

# The Structural Role Of Lead In Network Glasses

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Lead monoxide, PbO, has been described as both a glass network *modifying* oxide, playing a role analogous to alkaline earth oxides, *and* as a glass network *forming* oxide, the archetype of which is SiO<sub>2</sub>. The latter attribute stems from the fact that oxide glasses with very high molar concentrations of PbO can be obtained, for example, 83.3PbO.16.7SiO<sub>2</sub> (mol.%) glass has been obtained by twin roller-quenching [1]. Pure PbO glass cannot, however, be obtained from the melt at presently accessible cooling rates. The two structural roles of PbO are related to the stereochemical activity of a non-bonding electron lone-pair (LP) associated with the Pb<sup>2+</sup> cation, where an active LP results in a glass-former site with highly asymmetric coordination to oxygen atoms and low coordination number. Diffraction experiments on binary lead phosphate, silicate and vanadate glasses [2] indicate that the local structure about the Pb<sup>2+</sup> cations is more strongly a function of the nature of the glass-forming partner oxide than the concentration of PbO in the glass, despite earlier claims to the contrary [3].

To shed further light on the local structure around Pb in oxide glass systems, both the compositional range of binary systems can be expanded, and the range of binary systems conducive to glass formation explored. The first point is addressed in the present work using lead silicate glasses formed by rapid roller-quenching. Concentrations of up to 80 mol.% PbO allow, for the first time, exploration of the structure in lead silicate glasses in the regime above 67 mol.% PbO - the theoretical limit of glass formation if every added Pb<sup>2+</sup> cation contributes two non-bridging oxygen atoms towards the depolymerisation of the silicate subnetwork. The second point is addressed using a comprehensive set of 18 lead germanate glass compositions, from pure vitreous GeO<sub>2</sub> up to 75 mol.% PbO. This system combines many desirable optical properties and has not before been subject to detailed study by x-ray diffraction.

The methodology adopted is a multi-technique approach, necessary for extracting reliable structural information from highly disordered systems. The lead silicate glasses have previously been studied using spectroscopic techniques [1] including <sup>29</sup>Si NMR. Both the lead silicate and lead germanate systems have been studied using total neutron diffraction (ND), where scattering data with good signal-to-noise at high momentum transfers was collected using the GEM diffractometer [4] at the ISIS pulsed neutron source in the UK. The resulting real-space correlation functions have excellent resolution and are dominated by pair-correlations involving oxygen, i.e. Si-O, Ge-O, Pb-O and O-O. Information on the distribution of *short* Pb-O bonds is available from the neutron diffraction data alone, but overlap with O-O correlations means that the full distribution, including any longer Pb-O bonds present, is obscured. High energy x-ray diffraction provides the ideal means to extract such information, because pair-correlations involving lead dominate the coherent x-ray diffraction. The approximate Pb-Pb distances should also be apparent in x-ray correlation functions, since this term dominates at most of the compositions studied.

The use of high energy synchrotron x-rays is necessary for highly absorbing materials, such as the lead containing glasses used here. Tuning the monochromator of beamline BW5 to pass x-rays of 85 keV allowed for a huge reduction of the absorption cross-section of the glasses as compared to that at typical laboratory x-ray source energies, whilst also avoiding fluorescence excitation above the 88 keV Pb K-edge. The precise x-ray wavelength was calibrated using a LaB<sub>6</sub> standard. High quality data were collected for 25 glass powders in 1.5 mm diameter thin-walled quartz glass

capillaries, as well as an empty capillary and background scan. A Ge-detector was stepped over the angular range  $0.5 < 2\theta < 32.0^\circ$ , giving access to momentum transfers of magnitude up to  $23.8 \text{ \AA}^{-1}$ . Different attenuators were used over different sections of the angular range to avoid detector saturation on account of the natural form-factor dependence of the scattering. Raw scattering data were screened for bad points, normalised to the monitor counts, scaled according to the attenuator used, and corrected for detector dead-time and the experimental geometry prior to being further corrected and reduced using the GudrunX [5] software. GudrunX was used to correct for polarisation, Compton scattering, multiple scattering and attenuation in both sample and capillary, as well as to subtract the self-scattering, background and capillary contribution to the data. No fluorescence correction was necessary due to the choice of incident x-ray energy. Normalisation by the Krogh-Moe/Norman method yields scattering data on an absolute scale. The software performs the normalisation and corrections iteratively to allow for scaling by a calibration factor accounting for unknown detector efficiencies. Suitable Fourier transforms of the extracted distinct scattering,  $i(Q)$ , yielded the real-space correlation functions  $T(r)$ .

An example  $T(r)$  for the 80 mol.% PbO lead silicate glass is shown in figure 1. The corresponding  $i(Q)$ , shown inset, is typical in appearance to that for all of the high-lead glasses. These functions are strongly dominated by Pb-Pb scattering, which gives rise to the sharp peak in  $T(r)$  at  $3.72 \text{ \AA}$ . The smaller, asymmetric peak between 2 and 3  $\text{\AA}$  is dominated by the Pb-O pair function and the right panel of figure 1 shows the deconvolution of this based upon fitting of symmetric correlations to the ND  $T(r)$ . The residual clearly shows a peak at  $2.65 \text{ \AA}$ , fitting of which to a single Pb-O peak function yields a coordination number,  $n_{\text{PbO}}$ , of 0.66, and a sum total  $n_{\text{PbO}} = 3.80$ , with some small residual remaining. The combination of the ND and XRD data clearly shows an asymmetric distribution of Pb-O bonds in this glass and future work will involve extraction of compositional trends as well as comparison of isocompositional silicate and germanate analogues via calculation of x-ray/neutron difference functions and empirical atomistic modelling, driven by the ND and XRD scattering data.

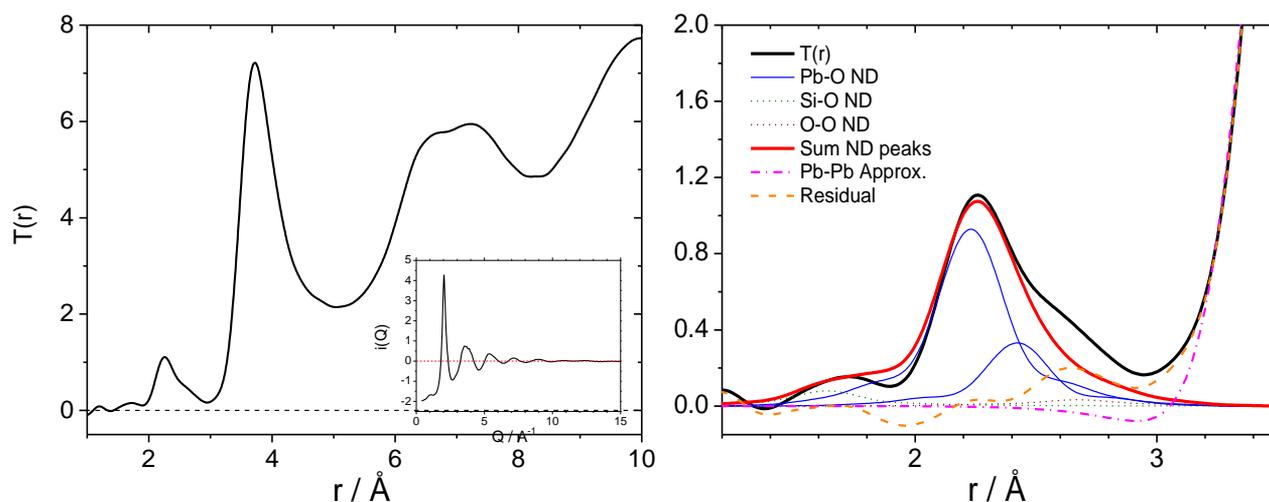


Figure 1: X-ray  $T(r)$  for  $80\text{PbO}.20\text{SiO}_2$  glass over an extended (left panel) and reduced (right panel) range. Inset shows the distinct scattering prior to Fourier transformation with maximum momentum transfer of  $23.64 \text{ \AA}^{-1}$ . Also shown in the right panel are correlations calculated from fits to the ND  $T(r)$ , their sum, an approximate Pb-Pb correlation and residual, which shows a peak at  $2.65 \text{ \AA}$ , attributed to longer Pb-O bonds.

## References

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