Scintillation and dosimeter properties of Ce-doped $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glasses

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In this study, we developed $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glasses doped with different concentrations (0, 0.1, 0.2, 0.5 and 1.0%) of Ce and studied the optical, scintillation and dosimeter properties. The scintillation and photoluminescence (PL) emissions showed an intense emission due to the 5d–4f transitions of Ce^{3+} . In addition, the scintillation and PL decay times of Ce^{3+} were obtained for 25–32 and 26–29 ns, respectively. These results were typical for Ce-doped scintillator. Moreover, as a dosimeter property, 0, 0.1, 0.5 and 1.0% Ce-doped glass samples showed thermally stimulated luminescence (TSL) around 150–200 and 350–400°C with a good liner response over 0.5–10 Gy.

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Key-words : Cerium, Glass, 5d–4f transition, Thermally stimulated luminescence, Scintillator, Dosimeter

[Received October 16, 2015; Accepted February 16, 2016]

1. Introduction

Scintillator is a type of phosphor that converts a single high energy (keV–GeV) radiation photon immediately to a several thousands of low energy photons such as ultraviolet and visible light.¹⁾ Further, scintillators are used in various fields such as medicine, security, resource mapping and high energy physics.^{2)–5)} On the other hand, dosimeter is another type of phosphor which temporarily stores the incident radiation energy until the signal is read out. The stored signal can be read out by two different ways, optical and thermal stimulations. Upon the stimulation, the dosimeter material emits light with an intensity proportional to the radiation dose absorbed. The light emission is referred as optically-stimulated luminescence (OSL) and thermally-stimulated luminescence (TSL) when the stimulation is done optically and thermally, respectively.^{6),7)} While the OSL and TSL dosimeters loses the stored signal once read out, another class of dosimeter using radio-photoluminescence (RPL) effect permanently stores the radiation signal; and it can be read out multiple times without fading. In RPL dosimeter, the radiation dose is represented as a form of photoluminescence (PL) intensity which is proportional to the incident radiation dose.^{8),9)}

In recent years, the most commonly used scintillators are doped with Ce^{3+} .¹⁾ For examples, Ce-doped Gd_2SiO_5 (GSO), Li_2SiO_5 (LSO) and $(\text{Lu}, \text{Y})_2\text{SiO}_5$ show notable performances; and these are mainly used for PET.^{10)–12)} Ce-doped materials tend to show two key characteristics which are intense emission and fast fluorescence decay time. Although Pr^{3+} -doped materials tend to show a faster emission, the emission wavelength is, in general, much shorter so the spectral response of conventional photo-

multiplier tubes (PMTs) does not match well.¹³⁾ For those reasons, Ce^{3+} -doped phosphors are of great interest for a scintillator material.

2. Experimental

In this work, we developed $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glasses doped with different concentrations of Ce, and we studied the optical, scintillation and dosimeter properties. Ce-doped $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glass sample was prepared by a conventional melt-quenching technique. The concentration of Ce varies as 0, 0.1, 0.2, 0.5 and 1.0 mol %, and the Ce ion was introduced in the glass formula as CeO_2 . The starting compounds of reagent grade were mixed first, and the mixture was melted in an alumina crucible inside an electric furnace at the temperature of 1300°C for 30 min in air atmosphere. The melt was then quenched on a pre-heated stainless plate at 200°C. The obtained glass samples were characterized by the following experiments.

The optical in-line transmittance spectrum was measured by using JASCO V670 spectrometer in the spectral region 190–800 nm. Further, the excitation-emission matrix and quantum yield (QY) were observed by Hamamatus-QY (C11367-01). The measured spectral ranges for excitation and emission were 250–500 and 200–900 nm, respectively. In addition, PL emission spectra and PL decay curves were measured by using Quantaaurus τ (Hamamatsu). In these measurements, the excitation wavelength was 280 nm, and the monitoring wavelength for the PL decay measurement was 330 nm. These optical measurements were carried out at room temperature.

The X-ray induced scintillation spectrum was measured using our laboratory-made set-up, which was previously described in detail elsewhere.^{14),15)} The X-ray source used here is a conventional X-ray tube with an applied voltage and current of 40 kV and 5.2 mA, respectively. The scintillation emission from the samples by X-ray irradiation was fed into an optical fiber in order to guide the light to a monochromator equipped with a CCD detector (Andor iDUS420) to obtain a spectrum. The scintillation decay curve was measured by using our original lab-constructed

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[‡] This article was selected from the presentations at “STAC-9” (The 9th International Conference on the Science and Technology for Advanced Ceramics) held in Tsukuba, Japan (2015), through the regular reviewing procedure.

set-up in order to characterize the scintillation lifetime as well as afterglow.¹⁶⁾ The system is equipped with a pulsed X-ray tube, in which the applied tube voltage is 30 kV and the time resolution is ~ 1 ns.

The TSL glow curves of all the samples were measured by using a TSL reader (TL-2000, Nanogray Inc.) after an irradiation by X-rays at several different doses in order to study the dosimeter properties. The measurement temperature range is from 50 to 490°C, and the heating rate is 1°C/s. The dose response curve, which is the TSL intensity vs irradiation dose, was obtained over the range from 0.5 to 10 Gy.

3. Results and discussion

Figure 1 illustrates some of the Ce-doped $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glasses prepared in our research as an example. The synthesized samples look colorless, transparent in the visible range and homogeneous. The thickness of prepared samples are ~ 0.95 mm ± 0.2 mm. **Figure 2** shows the in-line transmittance spectra of the samples prepared. All the samples did not have any noticeable absorption band in the 370–800 nm region. In the non-doped sample, the absorption edge was obtained ~ 240 nm (5.2 eV) while the doped samples have the edge at longer wavelengths. This is due to a strong absorption located in the 250–350 nm ($\sim 4\text{--}5$ eV) region, which is due to the 4f–5d transitions of Ce^{3+} ion commonly seen in many Ce^{3+} -doped materials.^{17),18)} It is also possible that a fraction of Ce^{4+} is also included in the samples; however, a discussion for the presence of Ce^{4+} is beyond the scope of this paper. In addition, this absorption edge shifts towards longer wavelengths with increasing the Ce concentration.

Figure 3 shows the PL excitation-emission matrix of 1.0% Ce-doped sample (top) and non-doped samples (bottom). The former sample was chosen because 1.0% Ce-doped sample showed the most intense emission among the samples prepared. On one hand, the Ce-doped glass sample exhibited a strong emission at 340 nm under excitation at 290–310 nm. On the other hand, the non-doped sample did not show any measurable emission. Since

the 340 nm emission is only present in the Ce-doped sample, we attribute this origin to the typical allowed transitions from the 5d (t_{2g}) excited state to the 4f ($^2F_{5/2}$, $^2F_{7/2}$) ground states. Moreover, the excitation range measured in the Ce-doped sample is consistent with the absorption band of Ce-doped samples seen in Fig. 2.

In **Fig. 4**, the QY is shown as a function of Ce concentration. The QY value varies with the concentration in the range approximately 30–40%, and it reaches to the highest value when the concentration of Ce is 0.5%. Because the QY value at 1.0% is lower than that of 0.5%, it indicates that a concentration quenching takes place at concentrations higher than 0.5%.

The PL emission spectra were measured by an excitation at 280 nm, and the obtained spectra are shown in **Fig. 5**. In this measurement, emissions by non-doped samples were observed around 310 and 410 nm, although it is much weaker than those in Ce-doped samples. The measured emission structures of Ce-doped samples were broad with the peak around 340 nm. The emission peak position, in fact, shifts towards longer wavelength, and the intensity increased with increasing the Ce concentration. This observation is explained as follows. Since the concentration

Fig. 3. Excitation-emission matrix of 1.0% Ce doped (top) and non-doped samples (bottom).

Fig. 1. Ce doped $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glass.

Fig. 2. Optical transmittance spectra of Ce-doped and non-doped $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glasses.

Fig. 4. QY as a function of Ce concentration.

Fig. 5. PL emission spectra of non-doped and Ce-doped glass samples. The excitation wavelength is 280 nm.

Fig. 6. PL decay times of the glass host and 5d-4f transitions of Ce^{3+} against the Ce concentration. The inset is PL decay curves of non-doped and Ce-doped glass samples. The monitoring wavelength is 340 nm while the excitation is at 280 nm.

Fig. 7. Scintillation spectra of non-doped and Ce-doped glass samples with different dopant concentrations.

of Ce increases, the 4f-5d absorption band of Ce^{3+} red-shifts; consequently, the left-hand side of the emission band in the figure is strongly absorbed and the peak position is seen to be red-shifted. The inset of **Fig. 6** shows the PL decay curve of the non-doped and Ce-doped glass samples. The emission was monitored at 340 nm under the excitation at 280 nm. Further, the derived lifetimes from the decay curves are plotted in **Fig. 6**. Here, the PL decay curve of non-doped sample was approximated by a double-exponential decay function. We think that the faster component is due to the instrumental response because the timing resolution of the instrument was around 1 ns. The slower PL decay component was believed to be by the host emission, and the derived lifetime is 19.4 ns. This host emission was not measurable in the earlier measurements shown in **Fig. 3**. On the other hand, the PL decay curves of all the Ce-doped samples were approximated by a single-exponential decay function. It should be pointed out here that the host emission should be present in the Ce-doped sample, but the signal was negligibly smaller than that by Ce^{3+} . The obtained PL decay time of Ce doped samples ranged from 26 to 29 ns as shown in **Fig. 6**.

Figure 7 shows the scintillation spectra of 0–1.0% Ce-doped samples. As observed in PL, the spectral emission shape was broad, and the intense emission peak appeared at 340 nm except for the non-doped sample. The origin of the emission seen in the Ce-doped samples was attributed to the 5d-4f transitions of Ce^{3+} . The scintillation intensity increases with increasing the concentration of Ce, but this increase seems to saturate above 0.5%. The scintillation decay curves and extracted decay time constants are shown in **Fig. 8**. The latter values were obtained by approximating the measured decay curve as a double-exponential decay function. The initial rapid decay seen for all the samples was due

Fig. 8. Scintillation decay plots of non-doped and Ce-doped glass samples with different dopant concentrations. The scintillation emission was induced by X-rays. The inset shows scintillation decay profiles of non-doped and Ce-doped glass samples.

Fig. 9. TSL glow curves of non-doped and Ce-doped glass samples with different dopant concentrations after 1 Gy irradiation.

to the instrumental response, so this component was disregarded in the analyses. The derived lifetimes of faster component were around 10 ns. We attribute the origin of this component to the host emission rather than Ce because the non-doped sample shows an emission with a similar lifetime. Although the host emission was not measurable by the spectrum measurements, it was measurable by the decay measurement which is based on the photon-counting technique using a photomultiplier tube. In addition, the slower decay time components of Ce-doped samples were between 25 and 32 ns, and the origin of these emissions are due to the 5d-4f transitions of Ce^{3+} . The slower decay time of the 5d-4f transitions of Ce^{3+} increased slightly as the concentration increases from 0.1 to 0.2%. We think this is due to a self-absorption of emission as observed in an Er-doped system.¹⁹⁾

Figure 9 shows the TSL glow curves of non-doped and Ce-doped glass samples with different dopant concentrations. Prior to the measurements, the samples were irradiated by X-rays with the dose of 1 Gy. For the Ce-doped samples, two intense and broad glow peaks appeared around 150–200 and 300–400°C while the non-doped samples showed glow peaks at two different temperature ranges, 370°C and above 490°C. This observation

Fig. 10. TSL response as a function of X-ray dose for non-doped and Ce-doped glass samples with different dopant concentrations.

indicates a creation of new trapping centers due to an introduction of Ce^{3+} into the host. Moreover, the dose response curve is illustrated in Fig. 10. Here, the TSL intensity was defined as an integrated TSL peak at 350°C . The dose response curves were demonstrated in Fig. 10, and we have confirmed that 0, 0.1, 0.5 and 1.0% Ce-doped samples were found to exhibit a good liner response against the irradiation dose over 0.5–10 Gy. On the other hand, 0.2% Ce-doped sample shows a liner response in the range of 1–10 Gy. We think that the sensitivity needs to be improved for use in low dose measurement applications such as personnel dose monitoring. However, for use in large dose measurement applications such as radiation therapies, our new dosimeter material should cover the dose level to be measured and should be considered to be a candidate.²⁰⁾

4. Conclusions

We evaluated scintillator and dosimeter properties of $\text{Li}_3\text{PO}_4\text{-Al}(\text{PO}_3)_3$ glass doped with different concentrations of Ce. A lot of Ce^{3+} -doped materials observed dosimeter properties including TSL. Ce-doped samples show glow peaks around 150–200 and 300–400 $^\circ\text{C}$; in contrast, non-doped sample show glow peaks at 370 $^\circ\text{C}$ and above 490 $^\circ\text{C}$. In addition, dose response of all samples was confirmed to show a good liner response. However, only 0.2% Ce-doped sample show low sensitivity with a liner response over 1 Gy. Although these samples can not be used for monitoring low dose, these samples can be applied for radiotherapy which involves high dose.

Acknowledgements This work was supported by a Grant in Aid for Scientific Research (A)-26249147 from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese government (MEXT) and partially by JST A-step. Green Photonics Research from MEXT and the Cooperative Research Project of Research Institute of Electronics, Shizuoka University, are also acknowledged.

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