22.3-02 X-RAY DIFFRACTION STUDIES OF GLASSES IN THE SYSTEM $CaO-MgO-Al_2O_3-SiO_2$. By C. M. Shepperd and E. J. W. Whittaker, Department of Geology and Mineralogy, Parks Road, Oxford.

An investigation was made of five glasses in the quaternary system $CaO-MgO-Al_2O_3-SiO_2$ from the glass-forming region 10-20% CaO, 20% MgO, 5-15% Al_2O_3, 50-60% SiO_2, and also of a pure SiO_2 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. (1965) 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 polarisation 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 quite sharp peaks at low r in the PFD, followed by a rapid approach to the average atomic distribution. The first peak, at 1.65-1.69Å, was attributed to (Si,Al)-O distances, and that at ∿ 2.72Å to O-O 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 Ca^{2+} and Mg^{2+} ions.

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

Two glass compositions were investigated by the RDF method: a) 0.63 PbO. 0.37 B_2O_3 (yellow); b) 0.29 PbO. 0.71 B_2O_3 (colorless). The measurements were carried out on a Siemens 500 X-ray diffractometer using MoKα and Si/Li detector. Polarization, background and anomalous dispersion were all taken into account during calculations. Compton scattering was not corrected for, since it is completely eliminated for angles greater than θ∿11°. Normalization was performed by integration. G(r) in Fig. 1 and $4\pi r^2\rho(r)$ curves 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 B_2O_3 ordering. Red tetragonal coordination of PbO was also suggested.

In this work similarities were found between PbO ordering in 0.63 PbO. 0.37 B_2O_3 glass and the orthorhombic 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 orthorhombic PbO (Fig. 2a). The PbO chains are linked with B_2O_3 as shown in Fig. 2. The B_2O_3 network can also be present in the interlayer regions.

The 0.29 PbO. 0.71 B_2O_3 glass, compared to 0.63 PbO. 0.37 B_2O_3, exhibits a significant increase in the Pb–O and Pb–Pb distances. The displacement of the first maximum can be caused by the appearance of the O–O scattering in B_2O_3 (2.6–3 Å), but a similar displacement of the 2nd maximum corresponding to Pb–Pb indicated a loosening of the PbO structure. A pronounced fourfold decrease in the Pb–Pb coordination number is also observed. The decrease cannot be explained by the composition change alone, and it indicates that single PbO molecules appear in the B_2O_3 network. The proportionally larger further maxima (Fig. 1), e.g. Pb–2Pb, probably reflect the somewhat more regular pattern of PbO located in B_2O_3 network vacancies. The increase of Pb–Pb and Pb–O distances is caused by a modification of the chemical bonding in the oxide.

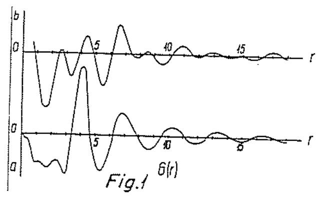

Fig.1

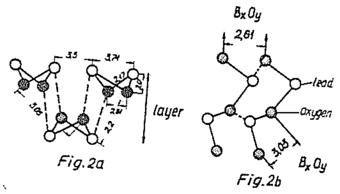

Fig.2a Fig.2b

Table. Interatomic distances in Å.

Atom Pairs	Glass (a)	Glass (b)	PbO ortho	PbO tetra
Pb–O	2.26	2.65	2.17–2.20	2.33
Pb–Pb	3.99	4.35	3.5 –3.74	3.7–3.98

22.3-04 LIQUID-LIQUID PHASE SEPARATION AND CRYSTAL NUCLEATION IN $BaO-SiO_2$ GLASSES*. By E.D. Zanotto, Departamento de Engenharia de Materials, Universidade Federal de São Carlos, Brazil, A.F. Craievich, Departamento de Física e Ciência dos Materials, Instituto de Física e Química de São Carlos, Universidade de São Paulo, Brazil and P.F. James, Department of Ceramics, Glasses and Polymers, The University of Sheffield, U.K.

The amorphous phase separation in SiO_2-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 26.9 mole% BaOin 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 Amer.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 Si 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