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LaCl₃:Ce Scintillator for Gamma Ray Detection


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Abstract

In this paper, we report on a relatively new cerium doped scintillator - LaCl₃ for gamma 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 gamma 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 gamma 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, gamma 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 - LaCl$_3$ with attractive scintillation properties has been discovered [3]. LaCl$_3$ (doped with 10% Ce$^{3+}$) has a very high light output (~49,000 photons/MeV), and fast principle decay time constant (26 ns) [3]. These properties make LaCl$_3$:Ce a very promising material for $\gamma$-ray spectroscopy.

In view of the attractive properties of LaCl$_3$:Ce for $\gamma$-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 in with 99.99% purity. A two zone vertical 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 material was adjusted to produce LaCl$_3$ samples with varying $\text{Ce}^{3+}$ concentration. Most growth runs were performed with 10% cerium concentration, 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 properties of LaCl$_3$. LaCl$_3$ crystals with size up to ~2.5 cm$^3$ which 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. Variations 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
γ-rays (137Cs source) to the response of a BGO scintillator (see Figure 1). These measurements involved optical coupling of a LaCl₃:Ce crystal (~1cm³ 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 LaCl₃: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 µsec with a LaCl₃:Ce crystal doped with 10% Ce. This experiment was then repeated with a BGO scintillator (which was assumed to have light output of ~8000 photons/MeV). Figure 1 shows measured pulse height spectra for both LaCl₃:Ce and BGO. Based on the recorded photopeak positions and by taking into account the photocathode quantum efficiency for BGO and LaCl₃:Ce, we estimated the light output of LaCl₃:Ce crystal with 10% Ce to be about 50,000 photons/MeV at 4 µs shaping time. This light output is amongst the highest values for inorganic scintillators [1].

We also studied variations in light output of LaCl₃: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 γ-ray spectra (241Am source) were recorded under identical operating conditions. Data was collected at shaping time of 4 µs and the results are shown in Figure 2. As seen in the figure, the light output of LaCl₃:Ce samples with Ce concentration up to 10% is similar while that of one with 20% Ce is slightly lower. The estimated values of light output for all four Ce concentrations are listed in Table 1.

Table 1
<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>

Fig. 2. 241Am spectra (60 keV photons) recorded with LaCl₃:Ce crystals of different Ce concentrations. From the peak position light output was estimated for each crystal, see Table 1.

3.2. Emission Spectra

We measured the emission spectra of LaCl₃:Ce samples under x-ray exitation 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. Figure 3 shows the normalized emission spectra for LaCl₃: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 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 LaCl\(_3\):Ce emission with varying Ce concentration.

3.3. Decay Time Profiles

The scintillation time profiles of LaCl\(_3\):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 LaCl\(_3\):Ce samples were placed in the x-ray beam and their fluorescent emanations 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 LaCl\(_3\):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 Figure 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 LaCl\(_3\):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 LaCl\(_3\):Ce samples. As seen in Figures 3 and 4, for higher Ce concentrations (10 and 20%), much of the emitted light appears in the scintillation peak with \( \lambda_{\text{max}} = 350 \) nm, and the principal decay time constant for these LaCl\(_3\):Ce 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 LaCl\(_3\):Ce samples with lower Ce concentration (0.1 and 1%).
samples with higher Ce concentration is also very fast (20-25 ns). However, for lower Ce concentrations (0.1 and 1%), a significant fraction of the emitted light is present in the broader scintillation peak with $\lambda_{\text{max}} \approx 420$ nm. Furthermore, the principal decay time constant for LaCl$_3$:Ce samples with lower Ce concentration is slower (~213 ns). This behavior has also been observed by other researchers [3, 6], and can be explained by considering different scintillation mechanisms in LaCl$_3$:Ce samples. The emitted light with fast decay constant (20-25 ns) is probably due to direct electron-hole capture on Ce$^{3+}$ site, since the observed decay time constant (20-25 ns) is characteristic for Ce$^{3+}$ luminescence. The contribution of this component to the total light output in LaCl$_3$:Ce increases as Ce concentration increases because more Ce$^{3+}$ ions would be available for electron-hole pair capture. The trends seen in Figures 3 and 4 also indicate that the emitted light appearing in scintillation peak with $\lambda_{\text{max}} = 350$ nm is probably due to the direct electron-hole capture (on Ce$^{3+}$) mechanism. Other scintillation mechanisms such as luminescence from self trapped excitons and binary electron-hole recombination have been proposed to explain the slower components observed in LaCl$_3$:Ce and other related materials [3, 6].

4. Gamma Ray Detection with LaCl$_3$:Ce

4.1. Energy Resolution

We measured $\gamma$-ray energy resolution of LaCl$_3$:Ce scintillator. This involved coupling an unpackaged LaCl$_3$:Ce crystal (~1 cm$^3$ 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 $\gamma$-rays ($^{137}$Cs source), and the resulting PMT signal was processed with a preamplifier (Canberra 2005), and then shaped with a spectroscopy amplifier (Canberra 2022). A $^{137}$Cs pulse height spectrum was recorded with shaping time of 4 $\mu$s as shown in Figure 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 LaCl$_3$:Ce scintillators by optimizing the light collection at the PMT - LaCl$_3$:Ce interface, and by improving the overall quality and packaging of LaCl$_3$:Ce crystals.

4.2. Proportionality of Response

We have evaluated the proportionality of response (or linearity) of LaCl$_3$: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 LaCl$_3$:Ce under excitation from the following isotopes: $^{241}$Am (60 keV $\gamma$-rays), $^{57}$Co (122 keV $\gamma$-rays), $^{22}$Na (511 keV and 1275 keV $\gamma$-rays), and $^{137}$Cs (662 keV $\gamma$-rays). Sample was wrapped in Teflon tape and coupled to a PMT. From the obtained peak position and the known $\gamma$-ray energy for each isotope, the light output (in photons/MeV) at each $\gamma$-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 Figure 5) indicate that LaCl$_3$:Ce is a very linear scintillator. Over the energy range from 60 to

![Fig. 5. Energy response (relative light yield, normalized to the value at 662 keV, as a function of energy) for LaCl$_3$:10%Ce. The response of an ideal material would be independent of energy. Non-proportionality of measured sample is ~7% which is much better than that in established scintillators.](image-url)
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 LaCl$_3$: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 LaCl$_3$:Ce crystal (1 cm$^3$, 10% Ce) was measured. For this experiment, two Hamamatsu R-5320 photomultipliers (700 ps rise time 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 gamma ray pair ($^{22}$Na 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 BaF$_2$ scintillators, one in the start channel and the other in the stop channel (see Figure 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.

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