Journal of Non-Crystalline Solids 414 (2015) 51–58

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Structural and optical properties of $30Li_2O–55B_2O_3–5ZnO–xTiO_2–(10 - x)V_2O_5$, $(0 \le x \le 10)$ glasses

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ARTICLE INFO

Article history:
Received 20 September 2014
Received in revised form 3 January 2015
Accepted 8 February 2015
Available online 18 February 2015

Keywords:
X-ray diffraction;
UV–visible;
Optical basicity;
IR spectra;
PL spectra

ABSTRACT

The structural and optical properties have been investigated for the $30Li_2O–55B_2O_3–5ZnO–xTiO_2–(10 - x)V_2O_5$, $(0 \le x \le 10)$ glasses using different spectroscopic characterization techniques. The relationship between optical and structural properties has been established in light of the variation of TiO_2 content. The band gap shows a decreasing trend with a decrease in V_2O_5 content. Physical parameters like density, molar volume, ionic concentration and inter ionic distance have been obtained for all the glass compositions. Theoretical parameters like optical basicity, oxide polarizability and electronegativity have been obtained and discussed in relation to the non-bridging oxygen (NBO). Bulk modulus has been calculated theoretically and correlated with average stretching force constant and network bonds/volume.

1. Introduction

Glasses are being used in the field of solid-state ionic due to their applications in magnetic heads, cathode ray tubes, hybrid integrated circuits, batteries and solid oxide fuel cells [1–3]. Lots of research has been done on the heavy metal oxide containing ternary and quaternary glasses due to their application as reflecting windows, ray absorbers, optical filters as well as mechanical sensors [4–8]. In addition to this, heavy metal oxide glasses exhibit good chemical durability and non-linear optical properties [4,5].

Transition metal oxides containing borate glasses find a wide range of applications in solar energy converters and solid state lasers [7–9]. The presence of transition metal oxides in glass composition modifies the properties of glasses due to variable transition states which formed locally different structural units. For instance, the character of chemical bonds and structural rearrangement occurs in the glass network due to incorporation of vanadyl ion (VO^{2+}) [6–9] which changes the optical properties of the glasses. On the other hand, small amount of titanium oxide acts as a nucleating agent and it helps in reducing the band gap of material [10,11]. In addition to this, researchers have also found titanium oxide doped borosilicate glasses as suitable sealing materials for the solid oxide fuel cell technology [12,13]. On the other hand, glass compositions that contained ZnO have broad-spectrum applications as conducting electrodes for ferroelectric/piezoelectric layers, dielectric layers and barrier ribs for plasma displays [2,3]. When alkali metal oxides are introduced in the borate glass network, then a variety of structural and optical changes take place in the glasses.

The glass composition, thermal history and measurement temperature play an imperative role in determining the properties of final quenched glass. For any suitable optical device application of glass, it is indispensable to have a prior knowledge of certain parameters like optical band gap, optical absorption, optical basicity and Urbach energy particularly for polynary glasses (multi components). Tremendous flexibility of properties is observed for polynary glasses due to the synergistic effect of all the participating ions. Moreover, the replacement of Ti^{4+} by V^{5+} cations in the present system is expected to enhance the glass formation tendency. Addition of V_2O_5 and TiO_2 in glass composition increases the semiconducting properties due to their highly polarizable nature. Therefore, it is worthwhile to study the effect of replacement of one intermediate oxide TiO_2 by another intermediate oxide V_2O_5 on structural and optical properties of polynary glasses.

Based on these objectives, authors have investigated the structural, physical and optical properties for the $30Li_2O–55B_2O_3–5ZnO–xTiO_2–(10 - x)V_2O_5$, $(0 \le x \le 10)$ novel glasses using different characterization techniques like X-ray diffraction (XRD), high resolution electron transmission microscopy (HRTEM), Fourier transform infra-red (FTIR) spectroscopy, thermal gravimetric analyzer (TGA), ultraviolet–visible (UV–VIS) and photo luminescence (PL) techniques. The band gap energy and Urbach energy have been calculated. The obtained results have been discussed in light of the change in the ionic concentration and inter-ionic distance due to replacement of TiO_2 by V_2O_5 in glass composition. Physical properties of glasses have been studied using optical

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http://dx.doi.org/10.1016/j.jnoncrysol.2015.02.004
0022-3093/

basicity approach, oxide ion polarizability, theoretical bulk modulus and average stretching force constant.

2. Experimental methods

The glass compositions chosen for the present study are listed in Table 1. The glasses were prepared by taking required stoichiometric amounts of different constituent oxides or carbonates of high purity (99.9%). These constituents were first mixed together in an agate mortar–pestle in acetone medium. The powder obtained, after hand grinding, was melted at 1550 °C in a high resistance furnace. The melt was quenched in air using copper plates. The quenched glass was then annealed at 400 °C to remove the internal stress from the glasses. The XRD pattern of pristine glasses was recorded using a PANalytical Xperts Pro MPD diffractometer with Cu K_α radiations. The pattern was recorded at a scanning rate of 2° min^{-1} with an angular range of 10–60°. High-resolution transmission electron microscope (HRTEM) images and selected area diffraction pattern (SAED) were obtained using the model CM 12, Philips (The Netherlands). The powdered glass ceramics was dissolve in ethanol and agitated ultrasonically for 20 min. A drop of sonicated solution was put onto the carbon enhanced copper grid for HRTEM measurement. The density of glasses was calculated using Archimedes principle using xylen as an immersion liquid. Diffuse reflectance spectra of the glasses were recorded at room temperature using a double beam UV–VIS spectrophotometer (Model: Hitachi) in the wavelength range of 200–1200 nm on powder glass samples. The spectrum of each sample was normalized to the spectrum of the blank sample holder. Fourier transform infra-red (FTIR) spectroscopy was carried out at room temperature in the region 4000–400 cm^{-1} using Perkin Elmer Spectrum BX (2) spectrometer. The spectral resolution of FTIR spectroscopy was $\pm cm^{-1}$. 5 mg of each sample was mixed with 20 mg of KBr in an agate mortar and then this powder was used for recording the absorption spectra. The spectrum of each sample was normalized to the spectrum of the blank KBr. PL excitation spectra of powdered sample has been recorded with Edinburgh Instruments FS920 spectrometer equipped with 450W Xenon Arc Lamp and a cooled single photon counting photomultiplier (Hamamatsu R2658P).

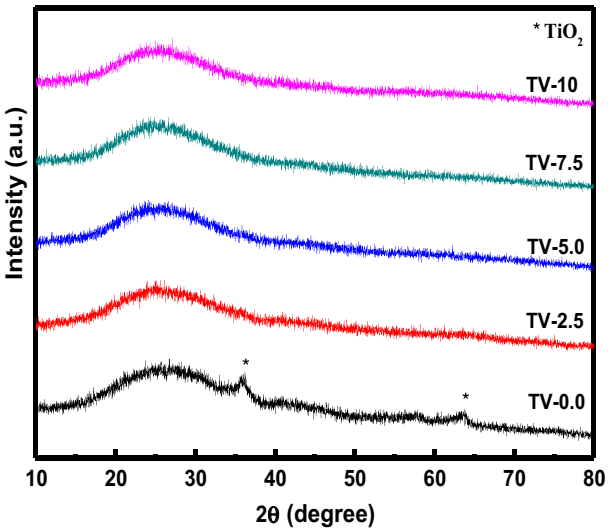

Fig. 1. XRD of all the glass samples. (* = TiO_2 rutile phase).

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of all glasses are shown in Fig. 1. No peaks are observed in the diffractogram, hence indicating the amorphous nature of pristine samples with long-range structural disorder. The broad halo at angles ≈ 20°–30° is observed for all the glass samples. However TV-0.0 shows two small peaks at 38° and 62°. These XRD peaks are indexed with the rutile phase of TiO_2 (ICDD card no. — 078–1509). The broad nature of the peaks indicates the formation of the in-situ nanocrystalline phase. In other words, the higher content of TiO_2 i.e. more than 7.5 mol% hinders the glass formation in the present case and leads to form the in-situ nanocrystalline phase TiO_2. Similar results have been observed in our earlier reports on TiO_2 contained glasses [14,15].

3.2. HRTEM studies

In order to confirm the presence of the in-situ nanocrystalline phase in sample TV-0.0 this sample was studied by HRTEM and SAED. The HRTEM images are shown in Fig. 2. The inset of Fig. 2 shows the diffuse rings along with random spots, confirming the presence of the nanocrystalline phase in this particular sample. This result is also supported by XRD pattern as shown in Fig. 1. Similar findings have been reported for various nanocrystalline glass ceramics [16,17]. It is clearly observed that the nanocrystalline crystals are inhomogeneous and are distributed unevenly in the glass ceramic matrix of TV-0.0.

3.3. Physical parameters

The molar volume is the volume occupied by one mole of substance and is given by the following relation:

$$V_m = {}^{M}\!/_{\rho} \quad (1)$$

Table 1
Glass compositions (mol %) along with the sample labels.

Label	Li_2O	B_2O_3	ZnO	TiO_2	V_2O_5
TV-10	30	55	5	0	10
TV-7.5	30	55	5	2.5	7.5
TV-5.0	30	55	5	5	5
TV-2.5	30	55	5	7.5	2.5
TV-0.0	30	55	5	10	0