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Structure and dynamics of silicate glasses and melts

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A one-day meeting was held in the Department of Earth Sciences, University of Cambridge, on the theme of the 'Structure and Dynamics of Silicate Glasses and Melts'. The meeting was sponsored by the Mineral Physics group of the Mineralogical Society, and was attended by ~80 people. The objective of the meeting was to bring together experts from the glass community with members of the mineralogical community who are interested in glasses and melts. The scope of the talks considered structural details over length scales from nearest-neighbour coordinations up to 1–2 nm, and dynamics in both the slow relaxational and fast vibrational ranges. The talks also covered both experimental (particularly neutron scattering and NMR) and computer simulation methods.

The meeting was organized into three groups of themes, namely structure and dynamics in glasses, structure and dynamics in melts, and vibrational dynamics in glasses.

The opening talk was by Neville Greaves (Aberystwyth), with the title 'Structure and ionic transport in disordered silicates' (Greaves, 2000). This was a wide-ranging talk which addressed issues that have puzzled glass scientists for some time, namely, ionic transport in silicate glasses and the mixed alkali effect. The way in which the microstructure of a glass may be extrapolated from an existing knowledge of local structure was described (Greaves *et al*., 1997). This influence of microstructure on ion dynamics and also on glass fracture raised some fundamental questions about glass structure. It was noted that using wide-angle X-ray scattering of glasses and photo-electron spectroscopy of freshly cleaved glass surfaces (Baker *et al*., 1995), experimental evidence of a microsegregation of modifier cations was being established.

The second talk continued the theme of structure. Phil Gaskell (Cambridge, Physics) presented recent ideas on the 'Relationships between the medium-range structures of glasses and crystals' (Gaskell, 2000), something that has been a topic of long-standing debate which has been sharpening up over the past few years. The talk highlighted the fact that the scattering vector of the first sharp peak in diffraction patterns of glasses is often close to that from the corresponding crystal, as in cristobalite for example. This suggests some similarities between the structures of glasses and crystals over some length scale, which were explored in the talk (Gaskell and Wallis, 1996; Gaskell, 1998, 2000).

The theme of the comparison between amorphous and crystalline materials was continued by David Keen (Rutherford Appleton Laboratory), with a talk entitled 'Comparing the local structures of amorphous and crystalline polymorphs of silica' (Keen and Dove, 2000). This described work on amorphous silica and some of the crystalline phases using Reverse Monte Carlo analysis of neutron diffraction data. It was noted that the amorphous silica shares many structural features with the high-temperature phases of tridymite and cristobalite over a length scale of up to 10 Å, but the similarities do not extend to quartz or to the low-temperature phases (Keen, 1997; Keen and Dove, 1999, 2000).

Georges Calas (Paris) spoke on 'Local environment around transition elements in synthetic and natural glasses' (Galoisy *et al*., 2000). The results presented were based on extended X-ray absorption (EXAFS) and neutron scattering with isotopic substitution (NSIS) of Ni and Ti in silicate glasses (Cormier *et al*., 1999; Cormier *et al*., 1997). The occurrence of 'unusual' five-fold coordination for these transition elements was described. In addition, considerable cation–cation correlations were reported of transition metal cations in corner or edge-linked polyhedra forming two-dimensional domains of cations (Cormier *et al*., 1996) consistent with the ideas presented by Gaskell earlier (Gaskell, 2000).

Alex Hannon (Rutherford Appleton Laboratory) gave another perspective on structure

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with his talk 'Three-coordinated oxygens in some network glasses', again using neutron diffraction data, but this time looking at the structure from the perspective of the oxygen atoms rather than that of the cations.

The second theme of melts was introduced by Ian Farnan (Cambridge, Earth Sciences) in his talk on 'Anionic structure and dynamics in silicate glasses and melts', which continued with the view of a structure from the perspective of oxygen with the additional aspect of the dynamics. This talk gave a comparison between the shear relaxation times of silicate melts at high temperature and the nutation effects in ^{17}O NMR. This provides evidence for a divergence of oxygen translational and rotational correlation times. A similar (but at much lower frequency) decoupling of motional modes, previously detected by ^{29}Si NMR (Farnan and Stebbins, 1994), close to the glass transition can also be observed by simulation of ^{17}O NMR exchange spectra. It was pointed out that the loss of the primary relaxation mechanism in silicate melts in this divergent way is responsible for the formation of the glass and detailed characterization of the time scale of oxygen rearrangements is pushing forward understanding of this process.

Simon Kohn (Bristol) gave a talk titled 'Recent advances in understanding the dissolution mechanisms of water in silicate melts and glasses' (Kohn, 2000). This talk concerned the quest for a microscopic interpretation of the dramatic effects on the viscosity and other transport properties of silicate melts containing dissolved water (Kohn *et al*., 1989). In particular the water dissolution mechanism as a function of composition was addressed. It was noted that different dissolution mechanisms existed for framework aluminosilicate melts and aluminium-free melts. The speciation of water into H_2O and OH^- entities in the melt in either system was also noted to be highly temperature dependent.

Sabyasachi Sen (Aberystwyth) gave the last talk in the session on melts on the theme 'Temperature-dependent structural and dynamical changes in borate, borosilicate and boroaluminate liquids: high-resolution and high-temperature NMR studies'. This talk brought together the connection between the configurational entropy of a melt, local structural rearrangement and transport processes. An impressive array of NMR results on borate, borosilicate and boroaluminate melts and glasses revealed that local species redistribution could explain changes in the configurational entropy of low-alkali borate melts which exhibit 'strong' behaviour. However, sources of configurational entropy other than local rearrangement would be required to explain the more fragile borosilicate systems (Sen *et al*., 1998). High-temperature ^{29}Si and ^{11}B NMR experiments on borosilicate melts showed that close to the glass transition there was a divergence in the rates of motion of the network-forming cations of B and Si. This is indicative of relaxation and flow taking place over longer distance scales (Stebbins and Sen, 1998) and the presence of incipient phase separation.

The final session considered dynamics in the vibrational time scale. This subject was introduced by Stephen Elliott (Cambridge, Chemistry), with a talk entitled 'Low-frequency vibrational excitations in vitreous silica: vibrational localization, Ioffe-Regel limit, the Boson peak and all that'. This wide-ranging talk presented results from molecular dynamics simulations, which were aimed at understanding some of the issues associated with the lower-frequency range of the vibrational dynamics. In particular, the effects of structural disorder on the propagation of sound waves was explored, and how the nature of vibrations changes when the wavelength becomes comparable to interatomic distances (Taraskin and Elliott, 1998*a,b*, 1999*a,b*).

Mark Harris (Rutherford Appleton Laboratory) presented the experimental perspective in his talk on 'Floppy modes in crystalline and amorphous silicates by inelastic neutron scattering' (Harris *et al*., 2000). This talk covered both low-energy vibrations and the origin of the Boson peak at ~5 meV, and showed how many features in the low-energy vibrational spectra of amorphous silica and silicates are also seen in inelastic neutron scattering data from polycrystalline materials (Dove *et al*., 1997; Harris *et al*., 1999), which reiterates the similarities between amorphous and crystalline materials discussed earlier in the talks on structure (Gaskell, 2000; Keen and Dove, 2000).

The final talk was given by Martin Dove (Cambridge, Earth Sciences), who presented some theoretical ideas and computer simulations in his talked entitled 'Amorphous silica from the Rigid Unit Mode approach' (Dove *et al*., 2000). The main point was that the similarities in structure and dynamics of crystalline and amorphous phases can be understood from the perspective of the Rigid Unit Mode model. The work has also shown how amorphous silica can support

reversible large-amplitude changes in the structure, which may be identified with tunnelling modes (Hammonds *et al*., 1996; Dove *et al*., 1998, 1999; Trachenko *et al*., 1998).

In conclusion, a number of important points in the study of amorphous silicates were aired at the meeting. Amongst these was the fact that the similarities between amorphous and crystalline silicates extends to both structure and vibrational dynamics. The complementarity of experimental and computational methods also came across as a strong point, and in particular the use of techniques (neutron scattering, NMR, molecular dynamics simulations) that have only recently begun to flourish within the mineralogical community.

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