



Crystal growth and characterization of europium doped KCaI_3 , a high light yield scintillator



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ABSTRACT

The presented study reports on the spectroscopic characteristics of a new high performance scintillation material $\text{KCaI}_3:\text{Eu}$. The growth of \varnothing 17 mm boules using the Bridgman–Stockbarger method in fused silica ampoules is demonstrated to produce yellow tinted, yet transparent single crystals suitable for use in spectroscopic applications due to very promising performance. Scintillation light yield of $72,000 \pm 3000$ ph/MeV and energy resolution of 3% (FWHM) at 662 keV and 6.1% at 122 keV was obtained from small single crystals of approximately 15 mm^3 . For a much larger 3.8 cm^3 detector, 4.4% and 7.3% for the same energy. Proportionality of the scintillation response to the energy of ionizing radiation is within 96% of the ideal response over an energy range of 14–662 keV. The high light yield and energy resolution of $\text{KCaI}_3:\text{Eu}$ make it suitable for potential use in domestic security applications requiring radionuclide identification.

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1. Introduction

Scintillator based detectors of X-ray and gamma rays are utilized within nuclear non-proliferation efforts as well as domestic security applications. The capability to detect and identify radio-nuclides has depended on the energy resolution capabilities of scintillation based detectors such as $\text{NaI}(\text{Tl})$ for many decades despite the rather low energy discrimination ability (6–7% FWHM at 662 keV). Advancement of the available technology has relied on either improvements to existing materials or the discovery of new scintillation materials which can attain improved spectroscopic performance over the previous generation of devices. Recently, a new generation of binary metal halide scintillators including $\text{LaBr}_3:\text{Ce}$ [1] and $\text{SrI}_2:\text{Eu}$ [2] have been developed which offer energy resolution of 3% FWHM or better at 662 keV, thus introducing alternative materials for fabrication of radiation detectors with enhanced capability. While technologically superior, these new scintillators remain costly to produce and thus their widespread use has been limited. Nevertheless, comparable yet cheaper alternatives are desired and the search for new scintillators suitable for spectroscopic applications has seen a recent surge of discovery and investigation into new ternary compositions comprised of Group I, Group II elements and the halides. The most

promising among them are $\text{KSr}_2\text{I}_5:\text{Eu}$ [3] and $\text{CsBa}_2\text{I}_5:\text{Eu}$ [4], two very high performance scintillators reported to obtain <2.6% FWHM at 662 keV. Mixed halides comprised of $\text{BaBrI}:\text{Eu}$ [4] and $\text{Ce}(\text{Cl}-\text{Br})_3$ [5] have also shown promising performance with energy resolution of $\approx 3.5\%$ and $<5\%$ respectively.

In this work, we present results from the recent crystal growth and characterization of $\text{KCaI}_3:\text{Eu}$. The orthorhombic crystal belongs to the ABX_3 family of perovskite-type compounds ($A = \text{Cs, K}$; $B = \text{Ca, Sr, Ba}$; $X = \text{Cl, Br, I}$) with a density of $\rho = 3.81 \text{ g/cm}^3$ and adopts the Cmcm space group ($a = 4.561 \text{ \AA}$, $b = 15.086 \text{ \AA}$, $c = 11.639 \text{ \AA}$) [6]. $\text{KCaI}_3:\text{Eu}$ was first reported as one of the most promising of the ABX_3 compounds with a previously reported light yield of $\approx 70,000$ ph/MeV and energy resolution of 3.8% at 662 keV [7]. The earlier report remarked upon our early attempts at crystal growth of $\text{KCaI}_3:\text{Eu}$ which often encountered difficulties in attaining sizable crystals which tend to grow with a needle-like morphology due to the somewhat layered structure. Since revisiting the crystal growth of $\text{KCaI}_3:\text{Eu}$ with an emphasis on controlling the self-seeding process, we have achieved improvements in the quality of Bridgman grown crystals which has resulted in an increase in spectroscopic performance for large and small crystals over previous reports, as we will illustrate.

In order to present a more complete study of the scintillation performance characterization of $\text{KCaI}_3:\text{Eu}$ we include the scintillation lifetime, radioluminescence emission spectra, photoluminescence emission and excitation spectra, and non-proportionality curves.

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2. Experimental

2.1. Crystal growth

Samples were mixed from 4–5 N purity materials, in beaded form, from commercial sources Sigma Aldrich and APL. KI and CaI_2 were used as-received while EuI_2 was further purified by zone refining to remove excess trace metal impurities in the as-received chemicals. A stoichiometric mixture of 1:0.97:0.03 KI:CaI₂:EuI₂ was used to attain a nominal incorporation of 3 at.% Eu²⁺ substituting for Ca²⁺ sites in the matrix. This initial dopant concentration was chosen due to previous experiences with related compounds. The charges were loaded into quartz ampoules within a dry nitrogen atmosphere glove-box maintained at less than 0.1 ppm oxygen and moisture. The loaded ampoules were then sealed with a torch after heating to 250 °C for several hours under a vacuum of 10⁻⁶ torr to rid the precursors of any trace oxygen or moisture introduced during handling and transfer.

A thin capillary tip at the bottom of the ampoule often used for self-seeding was modified by introducing a 20° bend away from the axis of the ampoule to aid in preventing multiple grains from reaching the iso-diameter section during growth. Crystal growth was preceded by melting the charges within the growth furnace by soaking above 750 °C for several hours. The Bridgman-Stockbarger furnace used for the growth and synthesis is comprised of two resistive heating zones enclosed in a gold coated quartz cylinder. More information about this setup can be found in reference [8]. Thermal gradients of 20–30 °C/cm were used with growth rates of 0.5–1.0 mm/h and cooling rates of 5–10 °C/h. After growth, the ampoules were opened and all subsequent handling, cutting, and polishing took place within a dry nitrogen glove-box.

It should be noted that $\text{KCaI}_3\text{:Eu}$ exhibits a level of hygroscopicity similar to that found in most iodides such as SrI_2 . Decomposition of the bare crystal surface occurs gradually from brief exposure to ambient moisture of several seconds to minutes at 40–50% relative humidity and is characterized by a clouding which impedes light emission from the bulk. Re-polishing of the surface after brief exposure is effective in restoring the scintillation properties. Further decomposition results in total deliquescence of the bulk after several hours or days of exposure. Crystals submerged in mineral oil or stored dry in molecular sieve under dry nitrogen or other inert gas appear to maintain their surface finish and do not degrade over time. As a result, a thin layer of mineral oil on the surface is sufficient protection during characterization lasting several minutes with total submersion in an oil filled quartz cuvette adequate for longer measurements. In our experience, a highly polished surface is less prone to rapid degradation.

Samples used for characterization were either cleaved or cut using a low speed wire saw, then ground and polished by hand using grinding papers and anhydrous lapping oil. The melting and freezing points of $\text{KCaI}_3\text{:Eu}$ were determined by differential scanning calorimetry (DSC) using a Labsys EVO instrument. Approximately 50 mg single crystal specimens within alumina crucibles were heated and cooled at 5 K/min under a flow of ultra-high purity argon. Each sample is ran concurrently using the same heating and cooling profile twice. For a baseline subtraction to the heat flow, the same crucible pan is ran empty in identical fashion prior to measuring with the sample.

2.2. Optical and scintillation performance characterization

The radioluminescence emission spectrum acquired in air atmosphere with a thin layer of mineral oil on the surface of a \varnothing 17 mm \times 2 mm crystal was produced in reflection mode under excitation from an X-ray source with a Cu target operated at

35 kV. The emission spectrum was recorded with a 150 mm focal length monochromator and broadband photomultiplier tube (PMT) over a wavelength range of 200–800 nm. Emission intensity was corrected for the spectral sensitivity of the measurement setup. Scintillation decay time under ¹³⁷Cs source excitation for a 5 \times 5 \times 5 mm³ crystal submerged in a mineral oil filled quartz cuvette was determined using the time correlated single photon counting method for a 10 μ s shaping time. The photoluminescence excitation and emission spectra of a \varnothing 17 mm \times 2 mm crystal covered with a thin layer of mineral oil was produced using a Horiba Fluorolog with a 450 W Xenon lamp and a Hamamatsu R928 PMT.

A small $\text{KCaI}_3\text{:Eu}$ single crystal \varnothing 2 mm \times 5 mm taken from the capillary region was used in the assessment of spectroscopic performance under excitation from a gamma source library consisting of ¹⁰⁹Cd, ²⁴¹Am, ⁵⁷Co, ¹³³Ba, ²²Na, ¹³⁷Cs, and ⁵⁴Mn. The source library produced responses to a range of energies from 14–1274 keV. Similarly, a larger crystal \varnothing 17 mm and 17 mm in length (\approx 3.8 cm³) was cut and polished to produce pulse height spectra under ¹³⁷Cs, and ⁵⁷Co source excitation in order to compare the energy resolution achievable with larger crystal volumes. All pulse height spectra were obtained with the crystal specimens submerged in a mineral oil filled quartz cuvette to prevent degradation during prolonged measurements. A measure of the absolute scintillation light yield from bare crystals directly coupled to the PMT was derived from the relationship between the 662 keV photopeak from a ¹³⁷Cs source to the single photo-electron response in a Hamamatsu R2059 PMT. The radioluminescence emission spectrum was convolved with the quantum efficiency of the PMT used to accurately estimate the number of collected scintillation photons from the photoelectron yield. The PMT signal processing chain consisted of a Canberra model 2005 pre-amplifier, an Ortec 672 amplifier, and a Tukan 8K multi-channel analyzer. A Hamamatsu R6231-100 Super Bi-alkali PMT was replaced in the setup and used for energy resolution measurements due to its greater quantum efficiency. A diffuse reflector comprised of a solid Teflon dome was used to maximize scintillation light collection in the photomultiplier tube (PMT).

3. Results

3.1. Crystal growth

The DSC curves are shown in Fig. 1. The melting point of $\text{KCaI}_3\text{:Eu}$ is 524 °C which is the same as that determined for pure KCaI_3 [6]. Under 5 K/min heating and cooling rate, this particular sample exhibited a relatively small degree of supercooling (melting point-freezing point = 20–25 °C). The small exothermic peak at 425° is believed to be a decomposition product formed once the sample is melted. The magnitude of this peak grows with subsequent scans and is accompanied by an endotherm only upon the second scan, meaning it is not present prior to melting in the first scan. The plot shown in Fig. 1 is from the first cycle. The absence of any additional endothermic or exothermic peaks other than the melting and freezing point isotherms indicates no solid–solid phase transitions occur between freezing and 25 °C. Thus the orthorhombic phase observed at room temperature is what crystallizes from the melt.

A \varnothing 17 mm single crystalline boule is shown in Fig. 2 which contained a singular transverse fracture seen at the top of the capillary region which occurred during the cooling process. The polycrystal-single crystal demarcation can be observed at the lower portion of the capillary which corresponds to the initial melt-crystal interface at the beginning of growth. The polycrystalline region at the bottom most section of the capillary contains a small amount (<0.2 g) of partially unreacted CaI_2 due in part to

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