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Structure-property correlations in TiO_2-Bi_2O_3-B_2O_3-TeO_2 glasses

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A B S T R A C T

Tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2 were prepared and structure-property correlations were carried out by density measurements, X-ray diffraction, Differential Scanning Calorimetry (DSC), Raman, FTIR, UV–visible and ^{11}B MAS-NMR studies. Titanium-tellurite and titanium bismuth tellurite glasses require high melt-cooling rates and were prepared by splat quenching. On adding B_2O_3, the glass forming ability (GFA) enhances considerably and bulk glasses could be synthesized at lower quenching rates. The density of glasses shows a direct correlation with molecular mass of the constituents. UV–visible studies were used to determine the optical band gap and refractive index. Raman studies found that the co-ordination number of tellurium ions with oxygen (N_{Te-O}) remains constant with variation in TiO_2 molar content, while the incorporation of B_2O_3 and Bi_2O_3 decreases N_{Te-O}. DSC studies show that the glass transition temperature (T_g) increases with B_2O_3 and TiO_2 concentrations and that T_g correlates well with bond enthalpy of the metal oxides. ^{11}B MAS-NMR studies found that the co-ordination number of boron with oxygen (N_{B-O}) decreases with increase in B_2O_3 content while increasing TiO_2 and Bi_2O_3 concentration does not significantly modify N_{B-O}.

1. Introduction

Tellurium-oxide based glasses have generated great interest due to their unique physical properties such as high refractive indices, good non-linear optical properties, high dielectric constant, low melting points, low phonon energies, semiconducting properties and wide optical transmission windows [1–6]. These noteworthy properties make them useful for applications such as window materials, optical memory, up-conversion lasers and optical communication [7]. Among the oxide glasses, TeO_2 based glasses have very high non-linear susceptibility values, which stimulate a special interest in the fundamental research of TeO_2 compounds. The values of non-linear indices depend upon the concentration and on the nature of cations used in TeO_2 glassy matrix [8]. The ab-initio studies performed on TeO_2 based glasses show that the higher order of hyper-polarizability [9–14] is inherent exclusively to the molecules having the form of linear chains, like the ones formed from 'n' polymerized Te−O species [15].

In tellurite glass network the basic building blocks are trigonal bipyramidal (tbp) (TeO_4) units and trigonal pyramidal (TeO_3) units [16,17], in which a lone pair of electrons occupy one of the equatorial sites [18]. The fraction of pyramidal (TeO_3) units increases with the increase in the monovalent or divalent cation content. TeO_2 is a conditional glass former [19] and forms glass easily with modifiers such as alkali, alkaline-earth and transition metal oxides or other glass formers such as V_2O_5 and B_2O_3. The poor glass forming ability (GFA) of TeO_2 is due to the presence of the lone pair of electrons that occupy the equatorial site. Earlier, pure TeO_2 glass was synthesized at very high quenching rate of $\sim 10^5$ K s^{-1} by twin roller quench technique [18] and recently, it has been synthesized in the bulk form by the intermittent quenching technique [20]. The two crystalline structures of tellurium dioxide, α-TeO_2 (paratellurite) and β-TeO_2 (tellurite) have been known for many years [21]. TeO_2 can be readily transformed into the α-TeO_2 on heating, whereas the β-TeO_2 phase is not observed during this process. On slowly heating the pure glass, the γ-TeO_2 structure was found to appear as the first crystalline phase. Pietrucci et al. [22] through molecular simulation studies reported N_{Te-O} to be 3.69 and neutron diffraction studies of glassy TeO_2 by Gulenko et al. [23] reported N_{Te-O} to be 3.73. The experimental results and theoretical predictions on co-ordination of tellurium with oxygen show good agreement. Moreover N_{Te-O} values calculated from neutron diffraction studies show good agreement with the results from Raman spectroscopy [18]. The addition of metal oxides in tellurite glasses decreases N_{Te-O}

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and improves its GFA and makes it more efficient for opto-electronic applications [24].

The addition of modifiers into TeO_2 decreases the non-linear properties of glass. The reason for this decrease in polarizability is associated with the fact that the oxygen atoms of the modifier react with the neutral TeO_2 units and produce the $[TeO_3]^{2-}$ units, leading to the evolution of complex tellurite anions. The addition of certain modifiers leads to the enhancement of non-linear refractive indices of tellurite glasses due to the high polarizability of involved cations. The two categories of these modifiers include cations of heavy p-elements and cations of d-elements. The later one includes Ti^{4+}, Zr^{4+} etc. which consist of weakly occupied highest orbitals while former one includes the cations like Pb^{2+} and Bi^{3+} which contain the lone pair of electrons [25].

The transition metal oxide glasses find wide applications in the field of switching devices and cathode materials in batteries [26] and opto-electronic devices. The addition of TiO_2 into tellurite glasses enhances the thermal stability and chemical resistance properties [27–29]. Vogel et al. [30] reported that, in silicate glasses containing only titanium or niobium, the non-linear refractive index coefficient is much larger for Ti than for Nb [31]. TiO_2 as a modifier holds special interest because, the addition of TiO_2 in TeO_2 glass does not significantly produces $[TeO_3]^{2-}$ units, thus maintaining the framework nature of the glass and hence favors the high polarizability and hyper-polarizability.

Bi_2O_3 belongs to the group of metal oxides that enhances the non-linear refractive indices of oxide glasses and the bismuthate glasses, exhibit some of the highest non-linear optical properties [32]. Among the heavy metal oxides, it holds great value in electrical and optical applications and ceramic production due to high polarizability of Bi^{3+} ions [33]. Earlier, it has been reported that borate glasses containing bismuth can be used as transparent nuclear radiation shielding windows [34]. Bismuth oxide due to its non-toxic nature, high refractive index and wide transmission range finds its use in thermal and mechanical sensors, reflecting windows and electronic devices [35]. Udovic et al. [36] has reported that the TeO_2 glass system containing TiO_2 jointly with the Bi_2O_3 proves to be an asset in the glasses as it offers the high non-linear optical characteristics along with high mechanical and thermal resistance. The glass transition temperature is found to increase in this case, which represents the relative strength of Ti—O—Te and Bi—O—Te bridges which replace the Te—O—Te bridges.

B_2O_3 is the best oxide glass former [37] and is widely used for synthesis of superionic conductors and thermal shock-resistant borosilicate glasses. B_2O_3 is also incorporated in silicate glasses to improve their chemical and thermal stability. Borate glasses have a random network consisting of tetrahedral (BO_4) and trigonal boron (BO_3) units and their combinations form diborate, triborate, tetraborate and pentaborate groups [38]. The borotellurite glasses contain BO_4 and BO_3 units, TeO_4 trigonal bipyramidal and TeO_3 pyramidal units at a high B_2O_3 content [39]. When two glass formers such as B_2O_3 and TeO_2 are mixed together, the co-ordination number and the concentration of structural units of both the species vary in a complex manner on incorporating a network modifier. Borate and tellurite units in borotellurite glasses connect together to form mixed structural units that enhance the electrical conductivity of borotellurite glasses [40]. In comparison to binary glasses, the multi-component tellurite glasses have good optical and electrical properties. Tellurite glasses belonging to the systems: TeO_2-Nb_2O_5 [41], TeO_2-BaO-TiO_2 [42], Al_2O_3–B_2O_3–TeO_2 [43] have been prepared and characterized for their remarkable non-linear optical properties, high refractive indices and good electrical conductivity.

In the present work, our aim is to study short-range order and the GFA of the tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2 and their effects on the optical, thermal and dielectric properties. To study the effects of varying B_2O_3 concentration on Te—O and B—O speciation; ^{11}B Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR) and Raman spectroscopic techniques were used.

2. Experimental

2.1. Glass preparation

Tellurite and borotellurite glasses containing TiO_2 and Bi_2O_3 of the composition:

1. $xTiO_2$-(100-x) TeO_2 with x = 5, 9, 10, 12 and 15-mol%
2. $xTiO_2$-yBi_2O_3-(100-x-y) TeO_2 with x = 5-mol% and y = 5 and 10-mol%
3. $xTiO_2$-yBi_2O_3-zB_2O_3-(100-x-y-z) TeO_2 with x = 5, 10-mol%, y = 5, 10, 20, 25 and 30-mol% and z = 10, 15, 20 and 30-mol%

were prepared using TeO_2 (Aldrich India 99%), Bi_2O_3 (Aldrich India 99.9%), H_3BO_3 (Aldrich India 99.9%), TiO_2 (Aldrich India 99.9%) by melt-quench technique. Appropriate amounts of chemicals were weighed, grinded in a mortar-pestle for about 30 min and then put in platinum crucible. The batch mixture was then sintered at 250°C for 24 h in an electric furnace. The temperature of the furnace was then slowly raised to 900°C and the melt was kept at this temperature for 1 h, before quenching it on a heavy brass plate. The crucible containing the melt was swirled several times inside the furnace to ensure its homogeneity.

The glass samples without B_2O_3 were prepared by splat-quench technique as these required higher cooling rates, however samples containing B_2O_3 were prepared by normal quenching in which a small quantity of the melt was poured on a brass plate and disk shaped glass was obtained, the later samples were subsequently annealed at 280 °C for 1 h. Splat-quenched samples were not given any post-quenching annealing treatment. All glasses were clear and highly transparent. The batch composition, density and molar volume data of samples are presented in Table 1.

2.2. X-ray diffraction (XRD)

XRD studies were performed on powdered and disk-shaped glass samples on Bruker D8 Focus X-ray diffractometer using Cu K_α radiation in the 2θ range of 15° to 55°. The X-ray tube was operated at 40 kV and 30 mA and the intensity of scattered X-rays was measured with a scintillation detector.

2.3. Density measurement

Density of glasses was measured by Archimedes method on an electronic balance of sensitivity 10^{-4} g, using di-butyl phthalate as an immersion liquid. Each measurement was repeated twice. The maximum uncertainty was in the range of ± 0.001–0.03 g cm^{-3}. Due to the smaller size of splat-quenched glasses in comparison of normal-quenched glasses, the uncertainty in density measurement was higher in case of splat-quenched samples.

2.4. Thermal studies

Thermal properties such as glass transition temperature (T_g), crystallization temperature (T_c) and the liquidus temperature (T_m) were measured by Differential Scanning Calorimetry (DSC). DSC analysis were performed on SETARAM SETSYS Evolution-1750 system in the temperature range of 200–750°C at a heating rate of 10°C/min, in air flow of 20 ml/min. Measurements were performed on powdered samples in platinum pans. Sample amounts of 20–40 mg were used. The maximum uncertainty in the measurement of glass transition, crystallization and liquidus temperatures was ± 1 °C.