Crystal growth of large diameter LaBr₃:Ce and CeBr₃

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Abstract

LaBr₃:Ce and CeBr₃ are novel inorganic scintillators for gamma-ray detection and spectroscopy. Both materials exhibit exceptional scintillation properties, such as very high light output, fast response and excellent energy resolution.

Custom equipment was built for crystal growth and handling of the moisture- and oxygen-sensitive materials. Crystal growth runs of large diameter crystals of LaBr₃:Ce and pure CeBr₃ were conducted in vertical multizone-zone Bridgman systems due to their operational simplicity and the potential for reduced thermal shock to the crystals. Procedures were developed to prepare clean charges, inhibit the formation of oxyhalides, and reduce the residual stresses and cracks in the crystals.

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1. Introduction

Gamma-ray spectrometers are an important tool for monitoring and preventing the worldwide proliferation of nuclear weapons. The desired systems need to detect and identify the characteristic X-ray and gamma-ray signatures of highly enriched uranium and weapons grade plutonium.

The systems also need to detect “dirty” bombs by monitoring for radioactive materials such as ¹³⁷Cs, ⁶⁰Co, ²⁴¹Am, radioactive medical waste and irradiated fuel from nuclear reactors. To facilitate routine monitoring at a multitude of locations and environmental conditions the ideal gamma-ray spectrometers should have high-energy resolution, high detection efficiency, compact size, light-weight, easy portability, and low-power requirements. Existing gamma-ray spectrometers based on hyper-pure Ge, CdZnTe, NaI:Tl, and CsI:Tl detectors have one or more deficiencies in these desired characteristics. The LaBr₃:Ce and CeBr₃ scintillator crystals we are reporting on have the desired properties for gamma-ray spectrometers that will meet the present day needs for nuclear non-proliferation [1–11]. Table 1 shows the properties of a number of inorganic scintillators that are routinely being used.

In this paper, we will report on our results to date for vertical Bridgman crystal growth and characterization of large diameter LaBr₃:Ce and CeBr₃ crystals. The scintillator properties of these crystals such as emission, light output, energy resolution, and proportionality of response will also be presented. These rare-earth halides have significant orientation-dependent differences in their thermal and mechanical properties and as a result are mechanically fragile and are susceptible to cleaving and cracking [12–14]. In addition, they are very sensitive in regards to reaction with moisture and oxygen. The rare-earth oxyhalides that form can lead to adhesion between the crystal and the ampoule wall. We will also report on our approach for dealing with these crystal growth challenges.

2. Experimental procedures

LaBr₃ and CeBr₃ crystals have a hexagonal (UCl₃ type) structure with P6₃/m space group [15]. LaBr₃ has a density of 5.06 g/cm³ and melts at 783 °C. CeBr₃ has a density of 5.18 g/cm³ and melts at 732 °C. The low melting points...
allowed us to grow the crystals in sealed quartz ampoules by using the Bridgman crystal growth technique.

The quartz ampoules were cleaned with acetone and methanol, lightly etched with a dilute HF solution, and rinsed with deionized water. The ampoules were vacuum baked in a horizontal tube furnace. Rare-earth oxybromides can be formed when rare-earth bromides are exposed to oxygen and moisture at elevated temperature [16]. To minimize this effect, all handling of the pure powder or beads was done in a nitrogen-purged glovebox as shown in Fig. 1. Gas in the glovebox was recirculated through a mixed bed of reduced copper catalyst and dry molecular sieve. The reduced copper catalyst and the dry molecular sieve lowered the respective oxygen and moisture concentrations in the glovebox to less than 10 ppm. After the crystals have been grown and removed from the growth ampoules, all handling was done in a glovebox or a dry room environment.

Anhydrous, 99.99% pure, −10 mesh beads of LaBr₃ and CeBr₃ from Sigma-Aldrich were loaded into quartz ampoules in the glovebox. The ampoules were attached to a Varian Vac Sorb pump, evacuated and sealed with an oxy-propane torch.

The crystals were grown in vertical Bridgman furnaces like the ones shown in Fig. 2. The MELLEN Company fabricated the high-temperature resistance furnaces. The top and bottom furnaces were separated with a thermal baffle that had a central hole for the ampoule to be lowered through. Gas-tight top and bottom insulation plugs prevented any chimney effect and uncontrolled air flow through the system. The ampoules were slowly lowered through the temperature gradient by stepper motor driven linear slides. Crystals up to 3” diameter can be grown in these furnaces. During the growth process, multiple random orientation crystalline grains are generated at the bottom of the ampoule capillary tip. As growth continues up the capillary, one crystal grain usually dominates. The full diameter crystal grows from this dominant grain. Random crystal orientation can lead to crystal cracking and cleaving. There are significant differences in the coefficients of expansion along the different crystal axes [17]. There is also a tendency of these halides to easily cleave along the cleavage planes that are parallel to the

<table>
<thead>
<tr>
<th>Material</th>
<th>Light output (photons/MeV)</th>
<th>Wavelength of maximum emission (nm)</th>
<th>Attenuation length at 511 keV (cm)</th>
<th>Initial photon intensity (photons/(ns MeV))</th>
<th>Principal decay time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaI(Tl)</td>
<td>38,000</td>
<td>415</td>
<td>3.3</td>
<td>165</td>
<td>230</td>
</tr>
<tr>
<td>CsI(Tl)</td>
<td>52,000</td>
<td>540</td>
<td>1.9</td>
<td>50</td>
<td>1000</td>
</tr>
<tr>
<td>LSO</td>
<td>24,000</td>
<td>420</td>
<td>1.2</td>
<td>600</td>
<td>40</td>
</tr>
<tr>
<td>BGO</td>
<td>8,200</td>
<td>505</td>
<td>1.1</td>
<td>30</td>
<td>300</td>
</tr>
<tr>
<td>BaF₂</td>
<td>10,000</td>
<td>220°, 310°</td>
<td>2.3</td>
<td>3400</td>
<td>0.6ᵃ, 620ᵇ</td>
</tr>
<tr>
<td>LaBr₃:10%Ceᶜ</td>
<td>80,000</td>
<td>360</td>
<td>2.1</td>
<td>3500</td>
<td>16</td>
</tr>
<tr>
<td>CeBr₃ᶜ</td>
<td>68,000</td>
<td>380</td>
<td>2.1</td>
<td>4000</td>
<td>17</td>
</tr>
</tbody>
</table>

ᵃFast component.
ᵇSlow component.
ᶜRMD results.
c-axis. The best orientation to grow from is a c-axis seed. This will minimize the expansion along the length of the crystal and it puts the cleavage planes parallel to the growth axis. This makes it less likely to cleave when the longitudinal contraction of the crystal occurs during the cool down at the end of the run. Once the crystals were in the lower furnaces, the furnaces were slowly cooled down to room temperature. This annealing and slow cooling step helped us to minimize the residual stress in the crystals. Fig. 3 shows a 2-in diameter crystal of LaBr$_3$:Ce.

In order to process the crystals, the quartz ampoules were carefully cut open with a low-speed O.D. saw. The crystals were cut with a diamond wire saw into test samples. During the sawing operation the samples were kept completely covered with mineral oil to minimize reaction with moisture in the air. The crystal samples were lapped and polished with oil-based diamond slurry on a Microcloth pad. The samples were then cleaned and characterized.

3. Results and discussion

Upon completion of the growth runs, the crystals that were still sealed in the quartz ampoules were viewed between crossed polarizers to observe any residual stress in the crystals. The visual absence of stress birefringence indicated that the crystals were stress free [18]. Large uncracked, single-crystal pieces were used for characterization and fabrication into scintillators.

The emission spectra of the LaBr$_3$:Ce and CeBr$_3$ samples were measured. A Philips X-ray generator was used to excite the samples. The X-ray generator had a copper target with settings of 30 kV and 15 mA. The emitted light of the scintillator was passed through a McPherson monochromator and detected with a calibrated Hamamatsu photomultiplier. Fig. 4 shows the emission spectrum of LaBr$_3$:Ce and CeBr$_3$ crystals.

The light outputs of LaBr$_3$:Ce and CeBr$_3$ samples were measured by comparing their response to 662 keV gamma-rays ($^{137}$Cs source) to the response of a calibrated BGO scintillator under the same test conditions. This measurement involved optical coupling of the crystals to a photomultiplier tube (with multi-alkali S-20 photocathode), irradiating the scintillator crystal with 662 keV photons and recording the resulting pulse height spectrums. In order to maximize light collection, the crystals were wrapped in thin layers of reflective, white Teflon tape on all faces except the one face coupled to the PMT. Teflon tape has always shown itself to be a very efficient optical reflector in the near-UV region. An index matching silicone fluid was used at the PMT–scintillator interface. A pulse height spectrum was recorded for the crystals. This measurement was then repeated with the calibrated BGO scintillator. Comparison of the photopeak position obtained with CeBr$_3$ for 662 keV photon energy to that with BGO provided an estimation of light output for the CeBr$_3$ crystal. The amplifier shaping time of 4 ms was long enough to allow full light collection from the BGO and CeBr$_3$ scintillators. The PMT bias and amplifier gain were the same for both spectra. Fig. 5 shows the room temperature light output of a CeBr$_3$ sample that has been exposed to a $^{137}$Cs source. Based on the recorded
photopeak positions for CeBr$_3$ and BGO, the light output of 8200 photons/MeV for BGO [19] and the photocathode quantum efficiency at the different emission wavelengths of BGO and CeBr$_3$, we estimated the light output of the CeBr$_3$ crystal to be about 68,000 photons/MeV. The energy resolution of the photopeak was 3.8% (FWHM). This compares quite well to other published results for CeBr$_3$ crystals [20,21]. The first author reported that the light output for CeBr$_3$ exposed to $^{137}$Cs 662 keV gamma-rays was about three times the value for a CsI(Tl) crystal with an energy resolution of 4.9%. The second author reported a photoelectron yield of 17,000 phe/MeV and an energy resolution of 3.9% at 662 keV on small irregular samples of CeBr$_3$.

An ideal scintillator will have a uniform optical response over a wide energy range. Proportionality or linearity of response was used to evaluate the LaBr$_3$:Ce and CeBr$_3$ samples. Fig. 6 shows the light output of a LaBr$_3$:10% Ce sample that was exposed to gamma-ray emissions from $^{241}$Am, $^{57}$Co, $^{22}$Na and $^{137}$Cs sources. The light outputs in photons/MeV from the different sources were all normalized to the light output from the $^{137}$Cs source at 662 keV. Fig. 7 shows the data plot of relative light yield versus energy for a LaBr$_3$:10% Ce and CeBr$_3$ samples. These plots indicate the proportionality or linearity of the scintillator material. For the energy range from 60 to 1275 keV the non-proportionality in light yield was about 6%. These results were much better than results seen for other scintillator materials like NaI:Tl, CsI:Tl, LSO, BGO or BaF$_2$. Fig. 8 shows the decay curves for LaBr$_3$:10% Ce and CeBr$_3$ samples.

4. Conclusion

During our research efforts we have investigated the scintillator crystals, LaBr$_3$:Ce and CeBr$_3$. These materials have been grown using the multizone vertical Bridgman process. Characterization of these large diameter crystals and devices has shown that these scintillators have high light output, fast response, high-energy resolution and good proportionality. The large diameter, high-quality
LaBr$_3$:Ce and CeBr$_3$ crystals have the desired properties for meeting the needs for advanced scintillator-based gamma-ray spectrometers for nuclear non-proliferation testing, nuclear physics, medical imaging, environmental remediation, and oil exploration.

Acknowledgments

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References