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Properties of optically and thermally stimulated luminescence of novel storage phosphor materials: Doped and undoped CsCaCl₃ ceramics

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We report the properties of CsCaCl₃, storage phosphors doped with Eu, Ce, or Cu. Both doped and undoped CsCaCl₃ samples were synthesized as ceramics. For undoped CsCaCl₃, thermally stimulated luminescence (TSL) spectrum showed a broad band around 360–390 nm, and optically stimulated luminescence (OSL) spectrum exhibited the same band with a shoulder near 320 nm. These bands were attributed to different kinds of defects or impurities. The OSL and TSL spectra of Eu-doped CsCaCl₃ showed a band around 440 nm arising from the 5d–4f transition of Eu²⁺. The Ce-doped CsCaCl₃ showed the OSL and TSL bands originating from the 5d–4f transition of Ce³⁺. An intense band at 345 nm appeared in the OSL spectrum of Cu-doped CsCaCl₃ due to Cu⁺, and an additional peak at 430 nm was ascribed to Cu⁺ ion perturbed by OH[−] ion. On the other hand, the TSL spectrum of Cu-doped CsCaCl₃ had a peak around 470 nm and it was assigned to Cu²⁺. The TSL glow curves of the undoped, Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ were different from each other. This suggested that the dopant ions influenced the trapping process of electron–hole pairs, which were formed upon irradiation.

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1. Introduction

In general, dosimetric and radiographic techniques have been developed based on thermally or optically stimulated luminescence (TSL or OSL) in storage phosphors. Upon X-ray irradiation, complementary defects, which are electron or hole trap centers, are generated in storage phosphors.¹⁾ The electron at the trap center can be thermally or optically stimulated and recombined with the complementary hole trap center.¹⁾ The recombination energy is often transferred to a doped activator, which emits light of a characteristic photon energy.^{1,2)} This process is called thermally or optically stimulated luminescence.

The dosimetric or radiographic techniques based on TSL or OSL in storage phosphors have simple processes in reading-out and erasing the information of radiation dose stored as trapped electron–hole pairs. However, the efficiency of TSL or OSL is still very low compared to the deposited ionizing radiation energy. For example, the efficiency is 0.039% in LiF: Ti, Mg as a commercial dosimeter, TLD-100.³⁾ To improve the efficiency, a novel material needs to contain or form a large number of electron and hole traps, which are efficiently occupied upon irradiation and can be thermally or optically stimulated.⁴⁾ An important class of materials exhibiting such a behavior is alkaline-earth halides or alkali halides doped with transition or rare-earth metal ions as a luminescence center.⁴⁾ In the previous studies, many binary alkali halides or alkaline-earth halides and their TSL and OSL properties have been reported. They have been used for the

dosimetric or radiographic applications, such as CsBr: Eu for digital radiography⁵⁾ and CaF₂: Tm (a commercialized dosimeter, TLD-200) for personal dosimetry.⁶⁾ BaFBr: Eu²⁺ is also well known as a good storage phosphor and has been used for digital radiography.¹⁾ However, there are only a few reports on storage phosphors based on multinary compounds. In addition, despite many efforts to understand the processes of storing and recombining electron and hole pairs, the mechanism has not been fully understood.¹⁾ Thus, it is important to find multinary compounds for good storage phosphor materials and to analyze their detailed properties to gain new knowledge about electron and hole pair storage and recombination.

In this study, we focused on a ternary alkali halide, CsCaCl₃—a novel scintillator material.^{7)–9)} Eu²⁺, Ce³⁺, and Cu⁺ were chosen as activators for CsCaCl₃ because their emission wavelengths, which are in the range 350–500 nm,^{8)–10)} can be easily detected with high sensitivity.¹⁾ The effects of X-ray irradiation on the TSL and OSL properties of undoped, Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ ceramics were analyzed.

2. Experimental procedures

The undoped or Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ samples (1 g) were prepared as ceramics. The starting materials for the CsCaCl₃ ceramics were CsCl (99.999%, Kojundo Chemical Laboratory Co. Ltd., Japan) and CaCl₂·2H₂O (99.9%, Kojundo Chemical Laboratory Co. Ltd., Japan) powders. The dopant supplying materials were EuCl₃·6H₂O (99.9%, Sigma–Aldrich, Japan), CeCl₃·7H₂O (99.9%, Sigma–Aldrich, Japan), and CuCl (99.995+%, Sigma–Aldrich, Japan). The dopant concentration was 1 mol % in each sample. The starting materials and dopant supplying material were mixed in a stoichiometric

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ratio. The mixed powder was formed into a tablet (13 mm × 13 mm × ~1 mm) and dried under vacuum at 473 K to remove water. Only CsCaCl₃:Cu tablets were dried at lower temperature (423 K) than the others to prevent change in the charge state of Cu⁺ ions. Subsequently, all tablets were sintered at 673 K under vacuum in sealed quartz tubes. The undoped, Eu-doped, and Ce-doped CsCaCl₃ ceramics were broken into shattered, reformed, and sintered again under the same condition since these ceramics were very fragile after the first sintering. All obtained ceramics were not transparent. The undoped and Ce-doped CsCaCl₃ ceramics were white. The Eu-doped ceramics were pale gray, whereas the Cu-doped CsCaCl₃ ceramics were white and pale yellow in places.

The obtained samples were analyzed based on their photoluminescence (PL) and PL excitation (PLE) spectra to confirm the luminescence center at room temperature (RT). These spectra were measured with a fluorescence spectrophotometer (F-7000, Hitachi High-Tech). The excitation source was a 150 W xenon lamp. The OSL spectra were measured as following. The samples were irradiated at RT with X-rays at 45 Gy using an X-ray generator (RINT2200, Rigaku) with a Cu X-ray tube operated at 40 mA and 40 kV. After waiting for the convergence of the phosphorescence intensity, the OSL photons from the sample were detected with a multichannel analyzer (Delta Flex 3000U-TMK2, HORIBA), while the irradiated sample was stimulated with 574 nm Nano LED (Horiba) at RT. To eliminate the stimulation light, we used a band-pass filter in the 270–500 nm wavelength range. Before the irradiation, all samples were heated at 600 K for 5 min. For the TSL analysis, TSL glow curves and TSL spectra of all samples were measured. The TSL glow curves were obtained with an original setup, which mainly consists of a heater (SAT0983a, Sakaguchi), a thermostat (SCR-SHQ-A, Sakaguchi), and a photomultiplier tube (PMT; H11890-210, Hamamatsu), following irradiation with X-ray at 45 Gy using RINT2200. The heating rate was 0.5 K/s and the temperature range was 308–658 K. To eliminate the background signal that was not induced by the irradiation, the samples were measured once without irradiation before the measurements of the TSL glow curves. A thermal radiation from the sample was cut with a radiation cut filter. The TSL spectra were measured as following. The samples were irradiated at RT with X-rays at 10, 17, or 55 Gy using an air-cooled conventional X-ray tube assembly (XRBP&N200X4550, Spellman) with a W anode target and a Be window operated at 40 kV and 5.2 mA. Subsequently, the TSL emission was collected with an optical fiber while the sample was heated from 298 to 658 K at the rate of 1 K/s on a ceramic heater system (SCR-SHQA, Sakaguchi). The TSL emission was guided to a spectrometer equipped with a Peltier-cooled CCD sensor (DU920P-BU2NC, Andor) and diffraction grating (SR163i-UV, Andor).

3. Results and discussion

3.1 OSL properties

Figure 1 shows the PL, PLE, and OSL spectra of the undoped CsCaCl₃ at RT. In the PL spectrum with the excitation at 250 nm, a broad emission band peaking around 360–390 nm is observed. The PLE spectrum for this emission at 360 nm has an intense peak at 245 nm. Considering the reported bandgap energy of 8.1–8.6 eV in CsCaCl₃,¹¹⁾ the excitation of around 250 nm corresponds to a transition inside the bandgap. Thus, we conclude that the PL peak at around 360–390 nm is attributed to intrinsic defects or impurities in CsCaCl₃. The OSL spectrum of undoped CsCaCl₃ has a broad band at around 360–390 nm with a shoulder

Fig. 1. PL, PLE, and OSL spectra of undoped CsCaCl₃ at RT.

Fig. 2. PL, PLE, and OSL spectra of CsCaCl₃ doped with Eu at RT.

at around 320 nm. Since the peak at 360–390 nm is associated with the PL peak at 360–390 nm, the defects or impurities contributing to OSL are the same as those contributing to PL in the undoped CsCaCl₃ ceramics. On the other hand, the shoulder near 320 nm is not observed in the PL spectrum. This indicates that the CsCaCl₃ ceramics also have different defects or impurities that cause the emission band at approximately 320 nm.

Figure 2 shows the PL, PLE, and OSL spectra of the Eu-doped CsCaCl₃. In the PL spectrum, a sharp peak at 440 nm corresponding to the 5d–4f transition of Eu²⁺ is observed.⁸⁾ The PLE spectrum for the PL band at 440 nm shows a bell-shaped band at around 220–270 nm and a staircase structured band at around 330–400 nm. These bands are featured with the 4f⁷–4f⁶5d transition of Eu²⁺ ions.¹²⁾ In the OSL spectrum, an intense peak at 435 nm with a weak peak around 320 nm is observed. The OSL band at 435 nm coincides with the PL band at 440 nm. Hence, the OSL band at 435 nm is attributed to the 5d–4f transition of Eu²⁺. The weak peak is assigned to defects or impurities observed in the OSL band of the undoped CsCaCl₃ near 360–390 nm with a shoulder at 320 nm.

Figure 3 shows PL, PLE, and OSL spectra of the Ce-doped CsCaCl₃. The PL spectrum exhibits an intense emission peak at 380 nm with shoulders near 320 and 360 nm. Some peaks at around 470 nm with a long tail are also observed. The PLE spectrum for the PL band at 380 nm has a peak at 255 nm. According to a previous study on CsCaCl₃:Ce,⁹⁾ the observed excitation band at 255 nm is attributed to the 4f–5d transition of Ce³⁺, while the emission band at 380 nm is ascribed to the 5d–4f transition of Ce³⁺. The PLE spectrum for the shoulder at around 360 nm is consistent with the PLE spectrum for the PL peak at 380 nm. The shoulder near 320 nm is associated with the OSL of the undoped

Fig. 3. PL, PLE, and OSL spectra of CsCaCl₃ doped with Ce at RT. Fig. 4. PL, PLE, and OSL spectra of CsCaCl₃ doped with Cu at RT.

CsCaCl₃ as shown in Fig. 1. Although other peaks at around 470 nm were unidentified, these emission bands are presumably due to defects or impurities. In the OSL spectrum of the Ce-doped CsCaCl₃, an intense peak at 390 nm with a feeble peak around 360 nm is observed and is attributable to the 5d–4f transition of Ce³⁺. Besides the Ce³⁺ band, a small band attributed to defects or impurities is observed in the wavelength range of 290–320 nm.

Figure 4 shows the PL, PLE, and OSL spectra of the Cu-doped CsCaCl₃. With the excitation at 270 nm, a peak at 470 nm with a shoulder at approximately 350 nm is observed. The PLE spectrum for the shoulder around 350 nm consists of an intense peak at 203 nm with two weak peaks around 250 and 270 nm. The shoulder at around 350 nm is assigned to 3d⁹4s–3d¹⁰ transition of an isolated Cu⁺ ion according to an intense PL band at 353 nm observed in the NaCl: Cu crystals with 255 nm excitation.¹⁰⁾ For the PL band at 470 nm, the PLE spectrum with an intense peak at 260 nm is observed. We consider the PL band at 470 nm is attributed to Cu²⁺ ions. The cations (Cs⁺ and Ca²⁺) in CsCaCl₃ are in six-fold coordination. The ionic radii of Cu²⁺ in the six-fold coordination is 0.073 nm¹³⁾ and is much smaller than that of Cs⁺ (0.167 nm). Based on the large difference in the ionic radii, some of Cu ions are considered to be incorporated as their divalent state into the Ca²⁺ site, because the ionic radius of Ca²⁺ in the six-fold coordination (0.100 nm) is much closer to that of Cu²⁺. The emission wavelength of 470 nm is slightly shorter than that of Cu²⁺ ions in CsBr at around 500 nm.¹⁴⁾ This difference is reasonable considering the difference in chlorides and bromides. In the OSL spectrum of the Cu-doped CsCaCl₃, an intense peak at 345 nm is observed in addition to a peak at 430 nm. The peak at 345 nm is close to the PL shoulder at around 350 nm and can be attributed to Cu⁺. Another peak at 430 nm is attributable to Cu⁺ ions perturbed by the OH[−] ions. According to a previous

Fig. 5. TSL glow curves of undoped, Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ irradiated at RT (X-ray dose: 45 Gy; heating rate: 0.5 K/s).

Table 1. Glow peaks observed in Fig. 5. Bold: The glow peak at maximum intensity; (): A shoulder or slight peak in the glow curve

Sample	Glow peak [K]
undoped CsCaCl ₃	340 , (390), 410, (520)
CsCaCl ₃ : Eu	400 , 470, 520, (580), (610)
CsCaCl ₃ : Ce	360 , (400–450)
CsCaCl ₃ : Cu	(360), (380), 420 , 540

study on the NaCl: Cu⁺ crystals containing OH[−] ions,¹⁵⁾ a PL peak appears at 420 nm, which can be attributed to Cu⁺ ions perturbed by OH[−] ions. Therefore, the OSL band at 430 nm can be attributed to Cu⁺ ions perturbed by OH[−] ions that are left in the sample. The starting material, CaCl₂·2H₂O, is known to dehydrate at 423 K,¹⁶⁾ and the CsCaCl₃: Cu tablets were synthesized after drying the starting materials at 423 K. However, the dehydration might not be sufficient to remove water and OH[−] ions, leading to the residual of OH[−] ions that can perturb Cu⁺ ions.

To detect OSL with less noise, the emission wavelength of the activator should be significantly shorter than that of the stimulation light.¹⁾ The observed OSL bands were in a spectral range, which is well separated from the stimulation light of 574 nm. Hence, all samples can be used as X-ray storage phosphors for radiographic applications.

3.2 TSL properties

Figure 5 shows thermally stimulated luminescence glow curves of the undoped, Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ ceramics. The peaks and shoulders observed in Fig. 5 are summarized in **Table 1**. Different TSL glow curves are obtained in the undoped, Eu-doped, Ce-doped, or Cu-doped CsCaCl₃. The TSL glow curve of the undoped CsCaCl₃ has two peaks at 340 and 410 K with shoulders at 390 and 520 K. The TSL glow curve of the Eu-doped CsCaCl₃ has three peaks at 400, 470, and 520 K and shoulders at around 580 and 610 K. For the Ce-doped CsCaCl₃ ceramics, the TSL glow curve has a peak at 360 K and some shoulders in the temperature range of 400–450 K. In the TSL glow curve of the Cu-doped CsCaCl₃, two peaks are observed at 420 and 540 K with shoulders around 360 and 380 K. Peaks or shoulders in the glow curves suggest the stability of complementary defects, which are electron or hole trap centers. All TSL glow curves have some peaks and shoulders in the different temperature range. Hence, this suggests that the stabilities of trapped electron–hole pairs are different for each dopant ion.

At the dominant peaks of each sample, the TSL spectra were measured as shown in **Fig. 6**. The TSL spectrum of the undoped CsCaCl₃ has a peak at 390 nm that matches the PL and OSL peaks

Fig. 6. TSL spectra of undoped, Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ (X-ray dose: 17 Gy in undoped CsCaCl₃, 55 Gy in Eu- and Ce-doped CsCaCl₃, 10 Gy in Cu-doped CsCaCl₃; heating rate: 1 K/s).

in Fig. 1. Hence, the defects or impurities inducing the TSL are the same as those causing PL or OSL in the undoped CsCaCl₃ ceramics. In the TSL spectrum of the Eu-doped and Ce-doped CsCaCl₃, Eu²⁺ and Ce³⁺ ions cause TSL centers because the observed peaks are consistent with those of PL and OSL. The broad peak observed at around 470 nm in the TSL spectrum of the Cu-doped CsCaCl₃ is due to Cu²⁺. In contrast, the TSL band attributed to isolated Cu⁺ ion is not observed, suggesting that the mechanism of TSL is different from that of OSL in CsCaCl₃: Cu. The emission from Cu⁺ was observed in the OSL spectra, whereas the emission from Cu²⁺ was observed in the TSL spectra. A possible mechanism of this difference is based on the scheme in Fig. 5 of Ref. 14. Based on the OSL result, after X-ray irradiations, the electrons and holes are considered to be trapped at some defects and Cu⁺, respectively. During the optical stimulation, electrons are released from the trap sites and recombine with holes at Cu⁺, resulting in the emission from Cu⁺. On the other hand, the TSL spectrum was obtained during heating. If some electrons are initially trapped at Cu²⁺ ions at the Ca²⁺ site and subsequently trapped holes are thermally migrated to the Cu²⁺ ions trapping an electron, the recombination would lead to the emission from Cu²⁺. The observed peaks and shoulders in the OSL and TSL spectra of all samples and their origins are summarized in Table 2.

4. Conclusion

It was confirmed that the OSL and TSL manifest in the undoped, Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ ceramics. The undoped CsCaCl₃ showed the OSL and TSL bands originating from defects or impurities. This study also confirmed that

Table 2. Summary of OSL and TSL for CsCaCl₃ ceramics

Sample		Peaks and shoulders [nm]	
undoped CsCaCl ₃	OSL	320: defects or impurities; 360–390: defects or impurities	
	TSL	390: defects or impurities	
CsCaCl ₃ : Eu	OSL	320: defects or impurities; 435: Eu ²⁺	
	TSL	440: Eu ²⁺	
CsCaCl ₃ : Ce	OSL	290–320: defects or impurities; 360, 390: Ce ³⁺	
	TSL	355, 385: Ce ³⁺	
CsCaCl ₃ : Cu	OSL	345: Cu ⁺ ; 430: Cu ⁺ perturbed by OH [−]	
	TSL	470: Cu ²⁺	

the OSL and TSL of the Eu- and Ce-doped CsCaCl₃ occur by the 5d–4f transition of Eu²⁺ and Ce³⁺, respectively. In addition to the OSL band attributed to Eu²⁺ or Ce³⁺, defects or impurities induced some OSL bands. For the Cu-doped CsCaCl₃, the TSL spectrum showed a broad band arising from Cu²⁺, and the OSL spectrum exhibited an intense band due to Cu⁺ with a peak originating from Cu⁺ ions perturbed by the OH[−] ions. It was shown that the mechanism of OSL differs from that of TSL in the Cu-doped CsCaCl₃.

The TSL glow curves of the undoped, Eu-doped, Ce-doped, and Cu-doped CsCaCl₃ were different from each other. This suggests that the stabilities of trapped electron–hole pairs are different due to the different dopant ions.

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