Structural studies of Bi₂O₃-Nb₂O₅-TeO₂ glasses.

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Abstract

Bi₂O₃-Nb₂O₅-TeO₂ glasses show unusual annealing behavior with appearance of spherulites within the matrix glass structure for the Bi_{0.5}Nb_{0.5}Te₃O₈ composition. The textures resemble those found previously among polyamorphic Al₂O₃-Y₂O₃ glasses containing metastably co-existing high- and low-density phases produced during quenching. However the spherulites produced within the Bi₂O₃-Nb₂O₅-TeO₂ glass are crystalline and can be identified as an "anti-glass" phase related to β-Bi₂Te₄O₁₁. We used high energy synchrotron X-ray diffraction data to study structures of binary and ternary glasses quenched from liquids within the Bi₂O₃-Nb₂O₅-TeO₂ system. These reveal a glassy network based on interconnected TeO₄ and TeO₃ units that is related to TeO₂ crystalline materials but with larger Te...Te separations due to the presence of TeO₃ groups and non-bridging oxygens linked to modifier (Bi³⁺, Nb⁵⁺) cations. Analysis of the viscosity-temperature relations indicates that the glass-forming liquids are "fragile" and there is no evidence for a LLPT occurring in the supercooled liquid. The glasses obtained by quenching likely correspond to a high-density amorphous (HDA) state. Subsequent annealing above T_g shows mainly evidence for direct crystallization of the "anti-glass" tellurite phase. However, some evidence may exist for simultaneous formation of nanoscale amorphous spherulites that could correspond to the LDA polymorph. The quenching and annealing behavior of Bi₂O₃-Nb₂O₅-TeO₂ supercooled liquids and glasses is compared with similar materials in the Al₂O₃-Y₂O₃ system.

1. Introduction

The phenomenon of "polyamorphism" recorded among ceramic glass-forming liquids and the amorphous solids derived from them is receiving increasing attention as a potential route to producing new classes of nano- to microscale composite materials. It can be implemented alongside metastable crystallization by annealing or synthesis schedules used to achieve ceramic-matrix composites (CMCs) with controllable mechanical, thermal and other properties [1]. The concept of polyamorphism recognizes the existence of different forms of a given amorphous substance with substantial variations in their local structure and physical properties. Different polyamorphs of a given glassy material or another type of amorphous solid can be produced by varying the synthesis route, or by subjecting the material to intense radiation or physical stresses including high pressure. In some cases, an abrupt transformation between polyamorphic forms with different densities has been recorded upon subjecting the glass to high mechanical stresses, which resembles a first order phase transition in crystalline solids. Density driven phase transitions have also been observed among liquids as a function of the pressure or temperature, and one or other of the glassy polyamorphs can be recovered by quenching at different rates. That was the case described for a range of compositions with between approximately 20-35 mole% Y_2O_3 in the Al_2O_3 - Y_2O_3 (AY) system [2-7]. Those results provided first evidence for the existence of liquid-liquid phase transitions (LLPT) occurring at constant chemical composition, that had been predicted theoretically on thermodynamic grounds [8-12]. Such LLPT are now thought to occur among a wide range of liquid systems [11, 12].

During initial quenching experiments Aasland and McMillan observed that "spherulites" of a different phase appeared spontaneously and grew within the supercooled liquids[2]. The spherulites were identified as mainly glassy in nature, and their chemical compositions were found to be indistinguishable both from the initial bulk liquid and the surrounding glassy matrix formed upon quenching to ambient conditions. The result was interpreted as due to a LLPT occurring between high- and low-density liquid (HDL, LDL) phases in the supercooled state that was arrested during the quench to provide metastably coexisting low- and high-density polyamorphs (LDA, HDA). In further series of quenching experiments, Wilding et al prepared new samples that exhibited different curvilinear textures separating different amounts of the LDA and HDA polyamorphs. Calorimetry studies could establish that the two glassy forms had different glass transition (T_g) values, as well as a value of ~ 30 kJ/mol for the enthalpy of the transition between them. The glassy structures were studied using X-ray and neutron scattering, as well as micro-beam Raman spectroscopy [5, 6]. The spherulites were shown to have $\sim 4\%$ lower density than the surrounding glassy matrix[7]. The calorimetric data permitted a prediction of the viscosity-temperature relationships in the stable and supercooled liquid states that led to a description of the LDL phase as less "fragile" with more Arrhenian relaxation properties than HDL.

In pioneering experiments using X-ray scattering combined with containerless levitation techniques, N. Greaves and co-workers showed that the LLPT gave rise to unusual periodic thermal fluctuations [13-15]. However, although these results and their interpretation were questioned initially, the LLPT interpretation appears to be validated by careful analysis of the data [13, 16-19]. The occurrence of a LLPT in the supercooled liquid is also supported by polarizable ion (PI) MD simulations, that exhibit random but persistent fluctuations between low- and high-density states of the supercooled liquid as the critical temperature is approached[20].

1 In the case of the AY polyamorphs, some authors have questioned the glassy nature of the LDA
2 material, observing that crystalline peaks are observed in some microbeam X-ray diffraction studies
3 [21, 22]. In fact, Aasland and McMillan already noted the crystalline aspect of certain spherulites
4 obtained during their quench studies of AY liquids, and crystalline Bragg peaks were present in
5 diffraction data for samples containing a large fraction of the LDA polyamorph [2] (Fig. 1). In samples
6 prepared for a Raman spectroscopic study using a quench technique that led to large regions of the
7 LDA and HDA polyamorphs separated by curvilinear boundaries[6], crystals were clearly observed
8 growing away from certain parts of the LDA-HDA interface into the LDA phase (Fig. 1). It is clear that
9 metastable crystallization can and often does compete with the LLPT or polyamorphic HDA/LDA
10 transition phenomena, either during the initial cooling event or following annealing of the quenched
11 glasses.

12 The observations and discussions concerning polyamorphism are now linked to new phenomena
13 observed among glasses within the $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ system [23-25]. In this case, partially ordered
14 crystalline materials have been described in terms of the "anti-glass" model introduced by Burckhardt,
15 Trömel and co-workers[26] for tellurite systems with fluorite-related structures [24, 25]. In this
16 situation, a metal sub-lattice based on large cations such as Sr^{2+} , Pb^{2+} , Ln^{3+} ($\text{Ln} = \text{Y}$, lanthanide ions)
17 along with Te^{4+} form an ordered array that gives rise to crystalline Bragg peaks in X-ray diffraction
18 experiments, but the anion positions can be disordered, and both sites might be incompletely filled.
19 A similar situation occurs for cubic ZrO_2 stabilized by substitution of Y^{3+} on some cation positions along
20 with vacancies present on the O^{2-} sites. Such materials typically exhibit crystalline X-ray diffraction
21 patterns due to the heavy atoms, but can appear amorphous to Raman and IR spectroscopy due to
22 the inability of phonons to propagate through the anion-deficient lattice[27]. Similar sub-lattice
23 disordering occurs in systems including AgI, PbBr, LaF, fluorite- and more complex-structured
24 materials that are known to be solid electrolytes and (super)ionic conductors.

25 Bertrand et al. first described the formation of $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ glasses produced by melt quenching.
26 Upon annealing, one sample with composition $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ developed spherulitic structures that
27 appeared similar to the LDA-HDA polyamorphic textures observed by Aasland and McMillan for AY
28 glasses[23](Fig. 1). However, X-ray and electron diffraction examinations indicated that the
29 spherulites were crystalline, and Bertrand et al. interpreted their results in terms of an "anti-glass"
30 model due to Trömel et al. that had been developed for tellurite systems[23].

31 Crystalline $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ has a cubic structure related to TiTe_3O_8 . Other "anti-glass" materials in the
32 $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ system include $\beta\text{-Bi}_2\text{Te}_4\text{O}_{11}$ with a fluorite-related arrangement of Bi^{3+} and Te^{4+}
33 cations occupying 1/3 and 2/3 of the cation sites, respectively, and O^{2-} vacancies occurring on 1/12 of
34 the anion sites[28]. Bertrand et al. proposed that the quenched matrix glass was fully structurally
35 disordered, but the spherulites that appeared had an "anti-glass" structure containing positional
36 ordering of the metal cations on the fluorite lattice as demonstrated by Raman experiments[23].
37 However, further TEM investigations have now indicated that some of the nanometer-sized
38 spherulites that appeared might be amorphous. Those experiments are continuing and their analyses
39 will be reported elsewhere (G. Delaizir et al., in prep).

40 In order to begin discussion of the relative behaviour of the metastable phase relations and glass-
41 ceramic materials produced by quenching and annealing in the $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ and $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$
42 systems we undertook an examination of the glassy structures using high energy synchrotron X-ray
43 diffraction (HE-XRD) techniques. We obtained data for fully glassy as well as partially recrystallized
44 samples along the $\text{TeO}_2\text{-Bi}_2\text{O}_3$ and $\text{TeO}_2\text{-Nb}_2\text{O}_5$ joins and within the ternary $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ system.
45 The glassy XRD data were analysed in terms of pair distribution functions to provide a first view of the

glass structure as it evolved from the parent TeO₂. The data do not reveal any rapid changes with composition that might indicate that a polyamorphic transition might have taken place. Instead, the XRD results and their analysis indicate that the glass structures can be extrapolated from the high temperature liquids existing prior to the quench. We then examine the viscosity-temperature relationships combining data for molten TeO₂ with new measurements for a Bi₂O₃-Nb₂O₅-TeO₂ supercooled liquid just above T_g. The two data sets can be fit by a common Volger-Tamman-Fulcher (VTF) curve indicating little dependence of the "fragility" (i.e., deviation from Arrhenius behaviour) is maintained throughout the compositional series. No evidence for a LLPT is found, by comparing with similar viscosity-temperature relations for the Al₂O₃-Y₂O₃ system.

2. Experimental

High energy X-ray diffraction (HE-XRD) data were obtained over a wide Q range for three series of tellurite glasses. TeO₂-Bi₂O₃, TeO₂-Nb₂O₅ and TeO₂-Bi₂O₃-Nb₂O₅ samples were prepared from mixtures of high purity TeO₂, Bi₂O₃ and Nb₂O₅ powders melted at 850°C in Pt crucibles and quenched by dipping the bottom of the crucible in water. Along the TeO₂-Bi₂O₃ binary join, glasses containing no distinguishable crystalline Bragg peaks could only be prepared very close to the TeO₂ composition (98 mole% TeO₂). Glass formation was found to extend further along the TeO₂-Nb₂O₅ binary, up to ~20 mole% Nb₂O₅. All of the ternary compositions studied here were found to be fully glassy to optical, X-ray and TEM examination.

HE-XRD measurements were performed at the Advanced Photon Source (APS) at Argonne National Laboratory (USA) at beamline 6-ID-C. Using high energy X-rays (100.131 keV, corresponding to $\lambda=0.123822\text{\AA}$) allowed data collection to high values of the scattering vector (Q) with minimal corrections for absorption and multiple scattering effects. The incident beam was collimated to 0.25 x 0.5 mm. XRD patterns were collected using a Perkin Elmer model 1621 detector mounted vertically on a platform that could be moved along the beam axis to select the distance between the sample and the active areas of the detector. For the measurements reported here the detector was typically set at ~45 cm from the sample. The sample-detector distance, coordinates of the direct beam and the angles of tilt and rotation were refined by calibration against crystalline CeO₂ standard. The detector had a 41 cm² active area using an a-Si active surface with spatial resolution 200 μm .

1D diffraction patterns were generated by integrating over all recorded pixels using Fit2D[29]. To maximize the value of scattering vector the detector was offset with the beam stop forming one corner of the area detector and a cake extracted to eliminate unresponsive pixels along the detector edge. Diffraction data were obtained up to $Q=28.5\text{ \AA}^{-1}$ at an instrumental resolution $\Delta Q/Q = 0.5\%$. Following background subtraction the total X-ray structure factor ($S(Q)$) was determined using PDFgetX2[30] as:

$$S(Q) = \frac{[I(Q) - C(Q) - \sum_i f_i^2(Q)]}{[\sum_i f_i(Q)]^2}$$

Here $I(Q)$ is the corrected initial scattered intensity, $C(Q)$ is the Compton scattering contribution and $f_i(Q)$ the set of X-ray (electronic) form-factors[31]. In Bi₂O₃-bearing samples the scattering intensity also contained fluorescence contributions that were accounted for by subtracting a constant value from $I(Q)$.

Our results are reported first as reciprocal space correlations of the total scattering ($S(Q)$) function that represents the weighted sum of partial structure factors, expressed using the Faber-Ziman formalism[32, 33]. The sine Fourier transform of the total, multi-component structure factor provides the total (pseudo-nuclear) pair distribution function, $G(r)$.

$$G(r) - 1 = \frac{1}{2\pi^2 r \rho} \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ$$

Here Q_{max} and Q_{min} represent the upper and lower limits of the finite range in reciprocal space studied and ρ is the atomic number density [32, 33]. The $G(r)$ function emphasizes local structure. In this study we use a Q_{max} of $28.5 \text{ \AA}^{-1}$ and the Lorch modification function to reduce termination ripples in the transform. For glassy materials it is convenient to express the pair distribution function in terms of the total correlation function, $T(r)$, or the differential distribution function ($D(r)$), that are used to highlight longer distance correlations. These are defined by:

$$D(r) = 4\pi r \rho [G(r)] - 1$$

$$T(r) = 4\pi r \rho [G(r)] .$$

Following our analysis of the X-ray scattering results for the glassy materials, we then wished to make a link with the behavior of the glass-forming liquids in the $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ system. The only available data are for liquid TeO_2 above its stable melting point. New viscosity data in the glass transition range were obtained for a ternary $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ composition using an indentation method [34, 35]. The indenter used was a 2 mm diameter SiC sphere and viscosities were measured using the rotating cylinder method[36]. The sample was placed in an Au crucible and heated up to 1113 K (840 °C) in air. The Au crucible was rotated at 70 rpm in order to collect the electrical voltage attributable to the torque on the inner cylinder. The measurement was performed during cooling the melt at decreasing temperatures in 20 K steps. Errors in the detected voltage (i.e. viscosity) measurements were estimated to be within $\pm 3\%$.

3. Results

Diffraction data obtained for $\text{TeO}_2\text{-Bi}_2\text{O}_3$ samples are shown in Figure 2. Only the sample containing 2 mole% Bi_2O_3 was fully glassy: the other patterns were dominated by Bragg diffraction peaks from crystalline TeO_2 and $\beta\text{-Bi}_2\text{Te}_4\text{O}_{11}$. As previously mentioned, the latter phase lies at the origin of the “anti-glass” model of Trömel et al. that was applied by Bertrand et al. to understand crystallization effects among the spherulites that appeared during annealing in the ternary $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ system[37]. Here we focus our analysis on the fully glassy materials at high TeO_2 content that we used to model the structural features present within a hypothetical pure TeO_2 glass.

The total structure factor for the 98% TeO_2 sample is shown in figure 2, the inset shows the data as $Q(S(Q)-1)$ which indicates oscillations that persist to the highest Q studied ($28.5 \text{ \AA}^{-1}$). A first strong peak in the diffraction pattern occurs at $2 \text{ \AA}^{-1}$. This principal peak [38, 39] can be associated with spatial correlations over medium range length scales and this often reflects the chemical ordering of different species [40-42]. In the $\text{TeO}_2\text{-Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$ samples the first observed peak in $S(Q)$ can be identified as Te...Te correlations occurring with real space periodicity $2\pi/Q \sim 3\text{-}4 \text{ \AA}$.

Oscillations in $S(Q)$ at $Q > 3 \text{ \AA}^{-1}$ reveal short range order occurring within the main glass-forming structural units. Fourier transformation leads to the real space function $T(r)$ that reveals characteristic distances within the glass structure. Faber-Ziman (FZ) weightings associated with the different pair correlations are given in Table 1. These are evaluated at $Q=0$ since there is a Q -dependence to the form factors. The FZ analysis indicates the relative contributions from each atom pair to the total X-ray scattering function and they show that the main contributions occur from Te-O and Te...Te correlations. The first main peak in $g(r)$ at $1.91 \text{ \AA}$ is due to Te-O distances within a glassy matrix dominated by TeO_3 and TeO_4 units[43-45] (Fig. 3c). That interpretation is supported by Raman

spectroscopic results[46, 47]. The second peak at 3.5 Å is mainly due to Te...Te correlations within the second coordination shell around the network-forming cations, and it gives rise to the principal peak at $\sim 2 \text{ Å}^{-1}$ in $S(Q)$. The peak in $T(r)$ has an obvious shoulder towards longer r that might initially suggest the presence of different populations of TeO_n polyhedra. Further analysis of the glass diffraction data was made using reverse Monte Carlo (RMC) modelling. An RMC model was constructed assuming a pure TeO_2 glass composition. A 3000 atom configuration generated with cut-off constraints similar to McLaughlin[48, 49] was used to establish the partial Te-Te, Te-O and O-O contributions to $S(Q)$ and $T(r)$ (Fig 3). The RMC simulations demonstrate that the asymmetric peak at 3.5 Å in the $T(r)$ comprises overlapping Te-Te and Te-O partial contributions. The Te-Te correlation is asymmetric in real space and the resulting configurations indicate that the glass is a mixture of both 3- and 4- coordinate Te-O polyhedra that can be both corner- and edge-shared. This modelled glass structure consistent with the data yields a structure that is considerably more disordered than the relatively open-structured face- or corner-shared structures of TeO_2 crystalline polymorphs [50, 51].

Table 1 : Faber-Ziman weightings (at $Q=0$) for TeO_2 - Bi_2O_3 - Nb_2O_5 glasses

(a) TeO_2 - Bi_2O_3 and TeO_2 - Nb_2O_5 compositions

TeO_2 - Bi_2O_3	98% TeO_2		TeO_2 - Nb_2O_5	98% TeO_2	95% TeO_2	90% TeO_2	85% TeO_2	80% TeO_2
Te-Te	0.51		Te-Te	0.54	0.49	0.40	0.34	0.27
Te-O	0.34		Te-O	0.35	0.34	0.32	0.30	0.27
Te-Bi	0.07		Te-Nb	0.04	0.08	0.15	0.19	0.23
Bi-Bi	0.00		Nb-Nb	0.00	0.00	0.01	0.03	0.05
Bi-O	0.02		Nb-O	0.01	0.03	0.06	0.08	0.11
O-O	0.05		O-O	0.05	0.06	0.06	0.07	0.07

(b) Ternary TeO_2 - Bi_2O_3 - Nb_2O_5 glasses

	95% TeO_2	90% TeO_2	85% TeO_2	80% TeO_2	75% TeO_2	70% TeO_2
Te-Te	0.47	0.37	0.29	0.24	0.19	0.19
Te-O	0.32	0.27	0.25	0.21	0.19	0.19
Te-Nb	0.04	0.07	0.08	0.09	0.09	0.10
Te-Bi	0.08	0.13	0.17	0.18	0.20	0.20
Nb-Nb	0.00	0.00	0.01	0.01	0.01	0.01
Nb-O	0.01	0.02	0.03	0.04	0.05	0.05
Nb-Bi	0.00	0.01	0.02	0.04	0.05	0.05
Bi-Bi	0.00	0.01	0.02	0.04	0.05	0.05
Bi-O	0.03	0.05	0.07	0.09	0.10	0.10
O-O	0.05	0.05	0.05	0.05	0.05	0.05

Within the TeO_2 - Nb_2O_5 system glasses are produced readily at up to 20 mole% Nb_2O_5 composition (Fig. 4). Analysis of $S(Q)$ and $D(r)$ data for the 98% TeO_2 (Te98Nb2) composition reveals very similar structural features to the 98 mol% glass produced along the TeO_2 - Bi_2O_3 binary. However as the Nb_2O_5 concentration is raised there are significant changes in $S(Q)$ that reflect the increased partial contributions of Te-Nb and to a lesser extent Nb-O correlations to the total structure factor and to the real space transform (Table 1).

We observe a slight decrease in the height of the first peak in the diffraction pattern that shifts to lower Q as the Nb_2O_5 content increases (Fig. 4a). The pair distribution function, shown as $T(r)$ in figure 4b, also shows continuous changes in the underlying structure as Nb_2O_5 is added. The first peak at 1.92 Å increases in intensity as Nb_2O_5 component is added. The radial distances for 4-6 coordinate NbO_n polyhedra lie between 1.83-1.98 Å for 4-6 coordinate NbO_n polyhedra based on tabulated values[43, 44] and the relative intensity changes are consistent with increasing contribution of an approximately Gaussian Nb-O correlation at 1.89 Å. Even for the most Nb_2O_5 -rich compositions the diffraction data are dominated by Te-O and Te-Te correlations. That result is consistent with the decrease in the intensity of the first peak in $S(Q)$ and the shift to slightly higher r value of the 3.5 Å peak in real space (Fig 4).

In the ternary TeO_2 - Bi_2O_3 - Nb_2O_5 system the glass-forming range is extended further to 70% TeO_2 (Fig 5). In this case there is an enhanced intensity of the first peak in $S(Q)$ at 1.98 Å⁻¹ as the Bi_2O_3 / Nb_2O_5 concentrations increase. This indicates that the partial contributions of Te-Te and Te-Bi correlations to the overall $S(Q)$ are of similar magnitude. At higher Q there is a change in the intensity of the peak at 3.6 Å⁻¹ and a decrease in intensity of its high Q shoulder with increasing Bi_2O_3 and Nb_2O_5 concentrations. In the real space transform the most TeO_2 -rich glass is structurally similar to the 98% compositions within the Bi_2O_3 - and Nb_2O_5 - TeO_2 binary joins. As expected from the Faber-Ziman weightings (Table 1) the main correlations are due to Te-O and Te-Te interactions.

As the TeO_2 content is reduced and the Bi_2O_3 and Nb_2O_5 concentrations increase the peak at 1.9 Å shows a decrease in intensity (Fig 5b), as this feature has overlapping contributions from Te-O and Nb-O correlations in 3-/4-coordination and 4-/6-coordination by oxygen. The Bi-pair contributions increase with Bi concentration, reflected by changes in the peak height at ~2.25 Å. Bond-valence calculations indicate Bi-O distances for 4- and 6-coordinated BiO_n units of 2.19 -2.35 Å, suggesting that a mixture of both coordination polyhedra contribute to the X-ray scattering data.

The correlations at higher r represent overlapping partial radial distribution functions of all partials with the greatest contributions arising from from Te-Te, Te-Bi, Te-Nb and Te-O correlations. As the Bi_2O_3 and Nb_2O_5 concentrations are increased there is no obvious evidence of any change in glass structure that might be expected if they had been produced from different structured liquids.

Finally, we examined the relaxation behavior by carrying out viscosity (η) measurements near the glass transition for the $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ glass composition. These results were combined with viscosity data for liquid TeO_2 [52]. The two data sets could be fit with a single $\log \eta - 1/T$ plot according to the Volger-Fulcher-Tamman (VFT) relation (Fig. 6). The VFT fit is strongly curved indicating a highly non-Arrhenian or "fragile" nature for the stable and supercooled tellurite liquids[53]. The fragility index (m) is obtained by considering the apparent activation energy (ΔH^*), obtained from the initial slope of the viscosity-temperature relation in the vicinity of the glass transition ($m = -\Delta H^*/RT_g$). The estimated value for these tellurite compositions is 78. "Strong" liquids such as SiO_2 have a fragility index of 20, while the most fragile liquid compositions, including Ca-K-nitrate and high-density aluminate liquids, have a fragility index of around 210[54]

Discussion

Pure TeO_2 is known to be a poor glass former but glasses are formed readily when small amounts of modifier components including metal oxides or fluorides. The crystalline polymorphs of TeO_2 contain TeO_4 polyhedra that are based on trigonal bipyramidal structures with two of the oxygen atoms are corner- or edge-linked between adjacent polyhedra [50, 51]. Adding modifier components to provide glass-forming compositions causes disruption of the network with the appearance of TeO_3^{2-} units

containing non-bridging oxygens that are coordinated to the modifier cations [55-58]. IR and Raman investigations of Nb^{5+} - and Bi^{3+} -bearing tellurite glasses indicate that they contain chains of corner-linked TeO_3 and TeO_4 units with non-bridging oxygens coordinating NbO_6 and BiO_6 units [46, 47]. Our HEXRD studies of these glass structures are consistent with these observations. The mean Te-O coordination numbers for TeO_2 -rich compositions are estimated to be 3.7 (98% Bi_2O_3) and 3.8 (98% Nb_2O_5) indicating a mixture of TeO_3 and TeO_4 coordination polyhedra (but dominated by TeO_4) that are both corner- and edge-shared. The similarity of the $S(Q)$ patterns indicate that this TeO_2 framework is only slightly perturbed by the addition of the modifier component, and structural correlations persist over a wide Q range. The first dominant peak in $S(Q)$ is associated with Te...Te correlations occurring at around 3.5 Å that corresponds to the Te...Te distances in Na_2TeO_3 and $\text{Na}_2\text{Te}_4\text{O}_9$ [49, 59-61], but is longer than those found in crystalline TeO_2 polymorphs [50, 51]. The addition of even small amounts of either Nb_2O_5 or Bi_2O_3 as modifier components causes the structure to relax internally while maintaining the highly ordered arrangement of the Te^{4+} cations. The improvement in glass forming ability thus likely results from the increased entropy associated with the linkage disorder caused by the random distribution of TeO_4 and TeO_3 units, along with the equatorial vs axial positions of the bridging vs non-bridging O^{2-} species. That finding immediately lends itself to the "anti-glass" model used to describe metastable crystallization features in Bi_2O_3 - Nb_2O_5 - TeO_2 glasses [23].

The viscosity data for tellurite yield a fragility index of 78 consistent with previous estimates of the fragility of sodium tellurite liquids [54] and comparable with moderately fragile liquids such as sodium silicates but are much less fragile than the most fragile liquids such as ZBLAN or Ca-K nitrate and the viscosities of the HD and LD Al_2O_3 - Y_2O_3 liquids. As outlined above this would indicate that the tellurite liquids are not highly cooperative smaller values of W would mean that the LLPT would not be intercepted before kinetic arrest at the calorimetric glass transition (T_g). Our interpretation of the viscosity-temperature data for the tellurite liquids is that they result in a high density amorphous (HDA) polyamorph upon quenching, with no indication of any structural or thermodynamic transition in the supercooled state that might be associated with transformation to a low-density (LDL) liquid. The structure and viscosity data for tellurites are not consistent with a discontinuous change in structure in the supercooled regime but do show textures that could suggest access to the LLPT on reheating. That behaviour is different from that observed for supercooled liquids in the Al_2O_3 - Y_2O_3 system [7].

The annealing process described for the $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ glass is consistent with the progressive access of low energy and more stable states. During annealing spherulitic structures appear that are mainly identified with "anti-glass" crystalline structures [28]. These changes occurred as the initial HDA glasses were heated above their glass transition temperature (T_g^{HDA}) and crystallization into the "anti-glass" phase might have occurred directly. On relaxation of the HDA glass formation of a more energetically stable phase is favoured and this is the anti-glass phase, which is clearly more ordered than the disordered glass but still with glassy-like properties in the form of anion disorder and glass-like Raman spectra. The presence of some amorphous spherulites on a nanometric scale could indicate that a possible transformation into a low-density (LDA) glassy polyamorph might have occurred simultaneously, in competition with the recrystallization event and indicating similar energetics of a LDA polyamorph and the "anti-glass" phase and a possible similarities in structure. Interestingly, no spherulites are developed for the specific $12.5\text{Bi}_2\text{O}_3$ - $12.5\text{Nb}_2\text{O}_5$ - 75TeO_2 glass composition that exhibits congruent crystallization upon annealing [62].

The behaviour can be compared with that found for the Al_2O_3 - Y_2O_3 supercooled liquids and glassy materials. As mentioned above the temperature of the LLPT is composition-dependent and glasses

can be produced that consist of the HDA form only. In these cases the LLPT transition temperatures occurred in the supercooled liquid range slightly above the glass transition (T_g^{HDA}) and can be accessed if these glasses are reheated. DSC curves for these glasses show two exothermic peaks in the supercooled liquid region, one attributed to partial recrystallization of a disordered AY_{ss} garnet and the second to a first order transition between the metastable supercooled HD liquid to a more stable LD glass. Similar behaviour is observed in HDA water. In the more Y_2O_3 -rich Al_2O_3 - Y_2O_3 glasses the glass produced is only that of the supercooled HDL phase, and the LLPT is not encountered during quench experiments. For more Y_2O_3 poor compositions that LLPT is encountered but not be completed. The emergence of crystalline material was observed both during initial quenching and subsequent annealing of the HDA-LDA glassy composite materials. In that case it was interesting that the crystalline material was produced within the LDA phase (Fig. 1). A similar situation is inferred for the tellurite glasses, a lower entropy amorphous form implied by a non-zero, non-ideal mixing parameter would result in formation of an LDA texture if a HDA glass were reheated. In tellurites, the textures are dominantly but not exclusively crystalline and implies that the "anti-glass" and LDA are structurally similar. In the case of TeO_2 - Bi_2O_3 - Nb_2O_5 glasses, it is not yet clear if the anti-glass crystals formed are structurally related to the potential LDA spherulites appearing within the system upon annealing. That will require further investigation.

Conclusions

Our HEXRD data for binary and ternary glasses in the Bi_2O_3 - Nb_2O_5 - TeO_2 system reveal a glassy network based on interconnected TeO_4 and TeO_3 units that appears to remain relatively unchanged from the parent TeO_2 system. The diffraction data are dominated by Te...Te correlations at distances greater than those found in pure TeO_2 phases but correspond to those for crystalline tellurites containing modifier cations. Analysis of the viscosity-temperature relations shows that the glass-forming liquids are highly "fragile" in nature. There no evidence for a LLPT occurring during cooling, and the glasses obtained by quenching likely correspond to a high-density amorphous (HDA) state. During subsequent annealing above T_g , X-ray diffraction, SEM and Raman spectroscopy data indicate crystallization of an "anti-glass" tellurite phase based on β - $Bi_2Te_4O_{11}$. Formation of this compound from the glassy material requires only small adjustments in the cation positions, sufficient to achieve an ordered array that results in positional (but not chemical) order and crystalline diffraction while the Raman spectra continue to exhibit broad "amorphous" signatures[23, 27]. It is possible that some nanoscopic spherulites appearing initially upon annealing are amorphous and that these could constitute examples of an LDA material produced simultaneously *via* a polyamorphic transformation occurring simultaneously with the anti-glass recrystallization event. The behaviour can be compared and contrasted with that reported previously for Al_2O_3 - Y_2O_3 glasses and glass-forming liquids. In that case the LLPT is sampled during supercooling but is not fully achieved during quenching to result in mixed HDA-LDA glasses. A metastable transition then occurs during re-heating above T_g for the HDA polyamorph, with appearance of the LDA phase below its glass transition[63]. However, both the initial quenching event and subsequent annealing result in simultaneous nucleation of a crystalline Al_2O_3 - Y_2O_3 solid solution phase. Our conclusion is that the transformations occurring within the Bi_2O_3 - Nb_2O_5 - TeO_2 system might be analogous to those observed among Al_2O_3 - Y_2O_3 and other rare earth (RE) oxide supercooled liquids, glasses and metastable crystalline phases, but with subtle but important differences in the relative temperatures and timescales over which they occur. Most importantly, the combination of metastable crystallization and polyamorphic transformation events provides a new routes to creating new families of nanocomposite materials with useful properties.

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FIGURE CAPTIONS:

Figure 1. Spherulites grown in $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ glass matrix when heated to 380°C . The two images for the tellurite glasses show formation of “anti-glass” spherulites at 4 (a) and 11 hour (B)[23]. The development of cracks in the spherulites indicates confined growth and differs from the congruent crystallisation characteristic of the vitrification process. The similar textures developed in yttrium aluminate glasses are shown from the paper by Aasland and McMillan[2] (c) and more recent publications (d).

Figure 2. The total structure factor for $\text{Bi}_2\text{O}_3\text{-TeO}_2$ glasses, $S(Q)$, obtained by HEXRD at sector 6 (6-ID-D), APS. Three compositions are shown (A), those with 80 and 85% TeO_2 show Bragg peaks consistent with the presence of TeO_2 and the anti-glass $\beta\text{-Bi}_2\text{Te}_4\text{O}_{11}$. The inset shows the high Q part of the glass diffraction data, shown as $Q(S(Q)-1)$. The real space transform for the 98% TeO_2 glass, shown as $T(r)$ is also shown (B).

Figure 3. The partial structure factors $S_{\alpha\beta}(Q)$ are shown for the 98% TeO_2 glass (A) from the RMC fit (assuming this structure is a pure TeO_2 glass). The partial contributions in real space, (shown as $g_{\alpha\beta}(r)$) are also shown (B) compared with the experimental data.

Figure 4. The total structure factors for $\text{Nb}_2\text{O}_5\text{-TeO}_2$ glasses, obtained from HEXRD data, these are shown displaced for clarity (A). The real space transforms (As $T(r)$) are also shown (B)

Figure 5. The HEXRD $S(Q)$ for $\text{Nb}_2\text{O}_5\text{-Bi}_2\text{O}_3\text{-TeO}_2$ glasses, also displaced for clarity(A) and the real space transform, as $T(r)$ B.

Figure 6. High and low-temperature viscosity data for $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ composition liquids (corresponding to 85% in this work) compared with rotating cylinder viscosity data for pure TeO_2 (Veber and Mangin, 2008). A Volger-Fulcher-Tamman (VFT) fit is also shown. ~~the~~The high-density liquid (HDL) phase of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ giving rise to HDA glassy polyamorphs also has a high fragility. This analysis is consistent with previous estimates of the fragility of sodium tellurite liquids[54].

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