Journal of Non-Crystalline Solids 404 (2014) 116–123

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Structural characterization of borotellurite and alumino-borotellurite glasses

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ARTICLE INFO

Article history:
Received 30 April 2014
Received in revised form 27 June 2014
Available online xxxx

Keywords:
Borotellurite and alumino-borotellurite glasses;
Phase separation;
Crystalline precipitates;
Infrared and Raman spectroscopy;
Chemical durability

ABSTRACT

Borotellurite (xB_2O_3–$(100-x)TeO_2$; x = 15, 20, 25, 30 and 35 mol.%) and alumino-borotellurite (yAl_2O_3–$10B_2O_3$–$(100-y)TeO_2$; y = 5, 10, 20 and 30 mol.%) glasses are prepared and studied by X-ray diffraction, density, differential scanning calorimetry, thermo-gravimetric analysis, UV–visible, infrared and Raman spectroscopy. Borotellurite glasses are hygroscopic and on crushing into powder, they absorb atmospheric water vapors to form crystalline precipitates of TeO_2 in an amorphous matrix; the chemical durability of these glasses deteriorates with increasing B_2O_3 concentration. The refractive index of borotellurite glasses decreases from 2.29 to 2.26 while the glass transition temperature increases from 339 to 366 °C with an increase in B_2O_3 mol.%. The short-range structure of glasses consists of TeO_4, TeO_3, BO_4 and BO_3 structural units. Using the ratio of the areas under TeO_4/TeO_3 and BO_4/BO_3 Raman and infrared bands respectively, the Te – O coordination is found to decrease from 3.63 to 3.56 and B – O co-ordination from 3.34 to 3.17 respectively on increasing B_2O_3 concentration from 5 to 30-mol.%. Alumino-borotellurite glasses show an amorphous–amorphous phase separation at an alumina concentration of 10-mol.% and above, while alumino-borotellurite sample with 30-mol.% of Al_2O_3 forms crystalline precipitates of α-Al_2O_3 in an amorphous matrix.

1. Introduction

TeO_2-based glasses have wide glass forming range and useful properties such as low melting temperature, high dielectric constant, high refractive index, low phonon energy and good transmittance of infrared radiation (0.4–6 μm); therefore, tellurite glasses have attracted significant interest over many years for application in non-linear optical devices, optical fiber amplifiers, lasers, solid state batteries, etc. [1–5]. Tellurite glasses have been reported to exhibit 30 times higher Raman gain coefficients than silica glass, and find application in Raman amplifiers and non-linear optical waveguides [6,7]. Silver–vanadium tellurite glasses show ionic conduction due to silver cations and mixed electronic–ionic conduction when doped with transition metal ions [8]. The synthesis of pure TeO_2 glasses requires melt-quenching rates of ~10^5 K s^{-1} [9]. The short-range structure of pure TeO_2 glass has been studied by neutron diffraction and Raman spectroscopy and it is reported that 64% of Te ions in the glass network exist in TeO_4 bipyramidal units. The addition of metal oxides modifies the Te – O network and simultaneously enhances the glass forming ability [1,2]. An interesting feature of the structure of tellurite glasses is that when the environment is more ionic, the addition of a modifier favors the formation of trigonal pyramidal, [$TeO_{3/2}$] (tp) units at the expense of trigonal bipyramidal, [$TeO_{4/2}$] (tbp) units [1,2,5,9–11]. Study of potassium tellurite glasses has shown that up to a K_2O molar concentration of 14.3%, non-bridging oxygens (NBO) are generated and TeO_4 tetrahedra do not transform into TeO_3 units, but at higher K_2O content, TeO_4 transforms into TeO_3 units [9]. Incorporation of TeO_2 in the alkali borate glasses decreases the latter's hygroscopic nature and enhances its infrared transmittance [12]. Borate glasses have a random network consisting of tetrahedral (BO_4) and trigonal boron (BO_3) units and their combination form diborate, triborate, tetraborate and pentaborate groups [13].

The presence of both B_2O_3 and TeO_2 in borotellurite glasses leads to complex speciation in the glass structure. Also a glass containing two network formers such as TeO_2 and B_2O_3 can lead to the formation of mixed structural units as in borosilicate glasses [14]. It is interesting to study the effect of TeO_2 on the fraction of tetrahedral borons in the glass network. Borotellurite glasses have potential application especially in micro-electronics and opto-acoustics owing to their favorable optical and electrical properties [15]. Raman study of B_2O_3–TeO_2 glasses by Sekiya *et al.* concluded that in glasses with low B_2O_3 content, there exists a continuous network of TeO_4, BO_4 and BO_3 groups [16]. On increasing B_2O_3 content, condensation of isolated BO_4, B_2O_5 and BO_3 units takes place and causes phase-separation. Glasses containing nearly 50-mol.% of B_2O_3 consist of sharing vertices of tellurite clusters, isolated BO_4, B_2O_5, BO_3 and condensed borate groups. Dimitriev *et al.* determined the phase diagram of a binary borotellurite system and reported the formation of two phases in glasses, one with high TeO_2 content was a transparent glass and the other phase richer in B_2O_3 was opaque and its structure consists of a complicated micro-heterogeneous network

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.08.002
0022-3093/

Table 1
Composition, density and molar volume of borotellurite and alumino-borotellurite glasses.

Sample code	Composition			Molar mass, M (g mol^{-1})	Density, d (g cm^{-3})	Molar volume, V_m (cm^3 mol^{-1})
	B_2O_3	TeO_2	Al_2O_3			
15BTe	15	85	–	146.04	5.110 ± 0.003	28.59
20BTe	20	80	–	141.59	4.906 ± 0.002	28.86
25BTe	25	75	–	137.09	4.728 ± 0.001	28.99
30BTe	30	70	–	132.59	4.472 ± 0.002	29.65
5Al–10BTe	10	85	5	147.72	5.047 ± 0.027	29.27
10Al–10BTe	10	80	10	144.84	4.811 ± 0.015	30.10
20Al–10BTe	10	70	20	139.07	4.416 ± 0.003	31.49
30Al–10BTe	10	60	30	133.31	4.303 ± 0.002	30.98

[17]. The binary borotellurite system is a simple eutectic and does not form any crystalline compounds. A wide stable miscibility gap was determined with TeO_2 concentration from 3.9 to 73.6-mol.% by Burger *et al.* [18]. Phase separation is also reported by Yardımcı *et al.* who determined the glass forming range of B_2O_3–TeO_2 system to be 5–25 mol.% of B_2O_3 [15]. Halimah *et al.* studied the ultrasonic and physical properties of the system: B_2O_3–TeO_2 and found an increase in the rigidity of the glass structure with the addition of TeO_2 [19].

The incorporation of a third component such as Al_2O_3 in borotellurite glasses influences B – O and Te – O coordinations and provides an opportunity to tailor glass properties for applications. Addition of Al_2O_3 in borotellurite glasses enhances their chemical durability [20]. In alumino-borotellurite glasses, there are reports of microcrystal distribution in an amorphous matrix [21].

The objective of this work is to elucidate changes that occur in glass short-range structure, in particular B – O and Te – O coordination as a function of B_2O_3 molar concentration in binary borotellurite glasses and the effect of addition of Al_2O_3 on glass structure and properties. Coordination numbers of boron and tellurium ions with oxygen are studied by FTIR and Raman spectroscopy respectively. Glass properties like density, optical band gap, refractive index and thermal properties are measured and structure–property correlations are made.

2. Experimental work

2.1. Glass preparation

Samples of borotellurite glasses: xB_2O_3–$(100 - x)TeO_2$ with x = 15, 20, 25, 30 and 35 mol.% and alumino-borotellurite glasses: yAl_2O_3–$10B_2O_3$–$(100-y)TeO_2$: y = 5, 10, 20, 30 mol.% were prepared using H_3BO_3 (Aldrich, 99.9%), α-Al_2O_3 (CDH, India 99.9%) and TeO_2 (Aldrich, 99%) as starting materials. The chemicals were mixed together in appropriate molar ratios in agate mortar pestle for about 30 min and then transferred to a platinum (Pt) crucible. The batch mixture was sintered at 250 °C for 24 h and melted at 800 °C for about 30 min in an electric furnace. The temperature of Pt crucible containing the melt was measured by a chromel–alumel thermocouple positioned close to it. For each borotellurite composition, a glass sample was prepared by normal quenching; in which the melt was poured on brass block and a button shaped sample was obtained and immediately transferred to another furnace where it was annealed at 300 °C for 30 min.

One sample containing B_2O_3 concentration of 35-mol.% was prepared but it was milky on its upper surface. Clear transparent glasses were obtained up to B_2O_3 concentration of 30-mol.%.

Alumino-borotellurite samples with a fixed B_2O_3 concentration of 10-mol.% and variable Al_2O_3 concentration of 5 to 30-mol.% were prepared by splat quenching. A small amount of melt was poured on a heavy stainless steel plate and then pressed by a massive brass block. Alumino-borotellurite glasses required higher quenching rates for the formation of glassy phase. Splat quenched samples were not given any annealing treatment. The composition, molar mass, density and molar volume of samples are given in Table 1.

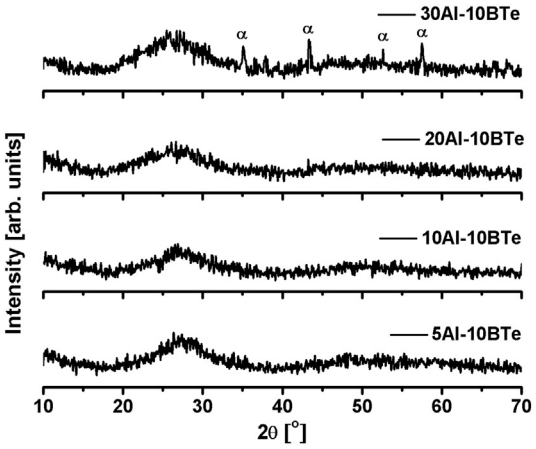

Fig. 2. XRD patterns of alumino-borotellurite glasses. All samples are amorphous except the sample with 30-mol.% of Al_2O_3, this sample shows sharp peaks due to crystalline precipitates of α-Al_2O_3.

2.2. X-ray diffraction

X-ray diffraction (XRD) studies were performed on powdered samples using Bruker D8 Focus X-ray diffractometer with Cu K_α

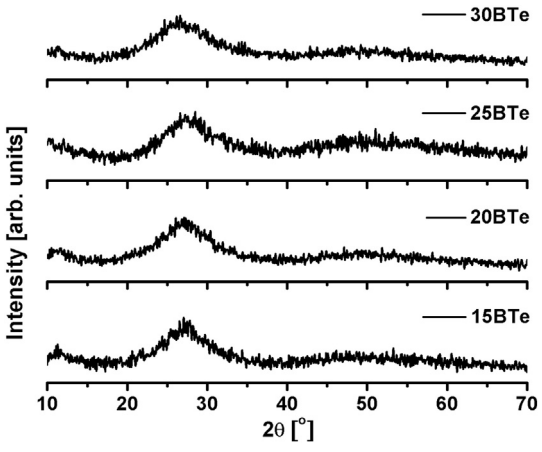

Fig. 1. XRD patterns of xB_2O_3–$(100 - x)TeO_2$ glasses.

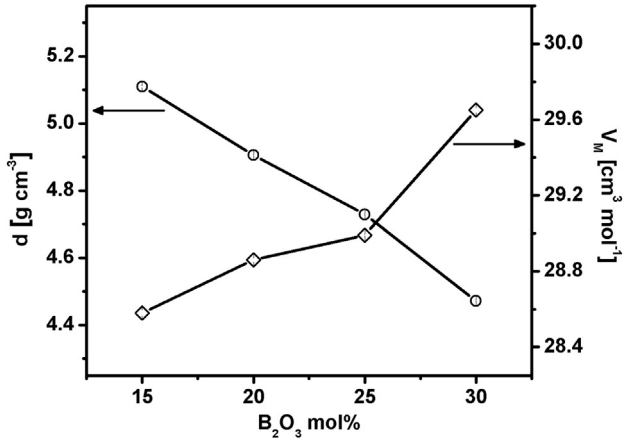

Fig. 3. Density and molar volume of borotellurite glasses as a function of B_2O_3 mol.% (error bars are of the size of the symbols).