MIXED ALKALI EFFECT IN $(40-x)\text{K}_2\text{O}-x\text{Li}_2\text{O}-10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3$ GLASSES—PHYSICAL AND OPTICAL ABSORPTION STUDIES

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So far only a handful of publications have been concerned with the study of the mixed alkali effect in borate glasses containing three types of alkali ions. In the present work, the mixed alkali effect (MAE) has been investigated in the glass system $(40-x)\text{K}_2\text{O}-x\text{Li}_2\text{O}-10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3$. ($0 \leq x \leq 40$ mol%) through density and modulated DSC studies. The density and glass transition temperature of the present glasses varies non-linearly exhibiting mixed alkali effect. We report the mixed alkali effect in the present glasses through optical properties. From the absorption edge studies, the various values of optical band gap (E_0) and Urbach energy (ΔE) have been evaluated. The values of E_0 and ΔE show non-linear behavior with compositional parameter showing the mixed alkali effect. The band gap energy based average electronic polarizability of oxide ions $\alpha_{02}(E_0)$, optical basicity $\Lambda(E_0)$, and Yamashita–Kurosawa’s interaction parameter $A(E_0)$ have been examined to check the correlations among them and bonding character. Based on good correlation among electronic polarizability of oxide ions, optical basicity and interaction parameter, the present $\text{K}_2\text{O}-\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses are classified as normal ionic (basic) oxides.

Keywords: mixed alkali effect, glasses, optical band gap.

1. Introduction

Many physical properties associated with the alkali ion movement and structure of the alkali oxide containing glasses show non-linear behavior exhibiting a minimum or maximum, as a function of alkali content, if one alkali ion is gradually replaced by another alkali ion, keeping the total alkali content constant. This behavior is called the “mixed alkali effect” (MAE) [1,2]. The mixed alkali effect is observed when two or three types of alkali ions are introduced into a glassy network [3, 4]. 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 ratio of alkali ions [5].

MAE is found in various glass systems like bismuthate, arsenate, tungstate and borate glasses [6,7]. In our previous papers [8,9] we reported the mixed alkali effect in density, glass transition temperature, optical absorption and electron paramagnetic resonance of the mixed alkali borate, boroarsenate and borobismuthate glasses.

The strength of the MAE depends on many factors [10], e.g., temperature, total alkali content, the size and mass difference of the involved alkali ions, etc. It has also been reported that the magnitude of the MAE increases with the difference in size or mass of the involved alkali ions [11, 12].

Most technical glasses containing a variety of different cations, but almost all studies on mixed alkali effects are focused on glasses with only two kinds of ions. Therefore, it is very important to study ion dynamics of glasses with three or more types of alkali ions. To the best of our knowledge dynamic conductivity spectra of few Li–Na–K-containing borate glasses have been reported [13]. More recently, Kim *et al.* [14] reported the results of the composition dependence of the ionic conductivity in borate glasses with three types of mixed alkali cations.

In the present study, we investigate the mixed alkali effect in $(40-x)\text{K}_2\text{O}-x\text{Li}_2\text{O}-10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3$ ($0 \leq x \leq 40$ mol%) glasses by measuring density and glass transition temperature as a function of compositional parameter R_{Li} which is defined as $R_{\text{Li}} = \text{Li}_2\text{O (mol\%)} / (\text{K}_2\text{O} + \text{Li}_2\text{O (mol\%)})$ which takes the values 0, 0.25, 0.5, 0.75 and 1. Further, optical studies have also been performed on glass samples.

2. Experimental

In the present study, the glass samples of composition $(40-x)\text{K}_2\text{O}-x\text{Li}_2\text{O}-10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3$ were prepared by melt quench technique at around 1050 °C. Density measurements were carried out at room temperature using Archimedes method with Xylene (density = 0.86 g/cc) as an immersion liquid. From the density data molar volume (V_m) and oxygen packing density (OPD) were determined and are given in table 1.

The glass transition temperature of the present glasses was determined using a modulated differential scanning calorimeter at a heating rate of 10°C/min. The refractive index measurements were carried out by using Abbe refractometer with an accuracy of ± 0.0002 . The room temperature optical absorption spectra for all the polished glass samples were recorded on a PerkinElmer (Lambda 950) UV–vis–NIR spectrometer in wavelength region of 200–1000 nm. The band position is measured with an accuracy ± 1 nm.

3. Results and discussion

The room temperature density of mixed alkali $(40-x)\text{K}_2\text{O}-x\text{Li}_2\text{O}-10\text{Na}_2\text{O}-50\text{B}_2\text{O}_3$ glasses as a function of compositional parameter R_{Li} is illustrated in figure 1. From the above figure, it is clear that the density varies non-linearly. The composition-dependent density appears to be ‘waved-shaped’, featuring two maxima and one minima. This non-linear behavior is a consequence of mixed alkali effect.

Fig 1. Density and glass transition temperature as a function of compositional parameter in $(40-x) K_2O-x Li_2O-10Na_2O-50B_2O_3$ glasses

The glass transition temperature (T_g) of all the glass samples are presented in Table 1. The variation of glass transition temperature as a function of compositional parameter R_{Li} is also presented in figure 1. The glass transition temperature varies non-linearly and exhibited negative deviation indicating the presence of mixed alkali effect.

The refractive index of the present glasses are given in table 1. It is observed that the refractive index remains constant as a function of glass compositional parameter R_{Li} . Generally the refractive index of any glass depends on the glass forming oxide. In the present glass system, since the glass former B_2O_3 is kept constant (50 mol%) the refractive index remains constant. From the optical absorption data the cut-off wavelengths were determined and are presented in table 1. The optical absorption coefficient $\alpha(\nu)$, near the fundamental absorption edge was determined from the relation

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

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 $\log(I_0/I_t)$ corresponds to absorbance. Davis and Mott [15] and Tauc and Menth [16] relate this data to the optical band gap, E_o through the following general relation proposed for amorphous materials.

$$(\alpha h\nu)^n = B(h\nu - E_o) \quad (2)$$

where B is a constant 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 , $2/3$ and $1/3$ for indirect allowed, direct allowed, direct forbidden and indirect forbidden transitions, respectively. By plotting $(\alpha h\nu)^n$ as a function of photon energy $h\nu$, one can find the optical energy band gap for all transitions. The values of optical band gap energy E_o can be obtained by extrapolating the absorption co-efficient to zero absorption in the $(\alpha h\nu)^n$ against photon energy $h\nu$ plots as shown in figure 2, 3, 4 and 5.

Fig 2. Tauc plots corresponding to $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for present glasses.

Fig 3. Tauc plots corresponding to $(\alpha h\nu)^2$ as a function of $h\nu$ for present glasses.

Fig 4. Tauc plots corresponding to $(\alpha h\nu)^{2/3}$ as a function of $h\nu$ for present glasses.

Fig 5. Tauc plots corresponding to $(\alpha h\nu)^{1/3}$ as a function of $h\nu$ for present glasses

The values of optical energy gap, E_o , thus evaluated for the glass samples at different values of n is listed in table 1. Since the obtained values of the optical band gap are varying according to the selected value of the exponent n , one cannot really decide which value of n is better to be selected. Therefore, the Eq. (2) may be rather used only for the determination of the type of conduction mechanism, and E_o itself should be determined using another parameter the imaginary part of the dielectric constant (ϵ_2) by which the exact value of exponent can be selected.

According to the theory of reflectivity of light, the refractive index and extinction coefficient can be expressed as

$$n^2 = (1+R^{1/2}) / (1- R^{1/2}) \quad \text{and} \quad k = \alpha\lambda/4\pi, \quad (3)$$

where λ is the wavelength of the incident photon and R is reflectivity of the sample in the transparent region. The real and imaginary parts of dielectric constant (ϵ_1 , ϵ_2) are related to the n and k values, through the formula

$$\epsilon_1 = n^2 - k^2 \quad \text{and} \quad \epsilon_2 = 2nk \quad (4)$$

Figure 6 plots the variation of the imaginary part of dielectric constant ϵ_2 with photon energy for the studied glass system. From the above figure, the optical band gap can be obtained by extrapolating the imaginary part of dielectric constant to zero as shown in the figure. On a comparison of the optical energy gap values obtained from absorption spectra in the case of indirect allowed transition are in good agreement with the values estimated from the dielectric measurements ϵ_2 . Thus, the type of electronic transition in the present glass system is indirect allowed. From the optical absorption data the values of Urbach energy (ΔE) were determined and are presented in table 1.

The energy gap based electronic polarizability of the oxide ions $\alpha_{O^{2-}}(E_o)$, optical basicity of the oxide medium Λ and the optical energy based interaction parameter $A(E_o)$ [17,18] of the present glasses were determined using the formulae presented in our previous paper [7]. The values of these parameters are presented in table 1.

Fig 6. Variation of imaginary part of dielectric constant (ϵ_2) as a function of $h\nu$ for present glasses.

Table 1

Parameters	Glass composition				
	x=0	x=10	x=20	x=30	x=40
Average molecular wt (g/mol)	78.684	72.252	65.821	59.390	52.958
Density (ρ) (g/cc) (± 0.001)	2.490	2.520	2.480	2.600	2.510
Molar Volume (cc/mol)	31.600	28.671	26.541	22.842	21.102
OPD (g-atm/l) (± 0.001)	63.291	69.756	75.537	87.558	94.777
T_g ($^{\circ}\text{C}$) (± 1)	379	394	404	388	427
Refractive Index (± 0.0002)	1.3490	1.3485	1.3490	1.3485	1.3489
Dielectric constant (± 0.001)	1.820	1.818	1.812	1.818	1.830
Cutoff Wavelength ($\pm 1\text{nm}$)	326	323	343	310	332
Band gap energy (eV) (± 0.01)					
Indirect allowed transition	3.81	3.72	3.59	3.85	3.71
direct allowed transition	3.56	3.57	3.75	3.83	3.73
indirect forbidden transition	2.96	2.96	2.94	3.19	3.16
direct forbidden transition	3.58	3.57	3.43	3.67	3.60
E_o from ϵ_2	3.76	3.74	3.53	3.80	3.74
Urbach energy (ΔE)	0.30	0.31	0.27	0.37	0.43
Electronic polarizability ($\alpha_{O^{2-}}$)(E_o)	3.18	2.97	2.84	2.44	2.47
Interaction parameter $A(E_o)$	0.025	0.036	0.044	0.053	0.074
Optical basicity $\Lambda(E_o)$	1.145	1.108	1.082	0.986	0.994
Optical basicity (Λ_{th})	0.885	0.845	0.805	0.765	0.725

Based on good correlation among electronic polarizability of oxide ions ($\alpha_{O^{2-}}$), optical basicity (Λ) and interaction parameter (A), the present $K_2O-Li_2O-Na_2O-B_2O_3$ mixed alkali glasses can be classified as normal ionic (basic) oxides. In general normal ionic (basic) oxides possess intermediate electronic polarizability of oxide ions ($2-3 \text{ \AA}^3$), optical basicity close to unity and intermediate interaction parameter ($0.02-0.08$).

4. Conclusions

In this paper, we report, the mixed alkali effect in optical studies in borate glasses containing three types of alkali ions. The composition-dependent density appears to be non-linear. This non-linear behavior is a consequence of mixed alkali effect. The molar volume of the glasses decreases where as oxygen packing density increases as Li_2O content increases, showing no MAE. The glass transition temperature T_g also varies non-linearly, indicating the mixed alkali effect. The various optical band gap energies and the Urbach energy in the present glass system varies non-linearly with compositional parameter. Based on good correlation among electronic polarizability of oxide ions, optical basicity and interaction parameter, the present $K_2O-Li_2O-Na_2O-B_2O_3$ glasses were categorized as normal ionic (basic) oxides.

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