Optical Materials 36 (2014) 1930–1933

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Scintillation and luminescence properties of a single $CsCaCl_3$ crystal

M. Koshimizu [a,]*, N. Yahaba [a], R. Haruki [b], F. Nishikido [c], S. Kishimoto [d], K. Asai [a]

[a] Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[b] Advanced Science Research Center, Japan Atomic Energy Agency, 2-4 Shirakata Shirane, Tokai, Ibaraki 319-1195, Japan
[c] Molecular Imaging Center, National Institute of Radiological Sciences, Anagawa 4-9-1, Inage-ku, Chiba 263-8555, Japan
[d] Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

ARTICLE INFO

Article history:
Available online 22 April 2014

Keywords:
Auger-free luminescence
Core-valence luminescence
Core hole
Scintillator
Self-trapped exciton

ABSTRACT

We synthesized a fast scintillation material based on a ternary halide crystal, $CsCaCl_3$, which is known to exhibit Auger-free luminescence (AFL) under core-level excitation. We characterized its luminescence properties using vacuum ultraviolet (VUV) light for excitation. We observed a broad AFL band centered at approximately 300 nm for the core hole excitation, with a decay time of 2.3 ns. In addition to AFL, we observed several luminescence bands for interband and sub-band-gap excitation. The scintillation light yield was estimated to be 410 photons/MeV. We observed a fast scintillation component due to the AFL having a decay time constant of 2.3 ns. This fast component accounts for 58% of the total scintillation. These results indicate that a fast scintillation material was successfully fabricated, employing AFL as the luminescence mechanism based on a ternary halide crystal.

1. Introduction

Auger-free luminescence (AFL), or core-valence luminescence, is a radiative electronic transition between the valence band and the outermost core band [1]. This luminescence is observed only for insulator crystals in which the band-gap energy is larger than the energy difference between the valence band and the outermost core band. AFL is known to be a fast luminescence process whose decay time constant is typically of the order of nanoseconds or less. Therefore, insulator materials that exhibit AFL are applicable as to fast-response scintillators.

Thus far, BaF_2 has been the most successful example of scintillators exhibiting AFL. Its scintillation has a fast component corresponding to AFL, whose decay time constant is as short as 0.8 ns [2]. Owing to this fast decay combined with relatively high light yields, BaF_2 has been used for applications in which good timing characteristics are necessary. However, its scintillation also has a long decay component corresponding to self-trapped excitons (STEs). The decay time constant of the long component has been reported to be 600 ns [2]. Thus, the long component limits the usage of BaF_2 in several applications, such as measurements with a high counting rate. AFL has also been observed in other binary halide crystals [3], such as RbF, CsF, CsCl, and CsBr. In those materials, the light output of AFL is lower than BaF_2, and they similarly have long components corresponding to STEs. Because the number of binary halides exhibiting AFL is limited, research should be extended to ternary or more complex halide crystals in order to develop novel scintillation materials exhibiting AFL.

Recently, AFL has been observed with several ternary halide crystals, such as $LiBaF_3$ [4], $MgBaF_4$ [4], $CsCaCl_3$ [4,5], Cs_2ZnCl_4 [6,7], Rb_2ZnCl_4 [8]. Among these, we have focused on the CsCl-based ternary crystals, because AFL occurs in the long wavelength region and so is suitable for detection with photomultiplier tubes (PMTs). In a study reported recently, we found a fast scintillation component due to AFL in Cs_2ZnCl_4 [9]. In this paper, we report the scintillation properties of another halide crystal, $CsCaCl_3$.

2. Experiment

Single crystals of $CsCaCl_3$ were fabricated using a vertical Bridgman-Stockbarger method. Powders of CsCl (99.999%, Kojundo Chemical Laboratory Co. Ltd., Japan) and $CaCl_2$ (99.99%, Sigma–Aldrich, Japan) were mixed in a stoichiometric ratio. The mixed powder was poured into a quartz ampoule and heated at 473 K in vacuum for 1 day in order to remove water. During the growth, the temperature gradient was 1.1 K/mm, and the ampoules were lowered at a rate of 1.0 mm/h. Transparent crystals were obtained. The photo of the sample crystal is shown in Fig. 1. The size was approximately $3 \times 5 \times 2$ mm^2. They showed a slight hygroscopy. When we left the crystals in air for several days, the surface of the crystals turned cloudy.

---

* Corresponding author. Tel.: +81 22 795 7219.
E-mail address: koshi@qpc.che.tohoku.ac.jp (M. Koshimizu).

http://dx.doi.org/10.1016/j.optmat.2014.04.004
0925-3467/© 2014 Elsevier B.V. All rights reserved.

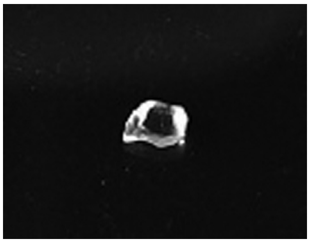

Fig. 1. Photograph of the sample crystal.

The luminescence properties were characterized using vacuum ultraviolet (VUV) light as an excitation source. The measurements were performed at beamline 7B of the UVSOR facility at the Institute for Molecular Science, Japan. The synchrotron radiation was monochromated using a 3-m normal-incidence monochromator. The samples were irradiated with the monochromated light in a vacuum chamber. The 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. The luminescence spectra were measured for various excitation wavelengths, and the excitation spectra were obtained from the luminescence spectra. In addition, luminescence decay behavior was observed by a single photon counting method. The single-bunch operation mode was used, and the period between successive pulses was 176 ns. The decay component longer than this period appeared as a time-independent component in the time profiles. The luminescence photons were detected with a multi-channel-plate (MCP) mounted PMT (R3809U-50, Hamamatsu, Japan). All measurements were performed at room temperature.

The scintillation properties and X-ray detection capability were characterized at BL-14A at the Photon Factory, KEK, Japan. The X-ray energy was 67.4 keV. For the characterization of the X-ray detection capability, the sample crystals were attached to a PMT (R7400P, Hamamatsu, Japan) with a small amount of optical grease. The pulse-height spectra were measured using a charge sensitive preamplifier (2005, Canberra, CT, US), a main amplifier (572A, Ortec, TN, US), and a multichannel analyzer (MCA; 5004, Aptec, NY, US). The single bunch operation mode was used for the measurements of scintillation time profiles,. The period between each successive pulse was 624 ns. The spacing between the samples and the PMT was ~38 mm. The single-photon detection signals from the PMT were amplified with a fast preamplifier (6954, Phillips Scientific, NJ, US). The timing of the amplified signals was determined with a constant-fraction discriminator (CFD; 935, Ortec, TN, US), and the timing signals were fed to a time-to-amplitude converter (TAC; 566, Ortec, TN, US) as start signals. The X-ray arrival timing signals were supplied from the synchrotron facility and fed to the TAC as stop signals. The time difference between the two signals was compiled into a histogram with the MCA, and yielding the time profiles.

3. Results and discussion

3.1. VUV spectroscopy

Fig. 2 shows the luminescence spectra of $CsCaCl_3$ excited at 170–200 nm. Considering the band-gap energy of 8.5–8.6 eV reported previously [5,10], these excitation wavelengths correspond to the sub-band-gap excitation. Thus, the observed luminescence originates from electronic transitions in the band gap, and we attribute this to impurities or defects. Because we did not use an optical filter to remove the scattered excitation photons, the second-order and third-order diffraction peaks appeared as sharp peaks. For excitation at 200 nm, we observed a broad band at 480 nm and a shoulder at approximately 290 nm. For shorter excitation wavelengths down to 170 nm, the intensity of the two bands reversed. In addition, we observed a band at 510 nm for excitation at 170 nm. The results indicate that the $CsCaCl_3$ crystal had at least two kinds of defect or impurity cites involved in the luminescence. One plausible origin is anion vacancies, which is common lattice defect in halide crystals. Another possible origin is cation vacancies due to a slight deviation of the cation composition from stoichiometry.

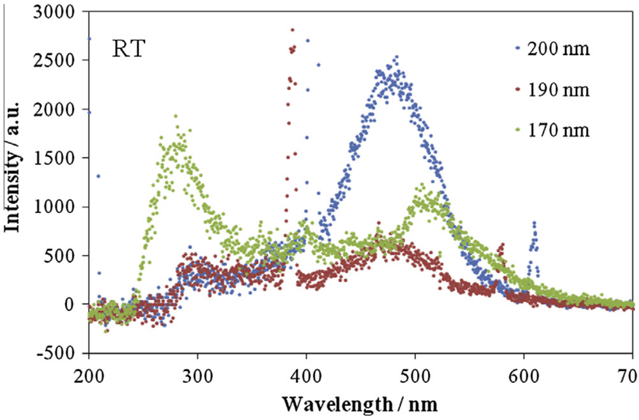

Fig. 2. Luminescence spectra of $CsCaCl_3$ for the excitation at 170–200 nm.

Fig. 3 shows the luminescence spectra of $CsCaCl_3$ excited at 160 and 130 nm. We observed a broad band peaking at approximately 440 nm for both excitation wavelengths or between them. The photoexcitation at 130 nm corresponds to the interband excitation. The photon energy at 160 nm is slightly lower than the band-gap energy, and may correspond to an exciton excitation [5]. Thus, this broad band is ascribed, presumably, to STEs.

Fig. 4 shows the luminescence spectra for excitation at 84–88 nm. Considering the position of the outermost core level of Cs, 14 eV below the conduction band [5,10], these excitation wavelengths correspond to core-level excitation. The spectrum for excitation at 84 nm differs considerably from those for the excitation wavelengths of 88 and 86 nm. For the excitation wavelength of 88 nm, the luminescence spectrum was quite similar to those for the excitation wavelengths of 130 or 160 nm shown in Fig. 3. For the excitation wavelength of 86 nm, in addition to the band centered at 440 nm, a small shoulder was observed at ca. 300 nm. For the excitation wavelength of 84 nm, a prominent broad band was observed at 300 nm, and a clear band was also observed at 500 nm. The spectrum for the excitation at 84 nm is quite similar to that in previous reports [5,10], and a broad band centered at

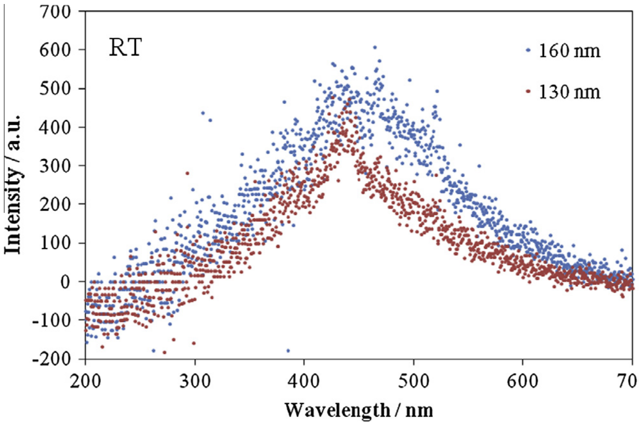

Fig. 3. Luminescence spectra of $CsCaCl_3$ for the excitation at 160 and 130 nm.