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Mixed alkali tungsten borate glasses – Optical and structural properties

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ABSTRACT

Glasses with composition xLi$_2$O-(30-x)Na$_2$O-10WO$_3$-60B$_2$O$_3$ (where $x = 0, 5, 10, 15, 20, 25$, and 30 mol%) were prepared by the melt quenching technique. Density, refractive index and glass transition temperature varies non-linearly with glass composition indicting the presence of mixed alkali effect. Optical energy band gap for various indirect and direct (allowed and forbidden) transitions were determined using Tauc plots. IR spectral study reveals the existence of BO$_3$ and BO$_4$ groups with W–O–W vibrations in the present glasses. Based on good correlation among refractive index based electronic polarizability of oxide ions, optical basicity and the Yamashita–Kurosawa's interaction parameter, the present Li$_2$O–Na$_2$O–WO$_3$–B$_2$O$_3$ glasses were classified as semi covalent oxides.

1. Introduction

A phenomenon known as mixed alkali effect (MAE) is observed when two types of alkali ions are introduced into a glassy network. It represents the non-linear variations in many physical properties associated with the alkali ion movement and structural 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 [1,2]. The most evident manifestation of this effect has been observed in DC electrical conductivity and in the activation energy exhibiting a deep minima and maximum as a function of composition in the intermediate mixing ratio of alkali ions [3–5]. Interestingly other "dynamical" properties such as internal friction, viscosity, glass transition, expansion coefficient also exhibit a more or less pronounced deviation. On the other hand, static properties like density appear to be linear [6]. Mixed alkali effect was found in mixed crystals [7], cation and anion conducting glasses [8,9] and also for glasses containing two glass formers [10]. So far, there are several theoretical attempts to explain the MAE in oxide glasses, but to date there is no success in explaining the MAE with respect to all glass systems [11–14]. MAE is found in various glass systems like silicates, phosphates and borate glasses. MAE can be used to design glasses with desired properties and tune their characteristics according to industrial needs.

Borate glasses are very interesting class of materials both from the fundamental and application point of view [15]. Alkali ion doping into borate glasses introduces interesting structural variations by converting three coordinated boron ions into four coordinated boron ions and by forming non-bridging oxygen ions (NBO's) [16]. These structural variations play vital role in controlling the physical parameters of borate glasses, pertaining to the mixed alkali effect.

Subhadra and Kistaiah [17,18] carried out physical and optical absorption studies in V$_2$O$_5$ doped Li$_2$O–K$_2$O–Bi$_2$O$_3$–B$_2$O$_3$ glass system to understand the effect of progressive doping of Li$^+$ ion with K$^+$ ion. The effect of mixed alkalis on the optical absorption and emission spectra of Sm^{3+} and Dy^{3+} doped chloroborate glasses was presented by Venkateswarlu et al. [19]. Recently, Raghavendra Rao et al. [20] studied and correlated the physical, optical and structural properties of transition metal ions doped ZnO–Li$_2$O–Na$_2$O–B$_2$O$_3$ glasses. More recently, in our previous papers [21–23] we reported the strength of mixed alkali effect in T_g, dc electrical conductivity and activation energy in xR$_2$O–(40-x)Na$_2$O–50B$_2$O$_3$–10Bi$_2$O$_3$ (R = Li, K) glass systems and mixed alkali effect in Li$_2$O–Na$_2$O–K$_2$O–B$_2$O$_3$ glasses. The magnitudes of the mixed alkali effect in T_g for the mixed Li/Na glass system are much smaller than those in the mixed K/Na glasses. The impact of mixed alkali effect on dc electrical conductivity in mixed Li/Na glass system is more pronounced than in the K/Na glass system and the results are explained based on dynamic structure model.

Tungsten ion containing glasses are the subject of a grate deal due to their important non-linear optical absorption and electrical properties for technological applications [24–26]. Tungsten ions exist in hexavalent W^{6+}, pentavalent W^{5+} and also in tetravalent W^{4+} state, regardless of the oxidation state of the tungsten ion

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[27]. W^{6+} ion participate in the glass network with different structural units like WO_4 (T_d) and WO_6 (O_h) structural units and W^{5+} ions participate in the form of $W^{5+}O_3^-$ and occupy octahedral positions [28]. Thus the concentration of different structural groups of tungsten ions with different oxidation states present in the glass matrix at a given temperature depends on the quantitative properties of modifiers, glass formers, size of ions in the glass structure, mobility of the modifier cation etc. W^{5+} ions are well known paramagnetic ions. The presence of tungsten in borate glasses, further, makes these glasses suitable for optoelectronic devices since they exhibit photochromism, electrochromism and thermochromism properties, which are known for provoking a color change due to the action of electromagnetic radiation, electric field and heat respectively [29,30].

To reveal the role of WO_3 in the glassy borate network Al-Shahrani et al. [31] studied the dc electrical conductivity of $Na_2B_4O_7$–WO_3 glasses. El-Kheshen and El-Batal [32] reported the effect of WO_3 on spectroscopic, thermal, density properties and structure of high lead borate glasses. El Batal [33] performed optical, infrared, EPR and Raman spectral studies of some lithium borate glasses containing varying WO_3 contents before and after gamma ray irradiation. Ali Abou Shama [34] carried out structural studies in lithium tungsten borate glasses and also correlated with the other measured physical properties (such as electrical conductivity, activation energy, etc). Sheoran et al. [35] measured the variation of density, molar volume, optical basicity with glass composition and complex impedance of alkali tungsten borate glasses. Deal et al. [36] reported Raman and luminescence studies on Na_2O–B_2O_3–WO_3 glasses.

Many investigations have been reported [37–41] on ternary alkali tungstate in phosphate, borate, tellurite, bismuthate and niobate glasses. More recently, Salem et al. [42] presented physical, structural, optical and dielectric properties of Li_2O–Bi_2O_3–GeO_2–WO_3 glasses. A recent investigation of density, glass transition temperature and electrical properties in Li_2O–Na_2O–$WO_3(MoO_3)$–P_2O_5 glass system showed the mixed alkali effect [43,44]. Gaffar et al. [45] studied the FTIR and ultrasonic properties on Li_2O–WO_3–B_2O_3 glasses. To the best of our knowledge, there are no reports on optical absorption and IR studies of mixed alkali borate tungsten glasses.

The present investigation is a part of an ongoing program to study the MAE in lithium sodium tungsten borate glasses. Therefore, in this work we have concentrated on the influence of mixed alkalis on optical absorption and infrared properties of xLi_2O–$(30\text{-}x)Na_2O$–$10WO_3$–$60B_2O_3$ ($0 \leqslant x \leqslant 30$ mol%) glasses. The physical properties of the glasses have also been determined with respect to glass compositional parameter R_{Li} defined as $R_{Li} = Li_2O$ (mol%)/($Li_2O + Na_2O$) (mol%) which takes the values 0, 0.166, 0.332, 0.5, 0.666, 0.832 and 1.

2. Experimental

In the present study, the glass samples of composition xLi_2O–$(30\text{-}x)Na_2O$–$10WO_3$–$60B_2O_3$ ($0 \leqslant x \leqslant 30$) were prepared by melt quench technique. Appropriate amounts of reagent grade Li_2CO_3, Na_2CO_3, H_3BO_3 and WO_3 were well mixed and melted in a porcelain crucibles in the temperature range of 1100–1150 °C depending on the glass composition in an electrical muffle furnace for about 60 min. The melt was swirled frequently to insure the homogeneity. The melt was then quenched in between a couple of brass plates pre-heated around 200 °C. Later, the samples were annealed below their respective glass transition temperature for about 24 h and slowly cooling them to laboratory temperature.

The amorphous nature of the glass samples was confirmed by X-ray diffraction study which shows no continuous or discrete sharp peaks but exhibit broad halo. The room temperature density (ρ) of the samples was determined by the Archimedes principle. Xylene was used as an immersion liquid. The densities of the present glasses were calculated by using the formula.

$$\rho = a * 0.865/(a - b) \quad (1)$$

where a is the weight of the sample measured in air, b is the weight of the sample measured in xylene (density of xylene at room temperature is 0.865 g/cc).

The room temperature refractive indices of the prepared glasses were measured using Abbe's refractometer. The thermal behavior of the glass samples was investigated using a modulated differential scanning calorimeter (TA Instruments model 2910). Glass samples in the form of powder weighing about 15 mg were sealed in aluminum pans and scanned with a heating rate of 10 °C/min. During all runs the sample chamber was purged with dry nitrogen. The uncertainty in glass transition temperature is ±1 °C. The room temperature optical absorption spectra of the polished glass samples were recorded using JASCO V670 spectrometer in the wavelength region 200–1000 nm. Infrared spectra of the powdered glass samples were recorded at room temperature in the range 400–1500 cm^{-1} using a spectrometer (Perkin–Elmer FT-IS, model 1605). These measurements were made on glass powder dispersed in KBr pellets.

3. Results

3.1. Physical parameters

The room temperature density of xLi_2O–$(30\text{-}x)Na_2O$–$10WO_3$–$60B_2O_3$ glasses measured by Archimedes method as a function of compositional parameter R_{Li} is illustrated in Fig. 1. From the above figure, it is clear that the density varies non-linearly. The composition-dependent density appears to be 'waveshaped', featuring two maxima and one minima. This non-linear behavior is a consequence of mixed alkali effect. The density of the present glasses varies from 2.724 to 2.918 g/cc. The molar volume and oxygen packing density of all the glasses were calculated using the density data and are presented in Table 1.

In the present glass system, the variation of molar volume and oxygen packing density as a function of compositional parameter is non-linear. This non- linear variation can be taken as a signature of mixed alkali effect. The change in the molar volume is a result of the creation of non-bridging oxygens (NBOs) which will break the bonds and increase space in the glass network. This result indicates that the glass structure becomes loosely packed. Similar observations were found in mixed alkali borate glasses [23,46].

Fig. 2 shows the compositional dependence of refractive index of the present glasses at room temperature. The refractive index of the present glasses are presented in Table 2, varies from 1.644 to 1.652 and it varies non-linearly, indicating the presence of mixed alkali effect. Similar mixed alkali effect in refractive index was observed in mixed alkali zinc borate glasses doped with cobalt [47]. Since the refractive index of the present glasses are less than 1.7, they can be used as optical glasses.

Modulated differential scanning calorimetry (MDSC) is used to characterize the glass and to determine thermodynamical parameters. The MDSC thermograms of all the glass samples are

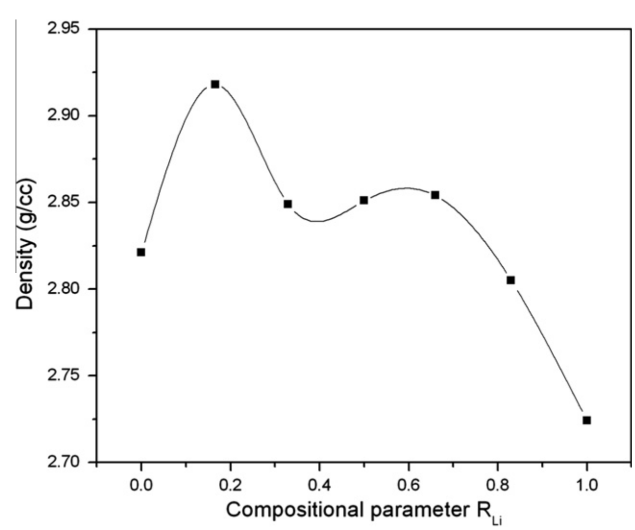

Fig. 1. Density as a function of compositional parameter R_{Li} in xLi_2O–$(30\text{-}x)Na_2O$–$10WO_3$–$60B_2O_3$ glasses.