Journal of Non-Crystalline Solids 495 (2018) 27–34

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Structural analysis of WO_3-TeO_2 glasses by neutron, high energy X-ray diffraction, reverse Monte Carlo simulations and XANES

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ARTICLE INFO

Keywords:
Tellurite glasses
Short-range structure
Neutron and high energy X-ray diffraction
RMC simulations
XANES

ABSTRACT

The structure of WO_3-TeO_2 glasses containing 15, 20 and 25 mol% WO_3 are studied by neutron diffraction (ND), high energy X-ray diffraction (XRD) and X-ray Absorption Near Edge spectroscopy (XANES). The short-range structural properties of glasses i.e. Te—O and W—O speciation, coordination number distributions, bond-lengths, and the O—Te—O, O—W—O and O—O—O bond angle distributions in the glass network are determined by the Reverse Monte Carlo (RMC) simulations of the ND and XRD data. RMC technique successfully determined all partial pair correlation functions and the coordination number distributions revealed that glass network consists predominantly of TeO_4 and WO_4 units with small amounts of triangular, penta and hexa co-ordinated units. The average W—O and Te—O bond lengths are in the ranges: 1.69–1.75 ± 0.01 Å and 1.99–2.00 ± 0.01 Å respectively. Both W—O and Te—O correlation peaks are asymmetrical, that indicate a distribution of their bond lengths in the respective structural units. The O-Te-O bond angle distribution has a peak at 107 ± 2°. Similarly the O-W-O bond angle distribution has a peak at 108 ± 5°. On increasing the WO_3 concentration from 15 to 25 mol%, the average Te—O coordination number decreases from 3.80 to 3.61 ± 0.02 due to the structural transformation: $TeO_4 \rightarrow TeO_3$, similarly the W—O coordination also decreases and is in the range: 3.79–3.67 ± 0.02. XANES studies found that the oxidation state of Te and W ions in the glasses are 4^+ and 6^+ respectively.

1. Introduction

TeO_2 is a conditional glass former, it forms glassy phase with difficulty at high melt-quenching rates of $\sim 10^5\,K\,s^{-1}$ [1–3], however on mixing it with alkali, alkaline-earth, heavy metal and transition metal oxides, the glass forming ability of TeO_2 enhances significantly and it forms a variety of binary and multi-component glasses rather easily at moderate quenching rates of $\sim 10^2$–$10^3\,K\,s^{-1}$ [4]. Tellurite glasses are technologically important materials for their applications in optical waveguides, Raman amplifiers and in non-linear optical devices for second and third harmonic generation [5–9]. Tungsten tellurite system forms clear and transparent glasses in the composition range of 11 to 33-mol% of WO_3 [4,10–12], and are promising materials for applications in optical waveguide and as optical windows for enhancing the efficiency of solar cells [13,14]. WO_3-TiO_2-TeO_2 glasses have a wide optical transmission window in the UV–visible-NIR range of 500 nm to 2800 nm and high refractive indices of 2.5–2.1 [15]. Tungsten based glasses find application for photochromatic, gas sensors and electrochromic devices [16].

There is an unresolved controversy about W—O coordination in tungsten tellurite glasses. According to the ab-initio simulations by Mirgorodsky et al. [17], the coordination number of W ions with oxygen (i.e. $N_{W\text{-}O}$) is 4 and not 6. On the contrary, Raman spectroscopy and quantum mechanical calculations by Sokolov et al. concluded that the W—O co-ordination number is 6 and not 4 in WO_3-TeO_2 glasses [18]. According to Shaltout et al. [19] up to 27.5-mol% of WO_3 in WO_3-TeO_2 glasses, mainly WO_4 units exist and that beyond this composition, WO_4 transform into WO_6 units. In an earlier work we reported the results on thermal, optical and Raman studies on WO_3-TeO_2 glasses [20]. In the present study, the structure of WO_3-TeO_2 glasses containing 15, 20 and 25-mol% WO_3 is studied by neutron and High Energy X-ray diffraction (HEXRD), Reverse Monte Carlo (RMC) simulations of the

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https://doi.org/10.1016/j.jnoncrysol.2018.05.003
Received 9 February 2018; Received in revised form 2 May 2018; Accepted 4 May 2018
0022-3093/

Table 1
Composition, density and atomic number density of WO_3-TeO_2 glasses.

Sample code	Composition	Density, d ($g \cdot cm^{-3}$) ($\pm$ 0.005)	Atomic number density [$Å^{-3}$]
15WTe	$15WO_3$-$85TeO_2$	5.850	0.0649
20WTe	$20WO_3$-$80TeO_2$	5.893	0.0652
25WTe	$25WO_3$-$75TeO_2$	5.941	0.0659

diffraction data and X-ray Absorption Near Edge Spectroscopy (XANES).

2. Experimental details

2.1. Glass preparation and density measurement

The binary xWO_3-$(100-x)TeO_2$ glasses with x = 15, 20 and 25 mol% (hereafter referred as 15WTe, 20WTe and 25WTe, respectively) were prepared by conventional melting of appropriate amounts of analytical reagent grade chemicals (TeO_2 and WO_3) in a platinum crucible and by splat-quenching the melt between two heavy metal blocks. Batch weights of the samples were about 10 g.

All samples were clear and transparent and their glassy nature was confirmed by laboratory source X-ray diffraction and Differential Scanning Calorimetric analyses [20]. Densities of glasses were measured by Archimedes method; the batch composition, density and atomic number density of samples are given in Table 1. Density measurement of each sample was repeated three times and the maximum uncertainty in the density is ± 0.005 g cm^{-3}, which was calculated from the precision (0.1 mg) of the electronic balance that was used for the measurement of the weight of samples in air and immersion fluid.

2.2. Neutron diffraction

Neutron diffraction measurements were performed on the pulverized samples kept in vanadium cans on the high-*Q* neutron diffractometer at Dhruva reactor of Bhabha Atomic Research Centre, Trombay, Mumbai, India [21]. Neutron diffraction data was collected on three glass samples in the *Q*-range of 0.5 to 13.5 $Å^{-1}$ using monochromatic neutrons of de-Brogile wavelength, $\lambda = 0.785$ Å. The procedures given by Eglestaff were used in carrying out the neutron data reduction, with corrections for background, multiple scattering and inelastic scattering. Vanadium normalization was used to put the data on an absolute cross-section scale [22]. The neutron structure factor, $S_N(Q)$ was calculated from the corrected and the normalized neutron scattering data.

2.3. X-ray diffraction

HEXRD studies were carried out on beamline 6-ID-D at the Advanced Photon Source, Argonne National Laboratory, USA. The powdered samples were filled into quartz capillary tubes of 2 mm in diameter (and wall thickness of ~0.01 mm, Charles Supper Inc., USA). X-rays of wavelength, $\lambda = 0.113$ Å were used in combination with an amorphous Si area detector to obtain data out to a $Q_{max} = 26.5$ $Å^{-1}$. The HEXRD structure factor, $S_X(Q)$ was calculated using the standard procedure [23–27].

2.4. XANES

W and Te L_3-edges XANES spectra were recorded at BL-9, Scanning EXAFS beamline of Indus-2 synchrotron at Raja Ramanna Centre for Advanced Technology, Indore, India [28]. The measurements were done in fluorescence mode using Vortex energy dispersive detector. The beamline consists of Rh/Pt coated cylindrical mirror for collimation and a Si (111) double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylinder which provided beam focused in the horizontal direction. The beam energy is perfectly calibrated by using Ta and Sb metal foils for experimental measurement.

2.5. RMC simulations

The experimental neutron and XRD structure factors, $S_N(Q)$ and $S_X(Q)$ were simulated by the RMC method using the software package RMC^{++} Version 1.5.1 to generate the partial pair correlation functions, coordination numbers and the bond-angle distributions, based on the practices [29–39].

The RMC simulation method is an effective tool for building large 3D structural models that are consistent with the experimental data and total structure factors obtained from ND and HEXRD experiments. During the calculation, the difference between the experimental and calculated curves is minimized by random moves of the particles; at the end of the simulation a particle configuration is obtained. From these final configurations, structural properties i.e. partial correlation functions, coordination numbers, bond-angle distributions can be calculated [35,37].

In neutron diffraction, the scattering amplitude is constant [40,41], scattering weighting factors, w_{ij}^N (independent of momentum transfer *Q* values), were calculated by the following formula [42–44] for all atom-pairs and their values are given in Table 2.

$$W_{ij}^{N} = \frac{c_i b_i c_j b_j \times (2 - \delta_{ij})}{\left[\sum_i^k c_i b_i\right]^2} \tag{1}$$

where δ_{ij} is Kroneker delta function, c_i, c_j are the molar fractions of the i^{th} and j^{th} atoms in the sample respectively, b_i, b_j are the corresponding neutron coherent scattering lengths and k is the total number of elements in the sample ($k = 3$ in the present glass system), thus $k(k+1)/2 = 6$ different atom pairs are present. The neutron scattering weighting factors were calculated for all atom-pairs and their values in the three samples are given in Table 2, parallel with X-ray weighting factors.

The X-ray scattering amplitude is *Q*-dependent [45] and their weight factor values, w_{ij}^X were calculated from the following formula:

$$W_{ij}^{X} = \frac{c_i f(Q)_i c_j f(Q)_j}{\left[\sum_i^k c_i f(Q)_i\right]^2} \tag{2}$$

where $f_i(Q)$ and $f_j(Q)$ are the X-ray scattering amplitudes of the i^{th} and j^{th} atoms in the sample respectively. In order to see the weight factors of the different atom pairs in the total $S(Q)$ for the two radiations, Table 2 presents w_{ij}^N and w_{ij}^X (at $Q = 2.5$ $Å^{-1}$) for all atom pairs.

The RMC simulation calculates the one-dimensional partial atomic pair correlation functions $g_{ij}(r)$, and these are Fourier transformed to calculate the partial structure factors, $S_{ij}(Q)$. Disordered atomic

Table 2
The neutron and X-ray scattering weight factors of atomic pairs in WO_3-TeO_2 glasses.

	Atom pair	15WTe	20WTe	25WTe
Neutron weight factors w_{ij}^N (%)	W-W	0.16	0.27	0.43
	W-Te	2.17	2.67	3.05
	W-O	5.52	7.34	9.15
	Te-Te	7.31	6.37	5.46
	Te-O	37.3	35.1	32.8
	O-O	47.5	48.2	49.2
X-ray weight factors w_{ij}^X (%) at $Q = 2.5$ $Å^{-1}$	W-W	2.67	4.55	6.81
	W-Te	20.4	24.5	27.4
	W-O	6.96	9.08	11.1
	Te-Te	38.87	32.91	27.68
	Te-O	26.55	24.43	22.42
	O-O	4.53	4.54	4.54