

Scintillation Properties of $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2:\text{Ce}$ Single Crystals

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$\text{Ca}_8\text{La}_{2(1-x)}(\text{PO}_4)_6\text{O}_2:x\text{Ce}$ ($x = 0.1, 0.3, 1, 3,$ and 10%) single crystals were synthesized by the floating zone method, and their photoluminescence and scintillation properties were investigated. X-ray diffraction patterns confirmed that all the samples had a single phase without any impurity phases. All the samples showed an emission peak due to 5d-4f transitions of Ce^{3+} ions under UV and X-ray irradiations. According to the pulse height spectra, the light yield of the 1% Ce-doped sample was estimated to be 30 photons/MeV under ^{241}Am α -ray irradiation.

1. Introduction

Scintillators are phosphor materials that immediately show luminescence when irradiated with ionizing radiation. In general, scintillators are used in combination with photodetectors such as photomultiplier tubes (PMTs) and photodiodes (PDs), and they are called scintillation detectors. Their applications are in the fields of security,⁽¹⁾ medicine,⁽²⁾ environmental measurement,⁽³⁾ well-logging,⁽⁴⁾ and so forth. The required properties for X- and γ -ray detection are, for example, high light yield (LY), large effective atomic number (Z_{eff}), and no hygroscopicity.^(5,6) So far, scintillators with various material forms such as glasses,^(7–12) polycrystals,^(13–16) and single crystals^(17–22) have been studied. Among them, single crystals have been mainly studied because of their high homogeneity and LY .

Ce-doped scintillators have attracted attention because luminescence due to the 5d-4f transitions of Ce^{3+} ions shows a short lifetime and an emission wavelength that matches the sensitivity wavelength of common PMTs.⁽²³⁾ The lifetime and wavelength are advantageous in photon-counting detectors, and $\text{Gd}_2\text{SiO}_5:\text{Ce}$,⁽²⁴⁾ $\text{Lu}_2\text{SiO}_5:\text{Ce}$,⁽²⁵⁾ and $\text{Gd}_3(\text{Al}, \text{Ga})_5\text{O}_{12}:\text{Ce}$ ⁽²⁶⁾ have been widely utilized in scintillation detectors so far. In recent years, Ce-doped silicate apatite scintillators have been actively studied^(27–29) because apatite with $M_{10}(\text{RO}_4)_6\text{X}_2$ as a basic component has attracted attention as a laser material since the 1970s.⁽³⁰⁾ Here, M , RO_4 , and X represent a metal cation (alkali-earth or rare-earth ions), an anion group (PO_4^{3-} , VO_4^{3-} , or SiO_4^{4-}), and a single anion (OH^- , F^- , Cl^- , or Br^-), respectively. Among the apatite scintillators,

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Ce-doped $\text{Sr}_2(\text{Gd}_{0.4}\text{Lu}_{0.6})_8(\text{PO}_4)_6\text{O}_2$ showed the highest LY of ~ 240 photons/MeV.⁽²⁹⁾ However, this LY was lower than that of commercial scintillators and should be improved. Therefore, Ce-doped phosphate apatite compounds ($R = \text{P}$) were investigated in this study. The photoluminescence (PL) properties of some phosphate apatite compounds were reported.^(31,32) Among them, only $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2$ (CLPA) single crystals were successfully synthesized,⁽³³⁾ and this composition was focused to begin with. There are three different types of cation sites of Ca(I), Ca(II), and La(I).^(34,35) Four Ca(I) sites are located at the 4f site of 9-fold coordination, and the other four Ca(II) sites and two La(I) sites are at the 6h site of 7-fold coordination. To date, the PL properties of CLPA:Ce have been reported,^(34,35) and CLPA:Ce has shown color-tunable emission under different excitation wavelengths. Despite its interesting luminescence characteristics, there have been no reports on the scintillation properties of CLPA:Ce. In this study, CLPA:Ce single crystals were grown by the floating zone (FZ) method, and their PL and scintillation properties were investigated.

2. Experimental Methods

$\text{Ca}_8\text{La}_{2(1-x)}(\text{PO}_4)_6\text{O}_2:x\text{Ce}$ ($x = 0.1, 0.3, 1, 3,$ and 10%) single crystals were grown by the FZ method. CeO_2 (Furuuchi Chemical, 4N), CaO (Furuuchi Chemical, 4N), La_2O_3 (Rare Metallic, 4N), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Sigma Aldrich, 4N) raw powders in a stoichiometric molar ratio were mixed using an agate mortar, and the powders were calcined at 1200°C for 8 h. After that, the powders were formed into a rod shape and sintered at 1200°C for 8 h. The rods were grown in an FZ furnace (Canon Machinery, FZD0192). The pull-down and rotating rates were 3 mm/h and 14 rpm, respectively. The obtained samples were polished to a thickness of ~ 0.5 mm.

To confirm whether the samples have a single phase, powder X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (Rigaku, MiniFlex600) over the 2θ range of $5\text{--}90^\circ$. PL emission and excitation spectra were obtained using a commercial spectrofluorometer (JASCO, FP-8600). PL decay functions and PL quantum yield (QY) were evaluated using Quantaaurus- τ (C11367, Hamamatsu Photonics) and Quantaaurus-QY (C11347, Hamamatsu Photonics). Radioluminescence (RL) spectra under X-ray irradiation were measured using our original setup.⁽³⁶⁾ RL decay curves under pulsed X-ray irradiation were obtained using an X-ray-induced afterglow characterization system.⁽³⁷⁾ To estimate LY , pulse height spectra (PHS) under ^{241}Am α -ray irradiation were measured with a shaping time of 2 ms for the samples and a reference.⁽³⁶⁾

3 Results and Discussion

Figure 1 shows the appearance of the obtained samples under room light and UV light. All the samples were transparent despite the presence of cracks and became yellow as the Ce concentration increased. Under UV light, blue luminescence was observed in the 3% and 10% Ce-doped samples by naked eyes. Figure 2 shows the XRD patterns of all the samples and the reference (JCPDS No. 33-0287). Since the XRD patterns of all the samples were consistent with the reference, the obtained samples had a single phase without any impurity phases. PL emission and excitation spectra are shown in Fig. 3. All the samples showed a broad emission peaking at

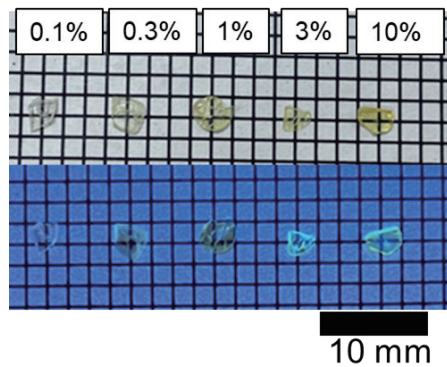


Fig. 1. (Color online) Appearance of CLPA:Ce.

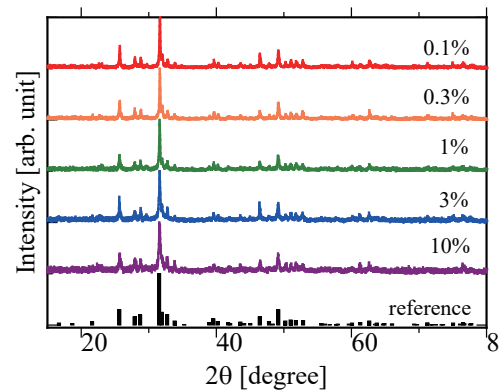


Fig. 2. (Color online) XRD patterns of CLPA:Ce.

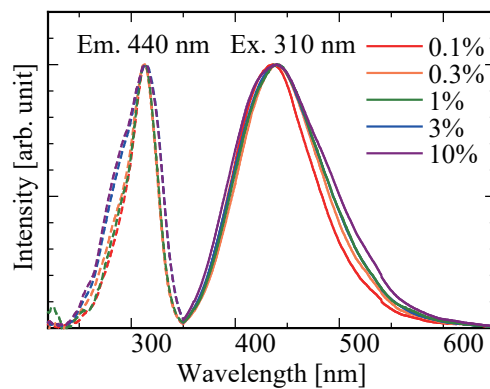


Fig. 3. (Color online) PL emission and excitation spectra of CLPA:Ce.

440 nm under excitation at 310 nm. From excitation spectra, a main peak (310 nm) and tail (280 nm) were observed, and these excitation bands would be due to Ce^{3+} that occupied the different sites. PL decay functions measured at 440 nm are presented in Fig. 4. The decay curves were approximated by an exponential function. The lifetime was 33.6–46.9 ns and decreased as the Ce concentration increased owing to concentration quenching. Since the lifetime was close to those of the other Ce-doped materials,⁽³⁸⁾ the luminescence would be due to the 5d-4f transitions of Ce^{3+} ions. The PL QY s in the 0.1, 0.3, 1, 3, and 10% Ce-doped samples were 5.0, 3.7, 5.6, 8.6, and 5.5%, respectively. The excitation and monitored wavelengths were 310 and 370–600 nm, respectively. The 3% Ce-doped sample showed the highest QY among all the samples.

RL spectra under X-ray irradiation are presented in Fig. 5. All the samples showed an emission peak at 500 nm. RL decay profiles under pulsed X-ray irradiation are shown in Fig. 6. The decay profiles consisted of an exponential function, and the lifetime was from 33.0 to 43.8 ns, which were close to those of PL. Therefore, the luminescence would be ascribed to the 5d-4f transitions of Ce^{3+} ions. The lifetime decreased with the increase in Ce concentration as well as PL. Compared with the PL spectra (Fig. 3), the emission wavelength was different, which would be due to the different geometric measurement setups and Ce^{3+} in different sites. Reflection measurements were used for PL, while transmission measurements were used for RL. Since transmission measurements were more affected by self-absorption, the emission peaks in RL

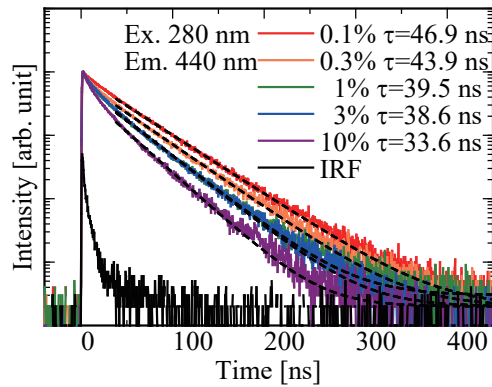


Fig. 4. (Color online) PL decay curves of CLPA:Ce.

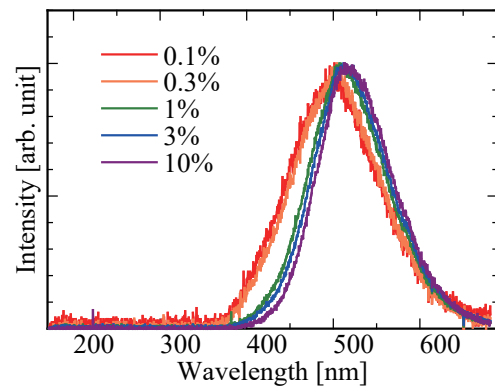


Fig. 5. (Color online) RL spectra under X-ray irradiation.

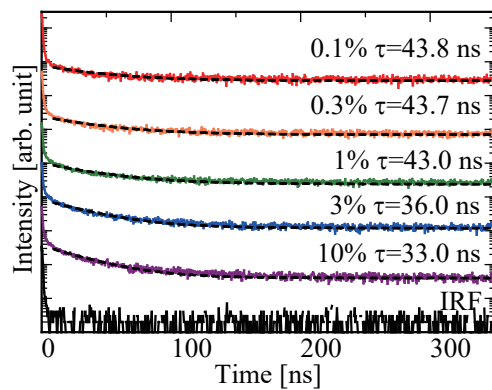


Fig. 6. (Color online) RL decay profile under X-ray irradiation.

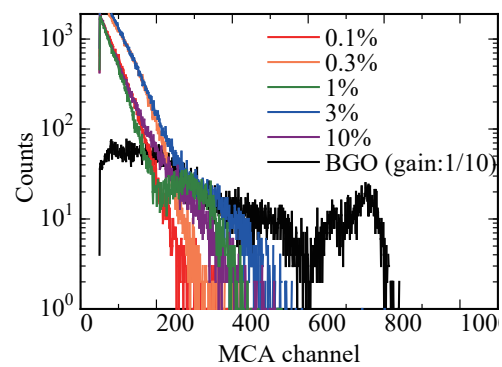


Fig. 7. (Color online) PHS of CLPA:Ce under ^{241}Am α -ray irradiation and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) under ^{137}Cs γ -ray irradiation.

spectra might be shifted to longer wavelengths. According to a previous report,⁽³⁴⁾ Ce^{3+} in Ca(I) and La(II) sites showed blue emission, and green emission was obtained when Ce^{3+} occupied Ca(I) sites. Therefore, in PL, the dominant emission would be Ce^{3+} ions located at the La(I) and Ca(II) sites. In contrast, the main emission in scintillation would be Ce^{3+} ions occupying the Ca(I) sites.

PHS of CLPA:Ce under ^{241}Am α -ray (5.5 MeV) irradiation and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) as a reference sample under ^{137}Cs γ -ray (0.662 MeV) irradiation are shown in Fig. 7. The LY of BGO was calibrated using a Si avalanche PD and the ^{55}Fe 5.9 keV peak, and the LY was determined to be 6,800 photons/MeV. Since the emission wavelength of CLPA:Ce was close to that of BGO,⁽³⁹⁾ the peak channel was directly compared to calculate LY . The 1% Ce-doped sample showed a full-energy peak, and the LY was estimated to be 30 photons/MeV (160 photons/5.5 MeV) under ^{241}Am α -ray irradiation. In the other samples, LY could not be determined because no clear full-energy peak was observed. The LY was comparable to those of Ce-doped apatite compounds reported so far (31–1300 photons/5.5 MeV^(28,29)). Since the samples became yellow, Ce^{4+} might be present in the crystals. Therefore, to improve LY , crystal growth under reducing atmosphere will be required in the future.

4. Conclusions

The PL and scintillation properties of $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2:\text{Ce}$ single crystals grown by the FZ method were evaluated. According to X-ray diffraction patterns, all the samples had a single phase without any impurity phases. All the samples showed luminescence due to the 5d-4f transitions of Ce^{3+} ions in PL and scintillation. According to PHS, the *LY* of the 1% Ce-doped sample was estimated to be 30 photons/MeV under ^{241}Am α -ray irradiation. This *LY* was comparable to those of Ce-doped apatite compounds reported so far. The samples look pale yellow, and Ce^{4+} might remain in the crystals. Therefore, to improve *LY*, crystal growth under a reducing atmosphere will be required in the future.

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