New Intrinsic Scintillator with Large Effective Atomic Number: Tl₂HfCl₆ and Tl₂ZrCl₆ Crystals for X-ray and Gamma-ray Detections

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We report on the photoluminescence and scintillation characterizations of new Tl₂HfCl₆ and Tl₂ZrCl₆ crystalline scintillators grown by the vertical Bridgman–Stockbarger method. Both Tl₂HfCl₆ and Tl₂ZrCl₆ crystals showed an intrinsic emission band peak at 450–470 nm under UV light and X-ray excitations. The scintillation light yields of Tl₂HfCl₆ and Tl₂ZrCl₆ reach 24200 and 50800 photons/MeV, respectively. Their energy resolutions at 662 keV are 17.7% for Tl₂HfCl₆ and 5.6% for Tl₂ZrCl₆. The scintillation decay time values of Tl₂HfCl₆ are 288 and 6340 ns; meanwhile, those of Tl₂ZrCl₆ are 696 and 2360 ns.

1. Introduction

Inorganic crystalline scintillators have been in use for decades to detect and measure X-ray and gamma-ray radiations as they provide an efficient means of converting a high-energy electromagnetic radiation into ultraviolet-visible photons of light that can be detected with photosensitive sensors such as a photomultiplier tube (PMT) and a photodiode (PD). The ultraviolet-visible photons are converted into a current pulse signal to be quickly counted and recorded by the PMT and PD, and thus, the scintillator-based radiation detectors belong to the indirect detector category. The number of scintillation photons as a response to a high-energy electromagnetic radiation is proportional to the current signal. Thus, the advancement of the radiation detector’s performance cannot be realized without the discovery of new scintillators with superior characteristics and the improvement of the existing scintillators. For X-ray and gamma-ray spectroscopy applications, the scintillator material must possess, in general, a large effective atomic number (Zeff), a high light yield with good energy resolution, and a fast decay time constant. In particular, the large Zeff provides high photoelectric conversion efficiencies of X-rays and gamma-rays [the probability of absorption by the photoelectric effect is proportional

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to $\rho Z_{\text{eff}}^{3-4}$ ($\rho$, density)].\(^{(1)}\) Although a classical NaI:Tl ($Z_{\text{eff}} = 50.8$) scintillator and some currently developed halide scintillators, such as SrI$_2$:Eu ($Z_{\text{eff}} = 50.3$) and CeBr$_3$ ($Z_{\text{eff}} = 47.6$), have demonstrated a high light yield and good energy resolution,\(^{(2-3)}\) their $Z_{\text{eff}}$ values are less than those of oxide-based commercial scintillators such as Gd$_2$SiO$_5$:Ce ($Z_{\text{eff}} = 59.4$), Lu$_2$SiO$_5$:Ce ($Z_{\text{eff}} = 65.4$), and Bi$_4$Ge$_3$O$_12$ ($Z_{\text{eff}} = 75.2$). Recent studies of a new scintillator material for X-rays and gamma-rays focus on Tl- and Hf-based halide scintillators because of the large atomic numbers of Tl (81) and Hf (72). Burger and co-workers have worked on the development of new Hf-based intrinsic halide scintillators and reported Cs$_2$HfCl$_6$ and Cs$_2$HfCl$_4$Br$_2$ crystals having high $Z_{\text{eff}}$ values, high light yields, and good energy resolution.\(^{(4,5)}\) Other research groups studied various Tl-based alkali halide elpasolite scintillators activated with Ce$^{3+}$.\(^{(6-9)}\) Among the elpasolite scintillators, the Tl$_2$LiYCl$_6$:Ce (TLYC) crystal shows good scintillation properties. Moreover, the TLYC crystal can distinguish gamma-ray and neutron radiations by pulse shape discrimination (PSD).\(^{(9)}\) Presently, our group has also reported some new halide scintillator materials with low hygroscopicity and large $Z_{\text{eff}}$ values, namely, CsPbCl$_3$,\(^{(10)}\) Cs$_3$BiCl$_6$,\(^{(11)}\) Rb$_2$HfCl$_6$,\(^{(12)}\) TlMgCl$_3$,\(^{(13)}\) TlCdCl$_3$,\(^{(14)}\) and Cs$_2$HfBr$_6$.\(^{(15)}\) In particular, Rb$_2$HfCl$_6$, TlMgCl$_3$, and Cs$_2$HfBr$_6$ scintillators were very interesting because they show high light yields and good energy resolution without any internal doping of an emission center. This study focused on two intrinsic halide scintillators containing Tl and Hf ions, namely, Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$. To the best of our knowledge, no other study on crystal growth, photoluminescence, and scintillation properties of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ has been reported so far. The two crystals have large $Z_{\text{eff}}$ values (72.7 for Tl$_2$HfCl$_6$ and 70.7 for Tl$_2$ZrCl$_6$), resulting in excellent photoelectric conversion efficiencies of X-rays and gamma-rays. We present and discuss results from the initial study of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystalline scintillators, grown by the vertical Bridgman–Stockbarger method, in the following sections.

## 2. Experimental Procedure

Samples of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals were prepared by the vertical Bridgman–Stockbarger method. Mixtures of TlCl (99.9%, Mitsuwa Chemicals Co., Ltd.) and HfCl$_6$ (99.9%, Mitsuwa Chemicals Co., Ltd.) or ZrCl$_6$ (99.99%, Sigma-Aldrich) raw materials in stoichiometric ratio were used for the growth of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals. The mixtures were then loaded into precleaned and prebaked quartz ampoules. The mixtures in the quartz ampoules were dried by heating overnight at 573 K in vacuum for 72 h before sealing. The crystal growth was carried out under vacuum in the sealed quartz ampoule using the vertical Bridgman furnace (TBR-30V, Techno Search Corp.). The ampoule was pulled down at a rate of 1.0–3.0 mm/h from top to bottom in a gradient temperature zone. The temperatures of the upper and lower zones in the vertical furnace were 1273 and 1073 °C, respectively, resulting in the temperature gradient of 1.3 K/mm across the solid-liquid interface. After the crystal growth was finished, the furnace was cooled to room temperature at a speed of 20 °C/h. As-grown crystals (shown in Fig. 1) were cut and polished into dimensions of $2.0 \times 1.0 \times 1.0$ mm$^3$ for use in photoluminescence and scintillation measurements. The measurements were carried out in air atmosphere because the visual observation indicated that the crystals are less hygroscopic than SrI$_2$:Eu and LaBr$_3$:Ce crystals.
The photoluminescence spectra were evaluated using an F-7000 (Hitachi High-Technologies) fluorescence spectrophotometer. The photoluminescence decay curves were measured with a DeltaFlex time-correlated single-photon counting system (Horiba). The crystal samples were excited at 250 nm using a pulsed NanoLED excitation source. The obtained decay curves were fitted to the appropriate exponential model after the deconvolution of the instrument response function.

The scintillation spectra were measured by excitation with X-rays from an X-ray generator (RINT2200, Rigaku) equipped with a copper target at power settings of 40 kV and 40 mA. The scintillation photons from the samples were counted with a SILVER-Nova multichannel spectrometer (Stellarnet Inc.) that was cooled to −15 °C using a Peltier module through an optical fiber. The crystal samples were optically coupled to the fiber head using optical grease, and Teflon tape was used as a reflector to enhance the light collection of diffuse reflections.

The scintillation decay time profiles were evaluated using a customized-setup, pulsed X-ray-induced scintillation characterization system (Hamamatsu Photonics). The main modules of the system are an R7400P-06 PMT (Hamamatsu Photonics) and an X-ray tube (N5084, Hamamatsu Photonics) controlled by a picosecond laser diode (PLP10-063, Hamamatsu). By combining the laser diode and X-ray tube, a pulsed X-ray was generated. The PMT was used to count scintillation photons in the photon-counting mode, and the detectable wavelength region of the PMT was 160 to 650 nm.

The scintillation pulse height spectra with 662 keV gamma-rays from a $^{137}$Cs source were evaluated using the sample crystals optically coupled to an R7600-200 PMT (Hamamatsu). The experimental details were described in our previous report. For better light collection, crystal samples were wrapped with Teflon tape on all sides, except the face in contact with the window of the PMT. The PMT was connected to an ORTEC 113 preamplifier, an ORTEC 572 shaping amplifier, and an Amptec 8000A multichannel analyzer (MCA). The spectra were recorded with a 10 μs shaping time. The quantum efficiency (QE) of the PMT was calculated using the wavelength response of the PMT and the scintillation spectra. The scintillation light yield was calculated by comparing the 662 keV gamma-ray-induced photopeak position of the samples with the position of the peak in spectra collected with a NaI:Tl commercial scintillator ($LY = \sim 40000$ photons/MeV).
3. Results and Discussion

Figures 2(a) and 2(b) illustrate the obtained photoluminescence spectra of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals. The intrinsic emission peak at 450–470 nm was observed upon ultraviolet light excitation for both Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals. This indicates that at least the emission process of Tl$_2$HfCl$_6$ is similar to that of Tl$_2$ZrCl$_6$. When monitoring emission at 465 nm, excitation bands at 255 nm for Tl$_2$HfCl$_6$ and at 270 nm for Tl$_2$ZrCl$_6$ were observed. Similar excitation bands were reported previously for Cs$_2$HfCl$_6$ and Cs$_2$ZrCl$_6$ crystals, and they correspond to charge transfer on HfCl$_6^{2-}$ and ZrCl$_6^{2-}$ complex ions. Considering the obtained photoluminescence spectra and referring to some previous studies about luminescence and optical characterizations of Cs$_2$HfCl$_6$ and Cs$_2$ZrCl$_6$ crystals, the origin of the blue emission band is possibly self-trapped excitons (STEs) that strongly depend on the Zr$^{4+}$ impurity in the host crystal.($^{18–20}$) Zr$^{4+}$ was detected as a major contaminant of the hafnium chloride (HfCl$_4$) raw material and grown Hf-containing halide crystals,$^{(4,19,21)}$ resulting in the creation of several types of STE states and the intrinsic luminescence of the Tl$_2$HfCl$_6$ crystal, which is similar to that of the Tl$_2$ZrCl$_6$ crystal.

The photoluminescence decay curves of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals are shown in Figs. 3(a) and 3(b), respectively. From the exponential fitting calculation, the decay time values of Tl$_2$HfCl$_6$ were approximately 324 and 3560 ns, whereas those of Tl$_2$ZrCl$_6$ were found to be approximately 360 and 3860 ns. The decay time value of Tl$_2$HfCl$_6$ was close to that of Tl$_2$ZrCl$_6$ because of the similar origins of the emission.

Figure 4 illustrates the scintillation spectra of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals. The spectrum of Cs$_2$ZrCl$_6$ (black dotted line) is also presented for comparison. The spectra of both Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals show an emission band peak at 450–470 nm. The spectra are consistent with the photoluminescence spectra, and thus, the peak can be assigned to the STEs. A similar emission band was observed for the Cs$_2$ZrCl$_6$ crystal. The slight shift in emission wavelength may be due to the difference in the monovalent cation between Cs$^+$ and Tl$^+$ since a similar emission shift was observed previously for Cs$_2$HfCl$_6$ and Rb$_2$HfCl$_6$.($^{12}$)
The scintillation decay profiles of $\text{Tl}_2\text{HfCl}_6$ and $\text{Tl}_2\text{ZrCl}_6$ crystals are shown in Figs. 5(a) and 5(b), respectively. The decay time values were calculated to be approximately 288 and 6340 ns for $\text{Tl}_2\text{HfCl}_6$ and 696 and 2360 ns for $\text{Tl}_2\text{ZrCl}_6$. From the measurements, the decay of $\text{Tl}_2\text{HfCl}_6$ and $\text{Tl}_2\text{ZrCl}_6$ crystals was found to be faster than that of $\text{Cs}_2\text{HfCl}_6$ (2200 and 8400 ns) and $\text{Cs}_2\text{ZrCl}_6$ (1500 and 7500 ns) reported previously. This is possibly caused by the difference in STE type between $\text{Cs}_2\text{MCl}_6$ and $\text{Tl}_2\text{MCl}_6$ ($\text{M} = \text{Hf, Zr}$). This difference is dependent on the crystal structure, crystalline quality, and localized electronic state. Understanding the mechanism of the difference in decay time value between photoluminescence and scintillation is clearly beyond the scope of our present study; however, we speculate that it is due to a complex energy transfer process from the host crystal lattice to emission centers under excitation by ionizing radiations.

Figure 6 illustrates the scintillation pulse height spectra of $\text{Tl}_2\text{HfCl}_6$ and $\text{Tl}_2\text{ZrCl}_6$ crystals, and the NaI:Tl commercial scintillator. In the spectra, the $^{137}\text{Cs}$-662 keV gamma-ray photopeaks of the $\text{Tl}_2\text{HfCl}_6$ and $\text{Tl}_2\text{ZrCl}_6$ crystals were located at the 250 and 525 channels, while that of the NaI:Tl commercial scintillator was observed at the 590 channel. Another peak at the 475 channel was also observed for $\text{Tl}_2\text{ZrCl}_6$ owing to the escape of $\text{K}\beta$ and $\text{K}\alpha$ X-rays from Tl atoms of the crystal. The QE of the R7600U PMT at 465 ($\text{Tl}_2\text{HfCl}_6$ and $\text{Tl}_2\text{ZrCl}_6$) and
415 nm (NaI:Tl) were about 28 and 40%, respectively. Thus, the light yields of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals were calculated to be approximately 24200 and 50800 photons/MeV on the basis of a comparison of NaI:Tl. The energy resolutions (FWHMs) of the 662 keV photopeak are approximately 17.7% for Tl$_2$HfCl$_6$ and 5.6% for Tl$_2$ZrCl$_6$. From the measurements, the Tl$_2$ZrCl$_6$ crystal was particularly found to show a high scintillation light yield with good energy resolution, possibly because crystalline quality depends on the purity of starting materials and the crystal growth conditions. The poor energy resolution for Tl$_2$HfCl$_6$ is possibly due to low crystalline quality and chemical composition uniformity because of the high vapor pressure of HfCl$_4$ during melt growth.$^{24}$ We expect that further improvement of the quality and composition uniformity of Tl$_2$HfCl$_6$ can result in a higher energy resolution.

4. Summary

Two new intrinsic crystalline scintillators, Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$, were reported. Crystal samples of Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ were successfully grown by the vertical Bridgman–Stockbarger method. For both Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals, the photoluminescence and scintillation spectra showed an emission band peak at 450–470 nm without any internal doping.
of an emission center. The scintillation light yields were calculated to be approximately 24200 photons/MeV with the energy resolution of 17.7% at 662 keV for Tl$_2$HfCl$_6$ and 50800 photons/MeV with the energy resolution of 5.6% at 662 keV for Tl$_2$ZrCl$_6$. For Tl$_2$HfCl$_6$, the scintillation decay time value was estimated to be approximately 288 and 6340 ns, while Tl$_2$ZrCl$_6$ gave the decay time values of 696 and 2360 ns. Both Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystals had an emission band peak at 450–470 nm with a high scintillation light yield, which well matched the sensitivity wavelengths of the commercial PMT and Si-based photodiodes. Future efforts toward understanding the origin of these emissions and growing high-quality crystals are expected to further improve the scintillation characteristics. This study indicates that the Tl$_2$HfCl$_6$ and Tl$_2$ZrCl$_6$ crystalline scintillators can be promising candidates for next-generation X-ray and gamma-ray detectors for various applications.

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