Scintillation and dosimetric properties of Tb-doped CaF$_2$ translucent ceramics synthesized by the spark plasma sintering method

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**ABSTRACT**

CaF$_2$ translucent ceramics with different concentrations of Tb were synthesized by the spark plasma sintering (SPS) method, and their photoluminescence, scintillation and dosimetric properties were characterized. The Tb-doped samples exhibited scintillation with several sharp peaks across the range from 365–630 nm due to 4 f–4 f transitions of Tb$^{3+}$ and with a broad peak at approximately 300 nm due to self-trapped excitons. Among the sample investigated, the scintillation intensity in the 365–630 nm range was highest for the 0.5% Tb-doped sample. As a dosimetric property, the Tb-doped samples exhibited thermally-stimulated luminescence (TSL) with a glow peak at approximately 90°C, and with a TSL response in a linear relationship to the X-ray dose over the dose range from 0.001 to 1 mGy. Optically stimulated luminescence (OSL) due to the 4 f–4 f transitions of Tb$^{3+}$ was detected in the Tb-doped samples, moreover and the lowest detectable limit of OSL was at most 100 mGy.

1. Introduction

The radiation dosimetric method has gained much attention as a means of determining accumulated radiation doses and spatial distribution. It has been used in a wide range of applications, such as retrospective accidental dosimetry, environmental dosimetry and individual radiation monitoring [1]. In this method, solid-state phosphor materials are often used due to their capability of showing storage luminescence such as thermally-stimulated luminescence (TSL) and optically-stimulated luminescence (OSL) [2,3]. When phosphor materials are irradiated by ionizing radiation, they function to store the radiation energy as a form of trapped carriers. Subsequently, the carriers recombine to exhibit TSL and OSL in response to such as external stimulation such as heat and light, respectively. The fundamental requirements of the phosphor materials include dose linearity, high sensitivity and low fading.

CaF$_2$ materials among especially TSL materials are the well-known host materials required for use with the radiation dosimetric methods. Dy-doped CaF$_2$ exhibits high TSL sensitivity, for instance, with a dynamic range reported to be from 0.1 µGy to 10 Gy. It is commercialized as TLD-200 for the environmental radiation dosimetry [4]. Furthermore, Mn-doped CaF$_2$, referred to TLD-400, shows efficient TSL with a dynamic range of 0.1 µGy – 10 Gy. Thanks to its high sensitivity and dose linearity, it is used for high dose measurement and environmental radiation dosimetry [4]. In addition, Tb-doped CaF$_2$ shows more efficient TSL than CaF$_2$ materials doped with other elements (Eu, Ho, Sm), and it shows efficient TSL with glow peaks at approximately 80, 100 and 185°C [5]. In addition to their TSL properties, the OSL properties of some CaF$_2$ materials have been investigated. It is reported that Tm-doped CaF$_2$ shows efficient OSL under 458 nm and 850 nm LED light, for example, and that its lowest measurable dose has been found to be 1 mGy and 100 µGy, respectively [6]. Furthermore, N-doped CaF$_2$ shows high OSL sensitivity, and its OSL dose response curve becomes linear for doses higher than 10 µGy [7]. In addition to those of the above materials, the OSL properties of Mn-doped CaF$_2$ and Ce-doped CaF$_2$ have been investigated [8,9]. In these past studies, the dosimetric properties were investigated mainly in their crystal and ceramic forms.

Recently, attention has been focused on translucent ceramics synthesized by the spark plasma sintering (SPS) method as candidate materials for radiation measurement. They have such industrial advantages as high mechanical strength, low fabrication cost and high uniformity according to the past studies [10,11]. Moreover, they can show efficient storage luminescence since many trapping centers responsible for storage luminescence can be formed owing to their high reducing atmosphere. Up to now, we have investigated the scintillation and dosimetric properties of CaF$_2$ translucent ceramics doped with impurities (Tm, Eu, Dy, Nd) for radiation measurement [12–15]. Among
them, Dy-doped CaF₂ translucent ceramics shows excellent TSL responses over the dose range of 0.001–1 mGy, and exhibit OSL due to 4 f-4 f transitions of Dy³⁺ under 630 nm excitation light.

In an attempt to continue developing phosphor materials based on CaF₂, we synthesized CaF₂ translucent ceramics with different concentrations of Tb (0.01, 0.05, 0.1 and 0.5%) by the SPS method. The Tb³⁺ ion is one of the luminescence centers commonly used for radiation measurement, and efficient storage luminescence can be observed in some Tb-doped materials such as Tb-doped MgO [16–18]. After the synthesis, we investigated the photoluminescence (PL) and scintillation properties. As dosimetric applications, the TSL and OSL properties were also evaluated. It should be noted that it is important to investigate both the scintillation and dosimetric properties because some compounds exhibit a complementary relationship between these two properties [9].

2. Experimental methods

CaF₂ translucent ceramics with different concentrations of Tb (0.01, 0.05, 0.1 and 0.5%) were synthesized by the SPS method using an SPS system (Sinter Land, LABOX-100). CaF₂ and Tb₄O₇ in a stoichiometric ratio were mixed for 30 min, and the mixed powder was loaded in a graphite die and held between two graphite punches. The sintering processes were as follows: The temperature was first increased at a rate of 23°C/min from 25°C to 1070°C temperature and then kept at 1070°C for 15 min under 70 MPa pressure. After these synthesis procedures, the surfaces of the fabricated translucent ceramics were polished mechanically for characterization.

Secondary electron images were then observed using a scanning electron microscope (SEM; JEOL, JCM-6000plus NeoScope). The in-line transmittance spectrum in the spectral range from 200–2500 nm was recorded using a spectrometer (JASCO, V670). The excitation and emission contour graph and quantum efficiencies were measured using Quantauret-τ (Hamamatsu Photonics, C11347). The PL decay curve was recorded using Quantauret-τ (Hamamatsu Photonics, C11367). The excitation wavelength for the measurement was 340 nm, while the monitoring wavelength was 540 nm. As scintillation properties, the X-ray induced scintillation spectra were measured using an X-ray generator equipped with a tungsten anode target (Spellman, XRB80P&N200 x 4550) [9]. The scintillation light from the samples was detected by a spectrometer (Andor, DU-420-BU2 CCD; Andor, Shamrock 163 monochromator) through optical fiber. The X-ray induced scintillation decay curve was recorded using an afterglow characterization system with a pulse X-ray source [19].

3. Results and discussion

3.1. Sample

Figure 1 shows a photograph of Tb-doped CaF₂ translucent ceramics. The thickness of the Tb-doped samples was about 1.0 mm. The 0.01–0.1% Tb-doped samples looked translucent, and striped patterns were visible on the backs of the 0.01–0.1% Tb-doped samples, while the underlying pattern on the 0.5% Tb-doped sample could not be seen clearly.

Figure 2 presents SEM images of Tb-doped CaF₂ translucent ceramics. The average grain sizes on the...
surfaces of the Tb-doped samples were approximately 10 µm (0.01% Tb), 10 µm (0.05% Tb), 10 µm (0.1% Tb) and 20 µm (0.5% Tb). The obtained sizes of the 0.01–0.1% Tb-doped samples were comparable to the previously reported value for 0.1% Eu-doped CaF$_2$ translucent ceramics [12]. No significant change in the grain size was observed with increase in the concentrations of Tb.

Figure 3 displays the in-line transmittance spectra of Tb-doped CaF$_2$ translucent ceramics in the spectral range of 200–2500 nm. The transmittance of the Tb-doped samples varied by 0–60% over the measurement range. The spectral features of the Tb-doped samples were similar to those of the previously reported CaF$_2$ translucent ceramics [12,20]. In addition, no absorption due to 4f–4f transitions of Tb$^{3+}$ was observed in the Tb-doped samples.

### 3.2. Photoluminescence properties

Figure 4 shows PL excitation and emission contour graphs of the Tb-doped CaF$_2$ translucent ceramics. Several emission peaks were observed for the 0.1% and 0.5% Tb-doped samples, while no clear PL signal was detected for the 0.01% and 0.05% Tb-doped samples using a spectrometer. These spectral features were in good agreement with those for the Tb$^{3+}$-doped CaF$_2$ ceramics [21], and the emissions were thus ascribed to 4f–4f transitions of Tb$^{3+}$. Furthermore, the QE values of the emissions across the 365–630 nm range were found to be 0.00 (0.01% Tb), 0.00 (0.05% Tb), 0.01 (0.1% Tb) and 0.04 (0.5% Tb) under an excitation wavelength of 340 nm. Among the sample investigated, the 0.5% Tb-doped sample exhibited the highest QE value.

![Figure 3](image1.png)

**Figure 3.** In-line transmittance spectra of the Tb-doped CaF$_2$ translucent ceramics.

![Figure 4](image2.png)

**Figure 4.** PL excitation and emission contour graph of the Tb-doped CaF$_2$ translucent ceramics.
Figure 5 displays the PL decay curves of Tb-doped CaF$_2$ translucent ceramics under 340 nm excitation light, monitored at 540 nm. The decay curves were approximated using an exponential decay function. The derived PL decay time constants were 8.2 ms (0.01% Tb), 6.9 ms (0.05% Tb), 6.8 ms (0.1% Tb) and 6.6 ms (0.5% Tb). These decay time constants were typical for the $^5D_4 \rightarrow ^7F_5$ transition of Tb$^{3+}$, and were thus attributed to the $^5D_4 \rightarrow ^7F_5$ transition of Tb$^{3+}$ [22–26]. These decay time constants remained almost constant with increase in the concentrations of Tb.

3.3. Scintillation properties

Figure 6 presents the X-ray induced scintillation spectra of the Tb-doped CaF$_2$ translucent ceramics. The Tb-doped samples showed sharp scintillation peaks at approximately 377, 412, 432, 486, 537, 583 and 618 nm. As in the previous studies on the Tb-doped materials [16,26], the origin of the scintillation peaks was the 4 f-4 f transitions of Tb$^{3+}$. The scintillation intensity in the spectral range of 350 – 650 nm increased with increase in the Tb concentration, and the results were consistent with the QE values for PL as shown in Figure 4. Furthermore, a broad scintillation peak appeared at approximately 300 nm in the Tb-doped samples. The broad peak originated from the self-trapped excitons in the CaF$_2$ host seen in the previous study [20]. The scintillation intensity of the broad peak decreased with increased in the concentrations of Tb. The cause of the decrease in scintillation intensity was unclear, and this phenomenon is also observed for Eu-doped CaF$_2$ translucent ceramics [12].

Figure 7 shows scintillation decay time profiles of the Tb-doped CaF$_2$ translucent ceramics. The spectral sensitivity of PMT used in the measurements was from 160 to 700 nm. Each decay time profile was approximated by an exponential decay function. The obtained decay time constants were 5.3 ms (0.01% Tb), 6.2 ms (0.05% Tb), 6.4 ms (0.1% Tb) and 6.1 ms (0.5% Tb). These were consistent with values for the 4 f-4 f transitions of Tb$^{3+}$ seen in other Tb-doped samples [16,22–26]. Thus, the origin of the components was the 4 f-4 f transitions of Tb$^{3+}$. The decay time constants for scintillation were found to be comparable to those in PL.

3.4. Dosimeter properties

Figure 8 shows TSL glow curves of the Tb-doped CaF$_2$ translucent ceramics. Prior to measurement, the Tb-doped samples were irradiated by X-ray (1 mGy). The Tb-doped samples showed a broad TSL glow peak at
approximately 90°C, and the overall glow curve features of the Tb-doped samples were similar to those of the undoped sample [20]. Among the samples investigated, the 0.1% Tb-doped sample exhibited the highest TSL intensity, whereas the PL and scintillation intensity of the 0.5% Tb-doped sample were the highest. This might be because the trapping centers responsible for TSL could not be generated effectively in the 0.5% Tb-doped sample. Furthermore, the glow peak temperature ($T_M$), peak top intensity ($I_M$), activation energy ($E$) and frequency factor ($s$) were derived by numerical approximations assuming first-order kinetics [27]:

$$I(T) = I_M \exp \left[ 1 + \frac{E}{kT} \left( \frac{T - T_M}{T_M} \right) - \frac{T^2}{2kT_M} \right] \exp \left( \frac{E}{kT} \left( \frac{T - T_M}{T_M} - \frac{2kT_M}{E} \right) \right)$$

where $k$ is the Boltzmann constant and $T$ is the absolute temperature. Moreover, the frequency factor ($s$) was obtained using the following formula: $s = \beta E/(k(T_M)^2)\exp(E/kT_M))$. In this measurement, the heating rate $\beta$ was 1°C/s. Table 1 summarizes the calculated results. The Tb-doped samples showed two glow peak temperatures at approximately 80 and 110°C. The frequency factors of the glow curves in the Tb-doped samples were estimated to be about $1.0 \times 10^{10}$, moreover, suggesting that the de-trapping process involved in TSL must be thermal ionization. In addition, the activation energy was about 0.8 eV regardless of the concentrations of Tb. The constant activation energy suggested that the origin of the trap sites responsible for TSL might be the CaF$_2$ host.

Figure 9 presents the TSL dose response curves of the Tb-doped CaF$_2$ translucent ceramics. Here, an integrated intensity of the observed glow peak at approximately 90°C in Figure 8 was defined as the TSL intensity. The Tb-doped samples exhibited a linear TSL response in the dose range from 0.001–1 mGy. The lowest detectable limit was found to be enhanced by Tb-doping compared with that of undoped CaF$_2$ translucent ceramics [20]. Furthermore, the TSL
sensitivities of the Tb-doped CaF$_2$ translucent ceramics were comparable to those of conventional TSL phosphors and the previously reported Dy-doped CaF$_2$ translucent ceramics [1]. Moreover, the dose linearity was calculated by coefficients of determination (R$^2$) obtained from a least-square fitting (y = ax + b). The obtained R$^2$ values were estimated to be 0.96 (0.01% Tb), 0.99 (0.05% Tb), 0.99 (0.1% Tb) and 0.99 (0.5% Tb). This linearity was essential, since it enabled us to measure the radiation dose accurately.

The OSL properties were also evaluated as dosimetric properties. Figure 10 shows the OSL decay curves of Tb-doped CaF$_2$ translucent ceramics under an excitation wavelength of 630 nm, monitored at 380 nm. Each decay curve was approximated by two exponential decay functions. The decay time constants of the faster component were 87 s (0.01% Tb), 85 s (0.05% Tb), 84 s (0.1% Tb) and 79 s (0.5% Tb), while the constants of the slower component were 900 s (0.01% Tb), 740 s (0.05% Tb), 760 s (0.1% Tb) and 810 s (0.5% Tb). The observed exponential signals suggested that the emissions should be attributed to OSL, and that at least two trapping centers for OSL should exist in the Tb-doped samples. Figure 11 shows OSL spectra of the Tb-doped translucent ceramics under 630 nm excitation light after X-ray irradiation at 10,000 mGy. All the Tb-doped samples exhibited several emission peaks at approximately 380, 415 and 440 nm. The spectral features were in good agreement with those in the PL spectra, and the emissions were therefore ascribed to the 4f-4f transitions of Tb$^{3+}$. The 0.1% Tb-doped sample showed the highest OSL intensity, and the result was consistent with the TSL result as shown in Figure 8. Figure 12 represents the OSL dose response curves of Tb-doped CaF$_2$ translucent ceramics. The excitation wavelength for the measurements was 630 nm, while the monitoring wavelength was 380 nm. Here, the top peak intensity at 380 nm was used as the OSL intensity. As shown in Figure 12, the OSL response of the Tb-doped samples showed linear characteristics over the X-ray dose range of 100–10,000 mGy. The lowest detection limit was found to be at most 100 mGy, which was higher than those of commonly used OSL phosphors such as C-doped Al$_2$O$_3$ [1]. However, the obtained detection limit could not be due mainly to the material properties but rather to technical limitations and might therefore be improved with more sensitive detectors and more powerful light sources.

4. Conclusions

The PL, scintillation and dosimetric properties of Tb-doped CaF$_2$ translucent ceramics were evaluated. The Tb-doped samples were synthesized by the SPS
method. The Tb-doped samples showed PL and scintillation originating from the 4 f-4 f transitions of Tb$^{3+}$ with a decay time constant of a few milliseconds. Furthermore, the Tb-doped samples exhibited efficient TSL responses with a dynamic range of 0.001–1 mGy. The lowest detection limit was almost equivalent to those of commonly used TSL phosphors. In addition, they showed OSL signals due to the 4 f-4 f transitions of Tb$^{3+}$ under an excitation wavelength of 630 nm, and their lowest measurable limit was found to be at most 100 mGy. The results showed that the Tb-doped CaF$_2$ translucent ceramics can be applied for use with the radiation dosimetric method.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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![Figure 11. OSL spectra of the Tb-doped CaF$_2$ translucent ceramics.](image1)

![Figure 12. OSL dose response curves of the Tb-doped CaF$_2$ translucent ceramics.](image2)
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