Scintillation and Dosimetric Properties
of Ce:CsCl Transparent Ceramics

Hiromi Kimura,* Fumiya Nakamura, Takumi Kato, Daisuke Nakauchi,
Go Okada, Noriaki Kawaguchi, and Takayuki Yanagida

Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma-shi, Nara 630-0192, Japan

Ce:CsCl transparent ceramics doped with different concentrations of Ce (0.01, 0.1, and 1 mol.%) were synthesized by spark plasma sintering, and their optical, scintillation and dosimetric properties were investigated. Regarding the scintillation properties, X-ray-induced scintillation spectra of the samples consisted of three emission peaks at around 280, 380, and 400 nm, which were due to the Auger-free luminescence and 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+}, respectively. In addition, the samples showed thermally stimulated luminescence (TSL) and optically stimulated luminescence (OSL) with emission peaks centering at around 400 and 480 nm, in which the origins were attributed to the 5d–4f transitions of Ce^{3+} and the host, respectively. In particular, the TSL was sensitive to X-rays, and the TSL signals as low as 0.1 mGy were measurable, while a linear response was confirmed up to 100 mGy.

1. Introduction

Phosphor materials are often used in radiation detectors, and such phosphors are classified into two types: scintillator and storage phosphors. Scintillators can immediately convert energy of the absorbed ionizing radiation into a large number of low-energy photons, and they have been widely used in fields requiring radiation detection, such as medicine,[1] security,[2] environmental monitoring,[3] and high-energy physics.[4] In general, the required properties of scintillators include high light yield, short decay time, and low afterglow. In contrast, storage phosphors store the absorbed energy of ionizing radiation. The energy is stored in the form of carriers trapped at localized centers. The trapped electrons and holes can be released by heat or light stimulation to emit photons. The resultant luminescence is called thermally stimulated luminescence (TSL) and optically stimulated luminescence (OSL), respectively. The luminescence intensity is proportional to the radiation dose; therefore, such storage phosphors are utilized in dosimetry applications. For this reason, they are often referred to as dosimeters. The materials showing TSL and OSL have been mainly used in individual radiation monitoring[5–7] and imaging plates (IPs).[8,9]

The recent trend of development of scintillators is based on a combination of inorganic materials as the host and rare-earth ions as emission centers, e.g., $Ce:Tb_3Al_5O_{12}$[10] and $Ce:Gd_2SiO_5$.[11] The host has the role of absorbing ionizing radiation effectively, while the emission center emits photons. Among such rare-earth ions, Ce^{3+} is often used in scintillators because of the fast emission due to the 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+}. Some Ce-doped chlorides are known to show high light yields, such as $Ce:LaCl_3$ (61000 ph/MeV)[12] and $Ce:Cs_2LiYCl_6$ (70000 ph/MeV).[13] CsCl is one of the chlorides, and it is potentially applicable to radiation detectors. CsCl has a high effective atomic number (Z_{eff} = 51.9) close to those of conventional scintillators such as CsI (Z_{eff} = 54.1) and NaI (Z_{eff} = 50.8), so CsCl can be applied in X- and gamma-ray detectors as the dosimeter material of scintillator and IPs. Ce:CsCl is known to show emission peaks at around 250, 360, and 380 nm, which are due to Auger-free luminescence (AFL) and 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+},[14] respectively. The decay time constants of the AFL at 8 K and the 5d–4f transitions of Ce^{3+} at room temperature are known to be ~2 and ~20 ns,[14,15] respectively. Up to now, some scintillation properties of Ce:CsCl have been reported in the literature; however, most studies were carried out on bulk single crystals, and no reports can be found for transparent ceramics.

Conventionally, most scintillator and dosimeter materials have been used mainly in the form of bulk single crystals because of their high optical qualities, even though single crystals have some industrial disadvantages such as low mechanical strength, high cost, and difficulty of upsizing. As an alternative, the use of transparent ceramics has recently attracted attention in the field of ionizing radiation detectors in order to overcome the above disadvantages. In addition, some transparent ceramics such as $Ce:Gd_3(Al, Ga)_5O_{12}$[16] and $Ce:Y_3Al_5O_{12}$[17] are known to show higher scintillation light yields than the single crystals.

In this study, we developed Ce:CsCl in the form of a transparent ceramic by spark plasma sintering (SPS) and then evaluated its optical, scintillation, and dosimeter properties. In recent years, it has been clarified that the scintillation and dosimetric properties of some materials are complementarily related.[18] Therefore, evaluations of both scintillation and dosimetric properties are important in order to comprehensively understand the luminescence phenomena induced by ionizing radiations.

2.   Experiment

Ce:CsCl transparent ceramics doped with different concentrations of Ce (0.01, 0.1, and 1 mol.%) were synthesized by SPS using Sinter Land LabX-100 in vacuum. Raw powders of CsCl (>99.999%, Mitsuwa Chemical) and $CeCl_3 \cdot xH_2O$ (>99.9%, Kojundo Chemical Laboratory) were homogeneously mixed using a mortar and pestle. Then, the mixture (total mass: 0.5 g) was loaded in a cylindrical graphite die (inner diameter: 10.4 mm), in which the mixture was held between two graphite punches inserted in the cylinder. SPS was performed by applying uniaxial pressure along the axis of graphite punches while applying a high-current DC pulse. The sintering temperature was increased from 20 to 580 °C at a rate of 56 °C/min and then held for 20 min while applying a pressure of 25 MPa. The wide surfaces of the obtained ceramic samples were mechanically polished by hand using sandpaper (2000 grits).

To investigate the optical properties, the in-line transmittance spectra were measured using a spectrophotometer (V670, JASCO) across the spectral range from 200 to 2700 nm with 1 nm intervals. The photoluminescence (PL) quantum yields and PL excitation/emission spectra were obtained using Quantaurus-QY (C11347, Hamamatsu Photonics). The PL decay curves were evaluated using Quantaurus-τ (C11367, Hamamatsu Photonics).

As a scintillation property, X-ray-induced scintillation spectra were measured using our original setup.[16] As the radiation source, an X-ray generator (XRB80P&N200X4550, Spellman) equipped with a conventional X-ray tube was used. The X-ray tube had a W anode target and was operated with a tube voltage and current of 40 kV and 1.2 mA, respectively. During irradiation, the scintillation photons were guided into a spectrometer (Andor DU-420-BU2 CCD and Shamrock 163 monochromator) through an optical fiber. X-ray-induced scintillation decay curves and afterglow profiles were evaluated using an afterglow characterization system equipped with a pulse X-ray tube. The details of the setup are described elsewhere.[19]

As dosimetric properties, TSL and OSL were characterized. TSL glow curves were measured using a TSL reader (TL-2000, Nanogray Inc.)[20] after irradiation with X-rays (100 mGy). Here, the heating rate was 1 °C/s, and the measurement temperature range was from 50 to 350 °C. Just before the measurement, the sample was kept at 50 °C for 5 min. Moreover, to obtain a dose response function, a series of TSL glow curves were measured with varying irradiation doses from 0.1 to 100 mGy. To obtain TSL spectra, the samples after X-ray irradiation (~10 Gy) were heated on a ceramic heater system (SCR-SHQ-A, Sakaguchi) increasing the temperature at a rate of 1 °C/s, and then the emission spectrum at 90 °C was recorded using a spectrometer (QEPro, Ocean Optics). OSL spectra were measured using Quantaurus-τ (C11367, Hamamatsu Photonics) after irradiating the samples with X-rays of 10 Gy. The stimulation wavelength was 630 nm.

3. Results and Discussion

3.1 Sample

Figure 1 shows photographs of the CsCl transparent ceramic samples doped with different concentrations of Ce (0.01, 0.1, and 1%) under (a) room light and (b) UV light (302 nm). Under UV irradiation, we observed a strong blue emission in all the samples. In addition, it was
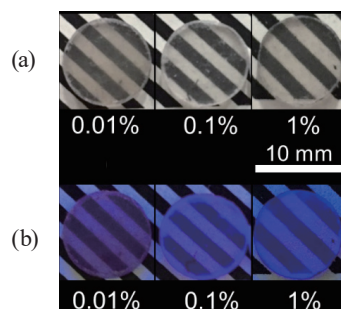

Fig. 1. (Color online) Synthesized Ce:CsCl transparent ceramics under (a) room light and (b) UV light (302 nm).

confirmed that transparency was such that the stripe patterns under the samples could be seen. The thickness of all the samples was fixed at approximately 1.3 mm. In-line transmittance spectra are illustrated in Fig. 2. The transmittance of the sample increased with increasing Ce concentration. A possible reason may be that the $CeCl_3 \cdot xH_2O$ was activated as a sintering acid and the densification was improved. The absorption due to 4f–5d transitions of Ce^{3+} was confirmed at around 340 nm.

3.2 PL properties

Figure 3 shows a PL excitation/emission contour graph of the Ce(0.1%):CsCl transparent ceramic sample as a representative example. The emission seems to consist of two broad band peaks at around 380 and 410 nm under an excitation of around 340 nm. The origins of these are attributed to the 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+}, respectively. In a previous study, two emission bands at 360 and 380 nm due to the 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+} were reported.[14] Our result is not highly consistent with that in the previous study. Typically, the difference in the energy levels between $^2F_{5/2}$ and $^2F_{7/2}$ is ~2000 cm^{-1}. In fact, our result matched this typical energy difference. The peak position shifted to a longer wavelength than that reported previously,[14] as a result of the self-absorption of Ce^{3+}. In the previous report, the sample was synthesized by the Czochralski method, and the Ce concentration was expected to be low. Furthermore, the optimum excitation wavelength agreed well with the absorption band observed in Fig. 2. The PL quantum yields of the samples with 0.01, 0.1, and 1% Ce were 10.7, 44.6, and 50.0%, respectively. The low PL QY of the Ce 0.01% sample was attributed to the small number of emission centers, and even in the 1% Ce-doped sample, concentration quenching did not occur.

PL decay profiles are presented in Fig. 4. Here, the excitation wavelength was 340 nm while the monitored emission wavelength was 400 nm. All the decay curves of the samples were well-approximated by a single exponential decay function. The decay time constants of
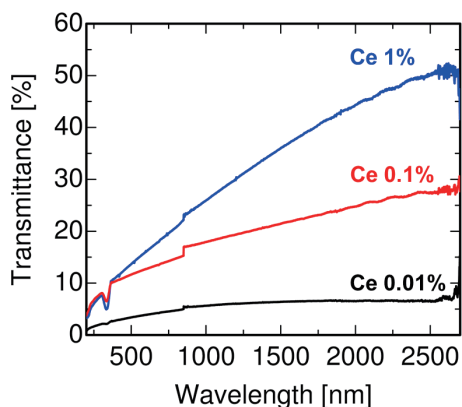

Fig. 2. (Color online) In-line transmittance spectra of Ce:CsCl transparent ceramics.
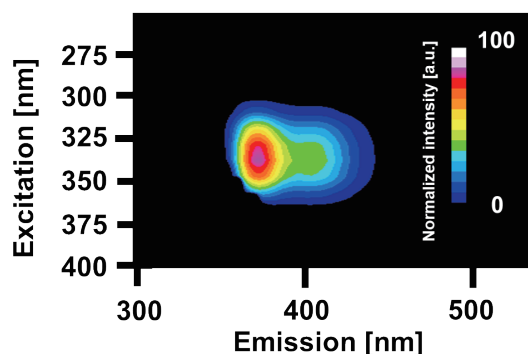

Fig. 3. (Color online) PL excitation/emission contour graph of 0.1% Ce-doped CsCl transparent ceramics. The vertical and horizontal axes represent excitation and emission wavelengths, respectively.
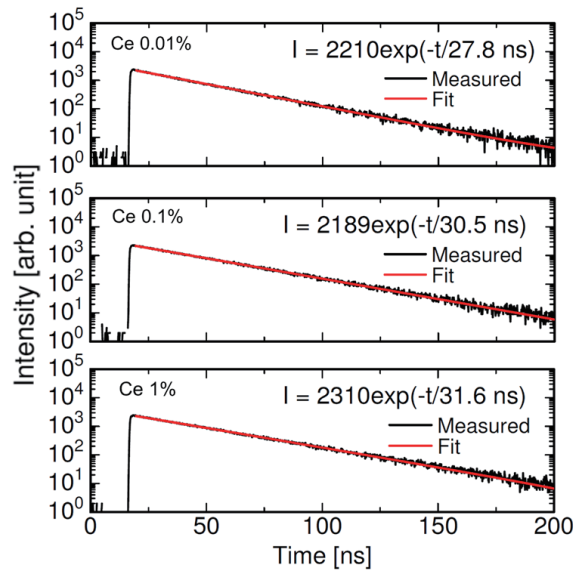
Fig. 4.   (Color online) PL decay profiles of Ce:CsCl transparent ceramics. The monitoring wavelength was 400 nm while the excitation wavelength was 340 nm.

the Ce:CsCl samples doped with 0.01, 0.1, and 1% Ce were 27.8, 30.5, and 31.6 ns, respectively. Those decay constants were of a typical order for the 5d–4f transitions of Ce^{3+}.[14] The decay time decreased as the Ce concentration increased.

3.3   Scintillation properties

Figure 5 shows X-ray-induced scintillation spectra of the Ce:CsCl samples. It was suggested that the emission consists of three bands centered at around 280, 380, and 410 nm. The origins of these emissions were attributed to the AFL and 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+}, respectively, according to the previous studies of single crystals.[14] The spectral features of Ce^{3+} were consistent with PL. Among the present samples, Ce(0.1%):CsCl showed the highest intensity. The emission wavelength is favorable for a typical photomultiplier tube. The emission intensity of the X-ray-induced scintillation spectrum is qualitative since the radiation stopping power cannot be accurately corrected; however, compared with Tl- and In-doped CsCl,[21] the emission intensity of our samples was weaker. In addition, a companion with the past result of Ce:CsCl[12] was not possible because the light yield under 45 MeV proton beam excitation, which is unavailable to us, was evaluated previously.

X-ray-induced scintillation decay time profiles of the Ce:CsCl samples are presented in Fig. 6. Each scintillation decay curve was well approximated by the sum of two exponential decay functions. The faster decay components of the samples with 0.01, 0.1, and 1% Ce were 1.6, 1.8, and 1.8 ns, respectively, and these faster decay components were attributed to the mixture of the AFL and instrumental response. The slower decay time components of the samples with 0.01, 0.1, and 1% Ce were 29.3, 32.2, and 32.3 ns, respectively. These values were of a typical order for 5d–4f transitions of Ce^{3+}. The decay time increased with the Ce concentration.
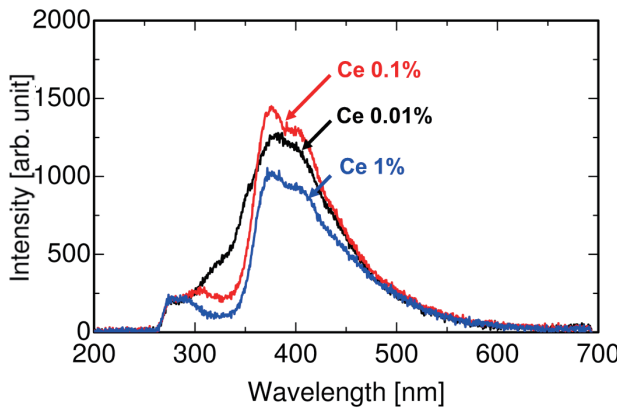
Fig. 5. (Color online) X-ray-induced scintillation spectra of Ce:CsCl transparent ceramics.
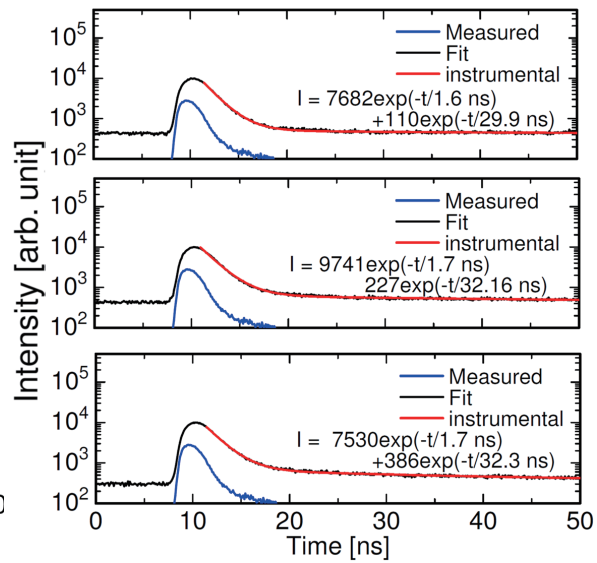
Fig. 6. (Color online) Scintillation decay profiles of Ce:CsCl transparent ceramics.

The afterglow curves of the Ce:CsCl samples are shown in Fig. 7. The afterglow level (A) is defined as A (%) = $100 \times (I_2 - I_{BG})/(I_1 - I_{BG})$, where I_1 is the signal intensity during X-ray irradiation, I_2 is that at 2 ms after the termination of irradiation, and I_{BG} is the background. The derived afterglow levels of the samples with 0.01, 0.1, and 1% Ce were 3.45, 4.43, and 1.14%, respectively. The afterglow levels of the current samples were higher than those of common scintillators such as Tl:CsI crystal.[22]

3.4   Dosimetric properties

Figure 8 shows the TSL glow curves of Ce:CsCl transparent ceramic samples measured after X-ray irradiation (~100 mGy). All the samples showed a major glow peak at around 100 °C. The origin of the glow peak is unknown, and we found no literature on the origin of the glow peak of Ce:CsCl. In previous works, more complicated features at a similar peak temperature were observed in Ni-doped and Eu-doped CsCl.[23,24] Therefore, the observed glow peak is possibly related to the CsCl host since these materials have only the CsCl host in common. TSL dose response functions of the samples are shown in the inset of Fig. 8. The TSL intensity represents the integrated signals between 50 and 190 °C of the measured glow curve. The samples showed good linearity from 0.1 to 100 mGy. The detection limit of 0.1 mGy was comparable to those of some commercial dosimeters.

The TSL spectra of Ce:CsCl transparent ceramic samples are presented in Fig. 9. The samples were irradiated with X-rays (~10 Gy) before the measurement, and the spectra were measured at 90 °C. Each TSL spectrum consists of two emission band peaks at around 400 and 480 nm. A previous study demonstrated that the TSL emission of nondoped CsCl appeared from 400 to 470 nm. Therefore, we consider that the origin of the TSL emission is both the CsCl host and 5d–4f transitions of Ce^{3+}.[25]
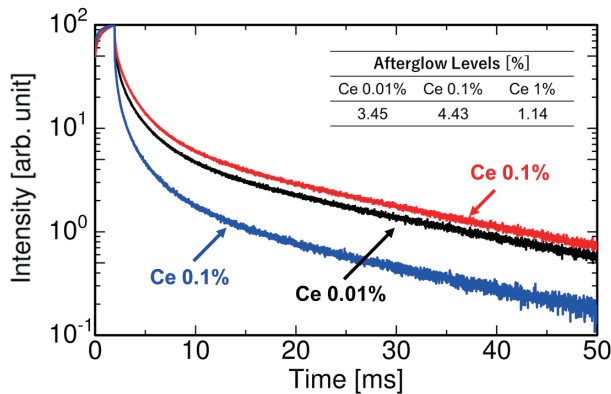
Fig. 7.   (Color online) Afterglow profiles of Ce:CsCl transparent ceramics. The inset shows the afterglow level of all the samples.
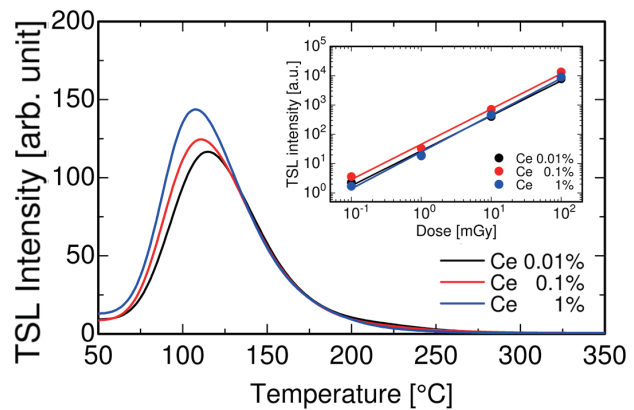
Fig. 8.   (Color online) TSL glow curves of Ce:CsCl transparent ceramic samples measured after 100 mGy X-ray irradiation. The inset shows the TSL dose response curves of the samples from 0.1 to 100 mGy.
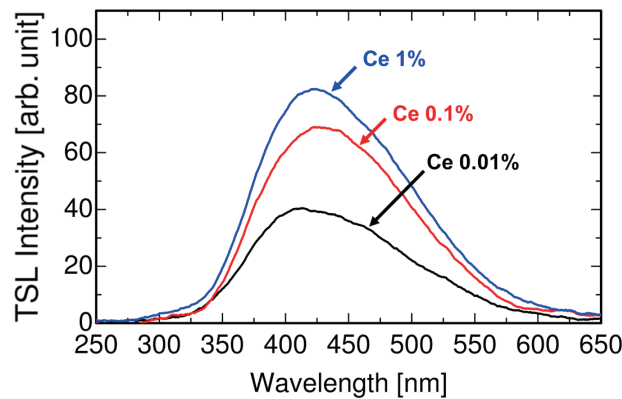

Fig. 9.   (Color online) TSL spectra of Ce:CsCl transparent ceramic samples measured at 90 °C after X-ray irradiation (~10 Gy).

Figure 10 shows OSL spectra of Ce:CsCl transparent ceramic samples. The samples were irradiated with X-rays (~10 Gy) before the measurements. The optical stimulation wavelength was 630 nm. The OSL spectral features of the samples were in approximate agreement with those of PL. Therefore, the origins of OSL spectra would be the 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+}.

OSL decay profiles of Ce:CsCl transparent ceramic samples are shown in Fig. 11. Before the measurements, the samples were irradiated with X-rays (~10 Gy). The monitoring wavelength was 400 nm while the stimulation wavelength was 630 nm. The OSL intensity exponentially decreased with time during the stimulation, which was a typical feature of OSL (if the observed signal is due to up-conversion, the signal intensity must not decrease with time). Each decay curve was best approximated by a sum of four exponential decay functions. This finding suggests that at least four different detrapping processes were involved. To the best of our knowledge, this is the first report of OSL in Ce:CsCl.
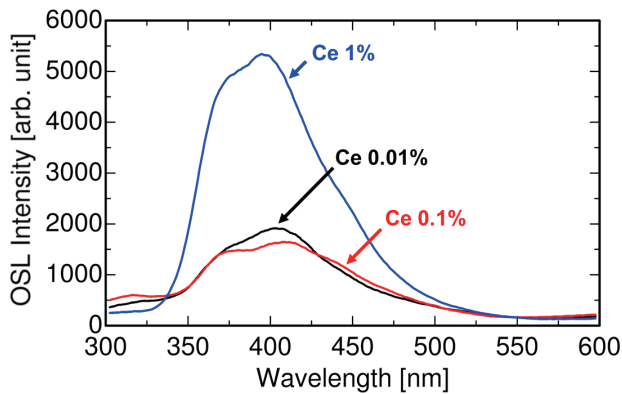
Fig. 10. (Color online) OSL spectra of Ce:CsCl transparent ceramic samples measured under 630 nm stimulation after X-ray irradiation (~10 Gy).
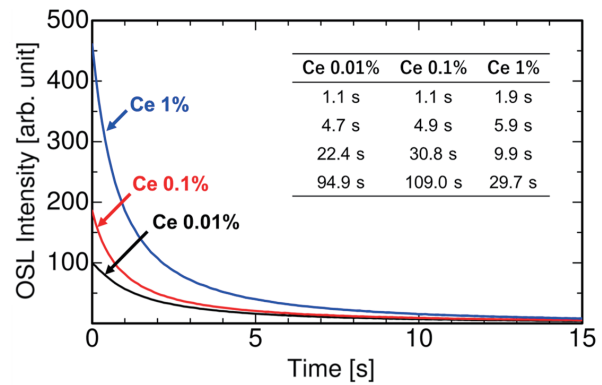

Fig. 11. (Color online) OSL decay profiles of Ce:CsCl transparent ceramic samples after X-ray irradiation (~10 Gy). The inset shows the OSL decay time constants of all the samples.

4. Conclusions

We synthesized Ce:CsCl transparent ceramics doped with different concentrations of Ce (0.01, 0.1, and 1%) by SPS and then investigated their optical, scintillation, and dosimeter properties. The PL spectra of all the samples showed two broad emission band peaks at around 380 and 410 nm under excitation of around 340 nm. The decay time constants of the samples doped with 0.01, 0.1, and 1% Ce were 27.7, 30.5, and 31.6 ns, respectively, which were of a typical order for the 5d–4f transitions of Ce^{3+}. The X-ray-induced scintillation spectra of all the samples contained three emission band peaks at around 280, 380, and 410 nm. The emission at around 280 nm was due to AFL, whereas the emission peaks at around 380 and 410 nm were attributed to the 5d→4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+}, respectively, as in PL. Concerning the dosimetric properties, the samples showed TSL and OSL. The main emission of both types of luminescence was observed at around 400 nm owing to the 5d→4f transitions of Ce^3. In particular, the TSL was very sensitive to the X-ray dose, and the TSL signal was measurable at as low as 0.1 mGy.

Acknowledgments

References

1   C. W. E. Van Eijk: Nucl. Instrum. Methods Phys. Res., Sect. A **509** (2003) 17.
2   J. M. Hall, S. Asztalos, P. Biltoft, J. Church, M. A. Descalle, T. Luu, D. Manatt, G. Mauger, E. Norman, D. Petersen, J. Pruet, S. Prussin, and D. Slaughter: Nucl. Instrum. Methods Phys. Res., Sect. B **261** (2007) 337.
3   K. Watanabe, T. Yanagida, and K. Fukuda: Sens. Mater. **27** (2015) 269.
4   T. Itoh, M. Kokubun, T. Takashima, T. Honda, K. Makishima, T. Tanaka, T. Yanagida, S. Hirakuri, R. Miyawaki, H. Takahashi, K. Nakazawa, and T. Takahashi: IEEE Trans. Nucl. Sci. **53** (2006) 2983.
5   R. W. Christy, N. M. Johnson, and R. R. Wilbarg: J. Appl. Phys. **38** (1967) 2099.
6   Y. Hirata, K. Watanabe, S. Yoshihashi, A. Uritani, Y. Koba, N. Matsufuji, T. Yanagida, T. Toshito, and K. Fukuda: Sens. Mater. **29** (2017) 1455.
7   G. Okada, T. Kato, D. Nakauchi, K. Fukuda, and T. Yanagida: Sens. Mater. **28** (2016) 897.
8   H. Nanto, A. Nishimura, M. Kuroda, Y. Takei, Y. Nakano, T. Shoji, T. Yanagita, and S. Kasai: Nucl. Instrum. Methods Phys. Res., Sect. A **580** (2007) 278.
9   N. M. Winch, A. Edgar, and C. M. Bartle: Nucl. Instrum. Methods Phys. Res., Sect. A **763** (2014) 394.
10 D. Nakauchi, G. Okada, N. Kawano, N. Kawaguchi, and T. Yanagida: Appl. Phys. Express **10** (2017) 72601.
11 K. Takagi and T. Fukazawa: Appl. Phys. Lett. **42** (1983) 43.
12 E. V. D. Van Loef, P. Dorenbos, C. W. E. Van Eijk, K. Krämer, and H. U. Güdel: Appl. Phys. Lett. **79** (2001) 1573.
13 A. Bessiere, P. Dorenbos, C. W. E. Van Eijk, K. W. Krämer, and H. U. Güdel: Nucl. Instrum. Methods Phys. Res., Sect. A **537** (2005) 242.
14 J. Kim, S. Ra, W. Kim, H. J. Kim, H. Park, S. H. Lee, H. Kang, S. Kim, D. Kim, and S. Doh: J. Korean Phys. Soc. **50** (2007) 1514.
15 D. K. Ingole, C. P. Joshi, S. V. Moharil, P. L. Muthal, and S. M. Dhopte: J. Lumin. **130** (2010) 1194.
16 T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi, and T. Yanagitani: Opt. Mater. **35** (2013) 2480.
17 T. Yanagida, H. Takahashi, T. Ito, D. Kasama, T. Enoto, M. Sato, S. Hirakuri, M. Kokubun, K. Makishima, T. Yanagitani, H. Yagi, T. Shigeta, and T. Ito: IEEE Trans. Nucl. Sci. **52** (2005) 1836.
18 T. Yanagida: J. Lumin. **169** (2016) 544.
19 T. Yanagida, Y. Fujimoto, T. Ito, K. Uchiyama, and K. Mori: Appl. Phys. Express **7** (2014) 62401.
20 T. Yanagida, Y. Fujimoto, N. Kawaguchi, and S. Yanagida: J. Ceram. Soc. Jpn. **121** (2013) 988.
21 T. Sakai, M. Koshimizu, Y. Fujimoto, D. Nakauchi, T. Yanagida, and K. Asai: Jpn. J. Appl. Phys. **56** (2017) 62601.
22 S. C. Thacker, B. Singh, V. Gaysinskiy, E. E. Ovechkina, S. R. Miller, C. Brecher, and V. V. Nagarkar: Nucl. Instrum. Methods Phys. Res., Sect. A **604** (2009) 89.
23 P. C. Selvan and S. Selvasekarapandian: Mater. Chem. Phys. **37** (1994) 94.
24 J. K. Radhakrishnan and S. Selvasekarapandian: Phys. Status Solidi **141** (1994) 457.
25 J. K. Radhakrishnan and S. Selvasekarapandian: Phys. Status Solidi **136** (1993) 229.