

X-ray Induced Luminescence Spectroscopy of Samarium Doped Barium Sulfate Prepared by Sintering Method

T Kumeda^{*1}, K Maeda¹, Y Shirano¹, K Fujiwara¹, K Sakai², T Ikari¹

¹ Faculty of Engineering, University of Miyazaki, 1-1 Gakuen-Kibanadai-Nishi, Miyazaki City 889-2192, Japan

² Cooperative Research Center, University of Miyazaki, 1-1 Gakuen-Kibanadai-Nishi, Miyazaki City 889-2192, Japan

E-mail: tc13006@student.miyazaki-u.ac.jp

Abstract. X-ray induced luminescence (XL) properties of phosphor materials made of samarium doped barium sulfate have been investigated. The samples were prepared by sintering method heated at 900-1250 °C for 3 hours in air from the mixture of BaSO₄ and Sm₂O₃. The concentration of Sm were prepared from 0.01-6 at.%. In as-prepared sample, the Sm³⁺ was detected by photoluminescence (PL). The PL intensity is maximum about 2 at.% with Sm, and then starts decreasing. The PL intensity showed concentration quenching. The XL observed Sm²⁺ and Sm³⁺ ions. The XL was shown from the sample sintered up to 1200 °C. The XL intensity increased with Sm concentration up to 1 at.%. The intensity was almost constant larger than 1 at.% Sm. These concentration dependences is different since the X-ray energy absorbed to the host material at once, and the energy transferred to both Sm³⁺ and Sm²⁺ ions. Sm doped BaSO₄ is found a host for XL phosphor materials.

1. Introduction

X-ray imaging techniques are used in such as medical fields and non-destructive testing. Various materials such as BaSO₄ and SrSO₄ have been developed for X-ray detection materials [1]. Indirect imaging method for obtaining X-ray images using fluorescent materials is required high sensitivity phosphor and, large area and high resolution [2]. In addition, an observation of X-ray induced luminescence (XL) has a merit of real-time measurement.

Rare earth ions exhibit high intensity and stable optical property in host materials. Samarium (Sm) ions emitted in the red region with high efficiency, and it can be coupled with Si photo-detector. Samarium ions were divalent and trivalent state in phosphor. The photoluminescence from Sm²⁺ ions are more efficient than that of Sm³⁺ ions [3]. After X-ray irradiation, some electrons can be trapped by Sm³⁺ ions, leading to the formation of Sm²⁺ ions while holes are trapped by other defects [4]. However, divalent ions are usually unstable as compared to trivalent. Following points are required to host material of X-ray phosphor of guest ions: a good solubility, a low phonon energy material and contain a heavy atom. In our previous paper [5, 6], we have studied X-ray phosphor of Sm -doped BaS. However Sm²⁺ ions were not presented in the material. In this paper, we choose the other host material, BaSO₄, because the emission from Sm²⁺ ions has been reported in the photoluminescence (PL) [7]. We study the optical and X-ray luminescence properties of Sm -doped BaSO₄.



2. Experimental

2.1. Sample preparation

Samples were made by the mixture of barium sulfate (BaSO_4 , 99.9%) and samarium oxide (Sm_2O_3 , 99.9%) compounds. The concentration of Sm were prepared from 0.01-6 at.%. These were weighted with a total weight of 3 g. These were ground in an agate mortar. The mixtures were synthesized by solid state reaction method at 900-1250 °C for 3 hours using an electric furnace in air. The obtained bulk samples were polished to a disk shape with, about 2 mm thickness and 5 mm diameter.

2.2. Measurements and characterization

The samples were characterized by X-ray diffraction method (XRD) obtained by PANalytical, X'Pert Pro using a $\text{CuK}\alpha$ radiation (45 kV, 40mA, $\lambda = 0.154$ nm) with a Ge monochromator at room temperature. PL spectra were measured in the range of 530-770 nm at room temperature using TRIAX320 Imaging Monochromator (Jobin yvon) with a cooled CCD detector. The PL excitation source used a 405 nm laser diode operating at a power of 24 mW. The PL intensity was calculated from the integrated intensity. The intensity of each sample was calibrated to a laboratory standard sample to allow a meaningful comparison.

The X-ray luminescence (XL) was measured by following method. The X-ray source was that for the same source as XRD measurement. The X-ray irradiate to 45 degrees of incidence to a sample. A digital camera (Canon EOS50D) was set up parallel to the sample plate surface. The red light-emitting from the sample during the X-ray radiation was taken as a photograph in the dark condition. XL measurements were carried out in situ. An expose time is in the range of 1 to 8 sec. Emission by Sm^{3+} and Sm^{2+} ions were measured by using a band pass filter with a transmission wavelength is 600nm and 700nm, respectively. After that, a luminescent image is electrical developed to be proportional to light intensity in image analysis software on PC. The XL intensity was calculated from the average of emission intensity of the sample surface. Finally, the XL intensity of the sample was determined by the slope of the light intensity versus the exposure time. XL spectra were measured with a monochromator (Ocean Optics, USB4000-UV-VIS) of which focal length is 6.8 cm through an optical fiber.

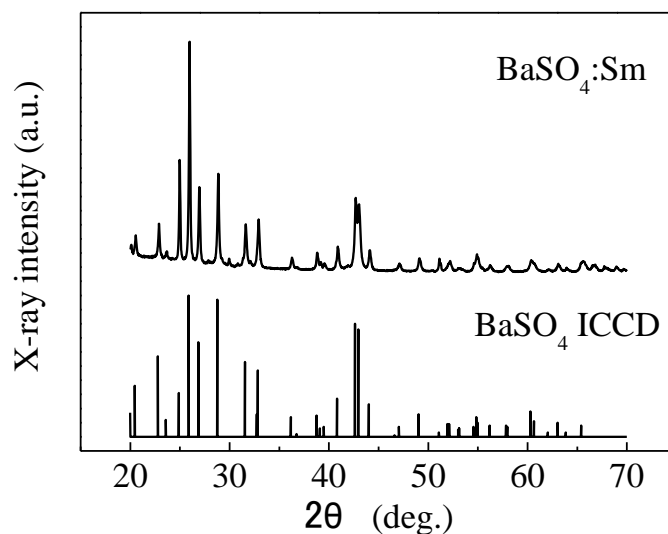


Figure 1. X-ray diffraction patterns of BaSO_4 ceramics samples doped (upper curve) 2 at.% of Sm and (lower curve) ICCD data base of card number 01-080-0512 .

3. Results and discussions

3.1. Characterization of samples

The X-ray diffraction of Sm doped BaSO₄ sample was shown in Figure 1. From the analysis of the XRD pattern of Sm doped BaSO₄ compound, it was found that the sample belongs to the orthorhombic structure at room temperature in correspondence with the ICDD data base of card number 01-080-0512. It was found that the sample is a single phase of BaSO₄.

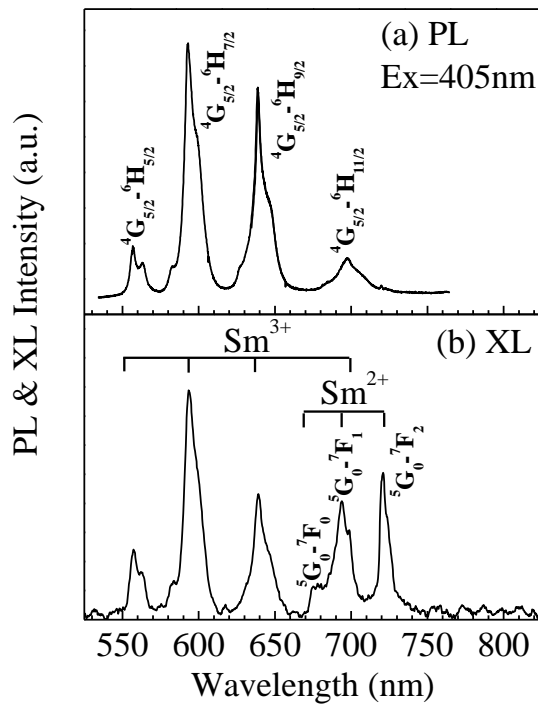


Figure 2. PL spectra excited at 405 nm light is shown in (a), and XL spectra is shown in (b).

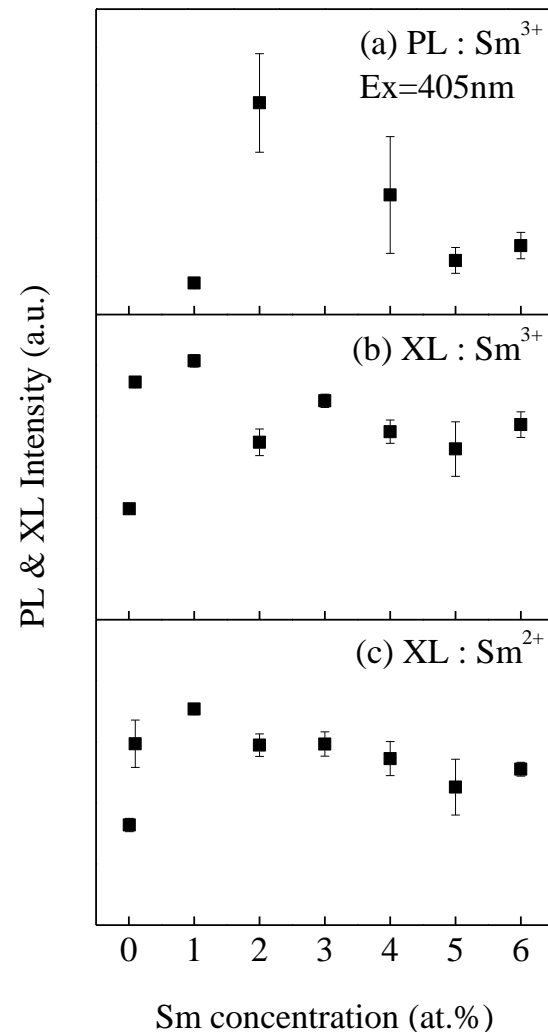


Figure 3. PL and XL intensity of BaSO₄:Sm ceramics as function of Sm concentration.

3.2. Photoluminescence

Figure 2 (a) showed the PL spectra of BaSO₄ doped Sm 2at.% excited at 405 nm. Four luminescence bands are obtained at around 557, 593, 639, 698 nm. These correspond to $^4G_{5/2}$ - 6H_J (J: 5/2, 7/2, 9/2, 11/2) transitions of Sm³⁺ [8]. All bands from Sm³⁺ consist of many peaks. The spectral bands from Sm²⁺ where are at 680, 694 and 721 nm [9] have not been observed. The PL intensity strongly depended on synthesized temperature. The PL intensity gradually increased with synthesized

temperature increasing. The PL intensity at synthesized temperature of 1250 °C was ten times larger than that of 900 °C.

The Sm concentration dependence of PL intensity excited at 405 nm is shown in Figure 3 (a). The PL intensity increased with Sm concentration up to 2 at.%, and then started decreasing with Sm. The phenomenon of these Sm concentration dependences seems as known effect of the concentration quenching [10].

3.3. X-ray luminescence

The red XL light could be seen in the dark during exposing X-ray. The X-ray luminescence was obtained from Sm doped BaSO₄ sample sintered up to 1200 °C. The XL spectrum of BaSO₄ including 2 at.% of Sm are shown in Fig. 2 (b). The spectra had a typical four luminescence bands of Sm³⁺ presented in the PL spectrum, previously. Also, three luminescence bands are obtained at around 680, 694, 721 nm. These correspond to ⁵D₀₋₇F_J (J: 0, 1, 2) transition of Sm²⁺ [10]. Some Sm³⁺ ions are reduced into Sm²⁺ ions by X-ray irradiation [7].

The Sm concentration dependence of XL intensity is shown in Figure 3 (b) and (c). The XL intensity increased with Sm concentration up to 1 at.%. The intensity was almost constant larger than 1 at.% Sm. The dependence of XL did not show concentration quenching different to that of PL. The energy of excited light corresponds to the energy difference between ⁶H_{5/2} and ⁶P_{3/2} in Sm³⁺ ion [11]. Then, the light could directly excite Sm³⁺ ions. In the case of XL [3], the X-ray energy absorbed to the host material at once, and the energy transferred to both Sm³⁺ and Sm²⁺ ions. The mechanism is indirectly excitation. It seems that these concentration dependence is dissimilar since the difference in the emission mechanism of PL and XL. Sm doped BaSO₄ is expected as the XL phosphor.

4. Conclusions

We have investigated the optical properties and X-ray luminescence of BaSO₄ ceramics doped Sm. All samples sintered up to 1200 °C showed X-ray luminescence. The PL spectral bands were identified to the transitions in Sm³⁺ ions. The XL spectral bands were identified to the transitions in Sm³⁺ and Sm²⁺ ions. Some Sm³⁺ ions are reduced into Sm²⁺ ions by X-ray irradiation. The dependence of XL did not show concentration quenching. Sm doped BaSO₄ is found a host for XL phosphor materials.

References

- [1] Yamashita N, Yamamoto I, Kiyotake N 1985 *Jpn. J. Appl. Phys.* **24** pp 1174-1180
- [2] Lanca L and Silva A 2009 *Radiography* **15** pp 58-62
- [3] Koughia C, Edgar A, Varoy C R, Okada G, Seggern H von, Belev G, Kim C Y, Sammynaiken R and Kasap S 2011 *J. Am. Ceram. Soc.* **94** pp 543-550
- [4] Wang J, Li Y, Huang Y, Shi L and Seo J H 2010 *Mater. Chem. Phys.* **120** pp 598-692
- [5] Maeda K, Tsudome R, and Ido M 2011 *Phys. Status Solidi C* **8** pp 2692-2695
- [6] Maeda K, Kawaida N, and Tsudome R 2012 *Phys. Status Solidi C* **9** pp 2271-2274
- [7] Stefani R, Maia A D, Teotonio E E S, Monteiro M A F, Felinto M C F C and Brito H F 2006 *J. Solid Status Chem.* **179** pp 1086-1092
- [8] Sidike A, Kusachi I and Yamashita N 2003 *Phys. Chem. Minerals* **30** pp 478-485
- [9] Edgar A, Varoy C R, Koughia C, Tonchev D, Belev G, Okada G, Kasap S O, Seggern H von and Ryan M 2009 *Opt. Mater.* **31** pp 1459-1466
- [10] Lei B, Man S Q, Liu Y and Yue S 2010 *Mater. Chem. Phys.* **124** pp 912-915
- [11] Venkatramu V, Babu P, Jayasankar C K, Troster Th, Sievers W and Wortmann G 2007 *Opt. Mater.* **29** pp 1429-1439