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# Improved Lithium Iodide neutron scintillator with $Eu^{2+}$ activation II: Activator zoning and concentration effects in Bridgman-grown crystals

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## ABSTRACT

We have previously reported on the formation of Suzuki Phase precipitate particles as a result of the addition of the divalent activator ion Eu $^{2+}$ to the monovalent alkali halide host LiI. [Boatner et al. (2017)]. These precipitates form during Bridgman or other melt-growth processes, even at low $Eu^{2+}$ concentrations (e.g., 0.1% $EuI_2$ doping), and scatter the scintillation light reducing the optical transparency of the scintillator and adversely affecting its radiation-detection performance. In our prior work, we developed a two-stage thermal-treatment method for the post-growth removal of the Suzuki Phase particles and the realization of a significant improvement in the optical transparency and associated neutron-detection of LiI:$Eu^{2+}$ scintillators. These improvements resulted in neutron-detection performance that is superior to GS-20 glass and that allows for the application of pulse height gamma-ray discrimination over a wide range of gamma ray energies as opposed to pulse shape discrimination. Here, we apply the two-stage thermal-processing method for the removal of Suzuki phase precipitates and carry out an in-depth study, first, of the neutron scintillator performance versus the $Eu^{2+}$ activator-ion-concentration spatial variation as a result of zoning effects during the Bridgman growth of LiI:$Eu^{2+}$ and, second, of the effects of varying the initial $Eu^{2+}$ activator ion concentration prior to crystal growth. The $Eu^{2+}$ zoning variation results allow one to identify and select the most efficient location of the scintillation performance in a directionally solidified single-crystal boule. The present study of the initial activator concentration levels shows that there are, in fact, two distinct types of luminescence centers with varying performance properties — one that occurs only at low $EuI_2$ addition levels (e.g., 0.01 to 0.06 %$EuI_2$) and that is quickly replaced by a second luminescing center with increasing $Eu^{2+}$ content (e.g., at ~0.1% $EuI_2$). The light yield for the luminescing center formed using a Eu activator in LiI is a critical function of the Eu concentration in the range of 0.01 to 0.1 % $EuI_2$, and a high light yield of 100,000 photons/neutron is observed at the 0.06 %$EuI_2$additive level prior to thermal processing.

## 1. Introduction

In our previous work [1,2], we have investigated the effects of a $Eu^{2+}$ activator ion on the performance of LiI:$Eu^{2+}$ neutron scintillators and have shown that the divalent Eu ion, when added to the monovalent LiI host at a level of approximately 3%, results in the formation of essentially opaque single-crystal scintillators. This opacity results from the formation of Suzuki Phase precipitate particles [3–5] that function as light scattering centers, and at a $Eu^{2+}$ level of a few percent, these particles render the neutron scintillator effectively non-functional. An example of the opacity of an as-grown 3% $Eu^{2+}$ LiI crystal is shown in the top-left photograph in Fig. 1, and the associated pulse-height spectrum for neutrons from an AmLi source is shown in the lower-left portion of the figure. In Refs. [1,2], we have described the development

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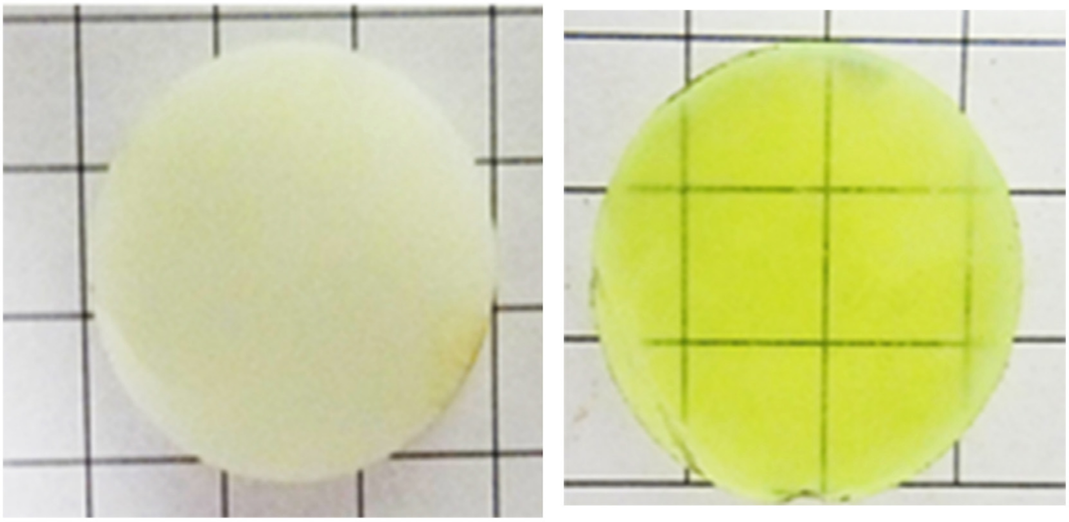
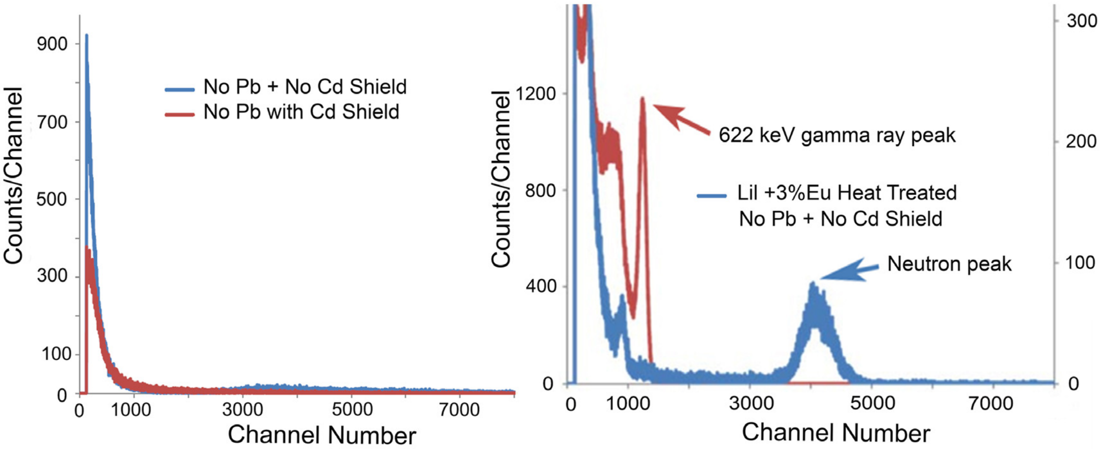


LiI: 3% Eu sample ~ 25 mm diameter X 5 mm thick.
Left: as-grown single crystal. Right: crystal after post-growth processing.



LiI: 3% Eu **Before** Heat Treatment AmLi Thermal Neutron Source Response.

LiI: 3% Eu **After** Heat Treatment AmLi Thermal Neutron Source + Cs-137 Gamma Response.

**Fig. 1.** Top Left: An as-grown, opaque single crystal of LiI with a 3% $EuI_2$ activator is shown prior to the two-stage thermal processing treatment described in Ref. [1]; Top Right: The same crystal is shown after the thermal processing sequence described in Ref. [1] — illustrating the difference in the optical transmission produced by the use of this processing method to remove the Suzuki-Phase precipitates that render the as-grown crystal opaque; Bottom Left: The pulse height spectrum using an AmLi thermal neutron source is shown for the as-grown crystal illustrated in the Top Left panel of the figure. This spectrum shows the essentially negligible response of the opaque crystal to thermal neutrons; Bottom Right: Pulse height spectrum using the AmLi thermal neutron source after the thermal processing treatment to produce the scintillator shown in the upper Right-Hand panel of the figure. This spectrum is plotted along with the 662 keV gamma-ray spectrum of $^{137}$Cs.
*Source:* Data excerpted from Figs. 1 and 6 of Ref. [1].

of a two-stage thermal-treatment process that can be used to eliminate the Suzuki Phase precipitates and significantly increase the optical transparency of the LiI:$Eu^{2+}$ crystal — as illustrated by a comparison of the upper right and upper left photographs in Fig. 1. The resulting dramatic improvement in the neutron detection response resulting from the altered scintillator properties produced by the two-stage thermal treatment is shown by a comparison of the two pulse height AmLi-source neutron spectra at the bottom left- and right-hand portions of Fig. 1. The lower right-hand pulse height spectrum in Fig. 1 also shows the spectrum of 662 keV $^{\mathbf{137}}$Cs gamma rays for purposes of comparison. The large difference in channel numbers between the $^{137}$Cs gamma-ray peak and the neutron peak indicates that direct pulse height discrimination between gamma rays and thermal neutrons can be used over a wide range of gamma-ray energies (including many energies that are useful for gamma ray spectroscopy) — instead of using pulse shape discrimination methods.

The work presented here extends the findings that are summarized above and described in Refs. [1,2]. Specifically, here we applied the two-stage thermal-treatment process for Suzuki Phase particle removal to an investigation of $Eu^{2+}$-activator spatial zoning effects that occur during the directional solidification process characteristic of single-crystal growth by means of the vertical Bridgman technique. These Eu-content zoning effects are then correlated with the variation in the neutron scintillator performance that occurs along the length of the Bridgman-grown single-crystal boule, and these results permit one to identify and select, for crystal cutting and detector-fabrication purposes, the optimal location of the neutron scintillator performance in the single-crystal boule.