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The characterization of Eu^{2+}-doped mixed alkaline-earth iodide scintillator crystals

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ABSTRACT

The high-performance inorganic scintillator, $SrI_2:Eu^{2+}$, when activated with divalent europium in the concentration range of 3–6%, has shown great promise for use in applications that require high-energy-resolution gamma-ray detection. We have recently grown and tested crystals in which other alkaline-earth ions have been partially substituted for strontium ions. Specifically, europium-doped single crystals have been grown in which up to 30 at% of the strontium ions have been substituted for by barium, magnesium, or calcium ions. In the case of the strontium iodide scintillator host, a material that is characterized by an orthorhombic crystal structure, three other column IIA elements are obvious choices for investigations intended to realize potential improvements in the performance of $SrI_2:Eu^{2+}$-based scintillators via the replacement of strontium ions with Mg^{2+}, Ca^{2+}, or Ba^{2+}. Light yields up to 81,400 photons/MeV with an associated energy resolution of 3.7% (fwhm for 662 keV gamma rays) have been observed in the case of partial substitution of Ba^{2+} for Sr^{2+}. The measured decay times ranged from 1.1 to 2.0 μs, while the peak emission wavelengths ranged from 432 to 438 nm.

1. Introduction

Many current radiation detection and monitoring applications require high-energy-resolution gamma-ray detection capabilities for isotope identification. The high-performance inorganic scintillator, $SrI_2:Eu^{2+}$, when activated with divalent europium in the concentration range of 3–6%, represents a promising candidate material for applications of this type [1]. The performance of europium-doped SrI_2 is, in fact, comparable with that of $LaBr_3$:Ce [2–4] in terms of energy resolution, and it is superior to $LaBr_3$:Ce in terms of light yield. Specifically, light yields up to 120,000 photons/MeV with an energy resolution of 2.7% (fwhm at 662 keV) have been reported for europium-doped strontium iodide and these performance characteristics have led to a number of recent extended studies of the single-crystal growth, synthesis, and characterization of $SrI_2:Eu^{2+}$ [5–10]. $SrI_2:Eu^{2+}$ has the potential to be significantly easier to fabricate in large single-crystal form than $LaBr_3$:Ce because of its lower melting point (~530 °C), and high-quality single crystals of $SrI_2:Eu^{2+}$ have been grown up to 5.0 cm in diameter in quartz ampoules by means of the vertical Bridgman technique.

In the present work, we have grown and characterized alkaline-earth iodide scintillator crystals in which other alkaline-earth ions have been substituted for strontium ions. Specifically, europium-doped single crystals have been grown in which up to 30 at% of the strontium ions have been substituted for by barium, magnesium, or calcium. The ionic substitution of aliovalent elements is a well-established method of altering the crystal field, phonon, and other physical characteristics of crystalline materials. Accordingly, the current effort to potentially improve the scintillation properties of the alkaline-earth iodide scintillators is based on an established practice of substituting like ions for constituent members of the original material. Subtle changes in the crystal field effects on activator centers resulting from compositional alterations of this type, however, may or may not lead to significant improvements in the scintillation properties. In the case of the strontium iodide scintillator host, a material that is characterized by an orthorhombic crystal structure, three other column IIA elements are obvious choices for investigations intended to realize potential improvements in the performance of $SrI_2:Eu^{2+}$-based scintillators via the replacement of strontium ions with Mg^{2+}, Ca^{2+}, or Ba^{2+}.

2. Synthesis of Eu^{2+}-doped mixed alkaline-earth iodide scintillator crystals

The europium-doped mixed alkaline-earth iodide single crystals investigated here were grown in sealed and evacuated quartz

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ampoules by means of the vertical Bridgman technique. Alkaline-earth iodides with the desired ratios of alkaline-earth cations plus the europium iodide dopant were placed in a quartz Bridgman ampoule in a glove box filled with dry nitrogen. The quartz ampoule was then transferred to a vacuum system equipped with a liquid-nitrogen-filled cold trap using a method that avoided intervening exposure to air. The mixed growth charge was then dried, vacuum melted, and sealed in the quartz ampoule. The ampoule containing the vacuum-melted material was then returned to the dry box, where it was loaded into a second quartz ampoule designed with two chambers that were separated by a porous quartz frit filter. This ampoule was then transferred back to the vacuum system, where the previously fused growth charge was vacuum remelted, and the molten salt was filtered from the upper chamber of the ampoule through the quartz frit into the lower Bridgman growth ampoule section, which was subsequently sealed off. This molten salt filtration procedure has previously been found to be an effective means of removing insoluble rare-earth oxyhalides that frequently form in materials of this type. The sealed Bridgman growth ampoule was placed in a two zone Bridgman furnace where the upper-zone temperature was set between 550 and 600 °C depending on the ratio of alkaline earth to iodide. The lower-zone temperature in the furnace was fixed at 250 °C, and the quartz ampoule was lowered between the two zones at a speed of ~0.25 mm/h. After the entire Bridgman growth ampoule had been lowered into the low-temperature zone, the furnace was programmed to cool down to room temperature over a 99 h time span. The quartz ampoule was then transferred back into the dry box for removal and subsequent double sealing of the scintillator single crystals in plastic envelopes, with the outer envelope containing a drying agent.

3. Experimental conditions and results

The characterization measurements carried out for the mixed alkaline-earth iodide single-crystal samples included (1) light-yield determinations using gamma-ray excitation by ^{137}Cs and ^{57}Co sources, made relative to a bismuth germanate (BGO) reference scintillator crystal; (2) decay-time measurements that were made using the single-photon counting method and using gamma-ray excitation; and (3) emission spectra determinations made using X-ray excitation. A brief description of the methods used for these measurements along with the respective results follows.

3.1. Light output measurements using gamma-ray excitation

Europium-doped mixed alkaline-earth iodide single-crystal samples (or a reference BGO crystal) were mounted on a Hamamatsu 6233 photomultiplier tube, covered by four layers of Teflon tape, and excited in turn by ^{137}Cs and ^{57}Co gamma-ray sources. The pulses were processed using a Canberra 2005 preamplifier, an Ortec 672 shaping amplifier, and an Ortec Trump PCI8k multichannel analyzer with a 6 μs shaping time. Fig. 1 shows the pulse-height distribution results for a mixed SrI_2 crystal with 10 at% BaI_2 plus a 6 wt% EuI_2 activator along with the results for the BGO scintillator reference crystal—both irradiated by ^{137}Cs or ^{57}Co gamma rays. The light yield determined using 662 keV gamma rays is 81,400 photons/MeV when the results are corrected for the photomultiplier tube response. The data, which are summarized in Table 1, show that a light yield of 73,300 photons/MeV is obtained even when the BaI_2 content is increased to 20 at%. With an increase in the BaI_2 atomic percentage to 30%, the light yield deceases to 55,700 photons/MeV. This represents a significant decrease, but the lower value is still higher than that characteristic of many scintillators. These results show that the SrI_2:Eu^{2+} system is relatively tolerant in terms of barium substitution for strontium and that significant amounts of barium can be substituted for strontium in the SrI_2:Eu^{2+} scintillator system while still maintaining a relatively high light yield.

The results for the energy resolution of the $Sr_{1-x}Ba_xI_2$:Eu^{2+} system are also summarized in Table 1. The energy resolution for the 10 and 20 at% BaI_2 mixed crystals is approximately the same: ~3.7%. This value is equivalent to that determined for many pure (i.e., unmixed) SrI_2:Eu^{2+} scintillator crystals with the best reported value for pure SrI_2:Eu^{2+} being 2.7%. The data given in Table 1, however, show a dramatic drop in the energy resolution when the BaI_2 content in the $Sr_{1-x}Ba_xI_2$:Eu^{2+} system is increased to 30 at%. At this level of BaI_2 substitution, the energy resolution decreased to 20%.

Fig. 2 shows the pulse height distribution results for a series of three mixed iodide scintillator crystals in which varying amounts

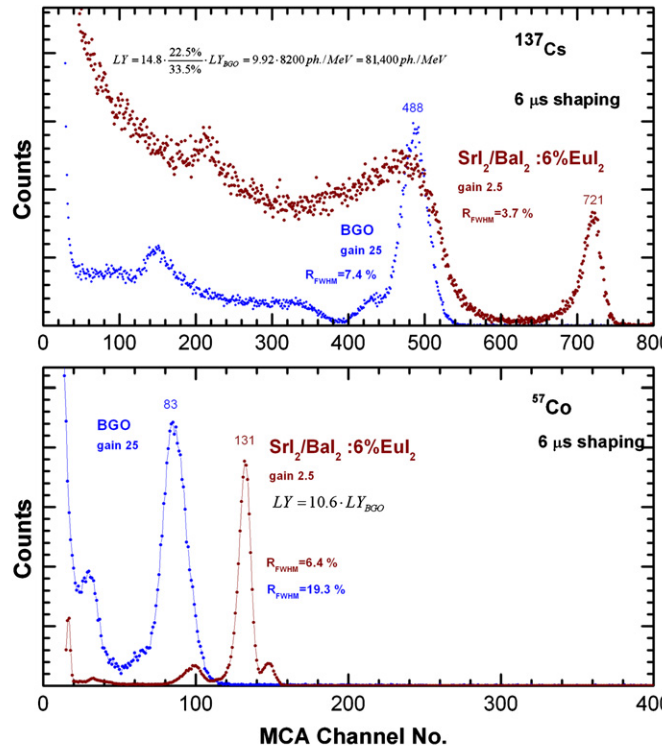

Fig. 1. Pulse-height spectra for SrI_2 with 10 at% BaI_2 plus a 6 wt% EuI_2 activator and a BGO reference scintillator irradiated by ^{137}Cs, 662 keV gamma rays (upper plot) or ^{57}Co (lower plot) gamma rays.

Table 1
Summary of light yield (as corrected for photomultiplier tube spectral response) and energy resolution (full width half maximum) data for europium-doped mixed crystals excited by 662 keV gamma rays.

$Sr_{1-x}A_xI_2$ with 6 wt% EuI_2		
A, *x*	**Light yield (photons/MeV)**	**Resolution (%, fwhm at 662 keV)**
Mg, 0.1	**55,500**	**7.8**
Mg, 0.2	**54,300**	**11.8**
Mg, 0.3	**55,100**	**5.5**
Ca, 0.05	**64,800**	**5.3**
Ca, 0.1	**64,900**	**8.7**
Ba, 0.1	**81,400**	**3.7**
Ba, 0.2	**73,300**	**3.6**
Ba, 0.3	**55,700**	**20**