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Growth and Characterization of Polycrystalline Lanthanide Halide Scintillators

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Abstract

We are exploring a novel time- and cost-efficient approach to produce robust, large-volume polycrystalline lanthanide halide scintillators using a hot wall evaporation (HWE) technique. To date, we have fabricated $\text{LaBr}_3\text{:Ce}$ and $\text{LaCl}_3\text{:Ce}$ films (slabs) measuring up to 7 cm in diameter and 7+ mm in thickness (20 to 25 cm³ in volume) on quartz substrates. These polycrystalline scintillators exhibit very bright emissions approaching those exhibited by their melt-grown crystal counterparts. Scanning electron micrographs (SEMs) and X-ray diffraction analyses confirm polycrystalline growth with columnar structures, both of which help in light piping, thereby contributing to the observed high light yields. The new scintillators also exhibit good energy resolution for γ -rays over the tested range of 60 keV (²⁴¹Am) to 662 keV (¹³⁷Cs), although they have not yet reached that of the corresponding crystals. The measured response linearity over the same energy range is comparable for both our HWE synthesized films and melt-grown commercially-available reference crystals. Similar consistency in response is also observed in terms of their decay time and afterglow behaviors. The data collected so far demonstrate that our HWE technique permits the rapid creation of scintillators with desired structural and compositional characteristics, without the introduction of appreciable defects, and yields material performance equivalent to or approaching that of crystals. Consequently, the deposition parameters may be manipulated to tailor the physical and scintillation performance of the resulting structures, while achieving a cost per unit volume that is substantially lower than that of crystals. In turn, this promises to allow the use of these novel scintillation materials in such applications as SPECT, PET, room-temperature radioisotope identification and homeland security, where large volumes of materials in a wide variety of shapes and sizes are needed. This paper describes our growth and testing of polycrystalline $\text{LaBr}_3\text{:Ce}$ scintillators and provides comparative characterizations of their performance with crystals.

Keywords

lanthanide halide; polycrystalline scintillator films; gamma ray imaging

1. Introduction

Lanthanide halide scintillators including cerium-doped lanthanum bromide ($\text{LaBr}_3:\text{Ce}$) and lanthanum chloride ($\text{LaCl}_3:\text{Ce}$) have shown great promise for medical imaging applications such as PET/SPECT and room-temperature radioisotope identification. $\text{LaBr}_3:\text{Ce}$ in particular has one of the highest conversion efficiencies among all scintillators ($>63,000$ photons/MeV), a rapid decay time (16 ns), very good linearity in energy response, excellent energy resolution ($\sim 3\%$ @ 662 keV), and a high absorption efficiency for γ -rays [1, 2].

Lanthanide halide scintillators are typically grown from a melt in vacuum, and crystals must be encapsulated immediately after removal from the growth ampoule to prevent rapid deliquescence from moisture in the atmosphere. This and other traditional growth techniques result in high production costs and limited availability for this material, and crystal sizes are normally limited to about a 5 cm x 5 cm right cylinder.

At RMD we have developed a new hot wall evaporation (HWE) method to grow thick polycrystalline films (slabs) of these materials efficiently and in large areas. At present we have fabricated up to 7 cm diameter, nearly 1 cm thick films, and developments are under way to make larger, thicker films. Here we report on the morphology of $\text{LaBr}_3:\text{Ce}$ polycrystalline films as well as their scintillator performance compared to commercial single crystals.

2. Materials and Methods

We have developed a new vapor deposition technique, which allows large-volume, time-efficient and low-cost production of high-quality lanthanide halide scintillators. HWE produces thick, large-area polycrystalline scintillators by co-depositing LaBr_3 and CeBr_3 salts, allowing precise control of Ce^{3+} dopant levels. Unlike standard crystal growth, physical vapor deposition is largely a function of the partial pressures of constituent materials, opening the possibility of developing chemical compositions not achievable directly from a melt. This allows the formation of unconventional compositions doped with various amounts of Ce^{3+} and possibly other co-dopants. Many of the problems associated with conventional crystal growth such as slow growth rate and low yields (resulting from crystal cracking and other difficulties) can be avoided with HWE. Perhaps the biggest advantage is the fact that robust large-area films can now be fabricated with thicknesses up to 1 cm being grown in a matter of hours instead of days. Due to the hygroscopic nature of this material, special precautions are still required to minimize exposure to air, and we successfully developed and employed methods to keep samples under dry N_2 at all times during transport and storage, until they were encapsulated.

Film morphology was evaluated with an ISI SS40 scanning electron microscope, revealing the range of crystalline structures that are possible by varying HWE fabrication parameters such as substrate temperature and constituent evaporation rates.

Scintillation performance was measured using pulse height analysis by coupling the scintillator specimens to a photomultiplier tube (PMT) (Hamamatsu R6233SBA). First, the photopeak position for thermally generated single photoelectrons in the PMT was measured

for energy calibration. Next, the scintillator, wrapped with several layers of reflective Teflon tape, was irradiated with 60 keV gamma rays, without altering the system gain. The PMT signal was shaped with a Canberra spectroscopy amplifier (#2020) with a shaping time of 4 μ s. The pulse height spectra for single photoelectrons as well as for 60 keV gamma rays were then recorded with an Amptek MCA 8000-A multichannel analyzer. By comparing these photopeak positions, the light outputs of the scintillator films were estimated using the known value of the quantum efficiency of the PMT at the LaBr₃:Ce emission ($\lambda_{\text{max}} \sim 380$ nm).

The energy resolution and proportionality of the HWE vapor-grown LaBr₃:Ce films was experimentally measured and compared to that obtained using a reference LaBr₃:Ce Saint-Gobain crystal. Energy spectra from the specimens were acquired by coupling them to the PMT setup and exposing them to ²⁴¹Am (60 keV), ¹²²Co (122 keV), ²²Na (511 keV, 1.2 MeV), and ¹³⁷Cs (662 keV) radioisotopes. The FWHM energy resolution was calculated using a Gaussian fit to the energy peak. Photopeak positions were recorded as a function of isotope energy to calculate the response proportionality in the range from 60 keV to 1.2 MeV. All specimens were compared to a Saint Gobain LaBr₃:Ce crystal with dimensions 1.3 cm diameter x 1.3 cm thick.

3. Results and Discussion

Our major technological accomplishment is that we have demonstrated the fabrication of polycrystalline LaBr₃:Ce films using a vapor-deposition technique, in particular our HWE method. The thick, nearly transparent polycrystalline films were made using low cost, relatively unpurified starting material, emphasizing the remarkable economy of growth using our HWE method. In addition, we have developed dry handling methods and successfully encapsulated these films to protect them from atmospheric moisture.

3.1. Morphology

Films grown with HWE are polycrystalline in nature, and with judicious control of temperature profiles during film growth we can control both film structure and stoichiometry. As shown in Figure 1, these films appear white (and not transparent) due to their polycrystalline nature; however, the scintillation light is indeed transmitted within the film, as evidenced by the light yield and linearity results described in the following sections. Figure 2 shows scanning electron micrographs (SEMs) of two sample films, showing densely packed polycrystalline columns that are ~ 150 μ m in diameter. By controlling the deposition conditions we can grow films in the forms shown here or with fine needle-like films which are more suitable for imaging applications [4, 3, 5].

3.2. Light yield characteristics

Light yield measured by the photoelectron method shows that our films produce 77,000 photons/MeV, compared to 52,000 for a commercial crystal, as shown in Figure 3. The validity of these data was verified by measuring the light yield of a calibrated BGO crystal, which showed 9965 ph/MeV yield, consistent with the published value of $\sim 10,000$ ph/MeV. The high light yield of the films compared to the reference crystal may be due in part to

specimen size differences. A similarly sized $\text{LaBr}_3\text{:Ce}$ crystal grown at RMD showed a conversion efficiency of 86,000 ph/MeV. Our data do suggest however that the light yield of the HWE films are at least on par with that of the crystal.

In spite of the higher brightness, our $\text{LaBr}_3\text{:Ce}$ films have not yet achieved the energy resolution of the reference crystal as shown in Table 1, which may be attributable to non-uniformities in dopant distribution, non-uniformity in light collection efficiency, and/or possibly phase variations in the polycrystalline structure. Our results for standard $\text{LaBr}_3\text{:Ce}$ crystals are in agreement with those previously reported in the literature [6]. Notably, the films demonstrate $1/e$ scintillation decay on the order of 8 ns, which is approximately a factor of two faster than that reported in literature for single crystals, and afterglow characteristics comparable to that of $\text{LaBr}_3\text{:Ce}$ crystalline material, indicating that the process of vapor deposition does not introduce any significant defect states that could compromise speed [3].

Figure 4 shows the proportionality results over a 60 keV to 1.2 MeV gamma ray energy range. As shown, the vapor-deposited $\text{LaBr}_3\text{:Ce}$ film demonstrates excellent proportionality, which is a characteristic of lanthanide halide scintillators, and is well preserved in the vapor-deposited specimens.

4. Conclusions

We have shown that the HWE method is an innovative technique for fabricating lanthanide halides with the advantage that large-volume scintillators can be fabricated quickly and cost-effectively. HWE offers the ability to control the film stoichiometry and scintillation properties, with performance approaching that of single crystals. In addition to lanthanide halide scintillators, the HWE technique is applicable to large volume production of other scintillators as well, which are currently being explored at RMD.

5. Acknowledgments

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Figure 1.
LaBr₃:Ce film measuring 7 cm in diameter and ~7 mm in thickness, deposited and hermetically sealed at RMD.

Figure 2.
SEM micrographs of a 3.5 mm thick $\text{LaBr}_3\text{:Ce}$ film (left) and the bottom portion of the film (right) showing densely packed polycrystalline columns.

Figure 3.

Light yield in photons/MeV based on the relative positions of a single photoelectron peak compared to the peak for the source-scintillator configuration (^{241}Am 60 keV γ -rays). PMT gain was maintained constant throughout measurements and showed that this particular RMD specimen yielded 76,617 ph/MeV compared to 51,351 ph/MeV for the reference crystal. PMT quantum efficiency for $\text{LaBr}_3:\text{Ce}$ ($\lambda_{\text{max}} \sim 380$ nm) is $\sim 31\%$.

Figure 4. Proportionality of the vapor-deposited $\text{LaBr}_3\text{:Ce}$ film compared to that of a crystal, showing the close match in linearity. Both datasets have been adjusted so that the 662 keV ^{137}Cs gammas have a pulse height of 1.

Table 1

Energy resolution of high temperature deposited LaBr₃:Ce film in comparison with a Saint-Gobain reference crystal when exposed to 60, 511, and 662 keV γ -rays.

Specimen	60 keV	Energy Resolution (%) 511 keV	662 keV
RMD LaBr ₃ :Ce 7 mm thick Film	14.3	8.6	8.5
Saint-Gobain LaBr ₃ :Ce reference crystal	10.8	3.5	3.0