Optical Properties of Nd$^{3+}$ Doped Sodium-Diborate Glasses Containing Heavy Metal Ions

M. Sudakara Reddy$^1$, N. Sivasankara Reddy$^2$, C. Renuka$^3$, Chikkahanumantharayappa$^4$ and C. Narayana Reddy$^{5*}$

$^1$ Department of Physics, SGS, Jain University, J.C.Road, Bangalore -560027, India.
$^2$ Department of Physics, Centre for Postgraduate Studies, Jain University, Bangalore -560011
$^3$ Research and Development Centre, Bharathiar University, Coimbatore, India.
$^4$ Department of Physics, Vivekananda First Grade College, Bangalore -560024, India
$^5$ Department of Physics, Sree Siddaganga College of Arts, Science and Commerce -572103, India

Abstract—There has been an increasing interest in the development of trivalent neodymium ion (Nd$^{3+}$) doped glasses for photonic devices viz: solid state visible and near IR lasers, frequency converters, up converters, wave guides, fibre amplifiers etc. We have prepared Nd$^{3+}$ doped Na$_2$B$_2$O$_7$ – PbO Glasses by melt quenching method. The samples were characterized by XRD and DSC studies. The glass transition temperature increases with Nd$_2$O$_3$ content. This paper reports on physical and optical properties of Nd$^{3+}$ doped lead-diborate glasses. In the case of Nd$^{3+}$ ion, the absorption takes place from the ground state $^4$I$_{15/2}$ to various excited states which are predominately 4f-4f induced electric dipole in nature. On the basis of the measured values of density, molar volume and optical band gaps, the refractive index, Nd$^{3+}$ ion concentration, electronic polarizabilities, polarizabilities of oxide ions and optical basicity were estimated and the results were analyzed on the basis of the structural modifications occur in the glass.

Keywords—Density, Optical band gap, Polarizability, Optical basicity and photoluminescence.

1. INTRODUCTION

Rare earth doped glasses have been studied with the aim to utilize their fluorescence properties. [1]Optically transparent glasses containing ferro electric and nanocrystals have received much interest as such materials can be used as Laser host materials, tunable wave guides or tunable fiber gratings [2]. The scientific interest of glasses containing Nd$^{3+}$ have gained importance after the demonstration of lasing action in Nd$^{3+}$ doped glasses by Snitzer [3]. There has been an increasing interest in the development of trivalent neodymium ion (Nd$^{3+}$) doped glasses for photonic devices viz; solid state visible and near IR lasers, frequency converters, up converters, wave guides, fibre amplifiers etc. [4-9]. Borate glasses are suitable for optical materials because of their high transparency, high thermal stability, different coordination numbers, and good solubility of rare-earth ions [10–12]. Further, heavy metal oxide glasses posses reduced phonon energy, high density, high refractive index, optimum band width, high mechanical and thermal stability, corrosion resistance and good solubility of rare earth ions. Thus, the incorporation of heavy metal oxides such as PbO or Bi$_2$O$_3$ into the borate glass matrix gives good luminescence properties of rare-earth ions in excited states. Further, it is well established that the addition of an alkali oxide has a strong influence on the boron coordination and the structural groups, depending on the type and concentration of the alkali oxide [13]. However, to the best of our knowledge, Nd$^{3+}$ doped lead sodium diborate glasses have not been studied in any great detail. Motivated by these considerations, in this paper we have prepared lead - sodium diborate glasses doped with Nd$^{3+}$ions, and studied the effects of the Nd$^{3+}$ concentration on physical and spectroscopic properties.

2. EXPERIMENTAL

The glass samples having the general chemical formula 30PbO - (70-x) Na$_2$B$_2$O$_7$ -x Nd$_2$O$_3$ with x=0, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 mol% have been prepared by the melt quenching technique. Required quantities of annular grade PbO, Na$_2$CO$_3$, H$_2$BO$_3$ and Nd$_2$O$_3$ were mixed together by grinding the constituents repeatedly to obtain an isotropic mixture. The mixture was melted in a porcelain crucible in an electrically heated muffle furnace under ordinary atmospheric conditions at a temperature of about 1000$^\circ$C for 1 h to homogenize the melt. The glass formed by quenching the melt between two pre-heated brass plates. The glass samples were annealed at 200$^\circ$C for 2 h to remove any thermal stresses that could have formed during the fast quenching process and the glasses were preserved under anhydrous atmosphere. The amorphous nature of the glass samples were confirmed using powdered X-ray diffraction (Model: Rigaku DMAX- IC employing Cr-K radiation). The XRD spectra did not show any sharp peaks, indicating that the samples were amorphous in nature. The densities of the
synthesized glasses were measured at room temperatures by applying Archimedes principle, with toluene as the immersion liquid. Molar volume was calculated for each sample using the relation, \( V = \frac{M}{\rho} \), where \( M \) is the molecular weight calculated according to the relation \( M = \sum x_i m_i \), \( x_i \) is the mole fraction of the component oxide and \( m_i \) is its molecular weight. UV–Visible Absorption spectra of synthesized glasses were recorded using Perkin Elmer (Lamda 35) spectrometer in the UV-Vis-NIR region in the range 200 to 1000 nm.

3. RESULTS AND DISCUSSION

Density and Molar volume—The Sample codes, composition and average molecular weights are tabulated in Table 1. The variation of the density and molar volume with \( \text{Nd}_2\text{O}_3 \) concentration is shown in Fig. 1. As can be seen in Fig.1, both the density and molar volume increases with the increase of \( \text{Nd}_2\text{O}_3 \) mol%. This indicates that replacing \( \text{Na}_2\text{B}_2\text{O}_3 \) by addition of a small amount of \( \text{Nd}_2\text{O}_3 \) results in the increase in the average molecular weight of oxide ions in the glass.

Table 1: Sample codes, composition and average molecular weights

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Sample composition in mol%</th>
<th>Molecular weight ( M ) (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0NDP</td>
<td>( \text{Na}_2\text{B}_2\text{O}_7 ) 70.0 ( \text{PbO} ) 30 ( \text{Nd}_2\text{O}_3 ) 0.0</td>
<td>113.87</td>
</tr>
<tr>
<td>1NDP</td>
<td>( \text{Na}_2\text{B}_2\text{O}_7 ) 69.8 ( \text{PbO} ) 30 ( \text{Nd}_2\text{O}_3 ) 0.2</td>
<td>114.40</td>
</tr>
<tr>
<td>2NDP</td>
<td>( \text{Na}_2\text{B}_2\text{O}_7 ) 69.6 ( \text{PbO} ) 30 ( \text{Nd}_2\text{O}_3 ) 0.4</td>
<td>114.94</td>
</tr>
<tr>
<td>3NDP</td>
<td>( \text{Na}_2\text{B}_2\text{O}_7 ) 69.4 ( \text{PbO} ) 30 ( \text{Nd}_2\text{O}_3 ) 0.6</td>
<td>115.48</td>
</tr>
<tr>
<td>4NDP</td>
<td>( \text{Na}_2\text{B}_2\text{O}_7 ) 69.2 ( \text{PbO} ) 30 ( \text{Nd}_2\text{O}_3 ) 0.8</td>
<td>116.02</td>
</tr>
<tr>
<td>5NDP</td>
<td>( \text{Na}_2\text{B}_2\text{O}_7 ) 69.0 ( \text{PbO} ) 30 ( \text{Nd}_2\text{O}_3 ) 1.0</td>
<td>116.56</td>
</tr>
<tr>
<td>6NDP</td>
<td>( \text{Na}_2\text{B}_2\text{O}_7 ) 58.0 ( \text{PbO} ) 30 ( \text{Nd}_2\text{O}_3 ) 2.0</td>
<td>119.26</td>
</tr>
</tbody>
</table>

Generally, as density increases the molar volume decreases. In the present glass system both the density and molar volume increases as a function of \( \text{Nd}_2\text{O}_3 \) concentration. The increase in molar volume could be due to the modifying role of \( \text{Nd}_2\text{O}_3 \). As concentration of \( \text{Nd}_2\text{O}_3 \) increases, the tightly packed diborate units opens up. Consequently, the non bridging oxygen’s in the glass network increases.

Also \( \text{Nd}_2\text{O}_3 \) has a higher relative molecular mass compared to \( \text{Na}_2\text{B}_2\text{O}_7 \). Based on the measured density, the \( \text{Nd}^{3+} \) ion concentration and other related physical properties such as polaron radius, internuclear distance and field strength can be determined using Eqs. in reference [14] and the results are tabulated in Table 2.

![Fig. 1: Variation of density and molar volume with Nd<sub>2</sub>O<sub>3</sub> mod%](image)

![Fig. 2: UV-Visible spectra of Nd<sup>3+</sup> doped PbO-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> glass system](image)

![Fig. 3: Direct band gap plots of Nd<sup>3+</sup> doped Na<sub>2</sub>B<sub>2</sub>O<sub>7</sub>-PbO glass system](image)

![Table 2: Nd<sup>3+</sup> concentration(N), polaron radius (r<sub>p</sub>), internuclear distance(r<sub>i</sub>) and field strength (F).](image)
UV-Visible Absorption Spectra—The UV-Visible absorption spectrum of Nd$^{3+}$ doped lead-sodium-diborate glasses is shown in the figure 2. The optical absorption edges are not sharply defined in glass samples under study, in accordance with their amorphous nature [15]. From this spectrum, It is observed that the absorption intensity of the observed bands increase with an increase in Nd$_2$O$_3$ concentration. The spectra consists of various absorption bands at 472 nm, 511 nm, 524 nm, 583 nm, 624 nm, 686 nm, 745nm, 802 nm and 874 nm are identified and these are assigned to the electronic transitions $^4$I$_{9/2}$ - $^2$G$_{5/2}$, $^2$G$_{5/2}$, $^2$G$_{7/2}$, ($^2$F$_{5/2}$ + $^2$F$_{7/2}$), $^4$F$_{5/2}$, ($^4$S$_{3/2}$ + $^4$F$_{5/2}$), ($^4$F$_{5/2}$)$^+$$^4$H$_{9/2}$ and $^4$F$_{5/2}$ respectively. Assignments to these bands have been made by using the reference [16]. For the absorption region, Mott and Davis proposed the following relation for amorphous materials [17]

$$\alpha(\nu) = B(\nu - E_g)^n / \nu$$

Where B is a constant and n=$\frac{1}{2}$ allowed transition gives direct optical band gap, n=2 allowed transition gives indirect optical band gap. By plotting $(\alpha\nu)^2$ as a function of photon energy $\nu$, optical band gaps for direct transitions could be found respectively by extrapolating to $(\alpha\nu)^2 = 0$ for direct transitions. Similarly indirect band gaps could be estimated by plotting $(\alpha\nu)^{\frac{1}{2}}$ as a function of photon energy $\nu$. The typical plots of $(\alpha\nu)^2$ vs $\nu$ for glass samples sample to calculate direct band gaps are shown in fig 3. The absorption coefficient, below and near the edge of each curve was determined at different wavelengths using relation

$$\alpha(\nu) = \frac{1}{d} \ln \left( \frac{I_r}{I_0} \right)$$

Where $I_0$ and $I_r$ are intensities of incident and transmitted beams, respectively and d corresponds to the thickness of each sample.

**Fig. 4: Variation of optical band gaps with Nd$_2$O$_3$ mol%**

The graph of optical band gaps as a function of Nd$_2$O$_3$ is shown in Fig.4. It is depicted from Fig 4 that the optical band gap energy decreases with the addition of Nd$_2$O$_3$ may be due to structural modifications. Addition of Nd$_2$O$_3$ may lead to an increase in the degree of electron concentration and thereby the increase of donor centres in the glass matrix. From the direct energy band gaps, refractive index of the samples has been calculated using the relation $n = a + \beta E$. Where $a = 4.68$ eV, $\beta = -0.62$ eV and E is the band gap energy. Glass optical basicity (A) and from refractive index values, Molar polarizability ($\alpha_m$), Glass oxide polarizability ($\alpha_o^2$) have been estimated using the formulæ given in reference [18] and are listed in Table 3.

**Table 3: Molar polarizability $\alpha_m (\AA^3)$, Glass oxide polarizability $\alpha_o^2 (\AA^3)$ and Glass optical basicity (A) values**

<table>
<thead>
<tr>
<th>CODE</th>
<th>$\alpha_m$ $\AA^3$</th>
<th>$\alpha_o^2$ $\AA^3$</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0NDP</td>
<td>4.0798</td>
<td>1.5022</td>
<td>0.5903</td>
</tr>
<tr>
<td>1NDP</td>
<td>4.1507</td>
<td>1.5326</td>
<td>0.5927</td>
</tr>
<tr>
<td>2NDP</td>
<td>4.2290</td>
<td>1.5670</td>
<td>0.5952</td>
</tr>
<tr>
<td>3NDP</td>
<td>4.2830</td>
<td>1.5887</td>
<td>0.5976</td>
</tr>
<tr>
<td>4NDP</td>
<td>4.3892</td>
<td>1.6371</td>
<td>0.6001</td>
</tr>
<tr>
<td>5NDP</td>
<td>4.4505</td>
<td>1.6626</td>
<td>0.6025</td>
</tr>
<tr>
<td>6NDP</td>
<td>4.5566</td>
<td>1.6858</td>
<td>0.6146</td>
</tr>
</tbody>
</table>

From the Table 3 it is noted that, optical basicity, molar polarizability and oxide polarizability values increases with increase in Nd$_2$O$_3$ mol%. This clearly establishes the fact that covalency in the glasses decreases with the increase of Nd$_2$O$_3$ mol% which correlates with the decrease in optical gaps.

4. CONCLUSION

Nd$^{3+}$ doped lead-sodium diborate glasses have been synthesized to study physical and optical properties. The properties such as density, molar volume, optical band gaps, refractive index, polarisabilities, and optical basicity of the glass reveals the structural changes occurred due to the network modifying role played by the rare earth oxide (Nd$_2$O$_3$). As concentration of Nd$_2$O$_3$ increases, the population of NBO’s in the network increases. Consequently the degree of electron localization and donor centers in the structure increases.

REFERENCES


