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Growth and characterization of potassium strontium iodide: A new high light yield scintillator with 2.4% energy resolution

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ABSTRACT

A new ternary metal halide scintillator, potassium strontium iodide, activated with divalent europium (KSr_2I_5:Eu) has been discovered. This material has a monoclinic crystal structure with a density of 4.39 g/cm^3. Differential scanning calorimetry indicates a congruent melting point of 470 °C and suggests that this compound has no solid–solid phase transitions. As is the case with most metal halides, the material is hygroscopic, and it has some internal radioactivity due to the presence of ^{40}K. Single crystals of KSr_2I_5 doped with 4% Eu^{2+} were grown in evacuated quartz ampoules via the Bridgman technique. The X-ray excited emission spectrum consisted of a single peak at ~445 nm due to the 5d–4f transition in Eu^{2+}. The measured light yield is ~94,000 photons/MeV with an energy resolution of 2.4% at 662 keV. The crystal has an excellent proportionality response over a wide range of energies from 14 keV to 1275 keV.

1. Introduction

Scintillators are common radiation detectors with a variety of applications, many of which have specialized requirements; as a result, scintillators are often developed with properties suitable for specific applications and devices in mind. Utilization for nuclear nonproliferation requires excellent energy resolution for spectroscopic differentiation of radioisotopes in order to minimize false alarms [1]. Medical imaging applications favor scintillators with high light output for improved spatial resolution of pixel arrays. Such arrays can then be used to produce high quality images to aid medical professionals in the early diagnosis of disease. Regardless of application, cost is a major consideration for widespread implementation of a detector. [2]

Current radiation detectors fail to satisfy all of these requirements to some extent. High purity germanium detectors offer an unparalleled energy resolution, but are expensive and require cryogenic cooling which is cumbersome to maintain. Another promising semiconductor radiation detector, CZT, is also expensive and growth technology has not advanced enough to produce crystals large enough for some applications [3]. One of the most common scintillators on the market, NaI:Tl, has become very cheap to manufacture in large quantities though its energy resolution limits its usability in next generation instruments [4]. Plastic scintillators are attractive for some applications because they can be made in a variety of shapes and sizes, but their very poor energy resolution limits their applicability.

Metal halide compositions have been used as scintillators since NaI:Tl was first discovered in 1948. More recently, $LaBr_3$:Ce [5] and SrI_2:Eu [6] have emerged as materials with potential to supersede NaI:Tl [7] due to their excellent scintillation properties.

Recently KSr_2I_5:Eu was discovered at the Scintillation Materials Research Center. KSr_2I_5:Eu 4% has a measured light yield of 94,000 ph/MeV and an excellent energy resolution of 2.4% at 662 keV [8]. The crystal structure of KSr_2I_5 was first reported by Schilling et al. It has a monoclinic structure with space group $P12_1/c1$ and a density of 4.39 g/cm^3 [9]. The effect of the ^{40}K background radiation on isotope identification sensitivity remains to be quantitatively analyzed, but these properties suggest that it may be well suited for uses in both homeland security and medical imaging where this high light output and excellent energy resolution are crucial for next generation applications.

2. Experimental

2.1. Crystal growth

The 99.99% pure KI, SrI_2 and EuI_2 raw materials from Sigma-Aldrich were mixed and loaded into quartz ampoules in a dry box with < 0.1 ppm moisture and oxygen. All ampoules were cleaned with deionized water and baked at 200 °C before use. The loaded ampoules were dried at 200 °C and sealed under a vacuum of 10^{-6} Torr.

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Single crystals of 13 and 22 mm in diameter were grown by the Bridgman technique. A two zone transparent furnace was used to allow the observation of melting, nucleation, and evolution of the solid–liquid interface shape. Crystal growth was initiated on a 2 mm diameter grain selector connected to the bottom of the ampoule. A relatively fast solidification rate of 5 mm/h and cooling rate of 10 °C/h were used for the ø13 mm crystal. For the ø25 mm crystal a pulling rate of 1 mm/h and cooling rate of 5 °C/h were used.

2.2. Characterization

The melting and crystallization temperatures were determined through differential scanning calorimetry–thermogravimetric analysis (DSC–TGA) using a Setaram Labsys Evo TG–DSC. The measurement was carried out on a ~50 mg specimen at 5 K/min, under a flow of ultra-high purity argon gas.

Moisture sorption profiles were recorded using a Dynamic Vapor Sorption technique with a DVS Intrinsic instrument by Particulate Systems [10]. Spherical samples with a surface area of $\sim 28 \pm 2$ mm^2 were prepared. The measurements were carried out at 25 °C for 60 min at a relative humidity of 40%.

Steady state photoluminescence spectra were measured at room temperature with a Horiba Jobin Yvon Fluorolog 3 Spectrofluorometer equipped with a Xe lamp and dual scanning monochromators.

The scintillation light yield was measured by coupling a sample to a Hamamatsu 3177-50 PMT and recording the response to 662 keV gamma rays from a ^{137}Cs source. The specimens were placed in a quartz container filled with mineral oil to protect them from moisture during the measurement. The mineral oil also served as optical coupling between the quartz container and PMT. A hemispherical dome of Spectralon was used to diffusely reflect the scintillation light into the PMT, and a shaping time of 10 μs was used to ensure the complete integration of the light pulse. The number of photoelectrons was calculated from the position of the 662 keV photopeak and the peak from single photoelectrons. The conversion from the number of measured photoelectrons to the number of photons/MeV emitted by the scintillator was accomplished by convolving the quantum efficiency of the PMT as a function of wavelength (measured by the manufacturer of our specific PMT) with the X-ray excited emission spectrum of the sample. We assumed 100% collection of photons by the PMT which likely gives a somewhat pessimistic estimate of the crystal's actual light output. Measurements of energy resolution for ^{137}Cs, ^{57}Co and ^{241}Am gamma rays were recorded by coupling the samples to a Hamamatsu R6231-100 PMT.

Radioluminescence spectra were measured at room temperature under continuous 30 keV X-ray irradiation. The emission spectra were recorded with a 150 mm focal length monochromator over a wavelength range of 200 to 800 nm.

The scintillation decay time was measured under irradiation from a ^{137}Cs sealed source with the time-correlated single photon counting technique [11].

3. Results and discussion

3.1. Single crystal of KSr_2I_5:Eu 4%

Large single crystals were obtained from both growth attempts. The ø13 mm boule was grown at a remarkably fast rate (5 mm/h) and fast cooling rate (10 °C/h), and the result was the highly transparent, virtually crack free, colorless single crystal shown in Fig. 1. The ø22 mm boule was growth rate at 1 mm/h and cooled to room temperature at 5 °C/h. The result was a highly transparent crystal, shown in Fig. 2. The growth parameters used for KSr_2I_5:Eu are at least 5 times faster when compared SrI_2:Eu. To achieve crystals of comparable quality, the reported growth rates for SrI_2:

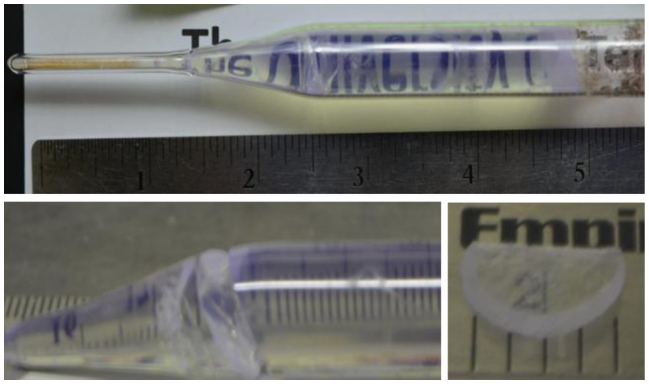

Fig. 1. Appearance of a 13 mm diameter single crystal of KSr_2I_5:Eu 4%: top—in the ampoule.

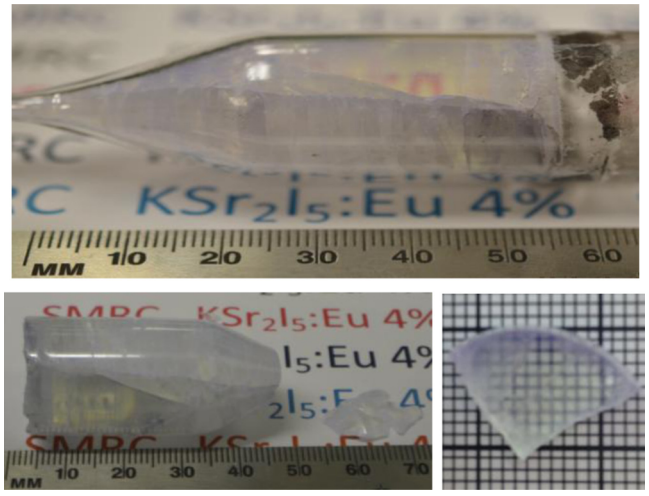

Fig. 2. Appearance of a 22 mm diameter single crystal of KSr_2I_5:Eu 4%: top—in the ampoule, bottom—bare crystal.

Eu are between 5 and 19 mm/day [12,13]. Note that a fast growth rate significantly lowers the ultimate cost of the scintillator.

Growth parameter optimization and zone-refining of the raw materials are expected to improve the general performance of the crystal. Pieces of various sizes were prepared for optical and scintillation characterization.

3.2. Melting point determination

Differential scanning calorimetry was performed on KSr_2I_5:Eu 4% to determine its melting point. The scan shown in Fig. 3 indicates that the melting point is 470 °C, and its crystallization point is 466 °C. A small feature at 410 °C needs further investigation.

3.3. Hygroscopicity evaluation

The dynamic vapor sorption technique was used to compare the moisture absorption rate of KSr_2I_5:Eu 4% to other scintillators as shown in Fig. 4. The moisture absorption rate of $LaBr_3$:Ce 5%, SrI_2:Eu 1% and NaI:Tl were measured under identical conditions. Attempting to reproduce typical operational conditions of detectors, a temperature of 25 °C and relative humidity of 40% were selected. The initial degradation effects from moisture can be seen almost instantaneously, and further moisture absorption continues during the 60 min acquisition time used for this measurement [14].

The moisture absorption rate of KSr_2I_5:Eu is ~2.5 times higher than the one of NaI:Tl, but when compared to SrI_2:Eu and $LaBr_3$:Ce, a ~20% reduction of the rate is observed. This