$LaBr_3$:Ce Scintillators for Gamma Ray Spectroscopy

K. S. Shah, J. Glodo, M. Klugerman, W. W. Moses, S. E. Derenzo, and M. J. Weber

***Abstract*—In this paper, we report on a relatively new scintillator - $LaBr_3$ for gamma ray spectroscopy. Crystals of this scintillator have been grown using Bridgman process. This material when doped with cerium has high light output (~60,000 photons/MeV) and fast principal decay constant (≤25 ns). Furthermore, it shows excellent energy resolution for γ-ray detection. Energy resolution of 3.2% (FWHM) has been achieved for 662 keV photons (^{137}Cs source) at room temperature. High timing resolution (260 ps - FWHM) has been recorded with $LaBr_3$-PMT and BaF_2-PMT detectors operating in coincidence mode using 511 keV positron annihilation γ-ray pairs. Details of its scintillation properties, and variation of these properties with changing cerium concentration are reported. Potential applications of this material are also addressed.**

***Index Terms*—Bromide compounds; Ce^{3+}; γ-detection; energy resolution; rare-earth trihalides; scintillation crystals.**

I. Introduction

Scintillation spectrometers are widely used in detection and spectroscopy of energetic photons (γ-rays) as well as neutrons at room temperature. 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 efficiency, fast response, low cost, good linearity, and minimal afterglow. These requirements cannot be met by any of the commercially available scintillators, and there is a continued interest in search for new scintillators with enhanced performance. Recently, a new cerium doped halide scintillator, $LaBr_3$ has been discovered which has attractive scintillation properties such as very high light output (~60,000 photons/MeV), and fast principle decay constant (30 ns) [3]. Based on these properties, $LaBr_3$:Ce is a promising scintillator for γ-ray spectroscopy.

In view of the attractive properties of $LaBr_3$:Ce and the evaluation of only very small crystals of this material so far, we have performed investigation of the crystal growth of this exciting material and explored its capabilities for γ-ray detection. In this paper, we report on $LaBr_3$:Ce crystal growth, evaluation of its scintillation properties with four different Ce^{3+} concentrations, and characterization of γ-ray detection properties of $LaBr_3$:Ce.

II. Crystal Growth of $LaBr_3$:Ce

$LaBr_3$ crystals have hexagonal (UCl_3 type) structure with P63/m space group and their density is 5.3 g/cm^3. The compound melts congruently at 783 °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 $LaBr_3$:Ce crystals because this technique is easy to implement, and can provide good indication of the feasibility of producing large crystals of $LaBr_3$:Ce from the melt. Ultra-dry forms of $LaBr_3$ and $CeBr_3$ were used with 99.99% purity. A two zone Bridgman furnace was used with temperature in the hotter zone above the melting point $LaBr_3$ (783 °C) and that of the cooler zone below the melting point. The amount of $CeBr_3$ in the feed material was adjusted to produce $LaBr_3$ samples with varying Ce^{3+} concentration. Most growth runs were performed with 0.5% cerium concentration, although in order to study the effects of variation in cerium concentration on the scintillation properties of $LaBr_3$ some runs were also performed with other Ce concentrations (0.2%, 0.5%, 1.3% and 5%). $LaBr_3$ crystals with size up to ~2.3 cm^3 were grown. These crystals were cut from the solid ingots and polished using non-aqueous slurries (due to hygroscopic nature of $LaBr_3$) 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 (Epoxy STYCAST#1266 Value23LV Titanium Oxide and EPO-TEK 301 between the crystal and window) with a thin quartz window (0.5 mm) placed on the crystal face, which would be coupled to an optical sensor.

III. Scintillation Properties of $LaBr_3$:Ce

We have performed characterization of the scintillation

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properties of $LaBr_3$ crystals grown by the Bridgman process. This investigation involved measurement of the light output, the emission spectrum, and the fluorescent decay time of the crystals. Variation of these scintillation properties with Ce^{3+} concentration was analyzed. Energy and timing resolution of $LaBr_3$:Ce crystals were also measured.

A. Light Output and Energy Resolution

The light output of $LaBr_3$:Ce crystals was measured by comparing their response and the response of a calibrated BGO scintillator to the same isotope (662 keV γ-rays, ^{137}Cs source, see Fig. 1). These measurements involved optical coupling of a $LaBr_3$:Ce sample to a photomultiplier tube (with multi-alkali S-20 photocathode), irradiating the scintillator with 662 keV photons and recording the resulting pulse height spectrum. In order to maximize light collection, $LaBr_3$:Ce crystals were wrapped in reflective, white Teflon tape on all faces (except the one coupled to a photomultiplier (PMT)). An index matching silicone fluid was also used at the PMT-scintillator interface. A pulse height spectrum was recorded with a $LaBr_3$:Ce crystal (~1 cm^3 size, 0.5% Ce). This experiment was then repeated with a calibrated BGO scintillator (which had light output of 8000 photons/MeV). Fig. 1 shows pulse height spectra for both $LaBr_3$:Ce and BGO under ^{137}Cs irradiation and amplifier shaping time of 4.0 μsec. This shaping time is long enough to allow full light collection from both the scintillators. The PMT bias and amplifier gain were the same for both spectra. Based on the recorded photopeak positions for $LaBr_3$:Ce and BGO, and by taking into account the photocathode quantum efficiency for BGO and $LaBr_3$:Ce, we estimated light output of $LaBr_3$:Ce crystal with 0.5% Ce to be about 60,000 photons/MeV. This light output is amongst the highest values for inorganic scintillators [1].

We also studied variation in light output of $LaBr_3$:Ce crystals as a function of the cerium concentration in these crystals. Crystals with cerium concentration of 0.2%, 1.3%, and 5% were investigated. Each crystal was coupled to PMT and 662 keV γ-ray spectra (^{137}Cs source) were recorded with these crystals under identical operating conditions. Data were collected at shaping time of 4 μs and the results reported in Table I, indicate that all Ce^{3+} concentrations provide high light output with highest values observed at the lower Ce^{3+} concentrations. The light output of the sample with 1.3% Ce^{3+} concentration is lower than expected, which is probably due to poorer quality of that crystal as compared to other samples.

The energy resolution of the 662 keV photopeak recorded with $LaBr_3$:Ce scintillator has been measured to be 3.2% full-width at half-maximum (FWHM) at room temperature as shown in Fig. 1. Such high energy resolution has not been achieved with any of the established inorganic scintillators. It should be noted that the energy resolution obtained with $LaBr_3$:Ce crystals approaches the energy resolution of room temperature semiconductor detectors such as CdTe and CdZnTe of similar size. We have also characterized a $LaBr_3$:Ce crystal (coupled to a PMT) using other gamma ray energies such as 511 keV (^{22}Na source) and 122 keV (^{57}Co source) and have found its energy resolution to be 3.6% (FWHM) and 6.8% (FWHM), respectively, at room temperature.

B. Emission Spectrum

We measured the emission spectrum of the $LaBr_3$:Ce scintillators. The $LaBr_3$:Ce samples were excited with radiation from a Philips X-ray tube having a copper target. The scintillation light was passed through a McPherson monochromator and detected by a Hamamatsu R2059 photomultiplier tube with a quartz window.

Fig. 2 shows the normalized emission spectra for $LaBr_3$:Ce samples with 0.2, 0.5, 1.3, and 5% Ce concentrations. As seen in the figure, emission peaks at 360 and 380 nm, which are characteristic for Ce^{3+} luminescence, are present for all four cerium concentrations. There appears to be no significant emission from these samples due to other mechanisms such as luminescence from self-trapped excitons or binary electron-hole recombination, which could cause slower component(s).

C. Decay Time

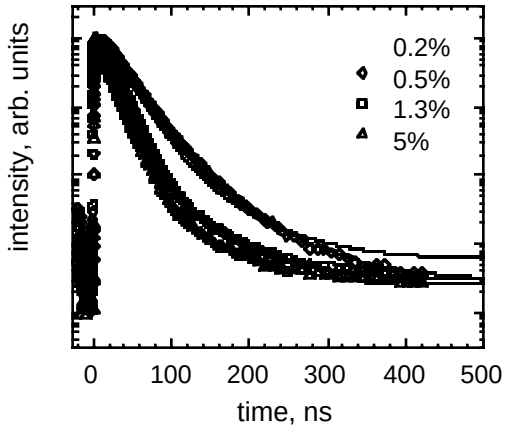

Fig. 3. Decay time spectra for $LaBr_3$ crystals with 0.2, 0.5, 1.3, and 5% Ce^{3+} concentrations, along with multi-exponential fits to the measured data.

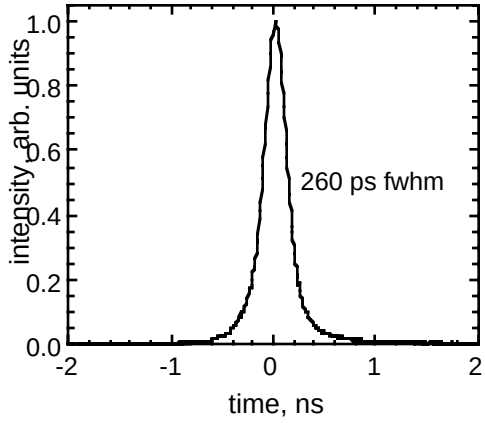

Fig. 4. Timing resolution spectrum measured for a $LaBr_3$:Ce (5% Ce^{3+}) crystal in coincidence with a BaF_2 crystal.

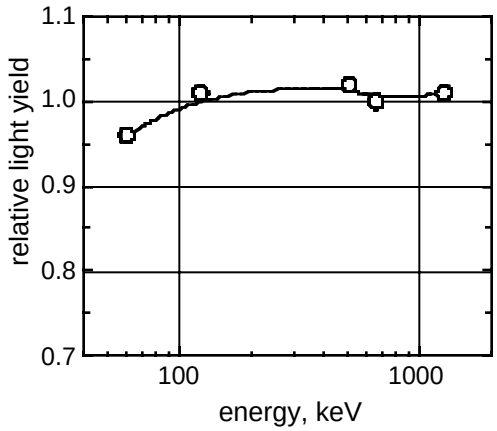

Fig. 5. Proportionality in light yield as a function of γ-ray energy measured for $LaBr_3$:Ce at room temperature.

The fluorescent decay times of $LaBr_3$:Ce samples (doped with 0.2, 0.5, 1.3 and 5% Ce) were measured using the delayed coincidence method [5]. Decay time measurements were made at the LBNL Pulsed X-Ray Facility. The x-ray source is a light-excited x-ray tube that produces 4,000 x-ray photons (of mean energy 18.5 keV) per steradian in each 1 ps FWHM pulse, with a 50 kHz repetition rate. The $LaBr_3$: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 emissions was measured using a TAC/ADC combination having 2 ps FWHM resolution. The total system response time is 100 ps FWHM. The decay time spectrum for each $LaBr_3$:Ce sample was measured up to 430 ns after x-ray exposure in this manner and was fitted to the sum of exponentials and a time-independent background. The fit results are shown in Fig. 3 and Table I. As seen in the table, all samples independent of Ce^{3+} concentration show very fast principal decay constant (≤ 25 ns). These results are consistent with the emission spectra shown in Fig. 2 where Ce^{3+} luminescence appears to be the primary scintillation component. Some evidence of rise time (in 1-4 ns range) was also observed in these studies. The light output, optical emission, and decay time data for all four Ce^{3+} concentrations in $LaBr_3$ are summarized in Table I.

D. Coincidence Timing Resolution

Coincidence timing resolution of $LaBr_3$:Ce crystals with various Ce^{3+} concentrations has been measured. This experiment involved irradiating a BaF_2 and $LaBr_3$:Ce scintillators, each coupled to a fast PMT (Hamamatsu R-5320, operated at –2000V) with 511 keV positron annihilation γ-ray pairs (emitted by a ^{22}Na source). The BaF_2-PMT detector formed a "start" channel in the timing circuit, while the $LaBr_3$-PMT detector formed the "stop" channel. The signal from each detector was processed using two channels of a Tennelec TC-454 CFD that had been modified for use with the MCP-PMTs. The time difference between the start and stop signals was digitized with a Tennelec TC-862 TAC and a 16-bit ADC, resulting in a TDC with 7.5 ps per bin resolution. There was a 5 ns cable between the "start" CFD and the TAC and a 20 ns cable between the "stop" CFD and the "TAC". Data were accumulated until the coincidence timing distribution had approximately 10,000 counts in the maximum bin. Fig. 4 shows a coincidence timing resolution plot acquired in this manner with $LaBr_3$:Ce crystal having 5% Ce^{3+} concentration and the timing resolution was measured to be 260 ps (FWHM). Similar measurements were also made with $LaBr_3$:Ce crystals having 0.2%, 0.5%, and 1.3% Ce^{3+} concentrations placed in the "stop" channel, and the coincidence timing resolution was measured to be 450 ns, 390 ns, and 320 ps (FWHM), respectively. The timing resolution for two BaF_2 detectors in coincidence with each other was measured to be 240 ps (FWHM) in this study. Overall, these results confirm that $LaBr_3$:Ce is well suited for applications requiring fast response, high count-rates, and good timing resolution.

TABLE I
SCINTILLATION PROPERTIES OF $LaBr_3$:CE WITH DIFFERENT Ce^{3+} CONCENTRATIONS

Ce^{3+} Concentration (%)	Light Output (Photons/MeV)	Rise Time (ns)	Decay Times (ns)
0.2	60,700	3.5	23 ns (93.4%), 66 ns (6.6%)
0.5	60,000	3.4	26 ns (93%), 66 ns (7%)
1.3	47,000	2.9	16.5 ns (97%), 66 ns (3%)
5	55,300	0.7	15 ns (97%),

E. Proportionality of Response

We have evaluated the proportionality of response (or linearity) of $LaBr_3$:Ce scintillators. 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) [6]. As a result, we have measured light output of $LaBr_3$:Ce under excitation from isotopes such as ^{241}Am (60 keV γ-rays), ^{57}Co (122 keV γ-rays), ^{22}Na (511 keV and 1275 keV γ-rays) and ^{137}Cs (662 keV γ-rays). A $LaBr_3$:Ce crystal (0.5% Ce) was wrapped in Teflon tape and coupled to a PMT. Pulse height measurements were performed using standard NIM equipment with the scintillator exposed to different isotopes. Same settings were used for PMT and pulse processing electronics for each isotope. From the measured 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 and the results (shown in Fig. 5) indicate that $LaBr_3$:Ce is a very proportional scintillator. Over the energy range from 60 to 1275 keV, the non-proportionality in light yield is about 6% for $LaBr_3$:Ce, 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) [7]. The higher proportionality of $LaBr_3$:Ce is one of the important reasons (in conjunction with its high light output) behind the high energy resolution of this scintillator.

Overall, these measurements clearly indicate that $LaBr_3$:Ce is a 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.

IV. Summary

In our research, we have investigated a new scintillation material, $LaBr_3$:Ce, for γ-ray detection. Our research concentrated on growth of high quality $LaBr_3$:Ce crystals using Bridgman method, as well as extensive characterization of the physical, optical, and scintillation properties of these crystals. Overall, these measurements indicate that $LaBr_3$:Ce is a promising scintillator. It has high light output, fast response and shows good energy and timing resolution. Based on successful performance as gamma ray detector, this new scintillation material can be applied to applications such as medical imaging, nuclear physics, X-ray diffraction, non destructive evaluation, treaty verification and non-proliferation monitoring, environmental cleaning, and geological exploration.

V. Acknowledgment

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References:

[1] G. Knoll, *Radiation Detection and Measurement (3rd ed.)*. New York: John Wiley and Sons, Inc., 1999.

[2] K. Kleinknecht, *Detectors for Particle Radiation (2nd ed.).* , Cambridge, U.K: Cambridge University Press, 1998.

[3] E. V. D. van Loef, P. Dorenbos, C. W. E. van Ejik, K. Kramer, and H. U. Gudel, "High Energy Resolution Scintillator: Ce^{3+} Activated $LaBr_3$", *Appl. Phys. Lett.*, vol 79, pp. 1573-1575, Sep. 2001.

[4] J. C. Brice, *Crystal Growth Processes.* UK: Blackie Halsted Press, 1986.

[5] L. M. Bollinger and G. E. Thomas, "Measurement of the time dependence of scintillation intensity by a delayed-coincidence method", *Rev. Sci. Instr.*, vol. 32, pp. 1044, 1961.

[6] P. Dorenbos, J. T. M de Haas, and C. W. E. van Eijk, "Non-Proportionality in the Scintillation Response and the Energy Resolution Obtainable with Scintillation Crystals", *IEEE Trans. Nucl. Sci.*, vol 42, pp. 2190-2202, Dec. 1995.

[7] O. Guillot-Noel, J. C. van't Spijker, J. T. M de Haas, P. Dorenbos, C. W. E. van Eijk, K. W. Kramer, and H. U. Gudel, "Scintillation Properties of $RbGd_2Br_7$:Ce Advantages and Limitations", *IEEE Trans. Nucl. Sci.*, vol 46, pp. 1274-1284, Oct. 1999.