Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Glass and anti-glass phase co-existence and structural transitions in bismuth tellurite and bismuth niobium tellurite systems

Nupur Gupta, Atul Khanna*

Department of Physics, Guru Nanak Dev University, Amritsar 143005, Punjab, India

ARTICLE INFO

Keywords:
Tellurite glass and anti-glass phases
Te-O co-ordination
phase-coexistence and liquid-liquid transitions
Glass transition
Spherulites
Micro-Raman

ABSTRACT

Glass and anti-glass samples of Bi_2O_3-TeO_2 and Bi_2O_3-Nb_2O_5-TeO_2 were prepared by ice-water quenching and normal-quenching respectively. The bismuth tellurite system has poor glass forming ability (GFA) and forms a glassy phase at low Bi_2O_3 concentration of 2 to 5-mol%. On increasing Bi_2O_3 concentration to 10 mol%, a mixture of glass and anti-glass phases are formed by rapid quenching of the melt. A further increase in Bi_2O_3 concentration to 20 mol%, produces a sample consisting of entirely $Bi_2Te_4O_{11}$ anti-glass upon melt-quenching. An anti-glass is a solid, which has long range order of cations (Te^{4+}, Bi^{3+}, Nb^{5+} etc.) but these are statistically distributed at their sites while the anion sites are partially vacant. Consequently the X-ray diffraction (XRD) patterns of bismuth tellurite and bismuth niobium tellurite anti-glass samples show sharp XRD peaks but the Raman spectra show broad phonon bands due to disturbed short-range order of the anions. The addition of Nb_2O_5 to the Bi_2O_3-TeO_2 system significantly enhances the GFA. Samples from the system: xBi_2O_3-xNb_2O_5-(100-2x)TeO_2 grow micro-inclusions or spherulites of size of several micron within the glass matrix on slow melt-cooling. Heat treatment of $7.5Bi_2O_3$-$7.5Nb_2O_5$-$85TeO_2$ sample show structural transitions from glass→anti-glass→crystalline phases.

1. Introduction

The family of oxide glasses is very wide and is being continuously developed to produce novel functional materials [1,2]. Researchers have focused their attention towards the oxide glasses due to their wide-ranging properties in combination with their wide composition range of formation, which renders them good candidates for many practical applications such as the dielectrics for super-capacitors [3], electrolytes in the electrochemical devices [4] and as sealants for high temperature oxide fuel cells [5,6]. Tellurium dioxide based glasses are outstanding materials for non-linear optical devices, up-conversion lasers and optical waveguides [7–11]. Some of the remarkable features of tellurite glasses are high refractive index, low phonon energies, high transparency in the infrared region and very high third order non-linear optical coefficients [12–14]. Tellurite glasses due to their large cross-section for stimulated Raman scattering are also used in optical amplifiers [7]. Specifically, the tellurite and bismuthate glasses have some of the highest values for third order non-linear optical coefficients. The high non-linearity of tellurites can be attributed to high hyper-polarizability of electron lone pair in the s-orbital of tellurium ions when bonded with oxygens [15]. More detailed study of tellurite glasses suggest that it is the nature of Te—O—Te linkages [16–18] itself which accounts to a large extent for high non-linear optical properties. The hyper-polarizability can be strengthened with either the addition of second lone electron pair ions such as Bi^{3+}, Pb^{2+} or with the addition of cations having empty d-orbitals such as Ti^{4+} or Nb^{5+} [19–21]. Moreover, the high values of hyper-polarizability also depend upon the electronegativity and the polarizability values of modifier ions and in general, the low electronegativity and high polarizability of heavy ions such as Nb^{5+} enhances the hyper-polarizability values. One shortcoming of tellurite glasses is that they are mechanically not strong, however these limitations can be overcome by providing heat treatment and converting them into glass-ceramics [22,23].

The short-range structural units of the tellurite network are trigonal bipyramidal TeO_4, TeO_{3+1} polyhedron and trigonal pyramidal TeO_3 units [9,24,25]. Barney et al. [26] measured the co-ordination of tellurium with oxygen to be 3.69(4) and reported that TeO_2 glass structure is composed of 2/3 trigonal bipyramidal units and 1/3 trigonal pyramidal units along with 16% of terminal oxygen atoms. The addition of modifier oxides leads to the progressive conversion of trigonal bipyramidal (TeO_4) units into TeO_{3+1} and TeO_3 polyhedra, and produces non-bridging oxygen (NBO) [26–30]. The pure tellurite glass is produced by roller quenching [26], and more recently by intermittent quenching [27]. According to the results of molecular dynamic studies

* Corresponding author.
E-mail address: atul.phy@gndu.ac.in (A. Khanna).

https://doi.org/10.1016/j.jnoncrysol.2017.12.002
Received 6 August 2017; Received in revised form 1 December 2017; Accepted 2 December 2017

carried out by Pietrucci et al. [28], the co-ordination of tellurium with oxygen ($N_{Te\text{-}O}$) is 3.69 while Gulenko et al. [29] determined $N_{Te\text{-}O}$ from neutron diffraction studies to be 3.79. Moreover, there is a good agreement between $N_{Te\text{-}O}$ values determined from neutron diffraction and Raman spectroscopy [26,27]. The glass forming ability (GFA) of TeO_2 increases considerably on mixing with the other glass formers such as B_2O_3 or P_2O_5 or by adding network modifiers such as WO_3, Nb_2O_5, Bi_2O_3, alkali and alkaline-earth metal oxides [31–33]. The addition of metal oxide modifiers to TeO_2 can both enhance and reduce its non-linear optical characteristics [32,34].

Incorporating Bi_2O_3 into the tellurite glass makes these glasses suitable to be used in the field of glass-ceramics, thermal sensors, optical fibers due to the fact that Bi_2O_3 enhances the refractive index and also lowers the melting temperatures. Earlier, it has been reported that borate glasses containing Bi_2O_3 demonstrate good gamma radiation shielding properties [35]. The glasses containing Bi_2O_3 have high infrared cut-off and high non-linear optical susceptibility which makes them excellent materials for infrared transmission components, photonic devices and optical switches [36]. Transition metal ions can exist in the multivalent states in the glass matrix due to which they are candidate materials for semiconductor applications such as in memory-switching devices and as cathode materials in batteries [37,38]. The addition of Nb_2O_5 stabilizes the glass system and strengthens the glass network due to high Nb−O bond enthalpy.

Heavy metal oxide tellurite systems are reported to form “anti-glass” phases. The first studies on the anti-glass materials were by Burckhardt and Trömel [39]. An anti-glass (also known as anion-glass) is a solid having long-range order of cations but the short-range order of anions is highly disturbed. This implies that the co-ordination number of network forming cations varies from an atom to atom within the material. Trömel et al. [40] reported that anti-glass phases in tellurite glasses are based on the CaF_2 fluorite-type structures where the Te^{4+} cations, along with the cations of the added modifiers are distributed statistically while the positions of anions (oxygen ions) are partly vacant. In such materials, the Te ions are present in such a way that the structures do not agree with the geometrical requirements of the usual tetragonal tellurium oxide. This disagreement leads to the large irregularities in the displacement of constituent atoms/ions which appear as Debye-Waller factors much larger than those generated by thermal motion of atoms. The modifiers added to the TeO_2, for the formation of anti-glass phases must have the ionic radii suitable for stabilizing the fluorite-type structure. The few reported anti-glass materials are $SrTe_5O_{11}$ [39], $Ln_2Te_6O_{11}$ [41] and $Bi_2Te_4O_{11}$ [42]. Crystallization of the Bi_2O_3-Nb_2O_5-TeO_2 glass shows spherulite like inclusions or droplets in the amorphous matrix [43]. It has been found from energy dispersive x-ray analysis that both the anti-glass inclusion and the amorphous matrix phases have the same elemental composition [23].

The observations and discussions concerning “anti-glass” structures can be related to the highly intriguing phenomenon of “poly-amorphism” discovered in amorphous ice [44], Y_2O_3-Al_2O_3 (YAG) glasses [45,46] and in triphenyl phosphite (TPP) [47]. The inclusions or droplets that appear in YAG glasses are similar to the LDA-HDA poly-amorphic textures observed in amorphous ice, moreover it was found by Aasland and Mcmillan that the droplet and matrix phases have the same chemical composition [48], this phenomenon is similar to what is observed in Bi_2O_3-Nb_2O_5-TeO_2 glasses, in which the droplet or inclusions have the same chemical composition as the matrix phase but possess different structures [23].

The X-ray diffraction (XRD) studies on bismuth–niobium–tellurite glasses indicated that these inclusions were crystalline while Bertrand et al. [49] inferred these in the terms of “anti-glass”. Hence, while YAG, TPP and amorphous ice show amorphous-amorphous phase separation (poly-amorphism), bismuth niobium tellurite system exhibit glass-anti-glass phase separation.

In the present work, we have studied the glass forming ability (GFA) of Bi_2O_3-TeO_2 and Bi_2O_3-Nb_2O_5-TeO_2 glass-anti-glass systems and characterized their short-range order by Raman spectroscopy. It is found that bismuth tellurite system forms either glass or anti-glass phases without any spherulite inclusions in the Bi_2O_3 composition range of 2 to 20-mol% by ice-water-quenching. However on adding Nb_2O_5 into the Bi_2O_3-TeO_2 system, GFA enhances significantly and co-existing glass and anti-glass phases are produced in Bi_2O_3-Nb_2O_5-TeO_2 system. The samples from the latter system show droplet like inclusions (spherulites) similar to the low density-high density polyamorphs reported earlier in YAG glasses [43]. The samples from the two systems were also studied for their structural and thermal properties by XRD, micro-Raman spectroscopy and Differential Scanning Calorimetry (DSC).

2. Experimental

Glass samples of the binary system: xBi_2O_3-(100-x) TeO_2 with x = 2, 3, 4, 5, 10 and 20-mol% were prepared by quenching the melt in a Pt crucible by immersing the bottom of crucible in ice-water bath. By this method small flakes of Bi_2O_3-TeO_2 glass and anti-glass materials were prepared.

Glasses of the composition: xBi_2O_3-xNb_2O_5-(100-2x)TeO_2 with x = 5, 7.5, 10 and 12.5-mol% were prepared by normal melt-quenching technique. The starting materials i.e. TeO_2 (Aldrich India 99%), Bi_2O_3 (Aldrich India 99.9%), Nb_2O_5 (Acros India, 99.9%) were weighed in an appropriate amount, ground in a mortar-pestle for about 30 min and transferred in a platinum crucible and melted in the furnace at 850°C for about 1 h. The melt was frequently homogenized by swirling the crucible inside the furnace. Disk shaped glass samples (diameter ~2 cm and thickness = 2 to 3 mm) were prepared by pouring the melt on a massive brass plate. After quenching, the samples were immediately annealed in the temperature range: 340–360°C for 30 to 60 min and then cooled slowly to room temperature.

Density measurements on disk shaped samples of Bi_2O_3-Nb_2O_5-TeO_2 were carried out by Archimedes method using di-butyl phthalate as the immersion fluid. The error in density was calculated from the precision of measurement of mass by electronic balance (10^{-4} g) and it is in the range: ± 0.001–0.005 g cm^{-3}.

Thermal studies were performed on the samples by DSC on a SETARAM Setsys Evolution-1750 system in the temperature range of 200–850°C at a heating rate of 10°C/min and in air flow of 20 ml/min. Measurements were performed on powdered samples in platinum pans. For DSC, sample amounts of 20–40 mg were used. The maximum uncertainty in the measurement of glass transition (T_g), crystallization (T_c), and liquidus temperatures (T_m) was ± 1°C.

Raman studies were performed on glass and anti-glass samples on Renishaw In-Via Reflex micro-Raman spectrometer using 2400 lines mm^{-1} diffraction grating, an edge filter for Stokes spectra and a CCD detector. The mapping mode was used to study the short-range structure of the matrix and droplet (spherulite) phases that co-exist with the amorphous matrix phase in the Nb_2O_5-Bi_2O_3-TeO_2 samples. Raman studies were carried out using 514.5 nm argon ion laser as an excitation source. All measurements were done at room temperature in the backscattering geometry with a 50× objective lens, in the Raman shift range of 30 to 1000 cm^{-1} and with the spectral resolution of better than 1 cm^{-1}.

The bismuth tellurite anti-glass sample containing 20-mol% Bi_2O_3 was heat treated at 450°C for 2 h in air. Another sample of composition: $7.5Bi_2O_3$-$7.5Nb_2O_5$-$85TeO_2$ was given sequential heat treatment at four temperatures of 380 °C(2 h), 450 °C(2 h), 500 °C(5 h) and 540 °C(5 h) in air. After each annealing treatment the sample was cooled to room temperature and analyzed by XRD and Raman studies to understand the phase formation and changes in the short-range structure.