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Thermoluminescence dose and heating rate dependence and kinetic analysis of ZnB_2O_4:0.05Dy^{3+} phosphor

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ABSTRACT

The intention of this study is to explore the thermoluminescence (TL) behavior of beta irradiated 5% Dy^{3+} doped zinc borate ($Zn(BO_2)_2$:0.05Dy^{3+}) phosphor prepared using the nitric acid method. The TL glow curve corresponding from 1 Gy to 80 Gy beta irradiation (preheated at 140 °C) shows a maxima at c.a. 180 °C. The dependence of heating rate was tested and found out that thermal quenching effect was dominating on TL glow curves as the heating rate increases. The dose response of the phosphor material exposed to beta radiation was investigated. Deconvolution was applied using the peak fit method on the glow curve for optimized conditions. Also peak shape (PS), various heating rates (VHR) and computerized glow curve deconvolution (CGCD) methods were used to evaluate the trapping level parameters, namely trap depth (*E*), frequency factor (*s*) and order of kinetics (*b*) associated with the main glow curve in $Zn(BO_2)_2$:0.05Dy^{3+} phosphor after beta irradiation of 20 Gy. The values of trap depth corresponding with the TL glow peak at 180 °C were found to be 0.93 eV, 0.92 ± 0.05 and 1.05 ± 0.02 respectively. Furthermore *W* and *c* parameters characterizing thermal quenching based on the Mott-Seitz theory were determined as 0.31 ± 0.04 eV and 162.55. The TL mechanism appears more likely to get second order kinetics, suggesting the probability of re-trapping of charge carriers by emptied traps.

1. Introduction

Over the past few decades, there has been a large amount of research dedicated to the radiation dosimetry using TL and the use of this technique explored many practical application potentials in various fields, such as personal, environmental, and clinical dosimetry. Although several luminescence materials used for various dosimetric applications have been produced [1–3], research and development of material are still going on the field for exploring new materials with low cost having better dosimetric properties. The TL studies of borate compounds have been drawn much attention owing to their near tissue equivalency [4], extremely low cost, easy handling process, lower synthesis temperature, outstanding thermal stability and mechanical properties and higher sensitivity [5–9]. Recently, TL characteristics of phosphors based on zinc borate are being reported. When the $Zn(BO_2)_2$ borate was doped with Ce^{3+} ions and exposed to beta irradiation the powder sample was observed to exhibited a prominent glow peak appeared at 230 °C and increases with increasing doses [10]. For the Tb doped zinc borate prepared by the solid state reaction method, TL and photoluminescence (PL) emission bands were found to be at about 490, 543, 584 and 620 nm [4]. Kucuk et al. (2013) have reported the TL properties of La-doped ZnB_2O_4 synthesized using the nitric acid method and found a main glow peak located at c.a. 200 °C [11]. Besides, it was shown that the shape of the glow curves were strongly related to the intensity of the beta dose. Juan et al. (2008) has studied PL and TL properties of Dy doped zinc metaborate, but TL data obtained using ^{60}Co gamma ray irradiation were very limited [12]. The study was mostly focused on PL and observed host material and 4*f*-4*f* transitions of Dy^{3+} ions. In the present study, $Zn(BO_2)_2$ phosphor doped with Dy^{3+} was obtained by nitric asid method in the air at high temperature. The shapes, intensities and positions of the TL glow curve can be correlated with various parameters of the trapping states associated with TL. This work has motivation in the potentialities of the borate phosphors for the application in the dosimetry at various irradiation doses and investigating their some TL characteristics. Here we have used PS, VHR and CGCD methods for the calculations and then evaluated the thermal quenching parameters. As far as we are aware, no work has been investigated from the point of view of TL dose response and corresponding kinetic parameters of this phosphor.

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2. Experimental details

$Zn(BO_2)_2$:0.05Dy^{3+} phosphor was prepared by using the nitric acid method [13]. In this technique, precursor powder chemicals, namely, ZnO (Alfa Aesar, 99.99% purity), H_3BO_3 (Alfa Aesar, 99.99% purity), and Dy_2O_3 (Alfa Aesar, 99.9% purity) were individually weighed in appropriate amounts to prepare ZnB_2O_4:0.05Dy^{3+} phosphor. These precursor powder chemicals were stirred during heating procedures at 80 °C, in 1 M nitric acid solution (HNO_3, standard solution) with a magnetic stirrer. The experimental study was performed in a 250 mL glass beaker. For 10 g of initial powders, 80 mL of nitric acid was used. It is worth mentioning that all oxides and boric acid were completely converted into the metallic nitrates [i.e. $Zn(NO_3)_2$, $B(NO_3)_3$ and $Dy(NO_3)_3$] through the reactions below:

$$ZnO + 2HNO_3 \rightarrow Zn(NO_3)2 + H_2O \quad (1)$$

$$H_3BO_3 + 3HNO_3 \rightarrow B(NO_3)3 + 3H_2O \quad (2)$$

$$(1/2)Dy_2O_3 + 3HNO_3 \rightarrow Dy(NO_3)3 + (3/2)H_2O \quad (3)$$

Mixing step was continued until a dry precursor was obtained. The dry precursor was ground in an agate mortar for 15 min in order to form powder and then calcined at 450 °C for 5 h to eliminate possible organic compounds. The most abundant nitrogen oxides in the air (i.e. N_2O, NO and NO_2) were also released up to this temperature, and metallic nitrates were converted into the oxides again. Finally, the dry precursor was pelletized under the pressure of 3 tons before annealing at 850 °C for 2 h which gives rise to the formation of $Zn(BO_2)_2$:0.05Dy^{3+} phosphor. Then the phosphor was cooled down naturally after completion of annealing and triturated in an agate mortar, and then placed into an Eppendorf tube [10,11,14,15].

All TL measurements were performed by using and automated Lexsyg Smart TL/OSL reader system having an internal Hamamatsu bialkaline photomultiplier tube (PMT) and an internal $^{90}Sr/^{90}Y$ source with the dose of 0.115 Gy s^{-1}. A filter (IRSL, TL wideband blue: BG39 + BG25 + KG3) was used in front of the PMT. The glow curve readouts were performed at a linear heating rate (HR) of 2 °C s^{-1} from room temperature (RT) to 400 °C. A preheat treatment at 140 °C were applied all TL measurements to erase the non-dosimetric maxima of the glow curves. A gas flow of nitrogen was used to reduce the oxidation of the heating element during the readout. Also the background was subtracted from all TL data to reach the final intensity.

3. Results and discussion

3.1. The effects of VHR on TL response

TL glow curves of $Zn(BO_2)_2$:0.05Dy^{3+} phosphor exposed to 20 Gy beta dose were studied using different HRs in the range of 0.5–10 °C s^{-1}. Fig. 1 shows the glow curves of the sample after preheat at 140 °C having a smooth shaped of maxima at c.a. 180 °C and 240 °C for the HR values of 0.5 °C s^{-1} and 10 °C s^{-1} respectively, it was observed as follows: (i) The temperature value at maximum TL intensity (T_m) shifts to higher temperatures (see Fig. 1) which is well known as temperature lag effect [16], mainly due to the temperature difference between the sample and the heating element. Indeed the sample heated with relatively higher HR needs shorter time than that of heated with relatively lower HR in order to release the same amount of electrons. (ii) Maximum TL intensity value of the glow peak decreases (see Fig. 1); a well recognize phenomenon, thermal quenching effect; increased probability of non-radiative transitions [17], in other words, thermally released charge carriers from trapping or luminescence centers, usually host defects or co-dopants, cannot recombine directly at recombination center and energy transfer takes place via non-radiative transitions. (It is proved by the subsequent items as well) (iii) The integrated peak area of the glow curve decreases (see Fig. 2a), indicating the evidence of thermal quenching affect. Otherwise the total area under the glow curve should have been independent of HR [18,19]. (iv) Full width at half maximum (FWHM) increased (see Fig. 2b); another consequence of aforementioned temperature lag effect and withal thermal quenching effect [20].

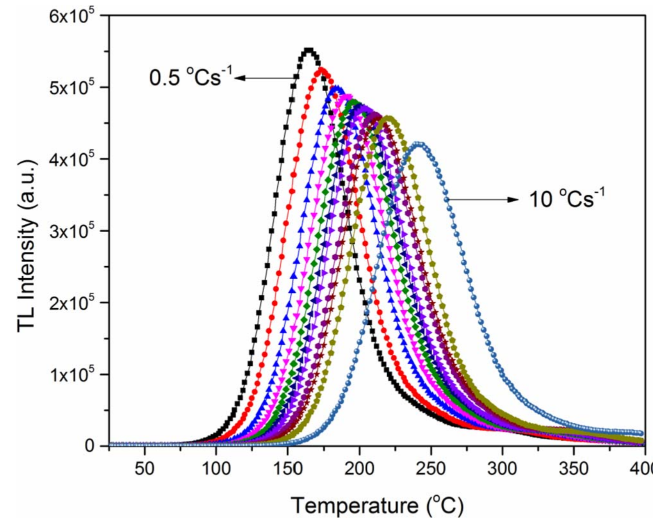

Fig. 1. Effect of heating rate on TL glow curve for 20 Gy beta dose exposed ZnB_2O_4:0.05Dy^{3+} phosphor.

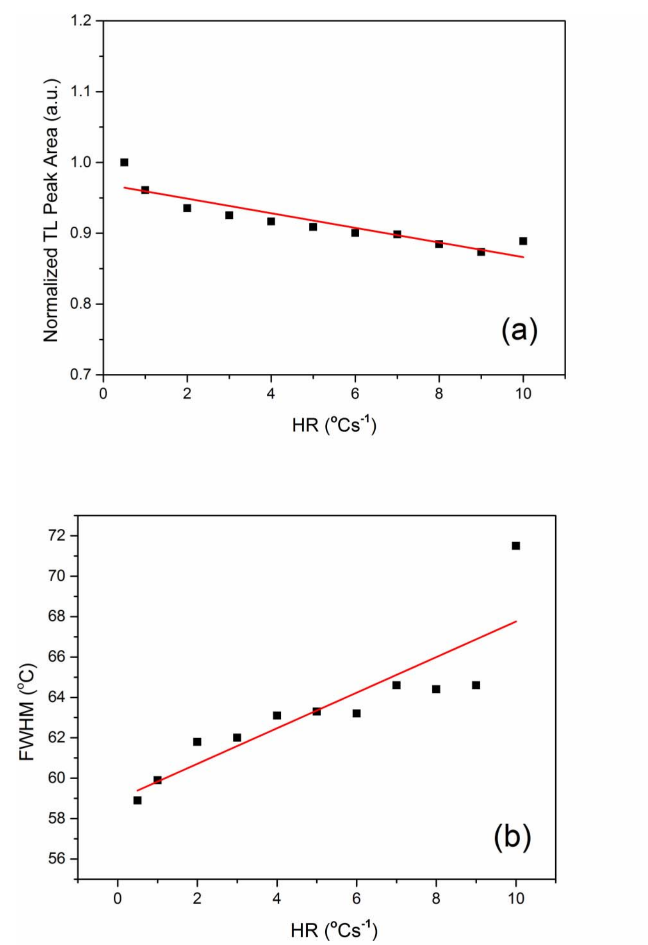

Fig. 2. a) Normalized TL peak area vs HR and b) FWHM vs HR curves of ZnB_2O4:0.05Dy^{3+} phosphor.