

## Optical and Optically Stimulated Luminescence Properties of Ce-doped CsCl–CaCl<sub>2</sub>–ZnCl<sub>2</sub> Glasses

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The optical and optically stimulated luminescence (OSL) properties of Ce-doped 20CsCl–20CaCl<sub>2</sub>–60ZnCl<sub>2</sub> (CCZ) glasses were evaluated. All the Ce-doped CCZ glasses showed a broad emission peak at 370 nm upon excitation at 320 nm, and the decay time suggested that the origin was the 5d–4f transitions of Ce<sup>3+</sup>. After X-ray irradiation, the Ce-doped CCZ glasses showed OSL around 370 nm under stimulation at 400 nm. All the glasses exhibited dose response functions with good linearity in the dynamic range of 0.1–10 Gy.

### 1. Introduction

Dosimeters using storage phosphors temporarily store the energy of ionizing radiation in the form of trapped carriers, and the stored information can be read out as luminescence by external stimulation. The obtained luminescence stimulated by thermal and optical stimulation is called thermally stimulated luminescence (TSL) and optically stimulated luminescence (OSL),<sup>(1,2)</sup> respectively. Radio-photoluminescence, in which the photoluminescence (PL) intensity increases with the radiation dose, has also been used for dosimetry. Such dosimeters have been used for various radiation measurements such as personal dose monitoring and also for imaging plates (IPs).<sup>(3)</sup> In general, the characteristics required for dosimeter materials include high emission intensity, low fading, and proportionality between emission intensity and irradiation dose. In addition, while personal dose monitoring applications require an effective atomic number ( $Z_{eff}$ ) close to that of the human body in terms of bioequivalence ( $Z_{eff} = 7.29$ ), based on the composition of C<sub>5</sub>H<sub>40</sub>O<sub>18</sub>N,<sup>(4)</sup> IP applications such as dental diagnostics require a large  $Z_{eff}$  for high detection efficiency. Various material forms such as single crystals,<sup>(5–7)</sup> ceramics,<sup>(8–13)</sup> and glasses<sup>(14,15)</sup> have been investigated for dosimeter applications, and glasses have industrial advantages such as a low production cost and high moldability in comparison with single crystals and ceramics.<sup>(16)</sup> However, only Ag-doped phosphate glasses have been commercially applied in practical use,<sup>(17,18)</sup> and there have been only a few reports on the TSL and OSL properties of glasses with

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a large  $Z_{eff}$ . Therefore, there is still plenty of room for studying heavy glasses for dosimetric applications.

In recent years, we focused on  $ZnCl_2$ -based glasses because of their large  $Z_{eff}$  in comparison with oxide glasses such as  $SiO_2$ -,  $P_2O_5$ -, and  $B_2O_3$ -based glasses. In addition, halide-based glasses have low phonon energy in comparison with oxide glasses.<sup>(19,20)</sup> The low phonon energy of the host glass leads to a low thermal relaxation rate because more phonons are excited at the same time; therefore, various halide glassy phosphors have been evaluated owing to their high luminescence efficiency.<sup>(21–31)</sup> In our previous studies, we investigated Eu- or Ce-doped  $20CsCl-20BaCl_2-60ZnCl_2$  (CBZ) glasses and clarified that Ce-doped samples showed high PL quantum yields ( $QY$ s) of 75.7%.<sup>(32,33)</sup> However, most previous studies on the dosimetric properties of glasses have examined the TSL and OSL properties of oxide glasses,<sup>(34–38)</sup> and there have been no studies evaluating the OSL characteristics of  $ZnCl_2$ -based glasses. In this study, we evaluated the OSL properties of Ce-doped  $20CsCl-20CaCl_2-60ZnCl_2$  (CCZ) glasses for the first time, and the effects of doping on optical and OSL characteristics were also investigated.

## 2. Materials and Methods

$xCeCl_3-20CsCl-20CaCl_2-60ZnCl_2$  ( $x = 0.01, 0.05,$  and  $0.1\%$ ) glasses (molar ratio) were prepared by the melt-quenching method. First,  $CsCl$  (99.99%, Mitsuwa Chemicals),  $CaCl_2$  (99.9%, High Purity Chemicals),  $ZnCl_2$  (99.99%, Wako Chemicals), and  $CeCl_3 \cdot 6H_2O$  (99.99%, High Purity Chemicals) were mixed and then placed in quartz ampules, with a total powder weight of 4 g for each sample. Then, the powders were dried under vacuum at  $200\text{ }^\circ\text{C}$  for 1 h, and the dried powders were enclosed in an ampule under vacuum. Following the drying process, the powders were heated for 1 h at  $700\text{ }^\circ\text{C}$  using an electric furnace, and the sealed ampule was placed in water at room temperature to rapidly cool the melt. After that, the thickness of the obtained glasses was standardized to 1 mm by polishing the top and bottom surfaces using a variety of sandpapers (600–3000 grit).

The diffuse transmission spectra of the Ce-doped CCZ glasses were measured using a spectrophotometer (SolidSpec-3700, Shimadzu). The PL  $QY$  and excitation/emission maps were measured using a Quantaaurus-QY spectrometer (C11347, Hamamatsu Photonics). PL decay curves were obtained using a Quantaaurus- $\tau$  spectrometer (C11367 Hamamatsu Photonics). OSL emission and stimulation spectra of the Ce-doped CCZ glasses were obtained using a spectrofluorometer (FP-8600, JASCO) after X-ray irradiation (1 Gy). To obtain the OSL dose response functions, OSL spectra were measured using the spectrofluorometer after X-ray irradiation with various doses during stimulation at 400 nm. Only the OSL properties were measured using the sample in a sealed ampule, while the other properties were evaluated using the polished samples. Because of the low chemical stability of the glass samples, each measurement except for OSL was performed within 10 min after taking them from a desiccator with silica gel.

### 3. Results and Discussion

Figure 1 is a photograph of the as-prepared Ce-doped CCZ glasses in a quartz ampule. All glasses synthesized in the quartz ampule were colorless and transparent. These quartz ampules were crushed to obtain the samples, and some pieces of the samples were used in the following characterizations after polishing. Figure 2 shows the diffuse transmission spectra of the Ce-doped CCZ glasses. The diffuse transmittance of all the prepared glasses was 50–60% in the wavelength range of 350–850 nm. A broad absorption band around 300–350 nm was observed, and the absorption became strong with increasing concentration of Ce. Since the Ce-doped glasses showed similar absorption bands at around 300–350 nm in a previous study,<sup>(39)</sup> the origin of the bands was concluded to be the 4f–5d transitions of  $\text{Ce}^{3+}$ .

Figure 3 presents the PL excitation/emission contour plots of the Ce-doped CCZ glasses. All the Ce-doped CCZ glasses showed a broad emission band around 370 nm with an excitation band around 320 nm. With increasing Ce concentration, the peak positions shifted to a longer wavelength, which is considered to be associated with self-absorption due to  $\text{Ce}^{3+}$ . Since the excitation and emission shapes were similar to those of Ce-doped glasses in previous reports,<sup>(40,41)</sup> the origin of the emission was ascribed to the 5d–4f transitions of  $\text{Ce}^{3+}$ . The PL QYs of the 0.01, 0.05, and 0.1% Ce-doped CCZ glasses upon excitation at 320 nm were 75.6, 87.6, and 81.5%, respectively. The PL QYs of the Ce-doped CCZ glasses were higher than that of a Ce-doped CBZ glass (~76%)<sup>(32)</sup> and comparable to that of a commercial GS20 Li-glass scintillator (~80%).<sup>(42)</sup> Figure 4 shows the PL decay curves of the Ce-doped glasses monitored at 380 nm under excitation with a wavelength of 340 nm. The decay curves of all the Ce-doped glasses were well approximated by a single exponential decay function. The decay time constants of the

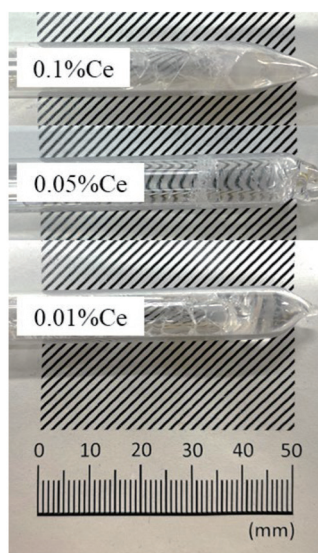


Fig. 1. (Color online) Synthesized CCZ glasses doped with various concentrations of Ce.

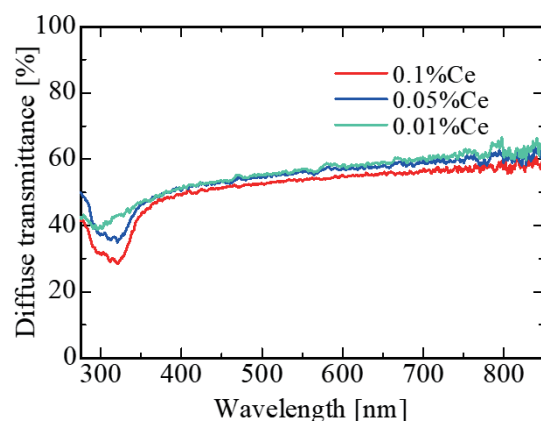


Fig. 2. (Color online) Diffuse transmittance spectra of Ce-doped CCZ glasses.

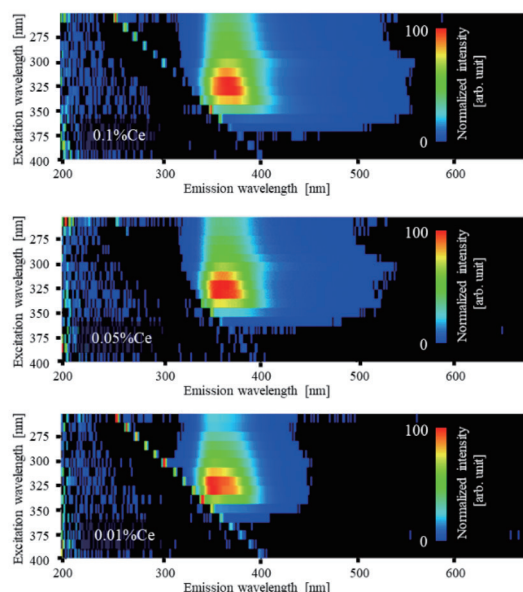


Fig. 3. (Color online) PL excitation/emission contour spectra of Ce-doped CCZ glasses. Top to bottom: 0.1, 0.05, and 0.01% Ce-doped samples.

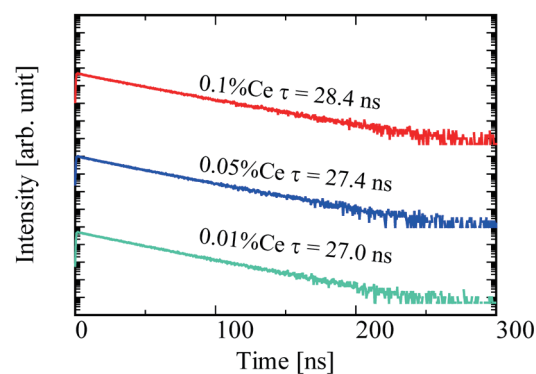


Fig. 4. (Color online) PL decay curves of Ce-doped CCZ glasses monitored at 380 nm under excitation at wavelength of 340 nm.

CCZ glasses were 27.0–28.4 ns, which are also typical of 5d–4f transitions of  $\text{Ce}^{3+}$ .<sup>(15,43)</sup> The decay time increased with increasing Ce concentration, and the concentration dependence was not consistent with that of PL *QY*. Such phenomena were also observed in Ce-doped CBZ glasses,<sup>(32)</sup> and the reason for them is still unclear. One possible reason is that as the concentration increased, energy transfer between the emission centers occurred without nonradiative quenching, resulting in a delay of the decay.

Figure 5 illustrates the OSL spectra of Ce-doped CCZ glasses after X-ray irradiation of 10 Gy. After the X-ray irradiation, all the samples showed OSL emission peaks at 370 nm under a stimulation wavelength of 400 nm. Since the spectral shapes matched those of the PL spectra, the emission was caused by the 5d–4f transitions of  $\text{Ce}^{3+}$ . Among the prepared samples, the OSL intensity of the 0.05% Ce-doped CCZ was the highest. This observation is the first report of OSL from  $\text{ZnCl}_2$ -based glasses. Figure 6 shows the OSL dose response functions of the Ce-doped CCZ glasses. All the glasses exhibited dose response functions with a good linear relationship in the range of 0.1–10 Gy. The detection limit of the Ce-doped CCZ glasses was worse than that of commercial dosimetric materials. In commercial OSL dosimeters and IPs, the read-out device has been optimized to enable the use of photodetectors as well as lasers for the stimulation light. Therefore, the detection limit of Ce-doped CCZ glasses may be improved by also optimizing the read-out device. The lowest detection limit of the glasses was lower than that of a practical glass badge of Chiyoda Ltd. (0.1 mGy).

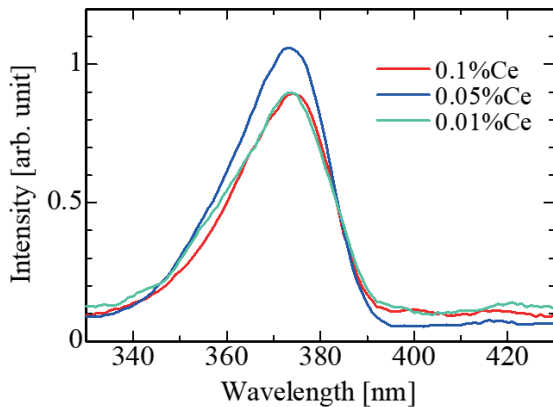


Fig. 5. (Color online) OSL spectra of Ce-doped CCZ glasses after X-ray irradiation of 10 Gy.

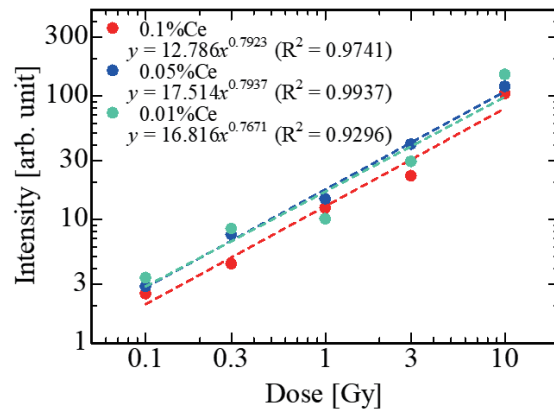


Fig. 6. (Color online) OSL dose response functions of Ce-doped CCZ glasses.

#### 4. Conclusions

CCZ glasses doped with various Ce concentrations were synthesized, and the optical and OSL characteristics were evaluated. The Ce-doped CCZ glasses showed a broad emission band around 370 nm with an excitation band around 320 nm that originated from the 5d–4f transitions of  $\text{Ce}^{3+}$ . After 10 Gy X-ray irradiation, OSL peaks due to the 5d–4f transition of  $\text{Ce}^{3+}$  were observed when the glasses were stimulated by light exposure at 400 nm. The dose responses showed good linearity in the dynamic range of 0.1–10 Gy. Although OSL has so far only been reported for oxide glasses, here, OSL was observed for the first time in chloride glasses. The dynamic range obtained in this study is insufficient for practical use, but we will improve the dynamic range by optimizing the composition of the material and the measurement conditions in the future.

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