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$LaCl_3$:Ce scintillator for γ-ray detection ☆

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Abstract

In this paper, we report on a relatively new cerium-doped scintillator—$LaCl_3$ 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 (^{137}Cs source) at room temperature. Also, high timing resolution (264 ps—FWHM) has been recorded with $LaCl_3$-PMT and BaF_2-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.

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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—$LaCl_3$ 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 γ-ray spectroscopy.

In view of the attractive properties of $LaCl_3$:Ce for γ-ray detection, and availability of only very

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small crystals, we have performed investigation of the crystal growth of this material and explored its capabilities for γ-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 P63/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 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 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 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_2O_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 (^{137}Cs source) to the response of a BGO scintillator (see Fig. 1). These measurements involved optical coupling of a $LaCl_3$:Ce crystal (~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 μs with a $LaCl_3$:Ce crystal doped with 10% Ce. This experiment was then repeated with a BGO

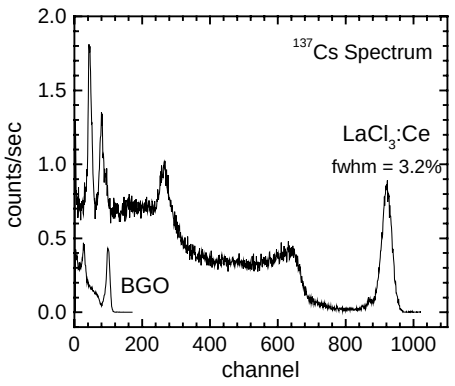

Fig. 1. ^{137}Cs spectra recorded with $LaCl_3$:10% Ce and BGO crystals coupled to PMT under identical operating conditions. Light output of $LaCl_3$:10% Ce was estimated to be ~50,000 photons/MeV from the calibration provided by BGO. The $LaCl_3$ spectrum shows resolution of 3.2% (FWHM) at room temperature.

scintillator (which was assumed to have light output of ~8000 photons/MeV). Fig. 1 shows measured pulse height spectra for both $LaCl_3$:Ce and BGO. Based on the recorded photopeak 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 μs 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 γ-ray spectra (^{241}Am source) were recorded under identical operating conditions. Data was collected at shaping time of 4 μs 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 λ_{max} of 350 nm is present for all four cerium concentrations. In addition, another broad emission peak with λ_{max} in 420–440 nm range is also present. For higher Ce concentrations (10% and 20%), almost all light is

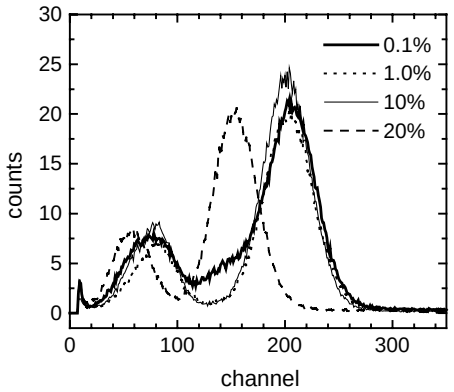

Fig. 2. ^{241}Am spectra (60 keV photons) recorded with $LaCl_3$:Ce crystals of different Ce concentrations. From the peak position light output was estimated for each crystal, see Table 1.

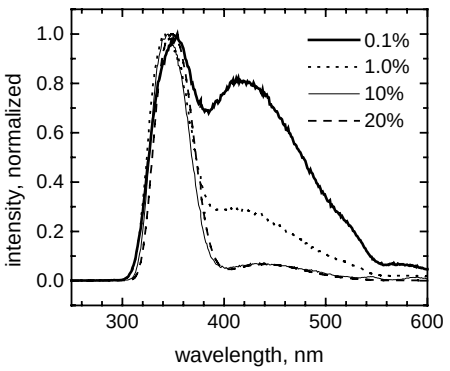

Fig. 3. Optical emission spectra for $LaCl_3$ samples with different Ce concentrations. Spectra were normalized with respect to 350 nm peak intensity.

Table 1
Scintillation properties of $LaCl_3$:Ce with different Ce concentrations

Ce concentration	Light output (photons/MeV)	Decay time (ns)	Emission peak (nm)
0.1	50,500	20 (15%), 213 (85%)	350, 430
1	50,500	20 (33%), 213 (67%)	350, 430
10	50,000	20 (70%), 213 (30%)	350, 430
20	38,000	25 (76%), 63 (13%), 213 (11%)	350, 430

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 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 $LaCl_3$: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 Figs. 3 and 4, for higher Ce concentrations (10% and 20%), much of the emitted light appears in the scintillation peak with $\lambda_{max} = 350$ nm, and the principal decay time constant for these $LaCl_3$:Ce samples with higher Ce concentration is also very

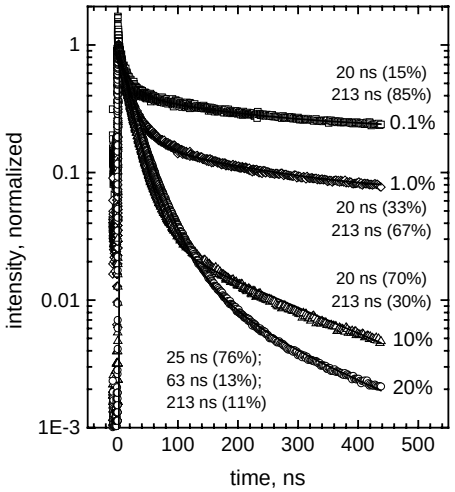

Fig. 4. Time profiles (points) measured for $LaCl_3$ crystals with 0.1%, 1.0%, 10%, and 20% Ce concentrations, along with multi-exponential fits (lines). As seen in plots, the principal decay constant is fast (≤25 ns) for samples with high (10–20%) Ce concentration.

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 $\lambda_{max} \approx 420$ 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 Figs. 3 and 4 also indicate that the emitted light appearing in scintillation peak with $\lambda_{max} = 350$ 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. γ-ray detection with $LaCl_3$:Ce

4.1. Energy resolution

We measured γ-ray energy resolution of $LaCl_3$:Ce scintillator. This involved coupling an unpackaged $LaCl_3$:Ce crystal ($\sim 1\,cm^3$ 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 γ-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 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 $LaCl_3$: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 γ-rays), ^{57}Co (122 keV γ-rays), ^{22}Na (511 and 1275 keV γ-rays) and ^{137}Cs (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 $LaCl_3$: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 $LaCl_3$:Ce is one of the important reasons (in conjunction with its high light output) behind the high-energy resolution of this scintillator.

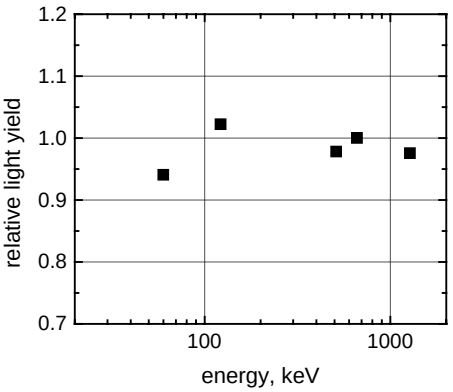

Fig 5. Energy response (relative light yield, normalized to the value at 662 keV, as a function of energy) for $LaCl_3$:10% Ce. The response of an ideal material would be independent of energy. Non-proportionality of measured sample of is ~7% which is much better than that in established scintillators.

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 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 (^{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 Fig. 6). The coincidence timing resolution was measured to be 273 ps (FWHM).

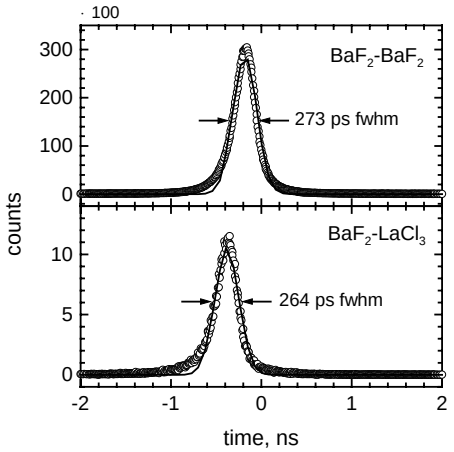

Fig. 6. Coincidence timing resolution results. Above coincidence timing resolution result for two BaF_2–PMT detectors, one in start channel and one in stop channel. Below coincidence timing resolution result for a $LaCl_3$-PMT detector in stop channel with a BaF_2-PMT detector in start channel.

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 γ-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 γ-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

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