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Optical absorption and EPR spectroscopic studies of $(30 - x)Li_2O–xK_2O–10CdO–59B_2O_3–1Fe_2O_3$: An evidence for mixed alkali effect

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ABSTRACT

Optical absorption and EPR spectroscopic studies were carried on $(30 - x)Li_2O–xK_2O–10CdO–59B_2O_3–1Fe_2O_3$ ($x = 0–30$) glass system to understand the effect of progressive doping of Li^+ ion with K^+ ion. Optical absorption results show typical spectra of Fe^{3+} ions and the various optical parameters such as, optical band gap, Urbach energy, oxide ion polarizability, optical basicity and interaction parameter were evaluated from the experimental data. The observed optical band gap and Urbach energy values show large deviation from the linearity where as the other parameters show small deviation from the linearity with the progressive substitution of Li^+ ions with K^+ ions. The observed EPR spectra are representative of Fe^{3+} ion in octahedral and axial fields in the glass network. The number of paramagnetic centers and paramagnetic susceptibility values were evaluated at different resonance lines for all the specimens and these parameters show non-additive nature with the progressive substitution of Li^+ ions with K^+ ions in the glass network. This is first ever observation of mixed alkali effect (MAE) in EPR and optical parameters of mixed alkali borate glasses.

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.

Borate glasses are very interesting class of materials both from the fundamental and application point of view [11]. Alkali doping into borate glasses induces interesting structural variations by converting three-coordinated boron structure into four-coordinated structures, famously known as “boron anomaly” and also with the formation of non-bridging oxygen (NBO) ions in the glass network [12]. Cation clustering also must have an effect on several physical properties of the system. Clustering may possibly play an important role in controlling the bulk properties of the glass [13]. Our recent IR and Raman studies on the changes in structural units with the mixed alkali (Li/K) doping have shown dramatic results with non-additive variation of the band intensities and positions [14]. Conductivity studies on Li/Na, Li/K & Li/Rb mixed alkali borate glasses show rather surprising results with higher MAE in Li/K system when compared to the other two combinations [15]. This is quite unusual when the MAE is understood on the basis of cation size or mass differences. Hence Li/K mixed alkali borate glasses are important class of materials for the study of MAE in spectroscopic properties. The optical properties of oxide based glasses vary with the local structural variations which modifies the glass network with different cation–anion covalent links. The variation in the cation–anion interactions in glass network induced by the alkali doping due to the formation of non-bridging oxide ions in glass

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network also modifies the optical properties of glasses like, optical basicity (Λ), interaction parameter (A) and optical polarizabilities ($\alpha_{O^{2-}}$). The interaction between the ions and their distribution in a glass network is important to study the glass structure. The presence or absence of heterogeneities as well as their size, morphology, and chemical composition, are significant parameters to be investigated. Electron paramagnetic resonance spectroscopy has been one of the major techniques used to study the local structural environments and variations in the paramagnetic center concentrations at different sites [16]. EPR spectroscopy of d^5 ions Mn^{2+}, has been used extensively in glasses to gather the local structural information and the spectra of these ions are also well understood in borate glasses [17–19]. So far, studies on spectroscopic and structural variations due to the alkali ion variation are meager and are of current research interest in various glass systems to understand the basic theory of mixed alkali effect in oxide glasses [20,21]. There are no papers to date reported on the mixed alkali effect in optical and EPR parameters in multi-component borate glass systems. Keeping these points in mind, a detailed study of Optical and EPR parameters in mixed alkali borate glasses is being carried out. In this article, the results of optical absorption and EPR studies in $(30 - x)Li_2O–xK_2O–10CdO–59B_2O_3–1Fe_2O_3$ (here after the glasses are labeled as LKCBF) system are reported with a detailed analysis of the observed spectra.

2. Experimental

Multi-component glass system with the chemical composition $(30 - x)Li_2O–xK_2O–10CdO–59B_2O_3–1Fe_2O_3$ ($x = 0–30$) was prepared through standard melt-quench technique and a thorough characterization of the glass system is presented in Ref. [14,22]. The optical absorption spectra of the glass samples were recorded at room temperature using Schimandzu 3100 UV–VIS–NIR spectrometer in the wavelength range of 200–800 nm. The uncertainty in the observed wavelength is about ±1 nm. The band position is measured digitally and the accuracy with which peaks were measured is about ±10 cm^{-1}. Electron paramagnetic resonance measurements were done on an EPR spectrometer operating in the X-band frequency (~9.44 GHz) with field modulation at 100 kHz. The magnetic field was scanned from 0 to 800 mT and the microwave power was 0.99 mW.

3. Results

3.1. Optical absorption

Fig. 1 shows the optical absorption spectra of LKCBF glass specimens. In LKCBF samples the spectrum observed shows a peak around 450 nm characteristic of $6A_{1g}(S)–4T_{2g}(G)$ transition of Fe^{3+} ions in the octahedral symmetry. The band position, absorption edge, band gap and Urbach energy values evaluated for LKCBF glasses corresponding to these transitions are presented in Table 1. The analysis of optical absorption edge leads to better understanding of the band structure and disorder present in the glass system. Borate glasses possess small and intermediate range ordering in glass network which makes these glasses interesting system for the study of optical properties. A detailed analysis of optical absorption spectra has been carried out on the present mixed alkali borate glasses. Optical band gap, Urbach energy, optical basicity, oxide ion polarizability, and interaction parameter values were evaluated to understand the mixed alkali effect on these parameters [22–32]. Fig. 2a–d shows the variation of optical parameters with the increase of K_2O content in the glass network. Optical band gap values fall in the range of 2.96–3.42 eV for LKCBF glasses. The Urbach energy values are in the range of

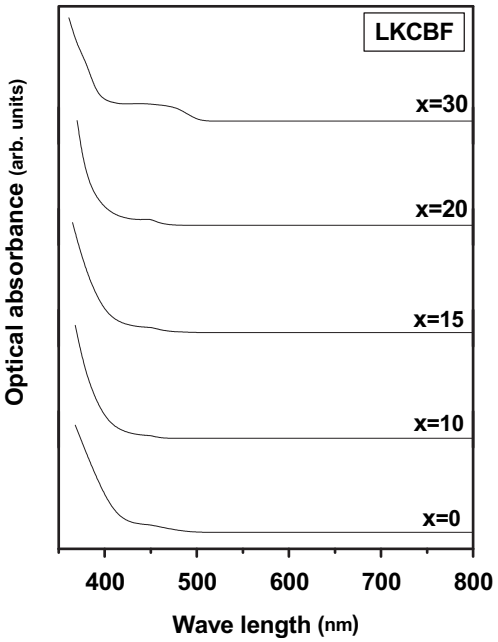

Fig. 1. Optical absorption spectra of LKCBF glasses.

0.081–0.297 eV for both LKCBF glasses. The optical band gap and Urbach energy values show a large deviation from the linearity with the progressive substitution of K_2O in to the glass network. The observed optical basicity values fall in the range of 0.508–0.525 for LKCBF glasses. The variation of the optical basicity with K_2O concentration in the glass network shows small deviation from the linearity. The calculated oxide polarizability and interaction parameter are in the typical range corresponding with the borate glasses. The polarizability shows an inverse dependence on the interaction parameter in these glasses.

3.2. EPR studies

EPR spectra which can be observed in d^5 systems, notably in systems containing Fe^{3+} and Mn^{2+}, is usually understood in terms of spin Hamiltonian given by [33]

$$H = g\beta\vec{H}\cdot\vec{S} + D\left[S_z^2 - \{(S(S+1))/3\}\right] + E\left(S_x^2 - S_y^2\right) \quad (1)$$

where D and E are constants for axial and rhombic fields respectively [34]. If D and E are zero then an isotropic absorption line with a g value slightly greater than 2 is observed. If D and E have finite but small value (0.001–0.1 cm^{-1}) five ESR transitions are observed. If D and E are larger compared to gβH, for the two limiting cases $D \neq 0$, $E = 0$ and $D = 0$, $E \neq 0$ the eigen values and eigen vectors of (1) in zero magnetic field are easily found to be three Kramer's doublets. In the first case lowest doublet has the effective g values $g_{\|} = 2$ and $g_{\perp} = 6$ and is exemplified experimentally in strong

Table 1
Optical absorption edge, band position, optical band gap and Urbach energies of LKCBF glasses.

Sample Code	Absorption edge (nm)	Peak position (nm) $6A_{1g}(S)–4T_{2g}(G)$	Band gap $E_{opt(ind)}$(eV)	ΔE (eV)
0LKCBF	437	442	3.09	0.104
10LKCBF	424	438	3.15	0.109
15LKCBF	423	432	3.2	0.068
20LKCBF	419	448	3.19	0.077
30LKCBF	415	463	3.24	0.079