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Luminescence Studies on Eu^{3+} Doped Telluro-Borate Glasses for Laser and LED Applications

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Abstract

A new series of Eu^{3+} ions doped telluroborate glasses have been prepared with the chemical composition $(55-x)B_2O_3 + 25TeO_2 + 10K_2O + 10Bi_2O_3 + xEu_2O_3$ (where x=0, 0.25, 0.5, 0.75, 1 and 2 in wt%) following the melt quenching technique. The Luminescence spectra for all the titled glasses exhibit five emission bands corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J=0, 1, 2, 3, 4) transitions located at 577 nm, 592 nm, 613 nm, 652 nm and 702 nm. The Judd-Ofelt intensity parameters have been used to calculate the radiative properties such as transition probability (A), branching ratio (β_R), stimulated emission cross-section (σ_P) and radiative lifetime (τ_R) for the various emission transitions of the Eu^{3+} ions. Luminescence quenching has been observed beyond 1 wt% Eu^{3+} ions concentration and is due to the interaction takes place between the Eu^{3+} ions at higher concentration. The decay curves possess single exponential behavior uniformly for all the titled glasses and the experimental lifetime values were obtained following the curve fitting method.

Keywords: Telluroborate glasses, luminescence, Judd-Ofelt parameters, stimulated emission cross-section

1. Introduction

Rare earth (RE) ions doped glasses play a most significant role in the field of photonics including the design and fabrication of new optical devices such as color display devices, solid state lasers, sensors, telecommunication and semiconductors induced LEDs etc., [1,2]. RE ions doped glasses draw a great deal of attraction among the researchers due to their key features such as inhomogeneous distinct visible emission, better thermal stability, less expensive and simple manufacturing process. Among the oxide glasses, telluroborate glasses are known to be the best host matrices because of their good optical quality, higher transparency, low melting temperature, high refractive index and high dielectric constant. Among the several RE^{3+} ions, Eu^{3+} ions acquire much attention because of their narrow band emission (almost monochromatic) around 613 nm (Red emission) due to the $^5D_0 \rightarrow {}^7F_2$ transition and higher quantum yield. The present work reports Luminescence behavior of the Eu^{3+} doped B_2O_3–TeO_2–K_2O–Bi_2O_3–glasses. The motivation of the present study is to (i) synthesis Eu^{3+} doped telluroborate glasses following melt quenching (ii) evaluate the Judd-Ofelt (JO) parameters (Ω_λ, λ=2, 4, 6) (iii) estimate the radiative properties of the Eu^{3+} ions and finally (iv) to determine the experimental lifetime of the $^5D_0$ metastable state of the Eu^{3+} ions.

2. Experimental

Eu^{3+} doped telluroborate glasses were prepared following the conventional melt quenching technique with high purity (99.99%) chemicals from

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Sigma-Aldrich as starting materials. The 15gm batch of the chemical composition (55–x) B_2O_3 + 25TeO_2 + 10K_2O + 10Bi_2O_3 + xEu_2O_3 (where x = 0, 0.25, 0.5, 0.75, 1 and 2 in wt% named as BTPxE) were weighed and thoroughly mixed in an agate mortar to obtain homogeneous mixture. The chemical mixtures were taken into a porcelain crucible and kept in an electrical furnace at 1080 °C for 2 hrs. The melt was then poured onto a preheated brass plate and pressed by another brass plate to obtain uniform thickness. The prepared glasses were annealed for 8 hrs at 350 °C to remove the thermal strain and to improve the mechanical strength. Luminescence spectra of the prepared glasses were recorded at room temperature (RT) using Perkin Elmer LS55 spectrophotometer with a spectral resolution of ±1.0 nm and the lifetime measurements were carried out employing Sciencetech modular spectrometer using xenon flash lamp an excitation source.

3. Excitation and Emission Spectra

The inset of figure 1 shows the excitation spectrum of the BTP1E glass and the sharp intense peaks around 200–600 nm are mainly attributed to the f–f transitions of Eu^{3+} ions. The observed excitation bands are assigned to the various electronic transitions of Eu^{3+} ions such as $^7F_0 \rightarrow {}^5D_4$ (363 nm), $^7F_0 \rightarrow {}^5G_2$ (376 nm), $^7F_1 \rightarrow {}^5L_7$ (381 nm), $^7F_0 \rightarrow {}^5L_6$ (395 nm), $^7F_0 \rightarrow {}^5D_3$ (415 nm), $^7F_0 \rightarrow {}^5D_2$ (465 nm), $^7F_0 \rightarrow {}^5D_1$ (526 nm), $^7F_1 \rightarrow {}^5D_1$ (533 nm) and $^7F_0 \rightarrow {}^5D_0$ (578 nm) transitions. It is observed from the excitation spectrum that, the $^7F_0 \rightarrow {}^5D_2$ band possesses strong excitation at 465 nm and is used as a source of excitation wavelength for the emission spectral measurements of the present glasses.

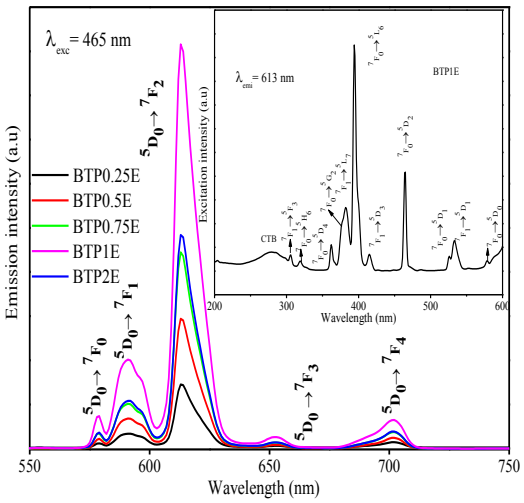

Figure 1. Luminescence spectra of the BTPxE glasses [Inset shows the excitation spectrum of the BTP1E glass]

The emission spectra of the prepared BTPxE glasses have been recorded as a function of Eu^{3+} ions concentration exciting at 465 nm and the same is shown in figure 1. The emission spectra exhibit five emission bands at around 577, 592, 613, 652 and 702 nm in the visible region corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) transitions and the $^5D_0 \rightarrow {}^7F_5$ emission transition found to occur in the near infrared region could not be observed because of the experimental limitations [3]. Among the emission bands, $^5D_0 \rightarrow {}^7F_2$ (613 nm) electric dipole allowed transition exhibit strong red emission and its intensity is hypersensitive to the environment around the Eu^{3+} ions. Whereas the $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole allowed and its intensity is independent of the environment around the Eu^{3+} ions [2]. It can be used for the estimation of transition probabilities of various excited levels. The luminescence intensity ratio (R) is defined as the ratio between the integrated intensity of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions and it is used to determine the nature of the chemical environment around the Eu^{3+} ions thus provides information pertaining to the

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strength of covalent/ionic bonding. Higher R values indicate the higher asymmetry around the Eu^{3+} ion site in the present glasses. It is observed from table 1 that the increase in R value upto 1 wt% of Eu^{3+} ions concentration thus indicate that asymmetry around the Eu^{3+} ions increases due to the formation of bonds between different network formers like B–O–Eu–O–Te [3]. The characteristic emission of the prepared glasses are made through CIE 1931 chromaticity coordinates and the (x,y) coordinates of the title glasses are presented in table 2. The inset of figure 2 shows the CIE 1931 chromaticity diagram and it is observed that the all the coordinates are found to lie in the reddish orange region.

Table 1. Luminescence intensity ratio (R), Judd-Ofelt parameters ($\Omega_\lambda \times 10^{-20} cm^2$) of the Eu^{3+} telluroborate glasses

Glass code	R	JO Parameters			Trends of Ω_λ
		Ω_2	Ω_4	Ω_6	
BTP0.25E	3.54	5.58	0.73	0	$\Omega_2 > \Omega_4 > \Omega_6$
BTP0.5E	3.63	5.69	0.77	0	$\Omega_2 > \Omega_4 > \Omega_6$
BTP0.75E	3.73	5.74	0.82	0	$\Omega_2 > \Omega_4 > \Omega_6$
BTP1E	3.91	5.95	0.89	0	$\Omega_2 > \Omega_4 > \Omega_6$
BTP2E	3.89	5.80	0.76	0	$\Omega_2 > \Omega_4 > \Omega_6$

4. Judd-Ofelt Analysis and Radiative Parameters

In case of Eu^{3+} ions, determination of Judd-Ofelt (JO) parameters following the least square fit procedure is not applicable due to the zero magnitude of matrix elements $\|U^\lambda\|^2$. The Judd-Ofelt intensity parameters (Ω_2, Ω_4, Ω_6) provide valuable information such as Ω_2 is related to the short-range effects such as polarizability of the ligand ions, Ω_4 and Ω_6 parameters are related to the long-range effects such as viscosity and rigidity of the glass [4]. The JO theory of trivalent europium ion possesses serious difficulties, because of the availability of few absorption transitions in the absorption spectra originate from the $^7F_0$ and $^7F_1$ states to the various excited states such as $^5D_1$, $^5D_2$ and $^5L_6$. Hence emission spectra of the Eu^{3+} ions are used to determine the JO parameters of the Eu^{3+} ions. Peng and Izumitani [3] used the electric dipole transitions $^5D_0 \rightarrow {}^7F_2$, $^7F_4$ and $^7F_6$ of the Eu^{3+} ions to determine the JO parameters. The luminescent intensity of the magnetic dipole allowed transition ($^5D_0 \rightarrow {}^7F_1$) is independent of the crystal field around the Eu^{3+} ions.

This property of the $^5D_0 \rightarrow {}^7F_1$ transitions is used to estimate the transition probability of the various electric dipole transitions such as $^5D_0 \rightarrow {}^7F_J$ (2,4,6) and are used to determine the JO parameters (Ω_λ, λ=2, 4, 6). The $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ emission transitions could not be observed due to the experimental limitations and the Ω_6 parameter is negligible in the determination of radiative lifetime of Eu^{3+} ions. The Judd-Ofelt parameters of the title glasses have been calculated and the results are presented in table 1. The trends of the JO parameters are found to be in the order $\Omega_2 > \Omega_4 > \Omega_6$ uniformly for all the prepared glasses. The higher Ω_2 value is often an indication of higher covalence and higher asymmetry around the Eu^{3+} ions site and is further confirmed through the luminescence intensity ratios of the prepared glasses.

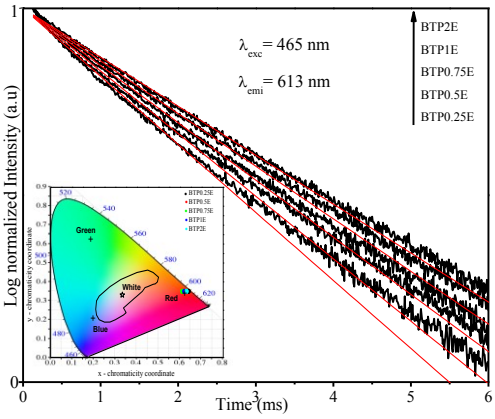

Figure 2. Decay curve of the $^5d_0$ excited state of the eu^{3+} doped teullroborate glasses

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Table 2. Emission band position (λ_p, nm), effective bandwidth ($\Delta\lambda_{eff}$, nm), radiative transition probability (A, s^{-1}), stimulated emission cross-section ($\sigma_p \times 10^{-22}$ cm^2), experimental, calculated branching ratio (β_R) and CIE 1931 coordinates of the BTPxE glasses

Transition	Parametes	BTP 0.25E	BTP 0.5E	BTP 0.75E	BTP 1E	BTP 2E
$^5D_0 \rightarrow {}^7F_0$	λ_p	578	578	579	578	578
	$\Delta\lambda_{eff}$	2.51	2.41	2.62	2.42	2.32
	A	0.00	0.00	0.00	0.00	0.00
	σ_P	0.00	0.00	0.00	0.00	0.00
	β_R(Exp)	0.022	0.023	0.024	0.026	0.024
	β_R(Cal)	0.00	0.00	0.00	0.00	0.00
$^5D_0 \rightarrow {}^7F_1$	λ_p	592	590	591	591	591
	$\Delta\lambda_{eff}$	6.27	6.48	6.08	6.38	6.17
	A	60.2	59.6	59.4	58.3	55.5
	σ_P	5.96	5.73	6.12	5.79	5.87
	β_R(Exp)	0.18	0.19	0.17	0.18	0.18
	β_R(Cal)	0.20	0.20	0.193	0.203	0.195
$^5D_0 \rightarrow {}^7F_2$	λ_p	613	613	613	613	613
	$\Delta\lambda_{eff}$	5.20	5.00	5.18	5.25	5.12
	A	223.4	208.7	231.7	244.5	214.3
	σ_P	30.9	30.1	32.4	33.1	31.6
	β_R(Exp)	0.707	0.692	0.708	0.713	0.712
	β_R(Cal)	0.749	0.734	0.754	0.758	0.755
CIE	x	0.64	0.64	0.61	0.62	0.63
	y	0.35	0.35	0.35	0.35	0.35

The JO parameters have been used to calculate the radiative properties such as radiative transition probability (A), stimulated emission cross-section (σ_p), radiative lifetime (τ) and branching ratios (β) for the $^5D_0 \rightarrow {}^7F_J$ (J=0,1,2,3,4) transitions and the results are presented in table 2. The radiative transition probability (A) and the stimulated emission cross-section value of the $^5D_0 \rightarrow {}^7F_2$ transition are found to be higher for all the prepared BTPxE glasses compared to the other transitions and the values are presented in table 2. The experimental branching ratio values of the $^5D_0 \rightarrow {}^7F_2$ transition are found to be 0.675, 0.707, 0.692, 0.708, 0.713 and 0.712 for the BTP0.1E, BTP0.25E, BTP0.5E, BTP0.75E, BTP1E and BTP2E glasses respectively and is quite comparable to the branching ratio values estimated using JO theory.

5. Decay Curve Analysis

Luminescence decay profile of the prepared Eu^{3+} doped telluroborate glasses have been recorded by monitoring an excitation at 465 nm and emission at 613 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition and the same is shown in figure 2. It is clearly observed from the figure that, the decay curve exhibits single exponential behavior for all the prepared glasses and the experimental lifetime values were evolved by fitting with a single-experimental function $I_t = I_0 e^{-t/\tau}$, where I_t and I_0 is the emission intensity at time 't' and at t=0 respectively, τ is the lifetime of the excited state energy level.

The calculated (τ_{cal}) and experimental (τ_{exp}) lifetime values for the $^5D_0$ level are found to be3.332, 3.355, 3.517, 3.260, 3.468, 3.527 ms and 1.192, 1.316, 1.517, 1.526, 1.878, 1.7694 ms corresponding to the BTP0.1E, BTP0.25E, BTP0.5E, BTP0.75E, BTP1E and BTP2E glasses respectively.

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