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Synthesis and TL emission properties of RE^{3+} (Tm, Tb, Ce, Gd and Dy) doped lithium based alkaline (Ca, Mg) earth metal borates

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ABSTRACT

In this paper we reported the preparation technique and thermoluminescence (TL) properties of rare earth (RE) doped lithium calcium borate (LCB) and lithium magnesium borate (LMB) phosphors. The phosphors were prepared by solid state diffusion reaction method. The TL glow curves were recorded for all the RE doped phosphors. In LCB phosphor thulium (Tm) doped LCB shows the good TL glow curve with high temperature glow peak at 430 ºC compared with other dopants. In the case of LMB phosphors terbium (Tb) doped phosphor gives the good TL sensitive glow peak at 250 ºC. The thermoluminescence emission spectra were recorded for RE doped LCB and LMB phosphors to know the luminescence emission centres. In LCB and LMB phosphors, TL emission spectra showed the emission of their dopants transition. The emission centres of TL glow curves were confirmed by TL emission spectra.

Keywords: Synthesis, TL emission, LCB, LMB

INTRODUCTION

Thermoluminescence (TL) is a well known phenomenon, which is produced by a release of the radiation induced electrons from the traps of the materials. Thermoluminescence is used in diverse fields such as dosimetry, archaeology, geology, biology, biochemistry, forensic science, space science, TSL photography, radiation physics and so on. During the past twenty years very considerable progress has been made in application of the thermostimulated luminescence technique for practical purposes. Borate compounds are currently attractive for research because of their wide range of applications [1]. TSL studies on borates were started from 1967. Alkaline earth metal borates are mainly used as a thermoluminescent materials and nonlinear optical (NLO) crystals for UV generation. Recently many researchers have developed new mixed alkaline earth metal borates. These are having good TL properties. First Wu et al. [2] determined the structure for a new compound namely lithium calcium borate (LCB). They developed this material for NLO applications. Jiang et al. [3] has reported the thermoluminescence properties of LCB because, of their Z_{eff} values. Continuously Li Panlai et al. [4] has reported the luminescent characteristics of Eu^{3+} doped LCB. Like this LCB material, Wu et al. [5] proposed the phase relations of the Li_2O-MgO-B_2O_3 system. Balaji Rao et al. [6] reported the structural, dielectric and optical properties of titanium ions doped Li_2O-MgO-B_2O_3 system. The same author has explained the effect of nickel ions in Li_2O-MgO-B_2O_3 system through spectroscopic characterization. So far no one has reported the TL properties on this Li_2O-MgO-B_2O_3 system [7].

The main aim of this work is to synthesis the lithium calcium borate (LCB) and lithium magnesium borate (LMB) compounds doped with different rare earths (RE). The ultimate aim of this work is to study the Thermoluminescence glow curve and thermoluminescence emission spectra of these compounds.

MATERIALS AND METHODS

Experimental Details

2.1. Synthesization technique

Rare earth doped compounds namely lithium calcium borate (LCB) and lithium magnesium borate (LMB) are synthesized by solid state diffusion reaction method. For the synthesis of LCB and LMB compounds, analytical grade lithium carbonate, calcium carbonate, magnesium oxide, boric acid and rare earth oxides were used as raw materials. The amounts of chemicals taken for the preparation of a typical batch of $LiCaBO_3$ phosphor with dopants are Li_2CO_3-0.73 g, $CaCO_3$-2 g, H_3BO_3-1.36 g and rare earth oxides-20 mg. Initially the raw materials were mixed with triply distilled water and the resultant paste was dried by controlled heating in a mantle heater. The dry powder was ground, placed in an alumina crucible, and sintered at 750±10 ºC for 3 hrs in an air atmosphere in a muffle furnace. The phosphor was cooled to 500 ºC inside the closed furnace itself; subsequently, the aluminium crucible was removed from the furnace and cooled to room temperature. For the TL characterization studies the phosphor powder was made into uniform grain size of ~100 μm by grinding in an agate mortar. The LCB compounds with different rare earth dopants were prepared by the same synthesis technique and recipes.

The lithium magnesium borate phosphor was prepared in the similar manner with different raw materials and sintered temperature. For the lithium magnesium borate synthesis analytical grade lithium carbonate, magnesium oxide, boric acid and rare earth oxides were used as raw materials. The amounts of chemicals taken for the preparation of a typical batch of lithium magnesium borate phosphor with dopants are Li_2CO_3-0.73 g, MgO-0.88 g, H_3BO_3-5.44 g and rare earth oxides (Tm, Tb, Ce, Dy and Gd) -20 mg. Here the sintering temperature is 850±10 ºC.

2.2. Instrumentation

The TL glow curves were recorded after gamma irradiation. The LCB and LMB materials were irradiated in gamma chamber containing Co-60 gamma ray source of dose rate 270 Gy/hr at room temperature. TL measurements were done using Nucleonix make TLD reader (Model-1007) at a linear heating rate of 10 ºC/s by electrical heating in kanthal tray. For the recording of the TL emission spectra, the optical cable outlet is fed to the emission monochromator of Jobin Yvon-Spex make Spectrofluorometer (Fluorolog version-3; Model FL3-11) with a xenon lamp in switched-off condition.

RESULTS AND DISCUSSIONS

3.1. TL glow curves of LCB doped with rare earths (RE)

TL glow curve of undoped and rare earth doped LCB phosphors (Tm, Tb, Ce, Dy and Gd) were recorded after gamma irradiation and the glow curves are shown in Figure 3.1.

The undoped LCB phosphor shows two peaks; one at 120 ºC and another shoulder peak at around 150 ºC. LCB doped with thulium (Tm) phosphor has three high sensitive peaks at 230 ºC and 430 ºC and one low sensitive peak at 100 ºC. Comparison made through TLD-100, the sensitivity of the peak at 230 ºC is 2.9 times than that of TLD-100. In the case of 430 ºC peak, the TL sensitivity is 8.3 times than that of TLD-100. Terbium (Tb) doped LCB phosphor has three glow peaks. First two glow peaks are situated at 100 ºC and 106 ºC. Third glow peak is at 170 ºC. This glow peak sensitivity is 5 times than that of TLD-100. Cerium (Ce) doped LCB phosphor has three peaks. The high sensitive TL peak is at around 250 ºC.

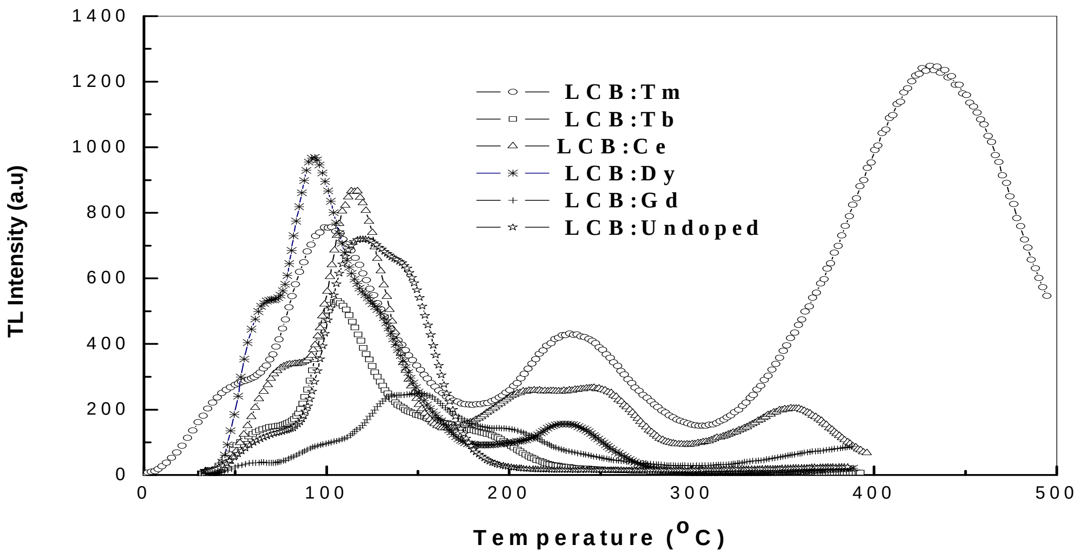
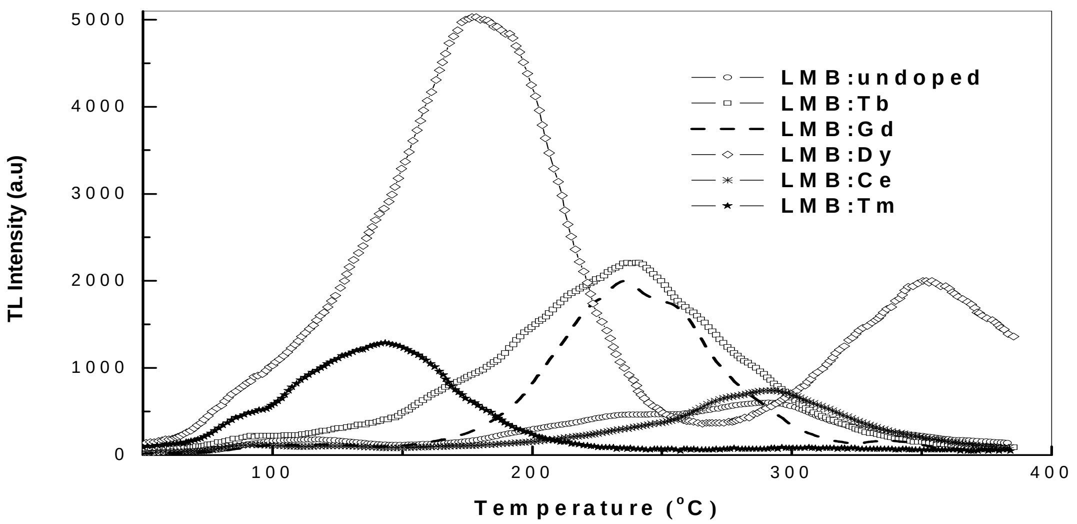


Figure 3.1. Gamma irradiated TL glow curves of undoped LCB and doped with different rare earths.



3.2. TL glow curves of LMB doped with rare earths (RE)

It is 1.7 times than that of TLD-100. The dysprosium (Dy) doped phosphor has a high temperature peak at 240 ºC. The intensity of this peak is relatively equal to TLD-100. Also it contains three low temperature peaks at 71 ºC, 93 ºC and 120 ºC. TL glow curve of LCB doped with gadolinium (Gd) shows a glow peak at low temperature around 150 ºC. Comparison made through TLD-100, the sensitivity of LCB:Gd phosphor is very less.

Thus it is observed that the sensitivity of Tm doped LCB phosphor is higher than the other dopant phosphor materials. Also Tm doped LCB glow peak is situated at higher temperature (230 ºC and 430 ºC) with good glow curve structure. Hence this may considered as dosimetric peaks.

The TL glow curves were recorded for undoped LMB and rare earths (Tb, Gd, Dy, Tm and Ce) doped LMB phosphors. TL glow curves were recorded after exposure to gamma dose 21.4 Gy (5 mins) by ^{60}Co gamma ray at room temperature by a linear heating rate at 10 ºC/s and are shown in Figure 3.2. The undoped LMB phosphor shows three glow peaks at 115 ºC, 235 ºC and 290 ºC. To improve the TL sensitivity of LMB, rare earths were doped. The Tb doped LMB phosphor consists only one glow peak at around 250 ºC. This glow peak shows high TL sensitivity with good glow curve shape. The TL glow curve of Gd doped LMB phosphor has given the glow peak at around 235 ºC with the shoulder peak at 255 ºC. Comparison made through the LMB:Tb^{3+} phosphor, the Gd doped LMB phosphor sensitivity is 0.8 times that of LMB:Tb phosphor. The LMB doped with Dy shows the glow peak at around 180 ºC and 350 ºC. Compared with LMB:Tb phosphor, Dy doped LMB sensitivity of the 180 ºC peak is higher than the LMB:Tb^{3+} phosphor. The gamma irradiated TL glow curve of thulium doped LMB consists two glow peaks at 92 ºC and 143 ºC. The sensitivity of these two glow peaks are less than that of LMB:Tb phosphor. The TL glow curve of Ce doped LMB phosphor has two glow peaks. The main glow peak is situated at around 290 ºC and the shoulder peak is at 124 ºC. The 290 ºC glow peak sensitivity is 0.3 times than that of Tb doped LMB phosphor. Among all the rare earth doped LMB phosphors, Tb doped LMB given the higher temperature peak at 250 ºC with good glow curve structure. The sensitivity of this glow peak is 4 times than that of TLD-100.

3.3. TL emission spectra of LCB phosphors

The TL emission spectrum is used to know the luminescence emission centres of the particular material. To know the emission centres of the undoped and RE^{3+}doped LCB phosphors, TL emission spectra were recorded for all LCB phosphors. Undoped LCB phosphor showed broad emission at 550 nm. Terbium doped phosphor showed Tb^{3+} characteristic emission at 413, 436, 487, 545, 583 and 621 nm correspond to electronic transitions $^5D_3\rightarrow{}^7F_5$, $^5D_3\rightarrow{}^7F_4$, $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_4$ and $^5D_4\rightarrow{}^7F_3$ respectively. The TL emission of LCB:Tm^{3+} show the characteristic of Tm^{3+} emission at 365 and 455 nm for the peaks at 100 ºC, 230 ºC and 430 ºC. In LCB:Tm, blue light emission at 455 nm, which is three times than 365 nm emission but in Ag codoped LCB:Tm phosphor, 365 nm is the dominant emission. However, the LCB:Tm^{3+} spectrum shows Tm^{3+} emission centre for all the peaks. The multilevel spectral transitions corresponding to Tm^{3+} in the free ion state are $^3P_0\rightarrow{}^3H_6$=285 nm, $^3P_0\rightarrow{}^3F_4$=341 nm, $^1D_2\rightarrow{}^3H_6$=365 nm, $^1D_2\rightarrow{}^3F_4$=455 nm, $^1G_4\rightarrow{}^3H_6$=472 nm, $^1G_4\rightarrow{}^3F4$=645 nm, and $^1G_4\rightarrow{}^3H_5$=769 nm. Most of these peaks are observed in the TL emission spectra and the similar spectra were observed in the Tm^{3+} doped $CaSO_4$ TL phosphor by Madhusoodanan et al. [8]. TL emission spectrum of gamma irradiated LCB doped Ce phosphor shows the peak at around 400 and 560 nm, which are the characteristics emission (78 ºC, 121 ºC and 317 ºC) of Ce^{3+}. All the three temperatures show the emission at the same centres. However, the intensity is varied. According to the Bangaru, [9] all the

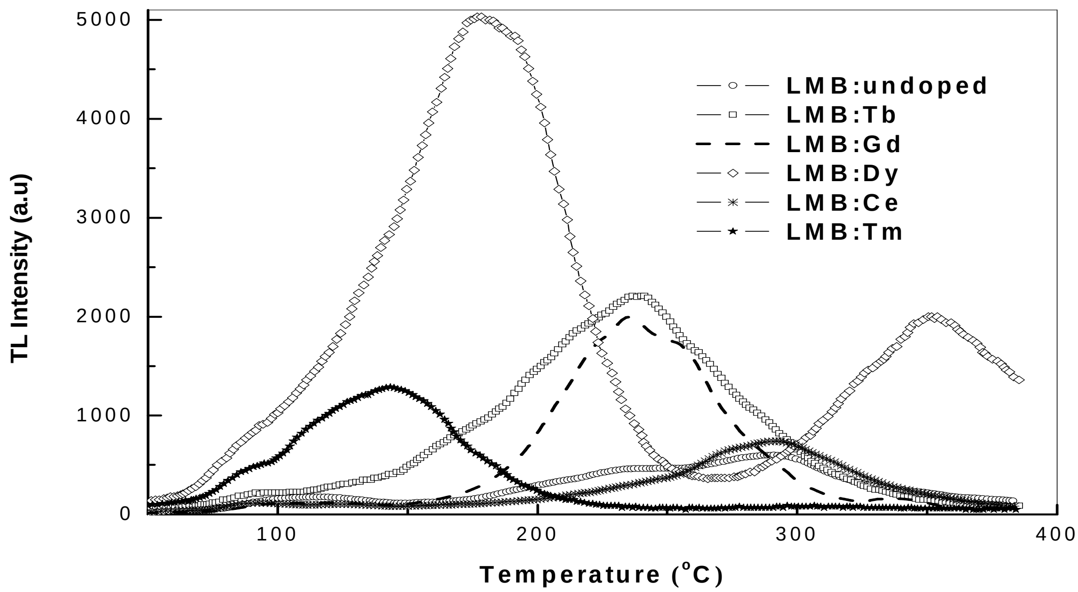


Figure 3.2. TL glow curves of LMB doped with different rare earths.

temperatures exhibit the strong emission around 400 nm. Dy doped LCB phosphor shows the emissions at 483 and 572 nm, which are the corresponding emission of dysprosium. These are due to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions of Dy^{3+} ion respectively [10]. The TL emission for Gd doped LCB phosphor is at around 350 nm for all the temperatures (150 ºC and 194 ºC). This 350 nm emission corresponds to the Gd^{3+} [11, 12]. The TL emission wavelengths of all the LCB phosphors are shown in Table 3.1. Representatively, the TL emission spectrum of Tm^{3+} doped LMB phosphor is shown in Figure 3.3.

3.4. TL emission spectra of LMB phosphors

Spectral measurements of TL provide useful information on the nature of luminescence centres, which are responsible for TL emission and may be formed by the presence of impurities and/or imperfections in the crystal. Emission spectra of the TL for undoped and doped gamma irradiated LMB phosphors measured by isothermal heating at various temperatures near each glow peaks. Emission spectra of the pure LMB phosphor recorded at the glow peak temperatures 110 ºC, 173 ºC 234 ºC and 286 ºC consists of a broad emission band at 555 nm in the green region. This emission is related to the host emission and not associated with the trivalent lanthanide ions. The LMB:Tb TL emission spectrum consists the wavelengths at 405, 436 and 544 nm. According to Yamashita et al. [13] and Jose et al. [14] TL spectrum of Tb^{3+} have the properties emission bands at 379, 412, 435, 487 and 544 nm, which are due to electronic transitions $^5D_3\rightarrow{}^7F_6$, $^5D_3\rightarrow{}^7F_3$, $^5D_3\rightarrow{}^7F_4$,

Table 3.1. TL emission wavelengths of all undoped and RE doped LCB phosphors.

Phosphor Name	TL emission wavelength (nm)
LCB:Undoped	550
LCB:Tm	365 & 455
LCB:Tb	413, 436, 487, 545 & 583
LCB:Ce	400 & 500
LCB:Dy	483 & 572
LCB:Gd	350

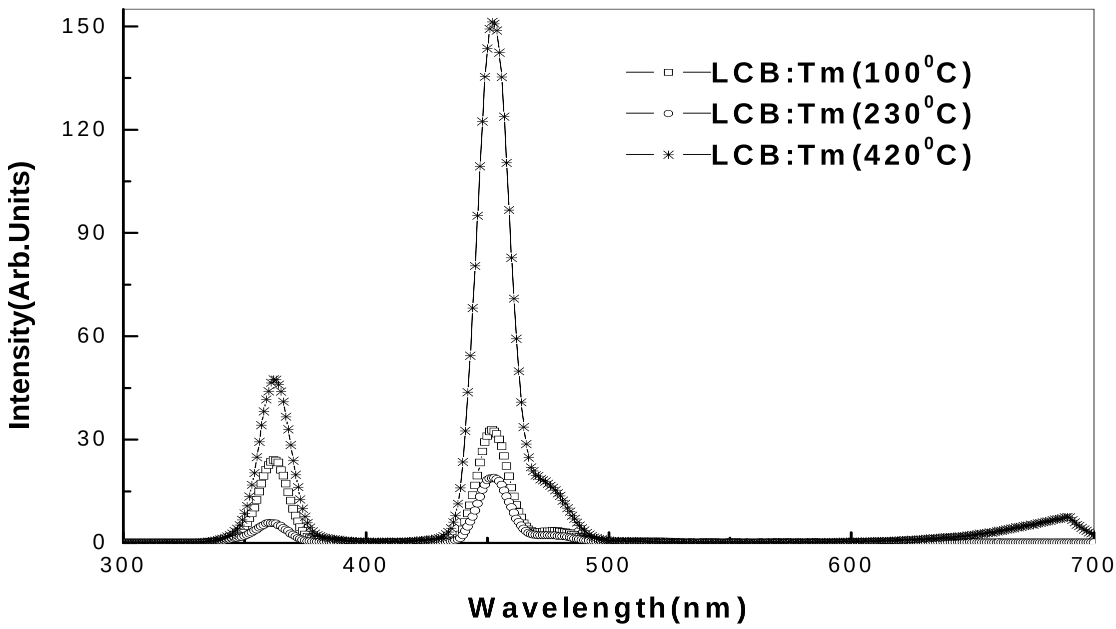


Figure 3.3. TL emission spectra of gamma irradiated LCB:Tm^{3+} at the main glow peak temperatures.

$^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ respectively. Gd doped TL emission spectra shows the emission at around 345 nm. This corresponds to the transitions of Gd^{3+}. TL emission spectra of Dy doped LMB shows the emission at 480 and 570 nm which corresponds to the transitions $^4F_{9/2} \rightarrow {}^6H_{15/4}$ and $^4F_{13/2} \rightarrow {}^6H_{13/2}$ of Dy^{3+}. The TL emissions of LMB:Tm phosphor are occurred at 360 and 450 nm, which is related to the blue light emission. The corresponding transitions are $^1D_2 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3F_4$. TL emission of Ce doped LMB phosphor for the glow peak temperatures at 124 ºC and 290 ºC is 403 nm, which is due to the Ce^{3+}. Table 3.2 shows the TL emission wavelengths of all the LMB phosphors. Representatively, the TL emission spectrum of LMB:Tb recorded for the glow peak temperature at 250 ºC is shown in Figure 3.4.

Table 3.2. LCB phosphors with their corresponding TL emission wavelengths.

Phosphor Name	TL emission wavelength (nm)
LMB:Undoped	555
LMB:Tb	405, 436 & 549
LMB:Dy	480 & 570
LMB:Gd	345
LMB:Tm	360 & 450
LMB:Ce	403

From the TL emission measurements, we identified the luminescence emission centres for both LCB and LMB phosphors. The rare earth doped LCB and LMB phosphors show their respective dopants emission. Prabahar et al. [15] also reported the defect related emission spectrum of PbSe thin films of different thickness. In this material the emission are related to the respective host materials.

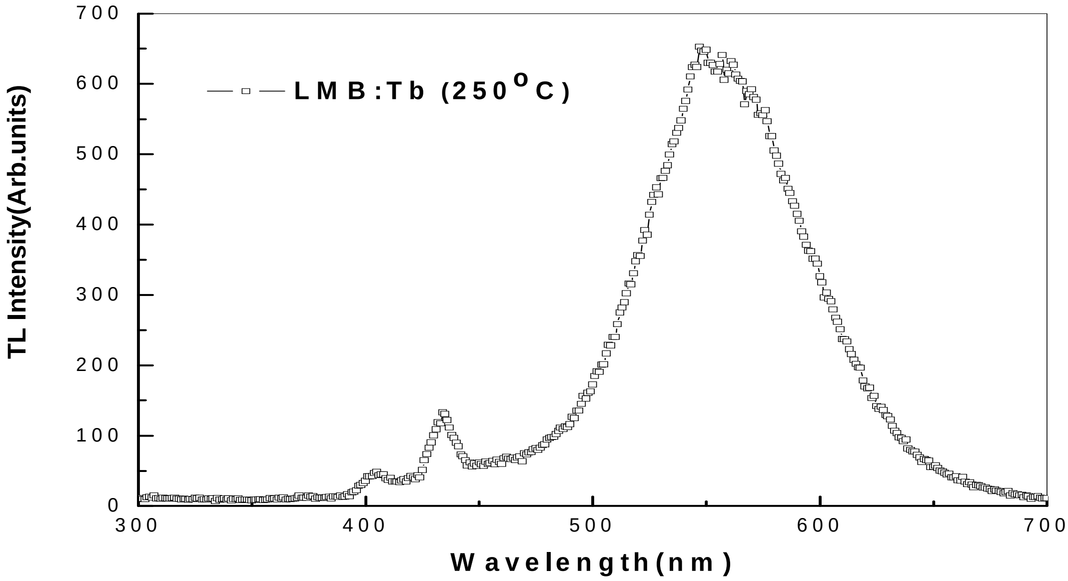


Figure 3.4. TL emission for gamma irradiated Tb^{3+} doped LMB phosphor.

CONCLUSION

Rare earths doped LCB and LMB phosphors were successfully synthesized by solid state diffusion reaction method. Among all the dopants Tm doped LCB phosphor showed the high intense and high temperature glow peaks (230 ºC and 430 ºC) with good glow curve shape. In the case of LMB phosphors, Tb doped phosphor has given the good glow curve shape with glow curve structure. TL glow peak of LMB:Tb^{3+} is situated at 250 ºC. The luminescence emission centres were confirmed by TL emission spectra. All the phosphors show the emission related to their rare earth dopants and the characteristic transitions. Thus, it is confirmed that the luminescence emission centres by TL emission spectra and the TL of the phosphors are due to the characteristic transitions of RE^{3+}.

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