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Letter to the Editor

On the germanium–oxygen coordination number in lead germanate glasses

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ABSTRACT

Knowledge of the Ge–O coordination number, n_{GeO} , in germanate glasses is of paramount importance for understanding the germanate anomaly and relating the glass structure to its thermophysical properties. By careful measurement using high resolution neutron diffraction on two samples of 40PbO.60GeO₂ glass, it is clearly demonstrated that the average Ge–O coordination number, n_{GeO} , is much less than the value, 4.77(5), previously obtained by use of neutron diffraction [Umesaki et al., *Physica B* 213 (1995) 490]. However, it is also clear that n_{GeO} is still significantly greater than four (~4.1), and this is supported by the observed asymmetry of the Ge–O peak in the real-space total correlation functions. The average Pb–O coordination number is a little in excess of three, typical of Pb²⁺ with a sterically active lone-pair of electrons.

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1. Introduction

The thermophysical properties of binary germanate glasses display a behaviour, known as the germanate anomaly, which involves a maximum or minimum at a particular composition. Examples of such observations in PbO–GeO₂ glasses include a minimum in molar volume [1] and maxima in resistivity [1] and elastic moduli [2] at ~30 mol% PbO. The average Ge–O coordination number, n_{GeO} , is thought to play a key role in the germanate anomaly [3,4].

Lead germanate glasses have shown much promise as optical materials, such as low loss fibres [5–7], Raman amplifiers [8], and hosts for optically active ions [9], among others [10–12]. However, despite numerous studies of the structure of PbO–GeO₂ glasses using neutron [13,14] and x-ray [15–17] diffraction, ²⁰⁷Pb NMR [18], Ge K-edge [18–21] and Pb L_{III}-edge [18,19,22] EXAFS, Raman spectroscopy [19,23,24] and molecular dynamics simulations [17,21,22,25,26], there is no consensus within the literature as to the detailed structural behaviour of Ge⁴⁺ and its (average) coordination states. To illustrate this point, Fig. 1 shows values of n_{GeO} reported by various authors, which are not only quantitatively inconsistent with each other, but which also show qualitative differences, i.e. for some studies n_{GeO} passes through a maximum as the PbO content increases, whilst in other studies it was found that n_{GeO} increases monotonically. However, in order to understand the structural mechanisms involved in the germanate anomaly, it is necessary to know reliably if n_{GeO} exceeds four, and if so by how much.

Some of the highest values of n_{GeO} have been reported for the 40PbO.60GeO₂ glass composition (up to 4.77(5) [13,14]), and the range of reported values is also large (0.87) (Fig. 1). This Letter presents neutron diffraction (ND) measurements of n_{GeO} in samples of 40PbO.60GeO₂ glass, including a re-measurement of the sample used in the only previously published ND study of lead germanate glasses [13,14]. We thereby resolve some of the apparent inconsistencies within the literature.

2. Experimental

2.1. Glass preparation

A sample of 40PbO.60GeO₂ glass was prepared by mixing quartz GeO₂ (Alfa Aesar, 99.98%) and Pb₃O₄ (Aldrich, 99%) in sufficient quantities to yield 20 g of glass. The powders were well mixed and placed into a large 90%Pt/10%Rh crucible inside an electric furnace at room temperature, under an air atmosphere. The furnace temperature was increased at a rate of 600 °C/h up to 1000 °C, and then held for 25 min. The melt was then quenched by pouring onto a steel plate and quickly pressing the upper surface with a brass plate to provide rapid quenching, of the order 10³ °C/s. The glass composition was estimated to be 38.3(3) mol% PbO by EDX spectroscopy, or 39.69(5) mol% PbO assuming excess mass lost during melting to be due to volatilisation of PbO. The latter value is used in all subsequent analyses. The same 5.5 mm diameter 40PbO.60GeO₂ glass rod as used by Umesaki et al. [13,14] was also obtained for re-measurement. The fictive temperatures, T_f , of the two 40PbO.60GeO₂ samples were measured to be 412(2) °C (rod) and 414(2) °C (plate quench) using differential scanning calorimetry (Mettler Toledo STAR^c), at a heating rate of 600 °C/h, and the analysis

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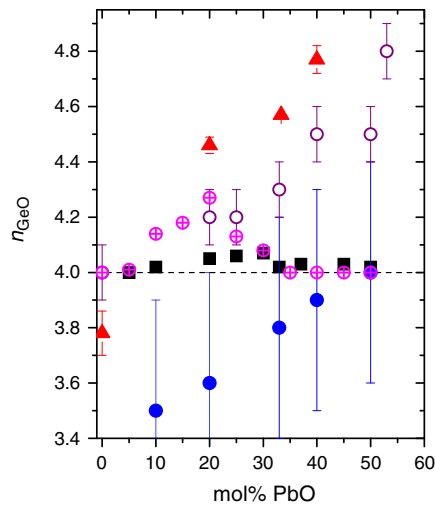


Fig. 1. Ge–O coordination numbers as a function of PbO–GeO₂ glass composition, as reported in the literature using neutron diffraction [13,14] (triangles), Ge K-edge EXAFS (circles: filled [21], open [19], with crosses [20]) and classical molecular dynamics [25] (squares).

method of Moynihan et al. [27]. Helium gas pycnometry (Micromeritics Accupyc 1330) was used to determine the mass and number densities of both 40PbO.60GeO₂ samples, as given in Table 1.

A sample of pure GeO₂ glass was prepared by melting quartz GeO₂ from the same source and under the same conditions as for the 40PbO.60GeO₂ sample, but with an increased maximum temperature of 1400 °C. After 45 min at this temperature, the melt was quenched to a glass by immersing the base of the crucible in water. The density for pure GeO₂ in Table 1 is an average of the literature values from the SciGlass database [28].

2.2. Neutron diffraction

Time-of-flight ND measurements were made using the GEM [29] diffractometer at the ISIS Facility, Rutherford Appleton Laboratory, UK. Small pieces (a few mm³) of the plate-quenched 40PbO.60GeO₂ glass and pure GeO₂ were each loaded into a cylindrical, thin walled (25 μm) vanadium container of internal diameter 8.3 mm. The 40PbO.60GeO₂ glass rod [13,14] was measured without a container. Measurements were also performed on an empty vanadium container, the empty instrument, and an 8.34 mm diameter vanadium rod for normalisation purposes and to allow for subtraction of background signals.

Table 1

Details of the first Ge–O and Pb–O peaks in $T^N(r)$ (and densities) for pure GeO₂ and 40PbO.60GeO₂ glasses.

| Parameter | Pure GeO ₂ | Plate-quenched 40PbO.60GeO ₂ | Re-measurement of 40PbO.60GeO ₂ glass rod | Reported by Umesaki et al. [13,14] for 40PbO.60GeO ₂ |
|---|------------------------|--|---|--|
| n_{GeO}^a | 3.98(1) | 4.06(3) | 4.17(3) | – |
| n_{GeO}^b | 3.99(4) | 4.00(3) | 4.11(3) | 4.77(5) |
| r_{GeO}^a (Å) | 1.7389(6) | 1.766(6) | 1.767(4) | 1.772 ^c |
| $r_{\text{GeO}}(1)^b$ (Å) | 1.7382(6) | 1.7556(3) | 1.7584(3) | 1.7572 |
| $r_{\text{GeO}}(2)^b$ (Å) | – | 1.944(4) | 1.967(5) | 1.877(15) |
| $\langle u_{\text{GeO}}^2 \rangle^{1/2}$ (1) ^b (Å) | 0.043(1) | 0.0540(4) | 0.0555(4) | 0.054 |
| n_{PbO}^b | – | 3.10(9) | 3.3(1) | 6.23(13) |
| r_{PbO}^b (Å) | – | 2.321(4) | 2.336(5) | 2.336(6) |
| $\langle u_{\text{PbO}}^2 \rangle^{1/2b}$ (Å) | – | 0.126(3) | 0.128(4) | 0.121(4) |
| Density (g cm ⁻³) | 3.65(2) ^d | 6.19(6) | 6.22(6) | 5.951 |
| Number density (atoms Å ⁻³) | 0.0630(6) ^d | 0.0640(7) | 0.0640(7) | 0.0613 |

^a By integration of $rT^N(r)$ over $1.50 \leq r \leq 2.06$ Å.

^b From fitting peaks to $T^N(r)$.

^c Area weighted average from two fitted peaks.

^d Average of values from SciGlass database [28].

3. Results

Data reduction and correction procedures were performed as described previously [30], using the GudrunN [31] software and the Atlas [32] suite of programmes, and the resulting distinct scattering functions, $i^N(Q)$, are displayed in Fig. 2. The distinct scattering for each sample was extrapolated to zero momentum transfer (see inset of Fig. 2) by fitting a symmetric function of the form $A + BQ^2$ to data at low Q (fitting in the region below 0.7 \AA^{-1} for the 40PbO.60GeO₂ samples). The sine Fourier transform of the interference function, $Qi^N(Q)$, performed using the Lorch [33] modification function $M(Q)$ with a maximum momentum transfer $Q_{\text{max}} = 40 \text{ \AA}^{-1}$, gives the differential neutron correlation function [34],

$$D^N(r) = \frac{2}{\pi} \int_0^{Q_{\text{max}}} Qi^N(Q)M(Q) \sin(rQ) dQ. \quad (1)$$

The total neutron correlation function, $T^N(r) = D^N(r) + T^0(r)$, is then obtained by the addition of an ‘average density’ term by

$$T^0(r) = 4\pi r g^0 \langle \bar{b} \rangle_{\text{av}}^2 = -S^0 r, \quad (2)$$

where g^0 is the atomic number density, and $\langle \bar{b} \rangle_{\text{av}}$ is the average coherent neutron scattering length. For a peak in $T^N(r)$ at distance r_{ll} and with area A_{ll} , due to the element pair $l - l'$, the average coordination number is

$$n_{ll} = \frac{r_{ll} A_{ll}}{(2 - \delta_{ll}) c_l \bar{b}_l \bar{b}_{l'}}, \quad (3)$$

where c_l is the atomic fraction for element l and δ_{ll} is the Kronecker delta. In order to obtain accurate coordination numbers from diffraction on a glass, it is essential that the total correlation function, $T^N(r)$, is normalised as well as possible and that the denominator in Eq. (3) is known as accurately as possible.

In the low r region before the first peak, in principle $T^N(r)$ is zero (i.e. there are no interatomic distances below a certain minimum) and $D^N(r)$ should equal $-T^0(r)$; in practice $D^N(r)$ is expected to oscillate about $-T^0(r)$, due to the presence of termination ripples and experimental noise. However, even after a full and careful set of experimental corrections have been performed, the measured differential correlation function, $D_{\text{meas}}(r)$, may not agree closely with $-T^0(r)$. For such datasets, we have developed a procedure whereby the first peak in $D_{\text{meas}}(r)$ (or the leading edge of the first peak, if it is an asymmetric peak) is fitted (usually by a single peak) together with a linear term, $-S_{\text{fit}} r$, where S_{fit} is a constant. If there are no interatomic distances in the region after the

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