LaCl₃:Ce scintillator for γ-ray detection

K.S. Shah*a,*, J. Glodoa, M. Klugermana, L. Cirignanoa, W.W. Mosesb, S.E. Derenzob, M.J. Weberb

Radiation Monitoring Devices, Watertown, MA 02472, USA
Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Abstract

In this paper, we report on a relatively new cerium-doped scintillator—LaCl₃ for γ-ray spectroscopy. Crystals of this scintillator have been grown using Bridgman method. This material when doped with 10% cerium has high light output (~50,000 photons/MeV) and fast principal decay time constant (~20 ns). Furthermore, it shows excellent energy resolution for γ-ray detection. For example, energy resolution as low as 3.2% (FWHM) has been achieved with 662 keV photons (¹³⁷Cs source) at room temperature. Also, high timing resolution (264 ps—FWHM) has been recorded with LaCl₃-PMT and BaF₂-PMT detectors operating in coincidence using 511 keV positron annihilation γ-ray pairs. Details of crystal growth, scintillation properties, and variation of these properties with cerium concentration are also reported.

Keywords: Scintillation crystals; Rare-earth trihalides; LaCl₃:Ce; γ-detection

1. Introduction

Scintillation spectrometers are widely used in detection and spectroscopy of energetic photons (γ-rays) as well as neutrons. These detectors are commonly used in nuclear and high-energy physics research, medical imaging, diffraction, non-destructive testing, nuclear treaty verification and safeguards, and geological exploration [1,2].

Important requirements for the scintillation crystals used in these applications include high light output, high stopping power, fast response, low cost, good linearity, and minimal afterglow. These requirements cannot be met by any of the commercially available scintillators thus there is a continued interest in search for new scintillators with enhanced performance. Recently, a new cerium-doped halide scintillator—LaCl₃ with attractive scintillation properties has been discovered [3]. LaCl₃ (doped with 10% Ce³⁺) has a very high light output (~49,000 photons/MeV), and fast principle decay time constant (26 ns) [3]. These properties make LaCl₃:Ce a very promising material for γ-ray spectroscopy.

In view of the attractive properties of LaCl₃:Ce for γ-ray detection, and availability of only very...
small crystals, we have performed investigation of
the crystal growth of this material and explored its
capabilities for $\gamma$-ray detection. In this paper, we
report on LaCl$_3$:Ce crystal growth and evaluation
of its scintillation properties with four different Ce
concentrations.

2. Crystal growth of LaCl$_3$:Ce

LaCl$_3$ crystals have hexagonal (UCl$_3$ type)
structure with P6$_3$/m space group and their density
is 3.9 g/cm$^3$. The compound melts congruently at
860°C and therefore its crystals can be grown
using melt-based methods such as Bridgman and
Czochralski. This is fortunate because these melt-
based processes are well suited for growth of large-
volume crystals [4]. In our research, we used
Bridgman method for growing LaCl$_3$:Ce crystals
because this technique is easy to implement, and
can provide good indication of the feasibility of
producing large crystals of LaCl$_3$:Ce from the
melt. Ultra-dry forms of LaCl$_3$ and CeCl$_3$
were used with 99.99% purity. A two-zone verti-
cal Bridgman furnace was used with temperature
in the upper zone above the melting point
LaCl$_3$ (860°C) and that of the lower zone below
860°C. The amount of CeCl$_3$ in the feed mat-
nerial was adjusted to produce LaCl$_3$:Ce samples
with varying Ce$^{3+}$ concentration. Most growth
runs were performed with 10% cerium concentra-
tion, although some runs were also performed
with other Ce concentrations (0.1%, 1.0% and
20%) in order to study the effect of variation in
cerium concentration on the scintillation prop-
ties of LaCl$_3$. LaCl$_3$ crystals with size up
to $\sim$2.5 cm$^3$ were grown using Bridgman method.
These crystals were cut from the solid ingots
and polished using non-aqueous slurries (due
to hygroscopic nature of LaCl$_3$) prepared by
mixing mineral oil with Al$_2$O$_3$ grit. The crystals
were then packaged to prevent long exposure
to moisture. This involved encapsulating the
crystal in an epoxy (EPO-TEK epoxy 301-2) with
a thin quartz window (0.5 mm) placed on
the crystal face which would be coupled to an
optical sensor.

3. Scintillation properties of LaCl$_3$:Ce

We have performed characterization of the
scintillation properties of LaCl$_3$ crystals grown
by the Bridgman method. This investigation
involved measurement of light output, emission
spectra, and the scintillation time profiles. Vari-
tions of these properties with Ce concentration
were measured.

3.1. Light output measurements

The light output of LaCl$_3$:Ce crystals was
measured by comparing their response to
662 keV $\gamma$-rays ($^{137}$Cs source) to the response of
a BGO scintillator (see Fig. 1). These measure-
ments involved optical coupling of a LaCl$_3$:Ce
 crystal ($\sim$1 cm$^3$ in size) to a photomultiplier tube
(Hamamatsu R2059), irradiating the scintillator
with 662 keV photons and recording the resulting
pulse height spectrum. In order to maximize light
collection, LaCl$_3$:Ce crystals were wrapped in
reflective white Teflon tape on all faces (except
the one coupled to PMT). An index matching
silicone fluid was also used at the PMT–scintillator
interface. A pulse height spectrum was recorded
with an amplifier shaping time of 4.0 $\mu$s with a
LaCl$_3$:Ce crystal doped with 10% Ce. This
experiment was then repeated with a BGO
scintillator (which was assumed to have light output of \( \sim 8000 \) photons/MeV). Fig. 1 shows measured pulse height spectra for both LaCl\(_3\):Ce and BGO. Based on the recorded photopoint positions and by taking into account the photocathode quantum efficiency for BGO and LaCl\(_3\):Ce, we estimated the light output of LaCl\(_3\):Ce crystal with 10% Ce to be about 50,000 photons/MeV at 4 \( \mu \)s shaping time. This light output is amongst the highest values for inorganic scintillators [1].

We also studied variations in light output of LaCl\(_3\):Ce crystals as a function of the cerium concentration. Crystals with cerium concentration of 0.1%, 1.0%, 10%, and 20% were investigated. Each crystal was coupled to PMT and 60 keV \( \gamma \)-ray spectra (\(^{241}\)Am source) were recorded under identical operating conditions. Data was collected at shaping time of 4 \( \mu \)s and the results are shown in Fig. 2. As seen in the figure, the light output of LaCl\(_3\):Ce samples with Ce concentration up to 10% is similar while that of the one with 20% Ce is slightly lower. The estimated values of light output for all four Ce concentrations are listed in Table 1.

### 3.2. Emission spectra

We measured the emission spectra of LaCl\(_3\):Ce samples under X-ray excitation using a Philips X-ray tube with a copper target and operating at 40 kVp and 20 mA. The emitted light was passed through a McPherson monochromator and detected by a Hamamatsu R2059 photomultiplier tube with a quartz window. The system was calibrated with a standard light source to enable correction for sensitivity variations as a function of wavelength. Fig. 3 shows the normalized emission spectra for LaCl\(_3\):Ce samples with 0.1%, 1.0%, 10%, and 20% Ce concentrations. As seen in the figure, an emission peak with \( \lambda_{\text{max}} \) of 350 nm is present for all four cerium concentrations. In addition, another broad emission peak with \( \lambda_{\text{max}} \) in 420–440 nm range is also present. For higher Ce concentrations (10% and 20%), almost all light is

![Fig. 2. \(^{241}\)Am spectra (60 keV photons) recorded with LaCl\(_3\):Ce crystals of different Ce concentrations. From the peak position light output was estimated for each crystal, see Table 1.](image1)

![Fig. 3. Optical emission spectra for LaCl\(_3\) samples with different Ce concentrations. Spectra were normalized with respect to 350 nm peak intensity.](image2)

<table>
<thead>
<tr>
<th>Ce concentration</th>
<th>Light output (photons/MeV)</th>
<th>Decay time (ns)</th>
<th>Emission peak (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>50,500</td>
<td>20 (15%), 213 (85%)</td>
<td>350, 430</td>
</tr>
<tr>
<td>1</td>
<td>50,500</td>
<td>20 (33%), 213 (67%)</td>
<td>350, 430</td>
</tr>
<tr>
<td>10</td>
<td>50,000</td>
<td>20 (70%), 213 (30%)</td>
<td>350, 430</td>
</tr>
<tr>
<td>20</td>
<td>38,000</td>
<td>25 (76%), 63 (13%), 213 (11%)</td>
<td>350, 430</td>
</tr>
</tbody>
</table>
emitted in the 350 nm band while for lower Ce concentrations (0.1% and 1.0%), a significant fraction of total light appears in the second, 420 nm band. These two peaks probably arise due to different light emission mechanisms [3,6] and may have considerable impact on the time profiles of LaCl₃:Ce emission with varying Ce concentration.

3.3. Decay time profiles

The scintillation time profiles of LaCl₃:Ce crystals (with 0.1%, 1.0%, 10% and 20% Ce) were measured by the delayed coincidence method [5] using LBNL Pulsed X-ray Facility. The X-ray source is a light-excited X-ray tube that produces 4000 X-ray photons (mean energy 18.5 keV) per steradian in each 1 ps FWHM pulse at a 50 kHz repetition rate. The LaCl₃:Ce samples were placed in the X-ray beam and their fluorescent emissions were detected with a sapphire-windowed microchannel plate photomultiplier tube (spectral range 150–650 nm, transit time jitter 40 ps FWHM). The time difference between the X-ray pulse and the detected fluorescent emission was measured using a TAC/ADC combination having 2 ps FWHM resolution. The total system response time is 60 ps FWHM. The time profile for each LaCl₃:Ce sample was measured up to 430 ns after X-ray exposure in this manner and was fitted to the sum of exponential components, and a time-independent background. The results are shown in Fig. 4 and Table 1. All data were consistent with an instantaneous (<200 ps) risetime. As seen in the figure, samples with high Ce concentration (10% and 20%) show very fast principal decay time constant (20–25 ns), while the principal decay time constant is slower (∼213 ns) for LaCl₃:Ce samples with lower Ce concentration (0.1% and 1%).

The emission spectra and time profile measurements reveal some interesting patterns in scintillation behavior of LaCl₃:Ce samples. As seen in Figs. 3 and 4, for higher Ce concentrations (10% and 20%), much of the emitted light appears in the scintillation peak with \( \lambda_{\text{max}} = 350 \text{ nm} \), and the principal decay time constant for these LaCl₃:Ce samples with higher Ce concentration is also very
4. γ-ray detection with LaCl₃:Ce

4.1. Energy resolution

We measured γ-ray energy resolution of LaCl₃:Ce scintillator. This involved coupling an unpackaged LaCl₃:Ce crystal (~1 cm³ size, 10% Ce) to a photomultiplier tube (Hamamatsu R2059). The sample was coated with Teflon tape to maximize the light collection. It was irradiated with 662 keV γ-rays (¹³⁷Cs source), and the resulting PMT signal was processed with a preamplifier (Canberra 2005), and then shaped with a spectroscopy amplifier (Canberra 2022). A ¹³⁷Cs pulse height spectrum was recorded with shaping time of 4 μs as shown in Fig. 1. Energy resolution for the 662 keV peak was calculated to be about 3.2% (FWHM) at room temperature, which is excellent for scintillator-based systems and has never been achieved with established inorganic scintillators (even with small crystals). We expect to further improve the energy resolution of the LaCl₃:Ce scintillators by optimizing the light collection at the PMT/LaCl₃:Ce interface, and by improving the overall quality and packaging of LaCl₃:Ce crystals.

4.2. Proportionality of response

We have evaluated the proportionality of response (or linearity) of LaCl₃:10% Ce scintillator. Non-proportionality (as a function of energy) in light yield can be one of the important reasons for degradation in energy resolution of established scintillators such as NaI(Tl) and CsI(Tl) [7]. As a result, we have measured light output of LaCl₃:Ce under excitation from the following isotopes: ²⁴¹Am (60 keV γ-rays), ⁵⁷Co (122 keV γ-rays), ²²Na (511 and 1275 keV γ-rays) and ¹³⁷Cs (662 keV γ-rays). Sample was wrapped in Teflon tape and coupled to a PMT. From the obtained peak position and the known γ-ray energy for each isotope, the light output (in photons/MeV) at each γ-ray energy was estimated. The data points were then normalized with respect to the light output value at 662 keV energy. The results (shown in Fig. 5) indicate that LaCl₃:Ce is a very linear scintillator. Over the energy range from 60 to 1275 keV, the non-proportionality in its light yield is about 7% which is substantially better than that for many established scintillators. For example, over the same energy range the non-proportionality is about 35% for LSO and about 20% for NaI(Tl) and CsI(Tl) [6]. The higher proportionality of LaCl₃:Ce is one of the important reasons (in conjunction with its high light output) behind the high-energy resolution of this scintillator.

4.3. Coincidence timing resolution

Coincidence timing resolution of LaCl₃:Ce crystal (1 cm³, 10% Ce) was measured. For this experiment, two Hamamatsu R-5320 photomultipliers (700 ps risetime and 160 ps FWHM single photoelectron transit time jitter) operated at ~2400 V were used. Upon irradiation of the crystals coupled to each PMT with 511 keV γ-ray pair (²²Na source), the signal from each PMT was processed with a TC-454 constant fraction discriminator. The resulting timing signals start and stop a time-to-amplitude converter whose output was digitized and processed by a computer to produce a timing spectrum. Data was first recorded for two BaF₂ scintillators, one in the start channel and the other in the stop channel (see Fig. 6). The coincidence timing resolution was measured to be 273 ps (FWHM).
The BaF$_2$ scintillator in the stop channel was then replaced with a LaCl$_3$:Ce scintillator and the coincidence timing resolution in this case was 264 ps FWHM. This experiment confirms that the timing resolution of LaCl$_3$:Ce is comparable to that of BaF$_2$, a benchmark in fast timing experiments. From the coincidence timing results with BaF$_2$–BaF$_2$ and BaF$_2$–LaCl$_3$ setups, we estimate the timing resolution of one LaCl$_3$:Ce sample to be 181 ps and of two LaCl$_3$:Ce samples in coincidence to be 256 ps (FWHM). To the best of our knowledge these are the first measurements of the timing resolution of LaCl$_3$:Ce.

5. Summary

In our research, we have investigated a new scintillation material, LaCl$_3$:Ce, for $\gamma$-ray spectroscopy. Our research concentrated on growth of high-quality LaCl$_3$:Ce crystals using Bridgman method as well as extensive characterization of the physical, optical, and scintillation properties of grown crystals. By and large, our measurements indicate that LaCl$_3$:Ce is a very promising scintillator. It has high light output, fast response and shows good energy and timing resolution. Our studies indicate that these properties are maintained as the crystal volume is increased. Based on the successful performance as a $\gamma$-ray detector, this new scintillation material can find its place in such applications as medical imaging, nuclear physics, X-ray diffraction, non-destructive evaluation, treaty verification and safeguards, environmental monitoring, and geological exploration.

Acknowledgements

This work was supported in part by US Department of Energy under SBIR Grant DE-FG02-01ER83268 and by the Director, Office of Science, Office of Biological and Environmental Research, Medical Science Division of the US Department of Energy under contract No. DE-AC03-76SF00098, and in part by Public Health Service Grant No. P01-CA48002 from the National Cancer Institute of the National Institute of Health.

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