Effect of vanadium on the optical and physical properties of lithium borate glasses

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ABSTRACT

In the present studies, the effects of vanadium substitution for $30Li_2O–55B_2O_3-(15-x)$ $ZnO–xV_2O_5$, $(0 \leq x \leq 7.5)$ glass system on the physical and optical properties have been investigated. V_2O_5 can work as a conditional glass former and its incorporation into glass yields vanadyl ions (VO^{2+}), which causes considerable change in the structure of glass. The glass composition can be tailored by optimizing the zinc and vanadium content so as to obtain the desirable semiconducting or optical applications. Physical parameters like density, molar volume, molar electro-negativity, oxide electro-negativity, basicity moderating parameters, ionic concentration, and inter-ionic distance are obtained for all the glass compositions. Characterization techniques like X-ray diffraction (XRD), UV–Visible and Fourier transforms infra-red spectroscopy (FTIR) are used to yield the structural and optical parameters. Average stretching force constant, network bond/volume and bulk modulus are calculated theoretically and correlated with each other. The Urbach energy as well as optical band gap shows a decreasing trend with decreasing concentration of V_2O_5 with respect to ZnO content.

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1. Introduction

Glasses have wide technological applications in electronic devices, optical filter, reflecting windows, ray absorbers, mechanical sensors, electro-optic devices and sealants [1–6]. The glass properties share strong intrinsic relation with its composition, nature of modifier/formers used and hence local structure. Borate based glasses have attracted the attention of researchers due to their stability and tendency of B–O groups to coordinate either trigonally $[BO_3]^{3+}$ or tetrahedral $[BO_4]^{3+}$ in glass matrix [4–6]. By choosing suitable modifiers and intermediate oxides for borate based glasses, the tremendous change in the local structure, optical band gap, randomness and orientations of glass network can be obtained.

The use of alkali and transition metal ions in borate glass compositions has been the potential area of research in non-linear optics [7–9]. The alkali ions like Li^+ possess ionic radius smaller than other ions in the network, hence, it easily enters interstitially into the glass network forming a new environment thereby changing the structure of the glasses. However, V_2O_5 can work as conditional glass former depending on the initial glass composition [10]. The incorporation of vanadium into the glass introduces vanadyl ion (VO^{2+}) causing change in its structure [11]. The B_2O_3 and V_2O_5 containing glass could be used for optical–electrical switching [12] and solid state devices [13]. On the other hand, glass compositions doped with ZnO have broad-spectrum applications in semiconductor industry as wide band gap semiconductors, because zinc can enter the glass network either as a former or modifier [14–16].

Before using the glass for any particular application, it is imperative to gain insight of certain parameters like ionic concentration, optical band gap, Urbach energy, optical absorption, optical basicity and thermal stability etc. Based on these objectives, authors have investigated the effect by systematic vanadium substitution on the optical properties for the $30Li_2O–55B_2O_3-(15-x)$ $ZnO–xV_2O_5$, $(0 \leq x \leq 7.5)$ novel glasses using X-ray diffraction, ultraviolet–visible (UV–VIS) and Fourier transform infra-red (FTIR) spectroscopy. The optical basicity, oxide ion polarizability, number of network bonds/volume, theoretical bulk modulus and average stretching force constant have been obtained for all the glasses. The optical basicity approach gives information on the electronic state of the oxygen atoms in terms of electron donor power. The direct/indirect band gap energy and Urbach energy have been calculated and discussed in light of non-bridging oxygens (NBOs). Furthermore, the change in ionic concentration as well as inter-ionic bond strength due to substitution of V_2O_5 by ZnO in glass composition has been obtained for all the glasses.

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 B_2O_3, ZnO, V_2O_5 and Li_2CO_3 of high purity (99.9%). These constituents were first mixed together in agate mortar–pestle in

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

Glass	Li_2O	B_2O_3	ZnO	V_2O_5
ZV-7.5	30	55	7.5	7.5
ZV-5.0	30	55	10.0	5.0
ZV-2.5	30	55	12.5	2.5
ZV-0.0	30	55	15.0	0.0

acetone medium for 1 h. The powder obtained after grinding was melted at 1200 °C in high resistance furnace. The melt was quenched in air using copper plates. The quenched glass was then annealed at 400 °C for 6 h to remove the internal stress from the glasses. The XRD pattern of pristine glasses was recorded using a PANalytical X'pert Pro MPD diffractometer with Cu K_α radiations. The pattern was recorded at a scanning rate of 2° min^{-1} with angular range of 10–80°. The TGA measurements were performed with Diamond Pyris TG/DTA (Perkin Elmer) using Al_2O_3 powder as reference material in oxygen atmosphere. During experiment the heating rate was 10 °C/min. The weight loss detection limit of the instrument was 0.001 mg. The samples were used in powder form without preheating before experiment.

The density of glasses was calculated using Archimedes principle using Xylene as an immersion liquid. Diffuse reflectance spectra of the glasses was 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 4000–600 cm^{-1} using PerkinElmer Spectrum BX (2) spectrometer. The spectral resolution of FTIR spectroscopy was 1 cm^{-1}. 0.5 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.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of all glasses are shown in Fig. 1. The absence of peaks in the diffractogram indicates the amorphous nature of
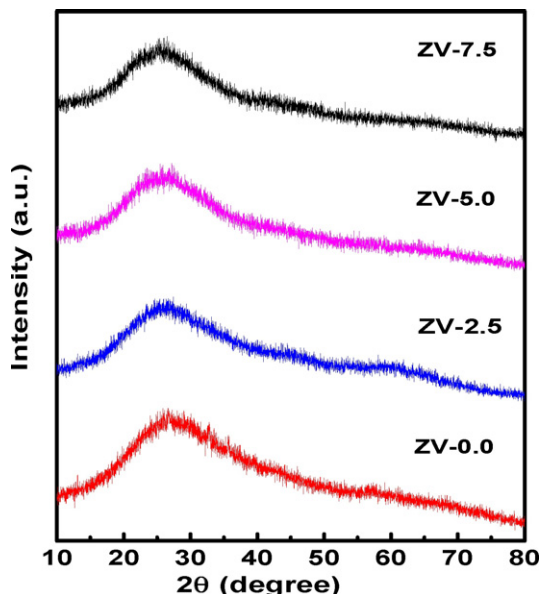
pristine samples with long-range structural disorder. For all the glass samples, broad halos at angles $\approx$ 20°–30° are observed.

3.2. Fourier transform infrared analysis

FTIR transmittance spectra of different vanadyl concentration doped glasses were recorded in 4000–600 cm^{-1} region at ambient temperature. As in 4000–2000 cm^{-1} region no peak has been observed, IR transmittance spectra of these glass samples are presented in Fig. 2 from 2000 to 500 cm^{-1} region. In this region, glass borate network peaks are observed as strong, medium and weak intensity broad bands of symmetric $(BO_3)^{3-}$, tetrahedral $(BO_4)^{4-}$, bridging and non-oxygen between B(III) and B(IV) units asymmetric vibrations of non-bridging oxygen groups. The broadness of bands in these oxide glass spectra has been attributed to the combination of degenerate vibrational modes, thermal broadening of the lattice dispersion band and mechanical scattering from powdered samples. The broad IR transmittance peak in 1500–1100 cm^{-1} region with two submerged components with maxima at 1327 cm^{-1} and 1210 cm^{-1} are assigned to B(III)–O–B(IV) of BO_3–O–BO_4 and B–O stretching vibration of $(BO_3)^{3-}$ group in meta-borate chains and orthoborates respectively. These peaks shift to higher wave numbers on increasing vanadyl concentration in glass matrix. i.e. (1337,1215), (1344,1223) and (1354,1224) cm^{-1} at 2.5 mol%, 5 mol% and 7.5 mol% vanadyl in glass matrix with loss in intensity has been explained in terms of the change in crystalline field effect and increase in lattice strain induced by doping more vanadyl in glass matrix [20–22]. The very weak B–O stretching mode arising from non-bridging oxygen in BO_4 vibration from tri-borate, tetra-borate, and penta-borate groups is observed at 1030 cm^{-1} which shifts to 1056 cm^{-1} in 7.5 mol% vanadyl doped glass sample [18–23]. The appearance of this peak indicates that there is a formation of four coordinated boron units with the addition of vanadyl oxide. The presence of a very weak 703 cm^{-1} peak has been attributed to B–O–B linkage due to B–O bond stretching of the trigonal BO_3 units [17], which shifts to 695 cm^{-1} on increasing vanadyl concentration in glass on substituting at Zn site. According to Central Force Model, the shifting of bands can be due to the structural changes associated with variation of inter-tetrahedral bond angles [23].

3.3. Thermo-gravimetric analysis

Fig. 3 gives the weight loss measurement for all the glass samples. The weight loss of glasses can be attributed to the release of trapped water molecules/water species during TGA measurement. The weight
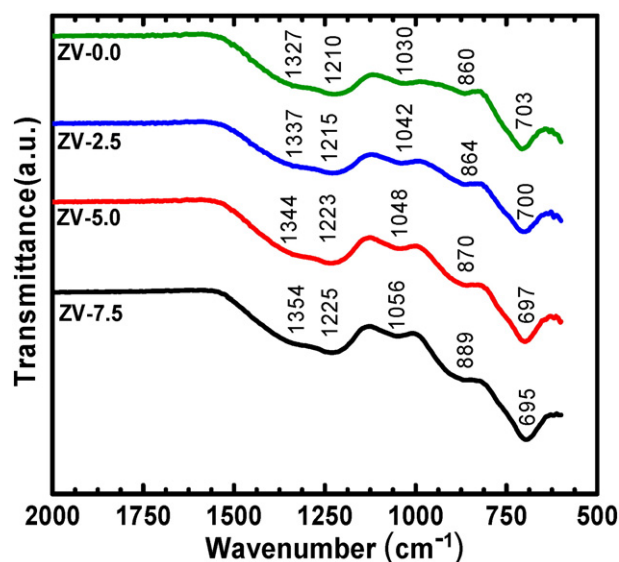

Fig. 1. XRD for all the glass samples.

Fig. 2. FTIR spectra for all the glass samples.