Luminescence Properties on Tb$^{3+}$ Doped Lead Fluoroborate Glasses

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Abstract—This article presents the optical properties of Tb$^{3+}$ in lead fluoroborate glasses of the type $X$ PbF$_2$ . (89 – $X$)B$_2$O$_3$.10 Al$_2$O$_3$.1Tb$_2$O$_3$ (where $X$ = 8, 12, 16, 20, 24, 28, 34 and 36). The standard Judd-Ofelt model was applied to the room temperature absorption intensities of Tb$^{3+}$ (4$f^8$) to determine the phenomenological intensity parameters $\Omega_2$, $\Omega_4$ and $\Omega_6$. These parameters have been used to calculate radiative transition probabilities ($A_{rad}$), lifetimes ($\tau_R$) and branching ratios ($\beta_R$) for the excited level $^7D_4$. The predicted values of $\tau_R$ are compared with the measured values for $^7D_4$ level for eight glass compositions (Glass (A-H)). Among the eight-terbium glasses Glass A with 8 mol% of PbF$_2$ (as the optimum content) has revealed an intense green emission with maximum life time and higher quantum efficiency. The stimulated emission cross section $\sigma(\lambda_P)$ is also evaluated for the $^5D_4\rightarrow^7F_J$ ($J = 6, 5, 4 & 3$) transitions.

Keywords— Glasses; Judd–Ofelt Theory; Luminescence; Optical Properties; Rare Earth.

I. INTRODUCTION

The study of spectroscopic properties of rare earth doped glasses has gained importance, since a complete knowledge on the fundamental data that includes optical efficiency, transition positions, transition probabilities, radiative and non-radiative decay rates, branching ratios etc. for the excited states is essential to estimate/design optical devices such as lasers, colour displays, upconverters, optical fibers and optical amplifiers and so on [1-5]. Rare earth ion doped glasses have obtained considerable interest due to their more homogeneous luminescence, low cost, greater ease of production and possibility of adjusting composition in comparison with other luminescent materials [6]. Among the trivalent rare-earth ions, the Tb$^{3+}$ has considerable interest due to its stimulated green emission through the $^5D_4\rightarrow^7F_5$ (543 nm) transition. The large energy difference (14663 cm$^{-1}$) between the $^1F_{J+1}$ multiplet levels and $^5D_4$ emitting level, the luminescence property of Tb$^{3+}$ has been proven to be useful in characterizing the energy level structure and optical transition mechanism. The absorption and luminescence spectra of Tb$^{3+}$ ion in different lattices have been studied by several workers [7–9]. In this paper an attempt has made to analyse the optical properties of Tb$^{3+}$ doped lead fluoroborate glasses of the type $X$ PbF$_2$. (89 – $X$)B$_2$O$_3$.10Al$_2$O$_3$.1Tb$_2$O$_3$ (where $X$ = 8, 12, 16, 20, 24, 28, 32, 36). The Judd-Ofelt theory [10, 11] has been applied to interpret the local environment of Tb$^{3+}$ ions and bond covalency of RE-O bond. Using Judd-Ofelt[10,11] theory, radiative transition probabilities ($A_{rad}$), radiative lifetimes ($\tau_R$) and branching ratios ($\beta_R$) have been computed for the excited level $^7D_4$ of Tb$^{3+}$ in these lead fluoroborate glasses. Emission spectra of these rare earth glasses are also studied. Luminescence decay curves of the $^7D_4$ level of Tb$^{3+}$ ions in lead fluoroborate glasses have been measured and analyzed.

II. EXPERIMENTAL STUDIES

The Tb$^{3+}$ doped lead fluoroborate glasses were prepared by using appropriate amounts of analar-quantity B$_2$O$_3$, PbF$_2$, Al$_2$O$_3$ and Tb$_2$O$_3$ with 99.99 % purity. For convenience these glass systems are designated as A, B, C, D, E, F, G and H according to the PbF$_2$ content in the glass matrix: GLASS A : 8 PbF$_2$. 81 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$ GLASS B : 12 PbF$_2$. 77 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$ GLASS C : 16 PbF$_2$. 73 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$ GLASS D : 20 PbF$_2$. 69 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$ GLASS E : 24 PbF$_2$. 65 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$ GLASS F : 28 PbF$_2$. 61 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$ GLASS G : 32 PbF$_2$. 57 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$ GLASS H : 36 PbF$_2$. 53 B$_2$O$_3$. 10 Al$_2$O$_3$. 1 Tb$_2$O$_3$

The samples are prepared by conventional melt quenching technique [12-14]. Absorption spectra were recorded at room temperature (RT) on a spectrophotometer (Varian Carry 5E model) in the wavelength range of 300 nm – 2500 nm with spectral resolution of 1nm. The excitation and emission spectra for the glass samples under study were recorded in HORIBA JOBIN YVON SPEX Fluorolog-3 -11 Spectrofluorometer. The decay profile of the glass samples under study was recorded using HORIBA JOBIN YVON SPEX Fluorolog-3 Model FL3-22 Fluorimeter. The measurement was carried out for the prominent fluorescent line $^5D_4 \rightarrow ^7F_5$ (543 nm) with 369nm UV excitation for all eight glass system. The experimental lifetime of the fluorescent level of Ln ions was determined by first e-folding time of the decay profile [8, 15,16].

III. RESULTS AND DISCUSSION

A. Excitation and emission spectra

The excitation spectrum was recorded in the wavelength region 300nm to 400nm for 543nm emission of Tb$^{3+}$ (with xenon excitation) is shown in the Figure 1, which is due to the

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4f-4f transitions. The transitions assigned to those bands are $^7\text{F}_6 \rightarrow ^5\text{H}_6$, $^5\text{D}_3$, $^5\text{L}_6$, $^5\text{G}_7$, $^5\text{L}_{10}$, $^5\text{G}_{10}$. The excitation spectrum shows an agreement with absorption spectra. Among different excitation transitions, $^7\text{F}_6 \rightarrow ^5\text{L}_0$ (369 nm) is more prominent. This has been used to measure emission spectra of Tb$^{3+}$ doped lead fluoroborate glasses as shown in Figure 2. The emission transitions have shown sharp emission bands due to the f-f inner shell transitions, from the excited level to the lower level such as $^5\text{D}_3 \rightarrow ^7\text{F}_J$ ($J = 3$ to $6$) for Tb$^{3+}$. From emission spectra, transitions such as $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (489 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (543 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_4$ (585 nm) and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ (622 nm) have been identified [17, 18]. The assignments of the transitions are taken from Dieke and Crosswhite [19] and are expressed formally in the LS coupling. Of them, 543 nm has shown bright green emission, arising from the Laporte-forbidden $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition [20]. The transition $^5\text{D}_4 \rightarrow ^7\text{F}_6$ obeys the magnetic dipole (MD) transition selection rule of $\Delta J = \pm 1$ [17, 21] When Tb$^{3+}$ ions excited by UV radiation, electronic transition of either $^5\text{D}_3 \rightarrow ^7\text{F}_J$ (blue emission) or successive $^5\text{D}_4 \rightarrow ^7\text{D}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_J$ (green emission) takes place, where $J = 3, 4, 5$ and 6. The energy level diagram of the luminescence and the resonant energy transfer processes in Tb$^{3+}$ doped lead fluoroborate glasses is as shown in Figure 3. The small energy gap between (5800 cm$^{-1}$) between the $^5\text{D}_4$ and $^5\text{D}_3$ emission levels causes a fast non-radiative decay and enhances the population of $^5\text{D}_4$ level much more at higher Tb$^{3+}$ concentrations resulting the enhancement of luminescence intensity. Luminescence from the higher excited state such as $^5\text{D}_3$ was not detected, indicating a very efficient non-radiative relaxation to the lowest excited $^5\text{D}_4$ levels. As shown in the Figure 2, it was noted that the blue emission from $^5\text{D}_3$ level to $^7\text{F}_J$ multiplets is absent in all eight glasses. The observation can be rationalized by the fact that the emission derived from $^5\text{D}_3$ level may be quenched by two types of nonradiative relaxation process, viz., cross-relaxation mechanism and multiphonon mechanism that result in the rapid population of the $^5\text{D}_4$ level at the expense of $^5\text{D}_3$ [22, 23]. The following cross relaxation may also occur:

$$\text{Tb}^{3+} ({}^5\text{D}_3 + \text{F}_J) \rightarrow \text{Tb}^{3+} ({}^5\text{F}_J) \rightarrow \text{Tb}^{3+} ({}^5\text{D}_4) + \text{Tb}^{3+} ({}^7\text{F}_0)$$

So that the $^5\text{D}_3$ to $^7\text{F}_J$ transitions of some high Tb$^{3+}$ (≥1.0 mol%) concentration materials are quenched by the energy transfer process as mentioned above. Thus only $^5\text{D}_4$ to $^7\text{F}_J$ emission can be observed. The Table 1 gives the peak wavelengths ($\lambda_p$), effective band widths ($\Delta\lambda_{eff}$), and the stimulated emission cross-sections $\sigma (\lambda_p)$, for the four transitions $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{F}_5$, $^5\text{F}_4$, $^5\text{F}_3$. The stimulated emission cross-section for the $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transition is the highest for all the eight glasses, which indicates that the laser efficiency for this transition is high.

**B. Radiative properties**

The JO intensity parameters ($\Omega_J$) have been used to compute the radiative properties of emission characteristics of the Tb$^{3+}$ doped lead fluoroborate glasses. Using the standard formulae available in literature [24-26] the radiative properties have been calculated for the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 3, 4, 5$ and 6) transitions for the eight glass systems and these values are presented in the Table 2. The radiative properties of Tb$^{3+}$ ions (or any of the Ln$^{3+}$ions) depend on the number of factors such as property of network former and modifier of glass. The parameter $\beta_R$ (i.e., the branching ratio) of the luminescent transitions characterizes the lasing power of the potential laser transitions. The $\beta_R$ values obtained for the luminescent transitions originated from $^5\text{D}_4$ for all the eight glasses are furnished in the Table 2. It is well established that an emission transition having branching ratio $\geq 0.50$ can emits laser radiation more efficiently [27]. Among various transitions the transition $^5\text{D}_4 \rightarrow ^7\text{F}_3$ is found to have the highest values of $\beta_R$ for all the eight glasses which is the characteristic property of Tb$^{3+}$ ion. This transition may therefore be considered as a possible laser transition. Higher the emission probability for a transition leads to faster decay of that level and hence shortening of the lifetime. It was seen from the Table 2 that the spontaneous emission probability ($A_0$) and the total emission probability ($A_1$) is smaller for Glass A and hence it is having higher excited state lifetimes compare to the other glass systems. The lifetimes ($\tau_0$) of $^5\text{D}_4 \rightarrow ^7\text{F}_3$ of all the eight glasses shows a decreasing trend with increasing PbF$_2$ content. The lower is the modifying action of the NWM in the glass network (Higher is the rigidity of the network), lower is the radiative lifetime and the greater presence of higher vibrational frequencies [28]. Such vibrations lead to non-radiative losses in the glass systems with increasing PbF$_2$. Even we have observed decrease in the intensity with increase PbF$_2$ content. The small difference in experimental and calculated lifetimes can be attributed to non-radiative decay. From the Table 2 it is observed that the Glass A (8% PbF$_2$) having higher values in both experimental and calculated lifetimes for $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transition is then the best glass to exhibit better lasing action among the 8 glasses with a higher quantum efficiency of 95.63%.

**C. Decay analysis**

Analysis of decay curves gives information about the measured life times of the excited states of trivalent RE ions in any host composition. For a detailed study of the quenching of the fluorescence, we have measured the decay profile for the $^5\text{D}_4 \rightarrow ^7\text{F}_3$ (green fluorescence) transition at 543nm of Tb$^{3+}$ in lead fluoroborate glasses excited with 369nm. The plots of the intensity of the $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transition for different concentrations of PbF$_2$ are shown in the Figure 4. At lower Tb$^{3+}$ concentrations (≤ 0.5 mol%), the decay curves exhibited single-exponential nature and at higher concentrations (≥ 1.0 mol%) they exhibited non-exponential behavior due to the resonance energy transfer among the excited Tb$^{3+}$ ions through $^5\text{D}_4$, $^7\text{F}_6$ transitions as shown in Figure 3. These curves were subjected to appropriate mathematical fitting procedures in order to determine the first e-folding times of the decay curves of the excited state using origin software and the values are presented in the Table 2, which shows that the Glass A is having higher fluorescence life time. The decay time was found to be decreasing as we go down the
order from Glass A to Glass H indicates a rapid energy transfer or resonant energy transfer (RET) among the excited T$^3_\text{b+}$ ions with increasing PbF$_2$ content. In such a case, the T$^3_\text{b+}$ ions may play an intermediate role in the recombination reaction either through bypassing or by resonant energy transfer condition, leading to a decrease in the radiative transitions [29].

IV. Conclusion

The emission spectra of all the eight glass systems show that the Glass A with 8% PbF$_2$ is having the higher intensity for the prominent green emission. The transition $^5\text{D}_4 \rightarrow ^7\text{F}_5$ is found to have the highest values of $\beta_{\text{R}}$ for all the eight glasses and therefore this transition is the potential laser transition. It is also observed that the stimulated emission crosssection for the $^5\text{D}_4 \rightarrow ^7\text{F}_4$ transition is the highest for all the eight glass systems, which indicates that the laser efficiency for this transition is high. In conclusion, this study shows that T$^3_\text{b+}$ doped lead fluoroborate glasses possesses several competitive spectroscopic properties, suggesting that Glass A with 8% PbF$_2$ has potential candidate for 0.54 $\mu$m laser operation.

REFERENCES