Nonproportionality and Scintillation Studies of Eu: SrI$_2$ From 295 to 5 K

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Abstract—The low temperature scintillation properties of 5 atomic % Eu: SrI$_2$ from ambient temperature down to 5 K were studied for the first time. With decreasing temperature, a shift in emission wavelength and a shortening of decay time were observed. Light yield and energy resolution exhibited notable changes with temperature, and were maximized as temperature was decreased. A degradation of light yield proportionality with decreasing temperature was observed.

Index Terms—Alkaline-earth halides, decay time, energy resolution, light yield nonproportionality, scintillation detectors, SrI$_2$.

I. INTRODUCTION

Efficient radiation detectors must be able to distinguish between different radioactive sources. For gamma-ray detection, scintillator materials with high energy resolution, high light yield, and a short decay time are required. Previous studies on Tl:NaI [1], Ce:LaBr$_3$ [2], Bi$_4$Ge$_3$O$_{12}$ (BGO) [3], Ce:Y$_2$Al$_5$O$_{12}$ (YAG) [4], Ce:Lu$_2$Si$_2$O$_7$ (LSO) [5], and Ce:YAlO$_3$ (YAP) [6] have shown that some scintillation properties can be temperature-dependent. However, the role of temperature on light yield nonproportionality remains to be better understood.

Light yield nonproportionality [7]–[13] refers to the non-proportional relationship between the number of visible photons produced in a scintillator and the energy deposited within that crystal. This is characteristic of most known scintillators and vitiates their ability to determine the energy of the gamma-radiation with precision [14], [15]. Nonproportionality has been attributed to various energy loss mechanisms that occur following the absorption of ionizing radiation, including the generation of secondary X-rays and Auger electrons from photoelectric absorption, multiple Compton scattering of electrons (which may then be followed by full-energy absorption), and the creation of delta-rays [9], [16]–[18]. Vasil’ev [19] and Bizarrì et al. [20] modeled these interaction mechanisms by studying the transformation of the electronic excitations and their recombination rates. Temperature has been found to play a role in these analyses since it affects charge mobility, trapping, and the probability of radiative recombination during the scintillation process [21].

Only a few experimental studies have been carried out on the thermal dependency of nonproportionality. In 1970, West and Collinson studied the light yield proportionality in NaI and found an improvement with increasing temperature in the range of 95 to 181 K [22]. On the other hand, a recent study on Ce:LaBr$_3$ by Khodyuk et al. revealed that light yield proportionality was degraded as the temperature was increased from 80 to 450 K [23]. From these few published studies, however, no straightforward relationship can be drawn between nonproportionality and temperature. It is evident that more experimental work is needed to elucidate this relationship.

In this investigation, we explored the thermal dependency of the scintillation properties and light yield nonproportionality of 5 atomic% Eu: SrI$_2$ (hereafter Eu: SrI$_2$) in the range of 5 to 295 K. This material, which is of great interest to the scintillator community, was selected because of its excellent light yield, energy resolution, and proportional behavior [24], [25]. Thus far, Eu: SrI$_2$ has only been characterized at room temperature [24]–[26], and between 80 to 600 K [27]. In our investigation, we extend the characterization to the low-temperature regime below 80 K.

II. EXPERIMENTAL

A. Materials Preparation

A 7 mm × 7 mm × 4 mm sample was sectioned from a single crystal boule of SrI$_2$ doped with Eu$_2$. Ultra-dry, 99.9% purity SrI$_2$ powder from Sigma–Aldrich was used as the starting material and was sealed in a clean and pre-baked quartz ampoule under high vacuum of 4 × 10$^{-6}$ torr. The material was zone-refined before crystal growth with a 5% doping level of Eu$_2$ using the Bridgman–Stockbarger technique. The dopant concentration of Eu$^{2+}$ in the sample was quantified to be (5.3 ± 0.3)% by the Evans Analytical Group using inductively coupled plasma mass spectroscopy. The sample was first wrapped with Vikuiti Enhanced Specular Reflective Film (ESR,
trademark of 3M), a highly efficient, specular reflector tailored to fit the crystal faces, and then wrapped with Teflon tape to secure the ESR, as explained in [28]. Due to the hygroscopic nature of the material, sample handling and preparation were performed in a glove-box with an H₂O content lower than 10 ppm, and then sealed for air-tight transfer to the experimental and measurement apparatuses.

B. Experimental Set-up and Measurements

Temperature studies were performed using an Oxford Instruments Optistat CF liquid helium continuous flow cryostat. Due to the hygroscopic nature of the sample, the cryostat was evacuated and flushed with dry He gas to remove moisture from the system prior to sample insertion. The cryostat includes a vacuum jacket for insulation (pumped down to 10⁻⁶ torr), and five optical ports with quartz windows. Four of the windows were blocked off and the remaining one was used for light collection. A Cernox 1030 temperature sensor mounted near the sample along with a temperature controller were used to monitor and regulate the temperature, respectively. The central system (cryostat body and photomultiplier tube) were located in a dark enclosure. A schematic of this system with the described customizations is shown in Fig. 1.

Using an Ocean Optics fiber-coupled reflection probe mounted on one of the cryostat’s optical ports, the sample was excited with 300 nm light (monochromated from a Xenon lamp) and the resultant fluorescence was collected with an Ocean Optics QE 65000 spectrometer. Pulse-height gamma-ray spectroscopy measurements were obtained using commercial solid sources (²⁴¹Am, ¹³³Ba, ¹⁰⁹Cd, ⁵⁷Co, ¹³⁷Cs, ¹³²Eu, ⁵⁴Mn, and ²⁷Na) from Eckert & Ziegler Isotopes Products GmbH. An XP Photonis 2060 photomultiplier tube (PMT) was coupled to an optical port of the cryostat with Bicron BC-630 optical grease. The PMT output signals were processed with a Canberra 2022 amplifier using a shaping time of 4 μs. Since Eu:SrI₂ is a bright scintillator, precautions were taken to select a PMT bias voltage that would prevent PMT saturation [28]. The amplifier output was collected and recorded with an Amptek MCA-8000A pocket multichannel analyzer. For each pulse-height spectra, at least 5000 counts under each photopeak were obtained to ensure a high signal-to-noise ratio. The photopeak centroid and full-width at half-maximum were determined by fitting the full-energy peaks in the pulse-height spectra using a Gaussian function and an exponential background. The light output trend was estimated from the location of the photopeak centroid at a given temperature normalized to the value at 295 K.

Decay times were obtained by recording 1600 pulses per temperature directly from the PMT using a Yokogawa DL6154 digital oscilloscope and a 50 Ω terminator to match the cable impedance. During data-processing, a pulse pile-up rejection algorithm was implemented using a ROOT macro.¹ The decay time for a given temperature was determined from averaging the calculated values derived from the fits of the 1600 pulses.

Furthermore, to verify that no sample degradation or damage occurred during the course of the experiment, pulse-height spectra were acquired at the beginning and end of the experiment at 295 K, and at 180 K during the cooling and heating of the cryostat. The shift in photopeak position was determined to be less than 0.5%, confirming that the sample remained unaltered.

III. RESULTS AND DISCUSSION

A. Decay Time

Only one decay component was observed in the 5 to 295 K range, which is in agreement with the findings of Cherepy et al. [26] and Glodo et al. [29] at room temperature. Fig. 2 shows a scintillation trace at 5 and 180 K. The measured decay time as a function of temperature is shown in Fig. 3. At room temperature, the decay time was determined to be (1.24 ± 0.07) μs. As the temperature was decreased to 5 K, the average decay time decreased, eventually leveling off at (0.37 ± 0.07) μs, which we take to be the radiative lifetime of the 5d-4f emission of Eu⁷⁺ in SrI₂. This value confirms the extrapolated predictions of Alekhin et al. [27].

The increase in the decay time for Eu:SrI₂ with increasing temperature is primarily due to an enhanced probability of emission re-absorption, or radiation trapping, which prolongs the time for the emitted light to exit the scintillator, resulting in a longer decay time [27], [29]. This is reflected in the larger overlap between the emission and absorption spectra, as was observed by [27] for the same material in the 80 to 600 K temperature regime. This radiation trapping phenomenon has also

¹Information on ROOT is available online at http://root.cern.ch
Fig. 3. Evolution of measured decay time as a function of temperature for Eu:SrI$_2$ under $^{137}$Cs gamma-ray excitation.

Fig. 4. Fluorescence spectra of Eu:SrI$_2$ at low temperatures under 300 nm excitation.

been observed in fluoride scintillators [30]–[32]. The relatively high concentration of dopant is also conducive to this phenomenon [33].

B. Emission Spectra

The 300 nm-excited fluorescence spectra of Eu:SrI$_2$ at each temperature had a single emission peak corresponding to the Eu$^{2+}$ $^4f^5d^1$ $^4f^7(^6S_{7/2})$ transition (Fig. 4). At room temperature, the emission peak was centered at approximately 440 nm. As the temperature was increased from 5 to 295 K, a red shift was observed, with a magnitude of 10 nm. This shift corresponds to the increase in emission-reabsorption that occurs with increasing temperature. This is in agreement with the trends observed by Alekhin et al. in [27], in which the emission peaks were shown to broaden and shift to longer wavelengths as the temperature was increased above 100 K. The maximum emission intensity was observed between 130 and 180 K (Fig. 4, inset).

C. Light Output

The light output, normalized to its value at 295 K, is shown as a function of temperature in Fig. 5. The relative light output increased as the temperature was decreased towards 130 K, with the maximum occurring between 130 and 180 K, where the emission intensity was also observed to be greatest. Although the local minimum at 150 K is a singular point that has not been verified, the overall trend in light output was confirmed. The increasing light output may be attributed to the reduction in nonradiative processes that typically dominate and reduce luminescence in alkali halides at higher (i.e., ambient) temperatures [34].

The light output fell rapidly as the temperature was decreased to 77 K, below which the light output remained relatively constant. The decrease in light output at the lower temperatures might be due to the presence of traps. A recent thermoluminescence study on 1 atomic % Eu:SrI$_2$ by Yang et al. [35] revealed a number of shallow traps below 100 K, as well as a series of deep traps (greater than half the calculated band-gap of 4.5 eV [36]) above 255 K. The decreased light output at lower temperatures may also be attributed to the fact that as temperature is decreased, the contribution to luminescence from the activator is reduced. This leaves only the contribution from the excitonic luminescence, which becomes more efficient since the self-trapped holes in the material become virtually immobile [34].

D. Energy Resolution

The total energy resolution as a function of gamma-ray energy is shown in Fig. 6. The energy resolution at ambient temperature was determined to be (11.4 ± 0.3)%), which is larger than the typically reported values [26]. This is due to the lack of direct optical coupling between the sample and the PMT. However, the general evolution of the total energy resolution with temperature should exhibit the same behavior. The total energy resolution was improved at lower temperatures, with an optimum occurring between 130 and 180 K. By comparing Figs. 5 and 6, it is clear that a strong correlation exists between the optimum in energy resolution and light output. This relationship can be explained by the fact that a high light output reduces the statistical uncertainty from the photomultiplier, which in turn improves the overall energy resolution [37].

E. Light Yield Nonproportionality

The relative light yield of Eu:SrI$_2$ was determined for temperatures ranging from 5 to 295 K. The gamma response at ambient temperature was found to have the same general trend as
the electron response presented by Payne et al. in [38]. The non-proportionality data for 5, 180, and 240 K are shown in Fig. 7. The spline curves (dashed lines) suggest that the light yield proportionality was degraded with decreasing temperature. The dip at 240 K corresponds to 31 keV and 32.1 keV K-alpha X-rays from the 133Ba and 137Cs sources. The dip is shifted towards 40 keV, however, due to contributions from the K-beta X-rays [39], [40]. It was difficult to determine the changes in non-proportionality as a function of temperature from the non-proportionality curves alone. However, since the light yield response of Eu:SrI2 was least proportional at the lower gamma-energies, focusing on the variations in this energy region made it easier to observe changes in the nonproportionality response. Therefore, for this analysis, the following definition was used [41]:

\[ NP_{E<\gamma/662} - \frac{Y_{E<\gamma \text{ keV}}}{Y_{662 \text{ keV}}} \]

with \( Y_{E<\gamma \text{ keV}} = 31, 32, \) and 41 keV. The variation of \( NP_{E<\gamma/662} \) with temperature is shown in Fig. 8, in which the dashed lines represent linear fits. The variation in the nonproportionality response was estimated to be 5% over the temperature range of the experiment. The increasing deviation from unity at lower temperatures for all three gamma-energies supports the initial conclusion that the light yield proportionality was degraded with decreasing temperature.

IV. CONCLUSION

Decay times, emission spectra, light output, energy resolution, and light yield nonproportionality were measured for 5 atomic % Eu:SrI2 from 295 down to 5 K. The already excellent scintillation properties are particularly enhanced in the lower temperature range of 130 to 180 K, with a reduction in decay time and increase in light output by approximately 50% and 35%, respectively. Finally, the light yield proportionality of Eu:SrI2 was degraded by approximately 5% with decreasing temperature. The phenomena responsible for the light output and energy resolution trends with temperature are still under investigation. In the meantime, we continue to explore new ways to improve the precision of our nonproportionality measurements. The focus of these nonproportionality studies will be on SrI2 with lower Eu concentrations.

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REFERENCES


