Synthesis and Photoluminescence Characteristics of Rare Earth Doped Lithium Based Alkaline Earth Metal Borates

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Rare Earth (RE) doped Lithium Calcium Borate (LCB) and Lithium Magnesium Borate (LMB) polycrystalline phosphors have been synthesized by high temperature solid state diffusion reaction method. Photoluminescence (PL) excitation and emission spectra of rare earth doped LCB and LMB phosphors were recorded for unirradiated and irradiated phosphors. LCB:Tm3+ phosphor showed the PL characteristic emission bands of Tm3+ at 455 nm along with a minor band at 480 nm under 360 nm excitation. No reduction in Tm3+ emission was observed in gamma irradiated sample. In the case of LMB phosphor, Tb3+ doped LMB showed the Tb3+ characteristic PL at 541 nm before irradiation. Gamma irradiation showed only negligible change in Tb3+ PL intensity. This shows that redox process do not play any significant role in the LCB:Tm3+ and LMB:Tb3+ phosphors.

Key Words: Luminescence; Lithium Calcium Borate; Lithium Magnesium; Thulium; Terbium

Introduction

Luminescence is the emission of light in the visible or near visible region from a material following the initial absorption of energy from an external source e.g., ultra-violet or high energy radiation. The materials and substances that are capable of emitting light in the visible range are termed `luminescent' [1]. The luminescence emission can be categorized as either fluorescence or phosphorescence, depending upon the characteristic lifetime $\tau$ between absorption of radiation and emission of light. For fluorescence, $\tau$ value is less than $10^{-8}$ sec and for phosphorescence $\tau$ value is greater than $10^{-8}$ sec [2]. The process in which incident electromagnetic radiation in the visible or near visible region causes a phosphor to give out luminescence is known as photoluminescence. A luminescence study of mixed alkaline earth metal borates has started very recently. Jiang et al. [3] have been studied mixed borate namely lithium calcium borate doped with rare earth elements recently. And Wu et al. [4] were prepared lithium magnesium borate compounds and determined the structure. The phase equilibria for Li$_2$O-MgO-B$_2$O$_3$ were measured by Bazaraa et al. [5]. Thermoluminescence (TL) studies are reported in impurity doped mixed metal borates such as SrMg(BO$_3$)$_2$ [6], LiBa$_2$B$_2$O$_7$:RE$_{2+}$ [7], LiSr$_2$(BO$_3$)$_3$:Ce$^{3+}$ [8], LiKB$_2$O$_7$ [9], K(SrBO$_3$)$_3$:Ce$^{3+}$ [10], NaSr(BO$_3$)$_3$:Ce$^{3+}$ [11], LiSrBO$_3$:RE$^{3+}$ [12] and LiCaBO$_3$ [13-14, 3]. We have synthesised the LCB and LMB polycrystalline phosphor doped with rare earths by solid state diffusion reaction method. The aim of the present work is to study the photoluminescence characteristics of Tm doped LCB and Tb doped LMB phosphors.

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Materials and Methods

Materials Preparation

In the present work, we have synthesised both lithium calcium borate (LCB) and lithium magnesium borate (LMB) phosphor materials by solid state diffusion reaction method. The preparation procedure is given below.

For the synthesis of lithium calcium borate samples, analytical grade lithium carbonate, calcium carbonate, boric acid and rare earth oxide were used as raw materials. The amount of chemicals taken for the preparation of a typical batch of LCB phosphor are Li₂CO₃-0.73 g, CaCO₃-2 g, H₃BO₃-1.36 g and for dopant, 20 mg of Tm₂O₃. Initially the raw materials were mixed with triple 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°C±10°C for 3 hrs in air atmosphere in a muffle furnace. The phosphor was cooled to 500°C inside the closed furnace itself; subsequently, the aluminium crucible was removed from the furnace and cooled to room temperature. For the characterization studies the phosphor powder was made into uniform grain size of ~100 μm by grinding using an agate mortar.

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 oxide were used as raw materials. The amount of chemicals taken for the preparation of a typical batch of lithium magnesium borate phosphor are Li₂CO₃-0.73 g, MgO-0.88 g, H₃BO₃-5.44 g and for dopant, 20 mg of Tb₄O₇. Here the sintering temperature is 850°C±10°C.

Characterization Methods

Source for Irradiation

The phosphor was irradiated at room temperature 1.5 Gy in a gamma chamber containing Co-60 source of dose rate 270 Gy/hr. Gamma chamber 900 containing the Co-60 γ-ray source supplied by Isotopic Division, Bhabha Atomic Research Centre (BARC), Mumbai (India) was used. With this unit it is possible to get a dose rate of 270 Gy/hr. The synthesized phosphor materials were subjected to irradiation without any chemical or annealing treatment. The particle size of the phosphors was >100 μm.

Spectrofluorimeter

The photoluminescence measurements were carried out by using a JOBINYVON-Spex spectrofluorimeter (Fluorolog version-3; model FL3-11) with a 450W high-pressure xenon lamp. The main components of the fluorolog-3 spectrofluorimeter system are optical components, a personal computer and Data max for Windows™ software.

Results and Discussion

Photoluminescence Spectra

Photoluminescence (PL) excitation and emission spectra of unirradiated LCB:Tm is shown in Fig. 1. The characteristic emission bands of Tm³⁺ corresponds to 1D₂→3F₄ observed as the major emission at 455 nm along with a minor band at 480 nm to the transition 1G₄→3H₆ under the 360 nm excitation corresponds to 3H₆→1D₂ transition. The PL excitation and emission spectra of irradiated LCB:Tm

![Fig. 1: PL excitation and emission spectra for unirradiated LCB:Tm phosphor](image-url)
has shown in Fig. 2. No reduction in Tm$^{3+}$ emission was seen in the gamma irradiated sample. This shows that no conversion of Tm$^{3+}$ to Tm$^{2+}$ takes place due to gamma irradiation. Gamma irradiation showed only negligible reduction in the Tm$^{3+}$ PL intensity, which means that redox processes do not play any significant role in the TL of LCB:Tm$^{3+}$ phosphors [14].

Fig. 3: PL excitation and emission spectra for unirradiated LMB:Tb phosphor

Fig. 2: PL excitation and emission spectra for irradiated LCB:Tm phosphor

Figs. 3 and 4 showed the PL excitation and emission spectra of LMB:Tb$^{3+}$ before irradiation and after irradiation. All the Tb$^{3+}$ characteristic peaks were seen in the excitation spectrum of the sample after irradiation. Major intense peak assigned to the parity-and spin-allowed transitions from the $^7F_g$ ground state of Tb$^{3+}$ (4f$^8$) to the different excited state of the $4f^75d^1$ configuration is seen except the minor peak at 232 nm. The narrow bands of parity forbidden f-f transitions within the 4f$^8$ configuration of Tb$^{3+}$ ions are seen as intense peak in this material. The excitation peaks at 379 nm from $^7F_6 \rightarrow ^5D_4$, 370 nm from $^7F_6 \rightarrow ^5D_3$, 350 nm from $^7F_6 \rightarrow ^5D_2$ and 318 nm from $^7F_6 \rightarrow ^5D_2$ electronic transitions are seen in the spectra. The PL spectra of LMB:Tb$^{3+}$ is measured under excitation at 379 nm where an efficient excitation band is observed in the excitation spectra. The spectrum of Tb$^{3+}$ will be consisting of many narrow bands which correspond to two series; very weak series between 375 and 475 nm, and a strong series above 475 nm. These narrow bands are characteristic of the spectra of trivalent rare earth ions in the crystals, because the 4f$^8$ valence electrons of RE$^{3+}$ ions are electrically shielded by the 5S$^2$ 5P$^6$ electron clouds. The weak and strong series are attributed to the electronic transitions from $^5D_3$ and

Fig. 4: PL excitation and emission spectra for irradiated LMB:Tb phosphor
respectively, to 7F_J (J = 6, 5, 4, 3, 2, 1 and 0) within 4f^8 configuration in Tb^{3+}. The intensity of the 5D_3 (blue) series is quenched by the cross-relaxation process between 5D_3→5D_4 of the emitting Tb^{3+} and 7F_6→7F_0 of the neighbouring Tb^{3+}. Due to the cross relaxation processes the 5D_3 (blue) emission is quenched as Tb^{3+} concentration increases because the lower energy 5D_4 emission (Green) level is favoured. Excitation by 379 nm light produced mainly the following emission in green region at 488 nm (5D_4→2F_5), 541 nm (5D_3→2F_5), 586 nm (5D_4→2F_5) and 619 nm (5D_4→3F_3) [15, 16] (Yamashita et al., 1999 and Jose et al., 2004). Gamma irradiations showed only negligible change in Tb^{3+} PL intensity which means that redox process do not play any significant role in the TL of LMB::Tb^{3+} phosphors [14].

**Conclusions**

Rare earth doped LCB and LMB phosphors were synthesised by high temperature solid state diffusion reaction method. PL excitation and emission spectra were recorded for unirradiated and irradiated LCB and LMB phosphors. For LCB::Tm^{3+} phosphor, unirradiated phosphor showed the PL emission at 455 nm and 480 nm under 360 nm excitation. The PL emission bands at 455 nm and 480 nm corresponds to the transitions 1D_2→3F_4 and 1G_6→3H_6 respectively. Irradiated LCB::Tm^{3+} phosphor also showed the Tm^{3+} emission at 455 and 480 nm under 360 nm excitation. There is no reduction in PL emission intensity. In the case of Tb^{3+} doped LMB phosphor, unirradiated LMB showed Tb^{3+} characteristics emissions bands at 488 nm, 541 nm, 586 nm and 619 nm by 379 nm excitation wavelength. After gamma irradiation LMB phosphor showed the same PL emission bands and negligible change has occurred in PL intensity. In both LCB and LMB phosphors unirradiated and irradiated materials showed the same PL emissions and no change in the PL intensity which means that the redox mechanism do not play any significant role during irradiation and thermoluminescence of LCB::Tm^{3+} and LMB::Tb^{3+} phosphors.

**References**

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