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SODIUM ENVIRONMENTS IN GLASS

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Abstract.— Sodium environments have been measured directly in several oxide glasses using EXAFS at the sodium K edge. The existence of local structure around sodium in glass contradicts the conventional Zachariasen model. Analysis of the EXAFS indicates there are significant differences relating to the glass modifier: glass former chemistry - the details of which demonstrate similarities with crystalline silicates and borates.

In the total diffraction spectrum of a glass the correlations associated with the modifying component (Na_2O in this case) are masked by those associated with the more strongly bound glass forming network (e.g. SiO_2 or B_2O_3). The EXAFS technique however enables these correlations to be separated out. Just this approach has been used for the first time with the following three glasses: sodium disilicate, soda-lime-silica glass and sodium diborate. At the Na K edge ($11.5 \text{ \AA}$) distinct EXAFS spectra have been measured demonstrating that the sodium environments in these widely different compositions are well defined for each glass. The fine structure, however, is weaker than the tetrahedral Si environment obtained from an earlier study (1) of the Si K Edge ($6.7 \text{ \AA}$). It is now clear using EXAFS why Na-O correlations are barely identifiable using x-ray or neutron diffraction techniques (2).

Normalized sodium EXAFS spectra for the three glasses are displayed in fig.1 (solid curves). These were obtained from transmission measurements of sub-micron thick specimens fabricated by blowing thin films from a molten pellet. Synchrotron radiation from the ACO storage ring was employed and monochromatized using the LURE two crystal soft x-ray spectrometer. Experimental details are given elsewhere (3). Fourier transforms of the normalized spectra are presented in fig.2. These were corrected using calculated phase shifts for sodium and oxygen. The broad features of the atomic distributions were then used as first attempts for curve-fitting the wave vector spectra. The final fits (dotted curves in fig.1) were obtained using Lee and Pendry's spherical wave formalism (4). Details of the derived clusters are listed in the accompanying table.

The Debye-Waller factors (σ_j) for all the glasses listed in the table are many times greater than those for silicon ($0.001 \text{ \AA}^2$ (3)). Specifically the Debye-Waller factor measured in EXAFS is the correlated bond length variance. It reflects the strength of the bond and the overall rigidity of the lattice. The large differences between the sodium and silicon Debye-Waller factors demonstrates why Na-O correlations are lost in the presence of Si-O or B-O correlations in the total diffraction spectrum. It also explains why the sodium related phonon band in the IR absorption spectrum of sodium disilicate glass (5) is so much broader than the bands relating to SiO_2 . In fact the respective stretching bands are separated in frequency by approximately an order of magnitude. This difference combined with the lighter weight of the atom pair implies Debye-Waller factors rather larger than

Fig.1

Normalized sodium EXAFS spectra for the three glasses sodium disilicate, soda-lime-silica and sodium diborate. For details see text.

the measured values given in the table. Evidently in glasses the rigid glass forming network of SiO_2 or B_2O_3 is important in correlating the motions of those oxygens coordinated with the sodium cations.

The Zachariasen model for glass (6) whilst emphasising the back-bone function of the covalent network subordinates the structural role of the ionic modifying component. Cations like sodium or calcium are pictured as providing a general filler for holes and voids present in the network as a result of topological disorder. It is clear from crystalline chemistry, however, that, even though the coordination of alkali or alkaline earth cations is never the same from compound to compound, for a given crystal it is usually fairly well-defined.

A very similar picture has emerged from the present study of the sodium EXAFS of silicate and borate glasses. The atomic distributions given in fig.2 confirm the average Na-O bond length to be 2.3 Å. The cluster calculations (see table) however show the actual oxygen coordination depends on the remaining composition. (Incidentally the coordination numbers, N_j , given in the table are essentially normalized with respect to the tetrahedral coordination of Si in the silicate glasses and as such are good to ~ 20% (see ref (3)). So there are approximately 5 oxygens around each sodium in sodium disilicate, 6 in sodium diborate but only 2 in the soda-lime-silica glass. Differences in local structure can also be seen beyond the oxygen ligand (fig.2). In sodium diborate there is a second shell of approximately 6 sodiums, the borons are not seen because the back-scattering is so much weaker compared to oxygen or sodium. For sodium disilicate a second shell is less obvious. Sodium and silicon shells are not pronounced probably because the similarity of the respective scattering factors makes the distinction of separate shells ambiguous. In the soda-lime-silica glass, however, the low oxygen coordination number suggests the second shell, which is distinct in the Fourier transform (fig.2), must also be made up of oxygens. The cluster calculations (fig.1 and the table) support this interpretation. Parallel compositionally related structural differences are to be

Fig.2

Atomic distributions around sodium
for the three glasses shown in fig.1
See text for details.

Sample	N_1	r_1	σ_1	N_2	r_2	σ_2	N_3	r_3	σ_3
		$\text{\AA}$	$\text{\AA}^2$		$\text{\AA}$	$\text{\AA}^2$		$\text{\AA}$	$\text{\AA}^2$
$\text{Na}_2 \text{Si}_2 \text{O}_5$	5 O's	2.3(0)	0.005(6)						
$\text{Na}_2 \text{CaSi}_5 \text{O}_{12}$	2 O's	2.4(3)	0.01(4)	1 O	2.8(6)	0.02(8)	3 O's	3.3(3)	0.02(6)
$\text{Na}_2 \text{B}_2 \text{O}_5$	6 O's	2.2(5)	0.02(8)	6 Na's	3.8(1)	0.02(8)			

Curve fitting parameters for the three glasses

N_j atom type and number

r_j shell radius

σ_j Debye-Waller factor

TABLE

found in the sodium environments of crystalline silicates and borates. In sodium diborate the oxygen coordination is between 6 and 7, in sodium disilicate it is 5 whilst in ternary alkali-alkaline earth silicates it is generally as low as 2 or 3 (7). The similarity with the local structure in the glasses is striking.

In addition to the Na EXAFS reported here for silicate and borate glasses, distinct EXAFS at Rb K edge ($0.82 \text{ \AA}$) in several germanate glasses has also been observed. Details of these measurements will be given in a future publication.

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