Publications
Characterization of Fe$^{3+}$ doped mixed alkali zinc borate glasses — Physical and spectroscopic investigations

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A B S T R A C T
The glasses of 19.9ZnO+xLi$_2$O+(30−x)Na$_2$O+50B$_2$O$_3$ (5≤x≤25) (ZLN) doped with 0.1 mol% of paramagnetic Fe$_2$O$_3$ impurity are prepared by melt quench technique. Physical parameters of all the glasses are evaluated and they reveal a non-linear behavior with respect to the composition. Powder XRD pattern has not revealed any crystalline peak which indicates its amorphous nature. The optical band gap and Urbach energies exhibited the mixed alkali effect. All the prepared glass samples are found to be strong and stable in structure with low values of Urbach energy which lie between 0.010 and 0.022 eV. Electron paramagnetic resonance exhibited three resonance signals around g values at 2.06, 4.24 and 8.34 in the all Fe$^{3+}$ doped glasses. The optical absorption spectrum of the samples exhibited three bands which are characteristic of Fe$^{3+}$ in distorted octahedral symmetry. The crystal field parameter (Dq) and Racah inter electronic repulsion parameters (B, C) are evaluated. The FT-IR spectra of Fe$^{3+}$ doped glasses exhibited characteristic vibrations of BO$_3$ and BO$_4$ units.

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1. Introduction

Oxide glasses formed with transition metal ions have received significant attention owing to their interesting optical applications. All the properties of glasses which are strongly affected by long-range motions of ions, show large deviations from a simple additive behavior upon mixing of two different types of mobile ions; this phenomenon is known as mixed alkali effect (MAE) [1]. While the mixed alkali effect might be of limited value for technological application, it is important in understanding the general problem of ionic transport in glasses. Borate glasses are particularly interesting model systems as they exhibit a variety of structural changes with alkali content. Zinc oxide enters in the glass structure in the form of both network former and network modifier. Since, zinc containing glasses have low melting point, they have been used as good sintering agents [2–5].

Though the spectroscopic investigations are meager, they are important and useful to gain insight into the microscopic mechanism responsible for the effect. Recent progress in understanding the mixed alkali effect has been initiated by the development of the dynamic structure model [6]. For alkali borate glasses, the abrupt property changes are observed near 15–20 mol% modified oxide [7]. This peculiar behavior is referred to as ‘borate anomaly’. On the other hand, the spectroscopic investigations such as EPR and optical absorption techniques are valuable to gain insight into the microscopic origin of the MAE.

Glasses containing Fe$_2$O$_3$ are used in electrochemical, electronic and electro-optic devices [8,9]. The stability and semiconductor properties of Fe$_2$O$_3$ allow it to be used as a photocatalyst [9]. At low concentrations, the ions act as modifiers similar to the alkali metals or alkaline earths [10]. EPR spectra of Fe$^{3+}$ in various glasses have been extensively studied. It is found that trivalent iron ions can take two different coordination sites, i.e., tetrahedral [11,12] or octahedral [13,14] in glasses. Recently effects of transition metal ions doped alkali zinc borate glasses are reported and they exhibit the mixed alkali effect [15–22]. No EPR study of Fe$^{3+}$ in alkali zinc borate glasses have been reported so far, the aim of the present study is to observe the physical and structural behavior of the new quaternary system of trivalent ion, Fe$^{3+}$ doped 19.9 ZnO + xLi$_2$O + (30−x)Na$_2$O+50B$_2$O$_3$ (5≤x≤25) (hereafter referred as ZLN) glasses by using spectroscopic techniques and to correlate their properties.

2. Experimental

2.1. Preparation

Glass samples are prepared by the melt quench technique. 0.1 mol% of Fe$^{3+}$ doped mixed alkali zinc borate glasses is prepared by using analar grade chemicals of ZnO, Li$_2$CO$_3$, Na$_2$CO$_3$, B$_2$O$_3$ and Fe$_2$O$_3$ as
starting materials with 99.9% of purity. Appropriate amounts of these starting materials are weighed and thoroughly mixed and ground in an agate mortar and pestle for about an hour. The batch mixture was transferred to a silica crucible and it is sintered at 750 K and melted in an electric furnace in a silica crucible around 1250 K for nearly 1 h. The silica crucible containing the melt was occasionally swirled inside the furnace for a few minutes to homogenize the glass melt. The melt is then quenched at room temperature in air to form a glass. The glass samples are quickly transferred to another furnace previously kept at 700 K, and annealed at this temperature for 1 h to reduce thermal stresses generated by rapid cooling. All glass samples are disk-shaped (about 1 cm diameter and thickness of 1–2 mm). The opposite faces of the samples are ground and polished with different grades of emery powder for UV–Visible spectrophotometric measurements. The glass compositions are taken as $19.9\text{ZnO} + x\text{Li}_2\text{O} + (30 - x)\text{Na}_2\text{O} + 50\text{B}_2\text{O}_3 + 0.1\text{Fe}_2\text{O}_3$ ($5 \leq x \leq 25$ or $x = 5, 10, 15, 20, 25$ mol%), hereafter named as ZLN glasses prepared at the temperatures 1175, 1188, 1213, 1223 and 1223 K respectively.

2.2. Characterization

The densities ($\rho$) of all glass samples are measured by using Archimedes method with xylene as an immersion fluid. Refractive indices of prepared glasses are measured by using Atago Abbe’s refractometer. Bruker FT-IR Spectrophotometer is used for recording FT-IR spectra of the prepared samples in the region of 200–1200 cm$^{-1}$. X-ray diffraction patterns of powdered glass samples are recorded on PANalytical Xpert Pro diffractometer with Cu K$_\alpha$ wavelength of 1.5406 Å. EPR spectra of powder samples are recorded at room temperature on JEOL JES-TE100 ESR spectrometer at X-band frequency with 100 kHz field modulation. The optical absorption spectra of polished glass samples are recorded on JASCO V-670 spectrophotometer in the region of 200–1400 nm.

3. Results

3.1. Powder X-ray diffraction studies

The X-ray diffraction patterns do not contain any sharp peaks which is a sign of amorphous material. All the prepared glass samples confirm the glassy nature. Fig. 1 shows the X-ray diffraction patterns of undoped and iron doped glasses.

3.2. Physical properties

The calculated values of densities and refractive indices of the prepared Fe$^{3+}$ doped ZLN glasses are given in Table 1 along with some other physical parameters. The error in density measurements and refractive indices are estimated to be ±0.004 g/cm$^3$ and ±0.0001. The effect of Li$_2$O content on density and refractive index of Fe$^{3+}$ doped ZLN glasses is shown in Fig. 2. For Fe$^{3+}$ doped ZLN glasses, ionic concentration and electronic polarizability are correlated with respect to Li$_2$O content and depicted in Fig. 3.

3.3. FT-IR studies

FT-IR spectra of Fe$^{3+}$ doped (19.9ZnO + xLi$_2$O + (30 – x)Na$_2$O + 50B$_2$O$_3$ (5 ≤ x ≤ 25)) glasses are shown in Fig. 4. B–O–B bending vibrations are observed at 551 and 553 cm$^{-1}$. B–O symmetric stretching vibrations of BO$_4$ units are observed in the region 1042–1085 cm$^{-1}$. B–O stretching vibrations of trigonal BO$_3$ units are observed in the region 1270–1500 cm$^{-1}$. The obtained absorption bands and their assignments are summarized in Table 2.

3.4. Optical absorption studies

The optical absorption spectra of Fe$^{3+}$ doped ZLN glass systems are shown in Fig. 5. The spectrum exhibits three bands around 450, 519 and 686 nm that represent the characteristic absorption of

<table>
<thead>
<tr>
<th>SL No</th>
<th>physical parameter</th>
<th>Glass code</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(units)</td>
<td>ZLN1</td>
</tr>
<tr>
<td>1.</td>
<td>Average molecular weight</td>
<td>81.3562</td>
</tr>
<tr>
<td>2.</td>
<td>Density ($\rho$) (g/cm$^3$) (±0.004)</td>
<td>2.6779</td>
</tr>
<tr>
<td>3.</td>
<td>Refractive index ($n$) (±0.0001)</td>
<td>1.6552</td>
</tr>
<tr>
<td>4.</td>
<td>Optical dielectric Constant ($\varepsilon$)</td>
<td>2.7397</td>
</tr>
<tr>
<td>5.</td>
<td>Reflection loss</td>
<td>0.0608</td>
</tr>
<tr>
<td>7.</td>
<td>Iron ion concentration ($N$) (10$^{22}$ ions/cm$^3$) (±0.005)</td>
<td>0.3165</td>
</tr>
<tr>
<td>8.</td>
<td>Electronic polarizability ($\alpha_e$) (×10$^{-26}$ ions/cm$^3$) (±0.005)</td>
<td>27.6921</td>
</tr>
<tr>
<td>9.</td>
<td>Inter-ionic distance ($r_i$) (Å) (±0.005)</td>
<td>6.8103</td>
</tr>
<tr>
<td>10.</td>
<td>Polaron radius ($r_p$) (Å) (±0.005)</td>
<td>2.7440</td>
</tr>
</tbody>
</table>

Table 1

Physical properties of $19.9\text{ZnO} + x\text{Li}_2\text{O} + (30 - x)\text{Na}_2\text{O} + 50\text{B}_2\text{O}_3 + 0.1\text{Fe}_2\text{O}_3$ ($5 \leq x \leq 25$) glass systems at room temperature.
distorted octahedral site symmetry. The band head data of Fe$^{3+}$ doped ZLNB glass system is given in Table 3.

3.5. Optical band gap and Urbach energies

For determination of optical band gap energies the plots ($\alpha h \nu$)$^2$ and ($\alpha h \nu$)$^{1/2}$ are drawn as a function of photon energy $h \nu$ as shown in Fig. 6. The respective values of $E_{\text{opt}}$ for direct and indirect transitions are obtained by extrapolating to ($\alpha h \nu$)$^2$ = 0 for direct transitions and ($\alpha h \nu$)$^{1/2}$ = 0 for indirect transitions. The optical band gap energy is obtained by extrapolating the linear region of the curve to the $h \nu$ axis. From these plots, the obtained optical band gap energies are given in Table 4. Urbach energies ($\Delta E$) are calculated by taking the reciprocals of the slopes of linear portion of the curves and are listed in Table 3.

3.6. Electron paramagnetic resonance studies

The EPR spectra of Fe$^{3+}$ doped ZLNB glasses are shown in Fig. 7. The EPR spectra exhibit intense resonance signal at $g$= 4.22, a weak signal at 2.04 and a shoulder in the region of 9.04. The EPR spectra of Fe$^{3+}$ in glasses consist of a sharp and intense resonance at $g$= 4.3, a weak resonance at $g$= 2.0 and a hump around $g$ = 10.0. The resonance signals at different $g$ values vary non-linearly with the increase of Li$_2$O content in the ZLNB glasses.

4. Discussions

Density of the amorphous materials is an important property for calculating the various physical properties like refractive index, elastic properties and thermal conductivity. The physical transport properties of semiconducting glasses are very interesting and provide useful information regarding the structure and conduction mechanism. The calculated values of densities and refractive indices of the prepared Fe$^{3+}$ doped ZLNB glass systems are given in Table 1, along with some other physical parameters. The error in density measurements and refractive indices are estimated to be ±0.004 g/cm$^3$ and ±0.0001. The effect of Li$_2$O content on density and refractive index of Fe$^{3+}$ doped ZLNB glass systems is shown in Fig. 2.

It is observed that the density and refractive index curves show non-linearity with Li$_2$O content, but oppositely directed. The density values at first increase with the increase of x mol% of alkali content and then decrease reach minimum at x = 15 mol% thereafter increase and then decrease. In the case of refractive index values, the curve initially decreases with x mol% of alkali content and then increases reaches a maximum value at x = 15%, thereafter it decreases. This non-linear behavior is due to the changes in the concentration of x mol% of alkali contents in the glass sample and is referred to as MAE. In pure alkali borate glasses, decrease in the density values was noticed due to the phenomenon of MAE within the composition [22].

<table>
<thead>
<tr>
<th>Assignment</th>
<th>ZLNBl</th>
<th>ZLNBl2</th>
<th>ZLNBl3</th>
<th>ZLNBl4</th>
<th>ZLNBl5</th>
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<tr>
<td>B–O–B stretching vibrations involving oxygen atoms outside borate ring</td>
<td>553</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
</tr>
<tr>
<td>Stretching vibrations of NBOs in BO$_x$ units</td>
<td>878</td>
<td>878</td>
<td>878</td>
<td>878</td>
<td>878</td>
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<tr>
<td>B–O symmetric stretching</td>
<td>1045</td>
<td>1045</td>
<td>1045</td>
<td>1045</td>
<td>1042</td>
</tr>
<tr>
<td>Vibrations of BO$_4$ units</td>
<td>1085</td>
<td>1088</td>
<td>1085</td>
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<tr>
<td>B–O stretching vibrations of trigonal BO$_3$ units</td>
<td>1275</td>
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<td>1449</td>
<td>1451</td>
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<td>1451</td>
</tr>
<tr>
<td>H–O–H bending vibrations</td>
<td>1646</td>
<td>1643</td>
<td>1642</td>
<td>1646</td>
<td>1646</td>
</tr>
</tbody>
</table>
Dielectric constant ($\epsilon$) can be calculated by using the following equation [23]

$$\epsilon = n_d^2$$  

(1)

where $n_d$ is the refractive index of the glass.

By using Fresnel’s formula, the reflection loss from the glass surface can be calculated [24].

$$R = \left( \frac{n_d - 1}{n_d + 1} \right)^2$$  

(2)

For each glass sample the molar refractivity ($R_m$) can be evaluated by using [25]

$$R_m = \left[ \frac{(n_d^2 - 1)}{(n_d^2 + 2)} \right] M / D$$  

(3)

where M is the average molecular weight and D is density in g/cm$^3$.

Electronic polarizability ($\alpha_e$) can be calculated by using the following expression [26]

$$\alpha_e = \frac{3(n_d^2 - 1)}{4nN(n_d^2 + 2)}$$  

(4)

where N is the number of iron ions per unit volume.

The polaron radius and inter-ionic separation can be determined by using the formulae [27]

$$r_p = \left( \frac{1}{2} \right) [\pi/6N]^{1/3}$$ and $$r_i = \left( \frac{1}{N} \right)^{1/3}$$  

(5)

The physical parameters like refractive index, density, molar refractivity, ionic concentration, electronic polarizability, inter-ionic distances and polaron radii are evaluated. With an increase in Li$_2$O content, it is pragmatic that the above physical parameters vary non-linearly.

**Table 3**

<table>
<thead>
<tr>
<th>Glass system</th>
<th>Transitions from</th>
<th>Wavelength (nm)</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>$D_q$ (cm$^{-1}$)</th>
<th>$B$ (cm$^{-1}$)</th>
<th>$C$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZLN1</td>
<td>$^{4}T_{1g}$ (G)</td>
<td>685</td>
<td>14,595</td>
<td>14,599</td>
<td>825</td>
<td>750</td>
</tr>
<tr>
<td>ZLN2</td>
<td>$^{4}T_{1g}$ (G)</td>
<td>526</td>
<td>19,006</td>
<td>18,888</td>
<td>845</td>
<td>770</td>
</tr>
<tr>
<td>ZLN3</td>
<td>$^{4}T_{1g}$ (G)</td>
<td>686</td>
<td>14,573</td>
<td>14,554</td>
<td>870</td>
<td>795</td>
</tr>
<tr>
<td>ZLN4</td>
<td>$^{4}T_{1g}$ (G)</td>
<td>686</td>
<td>14,573</td>
<td>14,568</td>
<td>880</td>
<td>790</td>
</tr>
<tr>
<td>ZLN5</td>
<td>$^{4}T_{1g}$ (G)</td>
<td>685</td>
<td>14,595</td>
<td>14,578</td>
<td>855</td>
<td>780</td>
</tr>
</tbody>
</table>

Fig. 5. Optical absorption spectra of Fe$^{3+}$ doped ZLN glasses.

Fig. 6. (a) Direct, (b) indirect band gap energies of Fe$^{3+}$ doped ZLN glasses.
The dielectric polarization is strong for borate glasses with compositions close to the diffusivity crossover composition where the ionic conduction is just like a mirror image of the electronic polarization curve. It is also observed that the inter-ionic separation \( r_1 \) and polaron radius \( r_p \) initially decreases up to \( x = 10 \) mol\% thereafter it increases and then decreases with an increase in \( \text{Li}_2\text{O} \) content.

The FT-IR spectra of \( \text{Fe}^{3+} \) doped ZLNB glasses are shown in Fig. 4. The obtained absorption bands and their assignments are summarized in Table 2. In the infrared spectral region, the vibrational modes of the borate network have four distinct frequency regions. The 1200-1600 cm\(^{-1}\) bands are in the first region, which are due to asymmetric stretching relaxation of the \( \text{BO}_3 \) units. The second region is reclined between 800 and 1200 cm\(^{-1}\), and is due to \( \text{BO}_3 \) bond stretching of tetrahedral \( \text{BO}_4 \) units. Deformation modes of both types of units are active between 600 and 800 cm\(^{-1}\) [29]. In the present IR analysis of the glasses, bands observed in the region 1270–1500 cm\(^{-1}\) are assigned to asymmetric stretching vibrations of \( \text{B}-\text{O} \) bonds in \( \text{BO}_3 \) units. The absorption bands around 878, 1045 and 1085 cm\(^{-1}\) are assigned to symmetric stretching vibrations of \( \text{B}-\text{O} \) bonds in \( \text{BO}_4 \) units. In general, the IR absorption band at 806 cm\(^{-1}\) is assigned to the boroxol ring in the borate glass network. In the present study, the peak at 806 cm\(^{-1}\) is found missing, which indicates the absence of boroxol ring in the glass network under investigation. The vibrational band observed at around 1646 cm\(^{-1}\) is ascribed to the vibrational modes of hydroxyl or water groups present in the glass systems. Absorption bands in the region 500–550 cm\(^{-1}\) are due to \( \text{ZnO} \) tetrahedron in glasses [30]. The band around 551 cm\(^{-1}\) is due to \( \text{B}-\text{O} \)-stretching vibrations involving oxygen atoms outside the borate ring [31].

Electronic configuration of \( \text{Fe}^{3+} \) \( (d^5) \) gives rise to free ion terms \( {6S, 4P, 4F, 4G} \), in addition to a number of doublet states of which \( {6S} \) occupies the ground state. \( {6S} \) and \( {4P} \) terms transform as \( {A_{1g}} \) and \( {T_{1g}} \), respectively, in crystal fields. \( {D^0} \) and \( {G^0} \) splits into \( {4E_1 + 4T_2} \) and \( {4A_1 + 4E_2 + 4T_1 + 4T_2} \), respectively. For all the glasses the optical absorption spectra are similar hence for Fe\(^{3+}\) doped ZLNB glass system (shown in Fig. 5) exhibited three absorption bands around 450, 519 and 686 nm representing the characteristic absorption of distorted octahedral site symmetry. The band around 686 nm is assigned to the transition \( {4A_{1g}(S) \rightarrow 4T_{1g}(G)} \) which depends on \( \text{Dq} \). The band around 519 nm is assigned to the transition \( {4A_{1g}(S) \rightarrow 4T_{2g}(G)} \) and the band around 450 nm is assigned to the transition \( {4A_{1g}(S) \rightarrow 4A_{1g}(G) + 4E_2}(G) \) as its energy expression is independent of \( \text{Dq} \). These transitions are assigned by using Tanabe–Sugano diagram [32]. Based on these assignments, the energy matrices for \( d^5 \) configuration with Tree’s correction \((\alpha = 90 \text{ cm}^{-1})\) are solved for different sets of crystal field parameter \( \text{Dq} \), Racah parameters \( B \) and \( C \). The values of \( \text{Dq} \), \( B \) and \( C \) give a good fit between the observed and calculated positions of the bands as shown in Table 3. Band positions are shifted with respect to \( \text{Li}_2\text{O} \) content. The \( {4T_{1g}(G)} \) band increases with \( x \) mol\% reaches a maximum at \( x = 15 \) % and then decreases, whereas \( {4T_{2g}(G)} \) and \( {4A_{1g}(G) + 4E_2(G)} \) bands initially decrease, reach a minimum value at \( x = 15 \) mol\% and then increase. The values of \( \text{Dq} \)/\( B \) and \( C \)/\( B \) represent structural distortion and vary non-linearly with \( \text{Li}_2\text{O} \) content, which is observed to be minimum at \( x = 20 \) mol\%. The free ion inter-electronic repulsion parameter \( B \) for \( \text{Fe}^{3+} \) ion is 1100 cm\(^{-1}\) [33]. In the present work, the value of \( B \) obtained for \( \text{Fe}^{3+} \) is in the range of 750–795 cm\(^{-1}\), thus indicating that the present value is about 31–27% of reduction from the free ion value indicating that bonding is partially covalent. It is observed that the shifting of bands is significant with increase of \( \text{Li}_2\text{O} \) content, which shows MAE.

The analysis of optical absorption spectra is one of the most productive tools for understanding and developing the band structure and energy band gap \( (E_g) \) of crystalline and non-crystalline material structures. There are two types of optical transitions that can occur at the fundamental absorption edge of crystalline and non-crystalline materials. They are direct and indirect transitions. In the case of glasses, the conduction band is influenced by the anions; the cations play an indirect but major role. The absorption co-efficient \( (\alpha) \) is a function of photon energy for direct and indirect transitions [34].
For direct transitions,

$$\alpha(v) = A (\nu - \nu_0)^n / \nu^n$$  \hspace{1cm} (6)

Here A is a constant, $$\nu_0$$ is direct optical band gap and n = 1/2 for allowed transitions. For indirect transitions, n = 2 for allowed transitions. Using the above equation, plots for $$(\nu_0)^2$$ and $$(\nu_0)^{-1/2}$$ as a function of photon energy $$\nu$$ are drawn and shown in Fig. 6. The respective values of $$\nu_0$$ for direct and indirect transitions are obtained by extrapolating to $$(\nu_0)^2 = 0$$ for direct transitions and $$(\nu_0)^{1/2} = 0$$ for indirect transitions. The optical band gap energy is obtained by extrapolating the linear region of the curve to the $$\nu_0$$ axis. From these plots, the obtained optical band gap energies are given in Table 4. Using the following equation, optical band gap energy can be calculated theoretically,

$$E_{\text{opt}} = \hbar c / \lambda$$  \hspace{1cm} (7)

The optical band gap energy shows the non-linear behavior of these ZLNB glasses and it is maximum at 20 mol%. The main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient $$\alpha(v)$$ with photon energy $$\nu$$ in accordance with the empirical relation [35].

$$\alpha(v) = \alpha_0 \exp(\nu / \Delta \varepsilon)$$  \hspace{1cm} (8)

Here $$\alpha_0$$ is a constant, v is the frequency of the radiation and $$\Delta \varepsilon$$ is the Urbach energy which indicates the width of the band tails of the localized states and depends on temperature, induced disorder, static disorder, and on average photon energies. Hence, Urbach energy provides a measure for the disorder in amorphous and crystalline materials [36,37]. The nature of disorder is different for crystalline and amorphous solids. In amorphous solids, the static atomic structural disorder dominates and can be due to presence of defects like dangling bonds or non-bridging oxygens in glasses [38].

Urbach energies ($$\Delta \varepsilon$$) are calculated by taking the reciprocals of the slopes of linear portion in the lower photon energy regions of the curves and are listed in Table 4. The Urbach energy increases initially and reaches to maximum at $$x = 15$$ mol% thereafter it decreases with the increase in Li2O content which shows MAE. It also shows the structural disorder of the system. Smaller is the value of Urbach energy, greater is the structural stability of the glass system. It is observed that the Urbach energy is maximum and density is minimum at $$x = 15$$ mol%. It is also observed that all the systems have low value of structural disorder, which indicates the strong structural stability. The band gap energy calculations indicate that the glass systems are direct semiconductors with the calculated band gaps close to the observed ones.

The EPR spectra of Fe3+ in general, can be analyzed by using the spin-Hamiltonian

$$H = g \beta S \cdot B + SDS$$  \hspace{1cm} (9)

where g is the isotropic factor, $$\beta$$ is the Bohr magneton, B is the external magnetic field, S is the vector operator of the electron spin momentum and D is the zero field splitting parameter. Zero field splitting describes various interactions of the energy levels of an electron spin (S > 1/2) even in the absence of an applied magnetic field. It is important in the electron spin resonance of various transition metal ions. That is, the degeneracy is removed as a consequence of molecular electronic structure and/or spin density distribution. Zero-field splitting causes magnetic anisotropy, and has profound effects on magnetic properties.

In undoped glasses, no EPR signal was detected indicating no paramagnetic impurities present in the starting materials. When 0.1 mol% of ferric oxide is added to ZLNB host glasses, the EPR spectrum exhibited three resonance signals. Fig. 7 shows the EPR spectrum of Fe3+ doped ZLNB glasses. Investigations of the EPR spectra of Fe3+ in a variety of glasses have been reported and the spectra have been characterized by an intense resonance signal at g = 4.22, a weak signal at 2.04 and a shoulder in the region of 9.04 [39]. The EPR spectrum of Fe3+ ions in glasses consists of a sharp and intense resonance at g = 4.3, a weak resonance at g = 2.0 and a hump around g = 10.0 [14]. Since Fe3+ belongs to d5 configuration with 5s ground state in the free ion and there is no spin–orbit interaction [40], the g value is expected to lie very near to the free ion value of 2.0023. However g value very much greater than 2.0 often occurs, in particular an isotropic g value at 4.2, due to the presence of certain symmetry elements. In the case of d5 transition metal ions, it is known that axial distortion of octahedral symmetry gives rise to the three Kramer’s doublets [41]. The sharp absorption at g = 4.3 is often associated with low-symmetry rhombohedral sites of either tetrahedral or octahedral coordination. However g = 2.0 resonance is associated with both axially; distorted sites and spin–spin interactions.

In the present work, the features of the EPR spectra can be qualitatively explained as follows: the resonance peaks for Fe3+ from g = 2.061 to 2.134 can only occur if Fe3+ is located in a site where the crystal field interaction energy is less than the magnetic Zeeman energy and arises due to isolated Fe3+ ions. The resonance signals from g = 4.236 to 4.243 are attributed to the strong tetragonally distorted octahedral symmetry in the presence of oxygen ligands and represent the population of one of the Kramer’s doublets [42,43]. The resonance signals from 7.859 to 8.575 may also be due to the population of one of the Kramer’s doublets as mentioned above. It is observed that all the g values vary non-linearly with the increase of Li2O content in the ZLNB glasses which conforms the mixed alkali effect. The anomaly behavior at x = 15% may be caused due to strong fields of iron ions, where its g value is large. The spectroscopic analysis of the obtained results confirmed distorted octahedral site symmetry for the Fe3+ impurity ion.

5. Conclusions

From the physical and spectral properties of 0.1 mol% of Fe3+ doped 19.92ZnO + xLi2O + (30 – x)Na2O + 50B2O3 (5 ≤ x ≤ 25) glasses, the following conclusions are drawn:

(i) Powder X-ray diffraction patterns confirm the glassy nature of all the ZLNB glasses.

(ii) Non-linear behavior is observed in the physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, inter-ionic distances and polaron radii with respect to the changes in the concentrations of alkali content (5 ≤ x ≤ 25 mol%). This is due to the phenomenon of MAE.

(iii) The FT-IR spectral analysis confirms the presence of BO3 and BO4 local structures in all the glass systems.

(iv) Optical absorption spectra confirm the distorted octahedral site symmetry for Fe3+ ions with partial covalency of ZLNB glasses.

(v) From optical absorption edges, optical band gap energies and Urbach energies are evaluated. A non-linear behavior is observed and found to be in good agreement with theoretical values. It also confirms the structural variations with x mol% of alkali ions.

(vi) EPR spectra of the prepared ZLNB glass systems exhibited well intense resonance signal which is the characteristic feature of Fe3+ ions. The non-linear behavior in g values was observed by changing the concentrations of alkali contents (5 ≤ x ≤ 25 mol%) which is the manifestation of mixed alkali effect in the present glass systems.

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References

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ABSTRACTS

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distorted octahedral symmetry. The PL spectrum shows that the prepared phosphor invariably emits red and IR luminescence at 700 nm excitation. The red luminescence indicates the presence of Cr(III) ions and is represented in CIE chromaticity diagram with coordinates \((x = 0.734, y = 0.265)\). Cr (III) ions doped NaCaAlPO₄F₃ nanophosphor is a novel of red emitting phosphor for fabrication of white light emitting diodes (W-LEDs). FT-IR spectrum exhibits various vibrational bands of host lattice.

**OP-34. Physical and Spectroscopic Investigations of Fe³⁺ Doped mixed Alkali Zinc Borate Glasses**

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Oxide glasses formed with transition metal ions have received significant attention owing to their interesting optical applications. Borate glasses are particularly interesting model systems as they exhibit a variety of structural changes with alkali content. Glasses containing Fe₂O₃ are used in electrochemical, electronic and electro-optic devices. The stability and semiconductor properties of Fe₂O₃ allow it to be used as a photo catalyst. The Alkali Zinc Borate Glasses doped with 0.1 mol% of paramagnetic Fe₂O₃ impurity are prepared by melt quench technique.

Physical parameters of all the glasses are evaluated and they reveal the non-linear behavior with respect to the composition. The optical band gap energies and Urbach energies exhibit the mixed alkali effect. All the prepared glass samples are found to be strong and stable in structure with low values of urbach energy which lie between 0.010 - 0.022 eV. Powder XRD pattern has not revealed any crystalline peak, which indicates its amorphous nature. The optical absorption spectrum of the samples exhibited three bands characteristic of Fe⁺⁺ in near octahedral symmetry. The crystal field parameter (Dq) and Racah inter electronic repulsion parameters (B and C) are evaluated. Three resonance lines are observed around g values at 2.06, 4.24 and 8.34 in the EPR spectra of all the Fe⁺⁺ doped glasses. From optical and EPR analysis it is confirmed that Fe⁺⁺ impurity occupies distorted octahedral site symmetry. FT-IR spectral investigations of Fe⁺⁺ doped glasses exhibit characteristic vibrations of BO₃ and BO₄ unit.

**OP-35. Spectral Characterizations of Co²⁺ doped CdO Nanopowder by Solid State reaction**


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To
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Title of the paper: Physical and Spectroscopic Investigations on TiO2 doped Alkali Zinc Bora Glasses

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