



Optical Absorption and Luminescence Properties of Sm^{3+} Doped Chlorofluoro Borate Glasses for Photonic Applications

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ABSTRACT

Sm^{3+} ions doped chlorofluoro borate glasses with compositions (in mol %) $(50-x)\text{B}_2\text{O}_3 + 20\text{PbO} + 15\text{NaCl} + 15\text{MgF}_2 + x\text{Sm}_2\text{O}_3$, $x = 0.2, 0.4, 0.6, 0.8$ and 1.0 have been prepared by melt quenching technique. For these glasses X-ray diffraction (XRD), optical absorption, emission and decay measurements were carried out. The glassy nature of the present glass matrices are confirmed by XRD profiles. From the optical absorption spectra, derived the spectral intensities (f) and Judd-Ofelt intensity parameters, Ω_λ ($\lambda = 2, 4, 6$) have been evaluated. Using Judd-Ofelt intensity parameters, radiative transition probabilities (A_R), and branching ratios (β_R) were calculated. From the photoluminescence spectra, stimulated emission cross-sections (σ_p) for all the observed emission transitions were calculated. To investigate luminescence potentiality of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ emission level of Sm^{3+} doped different chlorofluoro borate glasses, experimental lifetimes (τ_{exp}) were obtained from decay curve analysis for all glass matrices. Finally, these observed results were discussed and compared with the literature data.

Key Words: Borate glasses, J-O parameters, Photoluminescence, Lifetime, Emission cross-section

INTRODUCTION

Spectroscopy of rare earth ions integrated in different host glasses are used extensively in different scientific and technical applications such as solid state lasers, optical amplifiers and bar-code reading etc. In the development of rare earth (RE) doped optical devices, the selection of host glass matrix is very important because the spectral transitions of rare earth ions are host dependent [1].

Rare earth doped glasses were extensively researched due to their attractive advantages such as wide range of composition, flexibility, shape and wide range of potential applications like optical amplifiers, lasers and sensors. Among them, the borate family glasses have better application through the nature of low noise and high sensitivity character [2, 3]. Optical properties of borate glasses depend on the modifier oxide material of the composition. A large number of modifier oxides were used in glasses such as zinc oxide, alkali oxides,

alkaline oxides and heavy metal oxides. However, borate glasses still have quite a few disadvantages that restrict their further applications by high phonon energy of host glass matrix [4]. In this quest, an attempt has been made by borate glasses are a kind of glass former in which holoogens are used as an additional ligand environment to create low phonon energy in addition to the oxygen ligands. The Sm^{3+} ($4f^5$) ion is one of the most interesting Ln^{3+} ions to analyze the fluorescence properties as its emitting $^4\text{G}_{5/2}$ level exhibits relatively high quantum efficiency and also shows different quenching emission channels. In recent times, glasses containing Sm^{3+} ions have stimulated extensive interest due to their potential applications for high-density optical storage, under sea communication and colour display [5]. The decay of excited states in Sm^{3+} involves different mechanisms depending on the matrix [6]. Therefore the Sm^{3+} ion can be useful in lasers, solar energy converters, etc.

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In the present study, we first adopted simple melt quenching technique to prepare samarium doped different chlorofluoroborate glasses. The aim is to investigate the effects of Sm doping on optical properties of chlorofluoro borate glasses in detail. Now, we focus on to highlight the intimate connection between the rare earth concentration and spectroscopic parameters. From optical absorption spectra, Judd-Ofelt intensity parameters (Ω_2 , Ω_4 and Ω_6), radiative lifetimes (τ_R), radiative transition probability (A_R) and peak stimulated emission cross-sections (σ_p). The nature of decay curve profiles for the $^4G_{5/2}$ state of Sm^{3+} in all the glass matrices is analyzed. These prepared glasses could find application in the optical field.

EXPERIMENTAL

In the present work different concentration of Sm^{3+} doped lead magnesium fluoro borate glasses samples with the compositions $(50-x)\text{B}_2\text{O}_3+20\text{PbO}+15\text{MgF}_2+15\text{NaCl}+x\text{Sm}_2\text{O}_3$ (where $x = 0.2, 0.4, 0.6, 0.8$ and 1.0 mol%) were prepared using high purify chemicals, boric acid (B_2O_3), lead oxide (PbO), magnesium fluoride (MgF_2), sodium chloride (NaCl) and samarium oxide (Sm_2O_3) powders using a conventional melt-quenching method. The raw materials were thoroughly mixed in an agate mortar and melted in an electronic furnace at the temperature $950\text{--}1000^\circ\text{C}$ for 1h in porcelain crucible. After that, obtained liquid is poured on a preheated brass plate. The synthesized glass samples were subsequently annealed at 300°C to remove thermal strain to do spectral measurements. Refractive index (n) measurements were performed using an Abbe refractometer at sodium wavelength (589.3 nm) with one-bromonaphthalene as contact liquid. The density (d) was measured by Archimedes's principle using water as an immersion liquid. All these measurements were carried out at RT. For all the glass samples, the physical properties like density, thickness, refractive index and concentrations of Sm^{3+} ions doped have been calculated.

Structural investigations of prepared glasses were carried out by XRD. Optical absorption spectrum was recorded using Perkin-Elmer Lambda 950 spectrometer. The excitation and visible photo luminescence spectra (range $400\text{--}700\text{ nm}$) of Sm^{3+} doped glass matrices were recorded using JOBIN YVON Fluoro log-3 fluorimeter using flash lamp.

RESULTS AND ANALYSIS

XRD analysis

The X-ray diffraction pattern (XRD) of 0.8 mol \% of Sm^{3+} doped chlorofluoro borate glass is shown in Fig. 1. The XRD pattern does not contain any diffracting lines, suggesting the existence of long range structural disorder in the glass un-

der investigation. This confirms the amorphous nature of the Sm^{3+} doped chlorofluoro borate glass matrix.

Absorption spectroscopy and Judd-Ofelt theory

The study of optical absorption is a useful method for investigating optically induced transitions. Fig. 2 presents the absorption spectrum for 0.8 mol\% Sm^{3+} doped chlorofluoro borate glass matrix. Different absorption bands of Sm^{3+} ions in lead borate glass system were assigned with their appropriate transitions. Table 1, shows the spectral intensities of different absorption bands of 0.8 mol\% Sm^{3+} doped chlorofluoro borate glass matrix along with RMS deviations. Theory behind the work has been taken from our previously published paper [7]. There is a good correlation between calculated and experimental spectral intensities indicating that it is in accordance with intensity theory proposed by Judd-Ofelt [8,9]. Expected bands of Sm^{3+} in the visible region such as $^6P_{7/2}$, $^6P_{5/2}$ and $^4G_{9/2}$ are missing owing to strong absorption of host glass matrix.

Within the framework of the Judd-Ofelt theory, the absorption between any two states can be obtained as a function of three parameters (Ω_2 , Ω_4 and Ω_6) called the intensity or Judd-Ofelt parameters. These parameters characterize a rare earth ion in a given host matrix and are shown in Table 1. The Ω_2 parameter is strongly depending on short range effects, such as covalency of the rare earth ion and sensitive to the symmetry of rare earth ion site. While Ω_4 and Ω_6 are long range parameters related to the bulk properties of the glass such as rigidity and viscosity [10]. Order of intensity parameters is found to be $\Omega_2 > \Omega_6 > \Omega_4$. The obtained value of Ω_2 in chlorofluoro borate glass is $3.32 \times 10^{-20}\text{ cm}^2$ indicates that higher asymmetry/higher covalency is connected with surrounding.

Some transitions, whose spectral intensities are very responsive to a small change in the surrounding ligand environment, these transitions are called 'hypersensitive transitions (HST)'. HST transitions obey the selection rules $|\Delta J| \leq 2$, $|\Delta L| \leq 2$ and $\Delta S = 0$. Among various transition intensities, $^6H_{5/2} \rightarrow ^6F_{7/2}$ is the hypersensitive transition (HST) for Sm^{3+} ion and most intense one in the near infrared region [11] which is the same as those of a pure quadrupole transition. It has large $\|U^2\|$ reduced matrix elements. As the hypersensitivity, depends mainly on the atoms surrounding the samarium ions. The configuration of nearest- neighboring atoms has greater influence than atoms lying beyond the first and second- neighboring shells.

Emission analysis

The excitation spectrum of chlorofluoro borate glass was obtained by monitoring the emission of Sm^{3+} ion at 601 nm as shown in Fig.3 and the peak at 404 nm was found to be optimal excitation peak. The assignments of the samarium excited states were made in accordance with previous reported

works. For pure rare earth ion, the surrounding environment is homogeneous. So, their excitation bands are symmetric. In the present work, the excitation spectrum appears to be asymmetric owing to some disorder surrounding the environment of Sm^{3+} ion. The position of the emission transitions exhibits smaller variations and the invariance of the emission wavelengths can be explained by the shielded nature of the 4f–4f. The emission spectra of different chlorofluoro borate glasses are recorded using an excitation of 404 nm. Fig. 4 shows attributions of the corresponding luminescent transitions for different chlorofluoro borate glasses. Figure shows three emission peaks nearly at 569, 601 and 645 nm. From the emission spectra, it is observed that the main visible emission intensity of Sm^{3+} ion is in the reddish-orange part of spectra and corresponds to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition located at 601 nm. The intensity ratio between electric dipole and magnetic dipole transitions measures the symmetry of local environment of the trivalent 4f ions. The $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ transition is not observed due to its forbidden character ($\Delta J=3$), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ transition is a magnetic dipole (MD) transition. The $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition is magnetic dipole allowed but electric dipole dominated with the selection rule $\Delta J=\pm 1$ and the $^6\text{H}_{5/2} \rightarrow ^6\text{H}_{9/2}$ band is a forced electric dipole transition (ED). This transition is very sensitive to surrounding environment of Sm^{3+} ions due to its hypersensitive behavior. The greater the intensity of the ED transition, the more asymmetry is present in the glass matrix. In the present work, the spectral intensity of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (ED) transition of the Sm^{3+} ion is lower than the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ (MD) transition, which indicates that low asymmetric is predominant in the prepared glasses [12].

Intensity alteration was observed by changing samarium doping concentration. Among the three observed emission transitions (Figure 4), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition which has high emission intensity and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition which has low emission intensity. The narrow nature of emission band indicates that the Sm^{3+} coordination environment distribution is small. From the emission spectra, it is observed that the intensity of all the peaks increase up to 0.8 mol% Sm^{3+} ion concentration and then decrease at higher concentrations. The luminescence intensity is highly sensitive to the surrounding local environment of samarium ions. When the samarium ions are doped into a phosphate network, Sm^{3+} ions cannot be dispersed in the host glass matrix, but become closer Sm^{3+} - Sm^{3+} ion pairs at higher concentrations. This leads to quenching of the fluorescence intensity. Also, at lower concentrations of samarium ions (up to 0.8 mol%) the samarium coordinates with nonbridging oxygens which is responsible for the higher luminescence intensity. At higher concentrations (>0.8 mol%), samarium ions coordinate with bridging oxygens. The interaction between borate groups and oxygen groups through samarium ions decreases, i.e. connectivity decreases. Hence there is a possibility of decreasing fluores-

cence intensity. The cross relaxation channels are responsible for luminescence quenching in the studied glass matrix. This is mainly due to Sm^{3+} - Sm^{3+} interactions at higher concentrations. Certain luminescence properties for three emission transitions in all the glass matrices are shown in Table 2. It is noted that the transition, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ is the most probable transition. Also, it is noted that the predicted radiative transition probability for the transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ of 0.8mol% Sm^{3+} doped chlorofluoro borate glass is 169 s^{-1} .

The stimulated emission cross section (σ_p) of emission transition is one of the important parameter used to identify a laser active medium. A good laser transition can have a large emission cross section. It is observed that the transition, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ shows higher peak emission cross-section i.e. $7.68 \times 10^{-22} \text{ cm}^2$ at $\lambda_p = 601 \text{ nm}$ in 0.8mol% of Sm^{3+} doped chlorofluoro borate glass matrix, which is high. The large emission cross sections are attractive features for low threshold, high gain applications and are utilized to obtain continuous wave laser action [13].

Decay curve analysis

In the present work, it is observed that at lower concentrations of samarium (0.2 and 0.4 mol%), the decay profiles (Figure 5) are fitted to single exponential whereas at higher concentrations (0.6, 0.8 and 1.0 mol%), the decay profile becomes non-exponential due to the existence of non-radiative energy transfer. The energy gap between the $^4\text{G}_{5/2}$ level and next lowest level $^6\text{F}_{11/2}$ is nearly 6600 cm^{-1} and requires at least six phonons to bridge the energy gap. So, MPR channel is negligible in Sm^{3+} doped chlorofluoro borate glasses. The decreased luminescence decay constants are due to the energy transfer through cross-relaxation channels. It is predominant at higher concentrations of samarium ions, i.e. ≥ 0.6 mol% in the investigated glasses. The decrease of lifetime and non-exponential fit are characteristics of the existence of concentration quenching mechanism at higher concentrations of samarium ions.

CONCLUSIONS

From XRD analysis, it is confirm that the prepared glasses are of amorphous in nature. From the absorption spectra, various absorption transitions are assigned. From these transitions, one transition is chosen for excitation of samarium ions and emission spectra are recorded. From emission spectra, four luminescence transitions are observed. Among these transitions, emission transition at 601 nm has high in intensity. With the increases of content of samarium, concentration quenching is observed. From the results of these investigations, it is concluded that the 0.8 mol % of Sm^{3+} -doped chlorofluoroborate glass is more useful for photonic applications.

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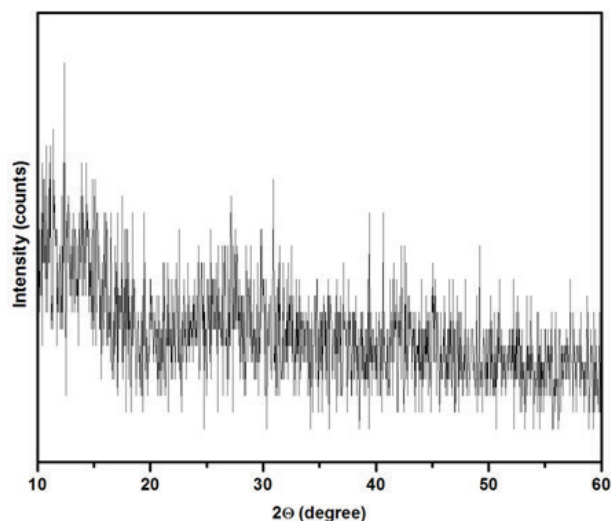


Figure 1: XRD profile for 0.8 mol% of Sm^{3+} doped chlorofluoro borate glass matrix.

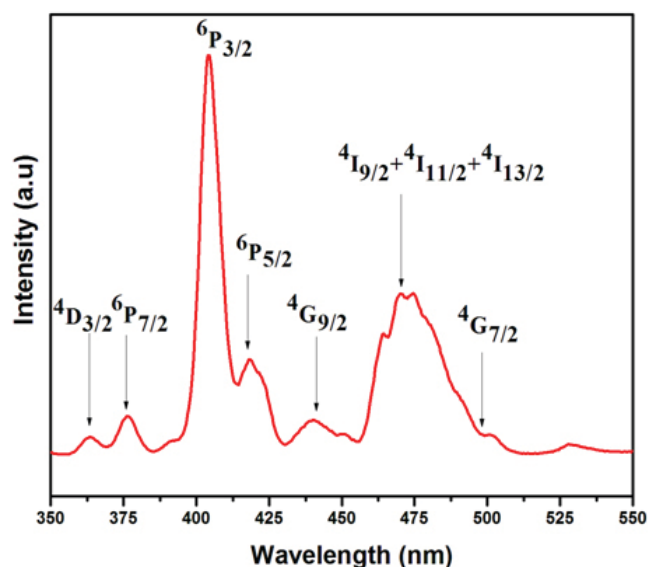


Figure 3: Excitation spectrum of 0.8 mol% Sm^{3+} doped chlorofluoro borate glass matrix.

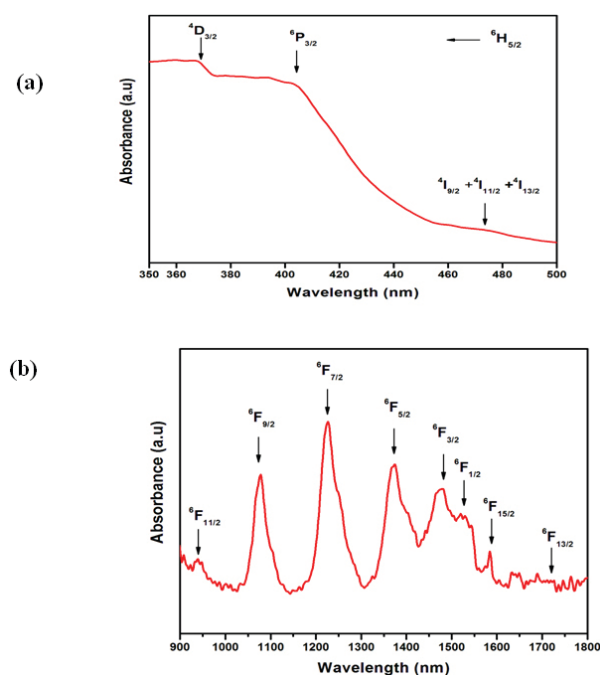


Figure 2: (a) UV-VIS (b) NIR absorption spectrum of 0.8 mol % Sm^{3+} doped chlorofluoro borate glass matrix.

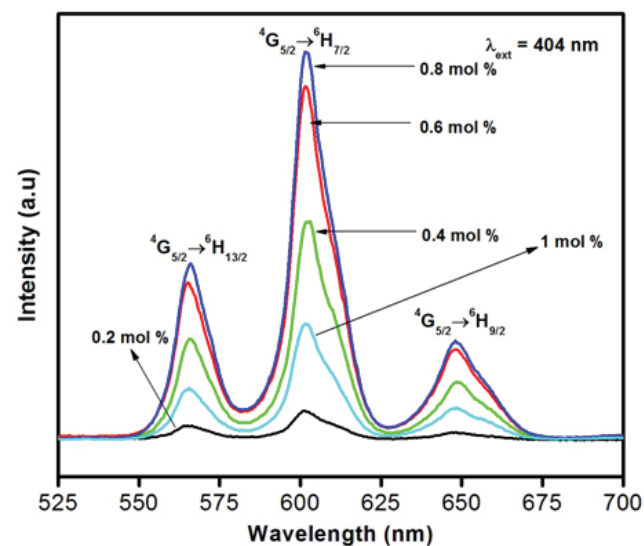


Figure 4: Emission spectra of Sm^{3+} doped chlorofluoro borate glass matrix for different concentrations.

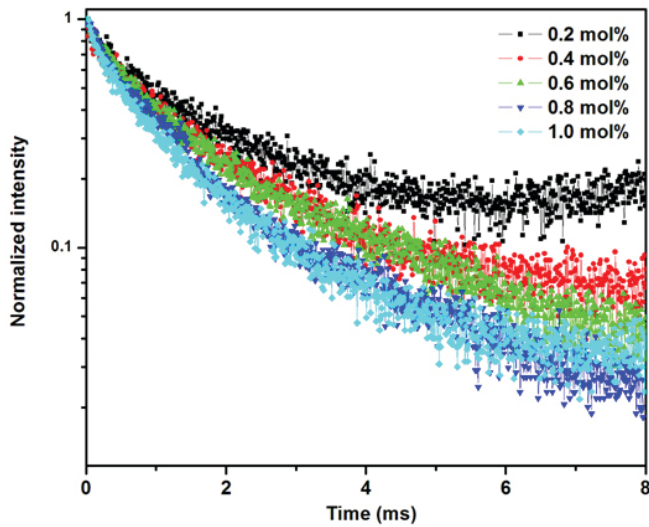


Figure 5: Decay profiles for Sm³⁺ doped chlorofluoro borate glass matrix for different concentrations.

Table 1: Observed band positions (nm) and their assignments, experimental (f_{exp}) and calculated (f_{cal}) spectral intensities ($\times 10^{-6}$) and Judd-Ofelt parameters (Ω_{λ} , $\times 10^{-20}$ cm²) for 0.8 mol% of Sm³⁺ doped chlorofluoro borate glass matrix.

| S. No | Energy level | | 0.8 mol% | |
|-------|--------------------------------|------|------------|-----------|
| | | | f_{exp} | f_{cal} |
| 1 | ⁶ F _{11/2} | 940 | 0.49 | 0.75 |
| 2 | ⁶ F _{9/2} | 1078 | 4.26 | 4.52 |
| 3 | ⁶ F _{7/2} | 1226 | 6.40 | 6.20 |
| 4 | ⁶ F _{5/2} | 1375 | 2.75 | 2.77 |
| 5 | ⁶ F _{3/2} | 1473 | 1.86 | 2.02 |
| 6 | ⁶ F _{1/2} | 1526 | 1.25 | 1.14 |
| 7 | ⁶ F _{15/2} | 1584 | 0.12 | 0.03 |
| | RMS deviation | | ± 0.18 | |
| | Ω_2 | | 3.32 | |
| | Ω_4 | | 4.56 | |
| | Ω_6 | | 4.90 | |

Table 2: Emission band positions (λ_p , nm), effective bandwidths ($\Delta\nu_{eff}$, cm⁻¹), radiative transition probabilities (A_R , s⁻¹), peak stimulated emission cross-sections ($\sigma_p \times 10^{-22}$ cm²) and branching ratios (β_R , %) of Sm³⁺ doped chlorofluoro borate glass matrix.

| S. No. | Transition | Parameter | 0.8 mol% |
|--------|---|-------------------|----------|
| 1 | ⁴ G _{5/2} → ⁶ H _{9/2} | λ_p | 645 |
| | | $\Delta\nu_{eff}$ | 374 |
| | | A_R | 97 |
| | | σ_p | 3.80 |
| | | β_R | 601 |
| 2 | ⁴ G _{5/2} → ⁶ H _{7/2} | λ_p | 601 |
| | | $\Delta\nu_{eff}$ | 390 |
| | | A_R | 169 |
| | | σ_p | 7.68 |
| | | β_R | 601 |
| 3 | ⁴ G _{5/2} → ⁶ H _{5/2} | λ_p | 569 |
| | | $\Delta\nu_{eff}$ | 398 |
| | | A_R | 128 |
| | | σ_p | 6.63 |
| | | β_R | 6.63 |