OPTICAL PROPERTIES ON $\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{WO}_3-\text{B}_2\text{O}_3$ GLASS SYSTEM

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Mixed alkali tungsten borate glasses $x\text{Li}_2\text{O}-(30-x)\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ ($0 < x < 30$) 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.

Keywords: Alkali tungsten borate, mixed alkali effect, optical band gap.

1. Introduction

Mixed alkali effect (MAE), a non-linear variation in various physical properties of oxide glasses when one alkali is progressively substituted with another alkali, has been topic intense research for the last few decades [1-3]. MAE is pronouncedly observed in ionic diffusivity, conductivity, dielectric relaxation, internal friction etc. On the other hand, bulk thermodynamic properties such as molar volume, density, refractive index, thermal expansion coefficient show small deviations from linearity [4,5]. MAE in oxide glasses could play a vital role in controlling desired properties for technology and industry, if well understood. This has been studied widely in transport properties with respect to various oxide glass systems (silicates, borosilicates, borates, and phosphates) [6,7]. Various models were also proposed to understand this phenomenon both based on geometrical and structural considerations [8-10]. Few models were successful in explaining this effect with respect to few properties in particular glass systems, but there is no single model which can provide universal explanation to this MAE. So far, the studies on MAE were concentrated on transport properties in oxide glasses. Recently interest into the study of MAE pertaining to spectroscopic parameters has been generated with few studies on borate glasses.

Tungsten ion containing glasses have gained much importance due to their non-linear optical absorption and electrical properties for technological applications. Tungsten ions

are predicted to have strong influence on physical properties of compounds. In oxide glasses, tungsten ions are generally assumed to attain multiple oxidation states, such as hexavalent W^{6+} , pentavalent W^{5+} and also tetravalent W^{4+} , regardless of the oxidation state of the tungsten ion in the starting glass batch. W^{6+} ions 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 $\text{W}^{5+}\text{O}_3^-$, and occupy octahedral positions. 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^{3+} 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 [11]. These glasses have several advantages over crystalline counterparts, such as easy formability over wide ranges of composition, isotropicity, absence of grain boundaries and ease of fabrication in complex shapes, which make them particularly attractive in practical applications [12].

The aim of the present work is to investigate the mixed alkali effect in $x\text{Li}_2\text{O}-(30-x)\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ ($0 \leq x \leq 30$ mol%) glasses by measuring the optical properties a function of compositional parameter R_{Li} , which is defined as $R_{\text{Li}} = \text{Li}_2\text{O}(\text{mol}\%)/(\text{Li}_2\text{O} + \text{K}_2\text{O})(\text{mol}\%)$. R_{Li} takes the values 0, 0.166, 0.33, 0.5, 0.66, 0.83 and 1.

2. Experimental

$x\text{Li}_2\text{O}-(30-x)\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ ($0 \leq x \leq 30$ mol%) glass samples were prepared through the standard meltquenching method. Details of the preparation and characterization of the glass specimens are given in ref. [13]. The optical absorption spectra of the glasses were recorded in the wavelength range 200–800 nm at room temperature using a Shimadzu 3100 UV-VIS-NIR spectrometer. The uncertainty in the observed wavelength was about ± 1 nm. The band position was measured digitally and the accuracy with which the peaks were determined was about $\pm 10 \text{ cm}^{-1}$.

3. Results and discussion

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.

The optical absorption spectrum of $25\text{Li}_2\text{O}-5\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glass is shown in Fig 1. Other glass samples in the present series also show similar spectral behavior. The analysis of optical absorption spectra (Fig.1) shows that the fundamental absorption edge

Fig.1. X-ray diffractograms of $x\text{Li}_2\text{O}-(30-x)\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glasses. (a) $x=0$, (b) $x=5$, (c) $x=10$, (d) $x=15$ and (e) $x=20$.

is not sharply defined, which characterizes the glassy nature of the samples. It is reported that the fundamental absorption edge shifts towards longer wavelengths in single alkali borate glasses with an increase in alkali content [14]. In the present study the optical absorption edge varies non-linearly.

The optical absorption co-efficient $\alpha(v)$, near the fundamental absorption edge of the curve in the above figure was determined from the relation

$$\alpha(v) = (1/d) \log(I_t/I_0) \quad (1)$$

where I_0 and I_t are the intensities of the incident and transmitted beams, respectively, and d is thickness of the glass sample. The factor $\log(I_t/I_0)$ corresponds to absorbance. Davis and Mott [15] and Tauc and Menth [1] relate this data to the optical band gap, E_{opt} through the following general relation proposed for amorphous materials

$$\alpha(v) = B(hv - E_{\text{opt}})^n / hv \quad (2)$$

where B is a constant related to the extent of the band tailing and $h\nu$ is incident photon energy. The index n determines the type of electronic transitions causing the absorption, and takes the values $1/2$, 2 , $3/2$ and 3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions. By plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy $h\nu$, one can find the optical energy band gap E_{opt} for indirect and direct transitions, respectively. The respective values of E_{opt} are obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for indirect transition and $(\alpha h\nu)^2 = 0$ for direct transition. Fig. 3 represents the Tauc plots $\{(\alpha h\nu)^{1/2} \text{ vs } h\nu\}$ for different glass samples. Similar behavior was also observed by other workers [17]. The values of the indirect optical energy gap, E_{opt} , thus obtained from the extrapolation of the linear region of Tauc plots are presented in Table 1. The values of direct optical energy gap were also determined and are presented in Table 1. In the present glasses, the indirect band gap energy varies from 3.41 to 3.83 eV and direct band gap energy vary between 3.66 to 3.99 eV respectively. In the present glasses, the compositional dependence of direct and indirect optical band gap energies is illustrated in Fig. 4. It is observed that the band gap energies

vary non-linearly with compositional parameter, indicating the existence of mixed alkali effect.

Fig 2. Optical absorption spectrum of $25\text{Li}_2\text{O}-5\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glass.

Fig 3. Tauc plots for the $x\text{Li}_2\text{O}-(30-x)\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glass system.

Fig 4. Indirect and direct optical band gap energy as a function of compositional parameter R_{Li} in present glasses.

Fig 5. Plots corresponding $\ln \alpha$ vs $h\nu$ for $x\text{Li}_2\text{O}-(30-x)\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glasses.

The non-linear variation of direct and indirect optical band gap in the present glass system (Fig.4) indicates the existence of mixed alkali effect in optical properties. In single alkali borate glasses, the optical band gap energy decreases monotonically with alkali content and has been attributed to the formation and increase in the non-bridging oxygens [18]. However, the non-linear variation in the optical band gap energy of the present glass system may be due to the formation of large number of non-bridging oxygens.

The main feature of the absorption edge of amorphous materials is an exponential increase of absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$, which is given by the Urbach rule [19]

$$\alpha(v) = C \exp(hv/\Delta E) \tag{3}$$

where C is a constant, and ΔE is the Urbach energy which is a measure of band tailing. Fig. 5 plots the variation of ln (α) as function of photon energy hv. The values of Urbach energy (ΔE) were determined by taking the reciprocals of slopes of the linear portion of ln(α) vs hv curves. The Urbach energy values of the present glass samples are presented in Table 1. The compositional dependence of Urbach energy ΔE is illustrated in Fig. 6. Urbach energy is varying non-linearly with compositional parameter indicating the existence of mixed alkali effect in present glasses.

Fig 6. Compositional dependence of Urbach energy (ΔE) in xLi₂O-(30-x)K₂O-10WO₃-60B₂O₃ glasses.

Table 1. Optical parameters of the xLi₂O-(30-x)K₂O-10WO₃-60B₂O₃ glass system.

Parameter	x=0	x=5	x=10	x=15	x=20	x=25	x=30
λ _c (nm)(±1)	338	312	277	312	307	304	313
Optical band gap energies (E _o) (eV) (±0.05)							
Indirect allowed	3.45	3.57	3.82	3.75	3.79	3.72	3.77
Indirect forbidden	3.45	3.78	3.79	3.58	3.76	3.71	3.85
Direct allowed	3.66	3.87	3.98	3.85	3.93	3.86	3.90
Direct forbidden	3.60	3.87	4.02	3.84	3.89	3.85	3.89
ΔE (eV) (±0.002)	0.285	0.342	0.394	0.266	0.288	0.265	0.235

It is generally assumed that absorption tail observed in various materials with different structures must have the same physical origin [20]. This origin can be attributed to the phonon-assisted indirect electronic transitions. For most of the glasses, and in the present glass system the value of ΔE lies between 0.245-0.397 eV and these results are in accordance with those reported for inorganic glasses.

4. Conclusions

Mixed alkali tungsten borate glasses in the form of $x\text{Li}_2\text{O}-(30-x)\text{K}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ ($0 \leq x \leq 30$) were prepared, and their physical and optical properties have been studied. The following conclusions were made:

- (i) XRD profiles have confirmed their amorphous nature more clearly.
- (ii) From optical absorption edges the direct and indirect optical band gap energies and Urbach energies were evaluated and their non-linear behavior confirms the mixed alkali effect.
- (iii) The optical band gap based oxide ion polarizability, optical basicity and interaction parameter have been estimated. Based on good correlation among these parameters the present $\text{Li}_2\text{O-K}_2\text{O-WO}_3\text{-B}_2\text{O}_3$ glasses were categorized as normal ionic (basic) oxides.

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