Fe³⁺ ions in alkali lead tetraborate glasses—an electron paramagnetic resonance and optical study

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Abstract

Glass systems of composition $90R_2B_4O_7 + 9PbO + 1Fe_2O_3$ (R = Li, Na and K) and $90Li_2B_4O_7 + (10 - x)PbO + xFe_2O_3$ (x = 0.5, 1, 3, 4, 5, 7and 9 mol%) have been investigated by means of electron paramagnetic resonance (EPR) and optical absorption techniques. The EPR spectra exhibit three resonance signals at $g \approx 6.0$, 4.2 and 2.0. The resonances at $g \approx 6.0$ and 4.2 are attributed to Fe³⁺ ions in rhombic and axial symmetry sites, respectively. The $g \approx 2.0$ resonance signal is due to two or more Fe³⁺ ions coupled together with dipolar interaction. The EPR spectra of 1 mol% of Fe₂O₃ doped in lithium lead tetraborate glass samples have been studied at different temperatures (123–433 K). The intensity of $g \approx 4.2$ resonance signal decreases and the intensity of $g \approx 2.0$ resonance signal increases with the increase of temperature. The line widths are found to be independent of temperature. The EPR spectra exhibit a marked concentration dependence on iron content. A decrease in intensity for the resonance signal at $g \approx 4.2$ with increase in iron content for more than 4 mol% has been observed in lithium lead tetraborate glass samples and this has been attributed to the formation of Fe³⁺ ion clusters in the glass samples. The paramagnetic susceptibility (χ) is calculated from the EPR data at various temperatures and the Curie constant (*C*) has been evaluated from $1/\chi$ versus *T* graph. The optical absorption spectrum of Fe³⁺ ions in lithium lead tetraborate glasses exhibits three bands characteristic of Fe³⁺ ions in an octahedral symmetry. The crystal field parameter D_q and the Racah interelectronic repulsion parameters *B* and *C* have also been evaluated. The value of interelectronic repulsion parameter *B* (825 cm⁻¹) obtained in the present work suggests that the bonding is moderately covalent.

Keywords: Fe3+ ions; Alkali lead tetraborate glasses; EPR; Optical absorption

1. Introduction

Due to their potential applications in various domains of modern technology, glasses containing transition-metal oxides have been the subject of intensive investigations [1]. For example, the glasses containing transition metal ion such as Fe_2O_3 is used in electrochemical, electronic and electro-optic devices [2–4]. The addition of iron to borate glass makes it electrically semiconducting and superparamagnetic [5]. Borate glasses are also of academic interest because of the boron anomaly [6] and also B_2O_3 is one of the best glass formers.

Among borate glassy family, alkali borate glasses have acquired greater significance (especially lithium borate glasses as solid electrolytes because of their fast ionic conduction) [7,8]. Electrical conductivity and infrared studies of the alkali borate glasses have been reported by many investigators [8,9] and these studies have provided very informative data on the nature of network, i.e., the type and concentration dependence of variety of boron–oxygen arrangement. The addition of heavy metal oxide like PbO to a glass will make them more stable. In addition to this, glasses containing lead or tungsten have a reputation of being good materials for IR transmission, electrochromic, photochromic and ferroelectric-like behaviour [10].

Therefore, we have made alkali lead tetraborate glasses, keeping in view of the possible applications and interested to study the structural evolution of these glasses using electron

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paramagnetic resonance (EPR). The EPR spectrum of transition metal ions in oxide glasses is an interesting research subject and affords a method to investigate the glass structure [11]. EPR spectra of Fe^{3+} ions in various glasses have been extensively studied [12–20]. It is found that the trivalent ions can take two different coordination sites, i.e., either tetrahedral or octahedral sites in glasses.

Recently, Ardelean et al. [20] studied the EPR and magnetic susceptibility of B_2O_3 –CaCl–Fe₂O₃ glasses. Bensimon et al. [21] studied the EPR in natural clay. No EPR and optical absorption studies of Fe³⁺ ions in alkali lead tetraborate glasses have been reported so far. In the present investigation, we have systematically studied the EPR and optical absorption spectra of Fe³⁺ ions in different alkali lead tetraborate glasses. We are also interested to know the effect of alkali ions on spin-Hamiltonian parameters and also to know the site symmetry around Fe³⁺ ions in these glasses. The effect of temperature (123–433 K) on EPR signals have also been studied.

2. Experimental

Table 1

The starting materials (Li₂B₄O₇, Na₂B₄O₇·10H₂O, K₂B₄O₇·5H₂O, PbO and Fe₂O₃) used in the preparation of glasses were of Analar quality. Table 1 lists the batch composition of glasses in mol% studied in the present work. The chemicals were weighed accurately in an electrical balance, mixed thoroughly and then ground to fine powder. The batches were then placed in porcelain crucibles and melted in an electrical furnace. The melting temperature of the batches is given in Table 1. The melts were, then, poured on a polished porcelain plate and pressed quickly with another porcelain plate. The glasses thus obtained were transparent and yellowish in colour. The colour is due to Fe^{3+} ions entering the glass matrix. Care was taken to obtain glasses of uniform thickness for recording optical absorption spectra. The glasses so obtained were annealed at 423 K for 3 h to remove the thermal strains. Glasses of good quality obtained after polishing were used for optical measurements.

EPR spectra were recorded at room as well as at different temperatures on an EPR spectrometer (JEOL FE-1X) oper-

ating in the X-band frequency (9.205 GHz) with a modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT with a scan speed of 25 mT min⁻¹. A powdered glass specimen of 100 mg was taken in a quartz tube for EPR measurements. The EPR spectrum of CuSO₄·5H₂O powdered material was also recorded at 9.205 GHz as a reference to calculate the number of spins.

The EPR spectrum of 1 mol% of Fe₂O₃ doped lithium lead tetraborate (LiPbTB:1Fe) glass sample was recorded at different temperatures (123–433 K) using a variable temperature controller (JES UCT 2AX). A temperature stability of ± 1 K was easily obtained by waiting for approximately half an hour at the set temperature before recording a spectrum, at each temperature.

The optical absorption spectrum of 3 mol% of Fe_2O_3 doped in lithium lead tetraborate (LiPbTB:3Fe) glass sample was recorded on a JASCO UV–vis–NIR spectrophotometer (model V-570) in the wavelength region from 300 to 900 nm.

3. Results and discussion

3.1. Electron paramagnetic resonance studies

No EPR signal was detected in the spectra of undoped glasses indicating that there are no paramagnetic impurities present in the starting materials. When various mol% of Fe³⁺ ions were added to alkali lead tetraborate glasses (see Table 1), the EPR spectra of all the samples under investigation exhibit resonance signals. Fig. 1 shows the EPR spectra of 1 mol% of Fe³⁺ ions in (a) lithium lead tetraborate (LiPbTB:1Fe), (b) sodium lead tetraborate (NaPbTB:1Fe) and (c) potassium lead tetraborate (KPbTB:1Fe) glass samples. For glass (a), the spectrum has an intense resonance signals at $g \approx 4.2$ and also at $g \approx 2.0$ and a shoulder in the region of $g \approx 6.0$. For glasses (b) and (c), the spectrum has an intense resonance signal at $g \approx 4.2$, a broad resonance signal at $g \approx 2.0$ and a shoulder in the region of $g \approx 6.0$.

Since the discovery of the unusual paramagnetic resonance lines in glasses by Sands [22], numerous publications have been devoted to the study of Fe^{3+} coordination in vitreous materials. EPR spectra of Fe^{3+} ions in various glasses

Composition (mol%) of glasses studied in the present work							
Glass code	$Li_2B_4O_7$	$Na_2B_4O_7\!\cdot\!10H_2O$	$K_2B_4O_7 \cdot 5H_2O$	PbO	Fe ₂ O ₃	Melting temperature (K)	
LiPbTB	90	-	-	10	_	1226	
LiPbTB:0.5Fe	90	_	-	9.5	0.5	1226	
LiPbTB:1Fe	90	_	-	9.0	1.0	1226	
LiPbTB:3Fe	90	_	-	7.0	3.0	1226	
LiPbTB:4Fe	90	_	-	6.0	4.0	1226	
LiPbTB:5Fe	90	_	-	5.0	5.0	1226	
LiPbTB:7Fe	90	_	-	3.0	7.0	1226	
LiPbTB:9Fe	90	_	_	1.0	9.0	1226	
NaPbTB:1Fe	_	90	-	9.0	1.0	1126	
KPbTB:1Fe	-	-	90	9.0	1.0	1126	



Fig. 1. EPR spectra for $1 \mod \%$ of Fe³⁺ ions in different alkali lead tetraborate glasses. (a) LiPbTB:1Fe, (b) NaPbTB:1Fe and (c) KPbTB:1Fe at room temperature.

have been extensively studied [23–29]. Usually, the occurrence of two resonance signals, at $g \approx 4.2$ and 2.0 has been reported [23,24]. In some cases, a resonance near $g \approx 6.0$ was also observed [23,24,30] as a shoulder of the resonance near $g \approx 4.2$. The resonance at $g \approx 4.2$ and 2.0 were discussed by many investigators [23–29]. Some investigators [23,24] suggested that the value of g in glasses containing Fe³⁺ ions is related to the coordination number. The absorption at $g \approx 4.2$ and 2.0 arise from Fe³⁺ ions in tetrahedral and octahedral coordinations, respectively [31].

Fe³⁺ ions belong to d⁵ configuration with ⁶S as the ground state in the free ion and there is no spin–orbit interaction [24]. The 'g' value is expected to lie very near to the free-ion value of 2.0023. However a g value very much greater than 2.00 often occurs, in particular an isotropic g value at 4.2 occurs and these large g values arise when certain symmetry elements are present.

When Fe³⁺ ions are placed in a crystal field environment, the ⁶S ground state splits into three Kramers doublets $|\pm 1/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$. The resonance signal at $g \approx 4.2$ results from the middle Kramers doublet $|\pm 3/2\rangle$ [32].

In the present study, the authors observed an intense resonance signal at $g \approx 4.2$ and 2.0 and a shoulder-like signal at g = 6.0 for all the glass samples under investigation. In sodium lead tetraborate and potassium lead tetraborate glasses, the intensity of the resonance signal at $g \approx 2.0$ is very small when compared to that of lithium lead tetraborate glasses. The resonances at $g \approx 4.2$ and 6.0 have been attributed to the isolated Fe³⁺ ions in rhombic and axial symmetry sites, respectively [23,33–35]. The $g \approx 2.0$ resonance may be attributed to either Fe³⁺ ions interacting by dipole–dipole interaction in sites of less distorted octahedral field or to their super exchange interactions within the pairs or Fe ions [23,35,36]. These *g* values observed in the present work indicate that the iron ions are in trivalent state and the site symmetry is distorted octahedral.

The EPR spectra of $90\text{Li}_2\text{B}_4\text{O}_7 + 9\text{PbO} + 1\text{Fe}_2\text{O}_3$ (LiPbTB:1Fe) glass sample was recorded at various temperatures (123–433 K) and are shown in Fig. 2. The peak-to-peak width of resonance signals at $g \approx 4.2$ and 2.0 are found to be independent of temperature. The intensity of the resonance signal at $g \approx 4.2$ decreases and the intensity of $g \approx 2.0$ resonance signal increases as the temperature increases. At low temperatures, we observed a prominent shoulder at $g \approx 6.0$. As the temperature increases, the intensity of $g \approx 4.2$ resonance absorption decreases. This may be due to the decrease in population of isolated Fe³⁺ ions. The increase in intensity at $g \approx 2.0$ resonance absorption with the rise of temperature may be due to the formation of clusters of Fe³⁺ ions containing two or more ions coupled together.

3.2. Calculation of number of spins (N) participating in resonance

The number of spins participating in resonance can be calculated by comparing the area under the absorption curve with that of a standard ($CuSO_4 \cdot 5H_2O$ in this study) of known concentration. Weil et al. [37] gave the following expression which includes the experimental parameters of both sample and standard.

$$N = \frac{A_x(\operatorname{scan}_x)^2 G_{\text{std}}(B_{\text{m}})_{\text{std}}(g_{\text{std}})^2 [S(S+1)]_{\text{std}}(P_{\text{std}})^{1/2}}{A_{\text{std}}(\operatorname{scan}_{\text{std}})^2 G_x(B_{\text{m}})_x(g_x)^2 [S(S+1)]_x(P_x)^{1/2}} \times [\text{std}]$$
(1)

where *A* is the area under the absorption curve which can be obtained by double integrating the first derivative EPR absorption curve, scan the magnetic field corresponding to unit length of the chart, *G* the gain, B_m the modulation field width, *g* the *g*-factor, *S* the spin of the system in its ground state. *P* is the power of the microwave source. The subscripts '*x*' and 'std' represent the corresponding quantities for Fe³⁺ glass sample and the reference (CuSO₄·5H₂O), respectively.

Fig. 3 shows the variation of number of spins at $g \approx 4.2$ and 2.0 resonances as a function of Fe₂O₃ content in lithium lead tetraborate (LiPbTB:*x*Fe where x = 0.5, 3, 4, 5, 7 and 9 mol% of Fe₂O₃) glasses. From the figure, it is also observed that the number of spins participating in resonance at $g \approx 4.2$ increases up to 4 mol% of Fe₂O₃, and thereafter, it decreases. The increase of number of spins at $g \approx 4.2$ resonance with Fe₂O₃ content is due to increase of 'isolated' Fe ions up to $x = 4 \mod \%$. The decrease of intensity for $x > 4 \mod \%$ may be due to the decrease in population of isolated Fe³⁺ ions. The



Fig. 2. EPR spectra for 90Li₂B₄O₇ + 9PbO + 1Fe₂O₃ glass sample at different temperatures.

progressive increase of iron content in the glass makes the iron ions to accumulate (at heavy doping $>4 \mod \%$), thereby making them to form clusters which in turn makes the 'isolated' Fe³⁺ ions a less in number. That may be the reason for the decrease in intensity for $g \approx 4.2$ resonance for x > 4 mol%. From the figure, it can also be observed that the number of spins participating in resonance at $g \approx 2.0$ increases with the mol% of Fe₂O₃. The increase in intensity for $g \approx 2.0$ resonance with Fe₂O₃ content also confirms the above arguments (formation of clusters). Recently, Ardelean et al. [35] observed a similar observation where the intensity of $g \approx 4.2$ resonance increases with Fe₂O₃ up to x = 5 mol%, and thereafter, it decreases strongly. They have attributed this due to a destruction of the configuration at the vicinity of Fe ions which assures their magnetic isolation. The gradual increase of iron content in the matrix destroys the local ordering of Fe³⁺ ion vicinities, thereby, the structural units as characteristic entities becomes less represented, and consequently, a decrease in the intensity of the resonance signal at $g \approx 4.2$.

Fig. 4 shows a plot of logarithemic dependence of the number of spins (log *N*) participating in resonance at $g \approx 4.2$

against the reciprocal of absolute temperature (1/T). 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. This is the phenomenon that can be expected from the Boltzmann law. The activation energy can be calculated from the slope of the straight line. The activation energy thus calculated is found to be 2.54×10^{-21} J (0.015 eV). This is of the same order as expected for a paramagnetic ion [38].

3.3. Calculation of paramagnetic susceptibility (χ) from EPR data

The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula [39]:

$$\chi = \frac{Ng^2\beta^2 J(J+1)}{3k_B T}$$
(2)

where *N* is the number of spins/m³ and the other symbols have their usual meaning. *N* can be calculated from Eq. (1) and *g* value is taken from EPR data.



Fig. 3. A plot of variation of intensity (*N*) at $g \approx 4.2$ and 2.0 resonances with different mol% of Fe₂O₃ concentration in 90Li₂B₄O₇ + (10 - *x*)PbO + *x*Fe₂O₃ (*x* = 0.5, 1, 3, 4, 5, 7 and 9 mol%) glass samples at room temperature.



Fig. 4. A plot of $\log N_g = 4.2$ against 1/T for $90Li_2B_4O_7 + 9PbO + 1Fe_2O_3$ glass sample.



Fig. 5. A plot of reciprocal of susceptibility $(1/\chi)$ as a function of absolute temperature (*T*) for 90Li₂B₄O₇ + 9PbO + 1Fe₂O₃ glass sample.

Fig. 5 shows a graph between reciprocal of paramagnetic susceptibility $(1/\chi)$ and absolute temperature (*T*) for the resonance signal at $g \approx 4.2$. The graph is fitted to be a straight line in accordance with the Curie's law. From the graph, Curie constant has been evaluated. The Curie constant is found to be 0.4×10^{-3} (emu/mol). The Curie constant calculated in the present work is of the same order to that of measured value 0.5×10^{-3} (emu/mol) reported for Fe³⁺ ions in oxide glasses by Moon et al. [40].

It is observed that the *g* values calculated does not vary in different alkali lead tetraborate glasses. These *g* values indicate that the paramagnetic ion is in the trivalent state and the site symmetry is distorted octahedral. As the *g* values are independent of alkali content, the symmetry around Fe³⁺ ions could not be changed with the alkali content.

The number of spins (*N*), the paramagnetic susceptibility (χ) of the glasses studied in the present work are given in Table 2.

Table 2

Number of spins (*N*), paramagnetic susceptibility (χ) and theoretical values of optical basicity (Λ_{th}) for the glasses studied in the present work

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Glass system	Number of spins, $N \times 10^{18}$	Paramagnetic susceptibility (χ) 10^{-6} m ³ kg ⁻¹	Optical basicity, Λ_{th}			
LiPbTB:1Fe	9.381	9.68	0.5029			
NaPbTB:1Fe	5.531	5.70	0.5233			
KPbTB:1Fe	11.937	12.32	0.5551			

4. Optical absorption studies

The optical absorption spectrum of 3 mol% of Fe₂O₃ in lithium lead tetraborate (LiPbTB:3Fe) glass sample is shown in Fig. 6. The optical absorption spectrum observed in the present work is a characteristic of Fe³⁺ ions in an octahedral symmetry. The spectrum exhibits three bands centred at 22215 cm^{-1} (450 nm), 25830 cm^{-1} (387 nm) and 27315 cm^{-1} (366 nm). These bands are denoted as A, B and C, respectively. These three bands have been assigned to the transitions ${}^{6}A_{1g}(S) \rightarrow {}^{4}T_{2g}(G), {}^{6}A_{1g}(S) \rightarrow {}^{4}A_{1g}(G),$ ${}^{4}E_{g}(G)$ and ${}^{6}A_{1g}(S) \rightarrow {}^{4}E_{g}(D)$. It is known that for Fe³⁺ ions, there are no spin-allowed transitions and the bands observed are due to spin-forbidden transitions only. The observed band positions are compared with those found for many glass systems containing iron, which indicates that iron ions are present in trivalent state with distorted octahedral symmetry [41–43]. The optical absorption spectra of other samples studied in the present work are similar to Fig. 6.

The energy matrices inclusive of Trees correction [44] are formed by adding appropriate Trees correction to the energy matrices of d⁵ configuration in a cubic field given by Tanabe and Sugano [45]. The inclusion of Trees correction ' α ' equal to 90 cm⁻¹ is necessary in order to obtain a good fit between the observed and calculated values. By dioganalising the energy matrices inclusive of Trees correction (α), the crystal field parameter $D_q = 1000 \text{ cm}^{-1}$ and Racah interelectronic repulsion parameters $B = 825 \text{ cm}^{-1}$ and $C = 3150 \text{ cm}^{-1}$ have been evaluated.

The observed and calculated band positions along with their assignments are given in Table 3. The crystal field parameters obtained in the present work are consistent with those for high spin octahedral Fe³⁺ ions [38]. The value of inter-electronic repulsion parameter *B* (825 cm^{-1}) obtained in the present work is far away from the free ion value (1300 cm⁻¹) [46]. This suggests that the bonding is moderately covalent.



Fig. 6. Optical absorption spectrum of $90Li_2B_4O_7 + 7PbO + 3Fe_2O_3$ glass sample at room temperature.

Table 3

The observed and calculated energies for Fe^{3+} ions in $90\text{Li}_2\text{B}_4\text{O}_7$ + 7PbO + 3Fe₂O₃ glasses at room temperature ($D_q = 1000 \text{ cm}^{-1}$, $B = 825 \text{ cm}^{-1}$ and $C = 3150 \text{ cm}^{-1}$; $\alpha = 90 \text{ cm}^{-1}$)

Band	Transition from ⁶ A _{1g} (S) to	Observed wavelength (nm)	Observed wave number (cm ⁻¹)	Calculated wave number (cm ⁻¹)
A	$^{4}T_{2g}(G)$	450	22215	22226
В	${}^{4}A_{1g}(G), {}^{4}E_{g}(G)$	387	25830	25800
С	${}^{4}T_{2g}(D)$	366	27315	28379

Also, it may be noted that the ionic radius of Fe^{3+} ions (0.064 nm) is close to the ionic radius of lithium (=0.068 nm) when compared to the ionic radius of Pb^{2+} (0.12 nm). Consequently, it is reasonable to assume that the Fe^{3+} ions occupy the lithium ion sites in these glasses.

4.1. Optical basicity (Λ_{th})

The optical basicity of an oxide glass will reflect the ability of glass to donate negative charge to the probe ion [47]. Duffy and Ingram [48] proposed that the optical basicity can be predicted from the composition of the glass and basicity moderating parameters of various cations present. The theoretical values of the optical basicity of the glass can be calculated by using the formula:

$$\Lambda = \sum_{i=1}^{n} \frac{Z_i r_i}{2\gamma_i} \tag{3}$$

where *n* is the number of cations present, Z_i the oxidation number of the *i*th cation, r_i the ratio of number of the cation to the number of oxides and γ_i is the basicity moderating parameter of the *i*th cation. The basicity moderating parameter γ_i can be calculated from the following equation

$$\gamma_i = 1.36(x_i - 0.26) \tag{4}$$

where x_i is Pauli electronegativity [49] of the cation. Λ_{th} can be used to classify the covalent/ionic ratios of the glass, since an increasing Λ_{th} indicates decreasing covalency. From Table 2, the Λ_{th} values are increasing from LiPbTB:*x*Fe glasses to KPbTB:*x*Fe glasses. Hence the covalency between Fe³⁺ ions and oxygen ligands should decrease as one moves from LiPbTB:*x*Fe glasses to KPbTB:*x*Fe glasses. Similar observations have been reported earlier by Rao et al. [50].

5. Conclusions

The EPR spectra of Fe³⁺ ions doped in different alkali lead tetraborate glasses exhibit three resonance signals at $g \approx 6.0$, 4.2 and 2.0. It is observed that the g values are independent of alkali ion. The resonances at $g \approx 4.2$ and =6.0 have been attributed to Fe³⁺ ions in rhombic and axial symmetry sites, respectively. The resonance signal at g = 2.0 is due to

two or more Fe³⁺ ions coupled together with dipolar interaction. It is observed that for Fe_2O_3 content >4 mol%, a cluster formation takes place in LiPbTB glasses. EPR spectrum of LiPbTB:1Fe glasses is studied at different temperatures. The linewidths are found to be independent of temperature changes for resonance absorptions at $g \approx 4.2$ and 2.0. The intensity of resonance absorption at $g \approx 4.2$ decreases and the intensity of resonance absorption at $g \approx 2.0$ increases with the increase of temperature (123-433 K). The number of spins (N) participating in resonance has been computed from the area under the absorption curve. A plot is drawn between $\log N$ and 1/T for the resonance signal at $g \approx 4.2$. Activation energy has been calculated from this graph and it is found to be 2.54×10^{-21} J (0.015 eV). The magnetic susceptibilities (χ) have been calculated from the EPR data at different temperatures. A linear relationship is observed between $1/\chi$ and T in accordance with Curie's law. The Curie constant has been evaluated from $1/\chi$ versus T graph. The optical absorption spectrum of LiPbTB:3Fe glasses exhibits three bands characteristic of Fe³⁺ ions in an octahedral symmetry. The crystal field parameter D_q and Racah interelectronic repulsion parameters B and C have been evaluated. The value of interelectronic repulsion parameter B (825 cm⁻¹) obtained in the present work is far away from the free ion value (1300 cm^{-1}) . This suggests that the bonding is moderately covalent.

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