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ABSTRACT

We find that the high-Z crystal Barium Iodide is readily growable by the Bridgman growth technique and is less prone to crack compared to Lanthanum Halides. We have grown Barium Iodide crystals: undoped, doped with Ce^{3+}, and doped with Eu^{2+}. Radioluminescence spectra and time-resolved decay were measured. BaI_2(Eu) exhibits luminescence from both Eu^{2+} at 420 nm (~450 ns decay), and a broad band at 550 nm (~3 μs decay) that we assign to a trapped exciton. The 550 nm luminescence decreases relative to the Eu^{2+} luminescence when the Barium Iodide is zone refined prior to crystal growth. We also describe the performance of BaI_2(Eu) crystals in experimental scintillator detectors.

Keywords: Scintillators, barium iodide, BaI_2, gamma ray detectors

1. INTRODUCTION

Detection sensitivity for weak gamma ray sources and rapid unambiguous isotope identification is principally dependent on energy resolution, and is also be enhanced by high effective atomic number of the detector material. The inorganic scintillator currently providing the highest energy resolution is $LaBr_3$(Ce), ~2.6% at 662 keV [1-3], but it is highly hygroscopic and its growth is still challenging. Barium Iodide is a candidate material offering higher Z (ρ=5.1 g/cm^3 and Z_{eff}= 54.1) and equivalent or higher light yield than $LaBr_3$(Ce). However, it apparently requires a monovalent or divalent activator, such as Tl^+ or Eu^{2+}, which have slower decay times compared to Ce-doped scintillators.

High light yields are found with many iodide scintillators, such as CsI(Tl) (65,000 Ph/MeV) and LuI_3(Ce) (about 100,000 Ph/MeV) [4, 5]. Many reports of scintillation from the family of alkaline earth halides have been published, originating with the work of Hofstadter on Calcium Iodide, in the 1960's [6] which exhibits light yields in the vicinity of 100,000 Photons/MeV and has been activated with many dopants, including Tl^+ and Eu^{2+}, though it is nearly impossible to grow substantial CaI_2 crystals due to its platelet growth habit. Efforts to demonstrate scintillation from Barium halides have indicated promising results, particularly for $BaBr_2$(Eu) measured at 32,000 Ph/MeV [7]. A few reports of scintillation from unactivated BaI_2 have appeared [8, 9], while the efforts of Selling, et al. to observe scintillation from Eu^{2+} doped BaI_2 were discouraging, with only 2,000 Ph/MeV [7]. We report here the scintillation characteristics of undoped, Cerium doped, and Europium doped Barium Iodide crystals. We find that zone refining the starting material results in very different scintillation spectra. Since we find that BaI_2 is a readily growable crystal with adequate mechanical properties and excellent overall light yield, we are modifying crystal growth parameters in order to produce a scintillator crystal with proportional, high light yield, and an acceptably fast decay in the blue spectral region where standard bialkali PMTs function well.

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2. EQUIPMENT AND METHODS

The single crystals of Barium Iodide were grown by the Bridgman technique at Fisk University. The melting point of BaI_2 is 711 °C and it possesses orthorhombic symmetry. Barium Iodide as-supplied powder, 99.995% pure ultra dry (Alfa Aesar) was yellowish. Crystals grown directly from the as-supplied powders retained a dark coloration. Zone refining was found to render the starting powders colorless, and resulting pure powders were used for the growth of several crystals.

Beta radioluminescence employed a ^{90}Sr source (beta endpoint energy 0.546 MeV). Radioluminescence spectra were collected with a Princeton Instruments/Acton Spec 10 spectrograph coupled to a thermoelectrically cooled CCD camera. A flashlamp pumped Nd:YAG laser at 10 Hz was operated at the 4^{th} harmonic of 266 nm, producing 20 ns FWHM pulses to excite the sample. Luminescence is collected with a monochromator coupled to an R928 Hamamatsu PMT and read out by an oscilloscope.

The scintillation light produced by the samples was detected by a commercially available Hamamatsu R980 bialkali PMT. The scintillators were optically coupled to the PMT by means of mineral oil and wrapped with several layers of Teflon tape. For all measurements, the scintillator was placed in the center of the entrance window of the PMT because in this region the photocathode has better uniformity and photoelectron collection at the first dynode is optimized. The signals from the PMT anode were collected on a 500 Ω load resistor, shaped with a Tennelec TC 244 spectroscopy amplifier (set with a shaping time equal to 8 μs for all the tested crystals) and then recorded with the Amptek MCA8000-A multi-channel analyzer for offline analysis.

3. RESULTS AND DISCUSSION

In this report, we describe the scintillation from Europium-doped Barium Iodide crystals grown from as-received powders and from zone refined materials (Figure 1). Additionally, we describe results from undoped Barium Iodide and Cerium-doped Barium Iodide, both grown from zone refined precursor.

3.1 Radioluminescence Spectra and Decay Times

We actuired the beta-excited luminescence of two BaI_2 crystals, both with Eu^{2+} doping of 0.5 mole percent, one of which was grown from zone refined (ZR) stock,; they are compared to a CsI:Tl standard crystal. The Eu^{2+} luminescence at ~420 nm is enhanced in the ZR crystal, while the broad ~550 nm band is reduced significantly (Figure 2). It is notable that the overall light yield is higher for the impurity-containing crystal; its integral light yield (including both the 420 nm band and the 550 nm band) is about 60,000 Ph/MeV. In Figure 3, the beta-excited luminescence of undoped BaI_2, BaI_2(Ce) (0.5mol%), BaI_2(Eu) (0.5 mol%) and BaI_2:Eu (1.5mol%) are shown for comparison. The weak band at 550 nm may be assigned to a trapped exciton, typically such luminescence is facilitated by the presence of impurity species. This is in good agreement with the reduction in the 550 nm band for zone refined crystals, compared to crystals grown from unrefined materials.

The alpha-excited luminescence of the ZR Ce-doped and the Eu-doped BaI_2 crystals show only luminescence consistent with Ce^{3+} and Eu^{2+} luminescence (Figure 4). Possible reasons include: (1) the de-excitation pathway for the higher dE/dx of alphas may favor the dopant luminescence, (2) the surface layer probed by alphas may differ in doping level or otherwise chemically from the bulk, resulting in a different observed spectrum.

Time resolved luminescence reveals that the Eu^{2+} band decays with a submicrosecond time constant (Figure 5), while the trapped exciton band is very long-lived, and cannot be fully integrated within a reasonable shaping time (<12 μs). It is interesting that the trapped exciton forms after excitation is transferred from the Eu^{2+}, as revealed by rise-time observed for 600 nm detection, and that it decays very slowly, on the tens of microseconds timescale (perhaps due to the exciton experiencing a triplet to singlet spin-forbidden transition).. For the ZR crystal, the Eu^{2+} decay is lengthened to 770 ns, which is still reasonable for scintillation counting. Further

improvements are likely with higher Eu^{2+} doping and the use of zone refined materials, such that light yields in the Eu^{2+} band could reach >60,000 Ph/MeV.

3.2 Pulse Height Spectra

The gamma ray pulse-height spectra of the 662 keV line of the Cs-137 radioactive source have been acquired with the Barium Iodide crystals and with a commercial CsI:Tl for comparison. The total absorption peaks have been processed with a Gaussian fit procedure to evaluate the peak position and the peak full width at half maximum, in order to estimate the scintillation light yield and the energy resolution, respectively. In Figure 6 the pulse-height spectrum of a BaI_2(Eu) (0.5 mol%) crystal is reported. Table 1 summarizes results of pulse height spectra acquired for all the crystals described above. The discrepancy between the integral light yield and the achievable energy resolution is in part due to delayed luminescence components, as well as poor spectral overlap between luminescence in the 550 nm band and the PMT quantum efficiency.

3.3 Conclusions

The high light yields observed under beta excitation and the improved light yield into the Eu^{2+} band with higher doping and zone refined materials suggest that Barium Iodide crystals could offer high energy resolution gamma ray spectroscopy.

Fig. 1. (left) Photograph of two Barium Iodide boules, showing the removal of a brownish coloration upon zone refining. (right) A BaI_2(Eu) crystal grown from zone-refined materials under room lights and under UV illumination.

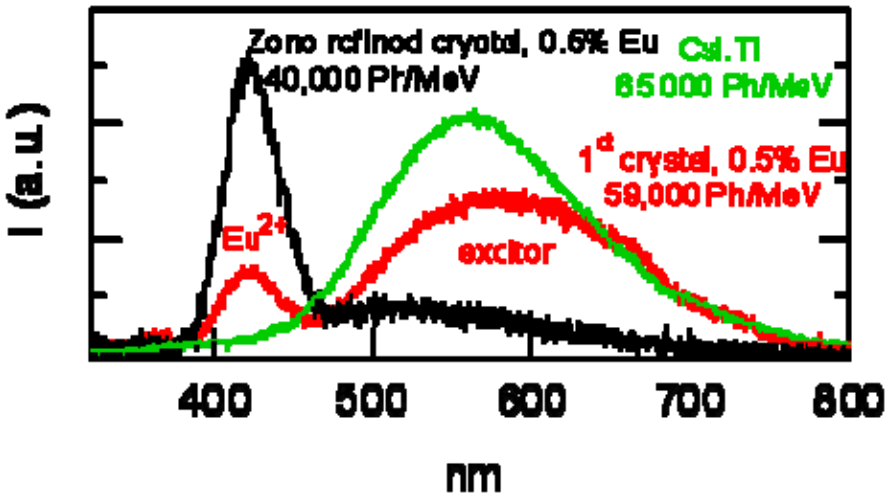

Fig. 2. Beta-excited radioluminescence spectra acquired of a two Eu-doped Barium Iodide crystals, one grown from as-received powders (black), the other from zone refined materials (red). Light yield is compared with that of Tl-doped Cesium Iodide (green), and may be compared in an absolute sense.

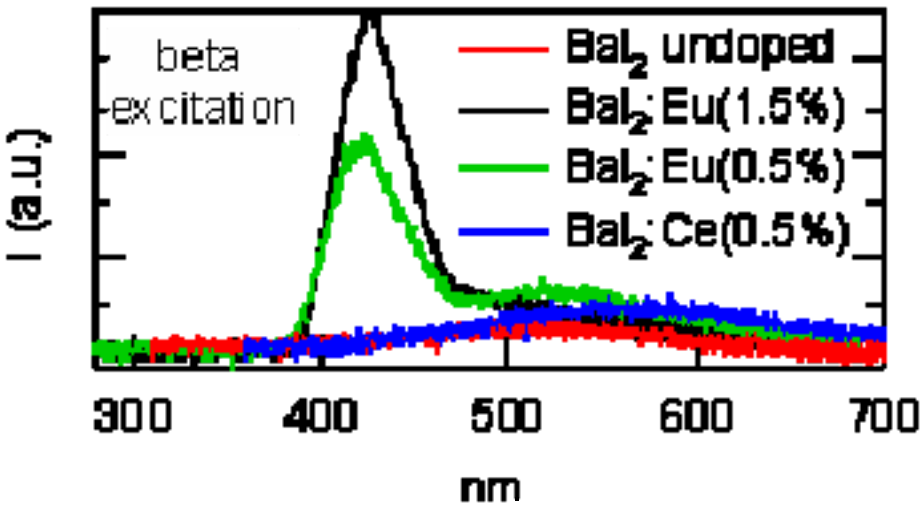

Fig. 3. Beta-excited radioluminescence spectra acquired of Barium Iodide crystals, all grown from zone refined materials. Light yields may be compared in an absolute sense.

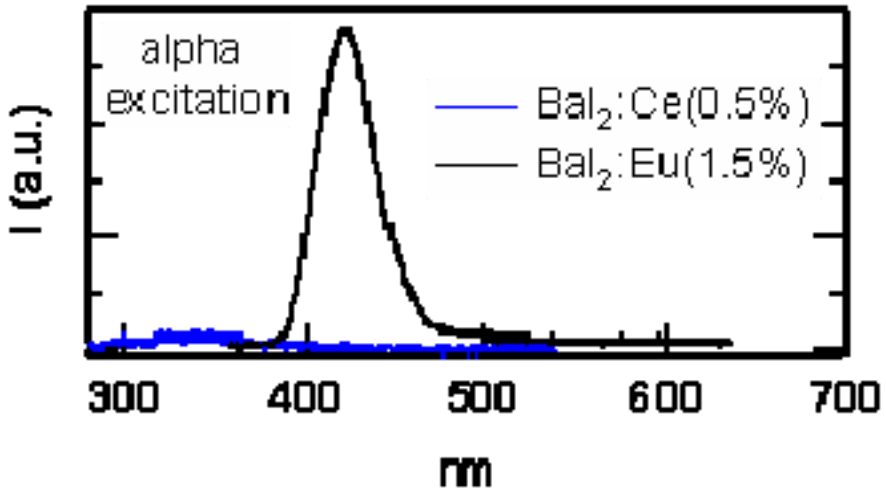

Fig. 4. Alpha-excited radioluminescence spectra acquired of a Ce- and a Eu-doped Barium Iodide crystal, both grown from zone refined materials. Light yields may be compared in an absolute sense.

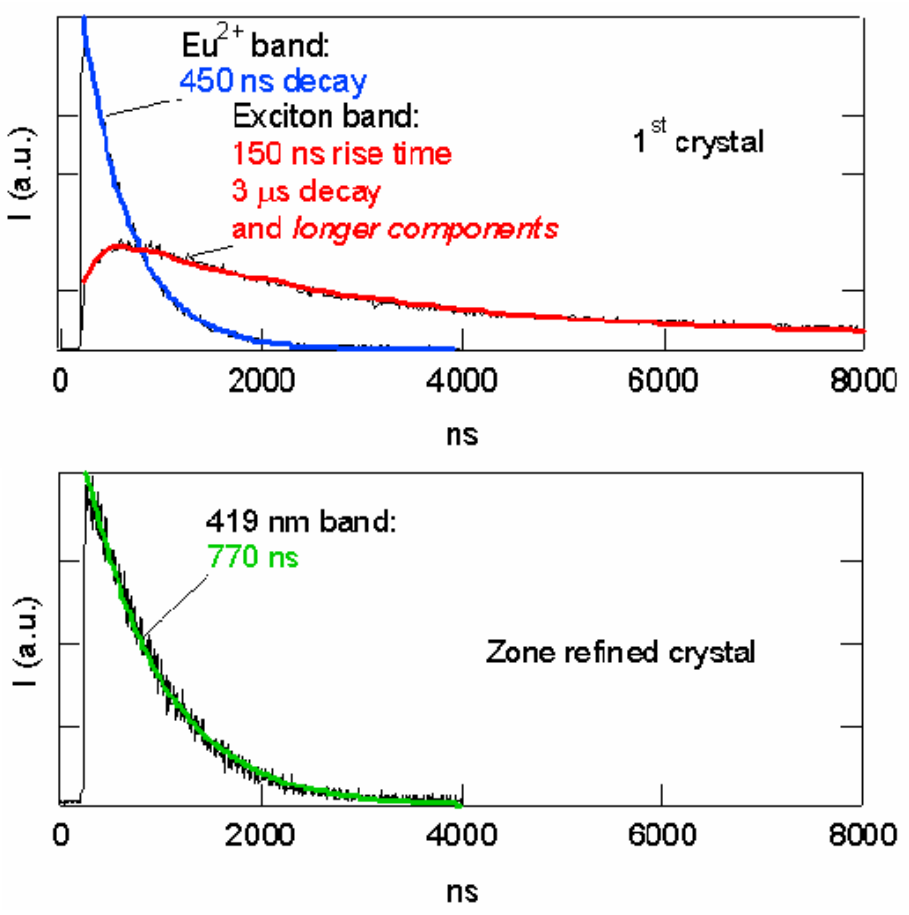

Fig. 5. Time-resolved luminescence decays acquired by excitation with 30 ns laser pulses at 266 nm.

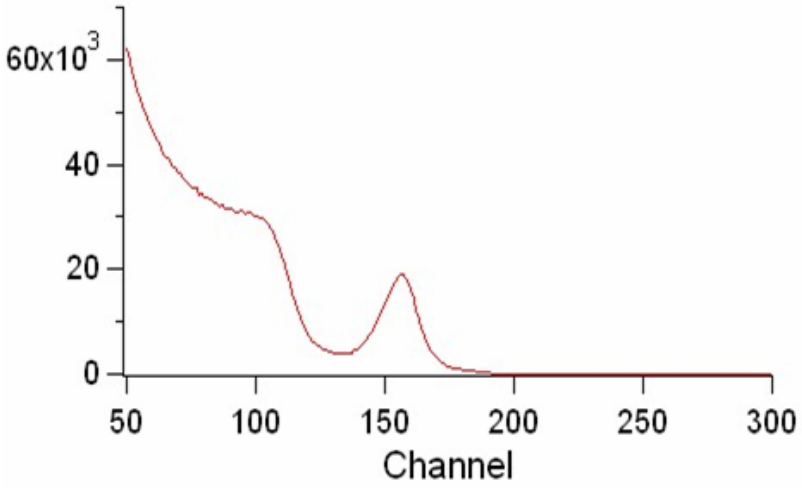

Fig. 6. Pulse height spectrum acquired of a BaI_2(Eu) (0.5 mol%) crystal grown from as-received powders, yielding energy resolution at 662 keV of 8%.

Table 1. Beta-excited light yields are acquired with silicon detector (CCD camera) with flat spectral response and integrate the measured luminescence spectrum over 30s, while the pulse height spectra acquired at 662 keV use a standard bialkali PMT, and a shaping time of 6-12 μs.

	Light Yield (all λ's, no timing gate, beta excitation)	**Energy Resolution** (662 keV)
CsI(Tl)	65,000	6.2%
BGO	9,750	12.7%
BaI_2 undoped (ZR)	5,850	--
BaI_2(Ce) 0.5% (ZR)	17,500	19%
BaI_2(Eu) 0.5% (ZR)	35,100	12%
BaI_2(Eu) 1.5% (ZR)	39,000	13.5%
BaI_2(Eu) 0.5% (not ZR)	59,000	8%

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