Journal of Luminescence 150 (2014) 59–67

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Study of anomalous emission and irradiation effect on the thermoluminescence properties of barium aluminate

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ARTICLE INFO

Article history:
Received 22 October 2013
Received in revised form
12 January 2014
Accepted 20 January 2014
Available online 28 January 2014

Keywords:
Anomalous emission
Aluminates
Combustion
Traps
Tracks
Deconvolution

ABSTRACT

The photoluminescence (PL) and thermoluminescence (TL) properties of $BaAl_2O_4:Eu^{2+}$ phosphor synthesized by the combustion method is studied. Electron beam and gamma rays are used for irradiating the phosphor while performing TL measurements. The structural and morphological analysis of the resulting phosphor was carried out by X-ray diffraction study and scanning electron microscopy, whereas their optical properties were examined by PL spectroscopy and TL glow curve measurements. The intense bluish green broad band emission near 494 nm that originates from 5d to 4f transition in Eu^{2+} ions was observed in the $BaAl_2O_4:Eu^{2+}$ phosphor. The broad band emission was further examined, showing that emission consist of two broad peaks originating due to occupation of two different lattice sites by Eu in $BaAl_2O_4$ host. The occurrence of two broad bands with large stokes shift and hence anomalous emission is explained by proposing energy level model. Calculations based on Dorenbos formulations were carried out which support the presence of anomalous emission in $BaAl_2O_4:Eu^{2+}$ phosphor. The TL response of $BaAl_2O_4:Eu^{2+}$ phosphor for two different radiations was compared and studied in detail. Detailed process and possible mechanisms for PL and TL are studied and discussed with the help of energy level models.

1. Introduction

Rare earth activated aluminate based phosphors have been extensively investigated because of their high chemical stability, long life and bright emission characteristics in the visible region of electromagnetic spectrum [1–6]. Several aluminate based compositions are investigated and used in PL, cathodoluminescence and plasma display panel applications due to their high quantum efficiency in the visible region [7,8]. The synthesis and spectroscopic study of $BaAl_2O_4:Eu^{2+}$ phosphor has attracted a tremendous amount of attention because of their potential use as long persistent phosphor [9–12]. $BaAl_2O_4$ which belongs to the family of stuffed tridymites is a high melting point material with good dielectric, pyroelectric, and mechanical properties. The structure of $BaAl_2O_4$ is derived from the structure of SiO_2 β-tridymite [13]. In this Al^{3+} replaces Si^{4+} in the tetrahedra of SiO_2 tridymite, Ba will occupy sites in channels parallel to the *c*-axis. It is observed from literature that at room temperature, $BaAl_2O_4$ is hexagonal and has a superstructure with unit cell parameters 2A, C; where, A and C are lattice parameters of hexagonal tridymite [14].

There is growing interest in developing oxide nanophosphors doped with transition metal or rare earth ions due to their ease of synthesis methods and chemical stability [5]. Lou et al. prepared thin films of barium aluminate ($BaAl_2O_4$) deposited by a spray pyrolysis method [15]. They investigated the effects of preparation conditions on the structural and luminescence properties of the films. Divalent europium ions (Eu^{2+}) have widely been used to obtain blue color emitting phosphors [16]. In rare earth activated phosphors Eu^{2+} doped phosphors usually show strong broadband PL emission in blue region and sharp peaks in red region. The emission of Eu^{2+} is strongly affected by host lattice and can occur from the blue to the red region of the visible region [17]. This is due to change in electric dipole of the $5d \leftrightarrow 4f$ transition and the variation of 5d excited state by crystal field effects. Recently, Rezende et al. studied X-ray excited optical luminescence of Ce-doped $BaAl_2O_4$ phosphor and found that decrease in the luminescence when excited at Ce L_{III}-edge. This is due to the energy transfer via X-ray fluorescence from Ce to Ba in the X-ray photon energy range of the Ce L_{III}-edge absorption [18]. Katsuma et al. studied the long afterglow phosphorescent characteristic of $BaAl_2O_4$:Eu,Dy films prepared by laser ablation. They correlated the poor afterglow with TL measurements [12].

Preparation of nano-sized phosphor is very promising in the field of photonics, luminescent displays, fluorescent lamps, TL dosimetry etc. Different methods such as spray pyrolysis, co-

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http://dx.doi.org/10.1016/j.jlumin.2014.01.057

precipitation, force hydrolysis [19] and sol–gel, have been used to fabricate nanophosphors. Amongst these methods co-precipitation and sol–gel are complicated and also consumes lot of time. The advantage of choosing the combustion method is the facile preparation of materials within short time. Furthermore no sintering is needed to change the ionizing state of Eu^{3+} to Eu^{2+} since the reducing atmosphere produced during synthesis is sufficient to accomplish this change [12].

$BaAl_2O_4:Eu^{2+}$ is good long persistent phosphor, to understand the mechanism of long persistence the thermoluminescence study of this phosphor has been done by many researchers [1,3,7,9]. Recently Bos et al. presented a new versatile facility to study photoionization processes in impurity doped compounds. In this facility they coupled additional monochromatic light with a TL reader, enabling a fully automated recording of glow curves as a function of photon excitation wavelength which provides detailed information on the mechanism of trap filling preceding persistent luminescence [20]. Therefore, we also took a small step to understand the variation in TL behavior and trapping parameters for two different types of radiations. In the present work, PL and TL study of this phosphor is carried out. The main interest of this study is to examine anomalous emission in $BaAl_2O_4:Eu^{2+}$ and variation of TL glow curves and trapping parameters for two different radiations.

2. Experimental section (chemical synthesis)

Recent investigations have focused extensively on various aluminates as host for luminescent materials doped with transition metal or rare earth ions [14,21]. It was noted that these aluminates have been prepared traditionally by solid state reactions, which demand generally long times and high annealing temperatures, which results in wastage of power [1,4,22]. Whereas some other preparation methods require, repeated heating, special equipments and expensive raw materials [9,23,24]. Indeed there is a growing demand for economically viable synthesis methods for manufacturing the aluminates. Combustion synthesis is very useful from this point of view [25]. In this work, we have successfully employed relatively a low temperature, fast and simple method for the preparation of $BaAl_2O_4$ material. $BaAl_2O_4$ phosphor was prepared by combustion synthesis route. The combustion synthesis is carried out at 550 °C, the starting materials used were $Ba(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Eu_2O_3 and urea (NH_2CONH_2) of analytical grade. Eu_2O_3 was converted into the nitrate form by mixing it into appropriate amount of nitric acid. All the starting materials were mixed and milled using a mortar and pestle, and a thick white paste was formed from water of crystallization present in the metal nitrates. The resulting paste was then transferred to silica crucible and kept inside a vertical muffle furnace, which is maintained at a constant temperature 550 °C. The paste melted, underwent dehydration and finally decomposed with the evolution of gases (oxides of nitrogen and ammonia). The mixture swelled, forming the foam that ruptured with a flame and glowed to incandescence. The combustion process was completed within 4 min (approximately). The ash formed after combustion results in $BaAl_2O_4$:Eu material which was milled to powder, using a mortar and pestle. Note that the synthesized samples were not sintered because the reducing atmosphere created during the reaction is enough to reduce Eu^{3+} to Eu^{2+}, which is confirmed from photoluminescence studies and detailed mechanism for reduction process is discussed in Section 3.3.5. To the best of our knowledge, the thermoluminescence properties of Eu^{2+} doped $BaAl_2O_4$ host, for different irradiation have not been studied yet. Therefore, in this study we focused on thermoluminescence properties of this phosphor in addition to photoluminescence properties.

SEM micrographs were obtained using a HITACHI S-4800 scanning electron microscope. The SEM micrographs were taken at 5000 V accelerating voltage, 8300 μm working distance, 7800 nA emission current, at high lens mode with fast scan speed and gray scale color mode. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using a X'pert-PRO PANalytical diffractometer (Cu-Kα radiation) at a scanning step of 0.001, in the 2θ range from 10 to 80°.The photoluminescence (PL) emission spectra of the samples were recorded using a Fluorescence spectrometer (Shimadzu, RF 5301 PC). Excitation and emission spectra were recorded using a spectral slit width of 1.5 nm. For TL studies, samples were exposed to gamma rays from a ^{60}Co source at room temperature at the rate of 0.58 kGy/h. After the desired exposure, TL glow curves were recorded with the help of Nucleonix 1009I TL reader, at a heating rate of 5 $°Cs^{-1}$. All the measurements were carried out in an open atmosphere.

3. Results and discussion

3.1. XRD and crystal structure

Fig. 1 shows the XRD pattern for $BaAl_2O_4$. The XRD pattern matched perfectly with standard data available in ICDD file no. 82-2001. No separate phases of constituents and other probable phases were observed which suggest formation of homogeneous $BaAl_2O_4$ phase. Although the Eu ions occupied the Ba ions, the small amount of the Eu dopant had no significant effect on the host structure of the $BaAl_2O_4$, as observed from XRD pattern and calculated lattice parameters. Aluminates are known for their stiff mechanical properties and $BaAl_2O_4$ has a very high melting point (1815 °C) and holds a stuffed tridymite (hexagonal) structure. The $BaAl_2O_4$ belongs to $C_6^6 - P6_3$ space group. In $BaAl_2O_4$ host there are two different sites of Ba^{2+}, one site (site-1) is twice as abundant as the other (site-2) [26]. Ba^{2+} has fairly large ionic radius $r = 1.47$ Å which is much bigger than most of the divalent/trivalent rare earth ions. Due to the bigger size of Ba the substitution of rare earth ions ($Eu^{2+} = 1.3$ Å) is easy at Ba^{2+} sites.

The crystal structure of $BaAl_2O_4$ phosphor projecting along [0 1 0] directions is shown in Fig. 2. In AlO_4 tetrahedra each oxygen atom is shared with two aluminum ions so that each tetrahedron has one net negative charge. Charge balance is accomplished by the large divalent cations (Ba^{2+}) which occupy interstitial sites

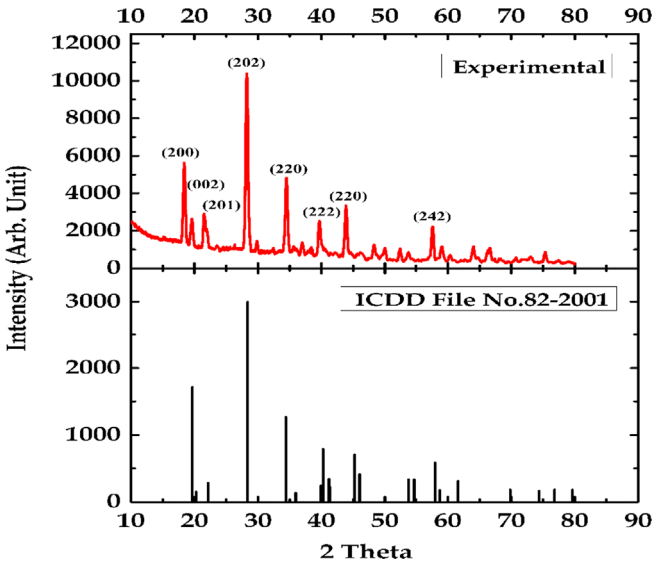

Fig. 1. XRD pattern of the as-prepared $BaAl_2O_4$:Eu(0.5 mol%) phosphor.