

Synthesis and Luminescence Properties of LaB₃O₆ Doped with Eu³⁺, Dv³⁺ and Tb³⁺

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ABSTRACT

In the present investigation, photoluminescence properties of rare earth doped LaB₃O₆ phosphors were investigated. Eu³⁺, Dy³⁺ and Tb³⁺ are used as rare earth ions for this investigation. Series of Eu³⁺, Dy³⁺ and Tb³⁺ doped LaB₃O₆ phosphors were synthesized sing solid state diffusion method. Powder X-ray diffraction technique (XRD) along with CIE color coordinates including their PL properties with emission intensity effect too were analyzed for the characteristics of prepared phosphors. Effect of heating time during synthesis and concentration of Eu³⁺ on PL properties of LaB₃O₆ was investigated and observed that increasing the heating time of synthesis changes the emission of Europium from blue to red i.e. Eu²⁺ to Eu³⁺. The emission spectra of Dy³⁺: LaB₃O₆ phosphors show two strong bands in blue and yellow regions and can be useful for solid state lighting in lamp industry. LaB₃O₆: Tb³⁺ may be predicted as a promising green phosphor candidate for applications in LED based solid state lighting or other display devices because of its excitation at 379nm.

Keywords : - Solid state method, X-ray diffraction technique (XRD), Photoluminescence, CIE, LED

I. INTRODUCTION

With the development of society, people requirements for display and relative light source are increasing continuously. Therefore from the past few years, much attention has been paid to the study of vacuum ultraviolet (VUV) and ultraviolet (UV) phosphors due to the demand of Plasma Display Panels (PDPs), emission Displays (FEDs) and light Emitting diodes (LEDs) [1–3]. To fulfill these requirements, high power light source such as high power LEDs and LASER (Light Amplification by Stimulated Emission of Radiation) has gradually become the research hotspot. Modern optoelectronic devices require phosphor materials (luminophores) to convert UV or near UV blue radiation into light. Lanthanide doped compounds have played outstanding roles as phosphors in lighting, flat panel displays, optical telecommunication, and as active materials in solid state lasers [4–6]. There are different kind of inorganic phosphors based on lanthanides such as oxides, silicates, aluminates (garnets), phosphates and borates. The last group rare earth borate phosphor is recently studied and reveals quite promising. Borate based compounds are of high

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chemical and photolytic stability and can be efficiently doped with Eu³⁺, Tb³⁺, Nd³⁺ and other lanthanide ions. Lithium tetra borate Li₂B₄O₇ (LTB) was the first borate synthesized in England [7]. About 65% of known borate compounds have crystallo chemical structures characterized by BO3 triangles which are either isolated or joined with each other. Such anionic units form ionic bonds with metal cations. Such structures are typically ortho, pyro and meta borates. In polyborates, the triangles are joined both with each other and with tetrahedrons by the common oxygen atom [8]. A large number of borate compounds are transparent over a wide spectral range, beginning from VUV and extending into infrared (IR). This is one of the reasons that borate compounds become important optoelectronics materials. Many researches are studying borate compound based materials for nonlinear optics, acousto electronics, piezotechnique and dosimeter and also because of large band gap, they are good choice as host lattices for luminescent ions. Borate compounds like BaB₂O₄ [9], LiB₃O₅ [10], CsLiB₆O₁₀ [11] and K₂Al₂B₂O₇ [12] possess high nonlinear optical (NLO) coefficient. Eu³⁺ and Tb³⁺ doped borates are often used as luminescent materials, because of their optimized properties which allow them to withstand the harsh condition in vacuum discharge lamps or screens. Rare earth doped borate phosphors have applications in various fields. Rare earth doped Ca₄GdO(BO₃)₃ [13,14] compounds are important solid state laser materials. YAl₃(BO₃)₄ doped with Nd³⁺ [15], as well as the 3d transition impurities also find applications in solid state lasers. Li2B4O7 can be useful for VUV laser [16]. Li₂B₄O₇: Cu²⁺ [17], and MgB4O7:Dy³⁺ [18] phosphors are used in commercial dosimetry systems based on thermoluminescence. Sr₂B₅O₉Cl: Eu also exhibits promising dosimetric characteristics [19]. doped Europium alkaline haloborates are also considered for the neutron radiography using photo stimulated luminescence (PSL). (Gd0.6Ce0.2Tb0.2) MgB5O10 is a green emitting phosphor used in the tricolour lamps [20]. SrB₄O₇:Eu²⁺

phosphor is used in commercial sun tanning lamps [21]. (La,Gd)B₃O₆: Bi is another borate based, UV emitting of phosphor commercial importance [22]. Cathodoluminescent phosphor InBO3:Tb³⁺ is used as a green emitting phosphor in projection color TV; application in neutrino detection has also been suggested [23], while Tb doped (Y,Gd)BO3 finds place as green emitting phosphor for plasma display panels (PDP) [24]. Other barium containing borates such as $Ba_5(B_2O_5)_2F_2$ [25] are good hosts for RE²⁺, while the RE stoichiometric borates are promising hosts for trivalent rare earth ions. Borate based luminophors may be applied in different devices like luminescent tubes and plasma display panels as well as LEDs. Borate phosphors are usually reported to be good luminescent material for plasma display panels [26]. Now a day, however it seems to be important to develop near UV to visible phosphors aimed for application in LED. In phosphor converted LEDs commercially available InGaN and GaN LED chips (420-480 nm and 360-370 nm, respectively) [4] are used as light source for phosphors excitation. This paper reports the synthesis of two borate compounds i.e. LaB₃O₆ doped with different concentrations of Eu³⁺, Dy³⁺ and Tb³⁺ using the high temperature solid state diffusion method. It also reports the investigations of synthesized borates morphology, structural and luminescence properties in detail, based on X-ray diffraction (XRD) profile and photoluminescence. CIE Color coordinates of prepared phosphors with standard one have also been reported.

II. Synthesis

The powder samples $La_{(1-x)}B_3O_6Eu_x$ (x=0.05,0.1,0.2,0.5,1m%) were synthesized using a solid state diffusion technique at high temperature. The starting materials used are of analytical grade La₂O₃, H₃BO₃ and rare earth oxide Eu₂O₃. The stoichiometric reactants were mixed and ground thoroughly in an agate mortar with acetone to get homogeneous mixture. Then the mixtures were heated at 800° C for



24 hrs and 48 hrs under air atmospheres. The final products were cooled down to room temperature and ground again into powder for further characterization. Other series of samples $La_{(1-x)}B_3O_6Ln_x$ (Ln = Dy, Tb and x=0.05,0.1,0.2,0.5,1m%) were synthesized by the same method at 800°C for 24 hrs.

The final products were cooled down to room temperature and ground again into powder for further characterization.

III. Measurements

The Phase of the prepared phosphor was examined by XRD with Cu-K α (λ = 15418Å) radiation at 40 kV and 30 mA. The photoluminescence measurements were carried out using Shimadzu RF-5301 PC fluorescence spectrophotometer equipped with a 150W Xenon lamp as the excitation source at room temperature and setting the excitation and emission slits at 1.5 nm. The Commission International de I'Eclairage (CIE) color co-ordinates were obtained using Radiant Imaging color calculator software.

IV. Results and discussion

4.1 Phase identification and morphology

In order to check the phase purity and phase structure, powder XRD measurements were carried out. Figure 1 shows the XRD pattern of LaB₃O₆: Eu³⁺ phosphor. The entire diffraction peaks are in good agreement with those in JCPDS file no. 01-073-1150, indicating that the obtained sample is single phase. The pattern exhibit the formation of single-phase compound with the monoclinic structure belonging to the I2/a space group with lattice parameter (a=7.9560Å, b=8.172 Å, c= 6.4990 Å, β =93.6300 Å), without any secondary or impurity phases.



Figure 1 : XRD pattern of LaB₃O₆: Eu and JCPDS standard card no. 01-073-1150.

4. 2 Infra red spectral analysis

To analyze the presence of functional groups in LaB₃O₆ qualitatively, we recorded Fourier transform infra-red (FTIR) spectrum in the range 375- 3975 cm⁻¹ using Shimadzu IR affinity-1 infrared spectrometer (Figure 2). The bands observed in the 900-1350 cm⁻¹ region in the FTIR spectrum are characteristics of BO₃ asymmetric and symmetric stretching vibrations and are in agreement with other compounds containing BO₃ anionic groups [27,28]. The bands observed between 400 and 750cm⁻¹ are attributed to the bending vibrations of the BO₃ and BO₄ groups.



Figure 2 : Infra-red spectra of Eu³⁺ doped LaB₃O₆

4.3 Luminescence properties 4.3.1 LaB₃O₆: Eu³⁺ phosphor

The excitation spectrum of La0.99B3O6Eu0.01 prepared at 800° C for 24 hrs, 48 hrs and guenched at 800°C for 1 hr, using solid state diffusion method is shown in figure 3 (a, b and c). It shows broad excitation band in the wavelength range 220 nm to 300 nm peaking at 263 nm, which can be attributed to the charge transfer from $O^{2\text{-}}$ to $Eu^{3\text{+}}.$ The charge transfer from $O^{2\text{-}}$ to $Eu^{3\text{+}}$ in La0.99B3O6Eu0.01 lattice is observed very strong. Apart from the charge transfer band, some sharp lines were also seen in the excitation spectrum of Eu³⁺ with host, which corresponds to the f-f transitions, all originated from transitions within Eu^{3+} 4f⁶ configuration [29]. Increasing the heating time decreases the intensity of CT band and all other excitation peaks as shown in figure 3. Very few trivalent lanthanide's f-f transitions are sensitive to the environment and become more intense but mostly of them are not affected by the environment. Such transitions have been called hypersensitive transitions [30]. This luminescence feature can yield structure information of a different character from that obtained by X-ray diffraction. All emission spectra were normalized to the intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole transition, which is known to be largely independent on the environment of Eu³⁺ ion. The ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ emission is a strictly forbidden transition with the selection rule $D_J = 0$, if Eu^{3+} ion occupies an inversion symmetry site in the crystal lattice [2,30]. The magnetic dipole transitions ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ are insensitive to the site symmetry, because they are parity-allowed. Particularly, the forced electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ with $D_{J} = 2$ is hypersensitive, and the intensity can vary by orders of magnitude, depending on the local site symmetry [2,30]. Upon excitation at 395 nm, the Eu³⁺ ions are promoted from the ground state to ⁵L₆ state and relax to ⁵D₀ energy level following a non- radiative process. The 5D0 level is populated and thus responsible for the fluorescence at $^{7}F_{J}$ (J = 0–2) energy levels.



Figure 3: Excitation spectra of sample LaB₃O₆:Eu³⁺ prepared (a) at 800° C for 24 hrs, (b) at 800° C for 48 hrs and (c) quenched at 800° C for 1 hr.

The emission spectrum of Eu³⁺ doped LaB₃O₆ prepared at 800°C for 24 hrs and 48 hrs is shown in figure 4 and 5 respectively. Figure 6 shows the emission spectrum of Eu³⁺ doped LaB₃O₆ quenched at 800°C for 1 hr. It is seen from figure 4 and 5 that with increase in temperature, Eu changes from Eu²⁺ to Eu³⁺. It can be seen from figure 5 and 6, the stark splittings of the ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{0}$, ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$ and ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$ emission lines are 1(580 nm), 3 (588, 592 and 599 nm) and 2 (616 and 624 nm), respectively. The strongest emission peak situated at 588 nm showing prominent and bright orange spectra is due to the



magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$. A peak at 610 nm can be attributed to Eu3⁺ forced electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$. It is relatively weak, which indicates the Eu³⁺ site has inversion symmetry and ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ electric dipole transition is very weak.



Figure 4 : Emission spectra of sample LaB₃O₆:Eu³⁺ prepared at 800° C for 24 hrs.



Figure 5 : Emission spectra of sample LaB₃O₆:Eu³⁺ prepared at 800° C for 48 hrs.



Figure 6 : Emission spectra of sample LaB₃O₆:Eu³⁺ quenched at 800° C for 1 hr.

The maximum splitting of the F_J levels for a given site is (2J+1) where J is the angular momentum. Figure 7 shows the emission mechanism of Eu³⁺ ion showing stark splitting in LaB₃O₆ phosphors under 395nm excitation. In general, when the Eu³⁺ ion is located at crystallographic site without inversion symmetry, its hypersensitive forced electric-dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ red emission dominates in the emission spectrum. If the Eu³⁺ site possesses an inversion center, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ orange emission is dominant. The distinct emission lines between 580 and 650nm are observed due to transitions from excited ⁵D₀ to the ⁷F_J (J = 0-3) levels of Eu³⁺ ions. The origin of these transitions (electric dipole or magnetic dipole) from emitting levels to terminating levels depend upon the location of Eu³⁺ ion in LaB₃O₆ lattice and the type of transition is determined by selection rule [31]. The most intense peak in the vicinity of 588 nm is ascribed to the magnetic dipole transition of ⁵D₀ and ⁷F₁ levels. The weak emission at 616 and 624 nm corresponds to the hypersensitive transition between the ⁵D₀ and ⁷F₂ levels due to forced electric dipole transition mechanism. The presence of unique emission line at 580 nm (${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{0}$) indicates that Eu³⁺ occupies only one site in the lattice. The presence of both ED and MD electronic transitions in the emission spectra confirms that the site occupied



by Eu^{3+} in this host i.e LaB₃O₆ is not strictly Centro symmetric.



Figure 7 : Emission mechanism of Eu³⁺ ion showing stark splitting in LaB₃O₆ phosphors under 395nm excitation.

4.3.2 LaB₃O₆: Dy³⁺ phosphor

In general there are nine obvious excitation peaks of Dy³⁺, and are assigned to the transitions from the ground level ⁶H_{15/2} to higher levels based on the energy levels reported by Carnall et al. [32]. Figure 8 shows the excitation spectra of Dy³⁺ doped LaB₃O₆ phosphor. The excitation spectra shows the peak at 348 nm which have been assigned to the transition from the ground level ${}^{6}\text{H}_{15/2}$ to higher levels ${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{P}_{7/2}$ of Dy³⁺ [59]. At 348nm excitation, emission spectrum was measured in the 400-650nm range as shown in figure 9. The emission spectra have similar pattern for all the asprepared samples. Two emission peaks at 475nm (blue) and 575nm (yellow) are corresponding to ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transitions of Dy³⁺ ion, respectively. The ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transition has mainly been magnetically allowed and hardly varies with the crystal field strength around the Dy³⁺ ions [33]. The ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition is a forced electric dipole

transition being allowed only at low symmetries with no inversion centre [33].

Figure 10 shows the dependence of the luminescence intensity at 475 nm with the dopant ion Dy³⁺ concentration. The pattern of emission spectrum does not vary with the Dy3+ concentration but the luminescence intensity changes more significantly. It can be found that the emission intensity of Dy3+ increases with an increase of dopant ion concentration (x), it reaches to a maximum value at x = 0.01, and then decreases with an increase of dopant (x) due to concentration quenching [33]. The reason must be that when the concentration of Dy³⁺ continues to increase, the interaction increases and leads to self-quench. Therefore the emission intensity decreases. The concentration quenching of Dy³⁺ luminescence is mainly caused by cross-relaxation, i.e. energy transfers from one Dy³⁺ to another neighbor Dy³⁺ by transition that match in energy. These transitions are mainly Dy³⁺ $({}^{4}F_{9/2}) + Dy^{3+}({}^{6}H_{15/2}) \rightarrow Dy^{3+}({}^{6}F_{3/2}) + Dy^{3+}({}^{6}F_{11/2})[34,35].$



Figure 8 : Excitation spectrum of LaB₃O₆ :Dy³⁺.



Figure 9 : Emission spectrum of LaB₃O₆ :Dy³⁺ λ_{ex} =348nm.



Figure 10 : Effect of concentration of doped Dy³⁺on relative luminescent intensity for LaB₃O₆: Dy³⁺.



Figure 11: Plot for the emission intensity per Dy ions as a function of Dy concentration.

Critical transfer distance (Rc) in LaB₃O₆: Dy³⁺ phosphor:

In the case of investigating the concentration quenching process of Dy³⁺ ions in LaB₃O₆: Dy³⁺ phosphors, the excitation and emission spectra of phosphors with different Dy^{3+} content (x = 0.05-1 mole %) excited by 348nm are shown in figure 10 and 11. No obvious changes for all the samples in the positions of emission bands. With increasing Dy³⁺ concentration, the emission intensity increase and reaches the maximum at x = 0.1 mole %. Concentration quenching occurs, when the Dy³⁺ concentration is more than 0.1 mole %. While considering the mechanism of energy transfer in oxide phosphors, Blasse has pointed out that if the activator is introduced solely on Z ion sits, then there is on the average of one activator ion per V/xcN, where x_c is the critical concentration, N the number of Z ions in the unit cell and V the volume of the unit cell. The critical transfer distance R_c is approximately equal to twice the radius of a sphere with the volume [36].

 $R_c = 2(3V/4\pi x_c N)^{1/3}$ ------ (1) By taking the appropriate values of V, N and x_c (421.13 Å, 4, 0.001) respectively, the critical transfer distance of Dy³⁺ in LaB₃O₆: Dy³⁺ phosphor is found to be 12.39 Å.

The intensity of multipolar interaction can be determined, if the energy transfer occurs between the same sorts of activators,. The emission intensity (I) per activator ion follows the equation [36]:

 $I/x=K/1+\beta x^{Q3}$ ------ (2) Where, x is the activator concentration; Q =3, 6, 8, 10 for the exchange interaction, dipole-dipole (d-d), dipole-quadrupole (d-q), quadrupole-quadrupole (q-q) interactions, respectively; whereas K and b are constant for a given host crystal under same excitation condition. The critical concentration of Dy³⁺ has been determined to be 0.1mole %. The dependence of the emission intensity of LaB₃O₆:Dy³⁺ phosphor excited at 348nm as a function of the corresponding concentration of Dy³⁺ for concentration greater than



the critical concentration is the determined. Equation-1, can be simply rearranged as follows:

log $[I/x] = A-Q/3 \log x$ $[A = \log K - \log \beta]$ ------(3) Considering these equations, we had calculated and plotted log (1/x) Vs. log(x) as shown in figure 11. The value of Q can be calculated approximately as 3, this indicates that the type of interaction is the exchange interaction.

4.3.3 LaB₃O₆ Tb³⁺ phosphor

The phosphors LaB₃O₆₆:Tb³⁺ with different doping concentrations of Tb3+ exhibit similar excitation and emission spectra except for their intensities. The excitation spectrum from 200 nm to 500 nm of LaB₃O₆:Tb³⁺ (1 mole %) monitored at λ_{em} = 545 nm is shown in figure 12. The overall excitation spectrum consists of two parts. One part in the range from 250 to 300 nm is attributed to the ${}^{4}f_{8} \rightarrow {}^{4}f_{7}{}^{5}d_{1}$ transition of Tb³⁺ shown in figure 12. The other part in the range of 300-500 nm contains several peaks, which can be assigned to the ${}^{4}f_{8} \rightarrow {}^{4}f_{8}$ transitions from the ground state ${}^{7}F_{6}$ to the excitation levels such as ⁵H₆ (303 nm), ⁵H₇ or ⁵D_{0,1} (317 nm), ⁵G₂ or ⁵L₆ (340 nm), ⁵L₉ or ⁵G₄ (351 nm), ⁵L₁₀ (368 nm), ⁵G₆ or ⁵D₃ (378 nm) and ⁵D₄ (486 nm) [37]. Among all the excitation bands, the strongest one is located in UV region (at 379 nm). Therefore, LaB₃O₆₆:Tb³⁺ phosphor can be effectively excited by ultra-violet light. Figure 13 exhibits the emission spectrum of LaB₃O₆₆:Tb³⁺ excited by 379 nm light. It consists of three Tb³⁺ emission peaks at 493, 545 and 588 nm, corresponding to the transitions from ⁵D₄ to $^{7}F_{6}$, $^{7}F_{5}$ and $^{7}F_{4}$ respectively, of which the green emission at 545 nm is the strongest one. The excitation and emission spectra reveals that LaB₃O₆₆:Tb³⁺ is suitable for being excited by ultra-violet (at 379nm) light and produces green emission. As seen in figure 13, concentration quenching is not observed till 1mole % of Tb³⁺.



Figure 12 : Excitation spectrum of La_{0.99}B₃O₆: 0.01Tb monitored at $\lambda_{em} = 545$ nm.



Figure 13 : Emission spectrum of La_{1-x} B₃O₆: xTb^{3+} (x= 0.2, 0.5, 1m %) monitored at λ_{exc} = 379 nm.

4.4 CIE Co-ordinates

The chromaticity co-ordinates of prepared samples were calculated using the photoluminescence data and Interactive CIE software. The calculated CIE coordinates of prepared phosphor are shown on 1931 CIE chromaticity diagram in figure 14. Figure 14 gives chromaticity coordinates of the the prepared LaB₃O₆:Ln³⁺ phosphors (Ln = Eu, Dy and Tb). Chromaticity co-ordinates of LaB₃O₆:Eu³⁺, LaB₃O₆:Dy³⁺ and LaB₃O₆:Tb³⁺ are A (x = 0.65, y = 0.33) red region, B (x = 0.31, y = 0.32) white region with correlated color temperature 6498 K and C (x = 0.33,

0.57) green region respectively. These coordinates are near to the National Television System Committee standards (x = 0.67, y = 0.33) and (x = 0.21, y = 0.71) for red and green region, respectively.



Figure 14: CIE chromaticity diagram of LaB₃O₆: Ln³⁺
(Ln = Eu, Tb, Dy), co-ordinate A of LaB₃O₆: Eu³⁺, B of LaB₃O₆: Dy³⁺ and C of LaB₃O₆: Tb³⁺.

V. Conclusion

The XRD pattern of LaB₃O₆: Eu phosphor matches well with those in JCPDS file no. 01-073-1150, indicating that the obtained sample is single phase. Effect of heating time during synthesis and concentration of Eu³⁺ on PL of LaB₃O₆ was investigated. Synthesis of this phosphor was done at 800°C for 24 and 48 hrs. In other case phosphor prepared for 24hrs was quenched at 800° C for 1hr. It was observed that increasing the heating time of synthesis changes the emission of Europium from blue to red i.e. Eu²⁺ to Eu³⁺. Quenching at 800°C for 1hr also showed the same results. This phosphor gives reddish orange emission under n-UV excitation (395 nm) making it promising candidate for LED. The emission spectra of Dy3+: LaB3O6 phosphors show two strong bands in blue and yellow regions. PL results of Dy³⁺: LaB₃O₆ phosphor shows the excitation peak at 348nm, which is away from Hg excitation and can be

useful for solid state lighting in lamp industry. LaB₃O₆ doped with Tb³⁺ have strong excitation band located at 379nm, which is suitable for being excited by user UV LED chip. It generates bright green emission at 545nm (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$) under 379nm excitation. So LaB₃O₆: Tb³⁺ may be predicted as a promising green phosphor candidate for applications in LED based solid state lighting or other display devices.

VI. REFERENCES

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