Journal of Non-Crystalline Solids 444 (2016) 1–10

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Structural, optical, dielectric and thermal properties of molybdenum tellurite and borotellurite glasses

Amandeep Kaur [a], Atul Khanna [a,*], Fernando González [b], Carmen Pesquera [b], Banghao Chen [c]

[a] Department of Physics, Guru Nanak Dev University, Amritsar, Punjab 143005, India
[b] Department of Chemistry and Process & Recourse Engineering, University of Cantabria, Spain
[c] Chemistry & Biochemistry Department, Florida State University, Tallahassee, FL 32306, USA

ARTICLE INFO

Article history:
Received 19 December 2015
Received in revised form 9 April 2016
Accepted 15 April 2016
Available online 26 April 2016

Keywords:
Molybdenum tellurite and borotellurite glasses
Short-range order
Raman spectroscopy
B^{11} MAS-NMR
Tellurium coordination
Boron coordination
Structural relaxation

ABSTRACT

Molybdenum tellurite and borotellurite glasses were prepared and structure-property correlations were carried out by density, X-ray diffraction, dielectric measurements, differential scanning calorimetry, UV–visible, infrared, Raman and B^{11} Magic Angle Spinning Nuclear Magnetic Resonance studies. The short-range structure of molybdenum tellurite glasses consists of TeO_4, TeO_3 and MoO_6 structural units. Increase in MoO_3 concentration from 20 to 50 mol% decreases the Te—O coordination from 3.48 to 3.26 and lowers the glass transition temperature (T_g) due to increase in the concentration of weaker Mo—O bonds at the expense of stronger Te—O bonds. Refractive index of molybdenum tellurite glasses increases while the dielectric constant decreases with increase in MoO_3 concentration. The addition of B_2O_3 in the tellurite network enhances T_g and suppresses the tendency towards crystallization. The effects of B_2O_3 are similar to that of MoO_3 and it produces structural transformations: $TeO_4 \rightarrow TeO_3$ and $BO_4 \rightarrow BO_3$. The addition of B_2O_3 does not significantly modify the optical properties but the dielectric constant decreases by a small amount. Glass sample of $20MoO_3$-$80TeO_2$ was annealed at 280 °C for ~500 h and changes in its density and thermal properties were studied; it was found that the annealing increases the glass density slightly, but it causes a drastic enhancement of T_g by 10 °C, due to the structural rearrangements in the intermediate range order without effecting Te—O and Mo—O speciation.

1. Introduction

TeO_2 based glasses have attracted considerable scientific interest due to their several useful properties such as good glass stability and durability, wide optical transmission window, low melting point, non-hygroscopic nature, high refractive indices and exceptional non-linear optical properties. Tellurite glasses find applications as gas sensors, memory switching devices and optical waveguides [1–5]. Crystalline α-TeO_2 contains Te^{4+} only in tetrahedral coordination with oxygen (i.e. $N_{Te\text{-}O} = 4$), but glassy TeO_2 has $N_{Te\text{-}O} < 4$ [6]. Glassy TeO_2 can be synthesized by twin roller quenching at melt-cooling rates of ~10^5 K s^{-1}. Ab initio molecular dynamic simulation studies on amorphous TeO_2 by Pietrucci et al. found $N_{Te\text{-}O}$ to be 3.69 [7] and neutron diffraction studies on glassy TeO_2 by Gulenko et al. [8] and by Barney et al. [6] determined $N_{Te\text{-}O}$ to be 3.73 and 3.68 respectively. Therefore experimental findings match well with theoretical predictions on the short range structure of glassy TeO_2. Further $N_{Te\text{-}O}$ from neutron diffraction analysis show good agreement with the values determined from Raman studies on tellurite glasses [6]. $N_{Te\text{-}O}$ decreases and the glass forming ability of TeO_2 enhances significantly on mixing it with alkali, alkaline-earth, heavy metal, rare earth and transition metal oxides [1]. The addition of metal oxides in tellurite glasses improves the functionality of glasses for optical applications [9,10].

MoO_3 has excellent optoelectronic properties [11]. It can act as a network former [12], and also as network modifier in the presence of other glass formers such as TeO_2 [13] and B_2O_3 [14]. On mixing it with TeO_2 it forms glasses in the composition range of 12.5 to 58.5 mol% of MoO_3 [15]. MoO_3 has the ability to control phase separation in glasses [16]. It produces structural modification in the tellurite network similar to WO_3 and V_2O_5 in WO_3-TeO_2 [17,18] and V_2O_5-TeO_2 systems [19] respectively. In TeO_2-MoO_3 glasses the basic structural units are fourfold coordinated TeO_4 tetrahedra, TeO_{3+1}, TeO_3 and six-fold coordinated single and paired MoO_6 octahedra [20,21]. The short-range atomic order in molybdenum tellurite glasses has been analyzed by variety of techniques: neutron and X-ray diffraction [22,23], X-ray photoelectron spectroscopy (XPS) [24] and Extended X-ray Absorption Fine Structure (EXAFS) [16] and it is found that the addition of MoO_3 decreases Te^{4+} coordination from 4 to 3 and that of Mo^{6+} from 6 to 4 [22].

Neov et al. [22] and Manisha et al. [25] reported that MoO_6 units transform into MoO_4 with increase in MoO_3 concentration in molybdenum tellurite glasses. Whereas Sokolov et al. [20] analyzed the structure of molybdenum tellurite glasses by quantum mechanical

---

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

http://dx.doi.org/10.1016/j.jnoncrysol.2016.04.033
0022-3093/© 2016 Elsevier B.V. All rights reserved.

calculations and Raman spectroscopy and concluded that only TeO_4, $O{=}TeO_2$, single octahedral ($O{=}MoO_5$) and paired octahedral ($2[O{=}MoO_5]$) units exist in the glass network. Moreover according to Sokolov et al. MoO_6 units with two double bonds and MoO_4 tetrahedra are unstable and do not exist in the glass network. Sekiya et al. [21] and Dimitriev et al. [26] also concluded from Raman and FTIR studies that at low MoO_3 concentration (<30 mol%) the intensity of the Raman peak at 920 cm^{-1} (due to Mo═O bond vibrations of single or paired MoO_6) is higher than the intensity of Raman peak at 870 cm^{-1} (attributed to vibrations of Mo—O—Mo linkages in MoO_6). On increasing MoO_3 mol%, the concentration of Mo═O bonds decreases and the peak at 870 cm^{-1} becomes more prominent due to the formation of Mo—O—Mo linkages. Dimitriev et al. found from X-ray diffraction radial distribution function analysis that $N_{Te\text{-}O}$ decreases with increase in MoO_3 concentration and that these glasses contain MoO_6 units [23].

Calas et al. [16] concluded from Mo—K edge EXAFS that isolated MoO_4 exist in molybdenum tellurite glasses which are not directly connected to the glass network. Mekki et al. [24] found from X-ray photoelectron spectroscopy (XPS) studies that the binding energies of 3d electrons of Te^{4+} in MoO_3-TeO_2 glasses is equal to that in α-TeO_2 crystals, similarly the binding energy of 3d electrons of Mo^{6+} in glasses is equal to that in α-MoO_3 crystals, hence these authors concluded that there exist only TeO_4 and MoO_6 units in molybdenum tellurite glasses containing 10 to 40 mol% of MoO_3 and that the oxidation state of Mo ions is only 6^+ and there are no Mo ions in 4^+ and 5^+ states.

Therefore, there are contradictory findings on Mo—O and Te—O speciation in these glasses and it is an unresolved issue that whether Mo^{6+} coordination changes or remains constant with MoO_3 concentration. It is necessary to carry out comprehensive studies on the thermal, optical and structural properties of MoO_3-TeO_2 glasses to resolve the questions on $N_{Te\text{-}O}$ and $N_{Mo\text{-}O}$.

B_2O_3 is the best oxide glass former [27], and is incorporated in silicate glasses to increase its chemical and thermal stability. Basic structural units of borate glasses are BO_4 and BO_3. An increase in the concentration of B_2O_3 in borotellurite glasses causes the transformation of BO_4 into BO_3 and decrease in boron oxygen coordination ($N_{B\text{-}O}$) [28, 29]. Decrease in the fraction of tetrahedral borons (N_4) in the glass network lowers the glass forming ability (GFA) of borotellurite glasses. The thermal stability and GFA of borate glasses depends on N_4 value in the glass network. Higher the N_4, more is its glass forming range [29], while in tellurite glasses, the opposite is true; it are the triangularly coordinated TeO_3 units which are the feature of the glassy phase and TeO_4 units are a feature of crystalline TeO_2. Borate and tellurite units in borotellurite glasses can connect with each other to form mixed structural units such as $BTeO_3$ and $BTeO_5$ which enhance the electrical conductivity of borotellurite glasses [30].

Multi-component tellurite glasses have good optical and electrical properties because of high refractive index and lower ability to devitrify as compared to binary tellurite glass system [31]. Tellurite glasses in the systems such as TeO_2–WO_3, TeO_2–Nb_2O_5 [18], TeO_2–Nb_2O_5-Bi_2O_3 [32], TeO_2–Nb_2O_5–ZnO [33], TeO_2–Nb_2O_5–ZnO-Gd_2O_3 [34] and TeO_2–TiO_2–Bi_2O_3 [3] have been prepared and characterized for their excellent nonlinear optical properties, high refractive indices and good electrical conductivity.

It is the objective of this work to analyze the changes in short-range structure of molybdenum and molybdenum borotellurite glasses and their thermal, optical and dielectric properties with varying MoO_3 and B_2O_3 concentrations in respective glasses. B^{11} Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR), Raman and FTIR methods are used to study the effects of addition of B_2O_3 and MoO_3 on B—O, Te—O and Mo—O speciation. Finally, the effects of long duration annealing on the density, thermal, optical, short-range and medium-range structure of one molybdenum tellurite glass (20MoTe) is studied.

2. Experimental

2.1 Glass preparation

Molybdenum tellurite and borotellurite glasses of composition: $xMoO_3$-(100-x) TeO_2 with x = 20, 30, 35, 40, 45 and 50 mol% and $20MoO_3$-xB_2O_3-(80-x) TeO_2 with x = 5 and 10 mol% respectively were prepared using MoO_3 (Otto Kemi, India, 99%), H_3BO_3 (Aldrich India, 99.9%) and TeO_2 (Aldrich India, 99%) as starting materials. Appropriate amounts of chemicals were weighed and mixed together in agate mortar pestle for about 30 min and then transferred to a platinum crucible. The batch mixture was melted at 850 °C for 30 min in an electric furnace. For each composition a glass sample was prepared by normal quenching method in which a small quantity of the melt was poured on a heavy brass plate and a disk-shaped sample was obtained and annealed at 300 °C for 30 min. Bubble free, clear and dark-brown colored samples were obtained, the color of glasses darkened with increase in the MoO_3 concentration. The composition, density and molar volume of samples are given in Table 1.

2.2 X-ray diffraction (XRD)

XRD measurements were performed on powdered glass samples on Bruker D8 Focus X-ray diffractometer with Cu K_α radiation (λ = 1.54056 Å) in the 2θ range of 10°–65°. The X-ray tube was operated at 40 kV and 30 mA and the scattered X-ray intensity was measured with a scintillation detector.

2.3 Density measurement

Density of glasses was measured by Archimedes method using dibutylphatalate (DBP) 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 was in the range of ±0.002 to ±0.004 g cm^{-3}.

2.4 Differential Scanning Calorimetry (DSC)

DSC studies were carried out on a SETARAM SETYS 16 TG-DSC system in temperature range of 200–800 °C at heating rate of 10 °C min^{-1}. Measurements were performed on powdered samples in platinum pans. Samples amounts of 20–50 mg were used for DSC analysis. Maximum uncertainty in the measurement of glass transition (midpoint), crystallization (peak point) and melting temperatures (peak point) is ±1 °C.

2.5 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of molybdenum borotellurite samples were recorded on Perkin-Elmer Frontier FTIR spectrometer using KBr disk technique in the wavenumber range of 400 cm^{-1} to 2000 cm^{-1} at room temperature. The mixture of powdered glass sample and spectroscopic grade KBr (1:100 by weight) was subjected to pressure of 10 tons cm^{-2} to prepare thin pellets. The FTIR absorption spectra were measured immediately after preparing the pellets.

2.6 Raman spectroscopy

Raman scattering studies were performed on samples with Renishaw In-Via Reflex micro-Raman spectrometer using 514.5 nm argon ion laser (50 mW) as excitation source, diffraction grating having 2400 lines mm^{-1}, an edge filter and a Peltier cooled CCD detector. Measurements were carried out in an unpolarized mode, at room temperature in the backscattering geometry, in the wave number range of 30 to 1000 cm^{-1} at a spectral resolution of 1 cm^{-1}.