Influence of alkaline earths on EPR spectra of lithium borate glasses doped with Fe (III) ions

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Abstract. Lithium borate glasses containing Fe (III) transition metal ion having composition 15RO-25Li₂O-59B₂O₃-1Fe₂O₃ (where R= CaO, SrO and BaO) are synthesized via melt quench route. These glasses were characterized using X-ray diffraction (XRD). Electron paramagnetic resonance spectra of prepared glasses have been studied. The recorded spectra mainly consists of an intense resonance signals at g ~ 4.282 and also at g ~ 2.0032 along with a shoulder in the region of g ~ 8.033 which is a characteristic of iron ions in the (3+) valence state in all the studied glasses. The number of spins participating in resonance (N) and its paramagnetic susceptibilities (χ) have also been evaluated. The spin concentration and the paramagnetic susceptibility at g = 2.0032 and at g = 4.282 increase by the substitution of alkaline earths from CaO to BaO respectively. The peak-to-peak line width ΔB for the resonance lines at g ≈ 4.282 and at g ≈ 2.0032 and the line intensity of the resonance centered at g ≈ 4.282 and at g ≈ 2.0032 have been evaluated. This EPR spectra has been analyzed in the light of different oxidation states of iron ions in order to understand the influence of alkaline earths as modifier oxide on the structure of glass matrix.

Keywords: Lithium borate glasses, X-ray diffraction, EPR spectra.

1. Introduction

Transition metal ion doping is commonly done using Cu, Fe, Cr, Mn ions to probe the glass network. Fe³⁺ and Cu²⁺ are both d⁵ ions and quite well studied through various spectroscopic studies. Glasses containing iron oxide are of high interest due to their effects on the physical properties of such glasses, i.e. mainly the electrical, magnetic and optical properties. Many studies have been reported in which it was concluded that the iron ion exists in different valence states with different coordinations simultaneously in the glass network: for example as Fe³⁺ with both tetrahedral and octahedral and as Fe²⁺ with octahedral environment. The co-existence of iron ions in two different valence states i.e. Fe³⁺ and Fe²⁺ is a general condition for semiconducting behavior of borate glasses [1-3]. Iron as an intermediate oxide in glasses is highly relevant to coloring commercial glasses [4, 5]. Iron doped oxides exhibit interesting electrical and magnetic properties that depend on the iron redox species and their coordination symmetry. The present investigation is aimed to provide a comprehensive understanding over the influence of three alkaline earth network modifiers, RO = CaO, SrO and BaO, on EPR spectra of lithium borate glasses doped with Fe (III) ions.

2. Experimental

Lithium borate glasses containing Fe (III) transition metal ion having composition 15RO-25Li₂O-59B₂O₃-1Fe₂O₃ (where R= CaO, SrO and BaO) are synthesized via melt quench route. The X-ray
diffraction patterns were recorded in the diffraction angle region of $2\theta$ from 10° to 80° insteps of 0.02° and 0.2 sec counting time per step using model Shimadzu XRD-7000 fitted with copper target and nickel filter operated at 40 kV and 30 mA at room temperature. The electron paramagnetic resonance (EPR) spectra of prepared glass samples were recorded at room temperature on Bruker spectrometer operating at X-band frequency with 100 kHz field modulation. The microwave frequency was kept at 9.729 GHz.

3. Results and Discussion
The X-ray diffraction pattern of all the prepared glass samples is shown in Figure 1. The observed pattern indicate a broad diffused hump in all the glasses. X-ray powder patterns further reveal that there are no crystalline features like appearing sharp peaks at different Bragg angles. This is an indicative of amorphous nature of the prepared glass specimens. In glasses the absence of small angle scattering means that the glass is a continuous medium with no discrete particles or breaks in the scheme of bonding [1-3].

Fig 1: XRD pattern of the present glasses
Fig 2: EPR spectra of studied glasses

The EPR spectra of all the prepared glass samples is shown in Figure 2. The recorded spectra mainly consists of an intense resonance signals at $g \sim 4.282$ and also at $g \sim 2.0032$ along with a shoulder in the region of $g \sim 8.033$ which is a characteristic of iron ions in the (3+) valence state in all the studied glasses. The resonance signal at $g \sim 4.282$ is characteristic for isolated $\text{Fe}^{3+}$ ions predominantly situated in rhombically distorted octahedral sites or tetrahedral oxygen environments where as the resonance signal at $g \sim 8.033$ arises from axially distorted sites. The resonance signal at $g \sim 2.0032$ have been attributed to either $\text{Fe}^{3+}$ ions interacting by dipole-dipole interaction in sites of less distorted octahedral field or to their super exchange interactions with in the pairs of $\text{Fe}^{3+}$ ions.

The magnetic properties of these glasses arise from the paramagnetic $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ ions with 3d$^5$ and 3d$^6$ electrons respectively. Since the iron ions are in $\text{Fe}^{3+}$ states belong to d$^5$ configuration with 6s as ground state and there is no spin-orbit interaction [4]. The $g$ value is expected to lie very near the free ion value ($g_e = 2.0023$). However a $g$ value very much greater than 2.0 often occurs; in particular an isotropic $g$ value at 4.28 occurs and these large $g$ values arise when certain symmetry elements are present. The theory of these large $g$ values is usually expressed by the spin Hamiltonian [6].

$$H = g\beta BS + D \left[ S_z^2 - \frac{S(S+1)}{3} \right] + E(S_x^2 - S_y^2)$$ ... (1)

where $S = 5/2$, $S_x$, $S_y$ and $S_z$ are the components of spin along three mutually perpendicular crystalline axis x, y and z. Here D and E are the axial and rhombic structure parameters, $\lambda = E/D$ lies within the limits $0 \leq \lambda \leq 1/3$ [6].

If D and E values are zero, the $g$ value is expected to lie very near the free electron value. If D and E values are large as compared with $g\beta H$, then in the two limiting cases of $D \neq 0$ and $E = 0$ and $D = 0$ and $E \neq 0$, the free ion $^3S$ ground state in zero magnetic field splits in to three Kramers doublets $|\pm 1/2>, |\pm 3/2>$ and $|\pm 5/2>$ with separations usually greater than the microwave quantum. In the first case ($D \neq 0$ and $E = 0$), the lowest doublet has effective $g$ values of $g = 2.0$ and 6.0. In the second case ($D = 0$ and $E \neq 0$), the middle doublet has an isotropic $g$ value of 4.3.

The intensity and the area of the resonance signals at $g = 2.0032$ and $g = 4.3$ increased by the substitution of alkaline earth oxides respectively indicates the increase of higher concentration of $\text{Fe}^{3+}$ ions. The reason might be as follows: whenever modifier oxides in the glass matrix were changed they alter the glass-forming ability associates with the cation capabilities due to the various levels of their ionic radii and polarizabilities. The observed increase in $g$ values from free electron $g$ value as presented in Table 1 is due to coupling of the iron orbitals involved in molecular orbitals containing the unpaired electrons, with the filled ligand orbitals. This increase in $g$ values is a consequence of amount of unpaired electron density at the donor sites of the oxide ions. Therefore, the covalency of Fe-O bond should decrease as $\Delta g$ value is increased [7-10].

**Table 1.** The $g$ values of studied glasses

| Sample | $g$ Values (±0.001) |
|--------|---------------------|
| CLBF   | 2.0694  4.2448  8.055 |
| SLBF   | 2.0712  4.2564  8.0584 |
| BLBF   | 2.0879  4.2722  8.0593 |

3.1. 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 help of a reference (CuSO$_4$·5H$_2$O in this study) by using the formula
\[
N = \frac{A_x (\text{Scan})^2 G_{\text{std}}(B_{m})x(B_{g})^2[S(S+1)]_{\text{std}}(P_{\text{std}})^{1/2}}{A_{\text{std}}(\text{Scan}_{\text{std}})^2 G_{x}(B_{m})x(B_{g})^2[S(S+1)]_{x}(P_{x})^{1/2}} \quad \text{[Std]} 
\]  
\[ \text{[2]} \]

3.2. Calculation of paramagnetic susceptibility from EPR data

Using these number of spin values, the paramagnetic susceptibility of the sample is evaluated using the formula

\[
\chi = \frac{N g^2 \beta^2 (J+1)}{3 K_B T} \quad \text{[3]} 
\]

Table 2 gives the number of spins participating in resonance at room temperature and the paramagnetic susceptibility of prepared glass samples at \(g = 2.0\) and \(g = 4.3\).

| Sample | Number of spins (per Kg) | Number of spins (per Kg) | Paramagnetic susceptibility (m\(^3\)-Kg\(^{-1}\)) | Paramagnetic susceptibility (m\(^3\)-Kg\(^{-1}\)) |
|--------|--------------------------|--------------------------|---------------------------------|---------------------------------|
|        | (N) \((10^{22})\) | (N) \((10^{22})\) | \((\chi) (10^{-3})\) | \((\chi) (10^{-3})\) |
| CLBF F | 0.605                   | 0.144                   | 3.552                          | 1.554                           |
| SLBF F | 0.657                   | 0.155                   | 3.863                          | 1.69                            |
| BLBF F | 0.676                   | 0.161                   | 4.043                          | 1.768                           |

The spin concentration (N) participating in resonance for studied glasses was calculated at \(g = 2.0\) and at \(g = 4.3\). The spin concentration and the paramagnetic susceptibility at \(g = 2.0\) and at \(g = 4.3\) increase by the substitution of alkaline earth oxides respectively.

3.3. Line intensity and peak-to-peak line width of EPR studies

The iron ion concentration dependence of the EPR parameters such as peak-to-peak line width \(\Delta B\) and the line intensity \(J = I (\Delta B)^2\), where \(I\) denotes the line height, gave us the possibility to follow the absorption line evaluation by the substitution of alkaline earth oxides respectively. For a fixed concentration of \(\text{Fe}_2\text{O}_3\) in these three series glass systems the signal intensity is increased by the substitution of alkaline earth modifiers respectively indicates the increase of higher concentration of \(\text{Fe}^{3+}\) ions. The reason might be as follows: whenever modifier oxides in the glass matrix were changed they alter the glass-forming ability associates with the cation capabilities due to the various levels of their ionic radii and polarizabilities.

The peak-to-peak line width \((\Delta B)\) for the resonance lines at \(g \approx 4.282\) and at \(g \approx 2.0032\) is increasing by the substitution of alkaline earth oxides respectively. A recent study on \(\text{Fe}_2\text{O}_3\) doped zinc borate glasses [11, 12] has concluded that \(\Delta B\) dependence on \(x\) mol\% reflects competition between the broadening mechanisms due to dipole-dipole interactions (the increasing disorder of glass matrix and the interactions between ions in multivalent states) and narrowing mechanisms arisen due to super exchange interactions between the pairs of iron ions. These mechanisms can act simultaneously but their strength strongly depends on iron ion concentration and the other components of the glass. In the present study an increase in peak-to-peak line width \((\Delta B)\) of the resonance absorption at \(g \approx 4.282\) and at \(g \approx 2.0032\) from CLBF to BLBF shows the dominant role of the broadening mechanisms.
4. Conclusions
The present study on Influence of alkaline earths on EPR spectra of lithium borate glasses doped with Fe (III) ions revealed the following conclusions.
1. Amorphous nature of the samples is confirmed by the broad diffused haloes in XRD patterns.
2. The intensity and the area of the resonance signals at $g = 2.0032$ and $g = 4.3$ increased by the substitution of alkaline earth oxides respectively indicates the increase of higher concentration of Fe$^{3+}$ ions.
3. An increase in peak-to-peak line width ($\Delta B$) of the resonance absorption at $g \approx 4.282$ and at $g \approx 2.0032$ from CLBF to BLBF shows the dominant role of the broadening mechanisms.

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REFERENCES
[1] B.E. Warren, J. Appl. Phys., 8 (1937) 645.
[2] S. R. Elliott, Physics of Amorphous Materials (Longmann Sci. & Tech. Essex), (1990).
[3] B.E. Warren, J. Appl. Phys., 13 (1942) 364.
[4] D. Loveridge, S. Parke, Phys. Chem. Glasses 12 (1971) 90.
[5] Ashok Bhogi, R.Vijaya Kumar, P. Kistaiah, J. Non-Cryst. Solids 426 (2015) 47.
[6] B. Bleaney, K. W. H. Stevens, Rep. Prog. Phys. 16 (1953) 108.
[7] B.V. Raghavaiah, P.N. Rao, P.Y. Reddy, N. Veeraiah, Opt. Mater. 29 (2007) 566.
[8] R.P.S. Chakradhar, B. Yasoda, J.L. Rao, N. O. Gopal, J. Non- Cryst. Solids 353 (2007) 2355.
[9] Ashok Bhogi and P. Kistaiah, Materials Today: Proceedings 5 (2018) 26199.
[10] Ashok Bhogi, R.Vijaya Kumar, P. Kistaiah, AIP Conference Proceedings 1731 (2016) 070038.
[11] Razvan Stefan, Petru Pascuta, Adriana Popa, Oana Raita, Emil Indrea, Eugen Culea, J. Phys. Chem. Solids 73 (2012) 221.
[12] P. Pascuta, G. Borodi, A. Popa, V. Dan, E. Culea, Mater. Chem. Phys. 123 (2010) 767.