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Synthesis and luminescence properties of rare earth doped gamma-ray-irradiated $GdCa_4O(BO_3)_3$ phosphors

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Abstract Undoped and rare earth (RE = Ce, Dy, and Eu) doped $GdCa_4O(BO_3)_3$ phosphors were synthesized by solid-state diffusion technique. Formation of the sample was confirmed by taking X-ray diffraction (XRD) pattern of the sample. Photoluminescence (PL) emission spectrum showed characteristic emission of RE doped in the $GdCa_4O(BO_3)_3$ sample. It is observed that doping of RE ion initially enhanced the TL yield, attained an optimum TL for a particular concentration of dopant (i.e., 0.5 mol%) then decreased with further increase in dopant concentration for all the samples. We found that Ce is the best activator for enhancing the TL yield in $GdCa_4O(BO_3)_3$ system. Fading of TL intensity of the sample was studied and it is found that fading of the TL is about 5% over the period of 15 days. The simple glow curve, linear response to γ-ray dose and less fading; makes the $GdCa_4O(BO_3)_3$:Ce(0.5 mol%) phosphors a suitable candidate for TL dosimetry.

Introduction

The effects of ionizing radiation in qualitative and quantitative terms has become very important in the present day context due to the influence of nuclear technology in various areas that include radiation medicine, radiotherapy, food processing, radiation based polymerization, and non-destructive testing techniques using radiography. Dependable radiation dosimetric procedures need to be developed over wide range of dose levels. As one of the most important method for radiation measurement, thermoluminescent dosimetry (TLD) has been known for a long time [1]. Up to now, much efforts has been taken to seek new and high performance TL material with the increasing need for dosimetry materials used in environment, personal, and clinical ionizing radiation protection. The TL studies of borate compounds are attractive because of their near tissue equivalent absorption coefficient. Investigations on a series of borate compounds have been reported, e.g., BaB_4O_7:Dy [2], $Li_2B_4O_7$:Cu,In [3], SrB_4O_7:Dy [4], MgB_4O_7:Dy,Na [5], $Ba_2Ca(BO_3)_2$:Tb [6], and $Sr_2Mg(BO_3)_2$ [7]. A new series of calcium containing rare-earth borates have been synthesised [8]. This family is isostructural with composition of $LnCa_4O(BO_3)_3$ (Ln = La^{3+}, Sm^{3+}, Nd^{3+}, Gd^{3+}, Er^{3+}, and Y^{3+}) and space group is monoclinic, non-centro-symmerty. They have good thermal and chemical stability and are good host for luminescent material under UV excitation.

In the present article, we are reporting very first time the TL of the rare earth (RE = Ce, Dy, and Eu) doped $GdCa_4O(BO_3)_3$ phosphors. For understanding the mechanism of TL emission, photoluminescence (PL) has also been recorded.

Experiments

Rare earth (RE) doped $GdCa_4O(BO_3)_3$ phosphors were synthesised by solid-state diffusion technique. In this

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technique, requisite amount of calcium carbonate, boric acid, gadolinium oxide, and rare earth oxide (Ce_2O_3, Dy_2O_3, and Eu_2O_3) were grounded thoroughly in a pestle and mortar. The mixture was then heated at 725 °C for 12 h and then cooled slowly. Obtained sample was grounded again, fired at 750 °C for another 12 h, and then cooled slowly up to room temperature. To confirm the formation of the samples, X-ray diffraction (XRD) pattern of the sample was recorded by X-ray Diffractometer (PW-1710). Photoluminescence (PL) of the rare earth doped samples were recorded using spectroflourophotometer (Shimadzu RF-5301 PC). The excitation monochromator isolates a band of a particular wavelength from the light from the Xenon lamp (150 W Xenon lamp serves as the light source) to obtain excitation light. Emission spectrum was recorded using a spectral slit width of 1.5 nm. The gamma-ray irradiation was carried out using ^{60}Co source. A PC based thermoluminescence analyser system (TL-1009I) was used for recording TL. TL was recorded with the heating rate 5 °C/s. For each measurement, at least three observations were taken and it was found that maximum variation in result was around 3–5%.

Results and discussions

Figure 1 shows the XRD pattern of the $GdCa_4O(BO_3)_3$ sample. The XRD data of prepared phosphor matched well with standard data of Joint Committee on Powder Diffraction Standards (JCPDS) [9] (File no. 89-1315).

Figure 2 shows PL emission spectra of $GdCa_4O(BO_3)_3$:Eu(0.5 mol%), $GdCa_4O(BO_3)_3$:Dy(0.5 mol%), and $GdCa_4O(BO_3)_3$:Ce(0.5 mol%) phosphors under 254, 353, and 247 nm excitations, respectively. Two peaks around 340 and 360 nm were observed in PL emission spectrum of Ce doped phosphors. For Dy doped sample, peaks were observed at 470 and 570 nm. In the PL emission spectrum of Eu doped phosphors, small peaks at around 590 and a prominent peak at 613 nm were observed.

In monoclinic $GdCa_4O(BO_3)_3$, polycrystalline Eu^{3+} occupies the low symmetry and energy level degeneration of $^7F_1$ and $^7F_2$ were released completely they were split into three and five states, respectively. There will be one $^5D_0 \rightarrow {}^7F_1$, three $^5D_0 \rightarrow {}^7F_2$, and five $^5D_0 \rightarrow {}^7F_2$ lines in spectra. The red emission at 613 is due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions and indicates that Eu^{3+} occupies the site of non-Centro symmetry. The other emission peaks are due to $^5D_0 \rightarrow {}^7F_0$ (580 nm) and $^5D_0 \rightarrow {}^7F_1$ (588, 592, and 600 nm) [10].

Two peaks observed around 340 and 360 nm in PL emission spectrum should be the existence of Ce^{3+} ion in $GdCa_4O(BO_3)_3$. The electron configuration of the ground states and excited states of Ce^{3+} are $4f^1$ and $5d^1$, respectively. The ^2F_J ground state of $4f^1$ is split by spin–orbit interaction into the $^2F_{5/2}$ and $^2F_{7/2}$ levels separated by $\sim$2200 cm^{-1}. On the other hand, the ^2D_J excited state of $5d^1$ is affected much more strongly by crystal–field interaction. If the crystal–field interaction for $5d^1$ is much larger than the spin–orbit interaction, then the ^2D_J excited state is split into five Kramer's doublet by low symmetry [11]. Ce^{3+} ions can be easily incorporated into different host materials and shows efficient broad band luminescence due to its $4f$–$5d$ parity allowed electric dipole transition. Ce^{3+} ion has high oscillator strength and a larger stokes shifts than the other rare earth ions. Optical absorption in Ce^{3+} doped compounds corresponds to the transitions from the $^2F_{5/2}$ ground state to the $5d^1$ excited states, where as emission occurs as the transitions from the lowest $5d^1$ excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground states. A large electron phonon coupling for the $5d^1$ state produces a large stokes shift energy between the absorption and emission spectra [12].

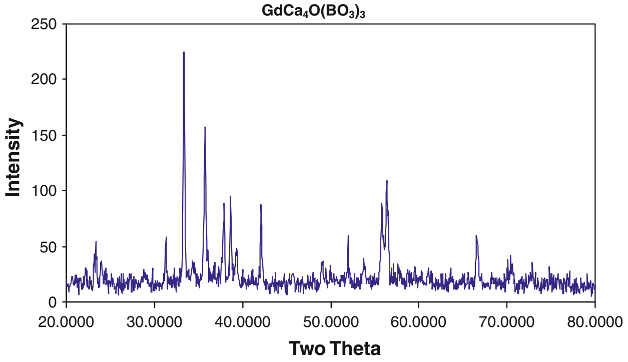

Fig. 1 X-ray diffraction pattern of $GdCa_4O(BO_3)_3$ sample prepared by solid state diffusion technique

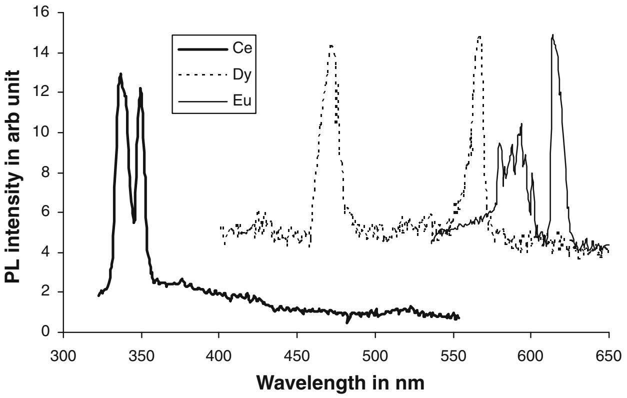

Fig. 2 PL emission spectra of $GdCa_4O(BO_3)_3$:RE(0.5 mol%) phosphors under 254, 353, and 247 nm excitations for Eu, Dy, and Ce, respectively

The emission of Dy^{3+} originates from the $^4F_{9/2} \rightarrow {}^6H_J$ ($J = 7/2, 9/2, 11/2, 13/2$, and $15/2$) transitions in the visible and near infrared regions. Within these transitions, the yellow band at ~575 nm corresponding to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition and the blue band at 485 nm corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition are predominant. It is well known that the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is hypersensitive ($\Delta L = 2$, $\Delta J = 2$) and therefore, its intensity strongly depends on the host, where as intensity of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is less sensitive to the host. The ratio of yellow to blue intensity depends on the environment of Dy^{3+} ions. At a suitable ratio of yellow to blue emission, Dy^{3+} will emit nearly white, so that luminescent materials doped with Dy^{3+} may be used as potential two-primary-color phosphors [13].

Figure 3 shows TL glow curves of γ-ray-irradiated (dose level 1.1 kGy) undoped and Eu doped $GdCa_4O(BO_3)_3$ phosphors. Two peaks at 150 and 290 °C were observed in the TL glow curve of undoped $GdCa_4O(BO_3)$ phosphors. As Eu was doped in the host lattice, initially TL intensity increased to reach an optimum TL intensity for 0.5 mol% of Eu in $GdCa_4O(BO_3)_3$ phosphors. It is also found that 290 °C peak shifts toward lower temperature side with increasing dopant concentration and an additional peak around 240 °C was observed in the TL glow curve of $GdCa_4O(BO_3)_3$:Eu(0.5 mol%) phosphors.

Figure 4 shows TL glow curves of γ-ray-irradiated (dose level 1.1 kGy) undoped and Dy doped $GdCa_4O(BO_3)_3$ phosphors. Dy enhances the TL intensity with an additional peak around 225 °C. An optimum TL was observed for 0.5 mol% of Dy.

Figure 5 shows TL glow curves of γ-ray-irradiated (dose level 1.1 kGy) undoped and Ce doped $GdCa_4O(BO_3)_3$ phosphors. It is observed that Ce enhanced the TL intensity of $GdCa_4O(BO_3)_3$ phosphors and enhancement was more for 290 °C TL peak. An optimum TL is observed for $GdCa_4O(BO_3)_3$:Ce(0.5 mol%) phosphors. For undoped γ-ray-irradiated (dose level 1.1 kGy) $GdCa_4O(BO_3)_3$ phosphors, intensity of 140 °C peak is 2.5 times greater than that of the 280 °C. While in Ce(0.5 mol%) doped γ-ray-irradiated (dose level 1.1 kGy) $GdCa_4O(BO_3)_3$ phosphors intensity of 290 °C peak is 4.5 times more than that of the 140 °C TL peak.

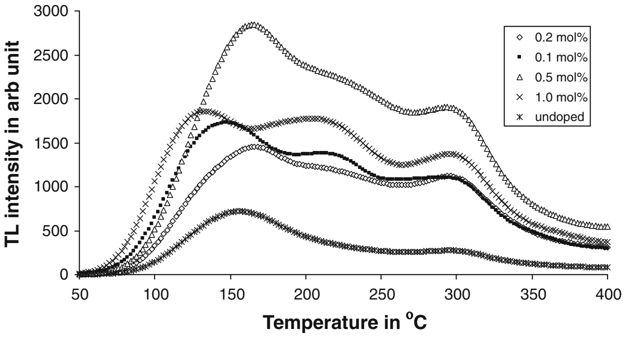

Fig. 4 TL glow curve of $GdCa_4O(BO_3)_3$:Dy phosphors. (Gamma-ray dose 1.1 kGy, rate of heating 5 °C per second, mass of the sample 1 mg)

Figure 6 shows relative total TL intensity of $GdCa_4O(BO_3)_3$:RE as a function of γ-ray doses given to the $GdCa_4O(BO_3)_3$:Ce(0.5 mol%) phosphors. It is found that the TL intensity of $GdCa_4O(BO_3)_3$:Ce(0.5 mol%) phosphors increases almost linearly with γ-ray doses up to 1.7 kGy.

PL emission spectra RE doped $GdCa_4O(BO_3)_3$ show that RE exists in trivalent ionic states. It seems when the borate based phosphors are exposed to γ-rays, various hole trapped centers like BO_3^{2-}, O_2^- are formed along with RE^{2+} ions [14] and TL emission may be caused by the recombination of holes from hole trapped radicals with RE^{2+} ions. The energy released in the electron–hole recombination process is used for the excitation of RE^{3+} resulting TL emission.

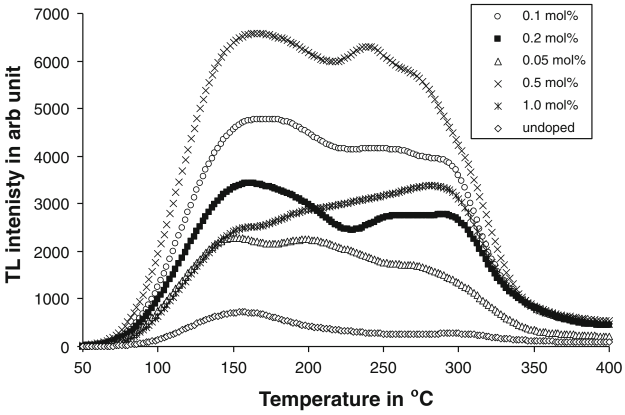

Fig. 3 TL glow curve of $GdCa_4O(BO_3)_3$:Eu phosphors. (Gamma-ray dose 1.1 kGy, rate of heating 5 °C per second, mass of the sample 1 mg)

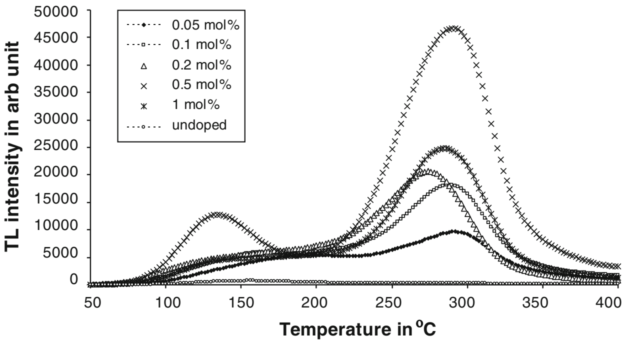

Fig. 5 TL glow curve of $GdCa_4O(BO_3)_3$:Ce phosphors. (Gamma-ray dose 1.1 kGy, rate of heating 5 °C per second, mass of the sample 1 mg)

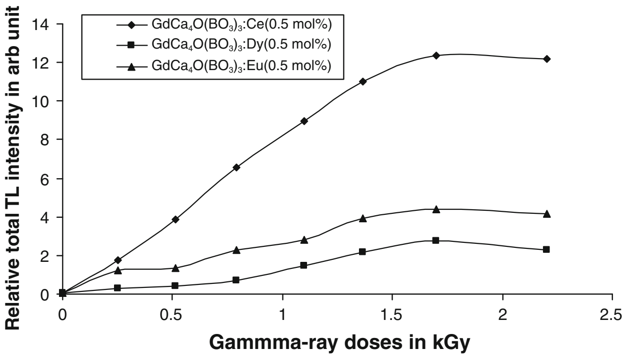

Fig. 6 Total TL intensity of GdCa$_4$O(BO$_3$)$_3$:RE phosphors as a function of γ-ray dose given to the sample

It is observed that the TL intensity initially increased with increasing the concentration of dopant attains an optimum value for a particular concentration and then decreased with further increase in the dopant concentration. Increasing the concentration of rare earth ions, more luminescence centers can be created and hence TL intensity is increased. However, the glow intensity cannot be expected to increase indefinitely with concentration, since the rate of formation of active luminescent centers by capturing the holes during irradiation might be fading rapidly and concentration quenching is occurred [1].

The increase in TL intensity with increasing γ-dose may be due to increase in number of active luminescent centers with γ-irradiation and subsequent emission of TL due to conversion of RE^{2+} → RE^{3+} during heating, thus intensity increases.

In order to find the possibility of GdCa$_4$O(BO$_3$)$_3$:Ce(0.5 mol%) phosphors as a TL dosimeter. Fading of TL was studied and it was found that the fading of the TL is about 5% over the period of 15 days.

Conclusions

Undoped and RE doped GdCa$_4$O(BO$_3$)$_3$ phosphors were synthesized by solid state diffusion technique. TL of the sample was recorded and it is found that the TL intensity in this system may be enhanced by doping the RE ions. Among three (Ce, Dy, and Eu) RE ions investigated here, we found that Ce is a suitable candidate for enhancing the TL intensity in GdCa$_4$O(BO$_3$)$_3$ system. On the basis of the PL emission spectrum of sample, we may conclude that RE ion acts as luminescence center in this system. The simple TL glow curve and linear dose response and less fading of TL over a period of 15 days of GdCa$_4$O(BO$_3$)$_3$:Ce(0.5 mol%) phosphors make the sample a suitable one for TL dosimetry.

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