Spectroscopic properties of lithium borate glass containing Sm$^{3+}$ and Nd$^{3+}$ ions

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ABSTRACT

Lithium borate glass samples mixed with a different concentration of Sm$^{3+}$ and Nd$^{3+}$ ions organized by quenching technique. Structural, vibration groups and spectral properties of glass samples investigated using X-ray diffraction, FTIR, UV/Vis/NIR and photoluminescence spectroscopy. The X-ray confirmed the lithium borate glass samples containing Sm$^{3+}$ and Nd$^{3+}$ ions in the amorphous state. Luminescence spectra of glass samples excited at 400 nm recorded, here three luminescence bands observed in Visible region, which due to spectra materials (Sm$^{3+}$, Nd$^{3+}$). These indicate that these glass samples responsible orange emission and used in the improvement of materials for LED, and optical devices. The functional vibration groups of the glass matrix studied using FTIR spectroscopy.

Keywords: Borate glass containing Sm$^{3+}$ and Nd$^{3+}$ ion, DTA, FTIR, Optical properties, XRD

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1. INTRODUCTION

Borate glasses act as host substances for studies the character, structure of the luminescence and useful practical applications. Specifically, the borate glass, free and containing rare earth or transition elements is a promising substance for nonlinear optics, quantum electronics, laser generation, scintillations, thermoluminescent dosimeters, detectors, transformers of the ionizing radiation, and many other applications [1-11].

Borate glasses are vital glass formers and perform a major function in diverse applications. The BO$_3$ group’s vibration and non-bridging oxygen (NBOs) increases in borate glass structure when the B$_2$O$_3$ content increase from 10 mol% to 30 mol% [12-14]. Silicate glasses are a host material for the luminescence of rare-earth and transition metal ions, because of the silicate glasses good optical and mechanical properties in addition to excellent chemical durability [15].

The physical and spectroscopic properties of lithium borate glasses containing Sm$^{3+}$ studied. And the rise of Sm$^{3+}$ content in glass samples increases the glass sample density due to the formation of BO$_4$ modules. The number of transitions peaks defined within the absorption spectra of glass containing Sm$^{3+}$ compared to samarium-free glass. These glass samples emitted sturdy peak at 598 nm which corresponds to $^4G_{5/2} \rightarrow ^4H_{7/2}$ transition. This indicates that these samples of glass can adjust for LED applications [16, 17]. From rare-earth ions, the Sm$^{3+}$ ion is considerable, Sm$^{3+}$ ion growing stipulate in various fluorescent gadgets, high-density optical storage, color displays, undersea communication and visible solid-state lasers because of its vivid emission in orange-red areas [18]. The $^4G_{5/2}$ level of Sm$^{3+}$ possesses relatively high quantum
efficiency and indicates numerous populating in addition to quenching emission channels [19]. Some authors studied the optical properties of Sm³⁺ ion-doped various host glass networks [20-22]. Neodymium is one of the maxima studied rare-earth ions and discovered to have vast applications in photonic gadgets [23, 24].

From the mentioned above and other many studies of synthetic and optical and physical properties have made on different types of glass groups containing component Nd³⁺ or Sm³⁺. But there have few studies of their presence together in the glass samples. The effect of changing the ratio of one of them with the stability of the ratio of the second element studied. It found that the emission intensity decreased by increasing the ratio of Nd³⁺ with the constant of Sm³⁺. As well as the emission intensity increase with increasing of Sm³⁺ and constant of Nd³⁺ content [25, 26].

In this study, we study the effect of replacing Sm³⁺ by Nd³⁺ on the structural, thermal, optical, spectroscopic properties of Sm³⁺ and Nd³⁺ ions on this glass. Judd-ofelt parameters calculated, for observed absorption spectra for Sm³⁺ and Nd³⁺ ions as well as the emission intensity.

2. EXPERIMENTAL WORK

Sm⁺³ and Nd³⁺ doped ion synthesized in the Borate glass system by conventional melt quenching method. The starting chemicals used reagent grade of H₃BO₃, Li₂CO₃, Sm₂O₃, and Nd₂O₃ with 99.99% purity. Chemical compositions prepared glasses as shown in Table 1.

Table 1. The code and glass sample’s composition (mol %).

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Li₂O</th>
<th>B₂O₃</th>
<th>Nd₂O₃</th>
<th>Sm₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33</td>
<td>66</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>33</td>
<td>66</td>
<td>0.75</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>66</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>33</td>
<td>66</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>5</td>
<td>33</td>
<td>66</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

The mixture melted in porcelain crucibles at the 1100 °C for 2h. The structure of each sample confirmed amorphous by X-ray diffraction with a Phillips diffractometer PW3700 using CuKα1 radiation. The density measured using the Archimedes method. Optical absorption spectra of samples recorded using the UV-Vis spectrometer (Model-JASCO V570). The IR spectra of the glasses recorded using the FTIR 4100 JASCO spectrophotometer Michelson interferometer type in the wavenumber region from 400 to 2000 cm⁻¹. The Differential thermal analysis of glass samples carried using a SHIMADZUDTA-50 ANALYZER. The emission measure using Spectrofluorometer type JASCO-FP-6300.

3. RESULTS AND DISCUSSION

Figure 1 demonstrates the XRD of the prepared glass sample containing a different Nd and Sm oxide content. That indicates the amorphous nature of the samples.

Figure 1. The XRD of glass sample containing a different concentration of Nd and Sm oxides.

The glass density tendency increase with the increase of Sm₂O₃ content as shown in Figure 2. It’s due to the structural atom arrangement change when Sm₂O₃ substitute Nd₂O₃ in the Li₂O-B₂O₃ glass network,
and the density of Sm$_2$O$_3$ (8.347 g/cm$^3$) greater than the density of Nd$_2$O$_3$ (7.24 g/cm$^3$). The excess density of the samples is due to the molecular weight of the samarium higher than any other component in the glass samples.

Figure 2. The relation between the density and samarium oxide content

Figure 3 shows the DTA curves obtained for Sm$_2$O$_3$-Nd$_2$O$_3$ doped lithium borate glass. This figure indicates the presence of endothermic peak Tg (glass transition temperature), the exothermic peak Tc (the crystallization temperature) and the endothermic peak Tm (melting temperature) which tabulated in Table 2. The Tg represents the strength or rigidity of the glassy structure [27].

Figure 3. The DTA curve of glass samples.

The difference ($\Delta x$) among Tx and Tg which employ the glass forming ability [28].

Table 2. Thermal stability, the glass transition, start crystallization, crystallization and melting temperatures

<table>
<thead>
<tr>
<th>sample</th>
<th>Tg(°C)</th>
<th>Tx(°C)</th>
<th>Tm(°C)</th>
<th>$\Delta x$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>519</td>
<td>689</td>
<td>839</td>
<td>170</td>
</tr>
<tr>
<td>2</td>
<td>533</td>
<td>671</td>
<td>828</td>
<td>138</td>
</tr>
<tr>
<td>3</td>
<td>529</td>
<td>697</td>
<td>832</td>
<td>168</td>
</tr>
<tr>
<td>4</td>
<td>530</td>
<td>676</td>
<td>822</td>
<td>146</td>
</tr>
<tr>
<td>5</td>
<td>530</td>
<td>646</td>
<td>835</td>
<td>116</td>
</tr>
</tbody>
</table>

According to DTA curves, the values of $\Delta x$ calculated. The impact substitution of Nd with Sm on the glass-forming ability can appear. From Table 2, observed that the quantity of $\Delta x$ of all samples $>$ 100, it means that all glass samples have glass-forming ability and thermal stability. Figure 4 shows the FTIR spectra of glasses doped with Nd$^{3+}$ and Sm$^{3+}$ ion with different concentrations. Three areas defined the borate glass transmission spectra, the band (1200 - 1600 cm$^{-1}$) is the primary region, the second region from 800 to 1200 cm$^{-1}$ and the last from 600 to 800 cm$^{-1}$.

Where the primary bands are the stretching, relaxation of the B—O bond of trigonal BO$_3$ units, the second attributed to BO$_4$ units, and the third due to the bending vibrations of B—O—B linkages inside the borate network [29-31]. The rare earth oxides doped borate glass outcomes within the conversion of BO$_3$.
units into tetrahedral BO$_4$ units, and create non-bridging oxygen. Every BO$_4$ unit connected two different units, the band at 485 cm$^{-1}$ due O−Sm or Nd shifted to higher wavenumber with the growing attention of Sm.

Figure 5 shows the Vis-NIR absorption spectrum acquired from the lithium borate glasses doped Nd$^{3+}$ and Sm$^{3+}$ with different concentrations. Figure 5 shows eight electronic f−f transition bands of Nd$^{3+}$ in Table 3. This result compared with the prior referenced recommendations [32]. Figure 6 shows the optical absorption spectra of the lithium borate glass doped with 1 mol % Sm$_2$O$_3$ or Nd$_2$O$_3$. The observed absorption bands assigned to appropriate fitting electronic f−f transitions inside Sm$^{3+}$ ion as shown in Table 4.

Figure 4. The IR spectra of glasses doped with Nd$^{3+}$ and Sm$^{3+}$ ion with different concentrations

Figure 5. The Vis-NIR absorption spectrum obtained from the lithium borate glasses doped Nd$^{3+}$ and Sm$^{3+}$ with different concentrations

Table 3. The 4f transition levels of Nd$^{3+}$ doped in lithium borate glasses compared with the reported (Rai and Rai 2006).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength (nm)</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Wavenumber reported (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2$F$_{5/2}$</td>
<td>428</td>
<td>23365</td>
<td>23140</td>
</tr>
<tr>
<td>$^2$G$_{5/2}$</td>
<td>472</td>
<td>21186</td>
<td>21171</td>
</tr>
<tr>
<td>$^2$G$_{7/2}$</td>
<td>510</td>
<td>19607</td>
<td>19544</td>
</tr>
<tr>
<td>$^2$G$_{9/2}$</td>
<td>524</td>
<td>19084</td>
<td>19018</td>
</tr>
<tr>
<td>$^4$F$_{5/2}$</td>
<td>582</td>
<td>17182</td>
<td>17167</td>
</tr>
<tr>
<td>$^2$H$_{11/2}$</td>
<td>624</td>
<td>16026</td>
<td>16026</td>
</tr>
<tr>
<td>$^4$F$_{7/2}$</td>
<td>680</td>
<td>14706</td>
<td>14854</td>
</tr>
<tr>
<td>$^4$S$_{3/2}$</td>
<td>746</td>
<td>13405</td>
<td>13460</td>
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<tr>
<td>$^4$F$_{9/2}$</td>
<td>802</td>
<td>12469</td>
<td>12573</td>
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<tr>
<td>$^4$F$_{3/2}$</td>
<td>868</td>
<td>11521</td>
<td>11527</td>
</tr>
</tbody>
</table>
Spectroscopic properties of lithium borate glass containing $\text{Sm}^{3+}$ and $\text{Nd}^{3+}$ ions (I. Kashif)
The distortion may contribute effectively to covalent or asymmetric environments. The parameters $\Omega_4$ and $\Omega_6$ indicate the large properties of the glass such as hardness and viscosity. In current glass systems, J-O parameter values presented in Table 7, Table 8 and follow the tendency as $\Omega_4 > \Omega > \Omega_2$. The same trend observed in other glass systems [38-41]. According Jorgensen and Reisfeld [42], the $\Omega_4$ extra affected the crystal- field asymmetry and the changes in the energy distinction relating to 4fN and 4fN−15d configuration. In other phrases, $\Omega_2$ will increase because of the nephelauxetic impact. This occurs due to the deformation of the electronic orbital within the 4f configuration. Increase the overlap the 4f of Nd$^{3+}$ ion and oxygen orbital induced the energy level of Nd$^{3+}$ ion contracts and shifting inside the wavelength. Furthermore, shifting all transitions to higher wavelength indicate the presence of Nd $\rightarrow$ O linkages in the glass system. The transition $^4S_{3/2}$ $\rightarrow$ $^2G_{5/2}$ observed is greater intense than the alternative transitions which well see from the intensity of the calculated oscillator strength increases empirically and relates to the structural changes of the location of the rare-earth ions. $\Omega_2$ rise significantly by reducing the symmetry of the rare-earth site and the more covalent its chemical bond with the ligands field. As a whole, the $\Omega_2$ increases because of the covalence among the rare earth ion and the ligand field increases, as the symmetry lowers, and as the electric gradient relating the rare earth ion and the ligand fields increases. The higher the value of $\Omega_2$ in the current glass indicates the higher the hardness of the glass network and the higher covariant around the Sm$^{3+}$ ions. The ratio between $\Omega_2$ to $\Omega_6$ indicates that all the samples containing Sm found this ratio greater than 1. These resulting analyses verify that the glass used as a laser generator.

Figure 8 shows the variation of emission intensity for the transition of Sm$^{3+}$-Nd$^{3+}$ containing glasses excited at 400 nm. It clears the three peaks at 561, 599 and 647 nm, which assigned to $^4G_{5/2}$ $\rightarrow$ $^6H_{5/2}$, $^6H_{7/2}$. 

\[ \delta_{\text{rms}} = \sqrt{\frac{\sum(\text{cal}_i - \text{exp}_i)^2}{N-3}} \]  

Table 5. Experimental energies (Eexp), experimental (fexp) and calculated (fcal) oscillator strengths for the energy levels of the Sm$^{3+}$ glass

<table>
<thead>
<tr>
<th>$^4S_{1/2}$</th>
<th>Eexp (cm$^{-1}$)</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fcal x10$^{6}$</td>
<td>fexp x10$^{6}$</td>
<td>fcal x10$^{6}$</td>
<td>fexp x10$^{6}$</td>
<td>fcal x10$^{6}$</td>
</tr>
<tr>
<td>$^4F_{7/2}$</td>
<td>6858</td>
<td>0.295</td>
<td>0.535</td>
<td>0.337</td>
<td>0.343</td>
</tr>
<tr>
<td>$^4F_{5/2}$</td>
<td>7363</td>
<td>0.582</td>
<td>0.959</td>
<td>0.841</td>
<td>0.832</td>
</tr>
<tr>
<td>$^4F_{3/2}$</td>
<td>8237</td>
<td>1.02</td>
<td>1.56</td>
<td>1.04</td>
<td>1.09</td>
</tr>
<tr>
<td>$^4F_{1/2}$</td>
<td>9380</td>
<td>0.681</td>
<td>0.869</td>
<td>0.591</td>
<td>0.537</td>
</tr>
<tr>
<td>$^4I_{11/2}$</td>
<td>10683</td>
<td>0.111</td>
<td>0.110</td>
<td>0.0914</td>
<td>0.0830</td>
</tr>
<tr>
<td>RMS x10$^{4}$</td>
<td></td>
<td>0.124</td>
<td>0.882</td>
<td>0.015</td>
<td>0.0952</td>
</tr>
</tbody>
</table>

Table 6. Experimental energies (Eexp), experimental (fexp) and calculated (fcal) oscillator strengths for the energy levels of the Nd$^{3+}$ glass

<table>
<thead>
<tr>
<th>$^4S_{3/2}$</th>
<th>Eexp (cm$^{-1}$)</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fcal x10$^{6}$</td>
<td>fexp x10$^{6}$</td>
<td>fcal x10$^{6}$</td>
<td>fexp x10$^{6}$</td>
<td>fcal x10$^{6}$</td>
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<tr>
<td>$^4F_{5/2}$</td>
<td>11320.74</td>
<td>0.928</td>
<td>0.623</td>
<td>1.59</td>
<td>1.64</td>
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<tr>
<td>$^4F_{7/2}$</td>
<td>12485.83</td>
<td>2.49</td>
<td>3.21</td>
<td>1.59</td>
<td>1.64</td>
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<tr>
<td>$^4F_{9/2}$</td>
<td>13404.83</td>
<td>3.36</td>
<td>1.72</td>
<td>1.60</td>
<td>1.45</td>
</tr>
<tr>
<td>$^4F_{11/2}$</td>
<td>14705.88</td>
<td>0.192</td>
<td>0.130</td>
<td>0.126</td>
<td>0.0598</td>
</tr>
<tr>
<td>$^4G_{7/2}$</td>
<td>17182.13</td>
<td>4.21</td>
<td>3.08</td>
<td>1.92</td>
<td>1.39</td>
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<tr>
<td>$^4G_{9/2}$</td>
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<td>0.400</td>
<td>0.776</td>
<td>0.373</td>
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<tr>
<td>$^4G_{11/2}$</td>
<td>19607.84</td>
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<td>0.332</td>
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<td>0.295</td>
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<td>0.112</td>
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<td>RMS x10$^{6}$</td>
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<td>1.26</td>
<td>0.609</td>
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</tbody>
</table>
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4. CONCLUSION

Samarium and neodymium ions doped Lithium borate glass prepared and studied. The density of glass samples indicates that the density measurement increases as samarium content increase and the distinction among the experimental and calculated density increase as the samarium content increase. The functional vibration groups within the glass matrix have studied and indicate the addition of rare earth ion transfer the BO$_3$ vibration groups to BO$_4$ and forming nonbridging oxygen. Judd—Ofelt (J—O) principle has applied and evaluates J—O intensity parameters. The general analysis of the results of the present study optical properties (absorption and emission) indicates that these glass samples are answerable for orange. Based on the results obtained from the J-O analysis, the parameters concluded that the glass under study is a promising luminescent and laser material. The current glasses in the study have the potential to act like an orange emission device as well as photovoltaic applications.

REFERENCES


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