Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Characterization of the intrinsic scintillator $Cs_2LiCeCl_6$

U.N. Roy*, G. S. Camarda, Y. Chen[†], Y. Cui, R. Gul, A. Hossain, G. Yang, P. Vanier, and R.B. James[††]
Brookhaven National Laboratory, Upton, NY 11973, United States
[†]Present address: Key Laboratory of Particle & Radiation Imaging, Tsinghua University, Ministry of Education, Beijing, 100084, China.
[††]Present address: Savannah River National Laboratory, Aiken, SC 29808, United States

Abstract

In this work, we report on the scintillation properties of the intrinsic scintillator $Cs_2LiCeCl_6$ (CLCC), which is potentially useful for dual gamma-ray and neutron detection. CLCC is from the elpasolite family with a cubic structure. We grew the crystals at BNL by the vertical Bridgman growth technique. The luminescence spectrum of CLCC showed a doublet with peak maxima at 384 nm and 402 nm. The light yield of CLCC was approximately 20,000 photons/MeV, and the energy resolution was about 6% for 662-keV gamma radiation. A scintillation decay of ~81% of the total light was observed to be ~ 90 nanoseconds.

Key words: A1. Characterization, A2. Bridgman, B1. Halides, B2. Scintillating materials.

*E-mail address: uroy@bnl.gov

1. Introduction:

Scintillators are widely used as X- and gamma-ray detectors in applications such as non-proliferation, homeland security and medical imaging. Since the discovery of NaI:Tl as a scintillator in 1948 by Hofstadter [1], significant efforts have been invested in the search of scintillator materials with superior performance, mainly better energy resolution to address the need for identification of radionuclides with relatively low-cost materials and with high efficiency. The highest energy-resolution (< 3% at 662 keV) scintillators available today for gamma-ray radiation detectors are $LaBr_3$:Ce and SrI_2:Eu [2-5]. For dual gamma- and neutron-detector applications, Cs_2LiYCl_6:Ce (CLYC) is possibly the most widely used scintillator material [6,7].

Most of the scintillators used today are doped with extrinsic activators. The performance of such doped scintillators may be significantly degraded with an increase in the detector's volume due to the segregation of the dopant (i.e., the activator) along the growth direction and the effects of microscopic growth striations, thus lowering the yield of large-volume detectors, reducing the efficiency for detection, and increasing their cost. In contrast, intrinsic compounds tend to avoid inhomogeneity of the material throughout the grown ingot, and thus are expected to produce a much more uniform response from the detector, potentially independent of its volume. There are a few intrinsic scintillators investigated previously by other researchers, such as $CeBr_3$, K_2CeCl_5 and K_2CeBr_5 for gamma-ray-only detector applications [8-10]. Recently, Burger et al. [11] discovered an efficient intrinsic scintillator Cs_2HfCl_6 for gamma-ray detection applications, which is non-hygroscopic and has an energy resolution of 3.3 % at 662 keV.

Recently, Rooh et al. [12] reported a new intrinsic scintillator material $Cs_2LiCeCl_6$ (CLCC), which has the potential for dual gamma- and neutron-detector applications based on the presence of ^6Li in the compound, which has a high capture cross-section for thermal neutrons plus the

conversion to energetic charged particles and gamma rays upon decay. The compound $Cs_2LiCeCl_6$ is from the elpasolite family with cubic structure [13]. The calculated density of the material is 3.141 gm/cm^3 [12]. In this paper we report the scintillator characteristics of $Cs_2LiCeCl_6$ grown by the vertical Bridgman method.

2. Experimental

The crystals were grown by the vertical Bridgman growth technique in a conically tipped quartz ampoule with an inner diameter of either 12 or 22 mm. The starting materials used were 99.999% pure anhydrous CsCl, > 99.99% pure anhydrous $CeCl_3$ and > 99% pure anhydrous LiCl, procured from Sigma Aldrich. The $Cs_2LiCeCl_6$ compound was synthesized in a sealed quartz ampule via the reaction, $2CsCl+CeCl_3+LiCl = Cs_2LiCeCl_6$. The synthesis and growth were carried out in the same ampoule. After loading the raw materials, the ampoule was evacuated and then heated at ~200 °C for 18 hours under dynamic vacuum prior to sealing under the vacuum of ~ $3x10^{-6}$ torr. The crystals were grown by the vertical Bridgman growth technique at a rate of 1.4 cm/day. The as-grown crystals are highly hygroscopic in nature and were stored in mineral oil after growth.

Optically excited emission spectra and excitation spectra were acquired using an ISS Photon Counting Spectrofluorimeter PC1 at BNL's Center for Functional Nanomaterials (CFN). The scintillation decay excited by 662-keV gamma rays using a ^{137}Cs source was measured from the output of a Hamamatsu R2059 photomultiplier tube using a Tektronix MSO 5104 digital oscilloscope. A Canberra model 2005 preamplifier was used to acquire pulse-height spectra for different excitation sources.

3. Results and discussion

Figure 1a shows the optically excited (λ_{exc}=280 nm) emission spectrum of $Cs_2LiCeCl_6$ at room temperature. The broad emission peak ranges from ~370 nm to ~440 nm with doublet peaks centered at 384 nm and 402 nm. This doublet is characteristic of Ce^{3+} emission due to the *d-f* transition, and it is similar to the emission peak of CLYC [6]. Rooh et al. [12] also observed a similar emission spectrum with two bands at 385 nm and 405 nm for CLCC grown by the Bridgman method, which agrees well with our present observation. The excitation spectrum for the same CLCC sample is shown in Figure 1b. The broad excitation spectrum shows two bands with the longer-wavelength intense peak at 366 nm. There is a fair amount of overlap of the emission and excitation spectra, which might contribute to self-absorption. However, the self-absorbed photons can be re-emitted as was observed for CLYC [7]. The decay time for the CLCC sample recorded at room temperature is shown in Figure 2. The sample was excited by 662-keV gamma radiation using a ^{137}Cs source. As expected, the decay curve exhibits multiple decay time constants similar to other known scintillators.

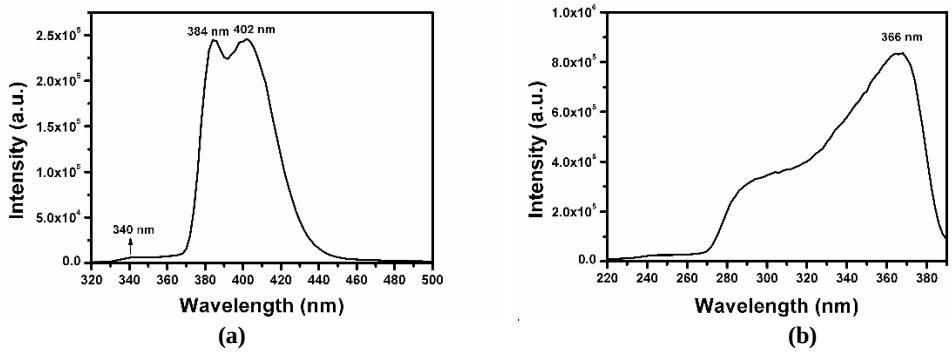

Figure 1. a) Optically pumped emission spectrum for an excitation wavelength of 280 nm, and b) the excitation spectrum of $Cs_2LiCeCl_6$.

The fastest decay time constant is ~90 ns and contributes to ~80% of the total light yield. The decay time constant agrees fairly well for the earlier reported value of ~100 ns for CLCC [12]. However, the decay time is much faster than the reported value of ~ 600 ns [6] for CLYC. The

intermediate decay time constant is 566 ns followed by the longest time constant of ~20 µs as shown in Figure 2. While the intermediate decay time constant agrees fairly well with the previous reported value of 557 ns [12], the longest decay time constant observed for the present sample is much longer than the previously reported value (~3 µs) [12]. However, in the present case, only 2.6% of the total light yield decays with the longest decay time constant, while for the previously reported value, 23% of the total light yield was part of the longest decay with a time

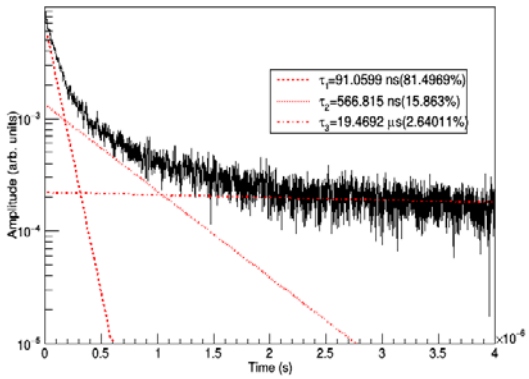

Figure 2. Fluorescence decay obtained from $Cs_2LiCeCl_6$ using 662-keV gamma excitation from a ^{137}Cs source.

constant of ~ 3 µs [12]. The light yield of the grown material was found to be ~20,000 photons/MeV, as estimated comparing the pulse height with a standard Bismuth Germanium Oxide (BGO) crystal using the 662-keV gamma line from a ^{137}Cs source. The light output value agrees fairly well with the reported value of 22,000 photons/MeV by Rooh et al. [12]. The pulse-height spectrum of the CLCC crystal at room temperature for a ^{137}Cs source is shown in Figure 3. The inset shows an optical photograph of the sample, immersed in mineral oil, used for the pulse-height measurement; its dimensions are~8x8x5 mm^3. The sample was optically coupled with a PMT window using optical grease, and the top and side walls of the sample were covered with teflon tape. The energy resolution obtained at 662 keV was ~ 6%. The energy resolution,

however, can be improved by purifying the synthesized material by a zone refining process and by improving the crystal growth to reduce the concentration of defects.

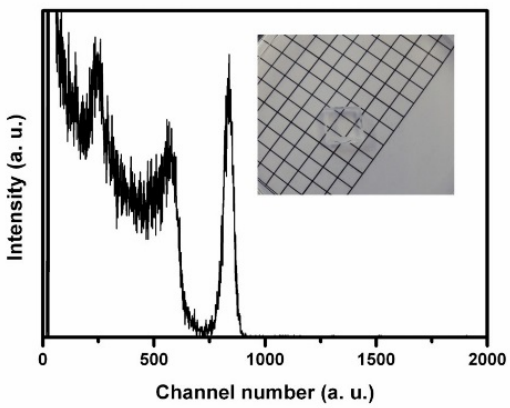

Figure 3. Pulse-height spectrum of $Cs_2LiCeCl_6$ measured with a ^{137}Cs source. The inset shows a picture of the CLCC sample.

4. Summary

We have demonstrated the growth of single crystals of $Cs_2LiCeCl_6$ scintillator material with diameter of 22mm. The $Cs_2LiCeCl_6$ scintillator material from the elpasolite family with cubic structure has potential for growth of large-volume single crystals. The light yield and the density of CLCC are comparable to CLYC, while its decay time is faster than CLYC. The energy resolution at 662 keV was found to be ~6%. Further improvements in the performance of CLCC are expected by growing better crystals with fewer defects and by additional purification of the initial charge by zone refining. The intrinsic scintillator CLCC holds tremendous promise to compete with CLYC based on its potential for growth of relatively uniform large-volume crystals and the possibility of dual gamma-neutron detector applications.

Acknowledgments

This work was supported by Laboratory Directed Research and Development (LDRD) funding at Brookhaven National Laboratory. The authors would like to acknowledge Crytur, Czech

Republic for providing the BGO crystal. This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science User Facility at Brookhaven National Laboratory under Contract No. DE-SC0012704. The manuscript has been authored by Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy.

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Captions to the figures

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