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Thermoluminescence and lyoluminescence in γ-ray irradiated and Ce^{3+}-doped $YCa_4O(BO_3)_3$ phosphors

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Abstract $YCa_4O(BO_3)_3$ crystal having various concentration of Ce ions were synthesized by solid-state diffusion technique. XRD pattern of the sample confirmed the formation of the sample. Thermoluminescence (TL) and lyoluminescence (LL) of the γ-ray-irradiated sample were recorded. Two distinct peaks around 160 and 277 °C were observed in TL glow curves. TL intensity increased with increasing dopant concentration up to 2 mol%. A single sharp peak was observed in the LL glow curve of the sample. It was found that both TL and LL increased almost linearly with γ-ray doses up to 1.5 kGy. Photoluminescence (PL) of the sample was recorded to find the role of rare earth ion doped in $YCa_4O(BO_3)_3$. PL emission spectrum showed two peaks lying very close to each other around 390 nm which are characteristics of $5d \rightarrow 4f$ transition of Ce^{3+} ions. When LL of samples was recorded after removing the TL peaks it did not show any emission. This indicates that emission centres responsible for TL are also responsible for LL.

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Introduction

The effect 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, thermoluminescence 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 iso-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-symmetry. They have good thermal and chemical stability and are good host for luminescent material under UV excitation. So far, as best of our knowledge TL of these phosphors have not been reported. That is why we have undertaken the TL study of Ce-doped $YCa_4O(BO_3)_3$ phosphors. It is reported that some of the thermoluminescent materials also show lyoluminescence (LL) [10–13]. LL is a phenomenon of light emission when certain substances irradiated with ionizing radiation, are dissolved in a suitable solvent. It was first reported in 1895, by Widdmann and Schmidt [9]. Like

TL, LL can also be used for radiation dosimetry. This article reports TL and LL of γ-ray-irradiated rare-earth-doped $YCa_4O(BO_3)_3$ phosphors. Photoluminescence (PL) has also been recorded to confirm the incorporation of Ce ions in the host material.

Experimental

Ce-doped $YCa_4O(BO_3)_3$ phosphors were synthesized by solid-state diffusion technique. In this technique requisite amount of calcium carbonate, boric acid, yittrium oxide and cerium oxide were grounded thoroughly in a pastel and mortar. The mixture was then heated at 725 °C for 12 h and then cooled slowly. Obtained sample was grounded again then fired at 750 °C for another 12 h then cooled slowly up to room temperature. To confirm the formation of the samples 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 γ-ray-irradiation was carried out using ^{60}Co source. A PC-based thermoluminescence analyser system (TL-1009I) was used for recording TL. A routine setup consisting of a photo-multiplier tube and nano-ammeter was used to record LL is shown in Fig. 1.

Results and discussion

XRD pattern of the sample is given in Fig. 2. XRD pattern of the sample was found similar to that of the reported by Norrestam et al. [8].

In order to find the role of rare earth doping, the samples were characterized by PL. PL emission spectrum of

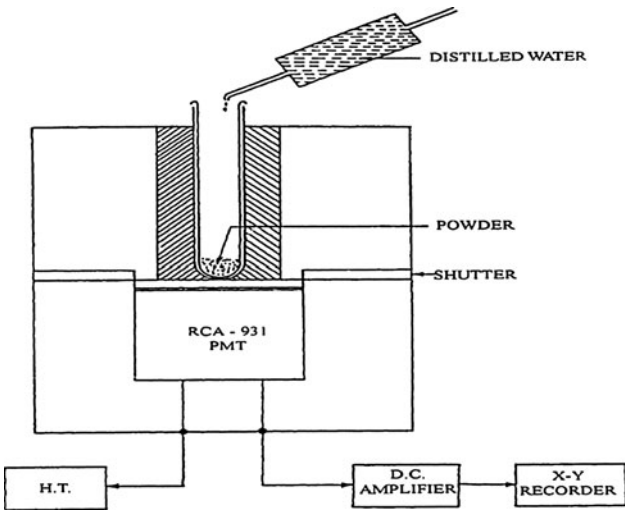

Fig. 1 Experimental setup used for LL measurement

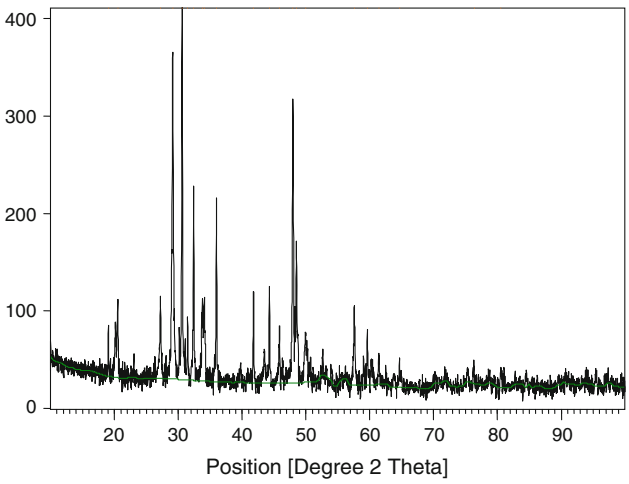

Fig. 2 XRD pattern of the $YCa_4O(BO_3)_3$ poly crystals

$YCa_4O(BO_3)_3$:Ce phosphors showed two peaks at 385 and 395 nm as shown in Fig. 3.

The Ce^{3+} ion has a single 4f electron outside the closed shells in its lowest energy state. Spin orbit coupling causes a split of a ground state into a $^2F_{5/2}$ and a $^2F_{7/2}$ states. The 5d → 4f transition being parity and spin allowed has large transition probabilities. Since the 5d electron orbital is much more strongly affected by the neighbouring ions, the 4f → 5d absorption transition is a strong broad band. The emission is similarly broad with two peaks corresponding to the $^7F_{5/2}$ and $^7F_{7/2}$ terminal states. [14]. PL emission confirms the incorporation of Ce ions in host lattice.

TL glow curves of the γ-ray-irradiated $YCa_4O(BO_3)_3$:Ce phosphors are shown in Fig. 4. Two distinct peaks one around 160 °C and another around 277 °C were observed in the TL glow curves. Peak TL intensity increases with increasing dopant concentration in the range 0.05–2.00 mol%.

When the borate-based phosphors are exposed to γ-rays, various hole trapped centres like BO_3^{2-}, O_2^- are formed [15] and TL emission may be caused by the recombination of holes from hole trapped radicals with Ce^{3+} ions. The

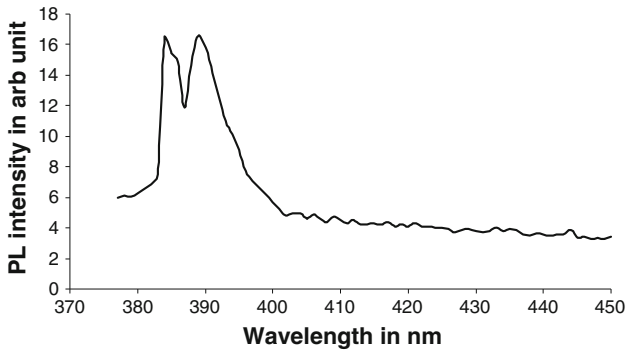

Fig. 3 PL emission spectrum of $YCa_4O(BO_3)_3$:Ce(2.0 mol%) phosphors under 247 nm excitation

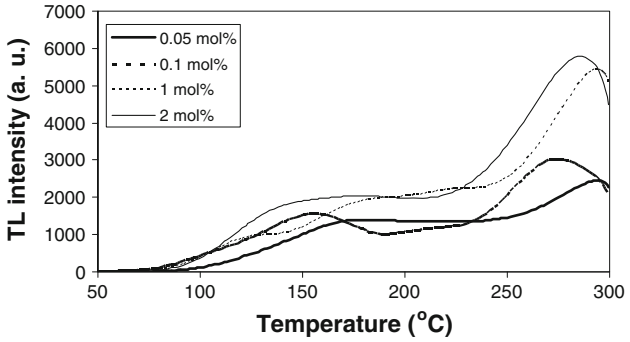

Fig. 4 TL glow curves of γ-ray-irradiated $YCa_4O(BO_3)_3$:Ce (2.0 mol%) phosphors. γ-ray dose 1.1 kGy. Material exposed to γ-ray dose by 1.1 kGy

energy released in the electron–hole recombination process is used for the excitation of Ce^{3+} resulting TL emission.

Figure 5 shows LL glow curves of γ-ray-irradiated Ce-doped $YCa_4O(BO_3)_3$ phosphors. When the sample was dissolved in dilute hydrochloric acid having concentration 0.36 g/L, LL intensity initially increased with time attained an optimum value and then decreased and finally disappeared. LL intensity also increased with increasing dopant concentration.

On dissolving the $YCa_4O(BO_3)_3$:Ce phosphors in dilute hydrochloric acid, the LL was observed due to release of trapped energy during dissolution.

$$e^-_{(\text{trapped})} + \text{water} \rightarrow e^-_{\text{aq}} \quad (1)$$

$$e^-_{(\text{aq})} + X \rightarrow X^*_{\text{aq}} \quad (2)$$

$$X^*_{\text{aq}} \rightarrow X_{\text{aq}} + h\nu \quad (3)$$

where X = radicals generated due to γ-ray irradiation.

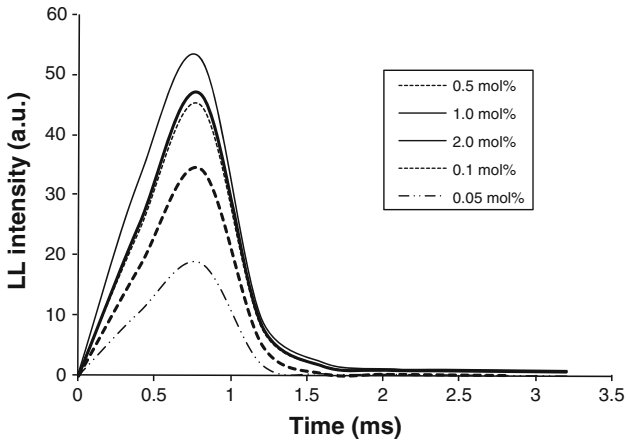

Fig. 5 Time dependence of LL intensity of γ-ray irradiated $YCa_4O(BO_3)_3$:Ce(2.0 mol%) phosphors. γ-ray dose 1.1 kGy when dissolved in dilute (0.36 g/L) hydrochloric acid

It is possible that steps (2) and (3) occur together without the intermediate state X^*_{aq}. A similar mechanism was also suggested by Ahnstrom [16].

Figure 6 shows TL and LL intensity as a function of γ-ray dose. TL and LL intensity increased with increasing γ doses given to the samples. Both TL and LL intensity increased almost linearly with the γ-ray dose.

The increase in TL/LL intensity with increasing γ-dose may be due to increase in number of active luminescent centres with γ-irradiation and subsequent emission of TL/LL due to conversion of $Ce^{2+} \leftrightarrow Ce^{3+}$ during heating or dissolution. Thus, intensity increases in initial stage. Difference in relative TL and LL intensities is probably due to the difference in energies imparted in different modes of excitation.

In order to understand the phenomenon of LL with the help of TL mechanism, we recorded the LL of post-irradiated annealed samples so that the TL of the samples can be removed. Interestingly, such samples did not show LL. This indicates that similar states are responsible for TL and LL in this system.

Conclusion

$YCa_4O(BO_3)_3$:Ce phosphors were synthesized by solid-state diffusion methods. PL emission spectrum shows the characteristic emission of Ce^{3+} ions. Both TL and LL intensity increased almost linearly with γ doses given to the sample. No LL was observed when it was recorded after annealing the post-irradiated samples at 280 °C for 5 min. It indicates that centers responsible for TL are closely related with LL and similar states are responsible for the emission of TL and LL.

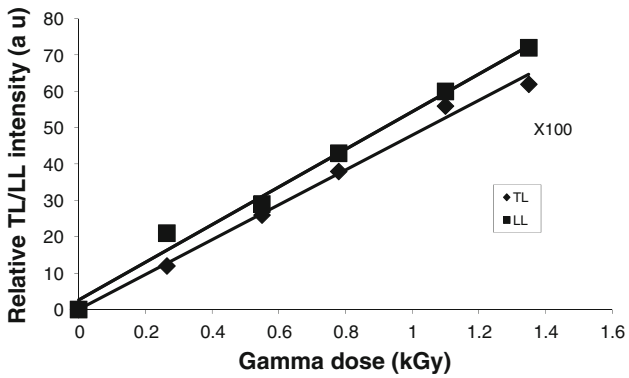

Fig. 6 Total TL/LL of $YCa_4O(BO_3)_3$:Ce(2.0 mol%) phosphors as a function of γ-ray dose given to the sample

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