Crystal Growth and Scintillation Properties of Strontium Iodide Scintillators

Edgar V. van Loef, Cody M. Wilson, Nerine J. Cherepy, Giulia Hull, Stephen A. Payne, Woon-Seng Choong, William W. Moses, *Member, IEEE,* and Kanai S. Shah

This work supported by the National Nuclear Security Administration, Office of Defense Nuclear Nonproliferation, Office of Nonproliferation Research and Development (NA-22) of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Crystal Growth and Scintillation Properties of Strontium Iodide Scintillators

Edgar V. van Loef, Cody M. Wilson, Nerine J. Cherepy, Giulia Hull, Stephen A. Payne, Woon-Seng Choong, William W. Moses, *Member, IEEE,* and Kanai S. Shah

***Abstract*— Single crystals of SrI_2:Eu and SrI_2:Ce/Na were grown from anhydrous iodides by the vertical Bridgman technique in evacuated silica ampoules. Growth rates were of the order of 5 – 30 mm/day. Radioluminescence spectra of SrI_2:Eu and SrI_2:Ce/Na exhibit a broad band due to Eu^{2+} and Ce^{3+} emission, respectively. The maximum in the luminescence spectrum of SrI_2:Eu is found at 435 nm. The spectrum of SrI_2:Ce/Na exhibits a doublet peaking at 404 and 435 nm attributed to Ce^{3+} emission, while additional impurity - or defected – related emission is present at approximately 525 nm. The strontium iodide scintillators show very high light yields of up to 120,000 photons/MeV, have energy resolutions down to 3% at 662 keV (Full Width Half Maximum) and exhibit excellent light yield proportionality with a standard deviation of less than 5% between 6 and 460 keV.**

***Index Terms*—Alkaline-earth halides, Crystal growth, Energy resolution, Scintillation detectors.**

I. Introduction

Security applications and nuclear non-proliferation depend on the rapid identification of highly enriched uranium, weapons grade plutonium, radioactive sources and other special nuclear materials. Efficient detection of their gamma-ray signature is the most common method for identification and requires a scintillator that has a high light yield, good energy resolution, fast scintillation and high effective atomic number. Currently, $LaBr_3$:Ce and $CeBr_3$ [1]–[3] provide the best combination of these properties. However, both are moisture sensitive and are prone to cracking during crystal growth [4]. Recently, the alkaline-earth iodides doped with divalent europium, i.e. SrI_2:Eu and BaI_2:Eu, have been rediscovered as inorganic scintillators that may rival $LaBr_3$:Ce and $CeBr_3$. Initially discovered by Hofstadter in 1968 [5], recent research indicates that these materials exhibit high light yields and show good energy resolution [6].

In this paper we report on the crystal growth and scintillation properties of strontium iodide scintillators doped with Eu^{2+} and Ce^{3+}. Radioluminescence, pulse height and scintillation decay time spectra are presented.

Manuscript received June 18, 2008. This work was supported in part by the Domestic Nuclear Detection Office in the Department of Homeland Security via Lawrence Livermore National Laboratory.

Edgar V. van Loef, Cody M. Wilson, and Kanai S. Shah are with Radiation Monitoring Devices, Inc., Watertown, MA 02472 USA (phone: 617-668-6922; fax: 617-926-9980; e-mail: EvanLoef@RMDInc.com).

Nerine J. Cherepy, Giulia Hull, and Stephen A. Payne are with Lawrence Livermore National Laboratory, Livermore, CA 94550 USA (e-mail: cherepy1@llnl.gov).

Woon-Seng Choong, and William W. Moses are with Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA (e-mail: wwmoses@lbl.gov).

II. Crystal growth

Single crystals of SrI_2:Eu and SrI_2:Ce/Na doped with different Eu^{2+} and Ce^{3+} concentrations were grown in silica ampoules using the vertical Bridgman technique. Sodium iodide was used as charge compensation, mandated by the substitution of trivalent cerium for divalent strontium. The melting point of SrI_2 is approximately 538°C. SrI_2 has the orthorhombic crystals structure with space group Pbca [7]. Based on structure and lattice parameters, the density of SrI_2 is 4.59 g/cm^3.

Anhydrous SrI_2 beads (Aldrich, 99.99%), EuI_2 powder (Aldrich, 99.9%), CeI_3 beads (Aldrich, 99.99%), and NaI beads (Aldrich, 99.999%) were used as starting materials. The starting materials were loaded into silica ampoules in a nitrogen-purged glovebox. Next, the ampoules were closed from the atmosphere by use of a vacuum valve and subsequently connected to a Varian Vac Sorb pump. The ampoules were evacuated to approximately 10^{-3} Torr while heated with a heating tape to approximately 150°C to remove any residual moisture. After several hours, the heating tape was removed and the ampoules were sealed. The strontium iodides were kept cool during the entire sealing operation by wrapping a wet towel around the ampoule. This prevented thermal decomposition of the iodides due to heat from the torch.

We used vertical Bridgman furnaces to grow the strontium iodides. Crystals were grown by melting the entire charge prior to the start of the run and subsequently lowering the ampoule through the hot zone. Sealed ampoules were lowered through the hot zone of the furnace at a predetermined rate of 5 to 30 mm/day. Subsequently, solidification starts at the capillary tip, which acts as a seed for the random crystal growth along the length of the capillary and the remainder of the crystal. The temperature maximum of the zone was set at 50°C above the melting point of the strontium iodide. The temperature gradient is typically 25°C/cm, but can vary from the outer core to the end of the furnace from 3 to 75°C/cm.

The highest quality strontium iodide crystals were obtained with SrI_2:Eu grown at rates of 5 – 10 mm/day. As an example,

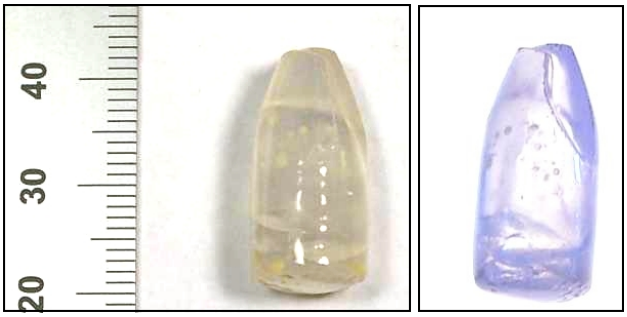

Fig. 1. Photograph of a SrI_2:8% Eu ingot. The photograph on the left was taken with ambient light, while the photograph on the right was taken with the ingot placed on a light box.

Fig. 1 shows a photograph of a SrI_2:8% Eu ingot. The ingot is about 10 mm in diameter and 24 mm long. The yellowish color of the ingot under ambient light is due to a thin layer of mineral oil on the surface of the ingot. The bluish haze of the ingot exposed to transmitting light is attributed to absorption and emission of Eu^{2+}. Almost all SrI_2:Eu ingots are optically clear, show minimal cracking and appear to have minimal Eu^{2+} segregation, whereas SrI_2:Ce/Na ingots have a pale yellow tint and show some Ce^{3+} segregation.

III. Scintillation Properties

A. Radioluminescence

Radioluminescence spectra were recorded with a Philips X-ray tube having a Cu anode operated at 30 kV and 20 mA. The scintillation light was dispersed through a McPherson 234/302 monochromator equipped with a holographic grating (1200 grooves/mm) and subsequently detected with a Hamamatsu R2059 photomultiplier tube (PMT). Radioluminescence spectra of SrI_2:0.5% Eu and SrI_2:0.5% Ce/Na are shown in Fig. 2. For SrI_2:0.5% Eu the spectrum consists of a single broad band due to Eu^{2+} 5d → 4f emission, peaking at 435 nm [6]. In contrast, the spectrum of SrI_2:0.5% Ce/Na exhibits a doublet peaking at 404 and 435 nm attributed to Ce^{3+} luminescence, while additional impurity - or defected – related emission is present at approximately 525 nm.

B. Scintillation Decay

Scintillation decay time spectra were recorded using a ^{137}Cs gamma ray source and a Tektronix TDS 220 oscilloscope connected to the output of a PMT. Fig. 3 shows the scintillation decay time spectra of SrI_2:0.5% Eu and SrI_2:0.5% Ce/Na under ^{137}Cs gamma ray excitation. A simple exponential decay time model was used to fit the data. In the case of SrI_2:0.5% Eu, the scintillation decay curve can be described by a single exponential decay time model with a time constant of 1.1 μs. For higher Eu concentrations, the time constant does not change significantly. The scintillation decay curve of SrI_2:0.5% Ce/Na can be described by a two-component exponential decay time model; a principle decay component that contributes about 25% to the total light yield with a 27 ns time constant, and a second decay component with a 450 ns time constant. The principal decay component of SrI_2:2% Ce/Na contributes about 46% to the total light yield and has a 33 ns time constant. The remaining light is emitted by a 570 ns decay component.

C. Light yield and Energy resolution

Pulse-height spectra were recorded with a Hamamatsu R2059 PMT. The output of the PMT was connected to a Canberra 2005 preamplifier and a Canberra 2020 spectroscopic amplifier. Crystals were optically coupled onto the window of the PMT using Bicron BC-630 optical grease. To minimize losses in light yield, crystals were wrapped in several layers of 0.1-mm UV reflecting Teflon tape. Nitrogen was flushed around the crystal to prevent hydration of the surface during measurement. Light yields expressed in photoelectrons per megaelectronvolt (MeV) of absorbed gamma ray energy (phe/MeV) were determined by comparing the peak position of the 662 keV full energy peak in the pulse height spectra with the position of the peak in the spectrum of single photoelectrons. The absolute light yield, expressed in

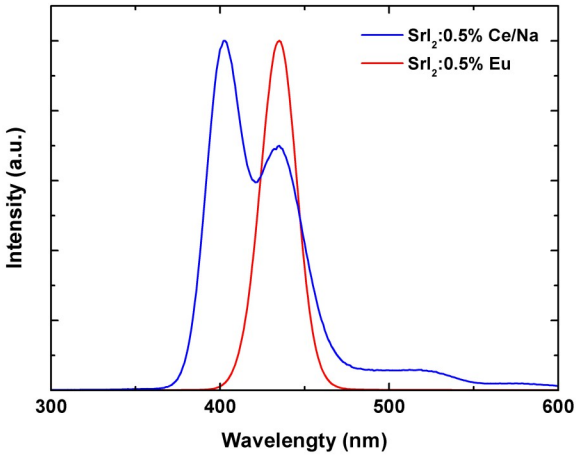

Fig. 2. Radioluminescence spectrum of SrI_2:0.5% Eu and SrI_2:0.5% Ce/Na.

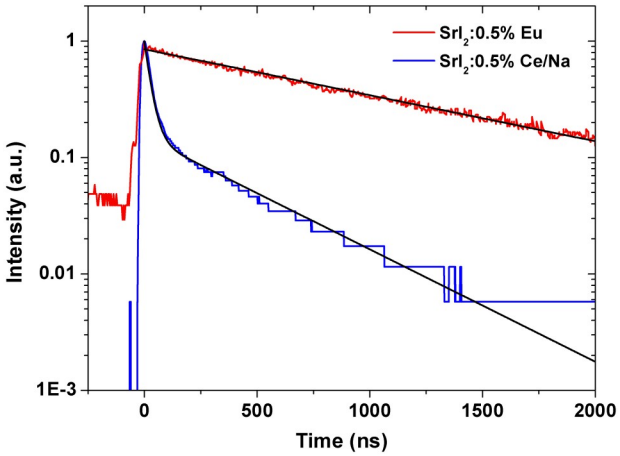

Fig. 3. Scintillation decay time spectra of SrI_2:0.5% Eu and SrI_2:0.5% Ce/Na under ^{137}Cs gamma ray excitation.

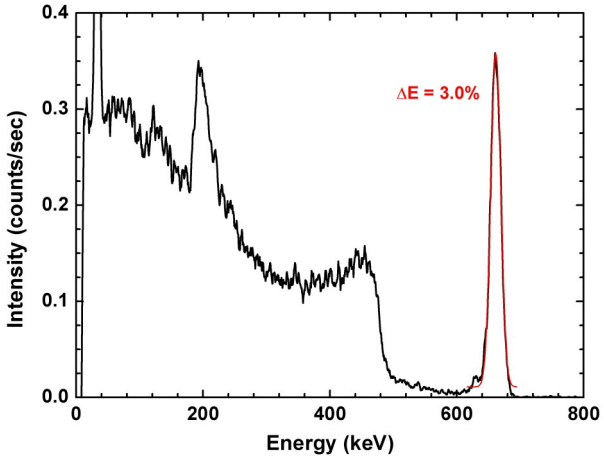

Fig. 4. Pulse height spectrum of SrI_2:5% Eu under ^{137}Cs gamma ray excitation using a shaping time of 4 μs.

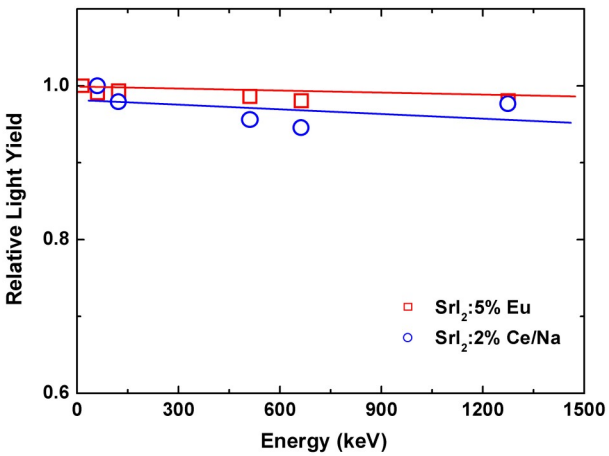

Fig. 5. Light yield proportionality as function of gamma ray energy of SrI_2:5% Eu and SrI_2:2% Ce/Na.

photons per MeV of absorbed gamma ray energy (ph/MeV) was determined from the detection efficiency of the PMT. The detection efficiency was assumed to be 21% and 23% for SrI_2:Eu and SrI_2:Ce/Na, respectively.

Fig. 4 shows the pulse height spectrum of SrI_2:5% Eu under ^{137}Cs gamma ray excitation using a shaping time of 4 μs. Based on the position of the full energy peak and the position of that for single electrons, we estimated light yield of this crystal to be about 120,000 ph/MeV. This light yield is among the highest values obtained with inorganic scintillators. A light yield of 85,000 ph/MeV was reported previously for SrI_2:Eu by Cherepy *et al*. [6]. The energy resolution of the 662 keV full energy peak measured with SrI_2:5% Eu is about 3% (FWHM). This is substantially better than the energy resolution of 6 to 7% (FWHM) at 662 keV obtained with established scintillators such as NaI:Tl and CsI:Tl, while rivaling that of $LaBr_3$:Ce scintillators.

In contrast to SrI_2:Eu, SrI_2:Ce/Na crystals show lower light yields and exhibit worse energy resolution. For SrI_2:0.5% Ce/Na we measured a light yield of 16,000 ph/MeV and obtained an energy resolution of 6.4% at 662 keV (FWHM), whereas for SrI_2:2% Ce/Na we measured a light yield of about 10,000 ph/MeV and an energy resolution of about 12% at 662 keV (FWHM) . Whether this is due to the large concentration gradient of Ce^{3+} and Na^+ in SrI_2, due to the lesser optical quality of the crystals, or a combination of both is unknown.

D.Proportionality

Light yield proportionality as function of electron energy was measured using the scintillation light yield non-proportionality characterization instrument (SLYNCI) at Lawrence Livermore National Laboratory [8]. SrI_2:Eu exhibits excellent light yield proportionality as function of electron energy [6], rivaling that of $LaBr_3$:Ce. Light yield proportionality as function of gamma ray energy was obtained by measuring the light yield of SrI_2:Eu under gamma ray excitation using different isotopes such as ^{22}Na (511 keV and 1.274 MeV), ^{57}Co (14 keV X-rays, 122 keV gamma rays), ^{137}Cs (662 keV), and ^{241}Am (60 keV). From the measured position of the full energy peak and the known gamma ray energy for each isotope, the light yield at each gamma ray energy was estimated. Subsequently, the data points were normalized with respect to the light yield at 662 keV. The results for SrI_2:5% Eu and SrI_2:2% Ce/Na are shown in Fig. 5. SrI_2:5% Eu demonstrates a remarkable linear response, similar to the response as function of electron energy. The deviation from linearity is less than 2% over the energy range from 14 to 1274 keV. SrI_2:2% Ce/Na also proves to be very proportional as function of gamma ray energy with a deviation of less than 6% over the energy range from 60 to 1274 keV. Although the energy resolution of SrI_2:Ce/Na at present is poor, its good proportionality indicates that when uniform crystals are produced with good optical quality, energy resolution may improve as well.

IV.Summary

Table I presents a summary of the scintillation properties of SrI_2:Eu and SrI_2:Ce/Na. Light yield, energy resolution, and scintillation decay times are presented. Strontium iodide scintillators doped with divalent europium are relatively easy to grow by the vertical Bridgman technique with minimal europium segregation. Crystals doped with trivalent cerium and monovalent sodium as charge compensation show a slight cerium segregation with $K < 1$. SrI_2:5% Eu shows a high light yield of up to 120,000 ph/MeV and has an excellent energy resolution of 3% at 662 keV. The proportionality of SrI_2:Eu and SrI_2:Ce/Na is much better than that of NaI:Tl and rivals that of $LaBr_3$:Ce. The already excellent performance of these scintillators holds much promise for future crystal growth and for the use of SrI_2:Eu and SrI_2:Ce/Na in applications where a high light yield and good energy resolution are required.

Table I. Scintillation properties of SrI_2:Eu and SrI_2:Ce/Na.

Crystal	Light Yield (ph/MeV)	Energy resolution at 662 keV (%)	Decay (ns)
SrI_2:0.5% Eu	68,000	5.3	1100
SrI_2:5% Eu	120,000	3.0	1200
SrI_2:8% Eu	80,000	6.7	1100
SrI_2:0.5% Ce/Na	16,000	6.4	27 (25%), 450 (75%)
SrI_2:2% Ce/Na	10,114	12.2	33 (46%), 570 (54%)

References

[1] E. V. D. van Loef, P. Dorenbos, C. W. E. van Eijk, K. Kramer and H. U. Güdel, "High-energy-resolution scintillator: Ce^{3+} activated $LaBr_3$," *Appl. Phys. Lett.*, vol. 79, no. 10, pp. 1573–1575, Sep. 2001.

[2] K. S. Shah, J. Glodo, M. Klugerman, W. W. Moses, S. E. Derenzo, M. J. Weber, "$LaBr_3$:Ce Scintillators for Gamma-Ray Spectroscopy," *IEEE Trans. Nucl. Sci.*, vol. 50, no. 6, pp. 2410–2413, Dec. 2003.

[3] K. S. Shah, J. Glodo, W. Higgins, E. V. D. van Loef, W. W. Moses, S. E. Derenzo, M. J. Weber, "$CeBr_3$ scintillators for gamma-ray spectroscopy," *IEEE Trans. Nucl. Sci.*, vol. 52, no. 6, pp. 3157–3159, Dec. 2005.

[4] W. M. Higgins, A. Churilov, E. van Loef, J. Glodo, M. Squillante and K. Shah, "Crystal growth of large diameter $LaBr_3$:Ce and $CeBr_3$," *J. Crystal Growth*, vol. 310, no. 7–9, pp. 2085–2089, Apr. 2008.

[5] R. Hofstadter, "Europium-activated Strontium Iodide Scintillators," US Patent 3,373,279 (1968).

[6] N. J. Cherepy, G. Hull, A. D. Drobshoff, S. A. Payne, E. van Loef, C. M. Wilson, K. S. Shah, U. N. Roy, A. Burger, L. A. Boatner, W.-S. Choong and W. W. Moses, "Strontium and barium iodide high light yield scintillators," *Appl. Phys. Lett.*, vol. 92, no. 8, pp. 083508 1–3, Feb. 2008.

[7] H. Bärnighausen, E. Th. Rietschel, "Die Elementarzelle und Raumgruppe von Strontiumjodid," *Z. anorg. allg. Chem.*, vol. 354, no. 1–2, pp. 23–26, Sep. 1967.

[8] W. S. Choong, W. W. Moses, K. M. Vetter, G. Hull, S. A. Payne, et al., "Design of a facility for measuring scintillator non-proportionality," *IEEE Trans. Nucl. Sci.*, vol. 55, accepted for publication, 2008.

[9] P. Dorenbos et al., "Non-proportionality in the scintillation response and the energy resolution obtainable with scintillation crystals," *IEEE Trans.Nucl. Sci.*, vol. 42, no. 6, pp. 2190–2190, Dec. 1995.