Mixed Alkali Effect in Li_2O -Na_2O-B_2O_3 Glasses Containing CuO-An EPR and Optical Study

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Abstract

The "mixed alkali effect" is one of the classical anomalies of glass science. We report here an interesting phenomenon "Mixed Alkali Effect" observed for a series of Cu^{2+} ions doped xLi_2O-(30-x)Na_2O-70B_2O_3 ($5 \leq x \leq 25$) glasses, investigated by EPR and optical absorption techniques. The EPR spectra of all the investigated samples exhibit resonance signals characteristic of Cu^{2+} ions in octahedral sites with tetragonal distortion. It is found that the spin-Hamiltonian parameters do not vary much with x. However, the number of spins participating in resonance (N) and the paramagnetic susceptibility (χ) exhibits the mixed alkali effect. The N is also measured as a function of temperature and the activation energy is evaluated. It is observed that the temperature dependence of paramagnetic susceptibility (χ) obeys Curie-Weiss law. The optical absorption spectra exhibit a strong band corresponding to the transition ($^2B_{1g} \rightarrow {}^2B_{2g}$) centered at 13280 cm^{-1}. By correlating the EPR and optical absorption data, the molecular orbital coefficients α^2 and β_1^2 are evaluated. It is interesting to observe that the optical band gap and Urbach energies show the MAE.

INTRODUCTION

The Mixed Alkali Effect (MAE) is one of the out standing problems and poorly understood phenomenon in glass science [1,2]. Usually the change of properties with chemical composition is linear and empirically determined factors for various oxides are often cited from which a particular property can be calculated with an accuracy of practical value. However, this is not the case in mixed alkali glasses, where the proprieties show pronounced non-linear nature of variations exhibiting minima or maxima and this phenomenon is known as mixed alkali effect.

The mixed alkali effect is not much studied in borate glasses. Further, the investigations of the spectroscopic properties are very few, but they would be important and useful to gain insight into the microscopic mechanisms responsible for the effect. In the present work we have shown that the mixed alkali effect can be viewed through EPR and optical spectroscopies also. We are also interested to know the effect of alkali ions on spin-Hamiltonian parameters and also to know the site symmetry around Cu^{2+} ions in these glasses. The effect of temperature (123 – 300 K) on EPR signals has also been studied.

EXPERIMENTAL

The Glass samples were prepared by splat quenching technique and the glass formation was confirmed by using X-ray diffraction experiments recorded with a Phillips type PW 1050 diffractometer, using copper tube and nickel filter. The EPR spectra were recorded on a EPR spectrometer (JEOL-FE-1X) operating in the X-band frequency. The optical absorption measurements were done on JASCO (V-570) UV–VIS–NIR spectrophotometer.

RESULTS AND DISCUSSION

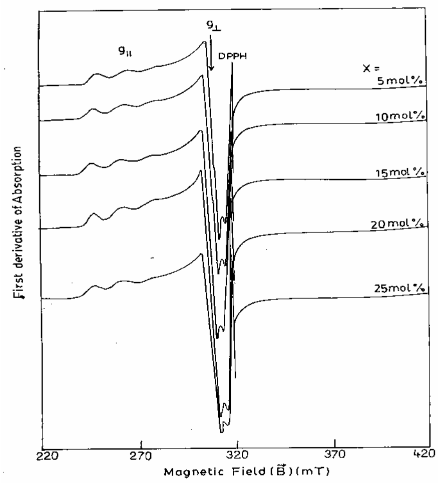

Fig. 1. EPR spectra of 0.5 mol% CuO doped xLi_2O-(30-x)Na_2O-69.5B_2O_3 ($5 \leq x \leq 25$) glass samples at room temperature.

Fig. 1. shows the X-band EPR spectra for 0.5 mol % of Cu^{2+} ions in xLi_2O-(30-x)Na_2O-70B_2O_3 ($5 \leq x \leq 25$) glasses. In the recorded spectra, we observe three weak parallel components in the lower field region and the fourth parallel component is overlapped with the perpendicular component; the perpendicular components is observed in the high field region. It is observed that the spin-Hamiltonian parameters (g and A) are nearly

independent of the mixed alkali content. The observed $g_{\parallel}$ and $g_{\perp}$ values are characteristic of Cu^{2+} ions co-ordinated by six ligands which form an octahedron elongated along the z-axis.

The number of spins (N) participating in resonance is calculated by comparing the area under the absorption curve with that of a standard ($CuSO_4.5H_2O$ in this study) of known concentration by using the formula

$$N= \frac{A_x\,(Scan_x)^2\, G_{std}\, (B_m)_{std}\, (g_{std})^2\, [S\,(S+1)]_{std}\, (P_{std})^{1/2}}{A_{std}\,(Scan_{std})^2\, G_x\, (B_m)_x\, (g_x)^2\, [S\,(S+1)]_x\, (P_x)^{1/2}}\,[Std]$$

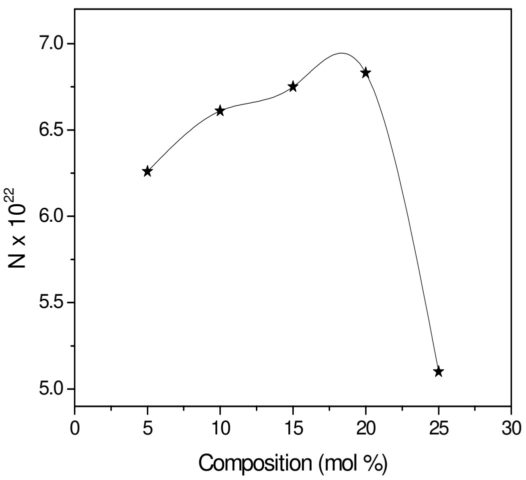

Fig. 2. The variation of N with x in xLi_2O-(30-x)Na_2O-$70B_2O_3$ ($5 \le x \le 25$) glasses .

From Fig. 2, it is interesting to note that the number of spins participating in resonance increases with x up to x = 20 reaching a maximum around x = 20 and thereafter it decreases showing the mixed alkali effect.

It is observed that as the temperature is lowered, the number of spins increases and a linear relationship between Log N and 1 / T is observed obeying the Boltzmann law. The activation energy thus calculated is found to be 2.086×10^{-21} J (0.013 eV).

It is also observed that the paramagnetic susceptibility χ increases with x up to x = 20 reaching a maximum around x = 20 and thereafter it gradually decreases showing the mixed alkali effect. Further, with increasing temperature, the susceptibility of the sample decreases obeying the Curie-Weiss law (Fig. 3). The data is fitted to a straight line in accordance with Curie-Weiss-type behavior $\chi = C/(T - \theta p)$. From the slope of the line the Curie constant ($C = 279 \times 10^{-3}$ emu mol^{-1}) and Cuire temperature ($\theta p = - 45K$) have been evaluated. The paramagnetic Curie temperature (θ_p) is negative for the investigated sample suggests that the copper ions are antiferromagnetically coupled by negative super exchange interactions at very low temperatures.

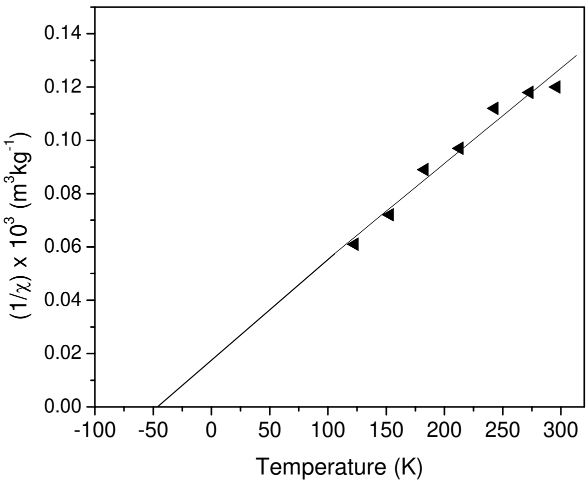

Fig. 3. A plot of ($1/\chi$) versus temperature (T) for $5Li_2O$-$25Na_2O$-$69.5B_2O_3$+0.5 CuO sample.

From ultraviolet absorption edges, the optical bandgap energies were evaluated for all the glass samples. It is interesting to note that the optical bandgap energies for these glasses increases slightly with increasing Li_2O content and reaches a maximum around 15 mol % and thereafter decreases showing the mixed alkali effect. The Urbach energy decreases with x reaching a minimum around x = 15 and thereafter it increases showing the MAE. The optical bandgaps obtained in the present work varies from 3.18 – 3.30 eV for indirect transitions. The theoretical values of optical basicities have also been evaluated.

REFERENCES

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