Auger-free luminescence characteristics of $\text{Rb}_{1-x}\text{Cs}_x\text{CaCl}_3$

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Fast scintillation materials based on ternary halide mixed crystals, $\text{Rb}_{1-x}\text{Cs}_x\text{CaCl}_3$ were synthesized. Broad luminescence bands were observed around 360 nm and can be ascribed to Auger-free Luminescence (AFL) for vacuum ultraviolet core-level excitation. Several luminescence bands for interband excitation were also observed. For X-ray excitation, the band that is ascribed to AFL could be clearly detected. The scintillation decay components due to the AFL had decay time constant of 0.8 ns for $\text{RbCaCl}_3$ and 2.0 ns for $\text{Rb}_{1-x}\text{Cs}_x\text{CaCl}_3$ ($x \neq 0$). $\text{CsCaCl}_3$ had the largest light yield of the AFL component, exceeding 1200 photons/MeV, which was slightly lower than that of $\text{BaF}_2$. The light yield of the AFL component increased linearly with Cs content.

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1. Introduction

Auger-free luminescence (AFL) is the radiative recombination of the outermost core hole and a valence electron $^{13–3}$ and is also called core–valence luminescence. AFL is observed in crystals having bandgap energies larger than the energy gap between the valence band and the outermost core band. Therefore, the number of the materials that are able to exhibit AFL is limited.

AFL is known to have decay time constants of a few nanoseconds or less. For example, the decay time constants of typical inorganic crystal scintillators are tens or hundreds of nanoseconds, namely, the decay time constants for BGO (Bi$_4$Ge$_3$O$_{12}$) is 300 ns, and that for YAP:Ce (YAlO$_3$-perovskite:Ce) is 30 ns. Compared with these cases, AFL is a very fast process for scintillation. Therefore, the materials that exhibit AFL can be expected to be applicable to fast-response scintillators.

One of the material groups that exhibit AFL is fluorides, such as RbF, K$_2$MgF$_4$, and BaY$_2$F$_8$. In this group, BaF$_2$ and CsF$^8$ have been applied as scintillators with BaF$_2$ being the most successful example. The fast component of BaF$_2$, which is due to AFL, has a decay time constant of 0.8 ns. In addition, BaF$_2$ has a relatively high light yield of 11000 photon/MeV. However, BaF$_2$ also has some undesirable characters. Firstly, BaF$_2$ has a long decay component corresponding to self-trapped excitons (STEs), whose decay time constant was reported to be 600 ns with 85% to the total scintillation amount, which means that the light yield of the AFL component is 1400 photon/MeV. Secondly, the emission wavelength of AFL of about 220 nm is too short to be detected with general photomultiplier tubes. Thus due to these unfavorable properties, BaF$_2$ has limited use in a number of applications. Therefore, the development of AFL materials with better properties are required.

Other materials that exhibit AFL are CsCl-based compounds, such as CsCl$^{10}$, Cs$_2$ZnCl$_4$,$^{11,12}$ and CsCaCl$_3$$^{13–15}$ In this work, the focus is on CsCl-based compounds because they exhibit AFL at longer wavelength, around 250–350 nm, which is compared with BaF$_2$, although the decay time constants of CsCl-based compounds are a few ns, which are longer than BaF$_2$. Furthermore, the light yields of the fast component in the conventional CsCl-based compounds are less than that of BaF$_2$. Therefore, it is necessary to identify new materials that exhibit more efficient AFL.

As an approach to identify such materials, ternary mixed crystals were considered. In this study, $\text{Rb}_{1-x}\text{Cs}_x\text{CaCl}_3$ is considered as a possible AFL material. The top and bottom of the valence band and the outermost core level are located at 8.1, 8.9, and 16.5 eV below the conduction band, respectively, in pure $\text{RbCaCl}_3$. Therefore, pure $\text{RbCaCl}_3$ partially satisfies the necessary condition of energy band structure for AFL. On the other hand, Cs doped $\text{RbCaCl}_3$ is known to clearly satisfy the condition. The
Rb$_{0.99}$Cs$_{0.01}$CaCl$_3$ and Rb$_{0.90}$Cs$_{0.10}$CaCl$_3$ are known to exhibit CsCl-based AFL$^{18),19}$ which appears for excitation at both the core levels of Cs and Rb. The outermost core level of Cs and Rb are about 14 and 16.5 eV, respectively, below the conduction band. These core levels are located nearby and may have some overlap. Therefore, a hole at the Rb core level may move up to that of Cs and subsequently recombine with a valence electron. Owing to the core hole transfer, it can be expected that a higher light yield of CsCl-based AFL in Rb$_{1-x}$Cs$_x$CaCl$_3$ is possible over that in pure samples. In this study, Rb$_{1-x}$Cs$_x$CaCl$_3$ crystals were investigated over the entire range of mole fractions (x). Luminescence and scintillation properties of Rb$_{1-x}$Cs$_x$CaCl$_3$ which are dependent on Cs/Rb proportion in the crystals are reported.

2. Experimental procedures

Crystal samples of Rb$_{1-x}$Cs$_x$CaCl$_3$ were fabricated using a solidification method. Powders of RbCl (99.9%, Mitsuwa Chemical Co. Ltd., Japan), CsCl (99.99%, Mitsuwa Chemical Co. Ltd., Japan) and CaCl$_2$ (99.9%, Kojundo Chemical Laboratory Co. Ltd., Japan) were mixed in a stoichiometric ratio. The x value representing Cs/Rb proportion are 0, 0.25, 0.50, 0.75, or 1.0. The mixed powder was poured into a quartz ampoule and heated at 400 K in vacuum for 1 day to remove adsorbed water. The ampoules were set in a tubular furnace. The furnace was heated up to 900°C, maintained for 12 h, and subsequently cooled down to room temperature in 24 h. The fabricated crystals appeared cloudy and confirmed to be in a single phase with XRD. Therefore, these crystals are considered to be solid solutions. The crystals were poor in water resistance. Therefore, they were preserved in an evacuated environment and used for experiments in a dry environment.

The luminescence properties were characterized with vacuum ultraviolet (VUV) light as an excitation source. Measurements were performed at beamline 7B of the UVSOR facility at the Institute for Molecular Science, Japan with synchrotron radiation being monochromatized with a 3-m normal-incidence monochromator. Samples were irradiated with the monochromatized light in a vacuum chamber and their luminescence spectra were measured using a charge coupled device (CCD) equipped with a monochromator. The luminescence was guided to the detector via an optical fiber and luminescence spectra were measured for different excitation wavelengths, and the excitation spectra were obtained from the intensity in luminescence spectra. Therefore, the excitation spectra were obtained as polygonal lines.

X-ray excited radioluminescence (XRL) spectra were measured under X-ray irradiation with a CCD-based spectrometer (Andor DU492A-1.7). X-rays were generated by using an X-ray generator which was equipped with a tungsten anode target (Spellman XRB80P) at a power setting of 60 kV and 2.5 mA.$^{20}$ Further, the scintillation temporal profiles were measured with a pulse X-ray tube that allowed the measurements by time-correlated single photon counting technique under X-ray excitation.$^{20}$ Gamma-ray-excited pulse-height spectra were measured at room temperature with a photomultiplier tube (PMT: Hamamatsu R7600-200) connected to a pre-amplifier (Ortec 113) and a main amplifier (Ortec 572A) with 0.5 μs shaping time. The crystals were irradiated with 662-keV gamma rays from $^{137}$Cs source, and scintillation was detected using the PMT.

3. Results and discussion

3.1 VUV spectroscopy

Luminescence spectra were measured with VUV excitation to analyze the emission process. Figure 1 shows the luminescence spectra of Rb$_{1-x}$Cs$_x$CaCl$_3$ for excitation at 150 nm which corresponds to the interband excitation. A broad band at 450 nm was observed for CsCaCl$_3$. On the other hand, the band at 450 nm for excitation at 200 nm that corresponds to excitation within the band gap was not observed. Therefore, this band may be ascribed to STE. The band at 380 nm was also observed for Rb$_{0.25}$-Cs$_{0.75}$CaCl$_3$ but was not observed for the other samples. Therefore, this band may be the luminescence at defect or impurity sites. The luminescence spectra were similar for Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$ and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$ that showed bands at 310, 400, and 600 nm for excitation at 84–88 nm. The bands at 310 and 600 nm were also observed for RbCaCl$_2$. The band at approximately 600 nm may be due to second-order diffraction of the 310 nm band. In addition, a broad band occurred at 380 nm for Rb$_{1-x}$Cs$_x$CaCl$_3$ (x ≠ 1) for excitation at 200 nm. Based on these results, the bands at 400 nm for Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$ and Rb$_{0.75}$Cs$_{0.25}$-CaCl$_3$ and at 380 nm for excitation can be ascribed to the luminescence at defect or impurity sites. In addition, the band at 310 nm for excitation at 150 nm may be ascribed to STEs.

Figure 2 shows the luminescence spectra of CsCaCl$_3$ for excitation at 84–88 nm for which the excitation wavelengths correspond to the outermost core level excitation of Cs. Two bands at 360 and 500 nm for excitation at 84 nm were observed, whereas these were not observed for excitation at 86 and 88 nm. The wavelength of the band at 360 nm with excitation at 84 nm was similar to that of that ascribed to AFL for CsCaCl$_3$ in a previous report.$^{15}$

![Fig. 1. Luminescence spectra of Rb$_{1-x}$Cs$_x$CaCl$_3$ with excitation at 150 nm.](image-url)
Accordingly, the band at 360 nm is ascribed to AFL. Although the band at 500 nm appeared with excitation at 84 nm as well as AFL, more research is needed to clarify its origin. For excitation at 88 and 86 nm, broad bands at 450 nm were found. These bands correspond to that for excitation at 150 nm. Therefore, these band at 450 nm also can be ascribed to STE. Figure 3 shows the excitation spectrum for the 360-nm luminescence band of CsCaCl₃ for which an increase in the intensity at 88–85 nm was observed. The threshold energy corresponds to the energy difference between the outermost core level of Cs and the bottom of the conduction band. AFL can be observed for higher energy excitation than this threshold energy. The result is similar to the excitation of AFL in CsCaCl₃ reported previously.¹⁵ Therefore, this result clearly indicates that the band at 360 nm is ascribed to AFL.  

Figure 4 shows the luminescence spectra of Rb₀.₂₅-Cs₀.₇₅CaCl₃ for excitation at 84–88 nm showing a broad band at 370 nm. This broad band is more clearly observed for excitation for 84 nm, and the emission wavelength was similar to AFL of CsCaCl₃. Figure 5 shows the excitation spectrum for the 370-nm luminescence band of Rb₀.₂₅-Cs₀.₇₅CaCl₃ that showed an increase in intensity at 90–86 nm. These excitation wavelengths mostly correspond to the position of the outermost core of Cs. Therefore, the band at 370 nm is also ascribed to AFL by excitation of Cs core band. Contrary to the literature, an increase in the luminescence intensity at the excitation wavelength corresponding to the core level of Rb, i.e., 74 nm was not observed, which indicates that AFL was not present in the Rb core-level excitation.  

Figure 6 shows the luminescence spectra of Rb₀.₅₀-Cs₀.₅₀CaCl₃ with excitation at 84–88 nm.
Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$ were similar to those of Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$ and emission bands were observed at 310, 400, 490, and 600 nm. In contrast, broad bands were found at 310 and 490 nm for RbCaCl$_3$. According to a previous report, RbCaCl$_3$ exhibits STE emission around 470 nm. Therefore, the band at 490 nm for RbCaCl$_3$, Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$, and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$ can be ascribed to STE. The bands at 310 nm for Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$, Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$, and RbCaCl$_3$ correspond to those that for excitation at 150 nm. Therefore, these bands at 310 nm also can be ascribed to STE. The band at 400 nm for Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$ and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$ correspond to those for excitation at 200 nm. Therefore, these bands can be ascribed to the luminescence at defects or impurity sites. In contrast to the cases of CsCaCl$_3$ and Rb$_{0.25}$Cs$_{0.75}$CaCl$_3$, no significant changes in the luminescence spectra were found with excitation at 84–88 nm for Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$ and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$. To investigate whether AFL appears, the excitation spectra were measured for the 360-nm luminescence band in Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$ and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$. Figure 7 shows the spectra and it can be seen that there was an increase in the luminescence intensity at 90–84 nm. This result is similar to that for CsCaCl$_3$ and Rb$_{0.25}$Cs$_{0.75}$CaCl$_3$, which indicates that AFL appears in Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$ and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$. A significant change in the luminescence spectra for excitation with 84–88 nm was not observed probably because other bands at 310 and 400 nm overlapped the AFL band. An increase in the intensity was also observed at the wavelength corresponding to the core level of Rb, although CsCaCl$_3$ also has a similar structure in the excitation spectra. Therefore, it could not be confirmed whether the core excitation of Rb leads to AFL. Figure 8 shows the energy band structure of Rb$_{1-x}$Cs$_x$CaCl$_3$ crystals and the observed transitions.

3.2 Characterization of scintillation properties

Figure 9 shows XRL spectra at 200–400 nm for the wavelength range that corresponds to AFL. Emission bands were present at around 250 and 350 nm for CsCaCl$_3$ and at 250 and 320 nm for Rb$_{0.25}$Cs$_{0.75}$CaCl$_3$, Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$, and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$, and at 310 and at 350 nm for RbCaCl$_3$. Although the wavelengths of the bands at 350 nm for CsCaCl$_3$ and at 320 nm for the others were slightly shorter than those of AFL observed with VUV excitation, they are ascribed to AFL at the Cs site. Thus, materials that exhibit AFL for X-ray irradiation could be fabricated. As discussed in a previous subsection, luminescence bands were observed that could be ascribed to defects or impurity sites and STEs at 300–350 nm with VUV excitation. Therefore, these origins may contribute to the band of CsCaCl$_3$ at 350 nm and those of Rb$_{0.25}$Cs$_{0.75}$CaCl$_3$, Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$, and Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$ at 320 nm. For RbCaCl$_3$, broad bands at 310 and 360 nm were present. Considering the luminescence spectra obtained with VUV excitation, the bands at 310 and 360 nm may be ascribed to the luminescence of STE and the luminescence at defect or impurity sites because the wavelength of the intrinsic AFL of RbCaCl$_3$ is estimated to be 140–190 nm. Therefore, Figure 10 shows the XRL spectra at 200–700 nm where a band at 450 nm can be clearly observed. The band was present in samples having high Cs content and corresponds to that in the luminescence spectra of CsCaCl$_3$ for the interband excitation allowing it to be ascribed to STEs.
Figure 11 shows the scintillation temporal profiles, and Table 1 shows the decay time constants and the proportion of the fast components. The decay behavior could be described by the sum of two exponential-decay components and a time-independent component. The decay time constant for RbCaCl$_3$ was about 0.8 ns, which is a shorter decay time than those of the samples containing Cs, and is equivalent to the fast component of BaF$_2$. This fast scintillation may correspond to the luminescence at defect or impurity sites, because it could not be clearly observed in the intrinsic AFL of RbCaCl$_3$. Regardless for the proportion of Cs in the samples containing Cs, the decay time constants are about 2.0 ns, which are typical for AFL in CsCl-based compounds. The proportions of the fast components are very large, at least 94%, in comparison to 15% for BaF$_2$.

Figure 12 shows pulse-height spectra for Rb$_{1-x}$Cs$_x$CaCl$_3$ ($x 
eq 0$) and Ce:Gd$_2$SiO$_5$ (GSO) for 662 keV gamma rays from a $^{137}$Cs source. It should be noted that the amplifier gain was ten times smaller for GSO. Broad peaks were observed at approximately 300 ch for CsCaCl$_3$, at 230 ch for Rb$_{0.25}$Cs$_{0.75}$CaCl$_3$, at 180 ch for Rb$_{0.50}$Cs$_{0.50}$CaCl$_3$, and at 130 ch for Rb$_{0.75}$Cs$_{0.25}$CaCl$_3$. Table 2 shows the estimated total light yields and fast component light yields. Assuming the light yield of GSO to be 10000 photons/MeV, and considering the wavelength dependent sensitivity of the PMT, the light yields of the Rb$_{1-x}$Cs$_x$CaCl$_3$ ($x 
eq 0$) crystals were estimated. The sample that had the largest light yield was CsCaCl$_3$, whose total light yield was about 1250 photons/MeV and the fast-component light yield is about 1200 photons/MeV. CsCaCl$_3$ had a slightly smaller light yield of the fast component than
whose light yield is estimated to be 1200 MeV
yields of the fast component was the largest for CsCaCl3
is typical for AFL in CsCl-based compounds. The light
ponent light yield increase linearly with
transfer from the Rb core level to Cs core level could
AFL owing to the hole
for Cs core-level excitation. The AFL exhibiting to the hole
in Rb1−xCsxCaCl3 mainly appears at the Cs site,
that AFL in Rb1−xCsxCaCl3 mainly appears at the Cs site.

4. Conclusions

Fast scintillation material were synthesized based on ternary mixed halide crystals (Rb1−xCsxCaCl3) exhibiting AFL. With VUV excitation, AFL was observed in samples for Cs core-level excitation. The AFL owing to the hole transfer from the Rb core level to Cs core level could not be observed. Luminescence of the other origins was present, such as STEs and the luminescence at defects or impurity sites, for the interband and within the band-gap excitation. For X-ray excitation, broad bands were present around 250 and 300 nm that are ascribed to AFL; bands at 450 nm are ascribed to STEs. RbCaCl3 had a scintillation decay time constant of about 0.8 ns, while Rb1−xCsxCaCl3 (x ≠ 0) had decay time constants of about 2.0 ns, which is typical for AFL in CsCl-based compounds. The light yields of the fast component was the largest for CsCaCl3 whose light yield is estimated to be 1200 MeV/photons and is slightly lower than that of BaF2. The light yields of fast components increased with Cs content which implies that AFL in Rb1−xCsxCaCl3 mainly appears at the Cs site.

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