Spectroscopic investigation of Tm^{3+} containing Lithium borate glasses

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Abstract. In the present study we investigated the spectroscopic properties of Tm^{3+} containing lithium borate glasses as a function of Tm^{3+} concentration. The physical properties were analyzed by using the density and molar volume of the glasses. The Judd-Ofelt theory was used to analyze the experimental data. The main focus of the present study was to study the effect of ion concentration on the emission properties of the glasses. The emission intensity of the glasses increased with the addition of Tm^{3+} ions up to 0.5 mol% and decreased with a further addition due to concentration quenching.

1. Introduction

Ongoing progress in the optical technologies is totally dependent on the rare earth materials in which photons are manipulated by using the change in the host materials or change in the concentration of singly or multi-doped rare earth materials. Glasses are the excellent host for the rare earth ions and their applications play an important role in photonics, nuclear waste management, household and other technologies. Among all rare earth ions Thulium (Tm^{3+}) is the best active ion because of its broad emission range. This emission range cover the applications in telecommunication up to the laser technology. Emission from Tm^{3+} ions at 2 μm is useful in the area of light detection and ranging (LIDAR), remote sensing and in the medical field [1].

The broad emission around 1460 nm is useful for the development of an optical amplifier for applications in fiber-optic communication. By using the 1860 nm emission of Tm^{3+} it is possible to build a mid –infrared laser [2]. Glass hosts can be utilized to attain both these properties. Among the available potential hosts, the lithium borate glasses are very interesting due to their easy formability, wide range of composition and good rare earth solubility [3-5].

The present work was to understand in detail the spectroscopic behavior of Tm^{3+} ions in the lithium borate glasses. We prepared the 27.5 Li$_2$O: (72.5-X) B$_2$O$_3$: X Tm$_2$O$_3$ glasses and analyzed their physical and spectroscopic properties. We also calculated the Judd-Ofelt (J-O) parameters by using the absorption data of the prepared glasses. J-O is a theory in physical chemistry describing the intensity of electron transitions within the 4f shell of rare earth ions in solids and solutions. By using the J-O parameters the estimated values of the radiative transition probabilities, radiative lifetimes of excited states and branching ratios are reported in the present study. Luminescence studies have been performed as a function of mol % of the Tm^{3+} ions.

2. Experimental

The 27.5 Li$_2$O: (72.5-X) B$_2$O$_3$: X Tm$_2$O$_3$ (Tm$_2$O$_3$ = 0, 0.25, 0.5, 0.75 and 1 mol%) glasses were prepared by the conventional melt quench technique. The appropriate quantity of high purity chemicals were weighed and mixed in an agate mortar by using acetone. The obtained mixture were transferred in an alumina crucible and melted in an electric furnace at 1273 K. To achieve the homogeneity of the melt, the melt was allowed to soak for 1 h with intermediate stirring. Samples of the desired shape were obtained by quenching the melt on the brass molds at room temperature. Samples were immediately transferred to an annealing furnace preheated at 573 K and collected the next day. The prepared sample were labeled as Tm0, Tm1, Tm2, Tm3 and Tm4 according to increasing doping concentration. The density of the samples were measured by the Archimedes principle using the METTLER TOLEDO weighing balance. A LAMBDA 950 Ultra violet/visible/near infra-red (UV/Vis/NIR) spectrophotometer (PerkinElmer) was used to measure the absorption spectra of the glasses. The excitation and emission spectra of the glasses along with the lifetimes were recorded by using an Edinburgh FLS980 system with a 450 W steady state Xe lamp as excitation source. The emission spectra were recorded by using a liquid nitrogen cooled Hamamastu R5509-72 near infrared photomultiplier tube (NIR-PMT) with the response time of 800 ps. The decay analysis were performed by 60 W pulsed microsecond Xe flash lamp and NIR-PMT.

3. Results and Discussion

Fig. 1 shows pictures of the glasses with different concentration of Tm$_2$O$_3$. The obtained glasses were colorless with a tint of yellow for the higher concentration Tm$_2$O$_3$ glasses and also have good transparency. The absorption spectra were normalized by using the thickness of the samples and concentration of the Tm^{3+} ions in the glass matrix and plotted as absorption cross section as shown in Fig. 2 for the 0.75 mol % Tm$_2$O$_3$ as representative. In these spectra five absorption bands centred at 464, 677, 782, 1208 and 1677 nm are assigned to the $^3H_6 \rightarrow ^1G_4$, $^3H_6 \rightarrow ^3F_2 + ^3F_3$, $^3H_6 \rightarrow ^3H_4$, $^3H_6 \rightarrow ^3H_5$ and $^3H_6 \rightarrow ^3F_4$ transitions of the Tm^{3+} ions [6]. The wavelength range of the observed transition, mean wavelength ($\overline{\lambda}$) and the integrated cross section ($\int \sigma(\lambda)\, d\lambda$) were determined and depicted in Table 1. These values were further used to calculate the Judd-Ofelt parameters for the prepared glasses.
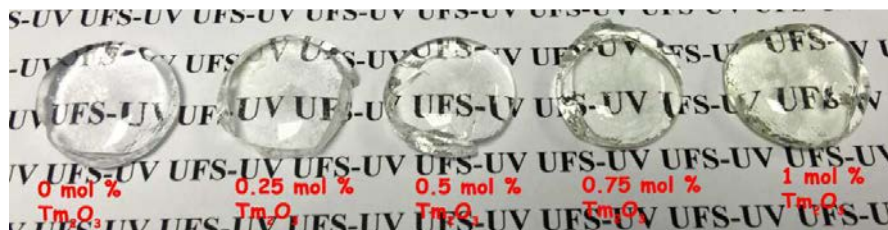
Figure 1. Glasses with different Tm$_2$O$_3$ content.

Table 1. Absorption parameters of 0.75 mol % Tm$_2$O$_3$ lithium borate glass.

Manifold	Range (nm)	$\overline{\lambda}$ nm	$\int \sigma(\lambda)d\lambda$ (cm^2 nm)
$^1G_4$	438-491	464	7.25
$^3F_2, ^3F_3$	618-726	677	20.14
$^3H_4$	733-841	782	21.92
$^3H_5$	103-1313	1207	39.04
$^3F_4$	1512-1911	1676	82.26
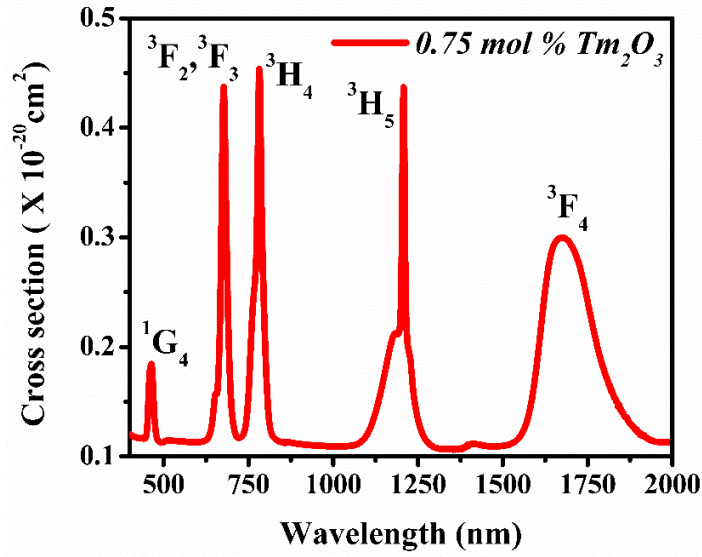
Figure 2. Absorption cross section spectra of 0.75 mol % Tm₂O₃ lithium borate glass.

Table 2. Variation of measured ($S^{ED}_{measured}$), calculated ($S^{ED}_{calculated}$) line strengths (X 10^{-20} cm²) and J-O intensity parameters Ω_t.

Manifold	0.25 mol% Tm₂O₃		0.5 mol% Tm₂O₃		0.75 mol% Tm₂O₃		1 mol% Tm₂O₃	
	$S^{ED}_{measured}$	$S^{ED}_{calculated}$	$S^{ED}_{measured}$	$S^{ED}_{calculated}$	$S^{ED}_{measured}$	$S^{ED}_{calculated}$	$S^{ED}_{measured}$	$S^{ED}_{calculated}$
$^1G_4$	0.60	0.12	0.52	0.1	0.23	0.07	0.26	0.07
$^3F_2, ^3F_3$	0.81	0.89	0.69	0.77	0.45	0.49	0.41	0.46
$^3H_4$	0.76	0.78	0.66	0.69	0.42	0.44	0.41	0.43
$^3H_5$	0.88	0.70	0.79	0.61	0.48	0.39	0.48	0.37
$^3F_4$	1.29	1.36	1.07	1.13	0.73	0.76	0.71	0.74
Ω_2 X10^{-20}	1.43		1.26		0.81		0.85	
Ω_4 X10^{-20}	0.62		0.44		0.33		0.29	
Ω_6 X10^{-20}	0.64		0.58		0.35		0.34	

By using the J-O theory [7,8] it's possible to calculate the manifold-to-manifold transition probabilities, radiative lifetimes and branching ratios of emission. The accuracy of the J-O parameter depend on accuracy of the absorption measurements. By using the values of integrated cross section, line strength of manifold to manifold electric dipole can be calculated by using the following equation:

$$S^{ED}_{measured} = \frac{3ch(2J'+1)}{8\lambda^2 e^2 \bar{\lambda}} n \left(\frac{3}{n^2+1} \right)^2 \int \sigma(\lambda)\, d\lambda \qquad (1)$$

where *n* is the refractive index and *J'* is the total angular momentum, and the other symbols have their usual meaning. By using the values of measured line strength J-O intensity parameters were obtained by solving

the equation for five observed transitions. J-O theory also provides the theoretical expression for line strength which is given by:

$$S_{calculated}^{ED} = \sum_{t=2,4,6} \Omega_t \left| f^n [SL] J \| U^t \| f^n [S'L'] J' \right|^2 \qquad (2)$$

where Ω_t are the Judd–Ofelt parameters, $\| U^t \|$ are the doubly reduced unit tensor operators, S is the spin operator and L is the angular momentum operator for L-S coupling scheme for ground state and first excited state [9]. The obtained values are provided in Table 2. The measured ($S_{measured}^{ED}$) and calculated ($S_{calculated}^{ED}$) line strengths have values relatively close to each other which justify the quality and accuracy of the fitting use in this study. The values or manifold $^1G_4$ has a very large difference between the calculated and experimental values. This difference may be due to the hypersensitivity of the $^1G_4$ transition. As the hypersensitive transition is strongly dependent on the host and surrounding and their predicted and experimental values may vary.

The variation of is Ω_2 strongly depends on the variation in the covalent bonding. Change in covalency between the Tm^{3+} ions and ligands anions directly affects the values of Ω_2 as it reflects the asymmetry of constituent's ions around the Tm^{3+} ions. Ω_4 and Ω_6 values are the measure of rigidity of the structure in which the rare earth ions are situated [10]. The values of Ω_2 were found to decrease with an increase in the concentration of the Tm^{3+} ions, which confirms an increase in the ionic nature of the bonding in the glasses.
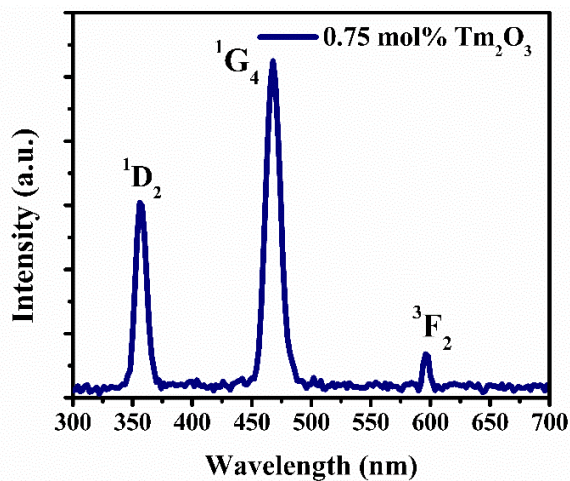

Figure 3 (a). Excitation Spectra of prepared 0.75 mol % Tm_2O_3 containing glass.
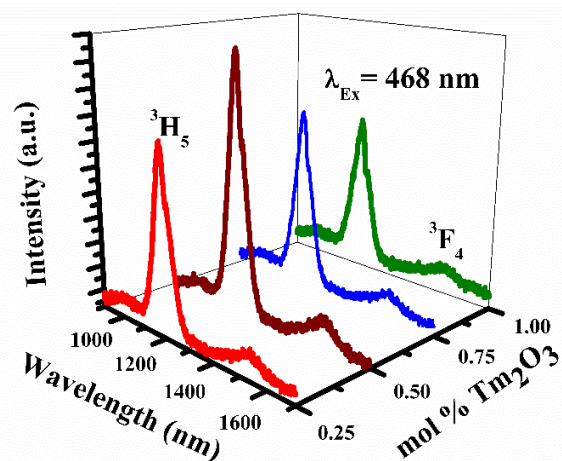
Figure 3 (b). Emission spectra of different mol % Tm_2O_3 glasses.

Fig. 3 (a) shows the excitation spectra of 0.75 mol % Tm_2O_3 containing glasses as representative at an emission wavelength of 1195 nm. The spectra show three excitation bands at 358, 468, and 596 nm from the ground state $^3H_6$ of the Tm^{3+} to various excited states. These bands are identified as $^1D_2$, $^1G_4$ and $^3F_2$ after comparing with the literature [2]. Amongst all, the $^1G_4$ was the most prominent band and it was selected to study the emission properties of the Tm^{3+} ion containing glasses. Fig. 3 (b) shows the emission spectra of glasses for different mol % of Tm^{3+} ions. These spectra contain a prominent band at 1195 nm along with a broad hump at around 1544 nm. These emission bands correspond to the $^3H_4 \rightarrow {}^3H_5$ and $^3H_4 \rightarrow {}^3F_4$ transitions of the Tm^{3+} ions. Fig. 4 (a) gives the intensity variation of the $^3H_4 \rightarrow {}^3H_5$ and $^3H_4 \rightarrow {}^3F_4$ transitions as function of composition. It is observed that the emission intensity increased up to 0.5 mol % Tm_2O_3 and decreased with further addition of the Tm^{3+} ions. This effect was due to concentration quenching and came in to effect because of the increase number of Tm^{3+} ions in the glass matrix [11].
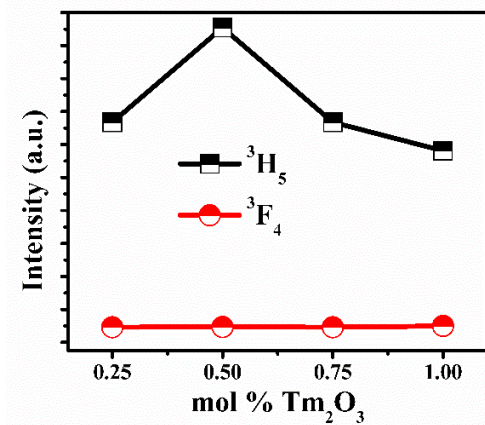
Figure 4 (a). Emission intensity variation with mol % Tm_2O_3.
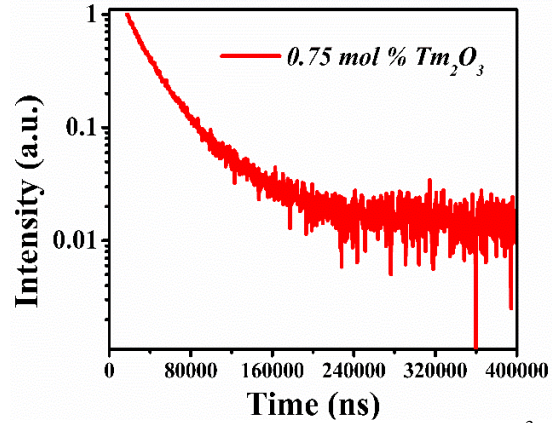
Figure 4 (b) Florescence decay profile of the $^3H_5$ state of the 0.75 mol % Tm^{3+} ion containing glass.

Table 3. Emission band positions (λ_p, *nm*), effective bandwidths ($\Delta\lambda_{eff}$, *cm^{-1}*), radiative transition probabilities (*A, s^{-1}*), peak stimulated emission cross-sections (σ_p x10^{-22}cm^2), branching ratios (β_R) and lifetime (τ_{exp} *μs*) of $^3H_4$ state of Tm_2O_3 containing glasses.

SN	Transitions	Parameter	Tm1	Tm 2	Tm 3	Tm 4
1	$^3H_4 \rightarrow {}^3H_5$	λ_p	1195	1195	1195	1195
		$\Delta\lambda_{eff}$	193.48	209.48	191.34	204.25
		A	2.2	12.35	9.23	8.2
		σ_p	164	968	668	730
		β_R *(exp)*	0.49	0.55	0	0.48
		β_R *(cal)*	0.001	0.01	0.02	0.01
2	$^3H_4 \rightarrow {}^3F_4$	λ_p	1544	1544	1544	1544
		$\Delta\lambda_{eff}$	274.73	257.24	242.31	239.14
		A	200	62.8	41	40.56
		σ_p	2943	6922	4915	6075
		β_R *(exp)*	0.51	0.45	0	0.52
		β_R *(cal)*	0.11	0.07	0.07	0.07
3	*Lifetime (τ_{exp} μs)*		53.88	38.61	29.13	22.18

By using the emission spectra of the prepared glasses the values of the branching ratio (β_R), stimulated emission cross-section (σ_P) and effective line width of the transition (λ_{eff}) were calculated by using the following relations [12, 13]:

$$\beta_R(\Psi J, \Psi' J') = \frac{A(\Psi J, \Psi' J')}{A_T(\Psi J)} \tag{3}$$

$$\sigma_P = \frac{\lambda_P^4 A}{8\pi c n^2 \Delta\lambda_{eff}} \tag{4}$$

where A is the transition probability of the upper excited state, A_T is the total transition probability, n is the refractive index, λ_P peak wavelength and λ_{eff} is the effective line width of the transition given by

$$\lambda_{eff} = \frac{1}{I_{max}} \int I(\lambda) \, d\lambda \tag{5}$$

I is the fluorescence intensity and I_{max} is the maximum intensity. The obtained values are presented in Table 3.

From the table it is clear that the emission cross section (σ_p) has the highest values for the 0.5 mol % Tm_2O_3 containing glasses. The $^3H_4 \rightarrow ^3F_4$ transition has the highest values of σ_p and branching ratio among the observed transitions. A big difference between the theoretical and experimental values was observed, the theoretical calculations, however, does not consider all the processes involved in the excitation and emission. These values are useful in justifying the application of these glasses for lasers. Thus the 0.5 mol % Tm^{3+} ions containing glasses are the best for laser application and telecommunication.

The decay curves of the $^3H_4$ transition were recorded at room temperature under 468 nm excitation by monitoring the emission at 1195 nm and are showed in Fig. 4(b) for different mol % of Tm_2O_3. On analyzing these curves it was observed that they were non-exponential in nature after 0.5 mol % Tm^{3+} containing glasses. The measured lifetimes of the $^3H_4$ state are depicted in Table 3 for the different concentrations of the Tm^{3+} ions. It is clear that the decay times decreased with an increase in Tm^{3+} ion concentration, the shorting of the life time and deviation from the exponential behavior was mainly due to the concentration quenching in the life time of the $^3H_4$ state. It is therefore clear that there was an energy transfer amongst the Tm^{3+} ions at higher concentrations.

Conclusions

The structural and spectroscopic properties of lithium borate glasses with different concentration of Tm_2O_3 were successfully studied. J-O intensity parameter were calculated for all prepared compositions. Ω_2 intensity parameter decreased with Tm^{3+} ion concentration showing an increase in ionic bonding in the glasses. A decrease in Ω_4 and Ω_6 parameter showed that the rigidity of the glasses decreased with Tm^{3+} ion concentration. Emission spectra of the prepared glasses showed four prominent bands which belongs to the $^3F_2$, $^3H_4$, $^3H_5$ and $^3F_4$ transitions. The emission intensity of the glasses increased up to 0.5 mol % Tm_2O_3 and decreased with further addition.

Acknowledgements

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