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Spectroscopic studies of single near ultraviolet pumped Tb^{3+} doped Lithium Lead Alumino Borate glasses for green lasers and tricolour w-LEDs

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ABSTRACT

Terbium ions (Tb^{3+}) doped Lithium Lead Alumino Borate (LiPbAlB) glasses with the chemical composition $10Li_2O$ – 10PbO – (10-x) Al_2O_3 – $70B_2O_3$ – xTb_2O_3 (where x = 0.5, 1.0, 1.5, 2.0 and 2.5 in mol%) were synthesized via melt quench method and characterized by absorption, photoluminescence (PL) and PL decay spectral measurements. The Judd-Ofelt (J-O) intensity parameters evaluated from the oscillator strength values are further used to evaluate the radiative parameters for the prominent fluorescent levels ($^5D_4 \rightarrow {}^7F_j$) of Tb^{3+} ions. The intensity of all the emission bands increases up to 2 mol% of Tb^{3+} and beyond concentration quenching took place. The decay profiles of $^5D_4$ show single exponential for lower concentration and non-exponential for higher concentration resulting decrease in experimental lifetime (τ_{exp}) with increase in rare earth ion concentration. Such decrease in τ_{exp} and decay conversion from single to non-exponential has been attributed to the cross-relaxation processes and subsequent concentration quenching observed. The Inokuti-Hiryama (I-H) model applied to the decay spectral profiles confirms the energy transfer process between Tb^{3+}-Tb^{3+} ions as dipole-dipole in nature. Higher values of stimulated emission cross-section, quantum efficiency, gain bandwidth and optical gain obtained for $^5D_4 \rightarrow {}^7F_5$ transition of LiPbAlB glass with 2 mol% of Tb^{3+} ions suggests its suitability for green lasers. The CIE-chromaticity co-ordinates, color purity (CP) and correlated color temperature (CCT) confirms the suitability of these glasses in tricolor w-LEDs.

1. Introduction

Recently the scientific interest in fabrication and characterization of glasses doped with rare earth (RE) ions have attracted many scientist because of their applications in diversified fields such as lasers, optical waveguides, hole burning memories and white Light Emitting Diodes (w-LEDs) [1–6]. RE doped glasses are also useful in fabricating visible and infrared optical devices due to the transitions observed within their 4f shells. Quite recently, the lighting industries have witnessed tremendous growth because of the replacement of conventional lighting sources with w-LEDs. It is because of the fabulous characteristics features of w-LEDs such as longer lifetime, environment friendly nature, higher reliability and lower fabrication cost [7,8]. The commercial approach for fabricating w-LED is to combine blue emitting LED InGaN chip with yellow emitting YAG:Ce^{3+}phosphor. However this method suffers from halo effect and poor Color Rendering Index (CRI) [9,10]. To overcome these drawbacks, scientists have adopted another method in which RGB phosphors are excited with Near Ultra Violet (NUV) LEDs. This method helps in improving CRI and minimizing the halo effect [8–10]. Nevertheless in both the methods, phosphors are encapsulated in an epoxy region, which gets deteriorated at higher temperatures, energy and excitation sources resulting in reducing the output gradually. Quite recently RE ions doped glasses are considered to be the potential candidates for fabricating w-LEDs as there is no epoxy region present in the glasses. The design as well as development of RE doped glassy systems for the aforementioned application needs the thorough study of optical properties by using absorption, PL and PL decay spectral analysis. The optical property of doped glasses highly depends upon the environment surrounded by RE ions in the amorphous matrix and on phonon energy of the host matrix.

Among the glass former available, borates are said to be the excellent hosts matrices for RE ions due to their unique properties such as high transparency, thermal stability, good RE ion solubility and lower melting point [11]. Despite having the aforementioned fantastic advantages, borate glasses are encountering a major setback due to their high phonon energies (1300 cm^{-1}). Presence of such redundant phonon energies in borate glasses can reduce the radiative emissions in them. Consequently emission cross-sections and quantum efficiency of borate glasses are getting effected very badly [12]. To overcome this drawback, some heavy metal oxides (HMO) such as lead oxide (PbO) or

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bismuth oxides (Bi_2O_3) can be added to B_2O_3 [13]. Depending upon the concentration of PbO in B_2O_3, it acts as a network modifier or as a network former. As the Pb^{2+} content in the boron network increases, conversion from BO_3 to BO_4 units takes place which may be a strong reason for suppressing the non-radiative decay process [14]. Addition of aluminium trioxides (Al_2O_3) to B_2O_3-PbO network can improve mechanical strength and thermal stability [15]. Al^{3+} ions involve in the glassy network along with AlO_4 and AlO_6 structural units and combine to evaluate the radiation sensitivity of glass system [16]. Introducing lithium oxide (Li_2O) in a ternary system (PbO-Al_2O_3- B_2O_3) can enhance stability, produce moisture resistance and remove air bubbles from the glassy matrix. Further, it can increase the glass transition temperature (T_g) and reduces thermal expansion coefficient [6,17]. Considering the aforementioned valuable scientific patronages offered by the chemical constituents such as B_2O_3, PbO, Al_2O_3 and Li_2O, in the present work we prepared a glassy system namely Lithium Lead Alumino Borate (LiPbAlB) glass.

Among the RE ions, Tb^{3+} is the most efficient ion for strong green emission, originating from $^5D_4 \rightarrow {}^7F_5$ transition located at 544 nm. The luminescence intensity of Tb^{3+} ions doped matrices depend upon the excitation wavelength, host matrix composition and Tb^{3+} ions concentration. Recently, Tb^{3+} doped glassy systems in large industrial scale were synthesized and studied by using their PL spectroscopy [18]. When Tb^{3+} ions doped glassy systems are pumped by NUV light, two types of energy transfer takes place from $^5D_3 \rightarrow {}^7F_j$ (blue emission) and $^5D_4 \rightarrow {}^7F_j$ (green emission) where $j = 0$ to 6, therefore the PL property is very useful for evaluating energy level structure as well as for identifying different transitions present in the system [19]. Tb^{3+} doped glasses can also be pumped by co-operative energy transfer process in which the excited Yb^{3+} ions simultaneously transfer its energy to an unexcited Tb^{3+} ion. Many researchers have reported the co-operative energy transfer between Yb^{3+} to Tb^{3+} [20–23]. Nowadays, Tb^{3+} doped materials are attracting researchers as well as industry due to their diversified applications in w-LEDs, solid state lasers, evolution of electromagnetic transmission window of sea water and green color emitting phosphors [24,25]. In this report, the role of Tb^{3+} ions in LiPbAlB glass has been studied thoroughly using spectroscopic techniques such as absorption, PL and PL decay spectra to understand the utility of these glasses in green lasers as well as in tricolor w-LEDs.

2. Experimental

Tb^{3+} doped LiPbAlB glasses with the nominal molar composition $10Li_2O$-10PbO-(10-x) Al_2O_3 $-70B_2O_3$-xTb_2O_3, where x is 0.5, 1.0, 1.5, 2.0 and 2.5 in mol% were synthesized by using conventional melt quenching technique. For convenience these glasses are designated as glass A, B, C, D and E. All the raw materials used in the present work such as Li_2O, PbO, Al_2O_3, B_2O_3 and Tb_2O_3 are of analar grade in quality. The above constituents in the given proportions were melted in a silica crucible by heating at 1100 °C in an electrical furnace for about 5 h and the desired melts were prepared. The melts were then quenched between two preheated brass plates to form the glass samples of uniform thickness. The glasses were annealed for 4 h in another electrical furnace at 350 °C to eliminate thermal strains and to improve structural stability. The resultant glasses are amorphous and transparent with 3 mm thickness and used directly for their optical characterization.

Densities of the as-prepared glasses were measured by using Archimedes principle taking water as an immersion fluid with an accuracy of ± 0.01 g/cm^3. Brewster's angle method was employed to determine the refractive index of titled glasses using He-Ne laser (650 nm line) with $\pm$ 0.01 accuracy. The optical absorption spectra for glasses were recorded by using a Perkin Elmer Tensor-27 UV–vis–NIR spectrophotometer in the wavelength range of 350–550 nm having a spectral resolution of 0.1 nm. The PL spectra for the titled glasses were recorded using Shimadzu RF-5310 PC-Spectrofluorophotometer with a spectral resolution of 0.5 nm in a steady state mode. The PL decay spectral recordings were done using an Edinburgh FLSP900 Fluorescence Spectrometer with a spectral resolution of 0.1 nm taking xenon lamp as an excitation source.

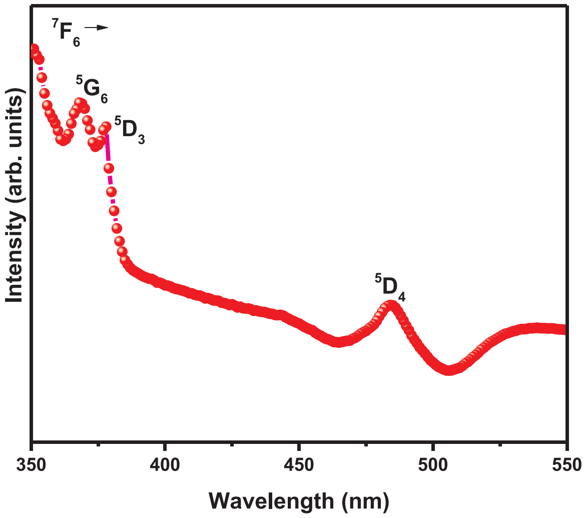

Fig. 1. Absorption Spectrum of 2.0 mol% of Tb^{3+} ions in LiPbAlB glass.

3. Results and discussion

3.1. Absorption spectral analysis and J-O parameters

The absorption spectrum of 2 mol% Tb^{3+} ions in LiPbAlB glass (Glass D) is shown in Fig. 1 as a representative. While the rest of the absorption spectra for various Tb^{3+} concentrations show similar band positions but their respective absorption intensities and absorption band edges shows systematic variation with concentration, which will be discussed in the following sections. From Fig. 1 it can be seen that all the transition starts from the ground state ($^7F_6$) of Tb^{3+} ions and consists of 3 transitions corresponding to $^7F_6 \rightarrow {}^5G_6$, $^5D_3$ and $^5D_4$. The band assignments have been done as per the Carnall report [26]. All the absorption bands are originated from induced electric dipole-dipole transition following the selection rules $\Delta S = 0$, $|\Delta L| \le 6$, $|\Delta J| \le 6$ [27]. From Fig. 1 it can be noticed that Tb^{3+} ions in LiPbAlB glass shows weak absorption in UV/blue region, which is due to the forbidden character of 4f-4f transition. The absorption spectra are used to evaluate oscillator strengths by taking area under the absorption curves using the procedure explained elsewhere [5,28–31]. The energy levels within the $4f^5$ configuration of the Tb^{3+} ion have been examined applying J-O theory [27,32] to the experimental oscillator strengths. The values of J-O intensity parameters thus estimated are presented in Table 1 along with some reported values [25,33–35].

The J-O intensity parameters (Ω_2, Ω_4 and Ω_6) will play a vital role in understanding the glass structure as well as transitions among the RE

Table 1
Judd-Ofelt Parameters ($\Omega_\lambda \times 10^{-20}$ cm^2) of Tb^{3+} ions in LiPbAlB glasses along with other reported values.

Glass System	Ω_2	Ω_4	Ω_6	Trend	References
Glass A	1.37	0.95	0.19	$\Omega_2 > \Omega_4 > \Omega_6$	present work
Glass B	1.39	1.06	0.23	$\Omega_2 > \Omega_4 > \Omega_6$	present work
Glass C	1.41	1.21	0.28	$\Omega_2 > \Omega_4 > \Omega_6$	present work
Glass D	1.48	1.34	0.32	$\Omega_2 > \Omega_4 > \Omega_6$	present work
Glass E	0.84	0.64	0.22	$\Omega_2 > \Omega_4 > \Omega_6$	present work
ZnAlBiBTb1.0	7.60	16.7	2.69	$\Omega_4 > \Omega_2 > \Omega_6$	[21]
$TbAlO_3$	40.5	8.74	2.26	$\Omega_2 > \Omega_4 > \Omega_6$	[29]
TbGAGSe	7.50	4.40	2.40	$\Omega_2 > \Omega_4 > \Omega_6$	[30]
TbSFB	0.45	5.53	1.39	$\Omega_4 > \Omega_6 > \Omega_2$	[31]