Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 39 (2013) 8975–8978

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Investigation of Eu^{2+} luminescence in barium tetraphosphate $Ba_3P_4O_{13}$ polycrystalline ceramics

Xinmin Zhang[a,*], Fangui Meng[a], Wenlan Li[a], Hyo Jin Seo[b,**]

[a]College of Materials Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, China
[b]Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea

Received 18 March 2013; received in revised form 26 April 2013; accepted 26 April 2013
Available online 4 May 2013

Abstract

In this paper, $Ba_3P_4O_{13}:Eu^{2+}$ phosphor was synthesized by a solid-state reaction. The photoluminescence (PL) emission spectrum and luminescence decay kinetics confirm that the doped Eu^{2+} ions can occupy two different Ba^{2+} sites. The PL excitation spectrum shows a broad band matching well with the emission of near-UV chip. $Ba_3P_4O_{13}:Eu^{2+}$ is a promising phosphor for near-UV chip excited white LEDs. The doped Eu^{3+} ions can also be reduced to Eu^{2+} ions in air atmosphere at high temperature. Charge compensation mechanism is applied to explain this kind of abnormal reduction.

Keywords: A. Powder: solid state reaction; B. Spectroscopy; C. Optical properties

1. Introduction

Recently, more and more attention is focused on phosphor converted white light-emitting-diodes (White LEDs) because of their advantages, such as high efficiency, long lifetime, energy saving and environment-friendly [1–3]. Developing the excellent phosphor materials matching well with near-UV or blue chips is the research focus in the field of solid-state-light (SSL) industry [4–6].

Up to now, Eu^{2+} ion has been widely investigated as an efficient activator in phosphors for display and lighting due to its intense broad excitation and strong emission band [7]. The excellent luminescent properties can be attributed to the allowed inter-configurational 4f→5d transitions with high oscillator strength [8,9]. In general, the 5d→4f emissions of Eu^{2+} depend strongly on the host composition, crystal structure and lattice symmetry [5,10,11]. So the colors of the Eu^{2+} emission can vary from long-wavelength ultraviolet to red. In addition, its emission peak can easily shift and its full width at half maximum will broaden if electron–phonon interaction is stronger [12].

Phosphates are a large family of compounds. The luminescent properties of rare earth doped materials have been investigated widely due to their application in the field of display and lighting [13]. For $Ba_3P_4O_{13}$ crystal, the structure has been reported by Gatehouse in 1991[14]. The luminescent properties of $Ba_3P_4O_{13}:Eu^{2+}$ phosphor has only been investigated simply by Lagos in 1968 [15]. In this paper, the PL emission spectrum at lower temperature and luminescence decay kinetics have been utilized to confirm that the doped Eu^{2+} ions can occupy two different Ba^{2+} sites. At the same time, it is found that the Eu^{3+} can be reduced to Eu^{2+} in $Ba_3P_4O_{13}$ host in air at high temperature. Charge compensation mechanism is applied to explain this kind of abnormal reduction.

2. Experimental

$Ba_3P_4O_{13}:Eu^{2+}$ phosphor was synthesized by a solid-state reaction. The stoichiometric amounts of materials $BaCO_3$ (Aldrich, 99.9%), $(NH_4)_2HPO_4$ (Aldrich, 99.9%) and Eu_2O_3 (Aldrich, 99.99%) were well mixed. The materials were prefired at 600 °C for 2 h in air to pyrolyze phosphate; then

---

*Corresponding author. Tel./fax: +86 731 85623303.
**Corresponding author.
E-mail addresses: zhangxinminam@gmail.com, hjseo@pknu.ac.kr (X. Zhang).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.04.097

the raw materials were re-ground and calcined at 750°C for 8 h in air atmosphere.

The crystalline structure of the final product was examined by using a Philips XPert/MPD diffraction system with CuKα ($\lambda = 1.5405$ Å) radiation. The photoluminescence (PL) excitation and emission spectra were measured with a Fluorescence Spectrophotometer (PTI) with a 150 W Xe lamp as an excitation source. The PL emission spectrum at 18 K was obtained by 355 nm pulsed Nd/YAG (yttrium aluminum garnet) laser (Spectron Laser Systems SL802G). The sample was placed at cold finger in a He gas recycled cryostat. The decay curves were recorded by the 500 MHz digital oscilloscope (LeCroy 9350A).

3. Results and discussion

3.1. Identification of crystalline phase of the sample

$Ba_3P_4O_{13}$ compound crystallizes in triclinic space group $P1^-$ with lattice constants of $a = 5.691$ (5), $b = 7.238$ (7) and $c = 8.006$ (5) Å; $\alpha = 83.65$ (5), $\beta = 75.95$ (8) and $\gamma = 70.49$ (7)° [14]. Fig. 1 shows X-ray diffraction pattern of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ sample. The XRD pattern of $Ba_3P_4O_{13}$ crystal (JCPDS, no. 79-1530) is also shown for comparison. The diffraction peaks are in good agreement with data given in JCPDS 79-1530, which indicates that doped Eu^{2+} ions do not change the crystal structure of $Ba_3P_4O_{13}$. Because the electric charges of Ba^{2+} and Eu^{2+} are identical and the radii of them are similar ($r_{Ba(+2)} = 0.142$ nm, $r_{Eu(+2)} = 0.125$ nm CN = 8) [16], we argue that the doped Eu^{2+} ions prefer to occupy Ba^{2+} sites.

3.2. PL properties of $Ba_3P_4O_{13}$:Eu^{2+} prepared in air

It is well known that Eu^{2+} usually gives broadband emission due to d → f transition, and the spectral position of the emission band depends strongly on the crystal structure of host [13]. The coordination numbers for the barium ions in $Ba_3P_4O_{13}$ crystal have been taken to be eight for Ba(1) and seven for Ba(2) (the crystal structure of $Ba_3P_4O_{13}$ emphasizing the coordination environment of Ba(1) and Ba(2) cations is shown in the inset of Fig. 1). The mean distance of Ba(1)–O bond is 2.82 (13) Å and that of Ba(2)–O bond is 2.76 (7) Å [14]. As discussed above, the doped Eu^{2+} ions will substitute Ba^{2+} ions sites in $Ba_3P_4O_{13}$. Two different Ba sites [Ba(1) and Ba(2)] can be partially occupied by Eu^{2+} ions. According to the above structure analysis, the mean distance of Ba(1)–O is longer than that of Ba(2)–O, so the Eu^{2+} ions substituting Ba(1) sites experience weaker crystal-field strength which is inversely proportional to R^5 (R: chemical bond length between a cation with d orbital electrons and the coordinating anion) [17].

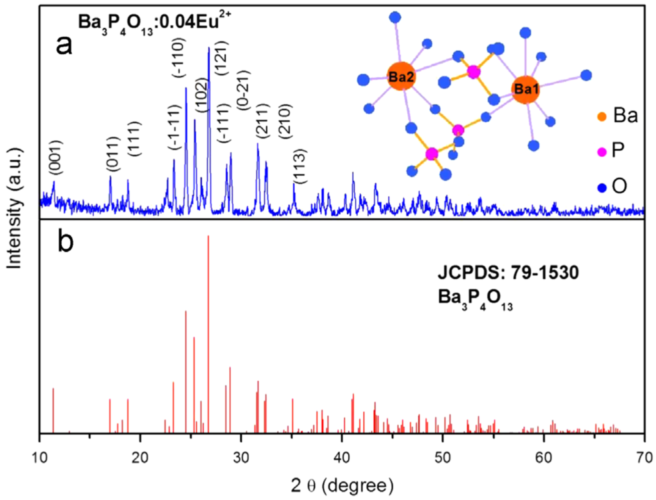

Fig. 1. XRD pattern of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ phosphor, the XRD pattern of $Ba_3P_4O_{13}$ crystal (JCPDS, no. 79-1530) is also shown for comparison (the inset shows the crystal structure of $Ba_3P_4O_{13}$ emphasizing the coordination environment of Ba1 and Ba2 cations).

Room temperature excitation and emission spectra of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ are depicted in Fig. 2. The excitation spectra show broadband in the near-UV region. Although the two excitation spectra show some difference when monitored by different emission wavelengths, they should be ascribed to the $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} ions. The 5d levels of Eu^{2+} that are not shielded from the outside environment are split under different ligand field strengths and the number of split levels is determined by the local symmetry around Eu^{2+} ions [18]. For $BaCl_2$:Eu^{2+} phosphor, Eu^{2+} ions occupy the Ca^{2+} site having O_h symmetry. So the 5d orbitals of Eu^{2+} are split into two levels, t_{2g} and e_g [19]. In the case of $CaSr_{1-x}Eu_xSi_5N_8$, the excitation spectrum is broadband and cannot be exactly resolved because Eu^{2+} could occupy two different Sr sites [20]. In the present case, the relative complicated environment of the Ba^{2+} also results in a broad excitation band, which is similar to $CaSr_{1-x}Eu_xSi_5N_8$ sample. Because the PL excitation spectra show strong absorption in the range of near-UV, $Ba_3P_4O_{13}$:Eu^{2+} could be a potential phosphor for white LEDs.

The broad emission band of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ sample is assigned to the allowed $4f^65d \rightarrow 4f^7$ transition of Eu^{2+}. It is found that the no Eu^{3+} emission (f–f transition) is observed within the sensitivity of our Fluorescence Spectrophotometer,

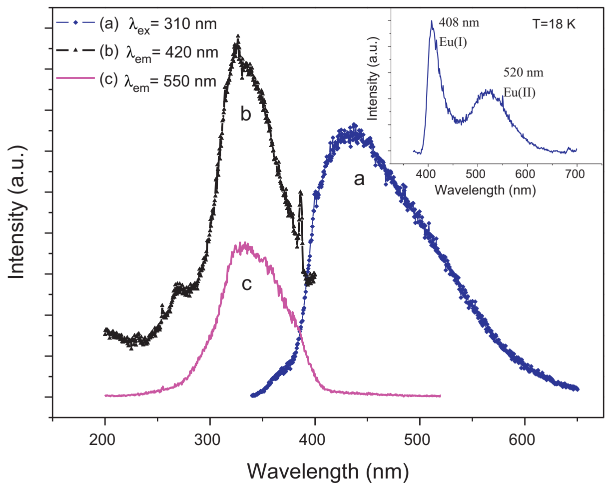

Fig. 2. Photoluminescence excitation ($\lambda_{em} = 420$, 550 nm) and emission ($\lambda_{ex} = 310$ nm) spectra of $Ba_{2.96}Eu_{0.04}P_4O_{13}$.