

Comparative Gamma Spectroscopy with SrI₂(Eu), GYGAG(Ce) and Bi-loaded Plastic Scintillators

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Abstract— We are developing new scintillator materials that offer potential for high resolution gamma ray spectroscopy at low cost. Single crystal SrI₂(Eu) offers ~3% resolution at 662 keV, in sizes of ~1 in³. We have developed ceramics processing technology allowing us to achieve cubic inch scale transparent ceramic scintillators offering gamma spectroscopy performance superior to NaI(Tl). Our bismuth-loaded plastic scintillator demonstrates energy resolution of ~8% at 662 keV, for samples of ~0.5 cm³.

Index Terms— Scintillators, strontium iodide, ceramic scintillators, gamma ray spectrometers, transparent ceramics, plastic scintillators

I. INTRODUCTION

Gamma ray spectroscopy can be used to identify the presence of weak radioactive sources within natural background. The ability to discriminate close-lying spectral lines is strongly dependent upon the energy resolution of the detector. In addition to excellent energy resolution, large volume detectors are needed to acquire sufficient events, for example, to identify a radioactive anomaly moving past a detector. We have employed a “directed search” methodology for identifying potential scintillator materials candidates [1], resulting in the discovery of Europium-doped Strontium Iodide, SrI₂(Eu) [2-4], Cerium-doped Gadolinium Garnet [5,6], GYGAG(Ce), and Bismuth-loaded polymers. These scintillators possess very low self-radioactivity, offer energy resolution of 3-8% at 662 keV, and have potential to be grown cost-effectively to sizes similar to the most widely deployed gamma spectroscopy scintillator, Thallium-doped Sodium Iodide, NaI(Tl).

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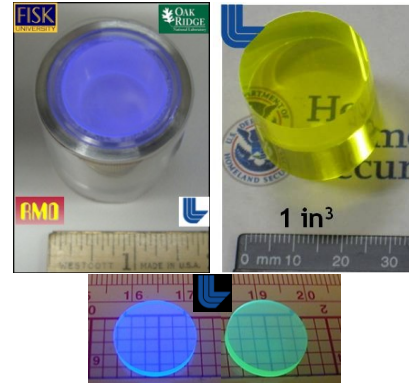


Fig. 1. New scintillators for gamma ray spectroscopy developed for DHS and DOE. (upper left) SrI₂(Eu) single crystal under UV excitation, (upper right) GYGAG(Ce) ceramic, (bottom) two Bi-loaded polymers under UV excitation.

In this study, gamma ray spectra of a variety of sources, were obtained employing SrI₂(Eu), GYGAG(Ce), Bi-loaded polymers, LaBr₃(Ce), and NaI(Tl). The effects of detector size, energy resolution, and background radioactivity (including self-radioactivity) on the ability to distinguish weak sources is quantified, based on a simple model, and qualitatively compared to laboratory data.

II. SAMPLES

A. Strontium Iodide

SrI₂(5 mol%Eu) crystals are being grown at RMD, Oak Ridge National Laboratory and Fisk University using the vertical Bridgman method. The crystals are grown in silica ampoules using anhydrous SrI₂ beads (Aldrich, 99.99%) and EuI₂ powder (Aldrich, 99.9%), as the starting materials [2-4]. Crystals from all three growers have offered similar performance. The crystal characterized in this report was grown at RMD, then packaged at LLNL. The crystal was cut into a tapered cylinder, polished and encapsulated in an aluminum can [7].

B. Gadolinium Garnet Transparent Ceramics

Transparent ceramic garnets were formed at LLNL using stoichiometric mixed metal oxide particles synthesized via flame spray pyrolysis (FSP), a nanoparticle production method developed by Pratsinis and co-workers [8] and Laine and co-workers [9]. Synthesis of FSP nanoparticles was carried out at LLNL, as well as by Nanocerox, Inc. The FSP nanoparticles are formed into a green body, vacuum sintered,

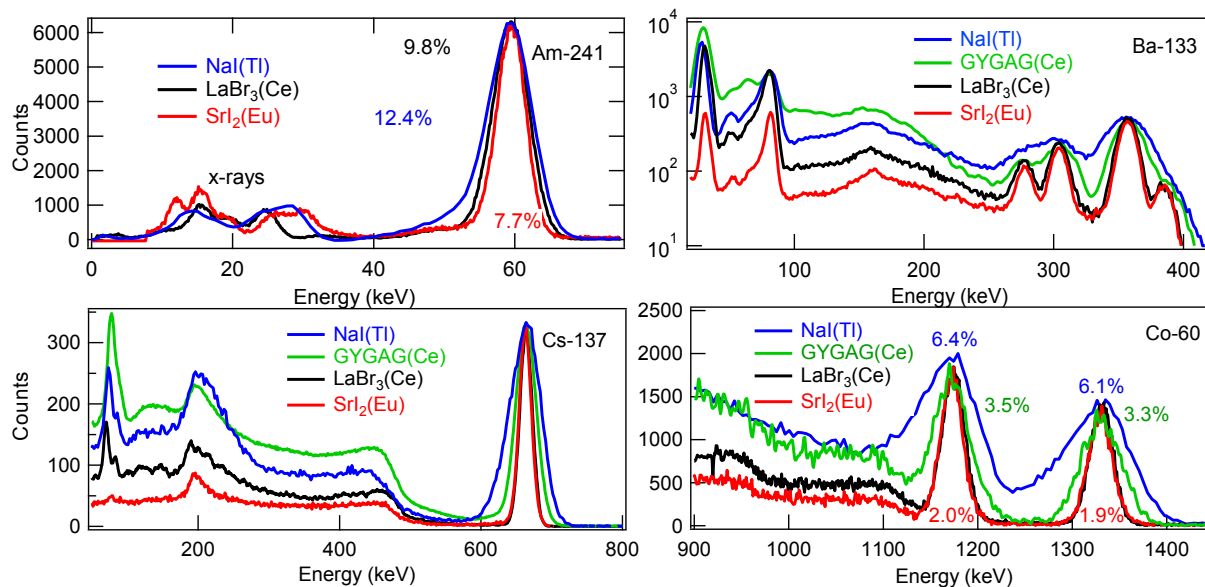


Fig. 2. Gamma spectra acquired with various sources using several scintillator materials. NaI(Tl) crystal is $\phi 2.54$ cm x 3.81 cm, LaBr₃(Ce) crystal is $\phi 1.8$ cm x 2 cm, GYGAG(Ce) ceramic is $\phi 2.77$ cm x 0.62 cm and the SrI₂(Eu) crystal is an encapsulated tapered cylinder with $\phi 2.54$ cm x 2.7 cm.

then hot-isostatic pressed into optically transparent parts [10]. The relative ease with which the GYGAG(Ce) ceramic is formed with high transparency is due to deliberate use of “intersubstitutional” ions, whereby the three different cation sites of the garnet unit cell are each occupied by more than one of the four cation species. This results in flexibility in stoichiometry, and ultimately, a high yield industrial manufacturing process due to excellent phase stability over a range of compositions.

C. Bismuth-loaded Polymers

Polymer scintillators with 40wt% Bismuth were formed at LLNL by mixing a Bismuth metallo-organic with monomer and 3% fluor, heating to melt, and subsequent polymerization of the homogeneous mixture. Two different fluors were investigated, an Iridium complex, emitting in the green, and diphenylanthracene, emitting in the blue.

III. GAMMA SPECTROSCOPY

Pulse height spectra were acquired with various radioactive sources, with scintillators coupled to a Hamamatsu R6231-100 PMT, a Tennelec TC243 amplifier (shaping times 8-12 microseconds), and recorded with an Amptek 8000A MCA. A comparison of the energy resolution obtained with the new scintillator materials and commercial LaBr₃(Ce) and NaI(Tl) crystals, using the Am-241, Ba-133, Cs-137 and Co-60 sources is shown in Figure 2.

To explore the ease of detection of a weak source with different scintillators, we measured a Cs-137 source at a 3 foot standoff with NaI(Tl), LaBr₃(Ce) and SrI₂(Eu), all ~ 1 in³ in size, with equivalent acquisition times. Figure 3 shows that the 662 keV peak is readily observed in the SrI₂(Eu) spectrum, while the poorer energy resolution of NaI(Tl) degrades its ability to detect the source, and the intrinsic background in LaBr₃(Ce) (La-138 gammas at 789 and 1436 keV, betas in 0-255 keV range, the Ba-138 32-37 keV x-rays, and sums of these) complicates its spectrum [11].

Pulse height spectra were acquired with Am-241, Co-57 and Cs-137 sources of 1.5 cm x 0.3 cm Bismuth-loaded polymer samples. Figure 4 shows that the energy resolution obtained for the sample containing the Iridium fluor is somewhat better than that of the diphenylanthracene activated polymer. This is likely due to the higher light yield with the Ir-complex, which collects both singlet and triplet excitons due to spin-orbit coupling [12]. Since the samples are so small and have only modest stopping power, escape peaks similar in intensity to the photopeak, are observed, from ²⁰⁹Bi K _{α} x-rays at 74.8 and 77.1 keV. These initial results suggest that it may be possible to produce polymer-based gamma spectrometers, with useful energy resolution for radioisotope identification, however, we

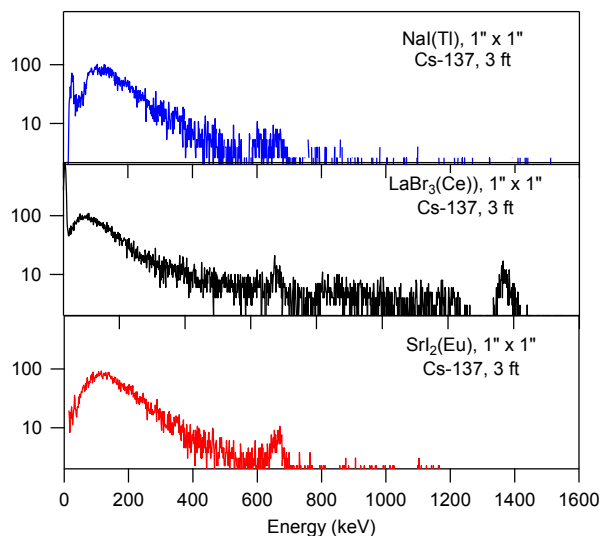


Fig. 3. Pulse height spectra of NaI(Tl), LaBr₃(Ce) and SrI₂(Eu), acquired under same conditions, for same scintillator size and acquisition time, using a low count-rate Cs-137 source.

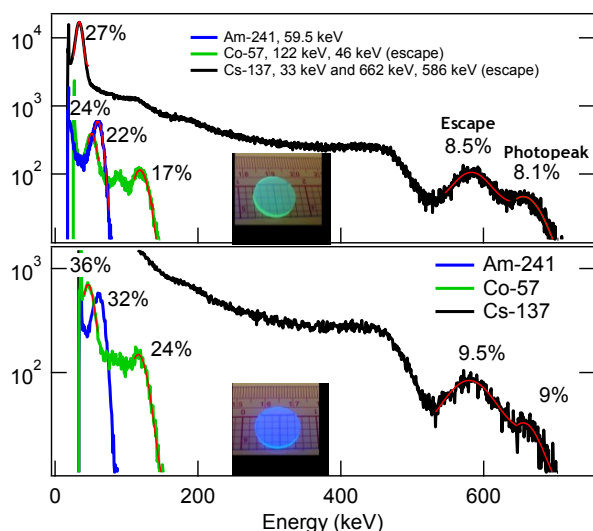


Fig. 4. Pulse height spectra of two 1.5 cm x 0.3 cm Bismuth-loaded polymer samples, acquired with Am-241, Co-57 and Cs-137 sources.

have yet to determine whether this performance can be maintained in large volume Bi-loaded polymer scintillators.

Figure 5 shows energy resolution obtained as a function of gamma ray energy for the scintillators described herein. The data may be fit to equation 1, comprised of the photon statistics term and a “B” factor that accounts for all non-idealities in the measurement, including intrinsic light yield non-proportionality, material response non-uniformity and light collection non-uniformity.

$$R = \{[(A/E)^{0.5}]^2 + B^2\}^{0.5} \quad (1)$$

In equation 1, A is a constant, E is the gamma energy, and B is required when there is deviation from pure photon statistics. For the data shown in Figure 5, the values for B obtained from the fits are shown in Table I. The large value of B for NaI(Tl) is thought to be due to its intrinsic non-proportionality. The much smaller value for SrI₂(Eu) likely results from light trapping, which may be addressed by careful optical design [13,7]. The origin of the B value for GYGAG(Ce) is under

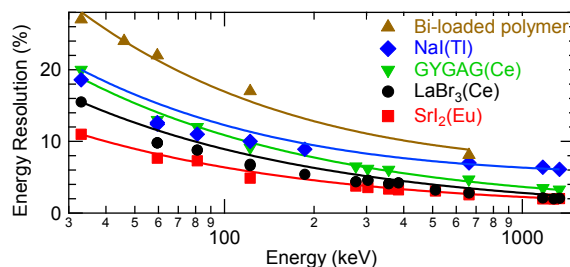


Fig. 5. Energy resolution as a function of gamma energy for several scintillators; data is fit to Eq. 1.

investigation. Material response non-uniformity is likely the origin of the large B value for the Bi-loaded polymer scintillator, possibly due to its amorphous structure and known phase segregation of Bi on the nanoscale, observable by electron microscopy.

From the analysis of Nelson, et al. [14], we have deduced that in the energy resolution range applicable to scintillators (4-15% at 200 keV) a false alarm rate (FAR) for identification of spectral anomalies can be expressed:

$$\text{FAR} \propto R^{3.4} / (S_{PP} / B_{TOT})^{0.54} \quad (2)$$

where R is the resolution of the instrument, S_{PP} is the photopeak efficiency (product of the stopping power and the photofraction), and B_{TOT} is the sum of the natural background (B_{NAT}) and the self-radioactivity (B_{SELF}) of the scintillator material. The self-radioactivity for LaBr₃(Ce) is approximately equivalent to the natural background rate, thus doubling the background. In terms of the FAR performance metric, SrI₂(Eu) and GYGAG(Ce) appear promising. For resolution in the 200-keV region, SrI₂(Eu) offers an overall reduction in false alarms of a factor of 3 compared to LaBr₃(Ce) and a factor of 14 better than NaI(Tl). These estimates may be qualitatively compared with the data shown in Fig. 3, where in low count spectra, the weak isolated gamma from Cs-137 is most readily identifiable with SrI₂(Eu). GYGAG(Ce) provides more than 2x better performance than NaI(Tl) in the 200 keV region, and in the 1200 keV region, as seen in the Co-60 spectrum in Figure 2, the advantage of

TABLE II
COMPARISON OF PROPERTIES AND PERFORMANCE OF SEVERAL SCINTILLATORS FOR GAMMA RAY SPECTROSCOPY

Scintillator	Light Yield (Photons/MeV)	Energy Resolution (662 keV)	NP Energy Resolution ^a (662 keV)	B (Eq. 1)	Energy Resolution (200 keV)	S _{PP} , %/cm (200 keV)	Radiation Background	Relative False Alarm Rate, ^d φ1.5 x 1.5 cm
NaI(Tl)	40,000	7%	5.0%	5.3	9%	0.30	B _{NAT}	1
LaBr ₃ (Ce)	63,000	3%	2.2%	0.003	5.4%	0.34	B _{NAT} + B _{SELF}	0.24
SrI ₂ (Eu)	90,000	3%	2.2%	1.1	4.3%	0.36	B _{NAT}	0.07
(Gd,Y) ₃ (Al,Ga) ₅ O ₁₂ (Ce)	50,000	4.8%	1.9%	1.3	7.3%	0.38	B _{NAT}	0.43
Standard PVT	15,000	8% ^b	3.6%	---	---	0.0006	B _{NAT}	---
Bi-loaded polymer	10,000-30,000	8%	3.5%	6.4	15%	0.08	B _{NAT}	12

^aNon-proportionality-limited energy resolution determined by fits to data from the Scintillator Light Yield Non-Proportionality Characterization Instrument, see Reference 14.

^bObtained from fitting the Compton Edge of the pulse height spectrum of Eljen EJ-200 plastic scintillator.

^cNot readily obtained due to extremely weak photopeak for this material.

^d False Alarm Rate (FAR) is described by Equation 2, for identifying a spectral anomaly in the vicinity of 200 keV.

GYGAG(Ce) becomes even more pronounced. The ease of manufacture and handling of transparent ceramic oxides, could additionally result in an economic advantage for GYGAG(Ce) over NaI(Tl). Finally, the intrinsic energy resolutions of SrI₂(Eu), GYGAG(Ce) and the Bi-loaded polymer, as estimated from fitting data from the Scintillator Light Yield Non-Proportionality Characterization Instrument, are better than the current experimental values, shown in Table 1, and therefore we expect that with improved material quality and device design, their energy resolution may improve further [15,16].

IV. SUMMARY

We have identified several new scintillator materials through a “directed search” methodology. Among them, SrI₂(Eu) offers the highest energy resolution. Transparent ceramic GYGAG(Ce) offers high light yield, and gamma spectroscopy with better resolution than NaI(Tl). We have synthesized and characterized Bi-loaded polymer scintillators that can be used for gamma spectroscopy, and larger size samples are under development.

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