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History and Current Status of Strontium Iodide Scintillators

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ABSTRACT

Eu-doped strontium iodide single crystal growth has reached maturity and prototype SrI_2(Eu)-based gamma ray spectrometers provide detection performance advantages over standard detectors. SrI_2(Eu) offers a high, proportional light yield of >80,000 photons/MeV. Energy resolution of <3% at 662 keV with 1.5" x 1.5" SrI_2(Eu) crystals is routinely achieved, by employing either a small taper at the top of the crystal or a digital readout technique. These methods overcome light-trapping, in which scintillation light is re-absorbed and re-emitted in Eu^{2+}-doped crystals. Its excellent energy resolution, lack of intrinsic radioactivity or toxicity, and commercial availability make SrI_2(Eu) the ideal scintillator for use in handheld radioisotope identification devices. A 6-lb SrI_2(Eu) radioisotope identifier is described.

Keywords: Strontium Iodide, scintillator, gamma ray spectroscopy, gamma spectrometer

1. INTRODUCTION

Gamma ray spectroscopy of weak radioactive sources requires large volume detector materials capable of sufficiently high energy resolution. Handheld gamma spectrometers for radioisotope identification devices (RIID's) generally employ crystals in the 1.5" x 1.5" size, for sensitivity at a manageable weight. $LaBr_3$(Ce) offers energy resolution of <3% at 662 keV, but is difficult to grow, as its crystal structure makes it somewhat prone to cracking [1]. Additionally, it is radioactive due to the intrinsic presence of ^{138}La, which is undesirable for low count rate applications. The most widely deployed scintillator, NaI(Tl), has no intrinsic radioactivity, and is available in large volumes for ~$5/cm^3, but provides poorer resolution of typically 7% at 662 keV. SrI_2(Eu) provides 3% resolution at 662 keV, has no intrinsic radioactivity, and offers easier growth compared to $LaBr_3$(Ce) [2-17]. Large SrI_2(Eu) crystals and the LLNL prototype RIID, called Mr. ID (Mobile Radioisotope Identification) are shown in Figure 1.

Figure 1a. Commercial large volume SrI_2(Eu) crystals.

Figure 1b. Prototype radioisotope identification detector engineered by Lawrence Livermore National Laboratory, incorporating a 1.5" x 1.5" SrI_2(Eu) crystal, and the radioisotope ID software, "RNAK" [18].

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The strontium iodide crystal, $SrI_2(Eu)$, offers high proportional light yield (>80,000 ph/MeV), high effective atomic number (Z=49), and easy growth from melt due to its moderate melting point (538^0C) and orthorhombic structure that undergoes only modest thermal expansion anisotropy between its three crystalline axes, resulting in robust mechanical properties and resistance to cracking [7]. It offers 3% energy resolution at 662 keV even in the largest size crystals measured so far (100 cm^3) [16]. Since the Eu^{2+} and Sr^{2+} ionic radii, at 1.41 Å and 1.40 Å, respectively, are nearly identical, there are no observable Eu^{2+} doping gradients in the crystal boule. Therefore, uniform light yields in large $SrI_2(Eu)$ boules are achieved, unless optically absorptive impurities are present, for example, as a result of co-dopants or contaminants that do not incorporate uniformly. The primary constituents, strontium and iodine, are Earth-abundant and non-toxic and therefore not subject to cost fluctuations or potential future environmental regulations.

Since its discovery in 2008 [2], the Europium-doped Strontium Iodide scintillator, $SrI_2(Eu)$, has become commercialized and is available from several US companies, including Radiation Monitoring Devices (Watertown, MA), Northrop Grumman Synoptics (Charlotte, NC), and CapeSym (Natick, MA). Encapsulated $SrI_2(Eu)$ crystals are also offered for sale several by Japanese companies, including Union Materials, Oxide Corporation and C&A (Crystals and Applications) Corporation. Sensor packages incorporating an encapsulated $SrI_2(Eu)$ crystal mounted on a photomultiplier tube (PMT), with basic readout electronics have been produced by Bridgeport Instruments (Austin, TX) and Scionix (Netherlands). The advent of affordable, high-quality feedstock powder, from vendors such as APL Engineered Materials (Urbana, IL) has provided growers with high growth yields of large boules (1.5" and 2" diameter) and finished crystal prices typically less than $LaBr_3(Ce)$ of comparable size.

Here, a few key aspects in the development of $SrI_2(Eu)$ scintillators are described: (1) the availability of high-quality feedstock for high yield growth, (2) the optical properties and how "light trapping" can be managed in $SrI_2(Eu)$, (3) gamma ray spectroscopy with $SrI_2(Eu)$, (4) a prototype gamma spectrometer based on $SrI_2(Eu)$, (5) and future directions for device development.

2. EQUIPMENT AND METHODS

Single crystals of SrI_2 were grown using a mixture of SrI_2 and EuI_2 commercially available beads at doping levels of 1.5-4% with the vertical Bridgman method in quartz ampoules, per standard procedures [3,6,13,17]. Radioluminescence spectra were acquired using a $^{90}Sr/^{90}Y$ source (~1 MeV average beta energy), and spectra were collected with a Princeton Instruments/Acton Spec 10 spectrograph coupled to a thermoelectrically cooled CCD camera. For scintillation measurements, pulse height spectra were acquired with various radioisotope sources, using a 2" Hamamatsu R6231-100 PMT or a 2" x 2" SensL silicon photomultiplier array. The signals from the photodetector anode were shaped with a Tennelec TC 244 spectroscopy amplifier and recorded with an Amptek MCA8000-A multi-channel analyzer; or with a Bridgeport Instruments eMorpho digitizer/multi-channel analyzer. Further details on gamma spectroscopy instrumentation used for the prototype detectors are found in refs. 14 and 16.

3. RESULTS AND DISCUSSION

3.1 Crystal growth of Strontium Iodide.

The volumetric coefficient of thermal expansion for SrI_2 is modest, at $<5 \times 10^{-5}$ ^{o}C, allowing fast growth rates to be employed [3]. While moderate quality feedstock may be used to successfully grow large $SrI_2(Eu)$ crystals, by employing frit filtration and melt-pumping, as developed by Boatner [13,15,17], the recent availability of high purity feedstock makes it possible for crystals to be grown with a single melt of the mixed constituents, followed by solidification, and resulting in high growth yield.

Figure 2a. Commercial samples of as-received EuI_2 feedstock. Over time, vendors have improved purity and stoichiometry.

Figure 2b. APL Engineered Materials EuI_2 feedstock.

In addition to high purity and on-stoichiometry strontium iodide feedstock, the dopant europium iodide feedstock must be pure. Figure 2a shows early EuI_2 feedstock from a several vendors, exhibiting off-stoichiometry, partial hydrolysis and impurities, the brown color generally due to decomposed iodine. Recent high-purity commercial EuI_2 is a greenish-white color, and incorporates into SrI_2 without deleterious side reactions or inclusions. APL Engineered Materials EuI_2 specifications are shown in Figure 2b. At this purity level, the EuI_2 does not require zone refining or other purification.

3.2 Optical properties of Strontium Iodide.

Due to substantial overlap between the Eu^{2+} optical absorption and emission (Figure 3), scintillation photons traversing a long path length have a high probability of re-absorption and re-emission from additional Eu^{2+} activators, lengthening the pulse lifetime, red-shifting the emission, and reducing the pulseheight for those events that have undergone "light trapping," as described in Glodo, et al. [11]. Light-trapping by the Eu^{2+} dopant may be addressed by: (1) the use of a physical taper, where the top of the crystal has a slight taper for uniform light collection, and/or (2) the use of on-the-fly correction of scintillation pulses by digital readout electronics [14]. The simplest remedy, fabricating the crystal with a slightly tapered top end, is described in Table 1, allows for a shorter and more uniform effective "flight path" for the scintillation photons [19]. For a 1"x2" long SrI_2(3%Eu) crystal, a small taper results in a volume loss of only 5%, but an improvement in energy resolution from 5.3% to 3.3% at 662 keV, with analog readout. In the digital correction technique, the scintillation pulses are digitized and processed on-the-fly prior to histogramming into a spectrum; this can provide R(662 keV) <3% FWHM, demonstrated for multiple 2-4 in^3 SrI_2(3%Eu) crystals read out with this approach.

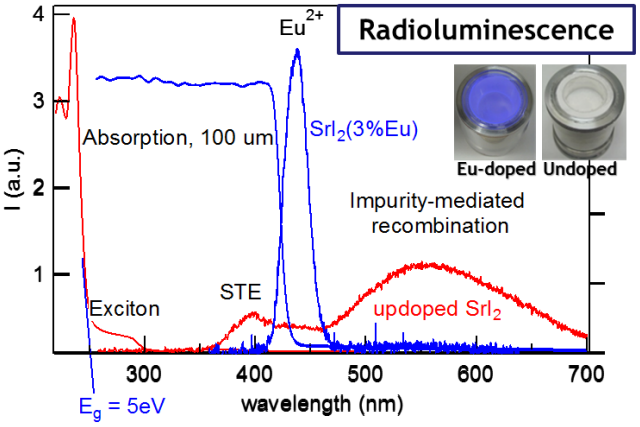
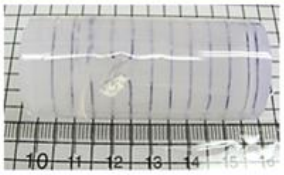
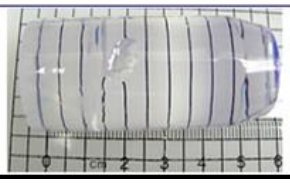


Figure 3. Optical absorbance and radioluminescence of undoped SrI_2 and 3%Eu-doped SrI_2 crystals. Inset shows encapsulated crystals illuminated with a UV lamp. The overlap between the Eu^{2+} absorbance and emission requires mitigation in the optical engineering of the detector or by digital pulse-processing.

Table 1. Comparison of SrI_2(Eu) gamma spectroscopy performance for a 1" diameter x 2" long crystal, first, as a right cylinder, and then after a small taper was applied to the top end (away from the PMT). Even with analog readout, energy resolution performance is excellent for the tapered cylinder, and greatly improved over the simple right cylinder.

Shape		% of Length Tapered	Vol (cm^3)	Vol Lost	R(662 keV) analog	R(662 keV) digital
Right Cylinder, 1" x 2"		0%	26.5	0%	5.3%	3.5%
Tapered, 1" x 2"		18%	25.2	5%	3.3%	3.1%

3.3 Gamma Ray Spectroscopy.

Figure 4a shows that energy resolution obtained with $SrI_2(Eu)$ is superior to that of NaI(Tl) and provides sufficient spectroscopy to distinguish most mixed gamma sources in the field, though the exquisite resolution of a Germanium detector is required for high quality assays of complex mixtures, usually performed in an analytical laboratory. For field use, low-power, rugged, moderate resolution scintillator detectors are normally employed. Search for weak sources in natural background is complicated when the $LaBr_3(Ce)$ scintillator is used, since background clutter due to the radioactive decay of ^{138}La overwhelms weak gamma lines, as shown in Figure 4b. $SrI_2(Eu)$ therefore has the advantage over NaI(Tl) of significantly better energy resolution, and lack of intrinsic radioactivity for $SrI_2(Eu)$ allows it to outperform $LaBr_3(Ce)$ for weak source detection.

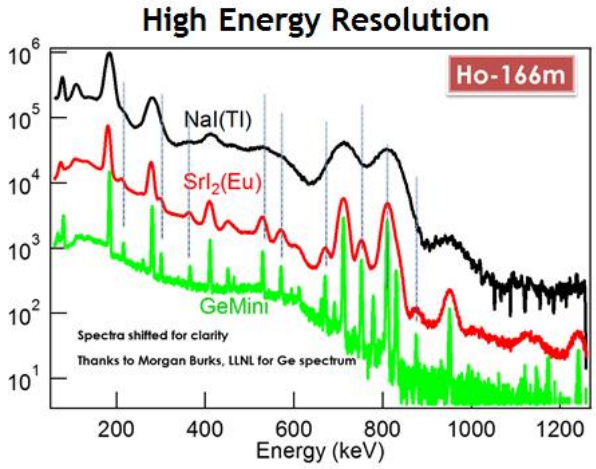


Figure 4a. Gamma ray spectrum of a Ho-166m source acquired with NaI(Tl), $SrI_2(Eu)$ and Germanium detectors. Many more gamma lines are readily resolved by $SrI_2(Eu)$, compared to NaI(Tl), providing accurate and rapid radioisotope ID for most combinations of sources.

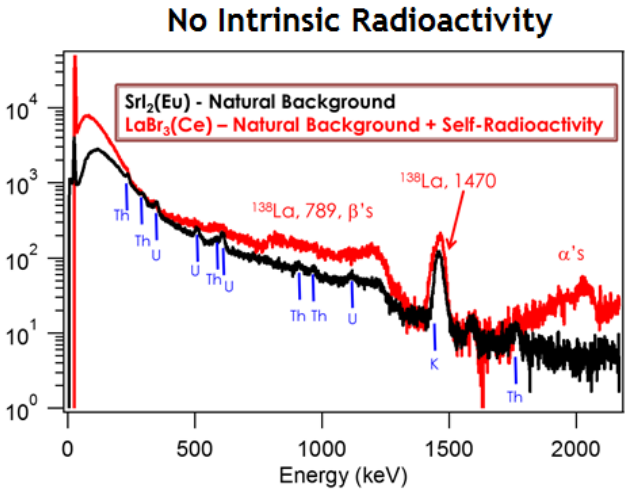


Figure 4b. Gamma ray spectrum of natural background in a laboratory setting, comparing equivalent volume $SrI_2(Eu)$ and $LaBr_3(Ce)$ detectors. While the $SrI_2(Eu)$ detector readily detects many natural background Th, U and K lines, the $LaBr_3(Ce)$ detector spectrum is mainly obscured by its intrinsic radioactivity features, beneath which the natural background is nearly imperceptible.

3.4 Gamma Spectrometer Prototypes.

Digital readout electronics (eMorpho, usbBase) available from Bridgeport Instruments have been used by LLNL for prototype detector development since 2011, and multiple prototype generations have been engineered up to the current Mobile Radioisotope Identification (Mr. ID) detector. This device employs a variety of practical features for robust performance, including temperature gain stabilization. As the development progressed, the detector moved from simply recording and displaying spectra (prior to 2014) to the incorporate the use of an embedded computer to run the high-performance software package, RNAK (Radionuclide Analysis Kit), developed by Karl Nelson, LLNL [18]. The RNAK package includes a library of radionuclide gamma energies that is overlaid on real-time data, providing full spectral radioisotope ID. Detailed specifications of the current device are shown in Figure 5. The software offers a range of information to suit different users, including: a list of up to 10 radioisotopes (if identified in the spectrum), a simple and rapid recalibration routine, waterfall plot of spectrum vs. time, dose rate details, spectrum zooming and data downloading.

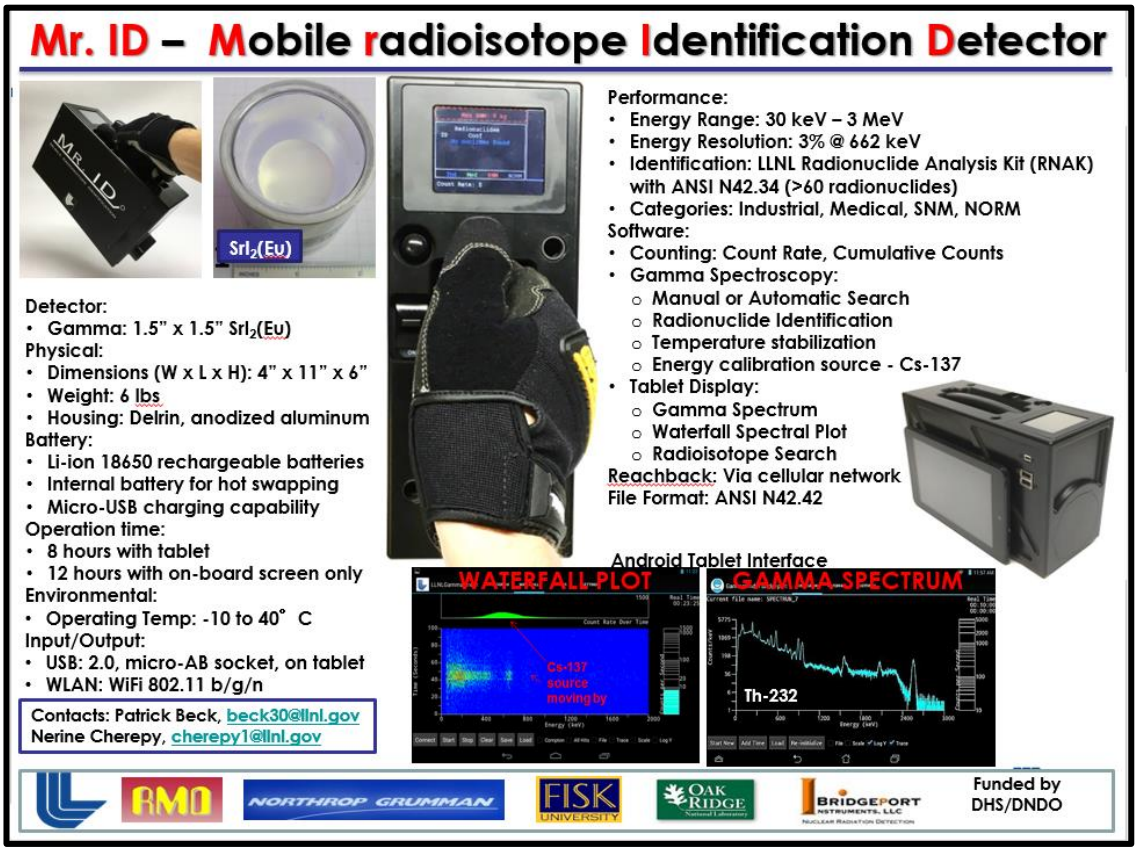


Figure 5. Main features of the most recent version of the Mr. ID gamma spectrometer based on $SrI_2(Eu)$.

3.5 Future directions for device development.

Current radioisotope identification devices employ crystals of 1.5" x 1.5" size, and manufacture of encapsulated $SrI_2(Eu)$ crystals in this size has been established at multiple vendors. End users prefer compact, lightweight detectors offering low false positives and false negatives, with an intuitive interface. The Mr. ID detector has been engineered for deployability with multiple innovations including digital readout, high performing radioisotope ID algorithms, and an easy-to-use graphical user interface. It may be further reduced in volume by using readout via a silicon photomultiplier (SiPM) array. Initial measurements reveal that there is no degradation in spectroscopy with SiPM array readout (Figure 6). The data stream, with file format in the ANSI N42.42 format, allows for integration with other tools and sensors in the field and this device architecture can be configured into networked nodes or read out by multiple readers.

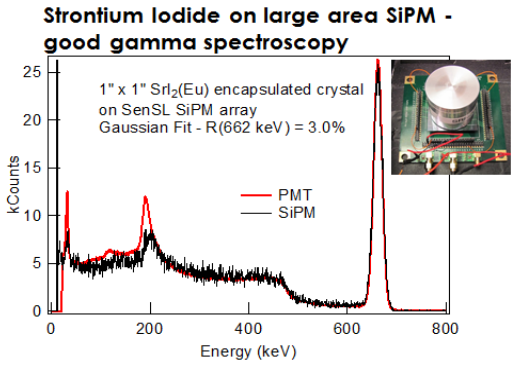


Figure 6. Pulse height spectra acquired using analog readout of a 12 cm^3 RMD $SrI_2(Eu)$ crystal with a Cs-137 source. Inset shows the encapsulated crystal mounted on a 2" x 2" silicon photomultiplier (SiPM) array. Both PMT and SiPM photodetectors provide R(662 keV) = 3%. Use of SiPM readout can provide greater detector robustness and a more compact footprint, without degrading gamma spectroscopy performance.

4. CONCLUSIONS

Strontium iodide doped with europium possesses excellent properties for successful large-size crystal growth with high, uniform light yield, as now established. Commercially available encapsulated crystals that provide excellent scintillation performance may now be purchased from multiple companies. Eu-doping leads to "light trapping" which complicates the acquisition of high resolution gamma ray spectra, but is readily mitigated with a small taper applied to the crystal and/or digital signal processing. SrI_2(Eu)-based gamma spectrometers can provide superior performance for field use compared to other scintillators, due to their high energy resolution and lack of intrinsic radioactivity. Integration of radioisotope identification software has provided a prototype device that allows non-experts to rapidly identify weak, unknown radiological sources with low false alarms. Efforts to further reduce the device volume for portability are underway.

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