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Mixed alkali effect in Cu^{2+} doped boroarsenate glasses—EPR and optical absorption studies

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ABSTRACT

The local structure around Cu^{2+} ion has been examined by means of electron paramagnetic resonance and optical absorption measurements in xK_2O–$(40-x)Na_2O$–$50B_2O_3$–$10As_2O_3$ ($0 \leqslant x \leqslant 40$) glasses. The site symmetry around Cu^{2+} ions is found to be tetragonally distorted octahedral and the ground state of Cu^{2+} is $d_{x^2-y^2}$. The spin-Hamiltonian parameter $g_{\|}$ goes through a minima whereas $A_{\|}$ goes through a maxima around $R_K = 0.5$, showing the mixed alkali effect. The glass exhibited broad absorption band centred 12,239 cm^{-1} corresponding to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$. By correlating the EPR and optical absorption data, the molecular orbital coefficients α^2 and β_1^2 are evaluated for the present glass system. The IR studies show that the glass system contains BO_3 and BO_4 units in the disordered manner.

1. Introduction

A phenomenon known as mixed alkali effect (MAE), one of the classical 'anomalies' of glass science is observed when two types of alkali ions are introduced into a glassy network. It represents the non-linear variations exhibiting a minima or maxima in many physical properties associated with the alkali ion movement and structural properties, when one type of alkali ion is gradually replaced by another, keeping the total alkali content constant [1–3]. The most evident manifestation of this effect has been observed in DC electrical conductivity, ionic diffusion, dielectric relaxation and internal friction [4]. However, spectroscopic investigations of MAE are meager, but they would be important and useful to gain insight into the microscopic origin of the MAE.

Electron paramagnetic resonance (EPR) and optical absorption are two experimental techniques capable of determining the coordination and environment of paramagnetic ions in glasses [5]. By correlating the EPR and optical absorption data, one can obtain information regarding the bond parameters which determine the metal–ligand bond in the glasses. Several studies have been made on optical absorption and EPR spectra of transition metal ions in various oxide glasses [6–8]. Recently, Chakradhar et al. [9] and Ramesh et al. [10] studied the EPR and optical absorption spectra of Cu^{2+} ions doped mixed alkali borate and alkaline earth alumino borate glasses.

Glasses containing As_2O_3 as main glass former has been studied during last two decades [11–14]. To our knowledge all studies are focused on the glass system containing single alkali arsenate glasses [11,15]. For the first time the authors reported the EPR and optical absorption studies in Li_2O–Na_2O–B_2O_3–As_2O_3 quaternary glasses [16]. In our recent article [17] we have reported the MAE in boroarsenate glasses by measuring the DC electrical conductivity. The results were explained based on the structural model proposed by Swenson and coworkers.

In the present study, we investigate the MAE in xK_2O–$(40-x)$-Na_2O–$50B_2O_3$–$10As_2O_3$ ($0 \leqslant x \leqslant 40$) glasses doped with Cu^{2+} ions using EPR and optical absorption techniques as a function of compositional parameter R_K defined as $R_K = K_2O/(K_2O+Na_2O)$ and R_K takes the values 0, 0.25, 0.5, 0.75 and 1.

2. Experimental

The method of preparation of the glass samples and the details of the apparatus used and the techniques employed for measuring EPR and optical absorption are similar to our earlier papers

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[16–18]. The amorphous nature of the glass samples was confirmed by the absence of any Bragg peaks in the X-ray diffraction pattern.

Infrared spectra of the powdered glass samples were recorded at room temperature in the range 400–2000 cm^{-1} using a spectrometer (Perkin-Elmer FT-IS, model 1605). These measurements were made on glass powder dispersed in KBr pellets.

3. Results and discussion

No EPR signal was detected in the spectra of undoped glasses. When Cu^{2+} ions were added to the glass, the EPR spectra exhibit resonance signals similar to those reported for Cu^{2+} ions in other glass systems. The room temperature EPR spectra of the present glasses are shown in Fig. 1(a) and (b). In the recorded EPR spectra, we observed three parallel components and the perpendicular hyperfine peaks were unresolved. The EPR spectrum was analysed using the spin-Hamiltonian.

$$\mathscr{H} = g_{\parallel}\beta H_z S_z + g_{\perp} b(H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y)$$

where the symbols have their usual meaning [19]. In this equation the nuclear quadruple interaction is neglected. The hyperfine peak positions are related to the principal values of g and A tensors by the solutions of spin-Hamiltonian. The spin-Hamiltonian parameters have been evaluated and their variation with the compositional parameter R_K is shown in Fig. 2. The spin-Hamiltonian parameters of present glasses are compared with other glass systems (Table 1) and are in good agreement with those reported in the literature.

From the EPR spectra of the present glasses it is observed that $g_{\parallel} > g_{\perp} > 2.0023$, which indicates that Cu^{2+} has an octahedral environment elongated along one of the cubic axis and the ground state of the Cu^{2+} is $d_{x^2-y^2}$ [20]. It is observed that in the present glass system $g_{\parallel}$ seems to go through a minima around $R_K = 0.5$ whereas $A_{\parallel}$ seems to go through a maxima, showing MAE. Abrupt or step wise changes in $g_{\parallel}$ and $A_{\parallel}$ have been reported by several research workers [20,21] in glass systems showing the borate anomaly. Ramdevudu et al. [22] reported spin-Hamiltonian parameters of Cu^{2+} in $MgO–Na_2O–B_2O_3$ glasses and found that $g_{\parallel}$ and $A_{\parallel}$ are dependent on the glass composition where as $g_{\perp}$ and $A_{\perp}$ remain constant. They reported that in $MgO–Na_2O–B_2O_3$ glasses as the MgO content increases $g_{\parallel}$ decreases and $A_{\parallel}$ increases which are attributed to the structural changes in the glass.

In the present investigation we have observed the MAE on the spin-Hamiltonian parameters ($g_{\parallel}$ and $A_{\parallel}$) as $g_{\parallel}$ goes through a minima and $A_{\parallel}$ goes through a maxima around $R_K = 0.5$. These changes are due to structural changes taking place with composition and also modification of the boron network with alkali content. However, $g_{\perp}$ does not show any dependence on compositional parameter.

Based on the definition of the strength of the MAE [17] in glass transition temperature and activation energy of electrical conductivity, the strength of the MAE in $A_{||}$ can be defined as

$$\Delta A_{\parallel} = A_{\parallel,\max} - A_{\parallel,\mathrm{lin}}$$

where $A_{\parallel,\max}$ represents the maximum value of $A_{\parallel}$ and $A_{\parallel,\mathrm{lin}}$ is determined at the composition which corresponds to $A_{\parallel,\max}$ and it is obtained by a linear interpolation between the $A_{\parallel}$ values of the two end members. The calculated value $\Delta A_{\parallel}$ using the above

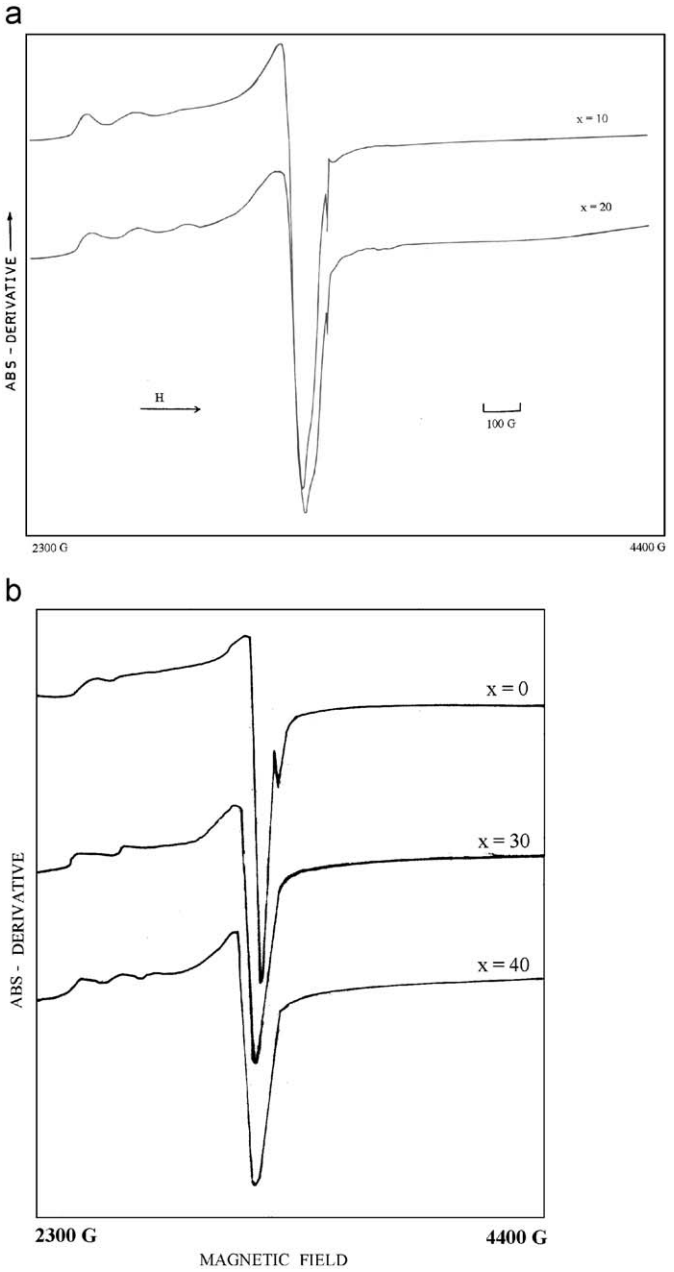

Fig. 1. (a) and (b). Room temperature EPR spectra of $xK_2O–(40–x)Na_2O–50B_2O_3–10As_2O_3$ glasses.

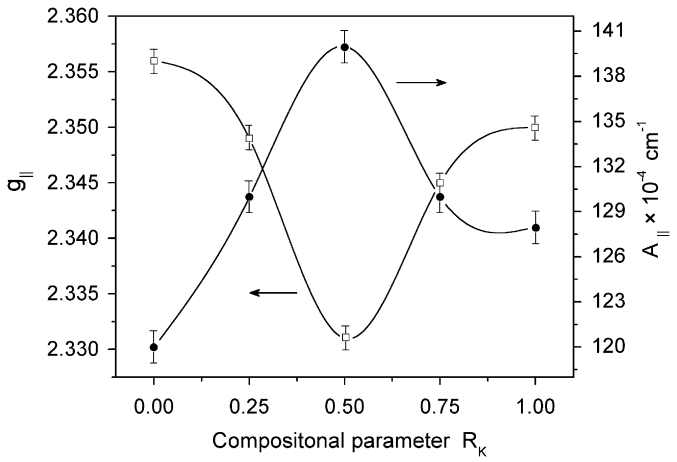

Fig. 2. Compositional dependence of spin-Hamiltonian parameters $g_{\parallel}$ and $A_{\parallel}$, in mixed alkali boroarsenate glasses.