



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Bonding and structure in network glasses

Alex C. Hannon

ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, UK

ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form 17 February 2016

Accepted 18 April 2016

Available online xxx

Keywords:

Glass structure

Bonding

Diffraction

ABSTRACT

The aim of this paper is to foster greater use of the concepts of electrostatic bond strength and bond valence in the interpretation of glass structure. Methods of applying these concepts to diffraction data to investigate the atomic bonding environments in network glasses are presented, and illustrated using neutron diffraction results on lead gallate glasses, which show that gallium atoms are tetrahedrally coordinated by oxygen, and lead atoms have an average oxygen coordination number between three and four. It is of great value to consider the oxygen anion-centred coordination numbers, as well as the cation-centred coordination numbers. Due to the requirement for charge balance, the dominant coordination for oxygen in lead gallate glasses is 3-coordinated, with both OGa_2Pb and OGaPb_2 motifs. A small fraction ($\sim 1\text{--}2\%$) of the oxygen atoms are bonded to four cations, either as $\text{OGa}_2\text{Pb}_0 + 2$ or $\text{OGaPb}_1 + 2$. By means of a valence sum function, it is shown that the number of long ($\sim 2.8 \text{ \AA}$) Pb–O bonds is not significant, and thus the number of Pb atoms on symmetric sites (with a stereochemically inactive lone pair of electrons) is not significant. It is shown that, even though glasses and crystals obey the same bonding rules, the structure of a glass can differ from that of a closely related crystal.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The interactions between the atoms (interatomic potentials, orbitals, etc.) in a solid are the same, whether it is a crystal or a glass. Consequently, in the interpretation of experimental results on glass structure, it is often assumed that the details of the structure (especially the local order) are the same as in a related crystal structure [1,2]. However, although the interactions between the atoms are the same, this does not necessarily imply that the details of the structure are exactly the same. Thus, it is preferable to interpret experimental results on glass structure by assuming that the interatomic bonding obeys the same rules as in crystals, instead of assuming that the local order is exactly the same.

The concepts of electrostatic bond strength (EBS) [3] and bond valence (BV) [4] are widely applied in structural studies of crystalline materials, and have proved to be immensely powerful (e.g., see recent studies of $\text{Pb}_9\text{Al}_8\text{O}_{21}$ [5] and $\alpha\text{-TeO}_2$ [6]). Contrastingly, with a few exceptions [7–22], these concepts have not been used in the interpretation of diffraction studies of glass structure. Nevertheless, in recent years the author and co-workers have successfully made use of EBS and BV to gain understanding of the structure of network glasses [23], including SnO–SiO₂ glasses [24], CaO–Al₂O₃ glasses [25,26], Cs₂O–GeO₂ glasses [27,28], PbO–Al₂O₃ glasses [29], SnO–Al₂O₃–B₂O₃ glasses [30], TeO₂–B₂O₃ glasses [31], Tl₂O–GeO₂ glasses [28,32,33], K₂O–TeO₂ glasses [34], and PbO–GeO₂ glasses [35]. This paper presents methods of applying the concepts of EBS and BV to specific sites in glass structure, illustrated

by neutron diffraction data for lead gallate ($\text{PbO-Ga}_2\text{O}_3$) glasses [36,37]. The methods described here are of application to any kind of network glass. However, they are the most highly developed for oxide glasses, and hence they are illustrated using experimental results for an oxide glass system.

The concept of EBS has surprisingly played almost no role in the interpretation of diffraction results on glass, but it has sometimes been used to interpret results from other experimental techniques [38], such as NMR [39–41]. The EBS concept is very simple, in that the only structural parameter considered is coordination number (see Section 3), whereas the BV concept is more sophisticated, because it considers interatomic distance as well as coordination number. Diffraction studies of glass yield information on both coordination number and interatomic distance, and hence the BV concept is well-suited to the interpretation of glass diffraction. It is thus surprising that BV is also not widely used to interpret glass diffraction studies.

Although it is well known, it is helpful to give here a brief description of the Zachariasen–Warren continuous random network (CRN) model for oxide glass structure [42,43]. In this model, the structure of a glass, composed of a glass-forming oxide AO_x (e.g. SiO₂), involves AO_n polyhedra (with a low value of n , say 3, 4, 5, or perhaps 6) that connect together by the sharing of oxygen corners between two polyhedra. There is a random distribution of bond and torsion angles at the shared oxygen bridge, so that the units connect together to form a network that fills three-dimensional space, and is random and continuous. Zachariasen [42] proposed a set of rules, describing which units are able to form glass structures, and how these units connect together, based upon what was known from X-ray diffraction about how similar units connect together in crystal structures. The strongest support for the CRN model

E-mail address: alex.hannon@stfc.ac.uk.

has come from diffraction studies of glasses, beginning with Warren's seminal X-ray diffraction studies [43]. The structural role of modifier oxides (e.g. Na₂O) is much less well defined in the CRN model, according to which the introduction of modifier into a glass network causes oxygen bridges to be broken, by the formation of non-bridging oxygens (NBOs), with the modifier cations filling suitably sized holes in the CRN.

2. Neutron diffraction

Pulsed neutron diffraction (ND) is arguably the single most important experimental technique for probing the structure and bonding in glasses [44]. As a consequence of its relatively high real-space resolution, and the ability to normalise the results reliably, pulsed ND can yield a combination of coordination numbers and bond lengths which is more accurate than provided by any other method [35,44]. Hence pulsed ND results for lead gallate glasses, $x\text{PbO} \cdot (100-x)\text{Ga}_2\text{O}_3$ [36,37], are used to illustrate the methods of interpreting glass structural data which are described in this paper. The experimental data used here are available from the ISIS Disordered Materials Database [45]. A further advantage of ND for oxide glasses is that it is much better than X-ray diffraction at locating light (i.e. low atomic number) oxygen atoms in the presence of heavy (e.g. Pb) atoms.

The former Liquids and Amorphous diffractometer, LAD [46], at the ISIS Facility pulsed neutron source was used to measure the ND patterns of two glasses with compositions of 66.6 and 80.1 mol% PbO. The diffraction patterns were measured up to a high maximum momentum transfer, Q_{max} , of 41 Å⁻¹, resulting in a narrow resolution width in real-space, and the other details of the experiment and the data analysis are described elsewhere [36,37]. Fig. 1 shows the total neutron correlation function [44,47–49], $T^{\text{N}}(r)$, measured for each of these glasses by Fourier transformation of the diffraction pattern, using the Lorch modification function [50]. Peaks in the correlation function indicate frequently occurring interatomic distances [44,47–49]. Table 1 gives the interatomic

distances, r_{jk} , root mean square variations in interatomic distance, $\langle u_{jk}^2 \rangle^{1/2}$, and coordination numbers, n_{jk} , obtained from the peak fits [37,51] shown in Fig. 1. The coordination number, n_{jk} , is the average number of atoms of type k that are bonded to (i.e. within a specified distance range from) an origin atom of type j [52,53]. The total neutron correlation function is a weighted sum of partial correlation functions,

$$T^{\text{N}}(r) = \sum_{j,k} c_j \bar{b}_j \bar{b}_k t_{jk}(r) = \sum_j c_j (\bar{b}_j)^2 t_{jj}(r) + \sum_{\substack{j,k \\ j>k}} 2c_j \bar{b}_j \bar{b}_k t_{jk}(r). \quad (1)$$

$t_{jk}(r)$ is the partial correlation function for origin atoms of element j , and coordinating atoms of element k . The summations are over the elements in the sample, and c_j and \bar{b}_j are the atomic fraction and coherent neutron scattering length for element j . If a peak in $T^{\text{N}}(r)$ at distance r_{jk} , due to j - k atom pairs, has area A_{jk} , then the corresponding coordination number is

$$n_{jk} = \frac{r_{jk} A_{jk}}{(2 - \delta_{jk}) c_j \bar{b}_j \bar{b}_k}. \quad (2)$$

For well-defined peaks in the correlation function, pulsed ND is now able to measure the coordination number reliably with an accuracy of ~1% [27,35,44], and hence the measured Ga-O coordination numbers in Table 1 are essentially four. Furthermore, there is only a very slight composition-dependence of the Ga-O bond lengths in Table 1; if there were a change with composition of the average Ga-O coordination number (e.g. if a fraction of Ga were 6-coordinated), then there would be a significant composition-dependence of the mean bond length [27]. The third peak in the correlation function occurs at a distance ~3.15 Å which is consistent with the O-O distance in a regular GaO₄ tetrahedron, and thus the experimental evidence is highly consistent with a structure in which all of the gallium atoms are tetrahedrally coordinated by oxygen [36,37]. However, the Pb-O correlation is more complex, in that it has an asymmetric peak in the correlation function that changes with composition. For the fits (with the parameters given in Table 1), two components (labelled Pb-O I and Pb-O II) were fitted to the Pb-O contribution to the correlation function. This is not a unique fit, and the peak positions obtained should not be interpreted as discrete, well-defined bond lengths. Nevertheless, this fit is a useful way to parameterise the asymmetric Pb-O distribution, and as is shown below it is essential to include the longer distance contribution in order to obtain chemically reasonable results [23]. The total Pb-O coordination number is between three and four, and it is lower for the high lead composition.

As is conventional for diffraction studies of glasses, the coordination numbers in Table 1 are given with cations as the origin atom, j . However, the coordination numbers may be converted so that the origin atom is an anion, k , according to the identity [44]

$$n_{kj} = \frac{c_j}{c_k} n_{jk}, \quad (3)$$

where c_j is the atomic fraction for element j . (The unlike-atom partial correlation functions $t_{jk}(r)$ and $t_{kj}(r)$ are not independent; this may be understood simply by considering that the number of j - k bonds is equal to the number of k - j bonds, provided that the same distance range defines both k - j and j - k bonds.) Table 2 gives the oxygen-centred coordination numbers calculated according to Eq. (3). In addition to the coordination numbers corresponding to the individual peaks of the fit, Table 2 also gives the total O-Pb coordination number, and the total O-X coordination number, where X represents any cation, Ga or Pb. It is notable that the total coordination number, n_{OX} , is very close to three for both glass compositions. This value may be understood by means of a consideration of the electrostatic bond strength of the bonds to an oxygen atom, as is discussed below.

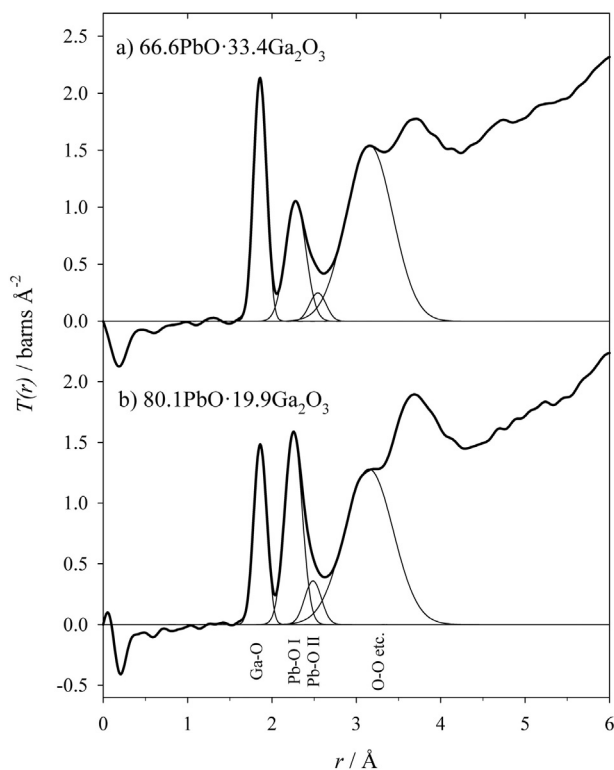


Fig. 1. The total neutron correlation function, $T^{\text{N}}(r)$, for lead gallate glasses with 66.6 mol% PbO (upper) and 80.1 mol% PbO (lower). The experimental measurement is shown as a thick line, and the individual components of the fit are shown as thin lines.

Download English Version:

<https://daneshyari.com/en/article/5441461>

Download Persian Version:

<https://daneshyari.com/article/5441461>

[Daneshyari.com](https://daneshyari.com)