

X-ray detection capability of a Cs₂ZnCl₄ single-crystal scintillator

Natsuna Yahaba¹, Masanori Koshimizu^{1*}, Yan Sun¹, Takayuki Yanagida², Yutaka Fujimoto², Rie Haruki³, Fumihiko Nishikido⁴, Shunji Kishimoto⁵, and Keisuke Asai¹

¹Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai 9800-8579, Japan

²Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Kitakyushu 808-0196, Japan

³Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

⁴Molecular Imaging Center, National Institute of Radiological Sciences, Chiba 263-8555, Japan

⁵Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan

E-mail: koshi@qpc.che.tohoku.ac.jp

Received April 19, 2014; accepted May 7, 2014; published online May 27, 2014

The X-ray detection capability of a scintillation detector equipped with a Cs₂ZnCl₄ single crystal was evaluated. The scintillation decay kinetics can be expressed as the sum of two exponential decay components. The fast decay component had a decay time constant of 1.8 ns, and its relative intensity was 95%. The total light output was 630 photons/MeV, and a subnanosecond timing resolution of 0.66 ns was obtained. The detection efficiency of 67.4 keV X-rays was 80% for a detector equipped with a 2.2-mm-thick Cs₂ZnCl₄ crystal. Thus, excellent timing resolution and high detection efficiency were achieved simultaneously. © 2014 The Japan Society of Applied Physics

Synchrotron radiation is an essential light source for many measurement techniques because it can produce intense narrow beams over a broad energy range from infrared to hard X-ray. Furthermore, a pulsed beam can be provided by an electron bunch, making it possible to perform time-resolved measurements. Time-resolved spectroscopy or high count rate measurements using high-energy X-rays are commonly adopted techniques in synchrotron radiation facilities, and detectors that show excellent time resolution, a short dead time, and high detection efficiency for such X-rays are in great demand.

One type of detector with a short dead time and high time resolution is the silicon avalanche photodiode (Si-APD).¹⁾ In X-ray detection events, electron-hole (e-h) pairs are created in the depletion layer of APDs by the photoelectric effect. The conduction electrons then generate further e-h pairs by an avalanche multiplication process. However, it is difficult to obtain both sufficient detection efficiency and excellent timing properties simultaneously for high-energy X-rays with the Si-APD. The depletion layer needs to be thin in order to obtain excellent timing properties, but the photoelectric absorption probability of X-rays inside such a thin depletion layer is quite small owing to the low atomic number of Si; thus, the detection efficiency is very low. To achieve a high detection efficiency, a certain thickness and constituent elements with high atomic numbers are necessary.

Another candidate is a scintillation detector equipped with fast scintillators. To realize scintillation detectors having a short dead time, the scintillation materials should satisfy the following two conditions: (i) The scintillation decay time constant should be small, and (ii) the contribution of the long components and afterglow should be negligible. Plastic scintillators, which typically have decay time constants on the order of nanoseconds, are examples. They are composed of a polymer matrix and organic phosphors. A commercial plastic scintillator, NE-142, is suitable for high-energy X-ray detection because it is loaded with lead (5 wt%) to enhance the stopping power for X-rays.²⁾ However, the enhancement is limited because of either the limited solubility of the loaded elements or severe degradation in light output at high loading concentrations. In terms of the detection efficiency, inorganic scintillators are advantageous owing to the high atomic numbers of their constituent elements. In doped scintillation

materials, relatively short scintillation decay time constants have been obtained by using Ce or Pr as a dopant. For example, YAlO₃:Ce (YAP:Ce) has a decay time constant of approximately 27 ns, much longer than that of plastic scintillators, although it exhibits a high detection efficiency and large scintillation yield.³⁾ Another approach is to use undoped insulator crystals. We recently examined the applicability of a BaCl₂ single-crystal scintillator.^{4,5)} The fast scintillation component in BaCl₂ may be attributable to self-trapped excitons (STEs).⁶⁾ Although the scintillator exhibits excellent timing properties, it still has a long lifetime component on the order of several tens of nanoseconds. A scintillation material having a quantum confinement structure was also tested, and nuclear resonant scattering measurements were successfully performed;⁷⁾ however, it is quite difficult to grow a large crystal of the compound.

Another approach to the development of fast scintillation materials is the use of the Auger-free luminescence (AFL).^{8,9)} AFL is a radiative transition from the valence band (VB) to the outermost core band, and its decay time constant ranges from subnanoseconds to several nanoseconds. For AFL to be observed, the energy difference between the top of the VB and that of the core band must be smaller than the band-gap energy. AFL has been used as a fast scintillation process. BaF₂ is a representative scintillation material exhibiting AFL with a decay time constant of approximately 0.8 ns;¹⁰⁾ thus, it is used as a fast inorganic scintillator in a wide range of applications. However, BaF₂ has a long scintillation component with a decay time constant of 600 ns due to STEs,¹⁰⁾ so it is not suitable for high count rate or short dead time applications. In addition, the wavelength of the fast component ranges from the vacuum ultraviolet (VUV) to the deep UV region, so a photomultiplier tube (PMT) with a quartz window is necessary. Other crystals exhibiting AFL, such as CsF,¹¹⁾ CsCl,⁸⁾ CsBr,⁸⁾ and CsCaCl₃,¹²⁾ also have long components, possibly due to STEs, in addition to a fast scintillation component due to AFL; thus, they are inappropriate for high count rate measurements.

In this paper, we report the X-ray detection capability of a Cs₂ZnCl₄ single crystal. A previous paper reported that AFL occurs in Cs₂ZnCl₄ on the basis of the excitation spectrum in the VUV region and that the luminescence bands due to AFL under VUV excitation are located at 3.3, 4.2, and 4.8 eV.¹³⁾

The long emission wavelength in the UV region, which is characteristic of AFL in CsCl-based crystals, makes this material advantageous over BaF₂ for application as a scintillation material.^{13,14} In this paper, the scintillation properties of Cs₂ZnCl₄ under high-energy X-ray irradiation are discussed, with particular emphasis on the scintillation time profile.

A single crystal of Cs₂ZnCl₄ was grown in a vacuum quartz ampule by the Bridgman–Stockbarger method. Before crystal growth, a stoichiometric mixture of CsCl and ZnCl₂ was dried by heating at approximately 500 K under vacuum. The purity of each raw material was 99.999%. The prepared sample crystal was colorless and transparent, and it was not deliquescent. The crystal was approximately 5 × 5 × 2.2 mm³ in size.

A scintillation spectrum was obtained using an X-ray tube as an excitation source. The spectrum was recorded by a Peltier-cooled charge-coupled device (Andor DU-420-OE) coupled with a grating monochromator (Oriel Instruments, 285 grooves/mm, blaze wavelength: 280 nm).

The X-ray detection capability was characterized using synchrotron X-rays at BL-14A, Photon Factory, KEK. Single bunch mode operation was used, and the period of the successive X-ray pulses was 624 ns. The impinged X-ray energy was 67.4 keV. The beam spot was approximately 1 mm in diameter. The duration of the X-ray pulse was 140–150 ps. A scintillation time profile was obtained by a single photon counting technique. The scintillation photons were detected with a photomultiplier tube (PMT; Hamamatsu R7400P) and a fast preamplifier (Phillips Scientific 6954). The rise time of the preamplifier was 220 ps. The X-ray arrival timing signals were supplied by the accelerator, and their time resolution was 20 ps. The timing of the signals was determined by a constant fraction discriminator (CFD; Ortec 935). The time difference between the signals was converted into the pulse height by a time-to-amplitude converter (Ortec 566), and the converted signal was accumulated to a histogram with a multichannel analyzer (MCA; Aptec 5004). The scintillation time profile was obtained as a histogram of the time difference. In this measurement system, the contribution of components having a decay time constant longer than the period of successive pulses appears as the time-independent component. We also characterized a scintillation detector equipped with the Cs₂ZnCl₄ crystal. The Cs₂ZnCl₄ single crystal was attached to the PMT with optical grease. For the measurement of the pulse-height spectra, the detection signal was amplified with a charge-sensitive amplifier (Canberra 2005) and a main amplifier (Ortec 572A, Ortec); a histogram was obtained with the MCA mentioned above. The shaping time of the main amplifier was set to 0.5 μs. To estimate the scintillation light yield, the pulse-height spectrum for 1-mm-thick YAP:Ce (OKEN) was also measured for comparison. A time resolution curve was also obtained with a setup similar to that for the scintillation time profile except for the use of a fast preamplifier (Ortec VT120A). In addition, the detection efficiency was determined by comparing the count rate of the current scintillation detector with that of a scintillation detector equipped with 5 mm thick NaI:Tl.

Figure 1 shows the scintillation spectrum of the Cs₂ZnCl₄ single crystal. Three bands were observed, at 390, 280, and 255 nm. The wavelengths of these bands were consistent with those observed under VUV irradiation.¹³⁾

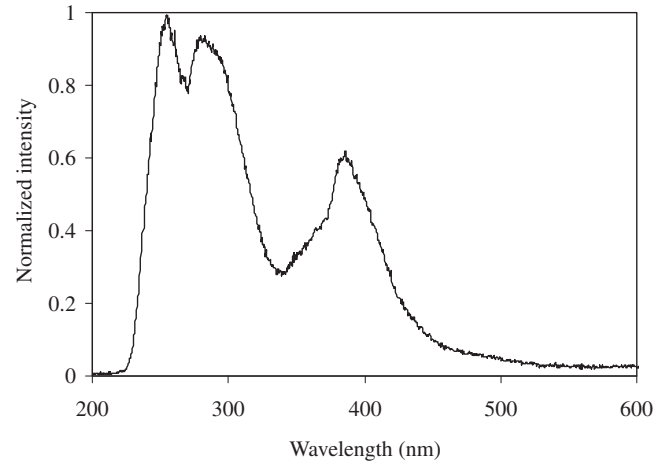


Fig. 1. Scintillation spectrum of Cs₂ZnCl₄ single crystal.

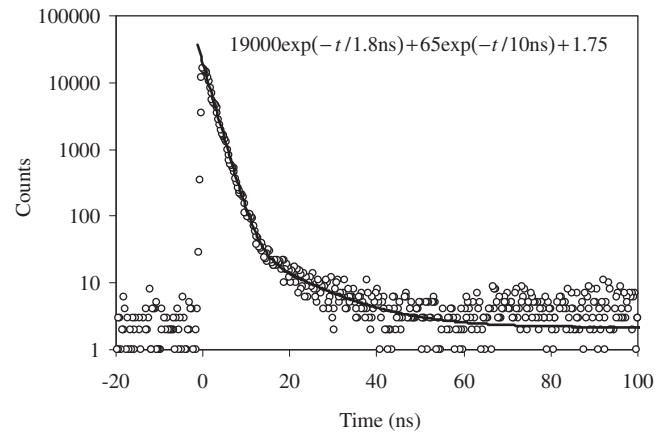


Fig. 2. Scintillation time profile of Cs₂ZnCl₄ crystal. Solid line represents function obtained by fitting.

Figure 2 is the scintillation time profile of the Cs₂ZnCl₄ crystal. The profile was reproduced as the sum of two exponential decay functions. The numerical formula for the fitted function is also shown in Fig. 2. The relative intensity of each component was calculated according to the formula. The intensity of each component was obtained by integrating the function for 624 ns, which is the period of the successive X-ray pulses. The decay time constant of the fast component was 1.8 ns, and its relative intensity was 95% of the total scintillation amount. The decay time constant of the slow component was approximately 10 ns, and its relative intensity was 2.5%. The remaining 2.5% consisted of decay components having much longer lifetimes, which are seen as time-independent components. When the X-rays were turned off, the photon count rate soon decreased to the background level. Thus, we observed no significant afterglow.

Figure 3 shows pulse-height spectra of Cs₂ZnCl₄ and YAP:Ce. The amplifier gain for the Cs₂ZnCl₄ crystal was 5 times that for YAP:Ce. In the Cs₂ZnCl₄ spectrum, a peak was observed at channel number 75. On the basis of a comparison of the peak channel numbers, the photoelectron yield of the Cs₂ZnCl₄ crystal was estimated to be 2.3% of that of YAP:Ce. Thus, the photoelectron yield is estimated to be approximately 100 photoelectrons/MeV, assuming the liter-

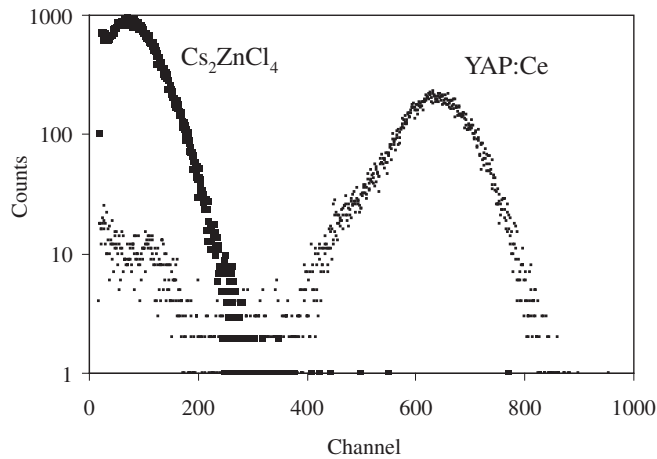


Fig. 3. Pulse-height spectra of Cs_2ZnCl_4 single crystal and YAP:Ce for 67.4 keV X-rays.

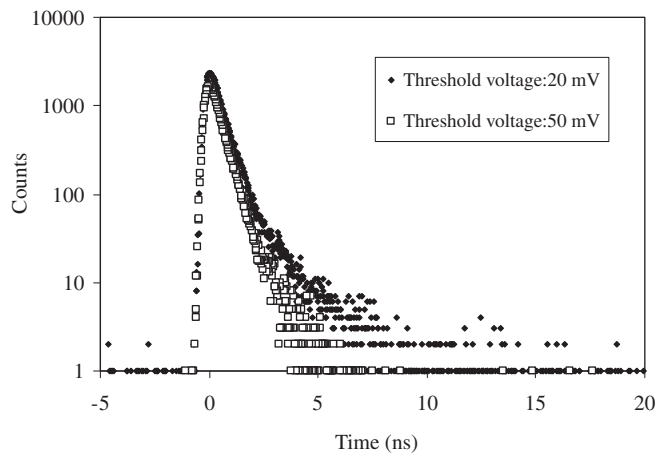


Fig. 4. Time-resolution curves of scintillation detector equipped with Cs_2ZnCl_4 crystal. Diamonds and open squares correspond to results with thresholds of 20 and 50 mV, respectively.

ature value of 4300 photoelectrons/MeV for YAP:Ce.¹⁵⁾ The average quantum efficiency of the PMT (R7400P) for the scintillation from Cs_2ZnCl_4 was estimated to be 16% on the basis of the scintillation spectrum in Fig. 1 and the wavelength-dependent sensitivity of the PMT. The photoelectron yield and average quantum efficiency led to an estimated light yield of 630 photons/MeV. The detection efficiency was calculated using the histogram shown in Fig. 3. The total count in Fig. 3 was approximately 9.4×10^4 counts, and the measurement time was 100 s. The arrival rate of the X-ray photons at the detector position was approximately 1.18×10^3 photons/s. Thus, a detection efficiency of 80% was obtained using a 2.2-mm-thick Cs_2ZnCl_4 crystal at 67.4 keV. The detection efficiency agrees well with the stopping probability for 67.4 keV X-rays of approximately 85%, which was estimated using the mass attenuation coefficients published by the National Institute of Standards and Technology.¹⁶⁾

Figure 4 shows the time-resolution curve of the scintillation detector equipped with the Cs_2ZnCl_4 crystal at a threshold voltage of 20 mV at the CFD. This threshold level corresponds approximately to the output of a single photon

Table I. Properties of fast scintillators.

	Atomic number	Slow component	Wavelength
Cs_2ZnCl_4	High	Negligible	UV-vis
BaF_2	High	Significant	VUV (fast) UV (slow)
Plastic	Low	Negligible	UV-vis

detection signal. The full width at half-maximum time resolution was approximately 0.66 ns. We observed a long tail up to 10 ns, which originated from the long scintillation components. At a threshold voltage of 50 mV, the time resolution did not differ significantly from that at the 20 mV threshold. The long tail was considerably suppressed. However, the count rate was approximately 35% less than that for the 20 mV threshold. In a crude approximation, the higher threshold level corresponds to the detection of lower-energy X-ray photons. The lower count rate at a higher threshold voltage indicates that the detection efficiency will decrease for X-rays of lower energy because of the small light yield of Cs_2ZnCl_4 .

The decay time constant of 1.8 ns for the fast scintillation component agrees well with the value of 1.6 ns for luminescence under VUV irradiation.¹³⁾ Thus, the fast scintillation component is ascribed to AFL. According to a previous paper,¹³⁾ in addition to AFL, two luminescence bands were observed at 2.4 and 6.2 eV at 10 K and were ascribed to defect luminescence. In addition, in insulators such as Cs_2ZnCl_4 , STE luminescence often contributes to the long component. The quite small contribution of the longer scintillation components in Cs_2ZnCl_4 may be ascribed to either quenching of the STEs or defect luminescence at room temperature.

Table I summarizes the properties of several fast scintillators. A Cs_2ZnCl_4 scintillator with a 2.2-mm-thick crystal exhibits high detection efficiency because of the high atomic numbers of its constituent elements and a moderate density of 2.93 g cm^{-3} . In addition, the decay time constant of the main component of 1.8 ns is comparable to or smaller than that of plastic scintillators. Thus, as a fast scintillation material for high-energy X-ray detection, Cs_2ZnCl_4 has several advantages over plastic scintillators, although the light output was rather low. In comparison to BaF_2 , the relative intensity of the fast component was much higher. In addition, the scintillation wavelength of 250–450 nm shown in Fig. 1 matches well the sensitive wavelength region of generic photon detectors, in contrast to BaF_2 , in which the wavelength of the fast component lies in the deep UV region. These advantages indicate that Cs_2ZnCl_4 is an appropriate scintillation material for high-energy X-ray detection with high detection efficiency, good timing resolution, and a high count rate.

In summary, the X-ray detection capability of a novel scintillation material, a Cs_2ZnCl_4 single crystal, was characterized. The dominant component of the scintillation time profile was a fast one having a decay time constant of 1.8 ns and a relative intensity of 95%. The scintillation light yield was estimated to be 630 photons/MeV on the basis of a comparison with YAP:Ce. A detection efficiency of 80% was achieved with a 2.2 mm thick crystal for 67.4 keV X-rays. Thus, this scintillation material is promising for high-energy

X-ray detection with high detection efficiency, good timing resolution, and a high count rate. This result indicates that the fast scintillation component is due to AFL.

Acknowledgments This research was partially supported by a Grant-in-Aid from the Adaptable and Seamless Technology Transfer Program through Target Drive R&D from the Japan Science and Technology Agency. This study was performed with the approval of the Photon Factory Advisory Committee (Proposal Nos. 2008G104, 2010G179, and 2012G062). Part of this work was carried out at the UVSOR facility, and it was supported by the Joint Studies Program (2011, No. 23-540) of the Institute for Molecular Science.

-
- 1) A. Q. R. Baron, S. Kishimoto, J. Morse, and J. M. Rigal, *J. Synchrotron Radiat.* **13**, 131 (2006).
 - 2) Data sheet of BC452 at http://www.detectors.saint-gobain.com/uploadedFiles/SGdetectors/Documents/Product_Data_Sheets/BC452-Data-Sheet.pdf (BC452 is equivalent to NE142).
 - 3) S. Kishimoto and T. Yamamoto, *Nucl. Instrum. Methods Phys. Res., Sect. A* **508**, 425 (2003).
 - 4) M. Koshimizu, K. Onodera, K. Shibuya, H. Saito, and K. Asai, *J. Appl. Phys.* **105**, 114912 (2009).
 - 5) M. Koshimizu, K. Onodera, F. Nishikido, R. Haruki, K. Shibuya, S. Kishimoto, and K. Asai, *J. Appl. Phys.* **111**, 024906 (2012).
 - 6) K. Onodera, M. Koshimizu, and K. Asai, *Radiat. Phys. Chem.* **78**, 1031 (2009).
 - 7) S. Kishimoto, K. Shibuya, F. Nishikido, M. Koshimizu, R. Haruki, and Y. Yoda, *Appl. Phys. Lett.* **93**, 261901 (2008).
 - 8) S. Kubota, J. Ruan (Gen), M. Itoh, S. Hashimoto, and S. Sakuragi, *Nucl. Instrum. Methods Phys. Res., Sect. A* **289**, 253 (1990).
 - 9) P. A. Rodnyi, *Radiat. Meas.* **38**, 343 (2004).
 - 10) M. Laval, M. Moszynski, R. Allemand, E. Cormoreche, P. Guinet, R. Odru, and J. Vacher, *Nucl. Instrum. Methods* **206**, 169 (1983).
 - 11) M. Moszyński, C. Gresset, J. Vacher, and R. Odru, *Nucl. Instrum. Methods* **179**, 271 (1981).
 - 12) M. Koshimizu, N. Yahaba, R. Haruki, F. Nishikido, S. Kishimoto, and K. Asai, *Opt. Mater.* (in press) [DOI: 10.1016/j.optmat.2014.04.004].
 - 13) A. Ohnishi, M. Kitaura, M. Itoh, and M. Sasaki, *J. Phys. Soc. Jpn.* **81**, 114704 (2012).
 - 14) A. Ohnishi, M. Saito, M. Kitaura, M. Itoh, and M. Sasaki, *J. Lumin.* **132**, 2639 (2012).
 - 15) M. Moszyński, M. Kapusta, D. Wolski, W. Klamra, and B. Cederwall, *Nucl. Instrum. Methods Phys. Res., Sect. A* **404**, 157 (1998).
 - 16) S. M. Seltzer, *Radiat. Res.* **136**, 147 (1993).