Fluorescence features of Sm$^{3+}$ ions in Na$_2$SO$_4$–MO–P$_2$O$_5$ glass system—influence of modifier oxide

Na$_2$SO$_4$–P$_2$O$_5$: Sm$^{3+}$ glasses mixed with three different alkaline earth modifier oxides viz., MgO, CaO and BaO were prepared. Optical absorption and photoluminescence spectra of these glasses have been recorded at room temperature; the Judd–Ofelt theory was successfully applied to characterize these spectra. From this theory, various radiative properties like transition probability $A$, branching ratio $\beta$, the radiative lifetime $\tau$, for various emission levels in the spectra of these glasses have been determined and reported. An attempt has also been made to throw some light on the relationship between the structural modifications and luminescence efficiencies in the change of scenario of modifying oxides in the glass network.
Fluorescence features of Sm$^{3+}$ ions in Na$_2$SO$_4$–MO–P$_2$O$_5$ glass system-influence of modifier oxide

4.1 Introduction

Sulphate containing alkali/alkaline phosphate glasses are well known due to their unique electrical properties that make the glasses suitable for electrolytic applications [1]. These glasses are also widely being used to incorporate radioactive waste for long time safe storage [2]. The SO$_4^{2-}$ ions largely dissolve in the phosphate glass matrix. However, SO$_4^{2-}$ ions and metaphosphate ions appear to be interacting weakly, resulting in a small dynamic concentration of dithiophosphate (DTP) units. The dynamic feature consists of association–dissociation equilibrium [3]. Such weak and variable interaction between these two ions is a welcoming facet for the incorporation of rare earth ions to give high luminescence efficiencies with minimal non radiative losses in these glasses. The interaction between sulphate and phosphate ions can further be modified with the introduction of different modifier oxides. As it is well known that, the incorporation of alkali-earth oxides (viz., MgO, CaO and BaO) in the glass structure leads to a disruption of the glass network and promotes the formation of non-bridging oxygens (NBO) groups [4]. The ionic field strengths I (I = Z/r$^2$ where Z is the charge number and r is the ionic radius) for Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ ions are 4.73 A$^\circ$-2, 2.04 A$^\circ$-2 and 1.49 A$^\circ$-2 respectively, indicating that the network modifier cation, Mg$^{2+}$
has larger ionic field strength than the other two ions. In view of these facts, when sodium sulphate-phosphate glasses are mixed with these network modifying ions there will be structural modifications and local field variations around the rare earth ion dopant in the glass matrix; in other words the symmetry and or covalency of the glass at the rare earth ion should be different for different modifier mixed glasses. Such variations will have strong bearing on various luminescence transitions of the lanthanide ion. It is with this view the present investigation is undertaken.

The lanthanide ion chosen for the present study is Sm$^{3+}$. Though some recent studies are available on emission characteristics of Sm$^{3+}$ ions in different glass systems [5–7], the thorough literature survey on rare earth doped glasses reveals that as such the studies on samarium containing glasses have received relatively less attention than other lanthanide ions despite many features of interest. Samarium exhibits promising characteristics for spectral hole burning studies [8, 9]. The decay of excited states in Sm$^{3+}$ involves different mechanisms depending on the composition of the glass matrix. Earlier studies on optical absorption, fluorescence and lifetime measurements of Sm$^{3+}$ ions in oxyfluoroborate glass have indicated the reduction of fluorescence intensity of Sm$^{3+}$ ions; it is attributed to the concentration quenching [10].

Although a large number of studies are available in the literature on alkali sulphate–phosphate glasses mixed with different modifiers, majority of
them are focused mainly on conductivity studies [3]. Even though this glass system offers excellent environment for hosting rare earth ions, very few studies are available on the emission features of samarium ions in some other sulphate glass systems [11]. Thus the objective of the present investigation is to characterize the optical absorption and the fluorescence spectra of Sm$^{3+}$ ion in Na$_2$SO$_4$–P$_2$O$_5$ glasses mixed with three interesting alkaline earth modifier oxides, viz. MgO, CaO and BaO and to shed some light on the relationship between the structural modifications in the glass network and luminescence efficiencies.

4.2 Brief review on the spectroscopic studies of Sm$^{3+}$ ions in various glass systems

Shanmuga Sundari et al. [12] have reported composition dependent structural and optical properties of Sm$^{3+}$ doped sodium borate and sodium fluoroborate glasses. In this study the authors have observed that the radiative parameters are decreasing with the decrease in the sodium content in the glass. Agarwal et al. [13] have reported radiative properties of Sm$^{3+}$ ions doped zinc bismuth borate glasses. In this study the variations of intensity parameters, radiative transition probabilities observed with variation in the content of Bi$_2$O$_3$ in the glass network have been discussed in detail. Sooraj Hussain et al. [14] have reported absorption and emission characteristics of Sm$^{3+}$ and Dy$^{3+}$ in lithium boro tellurite glasses. In this study the authors have reported a bright orange ($^4G_{5/2} \rightarrow ^6H_{7/2}$) along with a red ($^4G_{5/2} \rightarrow ^6H_{9/2}$) and a yellow
\((^{4}G_{5/2} \rightarrow ^{6}H_{5/2})\) emission transitions of Sm\(^{3+}\) ions. Udaya Bhaskar et al. [15] prepared the Sm\(^{3+}\) doped BiO\(_{2}\)-B\(_{2}\)O\(_{3}\)-Li\(_{2}\)O glass and examined the absorption, excitation and lifetimes of different measured emission bands. Biju et al. [16] have investigated up conversion fluorescence in Sm\(^{3+}\)-doped zinc phosphate glassy matrix. Jayasankar et al. [17] have studied optical properties of Sm\(^{3+}\) ions in zinc and alkali zinc borosulphate glasses and they also [18] studied fluorescence spectra and decay properties of the \(^{4}G\) \(_{5/2}\) level of the Sm\(^{3+}\) ions in lithium borate and lithium fluoroborate glasses as a function of the pressure up to 27.2 and 25.9 G Pa respectively, at room temperature.

Kumar et al. [19] have observed stark splitting in the upper and lower levels in the fluorescence and measured the life-time of \(^{4}G\) \(_{5/2}\) level as a function of Sm\(^{3+}\) ion concentration. Kojima et al. [20] have prepared and studied optical spectroscopy of 79.5 ZnCl\(_{2}\)-10 BaCl\(_{2}\)-10 KCl-glasses containing divalent and trivalent samarium ions. Souza Filho et al. [21] have investigated the high pressure dependence of Sm\(^{3+}\) emission in PbO-PbF\(_{2}\)-B\(_{2}\)O\(_{3}\) glasses. Annapurna et al. [22] reported the optical characterization of Sm\(^{3+}\) doped silicate glass from the measurements of optical absorption spectra at (300K), total luminescence spectra fluorescence life times in the temperature range (10–300K) of the prominent emission transitions. Mahapatra [23] studied optical absorption and photoluminescence for Sm\(^{3+}\) ions doped (in the range \(8.7 \times 10^{19}\) to \(7.8 \times 10^{20}\) ions cm\(^{-3}\)) calcium metaphosphate glasses. He analysed the
spectral intensities in terms of the Judd-Ofelt parameters $\Omega_\lambda$. Shimizugava et al. [24] have studied LIII XANES before and after X-ray or UV irradiation. XANES in this edge showed that a part of trivalent ion converted to divalent ion upon the irradiation of X-ray. Shimizugava et al. [25] have studied X-ray absorption fine structure of samarium–doped glasses using synchrotron radiation. Farries et al. [26] reported the laser emission at 651 nm in a Sm$^{3+}$-doped silica optical fibre in a Fabri-Perot type laser cavity.

**4.3 Results**

Within the glass forming region of Na$_2$SO$_4$–MO–P$_2$O$_5$ system, the following composition is chosen for the present study:

NSMgP: 19Na$_2$SO$_4$–20MgO–60P$_2$O$_5$: 1.0Sm$_2$O$_3$

NSCaP: 19Na$_2$SO$_4$–20CaO–60P$_2$O$_5$: 1.0Sm$_2$O$_3$

NSBaP: 19Na$_2$SO$_4$–20BaO–60P$_2$O$_5$: 1.0Sm$_2$O$_3$

The samples were prepared as per the procedure described in the chapter 2.

**4.3.1 Physical parameters**

From the measured values of the density and average molecular weight $M$ of the samples, various other physical parameters such as Sm$^{3+}$ ion concentration $N$, mean Sm$^{3+}$ ion separation $R$, in Na$_2$SO$_4$–MO–P$_2$O$_5$: Sm$_2$O$_3$ glass samples are computed and presented in Table 4.1.
Table 4.1 Physical properties of Na$_2$SO$_4$–MO (M = Ba, Ca and Mg)–P$_2$O$_5$: Sm$^{3+}$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density, d (g/cm$^3$) ($\pm$ 0.001)</th>
<th>Conc. of Sm$^{3+}$ ions, $N_i$ ($10^{20}$ ions/cm$^3$)</th>
<th>Inter ionic distance of Sm$^{3+}$ ions $R_i$ (nm) ($\pm$ 0.01)</th>
<th>Refractive index, $n_d$ ($\pm$ 0.001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSMnP</td>
<td>2.548</td>
<td>1.242 (0.2063 mol/l)</td>
<td>2.01</td>
<td>1.660</td>
</tr>
<tr>
<td>NSCaP</td>
<td>2.524</td>
<td>1.198 (0.1990 mol/l)</td>
<td>2.03</td>
<td>1.657</td>
</tr>
<tr>
<td>NSBaP</td>
<td>3.082</td>
<td>1.268 (0.2106 mol/l)</td>
<td>1.99</td>
<td>1.668</td>
</tr>
</tbody>
</table>

4.3.2 Optical absorption spectra

The optical absorption spectra (Fig. 4.1 (a) & (b)) of Sm$^{3+}$ doped Na$_2$SO$_4$–MO–P$_2$O$_5$ glasses recorded at room temperature in the wavelength range 300–2200 nm, have exhibited the following absorption bands:

Sm$^{3+}$: $^6$H$_{5/2} \rightarrow ^4$P$_{3/2}$, $^4$G$_{9/2}$, $^4$H$_{9/2}$, $^4$D$_{5/2}$+$^4$H$_{7/2}$, $^6$P$_{7/2}$, $^4$L$_{15/2}$, $^4$F$_{7/2}$+$^6$P$_{3/2}$, $^6$P$_{5/2}$+$^4$K$_{11/2}$,

$^4$G$_{9/2}$, $^4$I$_{13/2}$, $^4$I$_{11/2}$, $^4$M$_{17/2}$, (UV-visible region)

$^6$F$_{11/2}$, $^6$F$_{9/2}$, $^6$F$_{7/2}$, $^6$F$_{5/2}$, $^6$F$_{3/2}$, $^6$F$_{1/2}$, $^6$H$_{15/2}$ (NIR region)

The pattern of the absorption spectra for all the three modifier mixed glasses remains the same; however, the absorption strength under given peak is found to varied with the change of modifier oxide.
Fig. 4.1(a) Optical absorption spectra (UV-vis. region) of Na$_2$SO$_4$–MO–P$_2$O$_5$:Sm$^{3+}$ glasses recorded at room temperature, all the transitions are from the ground state $^6$H$_{5/2}$. 
Fig. 4.1(b) Optical absorption spectra (NIR) of Na$_2$SO$_4$-MO-P$_2$O$_5$:Sm$^{3+}$ glasses recorded at room temperature, all the transitions are from ground state $^6$H$_{5/2}$. 
Conventional Judd–Ofelt (JO) theory [27] has been used to perform analysis of the experimental absorption spectra. The reduced matrix elements $\|U^4\|$ of the unit tensor operators needed for calculations have been re-calculated, using newer literature data on the Sm$^{3+}$ Hamiltonian parameters taken from Ref. [28]; the experimental and calculated oscillator strengths are presented in Table 4.2.

The quality of fitting is determined by the root mean squared deviation (RMS) and given in Table 4.2. The value of rms ‘$\Delta f$’ is in the typical error range of the J–O fitting and indicates the good agreement between the experimental and calculated results.

The summary of the Judd-Ofelt intensity parameters $\Omega_\lambda$ ($\lambda = 2, 4, 6$) for the three glasses doped with Sm$_2$O$_3$ is presented in Table 4.3. The values of $\Omega_\lambda$ are found to be in the order of $\Omega_4 > \Omega_6 > \Omega_2$ for all the three glasses. The comparison of the data on $\Omega_\lambda$ parameters of Sm$^{3+}$ ion reported for various other glass matrices eg., lead oxyfluoride, fluorohafnate, ZNBS, YAG indicates the similar trend with few exceptions [29–31].
Table 4.2 The absorption band energies, the oscillator strength for the transitions of sm$^{3+}$ ion doped Na$_2$SO$_4$–MO (M = Ba, Ca and Mg) –P$_2$O$_5$. (Position of barry-centers of the absorption lines is determined as ± 5 cm$^{-1}$; r.m.s. deviations for the calculated oscillator strengths are also given).

<table>
<thead>
<tr>
<th>Transitions from $^6$H$_{5/2}$</th>
<th>NSMgP</th>
<th>NSCaP</th>
<th>NSBaP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy (cm$^{-1}$)</td>
<td>$f_{\text{exp}}$ (x$10^{-6}$)</td>
<td>$f_{\text{cal}}$ (x$10^{-6}$)</td>
</tr>
<tr>
<td>$^4$D$<em>{5/2}$ + $^4$H$</em>{7/2}$</td>
<td>27652</td>
<td>2.170</td>
<td>1.2651</td>
</tr>
<tr>
<td>$^6$P$_{7/2}$</td>
<td>26747</td>
<td>1.7195</td>
<td>2.0338</td>
</tr>
<tr>
<td>$^6$P$<em>{5/2}$ + $^4$K$</em>{11/2}$</td>
<td>24027</td>
<td>1.6967</td>
<td>1.3719</td>
</tr>
<tr>
<td>$^4$G$_{9/2}$</td>
<td>22781</td>
<td>0.5274</td>
<td>0.1242</td>
</tr>
<tr>
<td>$^4$I$<em>{13/2}$ + $^4$I$</em>{11/2}$ + $^4$M$_{17/2}$</td>
<td>21174</td>
<td>3.1046</td>
<td>1.2486</td>
</tr>
<tr>
<td>$^6$F$_{11/2}$</td>
<td>10556</td>
<td>0.4449</td>
<td>0.6380</td>
</tr>
<tr>
<td>$^6$F$_{9/2}$</td>
<td>9210</td>
<td>4.2371</td>
<td>4.0305</td>
</tr>
<tr>
<td>$^6$F$_{7/2}$</td>
<td>8048</td>
<td>6.0808</td>
<td>6.5692</td>
</tr>
<tr>
<td>$^6$F$<em>{3/2}$ + $^6$H$</em>{15/2}$ + $^6$F$_{1/2}$</td>
<td>6528</td>
<td>3.1619</td>
<td>3.0249</td>
</tr>
<tr>
<td>r.m.s. deviation</td>
<td>± 0.9665</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3 J–O parameters (evaluated to an accuracy ±0.001) of Sm$^{3+}$ ion doped Na$_2$SO$_4$–MO (M = Ba, Ca and Mg) –P$_2$O$_5$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\Omega_2$ ( x 10$^{-20}$) cm$^{-2}$</th>
<th>$\Omega_4$ ( x 10$^{-20}$) cm$^{-2}$</th>
<th>$\Omega_6$ ( x 10$^{-20}$) cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSMgP</td>
<td>1.599</td>
<td>8.295</td>
<td>4.168</td>
</tr>
<tr>
<td>NSCaP</td>
<td>1.427</td>
<td>8.151</td>
<td>3.761</td>
</tr>
<tr>
<td>NSBaP</td>
<td>0.327</td>
<td>8.605</td>
<td>3.919</td>
</tr>
</tbody>
</table>

4.3.3 Photoluminescence spectra

The excitation spectra for these glasses were recorded at room temperature by monitoring the emission at the wavelength corresponding to the transition $^4G_{5/2}\rightarrow^6H_{9/2}$. From these spectra, $\lambda_{exc}$ is identified as ~400 nm ($^6H_{5/2}\rightarrow^4F_{7/2}$) and the same was used for recording emission spectra for these glasses; the emission spectra (Fig. 4.2) exhibited bands due to the following transitions in the visible region:

$^4G_{5/2}\rightarrow^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$

Out of these, the band corresponding to $^4G_{5/2}\rightarrow^6H_{7/2}$ transition is found to be very strong whereas the bands due to $^4G_{5/2}\rightarrow^6H_{5/2}$ and $^6H_{11/2}$ transitions are nearly seven times weaker comparatively. The energy level diagram containing the observed absorption and emission transitions of Sm$^{3+}$ ion for BaO mixed glass is shown in Fig. 4.3.
Fig. 4.2 Photoluminescence spectra of Na$_2$SO$_4$–MO–P$_2$O$_5$: Sm$^{3+}$ glasses record at room temperature. All the transitions are from upper state $^4G_{5/2}$. 
Fig. 4.3 Energy level diagram of Na₂SO₄-BaO-P₂O₅: Sm³⁺ glass.
The comparison of the spectra of the three glasses indicate that the intensity and the half width of the band due to $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition are significantly higher for BaO mixed glass than that observed in CaO and MgO mixed glasses; this is expected due to the low phonon energy and the large refractive index of BaO mixed glass. The MgO mixed glass has the highest ionic character, i.e. the $4f^5 6s^2$ electronic states of Sm$^{3+}$-ion dopant are more localized compared to the delocalized states in covalently bonded BaO mixed glasses.

These delocalized electronic shells of dopant ions are also responsible for the observed red-shift (Fig. 4.2) in the emission peaks in BaO mixed glasses when compared with those of CaO and MgO mixed glasses.

By further application of the Judd-Ofelt theory with the standard procedure [32–34] the transition probabilities ($A$), radiative lifetimes ($\tau$) of excited states and branching ratios ($\beta$) of emission transitions are estimated and presented in Table 4.4(a). The comparison of lifetimes for the $^4G_{5/2}$ level (Table 4.4(b)) for the three glasses indicates higher value for the BaO mixed Na$_2$SO$_4$–P$_2$O$_5$ glass.
Table 4.4(a) Radiative emission lifetime estimations and branching ratios for The emission transitions from the $^4G_{5/2}$ level.

<table>
<thead>
<tr>
<th>Transitions from the $^4G_{5/2}$ level to:</th>
<th>Wavelength, $\lambda$ (±0.1) (nm)</th>
<th>Radiative probability, $A$ (s$^{-1}$)</th>
<th>Branching ratio, $\beta$% (±0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSMgP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^6H_{5/2}$</td>
<td>562</td>
<td>16.2</td>
<td>3.7</td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>598</td>
<td>230.6</td>
<td>52.2</td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>644</td>
<td>133.7</td>
<td>30.2</td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>706</td>
<td>61.5</td>
<td>13.9</td>
</tr>
<tr>
<td>Total probability, $A_T$ (s$^{-1}$)</td>
<td></td>
<td>442.0</td>
<td></td>
</tr>
<tr>
<td>NSCaP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^6H_{5/2}$</td>
<td>562</td>
<td>15.8</td>
<td>3.7</td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>598</td>
<td>219.4</td>
<td>52.0</td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>644</td>
<td>127.6</td>
<td>30.3</td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>706</td>
<td>59.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Total probability, $A_T$ (s$^{-1}$)</td>
<td></td>
<td>421.8</td>
<td></td>
</tr>
<tr>
<td>NSBaP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^6H_{5/2}$</td>
<td>563</td>
<td>15.6</td>
<td>3.8</td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>601</td>
<td>226.5</td>
<td>54.6</td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>645</td>
<td>112.0</td>
<td>27.0</td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>706</td>
<td>61.0</td>
<td>14.7</td>
</tr>
<tr>
<td>Total probability, $A_T$ (s$^{-1}$)</td>
<td></td>
<td>415.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4(b) A comparison of radiative lifetimes and quantum efficiencies.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Radiative lifetime, (±0.01) (ms)</th>
<th>Quantum efficiency ((\eta))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated $\tau$</td>
<td>Measured $\tau_m$</td>
</tr>
<tr>
<td>NSMgP</td>
<td>2.30</td>
<td>1.22</td>
</tr>
<tr>
<td>NSCaP</td>
<td>2.34</td>
<td>1.39</td>
</tr>
<tr>
<td>NSBaP</td>
<td>2.40</td>
<td>1.74</td>
</tr>
</tbody>
</table>
4.4 Discussion

Among different constituents of Na$_2$SO$_4$–MO–P$_2$O$_5$–Sm$_2$O$_3$ glass system, P$_2$O$_5$ is a strong glass forming oxide participates in the glass network with PO$_4$ structural clusters. The PO$_4$ tetrahedra are linked together with covalent bonding in chains or rings. The chains or rings of phosphate groups are subjected to modifications to various extents depending upon the nature of the modifier ions and MO/P$_2$O$_5$ ratio. Hence truncated chains in which a fraction of the phosphate tetrahedra possess three unshared oxygen corners produce the structure. These tetrahedra can be written as [POO$_{2/2}$O] with two bridging oxygens and [POO$_{1/2}$O$_2$]$^{2-}$ with one bridging oxygen.

The two bridging oxygen phosphate groups viz.,

\[
\begin{array}{c}
\text{POO}_3/2 + O^{2-} \rightarrow 2\text{POO}_{2/2}O^- \nonumber
\end{array}
\]

in the presence of the modifier oxide, can be written as

\[
2\ [\text{POO}_{3/2}]^0 + \text{MO} \rightarrow 2\ [\text{POO}_{2/2}O^-] + \text{M}^{2+}
\]

Similarly, the phosphate group with one bridging oxygen viz.,

\[
\begin{array}{c}
\text{POO}_2/2 + O^{2-} \rightarrow 2\text{POO}_{1/2}O_2^- \nonumber
\end{array}
\]

in the presence of modifier oxide can be written as

\[
2\ [\text{POO}_{2/2}O^-] + \text{MO} \rightarrow 2\ [\text{POO}_{1/2}O_2^-] + \text{M}^{2+}
\]
The glass formation with the combination of Na$_2$SO$_4$ and P$_2$O$_5$ is possible only if the phosphate network contains [POO$_{2/2}$O]$^-$ and [POO$_{1/2}$O$_2$]$^{2-}$ structural groups [3]. Further, there is every possibility for the formation of SPO$_7^{3-}$ (dithiophosphate) species in the glass matrix when sulphate and [POO$_{2/2}$O]$^-$ ions present simultaneously. The concentration of such species (which are expected to influence the emission probabilities of the rare earth ion) in the glass network will however, depend upon the nature of the modifier M$^{2+}$ ion. In other words, the atomic arrangement at short and intermediate range in the glass network can be considered as a decisive factor for the emission characteristics of the glass network. Following the order of the ionic size or radius of the three modifier ions ($r_{\text{Mg}^{2+}} < r_{\text{Ca}^{2+}} < r_{\text{Ba}^{2+}}$), one can understand that the replacement of MgO successively by CaO and BaO, causes to increase the degree of disorder in the glass network. Thus, the change of the modifier oxide causes substantial structural modifications at the lanthanide ion site in Na$_2$SO$_4$–P$_2$O$_5$: Sm$_2$O$_3$ glass network.

If we consider the varying modifier ions to be incorporated between the long-chain molecules in the vicinity of rare earth ion in the S–O–P network, then the symmetry and/or covalency of the glass at the rare earth ions should be different for different modifiers in the glass network. Additionally, the variations in the concentration of various structural units of phosphate, sulphate ions and linkages between them are also expected to modify the
crystal field around lanthanide ions in the glass network. Overall, there is a higher degree of structural depolymerization in the glasses mixed with BaO as modifier when compared with other two glasses.

The rare earth ions that occupy different coordination sites with non-centro symmetric potential contribute significantly to $\Omega_2$. Even with similar coordination, the differences in the distortion at these ion sites may lead to a distribution in the crystal field. The variations in the sites with non–centro symmetric potential (that may arise due to the influences of the dielectric of media, the environment of the rare earth ion and nephelauxetic effect) lead to changes in $\Omega_2$ value. Among the three J–O parameters, the parameter $\Omega_2$ is related to the covalency and structural changes in the vicinity of the Sm$^{3+}$ ion (short–range effect) and $\Omega_4$ and $\Omega_6$ are related the long-range effects and are strongly influenced by the vibrational levels associated with the central rare earth ions bound to the ligand atoms [35-37]. The comparison of $\Omega_2$ parameter for the three glass shows slightly lower value for glass mixed with BaO.

According to the Judd–Ofelt theory, the intensity parameters contain two terms: (i) Crystal field parameter that determines the symmetry and distortion related to the structural change in the vicinity of Sm$^{3+}$ ions. In the present context, this may be understood as follows: the larger the size of the modifier ion, the larger is the average distance between S–O–P, P–O–P chains causing the average Sm–O distance to increase. Such increase in the bond lengths
produces weaker field around Sm$^{3+}$ ions leading to a low value of $\Omega_2$ for the glass mixed with BaO. Additionally the variations in the concentration of phosphate groups with different number of non-bridging oxygens, as discussed above, also play an important role in the variation of value of $\Omega_2$. (ii) The covalency between the Sm$^{3+}$ ion and the ligand oxygen ion also contribute to $\Omega_2$. For oxide glasses this is related to the radial overlapping integral of the wave functions between 4f and admixing levels, e.g. 5d, 5g and the energy denominator between these two energy terms.

The luminescence spectra of Sm$^{3+}$ are similar to those reported for a number of other glass systems [31–33]. The high intensity or high quantum yield of the luminescence bands of Sm$^{3+}$ ion in BaO mixed glasses indicates that there is a lesser cross relaxation i.e., the transfer of energy from the excited state of Sm–ion by electric multipole interaction (more precisely dipole-dipole or dipole–quadrupole interactions) to neighboring Sm–ion lying in the ground state is low for this particular glass when compared with other two glass systems.

Branching ratio ‘$\beta$’ (that defines the luminescence efficiency of the transition) of yellow emission ($^4G_{5/2} \rightarrow ^6H_{7/2}$), among various transitions originated from $^4G_{5/2}$ is found to be the highest (~ 50%). Further, the comparison of $\beta$ values for the glasses viz., NSMgP, NSCaP and NSBaP suggests the highest value for the glass NSBaP. From these studies it is
identified that modifier BaO is more appropriate modifier in this glass matrix to produce high luminescence efficiency.

The fluorescence decay curve of the $^4G_{5/2}$ level for all the three glasses observed to be single exponential (inset of Fig. 4.2). The fluorescence lifetime $\tau$, evaluated from these graphs is apparently shorter than calculated lifetimes from the J–O theory (Table 4.4 (b)). Such difference obviously suggests multi-phonon relaxations. The higher value of lifetime either calculated or measured for the glasses NSBaP suggests a low phonon loses or higher concentration of dangling S–O–P bonds with more non–bridging oxygens.

The quantum efficiency ($\eta$) is defined as the radiative portion of the total relaxation rate of a given energy level:

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + W_{\text{nr}}} = \frac{\tau_{\text{exp}}}{\tau_{\text{rad}}}$$

(4.1)

where $A_{\text{rad}}$ is the total radiative relaxation rate, $W_{\text{nr}}$ is the rate of total non–radiative transition $\tau_{\text{exp}}$ –experimental lifetime and $\tau_{\text{rad}}$ –radiative lifetime.

The value of $\eta$ (for the $^4G_{5/2}$ level) determined for the three glasses is presented in Table 4.4(b). For the BaO mixed glasses, the value of $\eta$ is found to be 72.5 where as for CaO and MgO mixed glasses it is found to be 59.4 and 53.0 respectively. In general, for any common glass host, the quantum efficiency for Sm$^{3+}$ ions emission in the visible region is expected to be higher when compared with that of other rare earth ions. This is because, the energy gap
between $^4G_{5/2}$ and the first underlying level $^4F_{11/2}$ is $\sim 7000$ cm$^{-1}$; normally, the phonon energies in the phosphate glasses is $\sim 1100$–$1200$ cm$^{-1}$. The comparison of the two energies shows the non-radiative decay probability is low and hence higher values of $\eta$ are expected as is also observed for the present glasses. The comparison of the value of $\eta$ for the three studied glass systems here indicated the higher value for BaO mixed glass; as has been discussed earlier, the degree of disorder (ruffling of S–O–P linkages) in BaO mixed glasses is higher when compared with other two glasses. Such higher concentration of ruffled S–O–P linkages causes the presence of low energy phonons in these glasses, where as comparatively high energy phonons are expected in MgO and CaO mixed glasses. Hence, there is an electron–phonon coupling of the Sm$^{3+}$ ion with the high–energy phonons in the MgO mixed glass that lead to high non–radiative losses; such coupling in case of BaO mixed glasses is in between electron and low–energy phonons and hence minimal non-radiative losses are expected.

4.5 Conclusions

The optical absorption, photoluminescence of Sm$^{3+}$ in Na$_2$SO$_4$-MO-P$_2$O$_5$ glass systems have been studied. The optical absorption and emission spectra of these glasses are characterized using JO theory; out of the three J-O parameters ($\Omega_2$), the value of $\Omega_2$, which is related to the structural changes in the vicinity of the Sm$^{3+}$ ion, indicated the highest for MgO mixed glasses. The radiative transition probabilities and branching ratios evaluated for various
luminescent transitions observed in the luminescence spectra, suggested the highest values for $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition among various other transitions in all the three glass systems. The comparison of $\beta_k$ values of these transitions showed the largest value for BaO mixed glasses. The quantum efficiency is also found to be the highest for BaO mixed glasses indicating that these glasses exhibit better luminescence efficiency.
References


