Solid State Ionics 296 (2016) 54–62

Contents lists available at ScienceDirect

Solid State Ionics

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

Synthesis, characterization and AC conductivity of alkali metal substituted telluride glasses

Awadhesh Kumar Yadav [a], Priyanka A. Jha [b], Sevi Murugavel [c], Prabhakar Singh [b,*]

[a] Department of Physics, Dr.Bheem Rao Ambedkar Government Degree College, Anaugi, Kannauj, India
[b] Department of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India
[c] Department of Physics & Astrophysics, University of Delhi, New Delhi 110021, India

ARTICLE INFO

Article history:
Received 7 April 2016
Received in revised form 8 August 2016
Accepted 20 August 2016
Available online xxxx

ABSTRACT

A glass system $0.70TeO_2 \cdot (0.30\text{-}x)\ Na_2O \cdot xK_2O$ with $0 \le x \le 0.3$ was prepared using Quenching method. The structural, optical and electrical properties of these compositions were investigated. The structural analysis indicated that these glasses are composed of structural units of TeO_3, TeO_4, TeO_{3+d} and Te—O—Te. The optical band gap of the investigated glasses was found to lie between 3.43 and 3.74 eV range. With the increasing content of K_2O, the values of density, molar volume, optical basicity, refractive index, molar refractivity, electronic polarizability and electric susceptibility were found to increase, whereas Urbach energy and oxygen packing density decreased. The ion dynamics in these glass systems were studied using Dyre's free energy barrier model and Jonscher Power Law. The conductivity data followed both the models. The scaling behaviour of the two glass systems was studied using Ghosh and Dyre's scaling models. The conductivity spectra were found to follow the Dyre's scaling law, however, surprisingly, the spectra were failed to follow the Ghosh scaling law.

1. Introduction

Telluride glasses and glass ceramics are promising candidates for advanced photonics and optoelectronics because of high refractive index and very wide transmittance range in the IR region (up to 6 μm) [1–2]. It is well known that tellurium oxide (TeO_2) works as a conditional glass former in comparison with other oxide glass formers such as SiO_2, GeO_2, B_2O_3 and P_2O_5. It also requires very high quenching rate to form a glass [2,6–7]. Metal oxides not only modify the properties of glasses but also capable of changing the characteristic features of other ceramics [4–5]. Its glass forming ability can be improved by adding modifiers like alkali metal and alkaline-earth metal oxides. Moreover, the alkali metal substituted telluride glasses possess strikingly high non-linear susceptibility and superior chemical durability. They are also known for the potentially important family of optical devices [2–3]. Therefore, with the addition of alkali oxides into TeO_2 network ease the glass formation with a moderate cooling rate [8–12].

The anomalous behaviour of bulk properties of glasses is studied on the basis of local atomic structure. The pure TeO_2 glass network structure consists of TeO_4 trigonal bipyramids, in which one equatorial axis contains lone-pair of electrons and vertices are connected by Te–$_{eq}O_{ax}$–Te linkage [10,13]. Therefore, the structure of TeO_2 glass differs from conventional glass forming oxides. The Raman spectroscopy studies on M_2O-TeO_2 (M = alkali metal) glasses suggest the depolymerisation of the network structure and formation of polyhedral units with the change in alkali oxide content. The alkali metal substituted glasses possess a structure consisting of TeO_4 corner sharing trigonal bipyramids (tbp's) and TeO_{3+1} polyhedra with one non-bridging oxygen (NBO). On increasing network modifier content with 20–30 mol% alkali oxide, the network structure becomes depolymerized by the formation of TeO_3 trigonal pyramids (tp's) with NBOs [14–16].

The electrical properties of telluride glasses can also be tailored with the substitution of alkali metal and alkaline-earth metal oxides [17,18]. It is found that the alkali ion conductivity of telluride glasses is greater than that of the borate, silicate and borosilicate glasses [19–20]. As the electronegativity of alkali metal ions is smaller than those of Te and O and hence the charge transfer must occur from alkali ion to TeO_2. The charge transfer continuously varies as the alkali metal oxide content is increased. Thus, the charge transfer strongly depends on alkali ion content than the formation of non-bridging oxygen (NBO) [21]. Furthermore, due to lone-pair electrons in the TeO_2 structural units, the dielectric constant of these glasses is found to be higher than the other conventional glass forming oxides [22].

The understanding of ion dynamics in chalcogenide glasses has found much interest by the scientific community [23–24]. The characteristic property of electrical conductivity of disordered solids is dispersion in ac conductivity and has been reported in the wide variety of glasses. It is observed that conductivity is constant in the low frequency regions, while it becomes strongly frequency dependent at higher frequencies and varies approximately as a function of power of the frequency. The conductivity increases usually continue till phonon

* Corresponding author.
E-mail address: psingh.app@iitbhu.ac.in (P. Singh).

http://dx.doi.org/10.1016/j.ssi.2016.08.013
0167-2738/

frequencies. This behaviour is observed in a wide variety of non-metallic disordered solids.

This is true not only for the frequency but also for the temperature dependence of the conductivity. It is well known that conductivity increases with frequency due to the existence of hopping charge carriers in the solid. For this, various ion-ion interaction theories and models have been proposed to explain ac conductivity behaviour [25,26].

In the present report, we are discussing the synthesis and characterization of $0.70TeO_2 \cdot (0.30\text{-}x)Na_2O \cdot xK_2O$ with $0 \le x \le 0.3$ glasses by various analytical techniques. The impedance analysis of investigated glass systems has already been reported by the authors [27]. In this paper, it is concluded that bulk contribution was observed at low temperature along with some electrode contribution at high temperature. The scaling of Modulus analysis revealed temperature dependent phenomenon. The main objective of the present investigation is to report the qualitative explanation of ac conduction through a proper Hopping and scaling models. For this, the ion dynamics of the systems having potassium content <5 mol% is studied in detail using Jonscher Power Law and a model defined for alkali metal substituted glasses i.e. Dyre's random free energy barrier model. Bulk density, optical basicity, molar volume, refractive index, molar refractivity, electronic polarizability and electric susceptibility, optical band gap, Urbach energy and oxygen packing density have also been measured and evaluated for different concentration of K_2O.

2. Experimental procedures

Bulk glasses of $0.70TeO_2 \cdot (0.30 - x)Na_2O \cdot xK_2O$ with $0 \le x \le 0.3$ were synthesized using conventional melt quenching method. The high purity analytical reagent grade chemicals TeO_2 (Alfa Aesar, 99.995%), K_2CO_3 (Merk, 98%) and Na_2CO_3 (Rankem, 99.5%) were taken in stoichiometric amounts. The powders were then ground in acetone medium. The ground powder is then placed in high-grade alumina crucible in open air atmosphere into programmable glass melting furnace at temperature 1000 °C. The melt was then maintained at 1000 °C in the furnace for 1 h for refining and homogenization. The homogenous melt formed was quenched in an aluminium mould. The melt was then pressed by a thick aluminium plate. The quenched melt is kept it at 220 °C for 4 h to remove the internal residual stresses and finally cooled to room temperature with 1 °C/min.

The obtained glasses were characterized by X-ray diffraction (XRD) technique using Rigaku Miniflex-II X-ray diffractometer using Cu-$K_{\alpha 1}$ radiation to confirm the amorphous nature of these glasses. The differential scanning calorimetry (DSC) was carried out on powdered glass samples using a 'Perkin Elmer Thermal Analysis' from 25 to 275 °C with heating rate of 10 °C/min. The Infrared spectra of samples were recorded using JASCO FT/IR-5300 and Brucker FTIR Tensor-27 in the wave number range 400–4000 cm^{-1} at room temperature. In addition, UV–visible absorption spectra were carried out using UV–visible spectrophotometer (Varian, Carry-50Bio) in wavelength range 200–800 nm. For the electrical conductivity measurements, the bulk glass samples were cut to their requisite size and then polished with sand paper (grit size 600). Then metallic silver (Code No. 1337-A, Elteck Corporation, India) electrodes were painted onto both the surfaces of the glass sample for electrical conductivity measurement. Electrical conductivity measurements were carried out by using Novocontrol α-S high resolution impedance analyser in a frequency range from 10 mHz to 3 MHz, and temperature range between 273 K and 473 K.

3. Results and discussion

The composition in the glass system $0.70TeO_2 \cdot (0.30 - x)Na_2O \cdot xK_2O$ with $x = 0.00$, $x = 0.05$, $x = 0.10$, $x = 0.15$, $x = 0.20$, $x = 0.25$ and $x = 0.30$ have been designated as TNK0, TNK5, TNK10, TNK15, TNK20, TNK25 and TNK30 respectively. For example, TNK15 indicates the composition $0.70TeO_2 \cdot (0.15)\ Na_2O\ 0.15K_2O$. In Fig. 1, we illustrate the recorded X-ray diffraction patterns of investigated mixed alkali telluride glasses in the present investigation. The entire pattern reveals the short-range ordering of telluride network in the glassy matrix showing the characteristic feature of amorphous nature of the glasses.

3.1. Thermal properties

Fig. 2 shows the typical DSC patterns of the studied glass samples. In DSC patterns, a single endothermic peak is observed which corresponds to the glass transition temperature. Moreover, glass transition temperature is observed to depend strongly on composition. Some more endothermic peaks have also been observed (depending on the glass constituents) which correspond to the crystallization of the glass.

No systematic trend is observed in the value of glass transition temperature with the addition of K_2O content and it is found to lie in the range of 116–159 °C. The glass stability parameters are calculated by using the following relations:

$$\Delta T = T_x - T_p \tag{1}$$

$$\Delta T_p = T_p - T_x \tag{2}$$

$$S = \frac{\Delta T \Delta T_p}{T_g} \tag{3}$$

where, S = stability parameter, T_x = onset crystallization temperature, T_p = peak crystallization temperature, T_g = glass transition temperature. The magnitude of ΔT increases with increasing the content of K_2O in place of Na_2O. This indicates that stability of glasses increases with increase of concentration of K_2O in the glassy matrix [28]. It is also observed that the magnitude of stability factors, S, increases with addition of K_2O indicating that the stability of glass against crystallization is enhanced by K_2O addition [29].

The observed endothermic peak below 100 °C is attributed to release of water or hydroxyl group present in the glassy matrix as indicated in

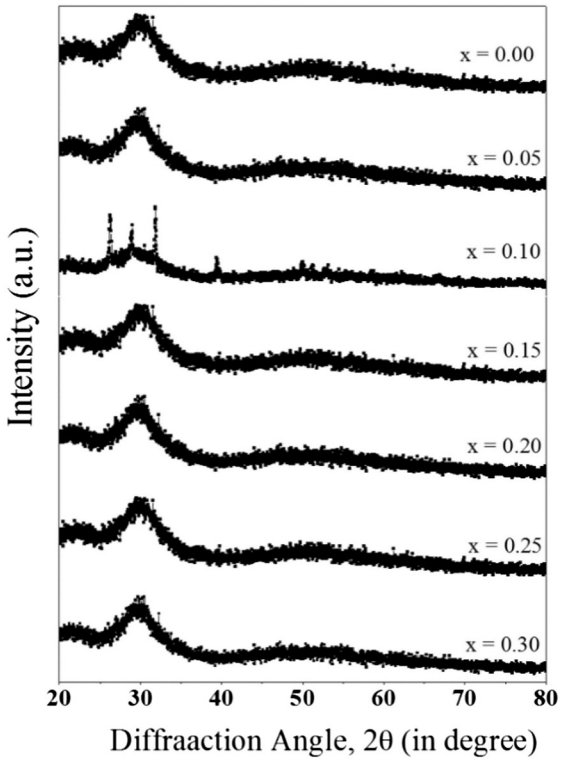

Fig. 1. X-ray diffraction patterns of glass samples TNK0, TNK5, TNK10, TNK15, TNK20, TNK25 and TNK30.