Crystal Field Parameters and Optical Parameters of Nd$^{3+}$ in Sodium Bismuth Silicate Glass

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ABSTRACT: Neodymium doped sodium bismuth silicate glasses were prepared by the melt quench technique. Optical absorption spectra of the Nd$^{3+}$ ion in the present glassy systems were recorded in the UV-Vis-NIR region. Taylor series expansion method was adopted for theoretical evaluation of various crystal field parameters such as the Slater-Condon ($F_2, F_4, F_6$), spin orbit ($\xi_{4f}$) and Racah parameters ($E_1, E_2, E_3$). Oscillator strength and electric dipole line strength of the observed transitions were evaluated with the help of Judd-Ofelt (JO) theory. Radiative transition probability (A), total radiative transition probability (A_t), radiative life time ($\tau_{rad}$), branching ratios ($\beta$) and integrated absorption ($\sigma$) cross section for stimulated emission between the meta stable state $^4F_{3/2}$ and $^4I_{11/2}$ (J= 15/2, 13/2, 11/2 and 9/2) levels were calculated using JO parameters. Optical basicity of the glass was found to increase with the addition of bismuth.

Keywords: Silicate glasses; Optical absorption spectroscopy; Racah parameters.

1. Introduction

Ever since the discovery of the solid state laser in 1961, a great deal of effort has been made to study the optical properties of rare earths and rare earth doped systems due to their unique uses in optical amplifiers, fiber lasers, telecommunications and display devices [1-3]. Attractive optical absorption and emission in the UV-vis-NIR region of the rare earths make them ideal candidates for optical applications in this region. A large variety of laser glasses doped with the Nd$^{3+}$ ion have been investigated with the purpose of generating efficient emission around 1050 nm [4]. Heavy-metal silicate glasses possess lower phonon energies compared to other oxide glasses and display strong visible and near infra-red fluorescence of rare earth ions within the system [5]. Though there have been a large number of reports on various rare earth doped glassy systems, the synthesis and optical analysis of neodymium doped bismuth silicate glasses has rarely been studied. At comparatively low Bi$_2$O$_3$ content ($\leq$10 mol%), Bi$_2$O$_3$ incorporates into the interstices of glass as a network changer which does not cause a large-scale structural rearrangement of the local glassy network. At higher concentrations of Bi$_2$O$_3$ (>10 mol%), Bi$_2$O$_3$ enters into glasses as a network former and a large-scale structural rearrangement of the local glass network takes place, which leads to significant variation of its optical properties [6-7]. In this context, an optical analysis of neodymium doped bismuth (10 mol%) sodium silicate glass is deserving of special attention and importance. The purpose of the present study is to derive various spectroscopic parameters such as Slater Condon, Racah, spin-orbit and Judd Ofelt parameters and to evaluate the
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radiative parameters, such as radiative transition probability, radiative life time and absorption cross section for
stimulated emission for the possible transitions.

2. Experimental

A neodymium (1.5 mol %) doped sodium bismuth silicate glassy system with composition (in mol%) 15 Na$_2$O-
10Bi$_2$O$_3$-75 SiO$_2$ was prepared by the well-known melt quenching method. Appropriate amounts of Bi$_2$O$_3$ (99.99% purity, Sigma Aldrich), Na$_2$CO$_3$ and SiO$_2$ (99.99% purity, Sigma Aldrich) were mixed and ground continuously using an agate mortar. The powder mixture was placed in a porcelain crucible and melted in a box furnace at a temperature of 1200 °C for 3 hours. The melt mixture was poured into a stainless steel mold heated to 100 °C. Then the sample was annealed at a temperature of 200 °C for 1 hour. The density of the sample was measured by Archimedes’ principle using xylene as the immersion liquid. The U-V Visible-NIR absorption spectrum of the sample was measured on a UV-Visible-NIR spectrophotometer Varian Cary 5000 in the wavelength span of 450 nm to 950 nm.

3. Results and discussion

Figure 1 shows the optical absorption spectra of 1.5 mol % Nd$_2$O$_3$ doped sodium bismuth silicate glass. The
transitions of the Nd$^{3+}$ ion occurs due to the transition from the ground state $^4$I$_{9/2}$ to various excited states [8-9]. The location intensity and breadth of the absorption bands are determined by the interaction of Nd$^{3+}$ ions with the local crystalline field. Each absorption band usually consists of a multiplicity of stark levels; unlike the regular local crystal field experienced by Nd$^{3+}$ in crystalline hosts, the crystal field’s sites in glass are randomly distributed. This distribution results in the inhomogeneous broadening of the absorption spectra of the Nd$^{3+}$ ion.

![Absorption spectra of Nd$^{3+}$ in sodium bismuth silicate glass.](image)

3.1 Bonding properties and nephelauxetic ratio

Indirect but convincing information regarding the RE-ligand bond strength can be obtained from the
nephelauxetic ratio(β). The nephelauxetic ratio is given by

$$\beta = \frac{\nu_m}{\nu_a}$$

where $\nu_m$ and $\nu_a$ are the wavenumbers (cm$^{-1}$) of the particular transitions in the host matrix and aqua, respectively. The larger value of the nephelauxetic ratio indicates a reduction in the strength of the covalent bond between the RE ion and ligand. The nephelauxetic parameter is directly related to the bonding parameter ($\delta$) as

$$\delta = \frac{1 - \bar{\beta}}{\bar{\beta}}$$

and $\bar{\beta}$ is the average value of the $\beta$ for observed transitions. The positive or negative sign of $\delta$ indicates covalent or ionic bonding of the rare earth-ligand bond. The small positive value of $\delta$ (0.0166) in the sodium bismuth silicate glass indicates the decrease in strength of covalency of the RE-O bond in the prepared sodium bismuth silicate glass compared to other silicate glass systems [10].

3.2 Crystal field parameters (Slater-Condon, Racah and spin-orbit parameters)

The Slater-Condon parameters ($F_{ij}$) generally represent the radial integral part of the electrostatic interaction
matrix elements of a trivalent rare earth ion and can be represented as [11]
The Racah parameters (E) are related to Slater-Condon parameters as

\[ E^+ = \frac{1}{9} \left[ 70F_2 + 231F_4 + 2002F_6 \right] \]

\[ E^- = \frac{1}{9} \left[ F_2 - 3F_4 + 7F_6 \right] \]

\[ E^' = \frac{1}{3} \left[ 5F_2 + 6F_4 - 91F_6 \right] \]  

The calculated values of all the spectroscopic parameters are given in Table 1.

All the spectroscopic parameters, viz. the Slater-Condon (F_2,F_4,F_6), spin-orbit (ξ_{4f}) and Racah parameters (E^*,E^,E^'), and the hydrogenic ratios (E^*/E^, E^'/E^, F^*/F^, F^'/F^) are found to be constants irrespective of the matrix composition. Therefore these parameters can be considered to be fundamental constants for trivalent neodymium in a given matrix.
Table 1. Calculated values of Slater-Condon (F_S), Racah (E^3) and spin-orbit (ξ_{ed}) parameters in sodium bismuth silicate glass and similar glasses.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F_0 (cm^−1)</td>
<td>284.36</td>
<td>330.05</td>
<td>314</td>
</tr>
<tr>
<td>F_2 (cm^−1)</td>
<td>46.54</td>
<td>50.8</td>
<td>47</td>
</tr>
<tr>
<td>F_4 (cm^−1)</td>
<td>2.642</td>
<td>5.14</td>
<td>4.8</td>
</tr>
<tr>
<td>ξ_{ed} (cm^−1)</td>
<td>865.61</td>
<td>870.47</td>
<td>926</td>
</tr>
<tr>
<td>E' (cm^−1)</td>
<td>3993.3</td>
<td>5001.5</td>
<td>4792</td>
</tr>
<tr>
<td>E'' (cm^−1)</td>
<td>18.13</td>
<td>23.89</td>
<td>22.6</td>
</tr>
<tr>
<td>E''' (cm^−1)</td>
<td>486.87</td>
<td>494.81</td>
<td>471</td>
</tr>
</tbody>
</table>

3.3 Judd-Olfet parameters

The electronic transitions of the trivalent lanthanides can be regarded as a sum of the electric dipole (f_{ed}) and magnetic dipole (f_{md}) contributions, i.e.

\[ F = f_{ed} + f_{md} \]  \hfill (9)

For rare earth ions, line strengths of magnetic dipole (md) transitions are much less than the line strengths of electric dipole (ed) transitions (S_{md} < S_{ed}) and are usually neglected in the calculation of oscillator strengths. The experimentally measured oscillator strengths of various absorption transitions of the Nd^{3+} ion in the present glassy systems are found to be in good agreement with those of other oxide systems (see Table 2). Oscillator strength (f) can be expressed in terms of the molar extinction coefficient (ε), and the energy of the transition in wave number (ν) by the relation (10) [14].

\[ f_{o} = 4.32 \times 10^{7} \varepsilon(\nu)d\nu \]  \hfill (10)

According to JO [15-16] theory, oscillator strengths of 4f→4f transitions of a rare earth ion can be described as a simple linear combination of three phenomenological parameters \( \Omega_{\lambda}(\lambda=2,4,6) \) as

\[ f_{ed} = \frac{\nu}{(2J+1)} \left[ \frac{8\pi^2mc(n^2+2)^2}{3h} \right] \Omega_{\lambda} \left( \nu \left| U_{\lambda} \right| \nu' \right)^2 \]  \hfill (11)

Table 2. Energy oscillator strength and electric dipole line strength of all observed transitions in sodium bismuth silicate glass.

<table>
<thead>
<tr>
<th>Transition from (^1I_{\gamma/2}) to</th>
<th>Energy (cm^−1)</th>
<th>F_{measured} (10^−5)</th>
<th>S_{ed} (10^−20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1G_{9/2})</td>
<td>19504</td>
<td>1.07</td>
<td>0.504</td>
</tr>
<tr>
<td>(^1G_{7/2})</td>
<td>18527</td>
<td>0.669</td>
<td>0.3324</td>
</tr>
<tr>
<td>(^1G_{5/2})</td>
<td>17390</td>
<td>1.239</td>
<td>0.665</td>
</tr>
<tr>
<td>(^1G_{3/2})</td>
<td>16946</td>
<td>1.543</td>
<td>0.837</td>
</tr>
<tr>
<td>(^1H_{11/2})</td>
<td>16621</td>
<td>0.268</td>
<td>0.148</td>
</tr>
<tr>
<td>(^1F_{9/2})</td>
<td>14602</td>
<td>0.138</td>
<td>0.086</td>
</tr>
<tr>
<td>(^1S_{9/2})</td>
<td>13467</td>
<td>1.562</td>
<td>1.066</td>
</tr>
<tr>
<td>(^1F_{7/2})</td>
<td>13260</td>
<td>0.269</td>
<td>0.186</td>
</tr>
<tr>
<td>(^1F_{5/2})</td>
<td>12500</td>
<td>0.459</td>
<td>0.3376</td>
</tr>
<tr>
<td>(^1H_{9/2})</td>
<td>12317</td>
<td>1.053</td>
<td>0.786</td>
</tr>
<tr>
<td>(^1F_{3/2})</td>
<td>11211</td>
<td>0.645</td>
<td>0.529</td>
</tr>
</tbody>
</table>

where (2J+1) is the degeneracy of the ground state, m the mass of the electron, and \( \nu \) the mean energy of the \( |\psi J\rangle \rightarrow |\psi' J'\rangle \) transition. \( U^{\lambda} \) is a unit tensor operator of rank \( \lambda \), and \( U^{\lambda} \)'s are parameters known as J-O intensity parameters. The calculated values of JO parameters (-0.41 x 10^{-20} cm^2, 3.14 x 10^{-20} cm^2, 2.61 x 10^{-20} cm^2) and the quality factor (\( \Omega_{2}/\Omega_{6} = 1.2 \)) for the sodium bismuth silicate glass are found to be in good agreement with those of other similar glasses [17].
3.4 Radiative transition parameters

Once the JO parameters $\Omega_2$ have been determined, they can subsequently be utilized to calculate the properties of transitions that have not been experimentally measured, including the radiative lifetime. The values of the radiative transition probability ($A$), total radiative transition probability ($A_T$), radiative lifetime ($\tau$), fluorescence branching ratio ($\beta$), and the integrated absorption crossection for stimulated emission are evaluated using the expressions:

$$A_{ed}^{J_J} = \frac{64\pi^2e^2}{3\hbar(2J+1)} \left[ \frac{n(n^2 + 2)^2}{9} \right] S_{ed}$$

$$A_{ed}^{J_J} = \tau^{-1}_{Rad}$$

$$\tau_{rad} = \sum J A_{JJ'}$$

The relative amplitudes of the fluorescence transitions or fluorescence branching ratio is given by

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum J A_{JJ'}}$$

The branching ratio is the ratio of the radiative transition probability to the total radiative relaxation rate. It measures the percentage of emission for a given transition from a state with respect to all other transitions from this state. For the Nd$^{3+}$ ion, the only excited manifold that is not relaxed predominantly by the multiphonon process is the $^4F_{3/2}$ manifold. This level fluoresces in four bands centered at approximately 880, 1060, 1350 and 1800 nm corresponding to the $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$ excited states respectively. Since the matrix elements $\langle {^4I_J} | U^2 | {^4F_{3/2}} \rangle$ are zero for the Nd$^{3+}$ ion, the $\Omega_2$ parameter will not have any effect on the stimulated emission parameters of Nd$^{3+}$ ions. The calculated values of the radiative transition probability ($A$), total radiative transition probability ($A_T$), radiative lifetime ($\tau_{rad}$) and fluorescence branching ratio are given in Table 3.

The integrated absorption crossection or effective crossection ($\sigma_a$) for a stimulated emission of the active ion are directly evaluated using the expression

$$\sigma_a = \frac{1}{v^2} \frac{A}{8\pi n^2}$$

From Table 3 it is clear that the $^4F_{3/2} \rightarrow ^4I_{15/2}$ transition has a promising stimulated absorption crossection and branching ratio and hence this transition in sodium bismuth silicate glass can be utilized for optical applications.
Table 3. Radiative transition rate, radiative life time, branching ratio and absorption crossection for stimulated emission for all the relevant transitions.

<table>
<thead>
<tr>
<th>Level from $^4F_{3/2}$</th>
<th>Energy (cm$^{-1}$)</th>
<th>$S_{td}$ x10$^{-2}$cm$^2$</th>
<th>$\Lambda$ (s$^{-1}$)</th>
<th>$\Lambda_{t}$ (s$^{-1}$)</th>
<th>$\beta$</th>
<th>Radiative life time $\tau_{rad}$($\mu$s)</th>
<th>Absorption cross section for stimulated emission $(\sigma_s)$ $10^{16}$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{15/2}$</td>
<td>5450</td>
<td>7.308</td>
<td>9</td>
<td>1760</td>
<td>0.005</td>
<td>568</td>
<td>0.12</td>
</tr>
<tr>
<td>$^4I_{13/2}$</td>
<td>7520</td>
<td>55.33</td>
<td>144</td>
<td></td>
<td>0.08</td>
<td></td>
<td>1.38</td>
</tr>
<tr>
<td>$^4I_{11/2}$</td>
<td>9520</td>
<td>150.8</td>
<td>794</td>
<td></td>
<td>0.451</td>
<td></td>
<td>4.69</td>
</tr>
<tr>
<td>$^4I_{9/2}$</td>
<td>11530</td>
<td>86.83</td>
<td>813</td>
<td></td>
<td>0.461</td>
<td></td>
<td>3.34</td>
</tr>
</tbody>
</table>

3.4 Optical basicity and ionic polarisability of the glass

Optical basicity represents the basicity of glasses in terms of electron density carried by oxygen. The theoretical optical basicity of a glass system is calculated using the relation [18-19].

$$\Lambda_{th} = \chi(Na_{2}O) \Lambda(Na_{2}O) + \chi(SiO_{2}) \Lambda(SiO_{2}) + \chi(Bi_{2}O_{3}) \Lambda(Bi_{2}O_{3})$$

where $\chi(Na_{2}O), \chi(SiO_{2})$ and $\chi(Bi_{2}O_{3})$ are the equivalent fraction of different oxides and $\Lambda(Na_{2}O), \Lambda(SiO_{2})$ and $\Lambda(Bi_{2}O_{3})$ are the optical basicity values assigned to the constituent oxides [5, 20].

The oxide ion polarisability can be calculated from the theoretical optical basicity as

$$\Lambda_{th} = 1.67 \left(1 - \frac{1}{\bar{\varepsilon}} \right)$$

It was observed that ionic polarisability increases when optical basicity increases. The bismuth free glass has an optical basicity of 0.787 which increased to 1.185 on addition of 10 mol % of $Bi_{2}O_{3}$. The glass hence possesses high optical basicity and ionic polarisability compared to other similar glasses [21].

4. Conclusion

UV-Vis-NIR absorption spectroscopy of Neodymium doped sodium bismuth silicate glasses, prepared by the melt quench technique, was carried out. From the detailed analysis of the spectra, various crystal field parameters such as Slater-Condon, spin-orbit and Racah parameters were calculated. Oscillator strength, electric dipole line strength and different radiative properties of the observed transitions were evaluated with the help of Judd-Ofelt theory. Optical basicity of sodium silicate glass was found to increase with the addition of bismuth.

References


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