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Alkali environments in tellurite glasses

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ABSTRACT

Neutron diffraction measurements are reported for five binary alkali tellurite glasses, $xM_2O \cdot (100 - x)TeO_2$ (containing 10 and 20 mol% K_2O, 10 and 19 mol% Na_2O, and 20 mol% $^7Li_2O$), together with ^{23}Na MAS NMR measurements for the sodium containing glasses. Differences between neutron correlation functions are used to extract information about the local environments of lithium and sodium. The Na–O bond length is 2.37(1) Å and the average Na–O coordination number, n_{NaO}, decreases from 5.2(2) for $x = 10$ mol% Na_2O to 4.6(1) for $x = 19$ mol% Na_2O. The average Li–O coordination number, n_{LiO}, is 3.9(1) for the glass with $x = 20$ mol% Li_2O and the Li–O bond length is 2.078(2) Å. As x increases from 10 to 19 mol% Na_2O, the ^{23}Na MAS NMR peak moves downfield, confirming an earlier report of a correlation of peak position with sodium coordination number. The close agreement of the maximum in the Te–O bond distribution for sodium and potassium tellurite glasses of the same composition, coupled with the extraction of reasonable alkali coordination numbers using isostoichiometric differences, gives strong evidence that the tellurium environment in alkali tellurites is independent of the size of the modifier cation used.

1. Introduction

The local structure of alkali M_2O–TeO_2 glasses (M = Li, Na, and K) has been studied extensively using neutron diffraction [1–5], X-ray diffraction [6,7], EXAFS [7,8], Raman scattering [7,9,10], NMR [2,11–13] and RMC modelling [2,14]. In these studies, particular emphasis was placed on determining the local environment of tellurium and there is a general consensus that the average tellurium coordination number, n_{TeO}, decreases as an oxide modifier is added to the glass network, the change being driven by the bonding requirements of the modifier. In a silicate glass, the number of non-bridging oxygens (NBOs) provided by 1 unit of M_2O cannot support the number of M–O bonds needed to satisfy the bonding requirements of the M^+ ions, necessitating the formation of less favourable bonds to bridging oxygens (BOs), as well as M–NBO bonds. However, in the tellurite glass system the local tellurium environment may be either pseudo-bipyramidal, [TeO_4E], or pseudo-tetrahedral, [TeO_3E] (where E denotes a lone-pair of electrons). The former are found in pure crystalline α-TeO_2 [15], whilst the latter have an arrangement of atoms similar to that present in M_2TeO_3 crystals [16–18]. The change in the local environment of a Te atom from [TeO_4E] to [TeO_3E] provides an additional NBO in the network, and hence reduces the total number of unfavourable M–BO bonds needed to fulfil the bonding requirements of the M^+ ions [19].

A detailed knowledge of the behaviour of the M–O coordination is important for the development of a reliable model for the composition-dependence of the Te–O network in M_2O–TeO_2 glasses [19]. However, there are few direct observations of the local environment of an *alkali* ion in alkali tellurite glasses and the results of these studies are now summarised. A neutron diffraction study of lithium tellurite glasses [1] was interpreted as showing that lithium is coordinated by 4 oxygen atoms with a Li–O bond length of ~2 Å. For sodium tellurite glasses, a ^{23}Na dynamic angle spinning (DAS) NMR study showed that the coordination number of sodium drops from ~5.8 to 5.2 with increasing Na_2O content [11]. Molecular orbital calculations have also been performed for cluster models of sodium tellurite glasses [4] and Na–O coordinations of 3, 4 and 5 were found. It was concluded that the 5-coordinated environment is more representative of the glass, based on the results of the previous ^{23}Na NMR study [11]. An extended X-ray absorption fine structure (EXAFS) and X-ray diffraction (XRD) study of two potassium tellurite glasses [7] indicated that the K–O coordination number, n_{KO}, is 6, with a K–O bond length of 2.71 Å. However, a second study, using neutron and X-ray diffraction to investigate three potassium tellurite glasses, determined that the K–O contribution to the results was too small to allow the coordination to be determined. To interpret the results, an assumed K environment of 3 oxygen atoms at 2.67 Å and 4 oxygen

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atoms at 2.88 Å was used [5]. Finally, a series of Reverse Monte Carlo (RMC) simulations of neutron and X-ray diffraction data for lithium, sodium and potassium tellurites has been performed [3], but the local environment of the alkali atoms was not determined; instead information from related crystal structures ($Na_2Te_4O_9$ [20], $K_2Te_4O_9$ [21], $Li_2Te_2O_5$ [22]) was used to constrain the coordination numbers and bond lengths of the alkali ions, in order to calculate the Te–O bond distribution for Li, Na and K modified glasses. The results obtained were difficult to interpret, showing no trends with modifier type, or concentration. This is likely to be due to the difficulties in deconvoluting the overlapping M–O and Te–O components in the correlation function, $T(r)$.

Neutron diffraction data are presented here for a series of alkali tellurite glasses, $x\mathrm{M_2O} \cdot (1-\mathrm{x})\mathrm{TeO_2}$, modified by 10 and 20 mol% K_2O, 10 and 19 mol% Na_2O, and 20 mol% $^7Li_2O$. Isostoichiometric difference functions, $\Delta T(r)$, for glasses of equivalent x but different M, may remove the Te–O and Te–Te contributions to $T(r)$, to leave only correlations arising from the modifier. However, this will only be the case if the Te–O bond distribution is independent of M. Several Raman studies of alkali tellurite glasses have shown that n_{TeO} is relatively unaffected by the size of modifying cation [10,23] and a quantitative model [19], proposed by the authors to predict the observed change in Te–O coordination number (measured by neutron diffraction) with potassium oxide content, is independent of the alkali coordination number, and hence alkali type. Therefore, the objectives of this study are two-fold; to extract information about the local environment of alkali ions in tellurite glasses and to investigate whether the Te–O environment in alkali tellurites is indeed independent of the modifier used.

2. Experimental detail

2.1. Sample preparation

Sodium tellurite glasses with nominal compositions of 10 and 20 mol% Na_2O were prepared at Warwick University by placing a suitable mixture of Na_2CO_3 (Alfa Aesar, 99.95 mol%) and TeO_2 (Alfa Aesar, 99.99 mol%) in Pt/Rh crucibles and heating to 800 °C, at a ramp rate of 5 °C/min. The glass melt was held at temperature for 15 min before being splat-quenched using steel plates. Density measurements were carried out using a Quantachrome micropycnometer with helium as the displacement fluid.

The lithium (Li20) and potassium (K10 and K20) tellurite glasses were made at Osaka Prefecture University, as described previously [7]. The potassium tellurites were made using K_2CO_3 and TeO_2 as precursors and the lithium tellurite glass was made using enriched $^7Li_2CO_3$. The reported lower limit of glass formation for lithium tellurites in older literature is about 13 mol% Li_2O [24]. Therefore, whilst it must be acknowledged that lower Li_2O containing glasses have subsequently been reported in the literature (see [10,23]) no attempt was made to produce a sample containing 10 mol% $^7Li_2O$ for this study.

2.2. Nuclear magnetic resonance

Quantitative ^{23}Na magic angle spinning (MAS) NMR spectra were recorded at Warwick University at an applied field of 14.1 T using a Varian 600 spectrometer operating at a Larmor frequency of 158.747 MHz. A known mass of sample was loaded into a 3.2 mm rotor which was subject to a spinning speed of 15 kHz in a Varian Chemagnetic probe. A single pulse program was used with a 0.7 μs pulse width and 1 s pulse delay (sufficiently long to give quantitative spectra). All the chemical shifts were referenced to the secondary reference, solid NaCl, at 7.2 ppm with respect to the primary reference, aqueous 0.1 M NaCl [25]. The Na content of each sample was determined by a comparison of its ^{23}Na signal with that from a known mass of sodium carbonate.

2.3. Neutron diffraction

Neutron diffraction measurements on the sodium tellurite glasses were made using the GEM diffractometer [26] at the ISIS Facility. Cylindrical 8.3 mm diameter vanadium containers with a wall thickness of 25 μm were used to contain the samples. The data were corrected using the Gudrun programme [27] and the Atlas suite of software [28], leading to the distinct scattering, $i(Q)$, shown in (Fig. 1). The former LAD diffractometer [29] at the ISIS Facility was used to measure $i(Q)$ for each of the potassium and lithium tellurite glasses (Fig. 1), in a 8.0 mm diameter container with a wall thickness of 25 μm. The experimental corrections were performed in the same way as for the sodium tellurite glasses, allowing the results to be directly compared. The neutron diffraction data, in both reciprocal- and real-space, are available from the ISIS Disordered Materials Database [30].

For each sample, the corrected $i(Q)$ was Fourier transformed (using the Lorch modification function [31] with a maximum momentum transfer, Q_{max}, of 35 $\mathrm{Å}^{-1}$) to yield the correlation function, $T(r)$ (see Hannon [32] for further theoretical details). A diffraction experiment is not element specific, and $T(r)$ is a weighted sum of all possible partial correlation functions, $t_{ll'}(r)$;

$$T(r) = \sum_{u'} c_l \bar{b}_l \bar{b}_{l'} t_{ll'}(r) \tag{1}$$

where c_l is the atomic fraction of element l, and $\bar{b}_l$ and $\bar{b}_{l'}$ are the coherent neutron scattering lengths for elements l and l' respectively. All the

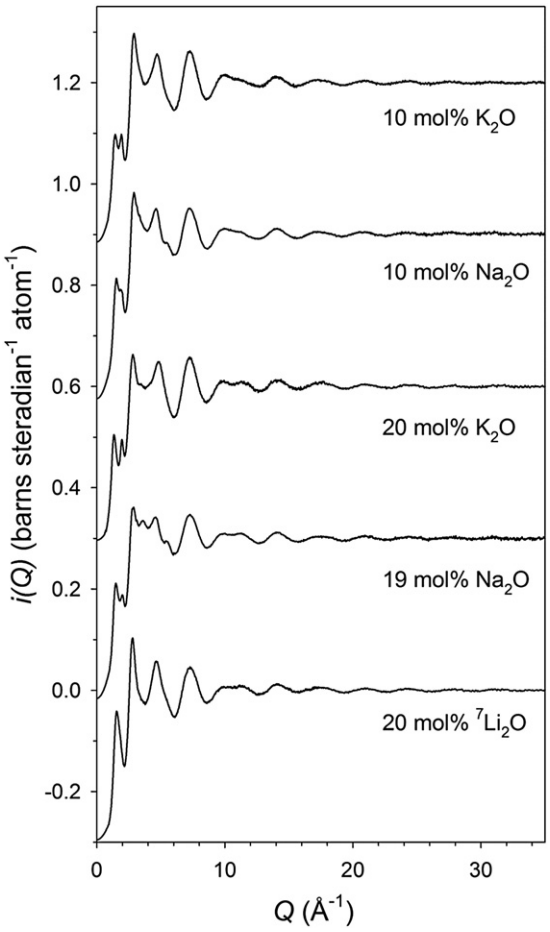

Fig. 1. The neutron distinct scattering, $i(Q)$, for binary alkali tellurite glasses containing 10 mol% K_2O, 10 mol% Na_2O, 20 mol% K_2O, 19 mol% Na_2O and 20 mol% $^7Li_2O$ respectively. Vertical shifts are shown between successive datasets for clarity.