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Effect of MoO_3 on electron paramagnetic resonance spectra, optical spectra and dc conductivity of vanadyl ion doped alkali molybdo-borate glasses

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ABSTRACT

Alkali molybdo-borate glasses having composition $xMoO_3\cdot(30-x)M_2O\cdot70B_2O_3$ and $xMoO_3\cdot(70-x)B_2O_3\cdot30M_2O$ (M = Li, Na, K) with $0 \leqslant x \leqslant 15$ (mol%) doped with 2.0 mol% of V_2O_5 have been prepared in order to study the influence of MoO_3 on electrical conductivity, electron paramagnetic resonance (EPR) and optical spectra. From EPR studies it is observed that V^{4+} ions in these samples exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and belong to C_{4v} symmetry. The tetragonal nature and octahedral symmetry of $V_{4+}O_6$ complex increase as well as decrease depending upon the composition of glasses with increase in MoO_3 but $3d_{xy}$ orbit of unpaired electron in the VO^{2+} ion expands in all the glasses. The decrease in optical band gap suggests that there is an increase in the concentration of non-bridging oxygen's. From the study of optical transmission spectra it is observed that for all the glasses the degree of covalency of the σ-bonding decreases with increase in MoO_3 content and the degree of covalency of the π-bonding also varies. These results based on optical spectroscopy are in agreement with EPR findings. It is found that dc conductivity decreases and activation energy increases with increase in MoO_3:M_2O (M = Li, Na, K) ratio in $MoO_3\cdot M_2O\cdot B_2O_3$ glasses, whereas the conductivity increases and activation energy decreases with increase in MoO_3:B_2O_3 ratio in $xMoO_3\cdot B_2O_3\cdot M_2O$ glasses, which is governed by the increase in nonbridging oxygen's. The variation in theoretical optical basicity, Λth is also studied.

1. Introduction

Recently many authors [1–10] devoted their work towards molybdenum doped oxide glasses but few of them [5–10] studied the effect of molybdenum ion on EPR, electrical and optical properties of mixed transition metal doped alkali borate glasses. In alkali oxide glasses the electrical conductivity depends on the mobility and concentration of mobile alkali ions. On the other hand, the oxide glasses containing transition metal ions exhibit a purely electronic conductivity with a polaronic conduction mechanism. The conduction process proceeds via a charge exchange among the transition metal ions of different valence states, owing to the loss of oxygens during the formation of the glasses and to the associated reduction of transition metal cation [11–13]. A glass based on a mixture of both transition and alkali metals exhibits a mixed ionic and electronic conductivity [14,15]. Electron paramagnetic resonance (EPR) spectroscopy can be used to study the microstructure around the transition metal ions in glasses [16–21]. The optical band gap studies of oxide glasses provide information related to their electronic structure [22–27]. Molybdenum containing glasses possess a variety of specific features, which arouse interest in view of their applications. It is known that MoO_3 adds to glass semiconductor properties with n-type conduction because of different valence states of molybdenum [28]. MoO_3 containing glasses are also used for the development of optical and radiation glasses [4,29]. In the present paper alkali molybdo-borate glasses doped with 2.0 mol% of V_2O_5 have been prepared in order to study the influence of MoO_3 on the EPR, optical spectra and electrical conductivity.

The compositions of the glass systems studied are given below:

(i) $xMoO_3\cdot(30-x)M_2O\cdot70B_2O_3$ (M = Li, Na and K): MB series
(ii) $xMoO_3\cdot(70-x)B_2O_3\cdot30M_2O$ (M = Li, Na and K): BM series with $0 \leqslant x \leqslant 15$ (mol%).

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2. Experimental

2.1. Glass preparation

The glass samples were prepared using melt-quench technique from analytical reagent grade chemicals (Himedia, India) M_2CO_3 (M = Li, Na, K), MoO_3, H_3BO_3 and V_2O_5. The chemicals were thoroughly mixed in the required proportions and were melted in crucibles using an electric muffle furnace with normal atmosphere for 30 min at 1373 K. To assure homogeneity, the melt was swirled frequently. The homogenized melt was poured onto a carbon plate and quickly pressed with another.

2.2. EPR measurements

The first derivative EPR spectra were recorded at the room temperature in the X-band ($\nu \sim 9.3$ GHz) on EPR spectrometer (Varian E-109). The magnetic field was modulated by 100 KHz. Polycrystalline DPPH was used as the standard g maker ($g \sim 2.0036$) for the calculation of the spin Hamiltonian parameters.

2.3. Optical spectra

The optical transmission and absorption spectra of the samples were recorded at room temperature using Perkin Elmer UV/Vis spectrometer (Lambda 20) in the wavelength range 350–850 nm.

2.4. dc conductivity

To measure dc conductivity, sample in the form of slice of nearly one-mm uniform thickness were ground to obtain parallel surfaces. The parallel surfaces of the samples were coated with colloidal silver paint as an electrode material. Conductivity measurements were made by the two terminal methods over a temperature range from about 373 K to 593 K. A constant voltage of 10 V was applied across the sample and the circulating current was measured by using a Keithley 6517 programmable electrometer/source.

3. Results

3.1. EPR

Figs. 1 and 2 show the EPR spectra of the VO^{2+} ions in xMoO$_3$·$(30-x)$Li$_2$O·70B$_2$O$_3$ and xMoO$_3$·$(70-x)$B$_2$O$_3$·30Li$_2$O glass samples. These spectra show structure which is due to a hyperfine interaction of a single unpaired electron with a ^{51}V nucleus whose nuclear spin (I) is 7/2. Similar EPR spectra were obtained for other glass samples. These spectra were analyzed by assuming [17–19] that vanadium is present as a vanadyl ion in a ligand field of C_{4V} symmetry. The spin Hamiltonian used is of the form as described by equation given by Hecht et al. [14]. The solutions of the spin Hamiltonian equation are given by suggested by Bleaney [15] for the parallel and perpendicular orientations, respectively.

The calculated value of Spin Hamiltonian parameters (SHP) of the VO^{2+} ion for the EPR spectra for all the glasses are presented in Tables 1 and 2. The uncertainty in the value of g is ±0.0010 and in the value of A is $\pm 1.0 \times 10^{-4}$ cm^{-1} satisfying the calculated value of line position with the corresponding experimental value. The dipolar hyperfine coupling parameter, $P = 2\gamma\beta\beta_N < r^{-3} >$, and the Fermi contact interaction term, K, are evaluated using the equations developed by Kivelson et al. [30].

K is found to be positive for transition metal ions [31]. From the molecular orbital theory, it can also be shown [32] that the compo-

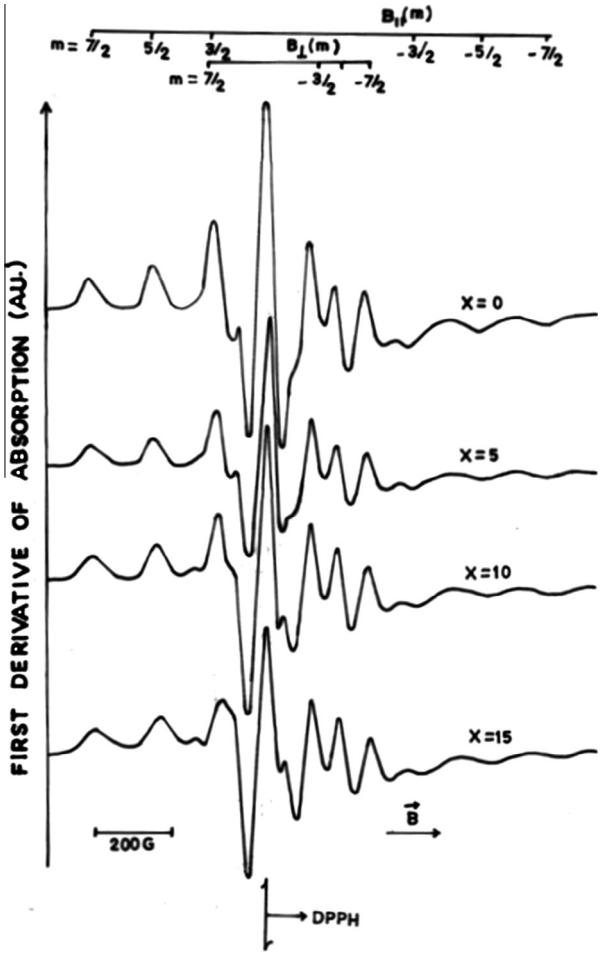

Fig. 1. The EPR spectra of xMoO$_3$·$(30-x)$Li$_2$O·70B$_2$O$_3$ glasses doped with 2 mol% of V_2O_5 in the X-band at 300 K.

nents $A_{\|}$ and $A_{\perp}$ consist of the contributions $A'_{\|}$ and $A'_{\perp}$ of the $3d_{xy}$ electron to the hyperfine structure and the PK term arises due to the anomalous contribution of the s-electrons. The values of $A'_{\|}$, $A'_{\perp}$ and $\Delta g_{\|}/\Delta g_{\perp}$, which measures the tetragonality of the vanadium site [32], are included in Tables 3 and 4. For vanadyl ion an octahedral site symmetry [14] with tetragonal compression would give $g_{\|} < g_{\perp} < g_e$ and $|A_{\|}| > |A_{\perp}|$, the values of SHP obtained in the present study satisfy these observations. Thus, it may be concluded that V^{4+} ions in the present glasses exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and belong to C_{4V} symmetry.

Theoretical optical basicity, Λth, has also been calculated and its calculated values are given in Tables 1 and 2.

3.2. Optical spectra

Figs. 3 and 4 show the optical transmission spectra of xMoO$_3$·$(30-x)$Na$_2$O·70B$_2$O$_3$ and xMoO$_3$·$(70-x)$B$_2$O$_3$·30Na$_2$O glass samples. Figs. 5 and 6 show the optical absorption spectra of xMoO$_3$·$(30-x)$Li$_2$O·70B$_2$O$_3$ and xMoO$_3$·$(70-x)$B$_2$O$_3$·30Li$_2$O glass samples. Similar spectra were obtained for other glass samples. From these spectra, it is observed that the optical absorption edges are not sharply defined which is a characteristic of amorphous material. The values of the cutoff wavelength (λ_{cutoff}) are shown in Tables 5 and 6 for all the samples. The absorption coefficient, $\alpha(\nu)$ was determined from the absorption spectra and Tauc's plots for xMoO$_3$·$(30-x)$Li$_2$O·70B$_2$O$_3$ and xMoO$_3$·$(70-x)$B$_2$O$_3$·30Li$_2$O glass