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Characterization and optical absorption studies of VO^{2+}:Li_2O–K_2O–Bi_2O_3–B_2O_3 glass system

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ABSTRACT

Mixed alkali bismuth borate glasses xLi_2O–$(30-x)$ K_2O–$10Bi_2O_3$–55 B_2O_3 ($0<x<30$) doped with 5 mol% vanadium ions were prepared from the melts. These glasses were characterized using X-ray diffraction, differential scanning calorimetry and density measurements. Optical absorption studies were carried out as a function of alkali content to look for mixed alkali effect (MAE) on the spectral properties of these glasses. From the study of ultraviolet absorption edge, the optical band gap energies and Urbach energies were evaluated. The average electronic polarizability of the oxide ion, optical basicity and the interaction parameters were also evaluated for all the glasses. Many of these parameters vary non-linearly exhibiting a minima or maxima with increasing alkali concentration, indicating the mixed alkali effect. An attempt is made to interpret MAE in this glass system in terms of its glass structure.

1. Introduction

Glasses have many technological applications due to their electrical and optical properties. B_2O_3 is established as glass forming oxide whereas Bi_2O_3 and V_2O_5 are conditional glass formers. Vanadium doped glasses are known to exhibit semiconducting properties. Growing attention has been given in the last two decades to glasses containing Bi_2O_3 owing to their optical properties [1–6]. The properties of bismuth glasses were studied by many authors to explain its role in glass structure [7–10]. Borate glasses containing Bi_2O_3 posses a high refractive index, show large polarizability, and high optical basicity [11]. These glasses have potential applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows and superconducting materials [12]. The Bi^{3+} ion has small field strength so Bi_2O_3 cannot form glass by itself [13]. However, in the presence of B_2O_3 glass formation is possible. The large glass formation region in bismuth borate glasses has been attributed to the high polarizability of the Bi^{3+} cations. This property of Bi^{3+} ions also makes the glass suitable as non-linear optical/photonic material with high non-linear optical susceptibility [14].

Mixed alkali glasses are unique from the point of view that certain properties change much more than normally anticipated from what appears to be a structurally and compositionally simple substitution of one alkali oxide for another. Mixed alkali effect in different physical properties is observed in silica, borate and phosphate glasses [15–17]. When two types of alkali metal ions are introduced into a glassy network, a phenomenon known as mixed alkali effect (MAE) is observed. It represents the non-linear variations in many physical properties, when one type of alkali ion in an alkali glass is gradually replaced by another while total alkali content in the glass being constant [18,19].

Considerable amount of work have been reported on bismuth borate glasses [13,20,1,21], but in the presence of alkali oxides and transition metal oxides, studies related to spectroscopic properties have been carried out to a little extent. In view of the aforementioned aspects, xLi_2O–$(30-x)$ K_2O–$10Bi_2O_3$–$55B_2O_3$:$5V_2O_5$ ($0<x<30$ mol%) glasses have been prepared and studied their optical properties to explore the relationship between the structure of the glass and its macroscopic behaviour. Further, some physical parameters have also been evaluated and their variation as a function of composition has been taken into account to supplement the results of MAE in optical properties.

2. Experimental

2.1. Glass preparation

Glasses having composition xLi_2O–$(30-x)$ K_2O–$10Bi_2O_3$–$55B_2O_3$:$5V_2O_5$ (LK glasses) with $x=5$, 10, 15, 20, 25 mol%, were prepared by conventional melt quench method. Analytical grade reagents of Bi_2O_3, Li_2CO_3, K_2CO_3, H_3BO_3, and V_2O_5 were used as starting materials. Table 1 lists the batch composition (the starting mixture) in mol% of glasses studied in the present work. The chemicals were weighed accurately in an electronic balance mixed thoroughly and ground to a fine powder. The batches were then placed in porcelain crucibles and melted in a programmable electrical furnace. The melt was held at a temperature of 1000 °C for 1 h and was shaken frequently to ensure proper mixing and homogeneity. The melt was then quenched

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Table 1
Glass composition of the samples in xLi_2O–$(30-x)$ K_2O–$10Bi_2O_3$–$55B_2O_3$:$5V_2O_5$ glass system.

Sl. no	Code	x (mol%)	Composition in mol%				
			Li_2O	K_2O	Bi_2O_3	B_2O_3	V_2O_5
1	LK-5	5	5	25	10	55	5
2	LK-10	10	10	20	10	55	5
3	LK-15	15	15	15	10	55	5
4	LK-20	20	20	10	10	55	5
5	LK-25	25	25	5	10	55	5

to room temperature in air by pouring it onto a polished steel plate and pressing with another steel plate. These glasses were then annealed at 300 °C to obtain strain free transparent glasses.

2.2. Glass characterization

The glass formation was confirmed by X-ray measurements using Philips X-ray diffractometer PW/1710 with Cu Kα radiation (λ = 1.5406 Å) powered at 40 kV and 30 mA.

By using the Archimedes principle, the glass densities have been determined with xylene as the immersion liquid on a single-pan electrical balance to the nearest 0.001 mg. The densities (D) were calculated by using the formula

$$D = \frac{a * 0.86}{a - b}\ \mathrm{g/cm^3} \quad (1)$$

where a is the weight of the sample measured in air; b is the weight of the sample measured in xylene and density of xylene at room temperature = 0.86 g/cm^3.

The molar volume (V_m) of each glass sample was calculated using the formula

$$V_m = \frac{\sum x_i M_i}{D}\ \mathrm{cm^3} \quad (2)$$

where x_i is the molar fraction and M_i is the molecular weight of the ith component.

From the density data oxygen packing density (OPD) was calculated using the formula [22]

$$\text{Oxygen packing density} = \left(\frac{D}{M}\right) \times \text{number of oxygen atoms per formula unit} \quad (3)$$

where M is the total molecular weight of the glass composition.

DSC is used to characterize the glasses. The glass transition temperature (T_g) was determined from differential scanning calorimetry (DSC) using DSC 821e METTLER TOLEDO model (TA Instruments). For this purpose the powdered glass sample was heated in an aluminum pan at a rate of 10 °C/min in the temperature range 30–600 °C using nitrogen as purge gas.

2.3. Optical measurements

The optical absorption spectra of these glasses were recorded in the UV region in order to measure the optical absorption edges by using a UV Elmer Lambda 700 spectrophotometer in the wavelength range 200–800 nm.

3. Results and discussion

3.1. XRD, DSC, density and molar volume

X-ray diffraction is a useful method to detect readily the presence of crystals in a glassy matrix if their dimensions are greater than typically 100 nm. The X-ray diffraction pattern of an amorphous material is distinctly different from that of crystalline material. The XRD patterns of the present glass system did not reveal any discrete or sharp peaks, but the characteristic broad humps of the amorphous materials. Fig. 1 shows the typical X-ray diffraction patterns for the glass system.

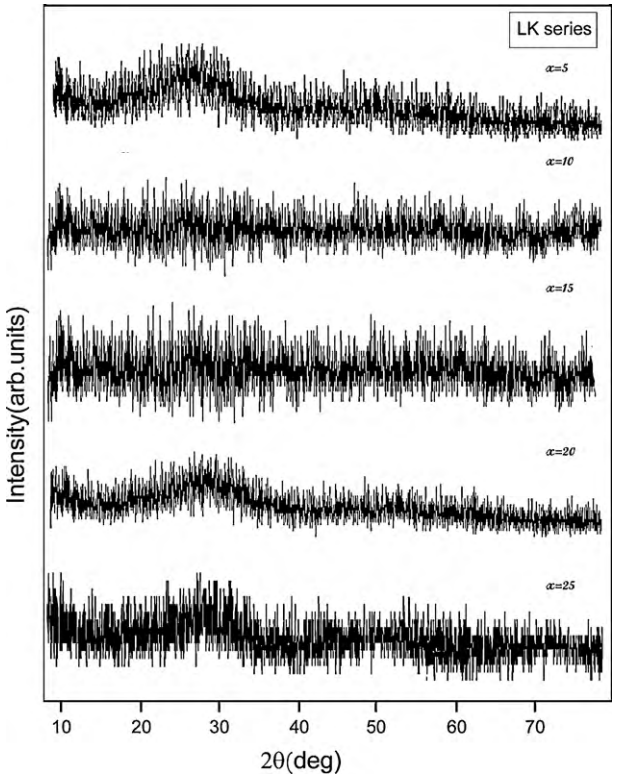

Fig. 1. X-ray diffraction patterns for different mixed alkali bismuth borate glasses: xLi_2O–$(30-x)$ K_2O–$10Bi_2O_3$–$55B_2O_3$–$5V_2O_5$ at room temperature.

The DSC pattern of LK-5 sample is shown in Fig. 2a. Fig. 2b shows the compositional dependence of glass transition temperature. In the present system all the glasses exhibit an endothermic peak due to the glass transition and the observed T_g lies in the range of 375–418 °C (Table 2). It is observed from Table 2 that glass transition temperature varies non-linearly with the concentration of Li_2O (x). The observed non-linear behaviour of glass transition temperature with x is a manifestation of mixed alkali effect in these glasses. The increase in the T_g is due to decrease in the number of non-bridging oxygen ions in the glass and is also associated with the formation of BO_4 tetrahedra which serve to cross-link the network by covalent B–O bonds. On the other hand the formation of borate network leads to a decrease in T_g. The non-linear variation of T_g with

Table 2
The density, molar volume, optical basicity, oxygen packing density, oxide ion polarizability, interaction parameter and glass transition temperature of the LK-series glass system.

Sample	Density (g/cm^3)	Molar volume (cm^3/mol)	Optical basicity (Λ_{th})	OPD (g-atm/l)	$\alpha_{O^{2-}}$ (E_o) (Å^3)	A	T_g (°C)
LK-5	3.27	36.43	0.688	68.63	3.25	0.0091	418
LK-10	3.30	35.08	0.680	71.26	3.16	0.0110	378
LK-15	3.36	33.47	0.672	74.68	3.04	0.0130	375
LK-20	3.43	31.84	0.664	76.88	2.98	0.0134	383
LK-25	3.43	30.94	0.656	80.8	2.91	0.0145	390