Storage Luminescence and Scintillation Properties of Eu-doped SrAl₂O₄ Crystals

Daisuke Nakauchi^{1*}, Go Okada¹, Masanori Koshimizu², Takayuki Yanagida¹

¹Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST)
8916-5 Takayama-cho, Ikoma-shi, Nara 630-0192, Japan

²Department of Applied Chemistry, Graduate School of Engineering, Tohoku University
6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

*corresponding author: nakauchi.daisuke.mv7@ms.naist.jp

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Abstract: Eu-doped SrAl₂O₄ (Eu:SrAl₂O₄) crystals are prepared by a floating zone (FZ) method. In photoluminescence (PL), an intense broad emission peak around 510 nm due to 5d-4f transition of Eu²⁺ appear under excitation at 250-450 nm. The PL decay time constants are about 800 ns due to the 5d-4f transitions of Eu²⁺. In the nondoped sample, emission peaks around 480 and 560 nm are observed upon excitation at 316 nm. The X-ray induced scintillation spectra also show an intense broad emission peak around 510 nm, and the decay time constants are approximately 500 ns. In the pulse height spectra of the 2.5% Eu:SrAl₂O₄ crystal, the absolute light yield is ~46000 ph/MeV. In thermally stimulated luminescence (TSL) after X-ray irradiation, strong TSL glow peaks are observed at 120 and 400 °C. In optically stimulated luminescence (OSL) after X-ray irradiation, emission peaks are observed around 510 nm while exposing the samples to the stimulation light at 800 nm.

1. Introduction

Luminescent materials have been utilized in radiation detectors, and they are classified into two types such as scintillators and dosimeters. Scintillators convert the absorbed energy of high energy ionizing radiation to thousands of low energy (1-8 eV) photons immediately, so they have been playing an important role in various fields of radiation detections including medical imaging [1], security [2], high energy physics [3], and geophysical and resources exploration, e.g. oil-dwelling [4]. On the other hand, dosimeters store and accumulate the incident radiation energy and emit a light with external stimulations of light (optically stimulated luminescence, OSL) or heat (thermally stimulated luminescence, TSL). So they are mainly used for personal dose monitoring [5-7]. In order to measure ionizing radiation more accurately, continuous efforts have been paid to develop new detector materials.

Eu²⁺ doped alkaline earth aluminates are known as phosphors in the visible wavelength with a strong photoluminescence (PL). Pioneering investigations on the MAl₂O₄ and MAl₁₂O₁₉ (M=Ca, Sr, Ba) were reported by Blasse et al. [8], and Palilla et al. studied the phosphorescent properties of SrAl₂O₄ doped with Eu (Eu:SrAl₂O₄) [9]. Matsuzaka et al. introduced the SrAl₂O₄ co-doped with Eu and Dy (Eu, Dy:SrAl₂O₄) as a long-lasting luminescent material, and they explained that the long-lasing phosphorescence mechanism resulted from the holes which are thermally released from the trap levels of Dy³⁺ [10, 11]. Beginning with this report, Eu, Dy:SrAl₂O₄ phosphors have been intensely studied and played important roles in industrial applications with a long-lasting luminescent material [12]. The scintillation from Eu, Dy:SrAl₂O₄ in the nano powder or sintered opaque ceramic forms have been also studied [13-18]. Although most radiation detectors utilize bulk crystalline phosphors mainly due to their high detection efficiency against ionizing radiations and high optical quality, most reports on SrAl₂O₄ were studied on the powder form. For detector uses, a bulk form is particularly important to absorb high energy ionizing radiation efficiently since the interaction probability of many kinds of ionizing radiation (e.g., X- and γ-rays) with materials simply depends on the detector volume. In addition, high transparency which is important to transport scintillation photons to photodetectors is also required so single crystalline scintillators are dominant in practical applications.

In this report, we investigated the storage luminescence properties such as TSL and OSL after X-ray irradiation of Eu:SrAl₂O₄. In addition to them, we also study the scintillation properties to grasp ionizing radiation induced luminescence comprehensively because it is recently pointed out that scintillation and ionizing radiation induced storage luminescence show a complementary relation in some material systems

[19]. Up to now, inspite of commonness of Eu and Dy doubly doped SrAl_2O_4 powder, no study can be found for Eu singly doped SrAl_2O_4 single crystal on scintillation and dosimeter properties.

2. Experimentals

$\text{Eu:SrAl}_2\text{O}_4$ crystals were synthesized by a floating zone (FZ) method using an FZ furnace (FZD0192, Canon Machinery Inc.). We used SrCO_3 (4N), Al_2O_3 (4N), and Eu_2O_3 (4N) powders as raw materials. The concentration of Eu varies as 0, 0.5, 1.0 and 2.0 mol%, and the Eu ion was introduced in the chemical composition of SrAl_2O_4 . The starting compounds of reagent grade were mixed first, and the mixture was shaped to the cylinder by the hydrostatic pressure. Then the cylinder was sintered at 1500 °C for 6 hours to obtain SrAl_2O_4 sintered rod. The sintered rod was put into the FZ furnace and the crystal growth was conducted with the pulling rate of 5 mm/h. After cutting the samples to adequate sizes, the synthesized sample was characterized by the measurements below.

The PL emission map and quantum yield (QY) were evaluated by using Quantaurus-QY (Hamamatsu Photonics) for Eu-doped samples while that of the nondoped sample under various excitation wavelengths were measured by using a spectrofluorometer (FP-8600, JASCO) since the excitation light intensity of Quantaurus-QY was not enough strong and we could not detect the emission from the nondoped sample. The PL decay time profile monitoring at 510 nm under 365 nm excitation was evaluated by using Quantaurus- τ (Hamamatsu Photonics). The decay times were deduced by the single exponential approximation.

As a scintillation property, X-ray induced radioluminescence (RL) spectra were measured by utilizing our original setup [20]. The irradiation source was X-ray generator equipped with a tungsten anode target (XRB80P&N200X4550, Spellman). During the measurements, the X-ray generator was supplied with the bias voltage of 80 kV and tube current of 2.5 mA. While the sample was irradiated by X-rays, the scintillation emissions from the sample were fed into the spectrometer through a 2 m optical fiber to measure the scintillation spectrum. The spectrometer (DU-420-BU2 CCD, Andor and SR163 monochromator, Shamrock) was cooled down to 188 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 [21]. In pulse height measurements, we mounted each crystal on the PMT (R7600-200, Hamamatsu) by using a silicon grease (6262A, OKEN). When γ -rays from ^{137}Cs was detected by the sample, scintillation photons were transferred to PMT, and the electrical signals from the anode of PMT were fed into a preamplifier (113, ORTEC), a shaping-amplifier (572, ORTEC) with 2 μs shaping time, a multichannel analyzer (AMPTK Pocket MCA), and finally to a personal computer.

In order to characterize the storage luminescence from relatively shallow trapping centers, TSL glow curves were measured by TL-2000 (Nanogray, Japan) with the heating rate of 1 °C/s over the temperature range from 50 to 490 °C [22]. On the other hand, for the storage luminescence from deeper trapping centers, OSL was also studied under 800 nm stimulation by using FP8600 spectrofluorometer (JASCO). Except for the TSL, the sample for all the other measurements mentioned above was at room temperature.

3. Results and Discussion

Fig. 1. Picture of the nondoped and $\text{Eu:SrAl}_2\text{O}_4$ crystals grown by the FZ method.

The synthesized nondoped and Eu:SrAl₂O₄ crystals are shown in Fig. 1. Typically, 4-5 mm $\phi \times 20$ -30 mm crystalline rods were grown. The nondoped sample looks white and translucent, and the Eu doped samples look yellow and translucent. Under UV lamp excitation (254 nm), a bright pale green emission can be seen by naked eyes from Eu doped samples. In order to characterize luminescence properties, we cut the transparent part with a typical size of 4-5 mm $\phi \times 2$ mm thickness.

Fig. 2. PL excitation and emission map of the 1.0% Eu:SrAl₂O₄ crystal as an example. The horizontal axis shows the emission wavelength and the vertical axis shows the excitation wavelength.

The PL emission and excitation map of the 1.0% Eu:SrAl₂O₄ crystal is represented in Fig. 2. Under excitation at 250-450 nm, an intense broad emission peak around 510 nm is observed. This emission origin is attributed to the 5d-4f transition of Eu²⁺ from the past study [12]. The *QY* of the 0.5, 1.0, 2.0, 2.5 and 3.0% Eu:SrAl₂O₄ crystals upon excitation at 374 nm are 35, 35, 49, 50 and 45%, respectively. In the nondoped sample, no emissions can be detected. Among present samples, the 2.5% Eu doped SrAl₂O₄ crystals showed the best PL *QY*.

Fig. 3. PL emission spectra of the nondoped SrAl₂O₄ crystal upon excitations at 316 and 366 nm.

Since we could not detect the luminescence from the nondoped sample by using Quantaaurus-QY, we investigated PL properties by using FP8600 which had a high power Xe excitation source. The PL emission spectra of the nondoped SrAl₂O₄ crystal are shown in Fig. 3. Under excitation with 316 nm, emission bands around 480 and 560 nm are observed. Under excitation with 366 nm, only an emission band around 550 nm can be seen. The emission wavelengths of the nondoped sample are obviously different with the Eu-doped samples, and this intrinsic or defect luminescence is suppressed by Eu-doping.

Fig. 4. PL decay time profiles of the nondoped (top) and the Eu:SrAl₂O₄ crystals (bottom).

The PL decay time profiles of all the samples are demonstrated in Fig. 4. The decay time constants of the Eu:SrAl₂O₄ crystals monitoring at 510 nm emission band upon 365 nm excitation are approximately 800 ns. These are slightly faster than the typical time constants of 5d-4f transition of Eu²⁺ [23], and the PL decay time constants became faster in the association with the Eu concentrations. The PL decay curves of the nondoped SrAl₂O₄ crystal monitoring at 480 nm emission band upon 280 nm excitation and at 550 nm emission band upon 365 nm excitation are composed of two components. The faster components is the instrumental response, and approximately 20 ns component is caused by the nondoped sample. Suggested by these results (similar emission wavelengths and decay times), emission bands around 480 and 550 nm are due to the same origin.

Fig. 5. X-ray induced RL spectra of the Eu:SrAl₂O₄ crystals.

The X-ray induced RL spectra are shown in Fig. 5. An intense broad emission peak around 510 nm [17] is observed as same as PL. The emission origin is ascribed to 5d-4f transition of Eu²⁺. In the nondoped sample, broad emission bands around 500 nm appear also as same as the PL. Although RL are qualitative evaluation since we cannot correct the stopping power of each scintillator material, the scintillation intensity of the nondoped one was quite weaker than Eu-doped ones.

Fig. 6. Scintillation decay time profiles of the Eu:SrAl₂O₄ crystals.

The X-ray induced scintillation decay time profiles of the Eu:SrAl₂O₄ crystals are represented in Fig. 6. The decay time constants are 400-600 ns which are faster than those in PL. In dense Eu-doping, the scintillation decay time becomes faster. In the nondoped sample, we could not observe the decay curve due to the low scintillation intensity (Fig. 5).

Fig. 7. Afterglow curves of the Eu:SrAl₂O₄ crystals.

We evaluated the afterglow properties of the Eu:SrAl₂O₄ crystals after an X-ray irradiation with a pulse duration of 2 ms in Fig.7. The afterglow levels of the 0, 0.5, 1.0, 2.0, 2.5 and 3.0% Eu:SrAl₂O₄ crystals are 0.090, 0.013, 0.011, 0.007, 0.016 and 0.028%, and the 2.0% Eu:SrAl₂O₄ crystal shows the lowest afterglow level among the present samples. In this evaluation, after glow levels (A) are represented $A (\%) = 100 \times (I_2 - I_0) / (I_1 - I_0)$ where I_0 , I_1 and I_2 denote the averaged signal intensity before the X-ray irradiation, the averaged signal intensity during X-ray irradiation and signal intensity at $t = 20$ ms after the X-ray cut off, respectively. We referred the formula from the evaluation manner of NIHON KESSHO KOGAKU CO., LTD. which is one of the famous companies for scintillation detectors for medical and security uses.

Table 1. Light yields of the Eu:SrAl₂O₄ crystals.

Eu [%]	Light yield [ph/MeV]
0.5	~30000
1.0	~29300
2.0	~45300
2.5	~46000
3.0	~42500

Fig. 8. Pulse height spectra of the Eu:SrAl₂O₄ crystals under ¹³⁷Cs exposure.

Pulse height spectra of the Eu-doped samples measured under ¹³⁷Cs exposure are shown in Fig. 8, and the light yield of them are summarized in Table 1. The 0.5% Ce:YAG transparent ceramic scintillator [24] was used as a reference which had an absolute light yield of ~20000 ph/MeV calibrated by using Si-APD and ⁵⁵Fe 5.9 keV X-ray source. The emission wavelength of Ce:YAG is similar to that of Eu:SrAl₂O₄ thus the correction of the wavelength dependence of the quantum efficiency of PMT is not required to deduce the light yield. All Eu-doped SrAl₂O₄ crystal show clear photo absorption peaks. Among the present samples, the 2.5% Eu:SrAl₂O₄ crystal gives the highest absolute light yield, which is ~46000 ph/MeV with typical error of 10%. Up to now, most Eu-doped scintillators are halide materials and most of oxide materials reported have powder form. The present result opens a new possibility of Eu-doped oxide crystal scintillators. In addition, observed light yield is similar levels with other famous oxide scintillator GAGG [20] and superior to LSO [25].

Fig. 9. TSL glow curves of the Eu:SrAl₂O₄ crystals after 2 Gy X-ray exposure.

Fig. 9 shows TSL glow curves of the present samples. In Eu doped samples, TSL glow peaks are observed below 50 °C and around 100, 170 and 400 °C, and these peaks were reported in past studies [26]. The lower temperature peak below 50 °C was suppressed by doping 2.0% Eu, while the intensity of the higher temperature peak does not depend on the Eu concentration. These results are consistent with the afterglow evaluations, and we interpret that shallow traps would be reduced by Eu-doping. On the other hand, TSL of the nondoped sample was very weak. From the afterglow, the nondoped sample should have the highest TSL intensity around low temperatures. This phenomenon could be understood that the nondoped sample may have very shallow traps, and carriers trapped in such shallow levels would be detrapped rapidly before we put the sample in the instrument. The time interval of X-ray irradiation and the setting of the sample in the TSL instrument is a few minutes in our setup.

Fig. 10. OSL spectra of the Eu:SrAl₂O₄ crystals upon 800 nm stimulation.

Fig. 11. A fading profile of OSL of Eu 2.0% sample monitoring at 510 nm with 800 nm stimulation.

Fig. 10 illustrates OSL spectra of the nondoped and Eu:SrAl₂O₄ crystals after 1 Gy X-ray irradiation. While exposing the samples to the stimulation light at 800 nm, emission peaks are observed around 510 nm which coincides with 5d-4f emission of Eu²⁺ in PL and scintillation [26]. The nondoped sample did not show OSL signal at all in spite of our effort to investigate various stimulation wavelengths. Fig. 11 shows the OSL fading curve of Eu 2.0 % doped sample. This emission intensity gradually decrease with the exposure time. The fading is ~ 4% at 10 minutes stimulation and this rate is lower than that of Eu, Dy:SrAl₂O₄ [27].

4. Conclusions

We evaluated the scintillation and storage luminescence properties of the Eu:SrAl₂O₄ crystals prepared by the FZ method. In PL and scintillation, Eu:SrAl₂O₄ crystals show luminescence peaks attributed to 5d-4f transition of Eu²⁺, and the decay time constants are slightly shorter than the typical Eu²⁺-doped materials. The *QY* of the 2.5% Eu:SrAl₂O₄ crystal is the highest among Eu doped samples. From pulse height spectra, the 2.5% Eu:SrAl₂O₄ crystal also shows the highest absolute light yield, which is ~46000 ph/MeV. TSL and OSL results suggest that Eu:SrAl₂O₄ work as the dosimeter. The present results open a new possibility to search Eu-doped oxide scintillators.

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6. References

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