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The growth and scintillation properties of $CsCe_2Cl_7$ crystal

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ABSTRACT

We report on a new scintillation crystal, $CsCe_2Cl_7$, for γ-ray spectroscopy. The crystal was grown using the Czocralski pulling method. X-ray excited luminescence measurements of the $CsCe_2Cl_7$ showed a broad emission band in the wavelength range from 370 to 470 nm with a peak centre at 410 nm. An energy resolution (FWHM of peak position) for the 662 keV full energy peak of 5.5% was observed at room temperature. The results showed a good proportionality for light output versus γ-ray energy. The light output deviation from the linear response is about 10% between the energy range of 31 and 1333 keV. We measured a light yield of 28,000 photons/MeV of absorbed γ-ray energy. The scintillation decay curve of $CsCe_2Cl_7$ can be described by a single exponential decay function with a decay time of 50 ns. Overall, these measurements clearly indicate that $CsCe_2Cl_7$ can exhibit attracting scintillation properties, and we believe that the $CsCe_2Cl_7$ crystal is a promising material for medical imaging and radiation detection.

1. Introduction

Scintillators are widely used for the detection of various kinds of ionizing radiation. Inorganic crystalline scintillators are used in devices for high-energy physics, tomography, astronomy, astrophysics, well logging, etc. Since the discovery of scintillation in NaI:Tl in 1948 by Hofstadter [1], significant efforts have been put into the search for scintillator materials with superior performance. For most applications, a good scintillation spectrometer should have high light output, high density, a fast decay time, good linearity, excellent energy resolution and low cost. These requirements cannot be met by any of the available scintillators, and as a result, there is a continued interest in the search for new scintillators with an enhanced performance [2–5]. It has been known for a long time that trivalent cerium emits fast scintillation (15–60 ns) in the 300–600 nm wavelength region. In recent years substantial research has been carried out in cerium-doped crystals; among these $LaCl_3:Ce^{3+}$ [6] and $LaBr_3:Ce^{3+}$ [7] showed excellent scintillation properties. The energy resolution obtained for $LaCl_3:Ce^{3+}$ and $LaBr_3:Ce^{3+}$ was 3.3% and 2.85% (FWHM), respectively, at 662 keV. The measured light output and decay time for these crystals were 46,000 and 61,000 photons/MeV at 662 keV and 26 and 35 ns, respectively. However, both materials are highly hygroscopic and have a high propensity to crack during the high-temperature growth and the subsequent cooling down processes.

In this article we report on the growth and scintillation properties of a new scintillation crystal, $CsCe_2Cl_7$. In this crystal Ce^{3+} is a constituent as well as a luminescence centre for the scintillation process. The scintillation properties measured were emission spectra, light output and fluorescence decay time of the crystal. The energy resolution and linearity response were also measured. The $CsCe_2Cl_7$ single crystal has a higher effective Z-number and is less hygroscopic than the $LaBr_3:Ce^{3+}$ crystal.

2. Experimental procedure

$CsCe_2Cl_7$ was identified and structurally characterized by Seifert et al. [8]. It has a hexagonal crystal structure with four formula units in the unit cell and lattice parameters a=9.72 Å and c=14.94 Å. The volume of the unit cell is 1222.8 (Å)^3. Based on its structure and lattice parameters, the $CsCe_2Cl_7$ single crystal has a calculated density of 3.60 gm/cm^3.

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In our research, we used the Czocralski technique to grow $CsCe_2Cl_7$ single crystal, since this technique is easy to implement and can provide a good indication of the feasibility of producing a large crystal of $CsCe_2Cl_7$ from the melt. Ultra-dry forms of CsCl and $CeCl_3$ (Sigma-Aldrich, >99.9%) were used as starting materials. The material was synthesized in an argon-filled glove box using the reaction

$$CsCl + 2CeCl_3 \rightarrow CsCe_2Cl_7$$

Polycrystalline $CsCe_2Cl_7$ powder was synthesized from the analytical reagents CsCl and $CeCl_3$ at a 1:2 molar ratio. A total of 30 gm of $CsCe_2Cl_7$ powder was thoroughly mixed by using a ceramic ball mill at an intermediate grinding speed for 48 h. The mixed polycrystalline $CsCe_2Cl_7$ material was transferred again to an argon-filled glove box and was loaded into a platinum crucible with a diameter of 30 mm and height of 30 mm. In order to sinter the mixed polycrystalline $CsCe_2Cl_7$ material, the crucible was heated at 600 °C for 12 h inside the Czocralski chamber and then the temperature was raised to about 710 °C for 5 h to ensure that the materials melted thoroughly. The temperature was then lowered to around 690 °C at a rate of 10 °C/h. A platinum bar with a diameter of 2.5 mm was lowered into the melt to induce the crystallization of the melt in order to obtain the seed. The platinum bar was rotated at a rate of 20 rpm at a pulling rate of 2 mm/h. In this way we obtained a 10 mm-long thin seed. The same rotation rate and pulling rate was reduced to 1 mm/h, and we successfully pulled a single crystal up to 10 mm in length and 10 mm in the diameter from the melt. After the growth process was over, the furnace was cooled to room temperature at the rate of 10 °C/h. Although the cooling rate was very slow, many cracks appeared in the ingot during the cooling process; however, a small crack-free sample having the dimensions of $3 \times 3 \times 1\,mm^3$ was successfully cut and polished from the ingot for the study of scintillation properties. It was found that there was only a narrow temperature range around the melting point in which the crystal could grow well. White polycrystals appeared when the temperature of the melt surface was a little bit lower than the melting point, whereas the seed crystal melted when the surface temperature was increased by only 3 °C. The possible reason responsible for this phenomenon can be attributed to a very narrow supercooling range for this compound. In order to measure the X-ray emission spectrum of the $CsCe_2Cl_7$ crystal, X-rays from a tungsten target were generated by the bombardment of an accelerated beam of electrons from a Linac (KD Siemens) at 6 MV. The X-ray emission spectrum was measured using a USB4000 fiber optic spectrometer made by ocean optics. The energy resolution and the scintillation decay time measurements at room temperature were performed with a pulse height analysis system equipped with a 2-in bialkali photocathode photomultiplier tube (9208B, Electron Tubes Ltd.). The crystal was covered with several layers of 0.1 mm-thick Teflon tape except for the surface, which was coupled to the PMT. The $CsCe_2Cl_7$ single crystal was then directly coupled with the entrance window of the PMT using the index matching optical grease. We used ^{133}Ba, ^{109}Cd, ^{57}Co, ^{137}Cs, ^{22}Na, ^{54}Mn and ^{60}Co γ-ray sources to excite the crystal at energies between the range of 31 and 1333 keV. Signals from the PMT were amplified using a home-made amplifier with a low noise and a high slew rate. The output signals were then fed into a 400 MHz flash analog-to-digital converter (FADC) [9]. The trigger was formed in the field programmable gate array (FPGA) chip on the FADC board. The FADC was located in the VERSA module eurocard bus (VME) crate and was read out by using a Linux operating PC through the VME-USB2 interface [10,11].

3. Results and discussion

We measured the emission spectrum of the $CsCe_2Cl_7$ single crystal. Fig. 1 shows the emission spectrum of the $CsCe_2Cl_7$ single crystal. The emission spectrum of $CsCe_2Cl_7$ consisted of a broad band spanning from 370 to 470 nm wavelength with a maximum at 410 nm. This emission wavelength is due to the $5d \rightarrow 4f$ transition of Ce^{3+}. The peak position wavelength of 410 nm is attractive for γ-ray spectroscopy, since it matches well with the spectral response of the photomultiplier tubes as well as a new generation of silicon photocathodes.

The proportionality of response is an important factor in the performance characteristics of scintillation detectors and one of the reasons for the degradation in the energy resolution of established scintillators such as NaI:Tl, CsI:Tl and LSO:Ce^{3+} [12,13]. We evaluated the proportionality of the $CsCe_2Cl_7$ single crystal and measured the light output of $CsCe_2Cl_7$ under excitation from different radio-isotopes such as ^{133}Ba (31, 81 and 384 keV γ-rays), ^{109}Cd (88 keV γ-rays), ^{57}Co (122 keV γ-rays), ^{137}Cs (662 keV γ-rays), ^{22}Na (511 and 1275 keV γ-rays), ^{54}Mn (835 keV γ-rays) and ^{60}Co (1333 keV γ-rays). The relative light output of the $CsCe_2Cl_7$ single crystal at each γ-ray energy was estimated from the measured peak position and the known γ-ray energy for each isotope. The data points were then normalized with respect to the light output value at 662 keV energy. The resulting proportionality plot is shown in Fig. 2. Over the energy range from 31 to 1333 keV, the non-proportionality is about 10%, and this is substantially better than that for many established scintillators. For example, almost over the same energy range, the non-proportionality is about 35% for LSO:Ce^{3+} and about 20% for NaI:Tl and CsI:Tl [14].

The energy resolution, $R=\Delta E(\mathrm{FWHM})/E$, of the full energy peak measured with a scintillator coupled to a photomultiplier tube can be written as $\Delta E/E=2.35\sigma(E)$ (in %), where ΔE is the full-width at half-maximum of a photo peak occurring at the pulse height E and $\sigma(E)$ is the standard deviation in the pulse height spectrum [15]. We measured the energy resolutions of the crystal for different γ-ray energies associated with various radio-isotopes. This involved the coupling of the $CsCe_2Cl_7$ single crystal to the PMT and irradiated with different radio-isotopes in order to obtain the respective energy photopeaks. From the recorded photopeaks, the energy resolutions were calculated by Gaussian fitting. The data plotted as a function of energy, as shown in Figs. 3(a) and (b), show the pulse height spectrum of 662 keV γ-rays from a ^{137}Cs

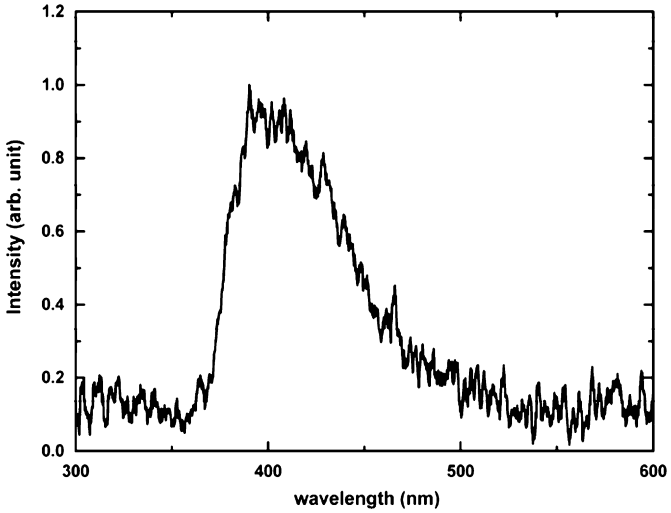

Fig. 1. X-ray emission spectrum of $CsCe_2Cl_7$ single crystal at room temperature.