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Synthesis, thermoluminescence and dosimetric properties of La-doped zinc borates

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ABSTRACT

Dependence on the dose of beta radiation of undoped and La-doped ZnB_2O_4 powder samples at 1%, 2%, 3%, 4%, 5% and 10% (by weight) was investigated by thermoluminescence technique. Powder samples were synthesized by the nitric acid method using the starting oxides [zinc oxide (ZnO), boric acid (H_3BO_3) and doped element oxide (La_2O_3)]. The samples were characterized by X-ray diffraction (XRD). The thermoluminescence (TL) properties of the powder samples were measured with Risø TL/OSL DA-20 reader. TL glow curves were obtained with heating at a constant heating rate of 5 °C/s up to 450 °C. The dose response curves of the powder samples exposed to ^{90}Sr beta radiation (40 mCi) were obtained in the dose range from 143 mGy to 60 Gy. Dose responses and minimum detectable dose (MDD) values for increasing radiation doses of the powder samples were determined. The dose responses of all the samples have shown a quite linear response to beta radiation. MDD value of 10% La-doped ZnB_2O_4 powder sample which shows a high temperature peak at 207 °C was determined as 4 mGy. MDD values for 1%, 2%, 3%, 4% and 5% La-doped ZnB_2O_4 powder samples were also determined as 10 mGy, 50 mGy, 10 mGy, 10 mGy and 30 mGy, respectively. Luminescence intensities of the powder samples were shown to be likely to be used for low radiation doses.

1. Introduction

The increasing use of thermoluminescence dosimeter (TLD) with application in areas such as clinical, personal and environmental monitoring of ionizing radiation has motivated research on new materials with adequate dosimetric properties [1]. Borates are attractive candidates in TLD for the quantitative measurement of radiation dose. The thermoluminescence (TL) of doped borates has been extensively investigated because of their near tissue equivalent absorption coefficient [2–6], very low cost, lower synthesis temperature, good thermal stability and mechanical properties, higher sensitivity and relatively easy preparation [7–12]. Therefore they are worth considering for personal dosimetry. The sensitivity and thermal stability of borates vary widely and depend not only on the starting materials, but also on the preparation method. This situation led to investigations into the mechanisms involved in thermoluminescence [13,14], and into how they depend on the synthesis methods [15–17].

Zinc borate (ZnB_2O_4) is a boron-based inorganic material widely used as flame retardant, antibacterial and additive to protect wood products above ground from insect and fungal attacks [18]. It is a white crystalline or amorphous powder insoluble in water. Its toxicity is low. Its melting point is 980 °C. Zinc borate can be isolated as crystalline material in various forms having different chemical compositions and structures [19].

Some researchers have made studies on photoluminescence, thermoluminescence and dosimetry properties of doped zinc borate [20–22]. To our knowledge, the luminescence and dosimetric properties of La-doped ZnB_2O_4 powder samples by beta irradiation have not been reported in the literature so far. In this paper, we first report the thermoluminescence and dosimetric properties by beta irradiation of undoped and various La-doped ZnB_2O_4 powder samples (ZnB_2O_4, $Zn_{0.99}La_{0.01}B_2O_4$, $Zn_{0.98}La_{0.02}B_2O_4$, $Zn_{0.97}La_{0.03}B_2O_4$, $Zn_{0.96}La_{0.04}B_2O_4$, $Zn_{0.95}La_{0.05}B_2O_4$ and $Zn_{0.9}La_{0.1}B_2O_4$) by the thermoluminescence technique.

2. Experimental details

2.1. Procedure for the synthesis of ZnB_2O_4

Powder samples of undoped and La-doped ZnB_2O_4 at 1%, 2%, 3%, 4%, 5% and 10% (by weight) were prepared by the nitric acid method. This method is relatively easy and cheap. ZnB_2O_4 powder samples were synthesized using zinc oxide (ZnO, with a minimum purity 99.99%) and boric acid (H_3BO_3, with a purity of

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99.99%). Appropriate amounts of ZnO and H_3BO_3 powders were separately weighted to prepare zinc borate. Starting materials were mixed, while heating at 80 °C, in 1 M nitric acid solution (HNO_3, standard solution) by using magnetic stirrer. All the experiments were carried out in a glass beaker of 250 ml volume. For 5 g of initial powders, 80 ml acid was used. During this process, all oxides and boric acid were converted into the metallic nitrates [i.e. $Zn(NO_3)_2$, $B(NO_3)_3$ and $La(NO_3)_3$] through the reactions below. La-doped ZnB_2O_4 powder samples were also prepared in a similar manner by taking the starting material in stoichiometric ratio and adding La_2O_3 to the mixture.

$$ZnO+2HNO_3 \rightarrow Zn(NO_3)_2+H_2O \quad (1)$$

$$H_3BO_3+3HNO_3 \rightarrow B(NO_3)_3+3H_2O \quad (2)$$

$$\tfrac{1}{2}La_2O_3+3HNO_3 \rightarrow La(NO_3)_3+\tfrac{3}{2}H_2O \quad (3)$$

Mixing was continued until dry precursor was obtained. The precursor was ground in an agata mortar for about 15 min. Then, it was calcined at 450 °C for 5 h to remove possible organic compounds. Gasses such as NO and NO_2 were also released up to this temperature and metallic nitrates were converted into the oxides again [23]. Finally, the precursor was pelletized under the pressure of 3 ton before annealing at temperatures from 700 °C to 900 °C for 2 h which leads to the formation of zinc borates. After annealing, the powder samples were cooled to room temperature and triturated in an agata mortar.

2.2. Measurements

The structure analysis of all the samples and the effect of doping on the structure of undoped ZnB_2O_4 powder sample were studied by X-ray powder diffraction. The X-ray diffraction (XRD) measurements were taken at the interval of Bragg angle 2θ from ($10^\circ < 2\theta < 90^\circ$), using a Rigaku Ultima IV X-ray diffractometer at 40 kV at 3 deg. min^{-1} and 30 mA with Cu-K_α (λ=1.5405 Å) radiation.

The TL glow curves of undoped and various La-doped ZnB_2O_4 powder samples were recorded with Risø TL/OSL DA-20 reader using Corning 7/59 and Schott BG/39 optical filters in nitrogen atmosphere. The measurements were carried out on 10 mg samples. During measurements of all the powder samples, preheating process up to 140 °C for the heating rate of 2 °C/s and the reading process up to 450 °C for the heating rate of 5 °C/s were used. TL intensity for each glow peak was calculated by taking the area under dosimetric peak. The dose responses of all the powder samples exposed to ^{90}Sr beta radiation (40 mCi) were obtained in the dose range from 143 mGy to 60 Gy.

3. Results and discussion

3.1. X-ray powder diffraction

In this work the ZnB_2O_4 phase formation condition has been investigated by XRD. Fig. 1 shows the XRD patterns of ZnB_2O_4, $Zn_{0.99}La_{0.01}B_2O_4$, $Zn_{0.98}La_{0.02}B_2O_4$, $Zn_{0.97}La_{0.03}B_2O_4$, $Zn_{0.96}La_{0.04}B_2O_4$, $Zn_{0.95}La_{0.05}B_2O_4$ and $Zn_{0.9}La_{0.1}B_2O_4$ powder samples sintered at 900 °C. These XRD patterns were found to be consistent with that reported in JCPDS card no. 39-1126. The XRD data shown in Fig. 1 indicated that the La-doped ZnB_2O_4 powder samples were almost pure phase with high crystallinity. It is known that the ionic radii (r) of Zn^{2+} and B^{3+} are 0.60 Å and 0.21 Å [24], respectively. As the ionic radius of B^{3+} is too small, it is difficult for these elements to replace B^{3+} in ZnB_2O_4. Hence, in this study, it is believed that the Zn^{2+} sites are substituted by La^{3+} in the lattice. The decrease in

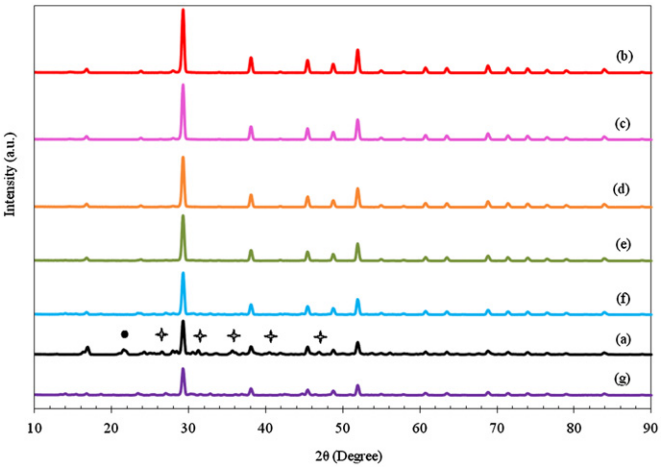

Fig. 1. The X-ray powder diffraction patterns of (a) ZnB_2O_4, (b) $Zn_{0.99}La_{0.01}B_2O_4$, (c) $Zn_{0.98}La_{0.02}B_2O_4$, (d) $Zn_{0.97}La_{0.03}B_2O_4$, (e) $Zn_{0.96}La_{0.04}B_2O_4$, (f) $Zn_{0.95}La_{0.05}B_2O_4$ and (g) $Zn_{0.9}La_{0.1}B_2O_4$ sintered at 900 °C; (✣) H_3BO_3, (●) B_2O_3. The standard XRD pattern of ZnB_2O_4 is taken from JCPDS card no. 39-1126.

crystallinity of La-doped ZnB_2O_4 with increasing La dopant content was observed from the XRD patterns, which can be attributed to the variation of charges of dopants that results in the defect formation in the lattice. Little impurity phases, such as H_3BO_3 and B_2O_3 were observed at 2θ=16.30°, 21.54°, 28.38°, 31.18° and 35.66°. The X-ray diffraction patterns of $Zn_{1-x}La_xB_2O_4$ (x=0 and x=0.01) powders sintered at 450 °C for 5 h and 700, 800, 900 °C for 2 h in air are also shown in Fig. 2a and b, respectively. It is clearly seen that the fraction of the zinc borate phase is considerably higher in the La-doped samples. At 900 °C, for example, ZnB_2O_4 is the major phase in the 1% La-doped sample while a fraction of impurity phases appears in the undoped specimen.

3.2. Thermoluminescence of undoped and La-doped ZnB_2O_4

Specification of thermoluminescence characteristics of a candidate for TL dosimetry is an important step in the production of a TL. Shape and structure of the glow curves, linear dose response, minimum detectable dose, sensitivity, the occurrence temperature and intensity of TL peaks, fading, sunlight susceptibility, and vulnerability against humidity should be studied [25]. In this study the TL properties of undoped and various La-doped ZnB_2O_4 powder samples, namely, glow curves, linear dose response and minimum detectable dose have been determined.

3.2.1. TL glow curves

The glow curves are particularly important since they are the main indicators of whether a material can be used for TL dosimetry purposes or not. Generally it is desired that the glow curve gives a simple, if possible single, peak at around 200 °C [25]. Glow curve shapes and peak temperatures are also affected by the synthesis and doping methods [26].

In this study it has been observed that the main TL peak is at around 200 °C on the glow curves of all the powder samples. Fig. 3 shows a set of the selected TL glow curves which were obtained from ZnB_2O_4 powder samples of undoped and La-doped with different amounts (1%, 4% and 10%) sintered at 900 °C for 143 mGy, 715 mGy, 1.43 Gy and 15 Gy beta radiation doses, respectively.

The glow curves of undoped and La-doped ZnB_2O_4 at 1%, 4% and 10% powder samples exhibit a very well defined main peak having the maximum temperature at around 191 °C (Fig. 3a), 201 °C with