1. Introduction

Luminescent materials have attracted much attention for various applications. Especially, bulk inorganic phosphors have been widely utilized in ionizing radiation detectors since ionizing radiations generally have a high penetrating power and bulk materials are required to absorb these radiations efficiently, and they are classified into mainly two types. One is a scintillator and the other is a dosimeter. Scintillators convert the absorbed energy of the ionizing radiation to thousands of visible photons immediately via electromagnetic interactions of materials and photons, and they have been playing an important role in various fields of radiation detection applications including medical imaging, security, astrophysics, and geophysical and resources exploration, e.g., oil-dwelling. On the other hand, dosimeters are mainly used for personal dose monitoring. In general, such materials store and accumulate the incident radiation energy via the carrier trapping at some defects levels, and the dose information can be recorded as an light emission while heating (thermally stimulated luminescence: TSL). Dosimeter is one of the optical memories that record the irradiated dose and the proportional relation between the emission intensity and the dose accumulated (dose response function) gives us the information about the exposed dose.

Strontium carbonate (SrCO3) has an orthorhombic crystal system and is an important compound in the production of ferrite magnets and cathode-ray tubes of televisions. SrCO3 is also widely used in the iridescent production and special glasses, driers, paints, pyrotechnics and chemical sensor (e.g., Eu3+), which have been widely utilized in the iridescent production and special glasses, e.g. oil-dwelling. On the other hand, dosimeters are mainly used for personal dose monitoring. In general, such materials store and accumulate the incident radiation energy via the carrier trapping at some defects levels, and the dose information can be read out as a light emission while heating (thermally stimulated luminescence: TSL). Dosimeter is one of the optical memories that record the irradiated dose and the proportional relation between the emission intensity and the dose accumulated (dose response function) gives us the information about the exposed dose.

Scintillation and dosimetric properties of Eu-doped SrCO3 ceramics prepared by spark plasma sintering method

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Eu-doped SrCO3 (Eu: SrCO3) ceramics are prepared by a spark plasma sintering (SPS) technique. In photoluminescence (PL), emissions around 615 nm due to 4f–4f transition of Eu3+ appear under several excitation wavelengths. The PL decay time constants are 314 ns due to the host and 600 μs due to Eu3+. The X-ray induced scintillation spectra show an intense emission peak and some small bands around 615 nm and scintillation decay time constants are 210–224 μs. In thermally stimulated luminescence (TSL) after X-ray irradiation, a strong TSL glow peak is observed in 450°C and TSL intensity increase in association with Eu concentration.

Key-words : Scintillation, Dosimeter, Ceramic, Europium, Strontium carbonate, Spark plasma sintering

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The photoluminescence (PL) emission map and quantum yield (QY) were evaluated by using Quantaurus-QY (Hamamatsu Photonics). The PL decay time profile monitoring at 600 nm under 460–510 nm excitation was evaluated by using Quantaurus-t (Hamamatsu Photonics). The excitation source was a white light source and the band pass filter (11E0304, OptoSigma) was used to select excitation photons. The decay times were deduced by the single exponential fitting.

As a scintillation property, X-ray induced radioluminescence (RL) spectrum was measured by utilizing our original setup.23) The irradiation source was an X-ray generator equipped with a tungsten anode target (XRB80P&N200X4550, Spellman). During the measurements, the X-ray generator was supplied with the voltage of 80 kV and tube current of 2.5 mA. During the sample was irradiated by X-rays, the scintillation photons from the sample were fed into the spectrometer through a 2.0 m optical fiber. The spectrometer (Andor DU-420-BU2 CCD and Shamrock 163 monochromator) was cooled down to 193 K by a Peltier module to reduce the thermal noise. Further, we have measured the scintillation decay time and afterglow profiles using a pulsed X-ray source equipped afterglow characterization system.24) In the scintillation decay, wavelength was not resolved. In order to obtain a basic curve as a dosimeter and characterize relatively shallow trapping centers induced by X-ray irradiations, the TSL glow curves after 5 Gy X-ray exposure were measured by using TL-2000 (Nanogray, Japan) with the heating rate of 1°C/s over the temperature range from 50 to 490°C.25) Except for the TSL, whole characterizations were conducted at room temperature.

3. Results and discussion

Figure 1 shows the picture of obtained samples. Visibly they look white. Under UV irradiation by using the UV-lamp (excitation wavelength was 254 nm), red luminescence due to Eu3+4f–4f transition can be clearly seen by naked eyes in Eu-doped ceramics while the blue luminescence is observed in the nondoped SrCO3. From SEM image (Fig. 2), the crystallization is good and well-defined morphology, the crystals are spherical. The typical particle size is approximately 20 μm.

Figure 3 shows XRD patterns of the Eu:SrCO3 ceramics. The patterns demonstrate diffraction peaks corresponding to the expected SrCO3 single phase. These materials belong to Pmcn space group of the orthorhombic crystal system. No impurity phases are observed in whole samples.

Figure 4 represents PL excitation and emission map of Eu 1.0% doped SrCO3. Emissions around 615 nm appear under several excitation wavelengths. These emissions are due to 4f–4f transition of Eu3+ (5D0→7F0, 5D0→7F1 and 5D0→7F2).16) The QY of the 0, 0.5, 1.0 and 3.0% Eu-doped samples show 3.0, 5.3, 6.1 and 4.5%, respectively. Figure 5 shows the PL emission spectrum of the nondope SrCO3 ceramic. The nondoped sample shows the blue emission due to the host around 450 nm under 365 nm excitation. The origin of the host emission was interpreted as the self-activated luminescence.11),12) Among the present samples, 1.0% Eu-doped sample shows the best quantum yield and the optimum Eu concentration in PL is around 1%.

PL decay time profiles of the samples are demonstrated in Fig. 6. PL decay time constants of Eu:SrCO3 ceramics are 400–600 μs depending on their Eu concentrations. They are a little...
faster than the typical decay time of 4f–4f transition of Eu$^{3+}$ (a few ms). As the Eu concentration increases, the decay time constants become faster and it is a typical phenomenon in rare-earth doped luminescent materials. On the other hand, the self-activated luminescence emission was 314 ns and it was not observed in Eu-doped samples.

The X-ray induced scintillation spectra of Eu:SrCO$_3$ ceramics show in Fig. 7. An intense emission peak and some small bands around 615 nm are observed in Eu-doped samples under X-ray excitation and these emissions are attributed to 4f–4f transition of Eu$^{3+}$ as same as PL. From this result, it is confirmed that Eu-doped SrCO$_3$ worked as a scintillator material. A broad emission peak around 450 nm observed in the nondoped sample is ascribed to the self-activated luminescence and this peak disappears by the Eu doping. Intensity of the peak around 615 nm increase according to Eu concentrations. Based on the Robbins model, scintillation intensity is roughly expressed the product of the energy migration efficiency from the host to emission centers and the PL QY. The present result suggests that the energy migration efficiency of the Eu 3.0% doped sample is largely higher than those of the other samples.

Figure 8 shows the X-ray induced scintillation decay time profiles. Scintillation decay of Eu-doped samples has one component and decay time constants are 210–224 s depending on their Eu concentrations. Concentration dependence shows the same trend as that in the PL-decay and the decay time become faster by dense Eu-doping. The scintillation decay time constant from the nondoped sample is 166 ns. Scintillation decay times are slightly faster than PL decay times. When we compare with other Eu$^{3+}$-doped scintillator, the scintillation decay times are faster and it suggests some kinds of quenching path may exist.

Figure 9 shows the X-ray induced afterglow profiles of Eu:SrCO$_3$ ceramics as the other important timing property for scintillation detectors. The afterglow level of 0, 0.5, 1.0 and 3.0% Eu-doped samples show 0.12, 0.03, 0.12 and 0.15%, respectively. Among these ceramics, Eu 0.5% doped sample shows the best afterglow level though all afterglow levels are similar. However, it is much bigger than commercial scintillators such as CdWO$_4$.
and BGO (~10 ppm) and these Eu-doped SrCO₃ are not preferable to high counting rate applications.

Figure 10 represents the TSL glow curves of the Eu:SrCO₃ ceramics. A strong TSL glow peak is observed at 450 °C and TSL intensities increase in association with Eu concentration. It is suggested that Eu-doping makes more defects in the SrCO₃ possibly due to the charge imbalance of Sr²⁺ and Eu³⁺, and these data are consistent with the afterglow where ceramics with higher Eu concentration shows worse afterglow. Therefore the origin of the TSL in Eu-doped SrCO₃ is the host emission and the present result suggests that the other trivalent ion doping would improve the TSL properties. The activation energy is derived using the initial rise method, which does not require the knowledge of frequency factor. The estimated value of the Eu 3.0% doped sample which has the deepest trap amount and the depth is 0.75 eV. In this analysis, we assume that the rise part of the glow peak is simply approximated by ln(I(T)) = const−Ε/kT, where I(T), E, k and T represent the TSL intensity, activation energy, Boltzmann constant and temperature, respectively. Assuming the occurrence of first order kinetics and using the trap depth derived above, the frequency factor can be calculated to be ~3 × 10^13 s⁻¹. This result suggests that the luminescence corresponding to the peak at 450 °C may occur by thermally assisted tunneling recombination.

4. Conclusion

We investigated the optical, scintillation and dosimetric properties of the Eu:SrCO₃ ceramics prepared by the SPS technique. Eu:SrCO₃ ceramics show photo- and radio-luminescence peaks due to Eu³⁺ 4f→4f transition and the decay time constants are determined in μs order. The scintillation efficiency is improved by the dense Eu doping. Afterglow and TSL results suggest that Eu-doping makes more defects in the SrCO₃ and the emission origin of the TSL is the host emission.

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References

1) T. Yanagida, A. Yoshikawa, Y. Yokota, K. Kamada, Y. Usuki, S. Yamamoto, M. Miyake, M. Baba, K. Sasaki and M. Ito, IEEE Trans. Nucl. Sci., 67, 1492–1495 (2010).
2) D. Totuka, T. Yanagida, K. Fukuda, N. Kawaguchi, Y. Fujimoto, Y. Yokota and A. Yoshikawa, Nucl. Instrum. Methods A, 659, 399–402 (2011).
3) K. Yamaoka, M. Ohno, Y. Terada, S. Hong, J. Kotoku, Y. Okada, A. Tsutsui, Y. Endo, K. Abe, Y. Fukazawa, S. Hirakuri, T. Hiruta, K. Itoh, T. Itoh, T. Kame, M. Kawahara, N. Kawano, K. Kawashima, T. Kishishita, T. Kitaguchi, M. Kubukun, G. M. Madejski, K. Makishima, T. Mitani, R. Miyawaki, T. Murakami, M. M. Murashima, K. Nakazawa, H. Niko, M. Nomachi, K. Oonuki, G. Sato, M. Suzuki, H. Takahashi, I. Takahashi, T. Takahashi, S. Takeda, K. Tamura, T. Tanaka, M. Tashiro, S. Watanabe, T. Yanagida and D. Yonetoku, IEEE Trans. Nucl. Sci., 52, 2765–2772 (2005).
4) C. L. Melcher, Nucl. Instrum. Methods B, 40/41, 1214–1218 (1989).
5) S. W. S. McKeever, Thermoluminescence of Solids, Cambridge University Press (1985).
6) T. J. Bastow, Chem. Phys., Lett., 354, 156–159 (2002).
7) A. F. Zeller, Chem. Tech., 19, 762–768 (1981).
8) J. Griffiths, Ind. Miner., 218, 21–35 (1985).
9) M. Erdemoglu and M. Canbazoglou, Hydrometallurgy, 49, 135–150 (1998).
10) G. Owsu and J. E. Litz, Hydrometallurgy, 57, 23–29 (2000).
11) S. Angelov, R. Stoianova, R. Dafinova and K. Kabasanov, J. Phys. Chem. Solids, 47, 409–412 (1986).
12) R. Dafinova and R. Stoianova, J. Mater. Sci. Lett., 6, 254–256 (1987).
13) M. J. J. Lammers and G. Blasse, Mater. Res. Bull., 21, 529–534 (1986).
14) H. F. Folkerts and G. Blasse, J. Phys. Chem. Solids, 57, 303–306 (1996).
15) J. J. Shi, J. J. Li, Y. F. Zhu, F. Wei and X. R. Zhang, Anal. Chim. Acta, 466, 69–78 (2002).
16) Y. Pan, M. Wu and Q. Su, Mater. Res. Bull., 38, 1537–1544 (2003).
17) J. Yanga, X. Liu, C. Li, Z. Quana, D. Konga and J. Lin, J. Cryst. Growth, 303, 480–486 (2007).
18) Y. Y. Zhang, J. L. Liu, Y. X. Zhu, Y. Shang, M. Yu and X. Huang, J. Mater. Sci., 44, 3364–3369 (2009).
19) S. Ni, X. Yang and T. Li, Mater. Lett., 65, 766–768 (2011).
20) F. Liao, L. Zhao, C. Zhai, Z. Zhang and X. Ma, Mater. Lett., 122, 331–333 (2014).
21) M. Tokita, Proc. 2000 PM World Congress (2000) pp. 729.
22) S. J. Duels, C. D. Greskovish and C. R. Oelair, “Electronic trap defects in Y₂O₃:Eu³⁺ and (Y, Gd)₂O₃:Eu³⁺ X-ray scintillators”, Eds. by M. J. Weber, P. Lecoq, R. C. Ruchti, C. Woody, W. M. Yen and R. Y. Zhu, Scintillators and phosphor materials (1994) pp. 503–509.
23) T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi and T. Yanagitani, Opt. Mater., 35, 2480–2485 (2013).
24) T. Yanagida, Y. Fujimoto, T. Ito, K. Uchiyama and K. Mori, Appl. Phys. Express, 7, 062401 (2014).
25) T. Yanagida, Y. Fujimoto, N. Kawaguchi and S. Yanagida, J. Ceram. Soc. Japan, 121, 988–991 (2013).
26) R. Yadav, A. F. Khan, A. Yadav, H. Chander, D. Haranath, B. K. Gupta, S. Virendra and C. Santa, Opt. Express, 17, 22023–22030 (2009).
27) D. J. Robbins, J. Electrochem. Soc., 127, 2694–2702 (1980).
28) H. Réot, S. Blahuta, A. Bessière, B. Viana, B. LaCourse and E. Mattmann, J. Phys. D Appl. Phys., 44, 235101 (2011).