Scintillation and Dosimeter Properties of CaF_2 Transparent Ceramic Doped with Eu^{2+}

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Abstract

We have developed CaF_2 transparent ceramics doped with Eu^{2+} ($\text{CaF}_2:\text{Eu}$) by using spark plasma sintering (SPS), and investigated the scintillation, dosimeter and photoluminescence (PL) properties. Under X-ray irradiation, all the samples showed emission due to self-trapped excitons (STE) and 5d-4f transition of Eu^{2+} at 300 and 430 nm, respectively. In addition, weak emission due to the 4f-4f transitions of Eu^{3+} at 570, 590, 615 and 625 nm were also present in all the samples. Under ^{137}Cs irradiation, the light yields of the 0.01, 0.02, 0.05 and 0.1 Eu-doped samples were estimated to be 16,400, 15,400, 17,700 and 14,300 photons/MeV, respectively. Thermally stimulated luminescence (TSL) glow curves of all the samples exhibited glow peaks at 100 and 180 °C, and these intensities increased linearity as a function of X-ray dose from 0.1 mGy to 1000 mGy. Furthermore, the $\text{CaF}_2:\text{Eu}$ showed not only TSL but also optically stimulated luminescence (OSL).

Keywords: Transparent Ceramic, CaF_2 , Scintillator, Dosimeter, Eu

1. Introduction

Phosphor materials are used in ionizing radiation detectors, and can be classified into two types: scintillator and dosimeter. The former has a function to convert the absorbed energy of ionizing radiation into low energy photons immediately, and has been widely used in practical applications including medicine [1], security [2] and high energy physics [3]. In practical applications, scintillators are required to have a high light yield. On the other hand, the latter has been mainly used to measure absorbed energy in the human body [4] because they function to store and accumulate the absorbed energy of ionizing radiation. The absorbed energy is stored in a form of carrier trapping, and the trapped charges can be de-captured by external stimulation. Subsequently, the de-captured charges recombine and then emit photons. When the stimulation is light, the resultant light emission is referred to as optically stimulated luminescence (OSL). In contrast, when the stimulation is heat, the resultant light emission is called thermally-stimulated luminescence (TSL). Ideally, the effective atomic number (Z_{eff}) of dosimeter material should be close to that of soft human body tissue ($Z_{\text{eff}} = 7.51$). If the Z_{eff} of dosimeter material is perfectly the same as that of the human body, it is expected that there is no energy dependence in a sense to measure radiation dose absorbed in the tissue. Therefore, no mathematical calibrations are needed in this ideal case. Furthermore, in recent years, the complementary relationship between scintillation and dosimeter properties was found [5, 6], so to understand ionizing radiation induced luminescence comprehensively both kinds of properties should be studied in one material.

Scintillation properties of CaF_2 doped with Eu^{2+} ($\text{CaF}_2:\text{Eu}$) have been studied since the first report was published in 1966 [7]. The $\text{CaF}_2:\text{Eu}$ shows scintillation emissions due to self-trapped excitons (STE) and Eu^{2+} 5d-4f transitions at 270 and 420 nm, respectively [8]. In addition, the $\text{CaF}_2:\text{Eu}$ is known to have high light yield (24,000 photons/MeV) [9]. The $\text{CaF}_2:\text{Eu}$ has been considered as a promising candidate in the search for dark matter because ^{19}F has the best figure of advantage for spin coupled dark matter search [10]. Therefore, the $\text{CaF}_2:\text{Eu}$ has been studied for potential use as a scintillator in astrophysics [11]. The $\text{CaF}_2:\text{Eu}$ has also been studied as a dosimeter material [12, 13] because its effective atomic number ($Z_{\text{eff}} = 17.1$) is low and relatively close to that of soft tissue. For these reasons, the $\text{CaF}_2:\text{Eu}$ is a good candidate for both scintillation and dosimeter materials.

There are a number of studies reporting the scintillation and dosimeter properties of $\text{CaF}_2:\text{Eu}$ [14-18]. However, most of these reports are on bulk single crystal $\text{CaF}_2:\text{Eu}$, and no reports are found for $\text{CaF}_2:\text{Eu}$ transparent ceramics. Transparent ceramics are of great interest because previous research has clarified that, compared with a single crystal form, some ionizing radiation induced luminescence properties were modified and improved [19-23]. In addition, transparent ceramics have some advantages, such as high mechanical strength, uniformity and low fabrication cost compared with single crystal, which are preferable properties for practical applications. For these reasons, in this study, we synthesize $\text{CaF}_2:\text{Eu}$ transparent ceramics using spark plasma sintering (SPS), and subsequently investigate both the

scintillation and dosimeter properties.

2. Experimental

A series of $\text{CaF}_2\text{:Eu}$ transparent ceramic samples with different Eu concentrations were synthesized using SPS. CaF_2 and EuF_3 powders were mixed using a mortar, and the concentration of Eu varied at 0.01, 0.02, 0.05 and 0.1 mol.% since the optimum concentrations in $\text{CaF}_2\text{:Eu}$ single crystal were around 0.05 [24]. The mixture was introduced into a cylindrical graphite die with a hole 10.4 mm in diameter. Subsequently, the sintering was executed with uniaxial pressure applied through the assembly while applying pulsed current to sinter. The sintering was carried out in two steps. First, the temperature was elevated from 15 °C to 800 °C within 10 min, then kept at 800 °C for 10 min while applying 10 MPa pressure. Next, the temperature was further increased from 800 °C to 1070 °C within 3 min and kept at 1070 °C for 15 min while applying 70 MPa pressure. The temperature was measured using a K-thermocouple attached onto the graphite die. After the sintering, wide surfaces of the obtained ceramic samples were polished with a polishing machine (MetaServ 250, BUEHLER). The sizes of the samples were comparable, and they were characterized in the same manner described below.

A scanning electron microscope (SEM; Hitachi TM3030) was used to observe backscattered electron images. Optical in-line transmittance spectra were evaluated by a spectrometer (V670, JASCO) over the spectral range of 190-2700 nm with 1 nm steps. Photoluminescence (PL) emission and excitation map and quantum yields were measured with a Quantaaurus-QY (Hamamatsu Photonics). PL decay profiles monitoring at 400 nm under 340 nm excitation were evaluated with a Quantaaurus- τ (Hamamatsu Photonics).

In order to characterize scintillation properties, X-ray induced scintillation spectra were measured using our original setup [25]. An X-ray generator equipped with a tungsten anode target (XRB80P&N200X4550, Spellman) was used as the excitation source, and operated with a tube voltage of 40 kV and current of 5.2 mA. Through a 2.0 m optical fiber, the scintillation photons from the sample were collected and then guided to a spectrometer (Andor DU-420-BU2 CCD and Shamrock 163 monochromator). Here, the spectrometer was placed off the irradiation geometry axis to avoid directly striking the X-rays onto the CCD. In order to reduce the thermal noise, the spectrometer was cooled down to 193 K by a Peltier module. A pulse X-ray source equipped with an afterglow characterization system was used to measure X-ray induced scintillation decay and afterglow profiles [26]. The applied voltage to the X-ray source was 30 kV. A pulse height spectroscopy measurement was conducted to evaluate scintillation light yields induced by γ -rays. In the measurements, a sample was firmly placed onto a window of the photomultiplier tube (PMT; R877-100, Hamamatsu) using an optical grease (6262A, OKEN), and covered by several layers of Teflon sheet to effectively guide the scintillation photons to the PMT. A pre-amplifier (113, ORTEC) was subsequently used to amplify the PMT output signals, and the signals processed by a shaping amplifier (572, ORTEC) with 2 μs shaping time. The signal output was integrated and registered using a multichannel analyzer (Pocket MCA 8000A, Amptek), and then a pulse

height spectrum was constructed on a personal computer. In this measurement, a sealed radioactive ^{137}Cs γ -ray was used as the radiation source.

TSL glow curves of the samples irradiated with various dose from 0.1 mGy to 1000 mGy X-rays were measured using a TSL reader (TL-2000, Nanogray Inc.) [27] after X-ray irradiation with various doses from 0.1 mGy to 1000 mGy. The heating rate was 1 °C/s, and the measurement temperature range was from 50 to 490 °C. In order to measure TSL spectra, the TSL emission was collected through an optical fiber while the sample was heated at a specific temperature on a ceramic heater system (SCR-SHQ-A, Sakaguchi). Subsequently, the light was guided to a spectrometer (QE Pro, Ocean Optics). Here, the samples were irradiated with the tube voltage of 80 kV and current of 2.5 mA for 10 min before heating. OSL was measured under stimulation with 650 nm light by using a spectrofluorometer (FP8600, JASCO). OSL decay profiles were also measured by the spectrofluorometer under the continuous stimulation light with wavelength of 650 nm.

3. Results and discussion

3.1. Sample

Fig. 1 shows a photograph of the $\text{CaF}_2\text{:Eu}$ transparent ceramic samples synthesized in this research. The top photograph shows the samples under ambient light. The stripe patterns on the back of the samples are clearly seen. The bottom photograph shows the samples under irradiated at 254 nm UV light. The samples showed blue PL emission. The sample size was typically $10\text{ mm}\phi \times 1\pm0.22\text{ mm}$. Fig. 2 shows the SEM image of the $\text{CaF}_2\text{:0.1\%Eu}$ transparent ceramic sample. From the SEM image, the average, maximum and minimum grain size on the surface of the sample was estimated at 101, 429 and $10\text{ }\mu\text{m}^2$, respectively. No significant difference from doping concentration was observed by SEM.

3.2. Optical properties

Fig. 3 shows the PL excitation/emission contour graph of $\text{CaF}_2\text{:0.05\%Eu}$ transparent ceramic sample as an example. Under excitation around 340 nm, an intense broad emission band around 420 nm was observed, with the origin of this emission ascribed to the 5d-4f transitions Eu^{2+} [28]. The excitation and emission spectra did not differ largely from the doping concentration. The intensity clearly depended on the doping concentration. The quantum yields of the 0.01, 0.02, 0.05 and 0.1 % Eu-doped samples were 1.8, 3.6, 27.2 and 2.3 %, respectively, and the 0.05 % Eu-doped sample showed the highest value among all the samples.

PL decay profiles of the $\text{CaF}_2\text{:Eu}$ transparent ceramic samples are shown in Fig. 4. The monitored emission wavelength was 420 nm, and the excitation wavelength was 340 nm. The decay curves were approximated by a single exponential function. The derived decay time constants of the 0.01, 0.02, 0.05 and 0.1 % Eu-doped samples were approximately 0.67, 0.68, 0.68 and 0.65 μs , respectively, and they were typical values of the 5d-4f transitions of Eu^{2+} [18].

Fig. 5 shows in-line transmittance spectra of the CaF₂:Eu transparent ceramic samples. The inset enlarges the spectral region of 200-500 nm. All the samples showed absorption bands in 320-420 nm due to the 4f-5d transitions of Eu²⁺, and this result was consistent with the PL excitation band (see Fig. 3). No clear relationship between transmittance and Eu concentration was observed.

3. 3. Scintillation properties

Fig. 6 shows X-ray induced scintillation spectra of CaF₂:Eu transparent ceramic samples. The inset shows an enlarged view in the 550-680 nm range. Intense emission peaks were observed at 300 and 430 nm in all the samples, and these peaks were ascribed to STE of CaF₂ and the 5d-4f transitions of Eu²⁺, respectively [8]. In addition, emission peaks at 570, 590, 615 and 625 nm appeared in all the samples, due to the 4f-4f transitions of Eu³⁺ [28]. The intensity ratio of the peak at 300 nm to the one at 420 nm decreased with an increase in the concentration of Eu.

X-ray induced scintillation decay time profiles of the CaF₂ transparent ceramic samples are shown in Fig. 7. The scintillation decay curves of all the samples were approximated by single exponential decay function. The derived decay time constants of the 0.01, 0.02, 0.05 and 0.1 % Eu-doped samples were 0.84, 0.81, 0.78 and 0.75 μs, respectively, and ascribed to the 5d-4f transitions of Eu²⁺ [8]. The decay times became shorter as the Eu concentration increased. The decay times were slower than those of PL because there were differences in the energy transfer process between PL and scintillation.

Afterglow levels of the CaF₂:Eu transparent ceramic samples are shown in Fig. 8. The inset shows the afterglow profiles. Here, the afterglow level (*A*) was defined as $A (\%) = 100 \times (I_2 - I_{BG}) / (I_1 - I_{BG})$ where *I*_{BG} is the background signal, *I*₁ is the averaged signal intensity during X-ray irradiation, and *I*₂ is the signal intensity at 20 ms after the irradiation was cut off [29]. The afterglow levels of the 0.01, 0.02, 0.05 and 0.1 % Eu-doped samples at 20 ms showed 0.16, 0.15, 0.04 and 0.02 %, respectively. The afterglow levels decreased as the concentration of Eu increased.

Fig. 9 shows pulse height spectra of the CaF₂:Eu transparent ceramic samples under ¹³⁷Cs γ-ray irradiation. The Compton edge appeared in all the samples. Based on the position of the Compton edge, the light yields were deduced as relative values registered on the MCA channel by a conventional NaI:TI crystal scintillator [30]. The light yields of the 0.01, 0.02, 0.05 and 0.1 Eu-doped samples were estimated at 16,400, 15,400, 17,700 and 14,300 photons/MeV, respectively, with the 0.05 % Eu-doped sample showing the highest light yield among all the ceramic samples. Compared with CaF₂:Eu single crystal, the observed light yields were slightly less. Since the SPS method is highly reductive, some anion defects could have been introduced in the samples, subsequently degrading the scintillation light yield.

3. 4. Dosimeter properties

Fig. 10 shows TSL glow curves of CaF₂:Eu transparent ceramic samples measured after X-ray irradiation. The irradiation dose was fixed at 1000 mGy for all the measurements. All the samples exhibited major glow peaks at 100 and 180 °C, consistent with earlier work [13]. From our previous study,

the origin of the 100 °C peak was ascribed to the host since the same glow peak was observed in nondoped CaF₂ transparent ceramics [31]. Furthermore, an additional peak at 200 °C was observed only in the 0.01 % Eu-doped sample. The TSL intensities were inversely proportional to Eu concentration. Fig. 11 shows TSL emission spectra of the CaF₂:Eu transparent ceramic samples measured at 100 °C after the samples were irradiated. The inset shows an enlarged view. An intense emission peak was observed at 430 nm in all the samples, due to the 5d-4f transitions of Eu²⁺.

TSL dose response of the CaF₂:Eu transparent ceramic samples are shown in Fig. 12. Here, the TSL intensity represents integrated value of all the glow peaks (shown in Fig. 10). All the samples showed a good linearity from 0.1 mGy to 1000 mGy. Assuming the first order kinetics, trap depth and frequency factors were estimated using the initial rise method [32], and the derived values are summarized in Table 1. The values of frequency factor suggest that a primary cause of TSL was the tunneling effect for all the peaks.

Fig. 13 shows OSL spectra of the CaF₂:Eu transparent ceramic samples under 650 nm stimulation after irradiation by X-rays (~2 Gy). Here, the X-ray tube voltage was 80 kV and current was 2.5 mA. All the samples exhibited a peak at 430 nm due to the 5d-4f transitions of Eu²⁺ [8]. The OSL intensity decreased with an increase in the concentration of Eu, which was once again inversely proportional to the TSL intensity. OSL decay profiles of the CaF₂:Eu are represented in Fig. 14. The decay curves of all the samples were approximated by two exponential decay functions, suggesting at least two detrapping processes. The faster components of the 0.01, 0.02, 0.05 and 0.1 % Eu-doped samples were 22.50, 17.55, 8.77 and 3.73 s, and the slower components were 85.84, 61.26, 30.58 and 20.97 s, respectively. Both components became shorter with an increase in the concentration of Eu, since the probability of radiative recombination simply increases with Eu concentrations.

4. Conclusions

We have developed CaF₂:Eu transparent ceramics using SPS and investigated the scintillation, dosimeter and PL properties. Under X-ray irradiation, all the samples showed emission due to STE and 5d-4f transition of Eu²⁺ appearing at 300 and 430 nm, respectively. In addition, weak emission peaks due to the 4f-4f transitions of Eu³⁺, which appeared at 570, 590, 615 and 625 nm, were present in all the samples. Under ¹³⁷Cs irradiation, the light yields of the 0.01, 0.02, 0.05 and 0.1 Eu-doped samples were estimated to be 16,400, 15,400, 17,700 and 14,300 photons/MeV, respectively. The TSL glow curves of all the samples exhibited glow peaks at 100 and 180 °C, and the dose response curves showed good linearity from 0.1 mGy to 1000 mGy. Furthermore, the CaF₂:Eu showed not only TSL but also OSL.

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Table. 1 Derived trap depth and frequency factors of CaF₂ transparent ceramic doped with Eu²⁺ samples.

	Peak temperature (°C)	Trap depth (eV)	Frequency factor (s ⁻¹)
0.01 % Eu	100	0.51	1.23×10^5
	180	0.41	1.05×10^3
	200	0.39	2.40×10^2
0.02 % Eu	100	0.53	5.86×10^5
	180	0.40	1.03×10^3
0.05 % Eu	100	0.56	1.43×10^6
	180	0.40	1.03×10^3
0.1 % Eu	100	0.58	3.68×10^6
	180	0.36	3.23×10^2