Å-1, the final pair functions all displayed spurious features below the first main peak.

Results for the five glasses were very similar — a few sharp peaks at low k in the PPDF, followed by a rapid approach to the average atomic distribution. The first peak, at 1.65-1.69Å, was attributed to (Si,Al)-0 distances, and that at 2.72Å to 0-0 pairs. Fourfold coordination of (Si,Al) by O is indicated, with a slightly expanded tetrahedron compared to silica glass. Peaks at 2.1 and 2.4Å were interpreted as Mg-O and Ca-O distances respectively. The peaks beyond 3Å are broadened considerably and their differences from those in silica glass indicate a substantial modification of the tetrahedral network by the Ca2+ and Mg2+ ions.

22.3-03 PbO ORDERING IN LEAD-BORATE GLASSES. By H. Grigoriew, OBIEPO FOLKOLOR, Warszawa, Poland.

Two glass compositions were investigated by the RDF method: a) 0.63 PbO. 0.37 B2O3 (yellow); b) 0.29 PbO. 0.71 B2O3 (colorless). The measurements were carried out on a Siemens 500 X-ray diffractometer using MoKα and SI/Li detector. Polarization, background and aomalous dispersion were all taken into account during calculations. Compton scattering was not corrected for, since it is 3-6 times smaller in the low angular region than 90°. Normalization was performed by integration. O0(r) in Fig. 1 and 4πρ0(r) were obtained as a result. Because of the predominant scattering ability of PbO in these glasses, the curves basically supply information about the PbO coordination.

Earlier investigations carried out on lead-borate glasses were mainly concerned with the B2O3 ordering. Red tetragonal coordination of PbO was also suggested.

In this work, similarities were found between PbO ordering in 0.63 PbO. 0.37 B2O3 glass and the orthochromic structure of yellow PbO (Table, Fig. 2). They are as follows: 1. small PbO distance; 2. small Pb- Pb distance; 3. low PbO coordination number. The size of the ordered PbO regions is 10 Å (Fig. 1), i.e. 2-3 Pb-Pb distances. The following atomic pattern is proposed for this glass: Layer fragments made up of interlinked PbO chains are similar to the ones in orthochromic PbO (Fig. 2a). The PbO chains are linked with B2O3 as shown in Fig. 2. The B2O3 network can also be present in the interlayer regions.

The 0.29 PbO. 0.71 B2O3 glass, compared to 0.63 PbO. 0.37 B2O3, exhibits a significant increase in the Pb-O and Pb-Pb distances. The displacement of the first max-

22.3-04 LIQUID-LIQUID PHASE SEPARATION AND CRYSTAL NUCLEATION IN BAO-SIO2 GLASSES*. By E.D. Zanotto, Departamento de Engenharia de Materiais, Universidade Federal de Sao Carlos, Brazil, A.F. Craievich, Departamento de Fisica e Ciencia dos Materiais, Instituto de Fisica e Quimica de Sao Carlos, Universidade de Sao Paulo, Brazil and P.F. James, Department of Ceramics, Glassess and Polymers, The University of Sheffield, U.K.

The amorphous phase separation in B2O3-BaO glasses was studied by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). From the measured integrated SAXS intensities for glass samples containing 28.3 and 28.9 mole% BaO in the coarsening stage of phase separation, the low temperature boundary of the miscibility gap was determined. This result agrees with the binodal calculated by Haller et al. (J. of Am. Ceram. Soc. (1974) 57, 120). From the integrated SAXS intensities for samples treated isothermally the time needed to reach the coarsening stage of phase separation was determined. The average diameter of the amorphous droplets and its variation with time at heat treatment temperatures of 743 and 760°C, was determined by means of Guinier plots of the SAXS intensities and also by TEM. Close agreement was found. Comparison of the SAXS studies with crystal nucleation curves of glasses heat treated inside and outside the miscibility gap, suggests that amorphous phase separation enhances the nucleation of barium disilicate crystals. This effect is attributed to a) the existence of a narrow SiO2 depleted zone around the droplets during the nucleation and growth stage and b) the enrichment in BaO of the amorphous matrix during phase separation.

* Work supported by FAPESP, CNPq and CAPES

<table>
<thead>
<tr>
<th>Atoms Pairs</th>
<th>Glass (a)</th>
<th>Glass (b)</th>
<th>PbO ortho</th>
<th>PbO tetra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-O</td>
<td>2.28</td>
<td>2.65</td>
<td>2.17-2.20</td>
<td>3.36</td>
</tr>
<tr>
<td>Pb-Fb</td>
<td>3.99</td>
<td>4.35</td>
<td>3.56-3.74</td>
<td>3.7-3.98</td>
</tr>
</tbody>
</table>