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Mixed alkali effect in Mn^{2+} doped $20ZnO + xLi_2O + (30 - x)K_2O + 50B_2O_3 (5 \leqslant x \leqslant 25)$ glasses

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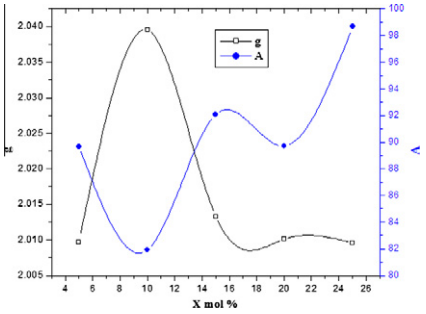
HIGHLIGHTS

- Various physical and structural parameters are evaluated and correlated.
- The phenomenon of MAE is established.
- Bandgap and Urbach energies are evaluated.
- Mn^{2+} ions occupied in distorted octahedral site symmetry.

GRAPHICAL ABSTRACT

Figure depicts the variation of spin-Hamiltonian and *g*-values of Mn^{2+} doped ZLKB glasses. Non-linear behaviour is observed with the increase of Li_2O content, but oppositely directed. The value of *g* for Mn^{2+} transition varies non-linearly along with *D*, reaches to maximum at $x = 10$ mol% where it's *A* value is minimum. The abrupt changes are observed in all the spin-Hamiltonian and bonding parameters at diffusivity crossover point i.e., at $x = 10$ mol%.



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ABSTRACT

Divalent Mn^{2+} ions containing $20ZnO + xLi_2O + (30 - x)K_2O + 50B_2O_3 (5 \leqslant x \leqslant 25)$ mol% glasses are prepared by using melt quench technique and are characterized by several spectroscopic techniques. Various physical parameters are evaluated from the measured values of density and refractive index for the observation of mixed alkali effect. Structural changes of Mn^{2+} doped ZLKB glasses are investigated by Powder XRD, UV–VIS absorption, Electron Paramagnetic Resonance and FT-IR spectroscopic studies. The XRD pattern indicates the amorphous nature of prepared glasses. FT-IR measurements of all glasses revealed that the network structure of glass system are mainly based on BO_3 and BO_4 units placed in different structural groups in which the BO_3 units being dominant. The EPR spectra of Mn^{2+} ions doped glasses exhibited a characteristic hyperfine sextet around $g = 2.0$. The spectroscopic analyses of the obtained results confirmed near octahedral site symmetry for the Mn^{2+} impurity ions. Crystal field and Racah parameters are evaluated from optical absorption spectra. The optical band gap and Urbach energies are determined which exhibited the mixed alkali effect.

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Introduction

The technological applications of glass materials have created many more arenas where it triggered to explore for new variety of glasses. The physical properties of glasses to a large extent are

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controlled by the composition, structure and the nature of the bonds of glasses. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition and dopants of transition metal ions is of considerable interest in the application point of view. Borate glasses have attracted much attention in the recent past because of their optical and electrochemical applications as solid-state batteries, optical waveguides and luminescent materials. Several works have been performed on borate glasses to study their structure, magnetic and electrical properties [1–5]. It offers promising choice especially for thermo luminescence applications due to its high sensitivity, low cost and easy preparation. The glassy material which consists of heaviest metal oxides, are more promising for photonics and optoelectronics. High electrical conductivity and ease in preparation of alkali-borate glasses has suggested as potential fast ion conducting solid electrolytes [6]. Of these, lithium-borate glasses have been studied most. The conductivity in this glass system increases as the mole fraction of lithium oxide is increased. While maintaining the vitreous nature, further increase in conductivity is achieved by adding lithium in the form of halides [7,8] or other lithium salts [9].

Most of the properties of the glassy materials are depend on the chemical composition of the glass system and the non-linear behaviour of certain properties with respect to modification of alkali content is known as mixed alkali effect [10]. The experimental and theoretical investigations on mixed alkali effect (MAE) of several glasses are reported in literature [11,12]. Mixed alkali glass is considered as an important class of material due to its scientific as well as technological aspect. Glasses doped with transition metals attract much attention because of their interesting optical [13], semi-conducting [14], memorizing and photo-conducting properties [15]. They also find potential applications in solid state lasers [16], luminescent solar energy concentrator and optical fibres for communication devices [17]. The states of transition metals in host glasses are known to be influenced by several parameters such as type and glass composition, melting conditions (including temperature and time) and oxygen availability in the furnace atmosphere. The ability to control the different species ratio is important for investigating its effect on the properties and structure of glasses. Recently authors investigated the phenomenon of MAE in the transition metal ions (TMI) doped ZLNB and ZLKB glass systems [18–23]. Manganese is next to iron element, one of the most common impurities in glasses and its intentional use as coloring and decolouring agent. Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous systems. As a continuation of our previous work, to understand the phenomenon of MAE in ZLKB glasses Mn^{2+} ions are taken as spectroscopic probe.

Experimental section

Preparation of glasses

The starting materials used in the present study are analar grade chemicals of ZnO, Li_2CO_3, K_2CO_3, B_2CO_3 and MnO with 99.9% of purity. These mixtures are sintered at 750 K and melted in an electric furnace in a silica crucible around 1250 K for nearly 1 h. The melt is then quenched at room temperature in air to form a glass. The glasses so formed are further annealed at 700 K for 1 h to relieve the structural stress. The glass composition here after named as ZLKB glass system. The composition of ZLKB glasses with prepared temperatures are given in Table 1.

Characterization techniques

The densities (ρ) of all glasses are determined by using Archimedes method with Xylene as an immersion fluid. Refractive indices (n_d) of the prepared glasses are measured by using Abbe's refractometer. The EPR spectra of powdered samples are recorded at room temperature on JEOL JES TE 100 ESR spectrometer at X-band frequency with 100 kHz field modulation. FT-IR spectra are recorded by using Bruker FT-IR spectrometer in the region 500–4000 cm^{-1}. The optical absorption spectra of polished glass samples are taken from JASCO V670 spectrometer in the region of 200–1400 nm. By using measured values of density (ρ), refractive index (n_d) some more physical parameters like molar refractivity (R_M), optical dielectric constant (ε), ionic concentration (N), electronic polarizability (α_e), polaron radius (r_p) and inter ionic distance (r_i) are evaluated [24–28].

Table 1
Composition of Mn^{2+} doped ZLKB glasses studied in the present work.

Glass system	Glass chemical composition	Prepared temp. (K)
ZLKB1	$19.9ZnO + 05Li_2O + 25K_2O + 50B_2O_3 + 0.1MnO$	1175
ZLKB2	$19.9ZnO + 10Li_2O + 20K_2O + 50B_2O_3 + 0.1MnO$	1188
ZLKB3	$19.9ZnO + 15Li_2O + 15K_2O + 50B_2O_3 + 0.1MnO$	1213
ZLKB4	$19.9ZnO + 20Li_2O + 10K_2O + 50B_2O_3 + 0.1MnO$	1223
ZLKB5	$19.9ZnO + 25Li_2O + 05K_2O + 50B_2O_3 + 0.1MnO$	1223

Results and discussion

Powder X-ray diffraction studies

The X-ray diffraction pattern does not contain any sharp peaks which is a sign of amorphous material. XRD pattern confirms the glassy nature of all the prepared glass samples.

Physical properties

Various physical parameters like optical dielectric constant, reflection loss, and molar refractivity like were evaluated from the measured values of densities and refractive indices of Mn^{2+} ions doped ZLKB glass systems [24–28].

The dielectric constant (ε) of the glass materials can be calculated by knowing the refractive index of the glass [24].

$$\varepsilon = n_d^2 \tag{1}$$

The reflection loss from the glass surface can be computed from refractive index using Fresnel's formula [25]:

$$R = [(n_d - 1)/(n_d + 1)]^2 \tag{2}$$

The molar refractivity R_M for each glass can be evaluated using [26]

$$R_M = [(n_d^2 - 1)/(n_d^2 + 2)]M/D \tag{3}$$

where M is the average molecular weight and D is density in g/cc. The electronic polarizability (α_e) can be expressed as [27]

$$\alpha_e = \frac{3(n_d^2 - 1)}{4\pi N(n_d^2 + 2)} \tag{4}$$

where N is the number of transition metal ions per unit volume.

The inter-ionic separation and polaron radius can be determined by using the following formulae [28]:

$$r_i = (1/N)^{1/3} \tag{5}$$

$$r_P = (1/2)[\pi/6N]^{1/3} \tag{6}$$

The calculated values are given in Table 2. The error in density measurements and refractive indices are estimated to be about ±0.004 g/cm^3 and ±0.0001 respectively. Figs. 1 and 2 show the effect of Li_2O content on density and refractive index, ionic concentration

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