Development of rare earth doped CaS phosphors for radiation detection

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CaS-based materials are known as highly efficient phosphors. CaS has excellent properties as host materials of phosphors under ultraviolet irradiation and is expected to have also for radiation detection. In this study, we fabricated CaS ceramic phosphors and measured their photoluminescence (PL), scintillation, and dosimetry characteristics to investigate the applicability of CaS ceramics as scintillators and dosimeters. The scintillation emission spectrum of CaS:Eu ceramics showed an emission peak at 656 nm, originating from the 5d–4f transitions od Eu²⁺ ions. The scintillation emission spectrum of CaS:Ce ceramics showed emission peaks at 510 and 570 nm that originate from the 5d–4f transitions of Ce³⁺ ions. The PL emission peaks of CaS:Ce and CaS:Eu were similar to those of the X-ray-induced radioluminescence emission peaks and were also assigned to the emission of Ce³⁺ and Eu²⁺ ions. The light yield of CaS:Ce and CaS:Eu were estimated to be approximately 1,700 and 4,400 photons/MeV, respectively. As for CaS:Eu, significant afterglow and strong thermoluminescence were observed, which indicates the sample contained trap sites at high concentration.

Key-words : Scintillator, Ceramic Scintillator, Rare-earth-doped, CaS

1. Introduction

Radiation detectors based on phosphors are widely used for astrophysical measurements, security inspection, nuclear medicine, and dosimetry. There are two types of phosphors for radiation detection, i.e., scintillators and dosimeters. Both of them are materials that emit photons utilizing the energy of incident radiation. Scintillators emit photons immediately upon receiving the energy of incident radiation and are used for astrophysics and elementary particle physics, security inspection, and medical diagnosis, such as positron emission tomography devices and X-ray computed tomography (X-ray CT). On the other hand, phosphors for dosimetry emit photons via three steps: at first, electrons and holes excited by radiation are trapped at defects or impurities, and are released by stimulation of heat or light, subsequently, recombine to emit photons. Dosimeters are used for personal exposure dose measurement, radiotherapy, and medical imaging. Although some properties, such as radiation resistances and high sensitivities to radiation, are commonly required, many different properties, such as fast response or energy storage are required for scintillators and dosimeters since they have different emission mechanisms. We investigated both scintillation and dosimetry properties with main focus on development of new scintillators in this study.

There are some conditions for good scintillators. First, high light yields are needed for discrimination between detection signals and noises and good energy resolution. Higher light yields reduce the statistical variation of the pulse heights of the detection signals and improves energy resolution. Third, fast decay time are needed for discrimination of successive detection signals of incident radiation. In addition, good detection efficiencies are needed. In the case of X-ray and gamma ray measurement, since the interaction probability is proportional to the 4th to 5th power of the effective atomic number (Zeff), the large Zeff is needed for scintillators that have good detection efficiencies.

There are some types of scintillator depending on the constituents, such as inorganic scintillators and organic scintillators, which have merits and demerits. Inorganic
scintillators are well known to have high light yields and good detection efficiencies, although their decay times are not fast, such as SrI$_2$:Eu single crystals (light yield: ~90,000 photons/MeV, decay time constant: 1,200 ns). Organic scintillators have fast response times but they have low light yields and low detection efficiencies, such as plastic and liquid scintillators. For X-ray and gamma ray detections, high light yields and good detection efficiencies are needed. From this reason, inorganic scintillators are generally suitable for X-ray and gamma ray detection.

Inorganic scintillators can be divided into two types: single crystals and ceramics. Both types of scintillators have strengths and weaknesses. Although crystalline scintillators are good for transparency and the transparency contributes good energy resolution, such as LaBr$_3$:Ce single crystals, they have the disadvantage that the uniformity of the dopant is not ensured, such as Lu$_2$SiO$_5$:Ce. For X-ray and gamma ray scintillators, high light yields and good detection efficiencies are needed. From this reason, inorganic scintillators are generally suitable for X-ray and gamma ray detection.

2. Experimental procedures

CaS (99.99 %, HIGH PURITY CHEMICALS), EuCl$_3$·6H$_2$O (99.9 %, ALDRICH), and CeCl$_3$ (99.99 %, ALDRICH) powders were used as the starting materials for the synthesis. For CaS:Ce, NH$_4$Cl (99.5 %, Wako) was used as the reducing agent. Owing to the charge neutrality, one charge-compensating Ca$^{2+}$ vacancy is expected to be created for two Ce$^{3+}$ dopant ions. The powders were mixed in a molar ratio of CaS:EuCl$_3$:6H$_2$O or CeCl$_3$ = 0.97:0.03, 0.995:0.005, and 0.999:0.001. For CaS:Ce, NH$_4$Cl powder was added as the reducing agent by the weight ratio of CaS:Ce to NH$_4$Cl of 0.5:0.02. The mixtures were pressured at 10 tons for 10 min and pelletized. The pellets were heated to 1273 K in a vacuum and then quenched in the air to ambient temperature to prepare the samples. The undoped CaS sample was also prepared by the same method. Figure 1 shows the photographs of the samples under room light and during ultraviolet (UV) irradiation with a wavelength of 302 nm.

We measured the X-ray diffraction (XRD) patterns using a Rigaku Ultima IV X-ray diffractometer. The sintered pellets were ground into a powder in a mortar to measure the XRD patterns. The PL spectra were measured using a fluorescence spectrophotometer (Hitachi High-Tech F-700) and a Xe lamp as an excitation source at room temperature. The photoluminescence (PL) quantum yields were measured using Hamamatsu absolute PL quantum yield spectrometer C11347 equipped with 150 W Xe light source at room temperature. The X-ray-induced radio-luminescence (XRL) spectra were recorded using a multi-channel spectrometer (SILVER-Nova multi-channel spectrometer, StellarNet Inc.). The X-ray source was an X-ray generator with a Cu target with power setting of 40 kV and 40 mA (SA-HFM3, Rigaku). The PL time profiles were recorded using a Delta Flex 3000U-TMK2 instrument at room temperature. The pulsed light-emitting diodes (HORIBA NanoLED-455 and HORIBA NanoLED-570) with an excitation wavelength of 451 and 574 nm, respectively, were used as the excitation sources. The scintillation decay time profiles were recorded using our original setup, a pulsed X-ray-induced afterglow characterization system (Hamamatsu) at room temperature. A detailed
description of this setup can be found in our previous report.\textsuperscript{22} The CaS:Ce samples were annealed at 673 K prior to the measurements to suppress the afterglow.\textsuperscript{137} Cs-gamma-ray pulse height spectra were recorded at room temperature and the scintillation light yields were estimated. The setup for the measurements of the pulse height spectra consisted of a photomultiplier tube (Hamamatsu R7600U-20) instrument biased at 700 V and connected to a preamplifier (ORTEC 572), and a multichannel analyzer (Amptek, MCA8000D). The CaS samples were annealed at 673 K to suppress the afterglow and subsequently coupled to the photomultiplier tube (PMT) window using optical grease and covered by Teflon tape as a reflector to increase light collection. The pulse height spectra were recorded with a 6-\mu s shaping time. The scintillation light yields were estimated by comparison with a Gd\textsubscript{2}SiO\textsubscript{4}:Ce (GSO) commercial scintillator (light yield = 10,000 photons/MeV). GSO single crystal crushed into pellet was used to compare correctly to the ceramics. TL was measured and the glow temperature was investigated to how the afterglow of the CaS:Eu samples occurred. The prepared samples were exposed to X-rays at a dose rate of 1 Gy/min for 1 min (total dose = 1 Gy) for the TL measurements. The X-ray source was an X-ray generator (SA-HFM3, Rigaku) with a Cu target with power settings of 40 kV and 40 mA. The TL glow curves were recorded at 303–673 K at a heating rate of 0.5 K/s in air. The temperature was controlled using a programmed heater (SCR-SHQ-A, Sakaguchi). TL photons from the sample were detected using a PMT (H11890-210, Hamamatsu) with a wide spectral sensitivity (230–700 nm). A radiation cut filter was used to limit thermal radiation from the samples.

3. Results and discussion

Figure 2 shows the XRD patterns of CaS, CaS:Ce (0.1, 0.5 and 3.0 mol\%), and CaS:Eu (0.1, 0.5, and 3.0 mol\%). The intensity is represented on a log scale. The XRD patterns were consistent to the data of CaS in the database (00-008-0464, ICDD). The structures of CaS are cubic. The lattice constant in a previous report was 5.6836 nm,\textsuperscript{23} and those estimated from the XRD patterns for CaS:Ce (0.1 mol\%), CaS:Eu (0.1 mol\%), and CaS are 5.660, 5.692, and 0.5690 nm, respectively. In addition, unknown peaks were observed in 0.5 and 3.0 mol\% CaS samples and those considered to be due to alien phases containing Ce or Eu. We attempted to assign the impurity phases by checking the database of XRD patterns, however, the peak angles for raw materials and Eu- or Ce-sulfide (EuS, CeS\textsubscript{2}, Ce\textsubscript{2}S\textsubscript{3}, Ce\textsubscript{2}S\textsubscript{4}, EuCl\textsubscript{3}, EuCl\textsubscript{3}, 6H\textsubscript{2}O, and CeCl\textsubscript{3}) did not match to the observed peaks. These peaks are considered to originate from some Ce- and Eu-base complex phases without data in ICDD database. In addition, (2 0 0) XRD peak, which had the highest intensity, depending on the concentration of dopants are shown in Fig. 3 to confirm the evidence in introducing the dopants. There are three factors that are presumed to influence the shift of XRD peaks according to the Vegard’s law.\textsuperscript{24} First, additions of dopants with larger ionic radii than those of host ions cause the increase in the lattice constant. The ionic radii of Ce\textsuperscript{3+} (0.101 nm) and Eu\textsuperscript{2+} (0.117 nm) are a little larger than that of Ca\textsuperscript{2+} (0.100 nm)\textsuperscript{25} and increase in the lattice constant is expected for this factor. Second, decrease in the lattice constant is expected in CaS:Ce in the case of the cation vacancies generation to maintain the charge neutrality. Third, increase in the lattice constant is expected in the case of the interstitial anion generation to maintain the charge neutrality. However, this is not plausible for the anion having larger ionic radii than those of cations.\textsuperscript{26} In the case of CaS:Ce, the ionic radius of S\textsuperscript{2–} (0.184 nm) is larger than those of cations.

The peaks of CaS:Eu ceramics did not significantly shift and the lattice constant of CaS:Eu (0.1 mol\%) was 0.0002 nm larger than that of CaS. CaS:Eu ceramic followed the first factor and its lattice constant increased slightly. However, the shift in the peak of XRD pattern was negligible owing to a slight increase in the lattice constant. The peaks of CaS:Ce ceramics shifted to the higher angle side with the dopant concentration except 3.0 mol\% sample, and the lattice constant of CaS:Ce (0.1 mol\%) was 0.0030 nm smaller than that of CaS which can be explained with the first and second factors. The shift to the higher angle side of XRD peaks indicates that the second effect was stronger than the first one in these samples. In summary, the dopants were successfully incorporated into the CaS matrix at 0.1 mol\%, and some rare earth elements appeared to be in alien phases in 0.5 and 3.0 mol% CaS samples. Therefore, the 0.1 mol\% samples were used for the all measurements.

Figures 4–6 shows the PL excitation and emission spectra of undoped CaS, CaS:Ce (0.1 mol\%), and CaS:Eu (0.1 mol\%) at room temperature, respectively. In the excitation spectrum of undoped CaS at the emission wavelength of 420 nm, an excitation peak at 250 nm was observed in Fig. 4. This excitation peak is attributed to the absorption of CaS since the bandgap energy of CaS was reported to be 5.38 eV in a previous paper.\textsuperscript{27} In the emission spectrum of undoped CaS at the excitation wavelength of 250 nm, the emission peaks at 430 and 600 nm and shoulder at 380 nm were observed. These emission peaks are attributed to the emission of CaS. The emission peaks were similar to those in a previous report,\textsuperscript{28} in which three emission bands were reported for pure CaS at 425, 490 and 580 nm.\textsuperscript{29} In the previous report, the emission band at 425 nm was assigned to intrinsic point defects, most probably S vacancies. The 490 nm emission was thought to be due to recombination of electrons from neutral S vacancy donors with acceptors. The emission at 580 nm was assigned to electronic transition of F\textsuperscript{−} centers. In the excitation spectrum of CaS:Ce (0.1 mol\%) at the emission wavelength of 510 nm, excitation bands at 270 and 458 nm were observed in Fig. 5. These excitation wavelengths are similar to those of CaS:Ce ceramics in a previous report (271 and 456 nm) and assigned to the E\textsubscript{g} and T\textsubscript{2g} of the 5d crystal field splitting levels.\textsuperscript{30} Besides, it is also considered that the peak at 250 nm is assigned to the host absorption of CaS since the peak wavelength is
similar to that of undoped CaS shown in Fig. 4. In the emission spectrum with excitation at 458 nm, emission bands at 510 and 570 nm were observed. These emission peaks have similar peak wavelengths to those of CaS:Ce ceramics in the previous report (508 and 568 nm) and are assigned to the transitions from the T2g level of the 5d-excited state to the 2F5/2 and 2F7/2 of the 4f ground state.30) The excitation spectrum of CaS:Eu (0.1 mol %) at emission wavelength of 656 nm exhibited a band at 270 and a broad band from 450 to 600 nm in Fig. 6. The excitation band at 270 nm is assigned to the host absorption of Ca since the peak wavelength is similar to that of undoped CaS shown in Fig. 4. The wavelength region of the excitation broad band from 450 to 656 nm is similar to that of SrS:Eu (1 mol %) single crystal in a previous report (2.1 to 3 eV) and is assigned to the 4f7–5d1 (T2g) transition of Eu2+.31) In the emission spectrum of CaS:Eu (0.1 mol %) with excitation at 450 nm, an emission band at 656 nm was observed. This wavelength is similar to that of CaS:Eu (0.06 %) single crystals in a previous report (emission at 650 nm) and is attributed to the transition from the T2g level of the 4f65d1-excited state to the 8S7/2 level of the 4f7
In summary, in the PL emission spectra, the emission peaks attributed to the CaS host excitation were confirmed in CaS ceramics. Besides, the emission peaks attributed to the Ce$^{3+}$ ions were confirmed in CaS:Ce ceramics, and the emission peaks attributed to the Eu$^{2+}$ ions were confirmed in CaS:Eu ceramics. In the PL excitation spectra, excitation peaks attributed to the absorption of host materials were confirmed in CaS, CaS:Ce, and CaS:Eu ceramics. In addition, the PL quantum yields of CaS:Ce and CaS:Eu (0.1 mol%) were estimated to be 0.095 and 0.627 with excitation at 250 and 470 nm, respectively.

Figure 7 shows the XRL spectra of CaS, CaS:Ce (0.1 mol%), and CaS:Eu (0.1 mol%).

The wavelengths of the scintillation peaks were longer than those of other scintillators, such as oxide and halide crystalline scintillators and ceramic scintillators. For example, the scintillation emission spectrum of LaBr$_3$:Ce (0.5, 4, and 10 %) single crystals$^{33}$ had a broad emission band peaked at 360 and 380 nm, which are much shorter than that of CaS:Ce (500 and 650 nm). The scintillation emission wavelength of Lu$_{2(1-x)}$Ce$_x$(SiO$_4$)O single crystal$^{34}$...
was 420 nm, which is also much shorter than those of CaS:Ce (500 and 560 nm). The scintillation emission wavelength of SrI₂:Eu²⁺ single crystals was ~340 nm, which is much shorter than that of CaS:Eu (667 nm). Some rare earth elements that emit in f¹⁻→d⁻⁺ transitions, such as Eu²⁺ and Ce³⁺, have a difference in the emission wavelength, which depends on the characteristics of the host materials, such as the type of ligands and positional relationship between ligands and dopants. The difference in the type of ligands was considered to be the most significant cause in this study. Ligands with strong covalent bond between ligands and dopant induce the decrease in the repulsive force between electrons of ligands and dopant. The decrease in the repulsive force between electrons results in nephelauxetic effect, in which the center of gravity of the 5d level energy is lowered. For the same dopant, the strength of covalent bond between ligands and dopant depends on the electronegativity of ligands. For example, the Pauling’s electronegativity scale of O, Br, I, and S is 3.44, 2.96, 2.66, and 2.58, and the strength of covalent bond increase in this order. The remarkably longer emission wavelength in the sulfides in this study than those oxide and halide scintillators is attributed to this effect.

Figure 8 shows the PL decay time profiles of (a) CaS:Ce (0.1 mol %) and (b) CaS:Eu (0.1 mol %). The decay time constants were estimated using a sum of two or three exponential

\[ I(t) = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \]  

where \( I(t) \) is the intensity at \( t \), \( I_0 \) is the intensity at \( t = 0 \), \( A_1 \), \( A_2 \), and \( A_3 \) are constants, and \( \tau_1 \), \( \tau_2 \), and \( \tau_3 \) are decay time constants. The decay time constants are shown in Table 1. \( \tau_1 \) of CaS:Eu (0.1 mol %, 19 ns) and \( \tau_1 \), \( \tau_2 \) of CaS:Ce (0.1 mol %, 1.3 and 20 ns) are components caused by scattering of excitation light. \( \tau_2 \) of CaS:Eu (0.1 mol %, 200 ns) is similar to that of CaS:Eu single crystals (2.5, 30.1, and 88.5 ns) and attributed to the 5d⁻→f transition of Ce³⁺. This slower component may correspond to the excited state ionization, in which the electron escapes from the Ce³⁺ 5d₁ excited state to the bottom of the conduction band and returns to the excited state of Ce³⁺ and recombines with the hole at Ce³⁺ 3d₁. \( \tau_1 \) and \( \tau_2 \) of CaS:Ce (\( \lambda_{em} = 451 \text{ nm}, 0.1 \text{ mol %}, 46 \text{ ns} \)) correspond to the peak at 460 nm in the PLE spectra. Their decay time constants are similar to those in other sulfides such as SrGa₂S₄:Ce (0.2 mol %, 60 ns) thin-films and KLu₂S₄:Ce single crystals (2.5, 30.1, and 88.5 ns) and attributed to the 5d⁻→f transiton of Ce³⁺. The slower component may correspond to the excited state ionization, in which the electron escapes from the Ce³⁺ 5d₁ excited state to the bottom of the conduction band and returns to the excited state of Ce³⁺ and recombines with the hole at Ce³⁺ 3d₁. \( \tau_1 \) and \( \tau_2 \) of CaS:Ce (\( \lambda_{em} = 255 \text{ nm}, 0.1 \text{ mol %}, 620 \text{ and } 3110 \text{ ns} \)) are attributed to the host excitation at 250 nm in the PLE spectrum and assigned to some defects in the host since \( \tau_1 \) and \( \tau_2 \) are similar to those of undoped CaS (834 and 3340 ns).

Figure 9 illustrates the scintillation time profiles of CaS:Ce (0.1 mol %). The scintillation time profiles of CaS:
Eu samples were not able to be measured since their afterglows were too strong. The decay time constants were estimated to 7 ns (~99%) and 46 ns (~1%) by using a sum of two exponential decay functions. The decay time constants of 7 ns was caused by scattering of excitation light. \(\tau_1\) of CaS:Ce (0.1 mol\%), 46 ns is similar to that in PL (46 ns) and attributed to 5d-4f transition of Ce\(^{3+}\). In addition, \(\tau_1\) of CaS:Ce (0.1 mol\%), 19 ns is significantly faster than those of the other Ce\(^{3+}\) activated scintillators, such as LaCl\(_3\):Ce (0.5 mol\%) single crystals [25 ns (60%)] and LaBr\(_3\) (0.5 mol\%) single crystals [35 ns (90%)].

**Figure 10** illustrates the pulse height spectra of CaS, CaS:Ce (0.1 mol\%), and CaS:Eu (0.1 mol\%) with 662-keV gamma-ray excitation from \(^{137}\)Cs. **Table 2** compares the pulse height spectra of GSO single crystals and powder. The spectrum edge of powdered sample and the photopeak channel of single crystal appear at similar channels as is shown for GSO powder crystal in Fig. 10. The light yields were estimated by comparing the spectrum edge position of each sample with the spectrum edge position of GSO powder. The quantum efficiencies of the PMT at the peak wavelengths of GSO and the samples were taken into account in the estimations. The light yields of the samples were estimated to be 1,700 photons/MeV (CaS:Ce 0.1 mol\%) and 4,400 photons/MeV (CaS:Eu 0.1 mol\%).

The material properties of CaS ceramics are compared with those of the other sulfide scintillators. Gd\(_2\)O\(_3\):Pr\(^{3+}\), Ce ceramic scintillators and Lu\(_2\)S\(_3\):Ce\(^{3+}\) crystalline scintillators are chosen for comparison since they have been well studied as scintillators and they are doped with Ce. The density of CaS ceramics was 2.59 g/cm\(^3\), which are lower than those of Gd\(_2\)O\(_3\):Pr\(^{3+}\), Ce (6.71 g/cm\(^3\)) and Lu\(_2\)S\(_3\):Ce\(^{3+}\) (6.26 g/cm\(^3\)). The effective atomic number of CaS (18.5) is quite lower than those of Gd\(_2\)O\(_3\):Pr\(^{3+}\), Ce (61.1) and Lu\(_2\)S\(_3\):Ce\(^{3+}\) (66.8). However, CaS ceramics are easier to prepare than Lu\(_2\)S\(_3\):Ce\(^{3+}\) crystals since their preparation temperatures (1273 K) are much lower than the melting point of Lu\(_2\)S\(_3\):Ce\(^{3+}\) crystals (2023 K). The light yield of CaS:Ce (0.1 mol\%) and CaS:Eu (0.1 mol\%) are 1,700 and 4,400 photons/MeV, which are lower than that of Gd\(_2\)O\(_3\):Pr\(^{3+}\), Ce ceramic scintillators (28,000 photons/MeV).\(^{40}\) The decay time constants of CaS:Ce (0.1 mol\%) are 19 and 325 ns, which are faster than that of Gd\(_2\)O\(_3\):Pr\(^{3+}\), Ce ceramic scintillators (6,890 and 790 ns). The scintillation emission wavelength of CaS:Ce (380 nm) is more suitable for PMT than those of Gd\(_2\)O\(_3\):Pr\(^{3+}\), Ce ceramic scintillators (510 nm).\(^{40}\) CaS:Ce ceramic scintillators have low light yield and slower decay time constants than Lu\(_2\)S\(_3\):Ce\(^{3+}\) crystalline scintillators (light yield: 28,000 photons/MeV, decay time constant: 32 ns).\(^{48}\) However, the scintillation emission wavelength of CaS:Ce ceramic scintillator (380 nm) is more suitable for PMT than those of Lu\(_2\)S\(_3\):Ce\(^{3+}\) crystalline scintillators (500 and 750 nm).\(^{15}\)

**Table 2.** Spectrum edge and light yield of CaS, CaS:Ce (0.1 mol\%), and CaS:Eu (0.1 mol\%)

| Spectrum edge | Light yield [photons/MeV] |
|--------------|--------------------------|
| CaS:Ce 0.1 mol\% | 220 | 1,700 |
| CaS:Eu 0.1 mol\% | 290 | 4,400 |
measurements, i.e., afterglow. That may contribute to the background noise in the PL decay measurements and an increase in the intensity of PL spectra. In the previous report on CaS:Eu (0.2 mol%), there was a peak at 403 K in TL grow curve after 10 to 50 Gy gamma rays irradiations.\(^{43}\) The peak temperature in the previous report is lower than that in our sample (473 K). The cause of the difference between samples has not been clarified since there are some possible reasons, such as the distance from the heater to the samples and thermal conductivity of the sample table. The trap responsible to the peak at 473 K in CaS:Eu can be attributed to Eu\(^{2+}\) ions since there is no similar peak in CaS:Ce. The intensity of TL grow peak in CaS:Eu was compared with commercially available dosimeter: TLD-100. The intensities were standardized by weights of samples. The intensity of a peak in CaS:Eu was significantly stronger than that in TLD-100, which means CaS:Eu ceramics have better sensitively than TLD-100. CaS:Eu ceramics have potential as dosimeter. Judged from the efficient TL emission, the relatively low light yield of CaS:Eu (0.1 mol%) of 4,400 photons/MeV can be explained for high quantum yield of PL. The relationship between the scintillation light yield and quantum yield of PL can be described with a following equation,\(^{44}\)

\[
L = \frac{10^6 \beta S Q}{2.3 E_g} \tag{3}
\]

where \(\beta\) is the number of electron–hole pairs actually produced by a one stopped gamma photon divided by the maximum possible number of electron–hole pairs, \(S\) is the efficiency of transfer process of the electron–hole pairs to the emission centers, and \(Q\) is the quantum yield of PL of the luminescence centers. \(L\) [photons/MeV] is the scintillation light yield, and \(E_g\) [eV] is the bandgap energy of the host. 2.3 \(E_g\) [eV/photons] is the minimum energy required to produce one electron–hole pair. \(E_g\) is the energy which depends on the band structure of the host material, and \(\beta\) is the efficiency of the conversion process to electron–hole pairs which depends on the electronic structure of the host materials. Both \(\beta\) and \(E_g\) have the same values for CaS:Eu and CaS:Ce. The light yield (\(L\)) of CaS:Eu (0.1 mol %, 4,400 photons/MeV) is higher than that of CsS:Ce (0.1 mol %, 1,700 photons/MeV), and the quantum yield (\(Q\)) of CaS:Eu (0.1 mol %, 0.627) is also higher than that of CsS:Ce (0.1 mol %, 0.095). The difference in the quantum yields is greater than the difference in the light yields. Hence, \(S\) of CaS:Eu should be significantly smaller than that of CaS:Ce according to the Eq. (3). This is consistent with the result of TL glow curve: the high TL intensity of CaS:Eu represents that the number of trapped electron–hole pairs is large, which results in a smaller \(S\) than that of CaS:Ce.

4. Conclusions

We fabricated CaS ceramic phosphors and measured their PL, scintillation, and dosimetry characteristics in order to investigate the possibility of CaS ceramics as scintillators. The scintillation emission spectrum of CaS:Eu ceramics showed an emission peak at 656 nm, originating from the 5d–4f transitions of Eu\(^{2+}\) ions. The scintillation emission spectrum of CaS:Ce ceramics showed emission peaks at 510 and 570 nm that originate from the 5d–4f transitions of Ce\(^{3+}\) ions. The PL emission peaks of CaS:Ce and CaS:Eu were similar to those of XRL emission peaks and were also assigned to the emission of Ce\(^{3+}\) and Eu\(^{2+}\) ions. The light yield of CaS:Ce (0.1 mol %) and CaS:Eu (0.1 mol %) were estimated to be approximately 1,700 and 4,400 photons/MeV. CaS:Eu exhibited a strong afterglow and TL, because of which the light yield was not obtained based on the pulse height spectrum. Considering their PL, TL, and scintillation properties, CaS:Ce and CaS:Eu have potentials for application as scintillators and dosimeters, respectively.

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