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Luminescence studies of zinc borates activated with different concentrations of Ce and La under x-ray and electron excitation

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ABSTRACT

Several ZnB_2O_4 powder samples having dopants concentrations of 0.1, 0.01, 0.04 wt% Ce and La were prepared using the nitric acid method via the starting oxides. Several complementary methods such as powder X-ray diffraction (XRD), thermal analyses environmental scanning electron microscopy (ESEM), Radioluminescence (RL) and Cathodoluminescence (CL) techniques were used. Unique luminescence properties of Ce doped ZnB_2O_4 powder samples are reported for the first time. A new luminescence bands appearing in red part of the spectrum and having all the characteristics of Ce^{3+} were obtained from RL results. Changing the Ce and La concentration of 0.01–0.1 wt% leads to an increase in RL and CL intensities of Ce^{3+} and La^{3+} ions and also CL emission spectra of ZnB_2O_4 show gradual shift towards longer wavelength. When we compare the luminescence intensity of the samples it is seen that Ce doped ZnB_2O_4 has the highest intense whereas La doped ZnB_2O_4 has the lowest one. However, emission spectra of both Ce and La doped samples kept unchanged.

1. Introduction

Zinc borate is a multifunctional boron based inorganic compound which is most commonly used as halogen free fire retardant material with different ratio of ZnO, B_2O_3, and H_2O. When comparing with other flame retardants zinc borates present major advantages in processing with several kinds of polymers. It is worth noting that toxic and corrosive substances are not produced in zinc borates during the combustion process. They can be used in halogen containing systems, plastic, paint, rubber or coating industry due to some advantages (i.e. innocuous to the environment, high thermal stability, density and good dispersion characteristics (Khalilev and Suzdal, 2013; Yan et al., 2004; Kim et al., 2007; Pang et al., 2008; Wu et al., 2009). As an important family of luminescence materials, zinc borates have been paid intense attention because of their excellence properties. Li et al. studied photoluminescence properties and thermoluminescence dosimetry characteristics following ^{60}Co gamma-ray irradiation of Tb^{3+} and Dy^{3+} doped ZnB_2O_4 phosphors. They suggested that ZnB_2O_4 incorporated with Tb^{3+} and Dy^{3+} had an important role as the materials for gamma-ray TL dosimeter in the clinical dosimetry field (Li et al., 2007) and (Li et al., 2008). Nil et al. reported luminescence and dosimetric characteristics of La activated ZnB_2O_4 powder samples after exposure to beta radiation (Kucuk et al., 2013). Annalakshmi et al. examined dosimetric characteristics of thulium doped ZnB_2O_4 phosphor and suggested that they have potential applications in radiation dosimetry (Annalakshmi et al., 2014). Liu et al. examined the luminescence properties of a new red phosphor, $ZnB_2O_4:Bi^{3+},Eu^{3+}$. They indicated that there was an improvement of luminescence intensity through the energy transfer from co-doped Bi^{3+} to Eu^{3+} in the host material (Liu et al., 2010). Mu et al. synthesized a series of Eu^{3+} doped ZnB_2O_4 phosphors prepared through solid state reaction method and suggested several applications to enhance the luminescence of Eu^{3+}(Mu et al., 2011a). Zheng et al. studied on Eu^{3+} doped ZnB_2O_4 prepared using co-precipitation method and investigated the luminescence properties of Eu^{3+} in the host material (Zheng et al., 2009). Boronat et al. studied the cathodoluminescence properties of $LaAlO_3:REE^{3+}$(REE = Dy, Pr and Eu) powders synthesized by the Pechini's method and a spray -drying technique (Boronat et al., 2017). Zou et al. synthesized $Zn_3(BO_3)_2:Ce^{3+}$ nanoparticles and $Zn_3(BO_3)_2:Ce^{3+},Al^{3+}$ nanoparticles by co-precipitation method and investigated the effect of Al^{3+} on luminescence

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properties of Ce^{3+}(Zou et al., 2005). Zhang et al. reported on luminescence properties of the $Zn_3(BO_3)_2$ nanocrystals and the $Zn_3(BO_3)_2$ samples doped with different mole fraction of Ce^{3+} and Mn^{2+} prepared by co-precipitate method (Zhang et al., 2012). They suggest that the Ce^{3+} ions substituted for Zn^{2+} in the host and acted as emission centers, and Mn^{2+} acted as activator. More recently Liang et al. investigated morphology and temperature dependence photoluminescence properties of Tb doped zinc borates by controlling the reaction temperature and the pH of the prepared solutions (Liang et al., 2017).

Most research done to date has focused on the preparation and luminescent properties of lanthanide phosphors. A variety of methods allowed preparation of an efficient phosphor materials are available in the literature, including solid-state reaction (Ayvacıklı et al., 2014), a gel combustion reaction (Muresan et al., 2016), hydrothermal technology, etc.

Hence in this work, the synthesis and the luminescence properties of La and Ce activated ZnB_2O_4 powder samples via nitric acid method have been prepared. As far as we are aware, there has been no literature on luminescence properties of these compounds up to now. Doping concentration effect of luminescent ions on the luminescence spectra have been studied. The motivation of this work is to suggest a comparative study of luminescence of the Ce and La doped in the zinc borate matrix and assess their potential use in display panels.

2. Experimental details

2.1. Sample preparation

2.1.1. Procedure for the synthesis of ZnB_2O_4:La

Undoped and La-doped ZnB_2O_4 at 0.01%, 0.04% and 0.1%wt phosphors were prepared using nitric acid method which is relatively simple and cheap process. Similarly, ZnB_2O_4 powder samples were synthesized using precursor chemicals namely, ZnO (Alfa Aesar, 99.99% purity) and H_3BO_3 (Alfa Aesar, 99.99% purity). Separately, powders were weighted according to desired composition to prepare zinc borate. These materials were agitated to obtain starting mixtures with a magnetic stirrer whilst being heated up at 80 °C, in a 1 M solution of nitric acid (HNO_3, standard solution). 80 ml acid was added to 5 g of initial powders for each experiment performed in a 250-ml glass beaker. 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 $La(NO_3)_3$] 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 into the mixture.

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

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

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

Mixing step was continued until a dry precursor was obtained. The precursor was grounded in an agate mortar for at least 15 min to form powders, and then calcined at 450 °C for 5 h to remove 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 precursor was pressed to form pellets by applying the 3 tons of pressure before annealing from 700 °C to 850 °C for 2 h which gives rise to the formation of zinc borates. After annealing, the pellets were cooled down naturally after completion of annealing (Kucuk et al., 2013).

2.1.2. Procedure for the synthesis of ZnB_2O_4:Ce

Undoped and various Ce^{3+} doped ZnB_2O_4 samples were prepared using nitric acid method. Undoped ZnB_2O_4 sample was prepared as given in Ref. Kucuk et al. (2013). Similarly, ZnB_2O_4:Ce^{3+} samples were also prepared using precursor chemicals namely, ZnO (Alfa Aesar, 99.99% purity), H_3BO_3 (Alfa Aesar, 99.99% purity). and CeO_2 (Alfa Aesar, 99.99%). The stoichiometric quantities of ZnO, H_3BO_3 and CeO_2 powders were separately weighted to prepare ZnB_2O_4:Ce^{3+} samples. The starting materials were mixed by using a magnetic stirrer at 80 °C in 1 M nitric acid solution (HNO_3). During this process, boric acid and all oxides were converted into the metallic nitrates [i.e. $Zn(NO_3)_2$, $B(NO_3)_3$ and $Ce(NO_3)_3$] (Kucuk et al., 2016). The expected reactions are given below:

$$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O \quad (4)$$

$$H_3BO_3 + 3HNO_3 \rightarrow B(NO_3)_3 + 3H_2O \quad (5)$$

$$CeO_2 + 3HNO_3 \rightarrow Ce(NO_3)_3 + 3/2H_2O + 1/4O_2 \quad (6)$$

Finally, the precursor was pressed to form pellets by applying the 3 tons of pressure before annealing from 700 °C to 850 °C for 2 h which gives rise to the formation of zinc borates. After annealing, the powder samples were cooled down naturally after completion of annealing and triturated in an agate mortar (Kucuk et al., 2016).

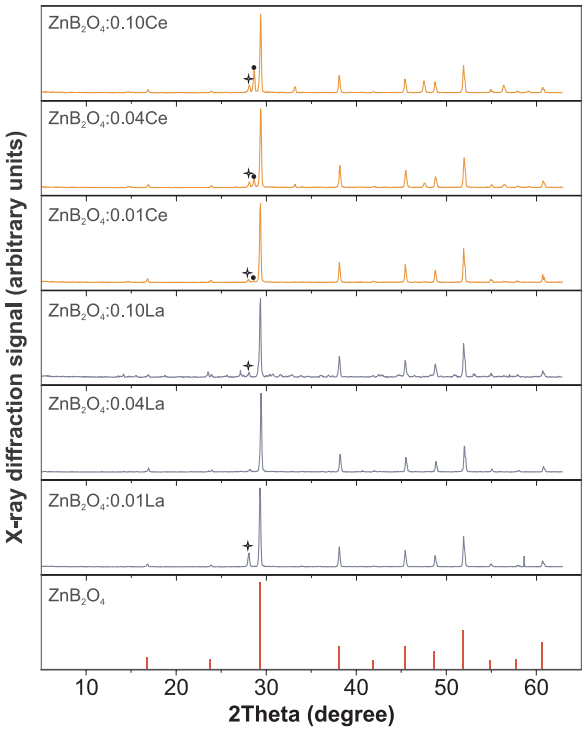

Fig. 1. XRD patterns of ZnB_2O_4 having dopants concentrations of 0.01, 0.04, 0.1 wt% Ce and La. Some impurity phases, namely H_3BO_3 and B_2O_3 were observed; (*) H_3BO_3, (.) CeO_2.

2.2. Sample characterization

Structural analysis of powdered Ce and La activated ZnB_2O_4 powder samples were performed using a Philips PW-1710 X-ray diffractometer (XRD) using Cu-Kα radiation. Data were recorded at RT using a step scanning with fixed time of 4 s per 0.020°2θ and XRD patterns were obtained from 2 to 80°2θ. The resultant XRD profiles of the powdered samples were refined by the ICCD-PDF2 and RRUFF databases.

The results of Thermal analysis (DTA) were performed using a thermal analyzer Model 4851e Mettler Toledo at a heating rate of 10 °C/min from RT up to 950 °C in nitrogen atmosphere. Each sample was weighted to be 55 ± 0.25 mg and the samples were held in an