Luminescence and scintillation properties of Ce-doped Cs₂ZnCl₄ crystals

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Abstract

In this study, we have synthesized scintillation materials based on Ce-doped Cs₂ZnCl₄ crystals. The light yield was enhanced by up to 20% by doping Cs₂ZnCl₄ with Ce³⁺ ions. In the scintillation time profiles, fast components exhibited decay time constants on the order of nanoseconds, which was ascribed to Auger-free luminescence (AFL). The light yield of the AFL component decreased at 10 mol% Ce³⁺ concentration, which is mainly attributed to the

reabsorption of AFL photons inside the crystals by Ce^{3+} ions, as seen in the scintillation spectra. Long components had decay time constants of approximately 30 ns. In addition, at 10 mol% Ce^{3+} concentration, a prominent band appeared at approximately 500 nm in the scintillation spectrum, which was not observed in the photoluminescence spectra. The long components in the scintillation time profiles and the 500 nm band in the scintillation spectra were tentatively attributed to self-trapped excitons perturbed by Ce^{3+} ions.

Introduction

Auger-free luminescence (AFL) or core-valence luminescence has long been used as a fast scintillation mechanism [1]. While the most famous scintillation material exhibiting AFL is BaF₂ [2], other halide crystals have also been considered in the study of fast scintillation materials [3]. Recently, we have developed fast scintillation materials based on Cs₂ZnCl₄ [4] and CsCaCl₃ [5] and reported that Cs₂ZnCl₄, in particular, exhibits relatively efficient AFL. In addition, we found that the contribution from the long component is very small in this compound, which is favorable for applications involving high counting rate measurements. However, the low total light yield (630 photons/MeV) renders the material unsuitable for applications in which a high light yield is necessary.

In this study, we attempted to increase the light yield of Cs₂ZnCl₄ crystals by doping with Ce³⁺ ions. We have analyzed the changes in the scintillation spectra and the time profiles, induced by Ce³⁺ doping. In addition, we have analyzed the total light yield based on the pulse height spectra.

Experimental

Single crystals of Ce-doped Cs₂ZnCl₄ were grown by the Bridgman-Stockbarger method. Prior to the growth of the crystals, a stoichiometric mixture of CsCl (99.999%, High-purity Chemical, Japan), ZnCl₂ (99.9%, Wako, Japan), and CeCl₃·7H₂O (99.9%, Wako, Japan) was dried in vacuum at 573 K for one day in order to expel water. The crystals were grown under vacuum in sealed quartz tubes. The concentration of Ce in the melt was either 1 mol% or 10

mol%. Hereafter, the samples will be referenced by their Ce concentration in the melt, i.e., Cs_2ZnCl_4 grown in melts with 1 mol% Ce and 10 mol % Ce will be referred to as $\text{Cs}_2\text{ZnCl}_4\text{:Ce 1\%}$ and $\text{Cs}_2\text{ZnCl}_4\text{:Ce 10\%}$, respectively. Single crystals larger than 1 mm were used for the optical and scintillation measurements. The crystals were not hygroscopic, and all the measurements were performed in air.

The Ce concentrations in the crystals were measured by ICP-MS (iCAP6500, Thermo Scientific), after dissolving the crystals in high-purity water. The luminescence spectra were obtained using a spectrofluorometer (F-7000, Hitachi, Japan), and the luminescence time profiles were measured by a time-correlated single photon counting method (Quantaaurus tau, Hamamatsu, Japan). Scintillation spectra were obtained using an X-ray tube as the excitation source. The spectrum was recorded using a Peltier-cooled charge-coupled device (CCD, DU-420-OE, Andor, UK), coupled with a grating monochromator (Oriel Instruments, CT, US, 285 grooves/mm, blaze wavelength of 280 nm). We did not carry out the correction for spectral sensitivity of detection systems. The scintillation time profiles were obtained by a time-correlated single photon counting method with pulsed X-ray beam as the excitation source. In order to obtain scintillation time profiles at certain wavelength regions, we used optical band pass filters. The pulse height spectra of the scintillation detectors equipped with Cs_2ZnCl_4 crystals were obtained using synchrotron X-rays at BL-14A, Photon Factory, KEK. The impinged X-ray energy was 67.4 keV. The sample crystals were attached to a PMT (R7400P, Hamamatsu, Japan) with optical grease. The detection signal was amplified with a charge-sensitive preamplifier (2005, Canberra, CT, US) and a main amplifier (572A, Ortec,

TN, US), and a histogram was obtained with a multichannel analyzer (MCA, 5004, Aptec, NY, US). The shaping time of the main amplifier was set at 0.5 μ s.

Results and Discussion

The Ce concentrations in $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% and $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% were found to be 0.091 mol% and 0.60 mol%, respectively, as determined by ICP-MS analysis. Cs^+ and Zn^{2+} ions in the Cs_2ZnCl_4 crystals are icosahedrally and tetrahedrally coordinated, respectively [6]. According to a previous report [7], the effective ionic radii for icosahedrally coordinated Cs^+ and tetrahedrally coordinated Zn^{2+} are 0.188 nm and 0.060 nm, respectively. The effective ionic radius of Ce^{3+} ranges from 0.10 nm to 0.13 nm, depending on the coordination number [7]. It is difficult to draw a conclusion on whether Ce^{3+} ions can replace Zn^{2+} or Cs^+ , based on the ionic radii. However, in either case, the actual concentration of Ce^{3+} ions is expected to be much lower in the $\text{Cs}_2\text{Zn}_2\text{Cl}_4$ crystals than in the melt due to large mismatch in ionic radii and different valence states. In view of this, the measured concentrations are reasonable.

Figure 1 shows the luminescence and excitation spectra of undoped and Ce-doped Cs_2ZnCl_4 crystals. For the undoped crystal, luminescence spectrum was obtained with an excitation of 300 nm, and excitation spectra were obtained with an emission wavelength of 470 nm. For the Ce-doped crystals, luminescence spectra were obtained with an excitation wavelength of 240 nm, and excitation spectra were obtained with an emission wavelength of 350 nm. A prominent band was observed at approximately 350 nm in the luminescence spectra of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% and $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% crystals. The energy position of the

luminescence band observed for Cs_2ZnCl_4 is quite similar to those observed for several other chlorides, such as CeCl_3 [8], NaCl:Ce [9], Ce-doped alkaline earth chlorides [10, 11], and Ce-doped complex chlorides [12-15]. Based on the similarity in luminescence band positions for all the above compounds, the observed UV luminescence band can be ascribed to the 5d-4f transition in Ce^{3+} ions. In the excitation spectrum of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%, an additional band was observed at approximately 300 nm. This band may be related with the host crystal. As shown in Fig.1 (a), an excitation band was observed at approximately 300 nm for the undoped crystal. The photon energy of 300 nm light was much smaller than the band gap energy of Cs_2ZnCl_4 (7.9 eV) [16], the luminescence band in the undoped crystal can be ascribed to lattice defects or impurities. Although the monitoring wavelength of the excitation spectrum in Fig.1 (b) is at the tail of the luminescence band of the undoped crystal as shown in Fig.1 (a), the excitation band at 300 nm in Fig.1 (b) may be the same origin as the luminescence band for the undoped crystal. For $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% crystal, the excitation band at 300 nm was not prominent because the Ce^{3+} concentration is higher and Ce^{3+} centers are more efficiently excited. Figure 2 shows the luminescence time profiles of Ce-doped Cs_2ZnCl_4 crystals. The luminescence time profiles were satisfactorily fitted with a single exponential decay function. The decay time constants were similar for $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% and $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% at 21.7 and 20.2 ns, respectively. The values obtained are typical for the 5d-4f transition in Ce^{3+} ions [18, 19].

Figure 3 shows the scintillation spectra of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%, $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% , and undoped Cs_2ZnCl_4 crystals. The scintillation spectrum of the undoped Cs_2ZnCl_4 crystal is

similar to the luminescence spectrum with core level excitation [16, 17] and the bands observed are ascribed to AFL. In the scintillation spectra of the Ce-doped crystals, the Ce^{3+} emission band is not obvious, possibly because the band would be located between the prominent AFL bands. A key deviation in the scintillation spectra of Ce-doped crystals from that of the undoped crystal is observed in the short wavelength region, where the intensity of the 250 nm band is significantly lower compared to the intensity of the other bands. This result is attributed to the reabsorption of AFL photons at the short wavelength by Ce^{3+} ions. Another feature of the scintillation spectra of the Ce-doped crystals is the appearance of a band at 500 nm. Since this band cannot be observed by luminescence measurement as shown in Fig.1, it is not related to electronic transitions within certain centers, such as Ce^{3+} or lattice defects. The band cannot be attributed to AFL either, since the concentration of Ce^{3+} ions is low and insufficient to alter the overall band structure of the crystal. The characteristics of this band are quite similar to so-called relaxed excited state in other halide crystals [20, 21]. Based on this similarity, the 500 nm band is tentatively ascribed to self-trapped excitons (STE) perturbed by Ce^{3+} ions. Based on this hypothesis, the absence of the band at 500 nm in the luminescence spectra can be explained because the excitation photons cannot generate electron-hole pairs and excitons, and thus STEs, in the luminescence measurement.

Figure 4 shows the scintillation time profiles of the $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% and $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% crystals. The time profiles were satisfactorily fitted with the sum of two exponential decay functions. For $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% crystals, the decay time constants of the two components were 3.0 ns and 32.7 ns with relative intensities of 87% and 13%, respectively. In

the case of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10%, the decay time constants of the two components were 1.6 ns and 30.5 ns with relative intensities of 23% and 77%, respectively. Considering that the decay time constant of AFL in an undoped crystal is 1.8 ns [4], the fast component can be reasonably ascribed to AFL, although the decay time constant of the fast component in $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% is relatively long. For $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%, the value of the fitted function is lower than the experimental value at around $t = 0$. The long decay time constant of the fast component for $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% may originate from this deviation. Figures 5 and 6 represent scintillation time profiles of Ce-doped Cs_2ZnCl_4 crystals using optical band pass filters at 340–390 nm or 460–510 nm. These wavelength regions correspond to those of the luminescence bands of Ce^{3+} ions and perturbed STE, respectively. In the case of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% at 340–390 nm, the decay time constants of the two components were 1.0 ns and 2.8 ns with relative intensities of 53% and 47%, respectively. At 460–510 nm, the decay time constants of the two components were 1.0 ns and 4.4 ns with relative intensities of 68% and 32%, respectively. For $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%, the scintillation time profiles are dominated by fast components possibly ascribed to AFL. In the case of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% at 340–390 nm, the decay time constants of the two components were 1.5 ns and 21.5 ns with relative intensities of 70% and 30%, respectively. At 460–510 nm, the decay time constants of the two components were 0.9 ns and 7.2 ns with relative intensities of 85% and 15%, respectively. For $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10%, the long components at 340–390 nm and 460–510 nm can be ascribed to luminescence bands of Ce^{3+} ions and perturbed STE, respectively. Based on the time profiles in Figures 5 and 6, the long components in Figure 4 are ascribed to the emission at Ce^{3+} ions.

Figure 7 shows the pulse height spectra of scintillation detectors equipped with undoped or Ce-doped crystals. The peaks at around 80 channel correspond to the full-energy peak. The peak position of the pulse height spectrum shifted towards higher channel numbers as Ce^{3+} concentration in the crystals increased. This result indicates that the light yield improved with doping, although the improvement is limited. For example, approximately 20% improvement in light yield was seen for 10% Ce^{3+} doping. When considered in combination with the results of the scintillation time profiles, this result indicates that the light yield of the AFL component decreased significantly in $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10%. The decrease is mainly ascribed to reabsorption of the AFL component by the Ce^{3+} ions, as was observed in the scintillation spectra in Figure 3.

Conclusion

We have fabricated scintillation materials by doping Ce^{3+} ions in Cs_2ZnCl_4 . We recently reported fast scintillation due to AFL in this system. The actual dopant concentration was determined to be an order of magnitude lower than that in the melt. A clear photoluminescence band was observed at approximately 350 nm, and the decay time constant of luminescence was approximately 20 ns. Photoluminescence is ascribed to the 5d-4f transitions within Ce^{3+} ions. In the scintillation spectra, a scintillation band appeared at approximately 500 nm in addition to the AFL bands. This band is tentatively ascribed to STE perturbed by Ce^{3+} centers. By comparing the pulse height spectra, it was determined that the light yield in Ce-doped crystals improved by up to 1.2 times the value obtained from undoped

crystals.

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Figure 1. Luminescence and excitation spectra of undoped and Ce-doped Cs_2ZnCl_4 crystals. (a): undoped Cs_2ZnCl_4 ; (b): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%; (c): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10%. For the undoped crystal, luminescence spectrum was obtained with an excitation of 300 nm, and excitation spectra were obtained with an emission wavelength of 470 nm. For the Ce-doped crystals, luminescence spectra were obtained with an excitation wavelength of 240 nm, and excitation spectra were obtained with an emission wavelength of 350 nm.

Figure 2. Luminescence time profiles of Ce-doped Cs_2ZnCl_4 crystals. (a): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%; (b): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10%. Excitation wavelength was 280 nm. Luminescence detection wavelength was 360 nm.

Figure 3. Scintillation spectra of undoped and Ce-doped Cs_2ZnCl_4 crystals. (a): undoped Cs_2ZnCl_4 ; (b): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%; (c): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10%.

Figure 4. Scintillation time profiles of Ce-doped Cs_2ZnCl_4 crystals. (a): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1%; (b): $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10%.

Figure 5. Scintillation time profiles of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 1% crystal using optical band pass filters

at (a): 340–390 nm; (b): 460–510 nm.

Figure 6. Scintillation time profiles of $\text{Cs}_2\text{ZnCl}_4\text{:Ce}$ 10% crystal using optical band pass filters

at (a): 340–390 nm; (b): 460–510 nm.

Figure 7. Pulse height spectra of scintillation detector equipped with undoped or Ce-doped crystals for X-ray detection at an energy of 67.4 keV. (a) Entire region of the spectra; (b) Enlarged view around the peak position.