Improved lithium iodide neutron scintillator with Eu^{2+} activation: The elimination of Suzuki-Phase precipitates

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ABSTRACT

Monovalent alkali halides such as NaI, CsI, and LiI are widely used as inorganic scintillators for radiation detection due to their light yield, the capability for the growth of large single crystals, relatively low cost, and other favorable characteristics. These materials are frequently activated through the addition of small amounts (e.g., a few hundred ppm) of elements such as thallium - or sodium in the case of CsI. The monovalent alkali halide scintillators can also be activated with low concentrations of Eu²⁺, however Eu activation has previously not been widely employed due to the non-uniform segregation of the divalent Eu dopant that leads to the formation of unwanted phases during Bridgman or other solidification crystal-growth methods. Specifically, for Eu concentrations near and above ~0.5%, Suzuki Phase precipitates form in the course of the melt-growth process, and these Suzuki Phase particles scatter the scintillation light. This adversely affects the scintillator performance via reduction in the optical transmission of the material, and depending on the crystal thickness and precipitated-particle concentration, this reduction can occur up to the point of opacity. Here we describe a post-growth process for the removal of Suzuki Phase precipitates from single crystals of the neutron scintillator LiI activated with Eu²⁺ at concentrations up to and in excess of 3 wt.%, and we correlate the resulting neutron-detection performance with the thermal processing methods used to remove the Suzuki Phase particles. The resulting improved scintillator properties using increased Eu activator levels are applicable to neutron imaging and active interrogation systems, and pulse-height gamma-ray spectroscopy rather than pulse-shape discrimination can be used to discriminate between gamma ray and neutron interaction events.

1. Introduction

An impressive number of new scintillator materials, including NaI [1-4], KI [2], CsI [5], and LiI [6] - plus the alkaline-earth halides SrI₂ [7] and CaI₂ [8-10] were discovered, developed, and patented by R. Hofstadter (along with some of his colleagues) – starting with his initial discovery of NaI activated with thallium in the period beginning in 1947 and ending with a scintillator patent by Hofstadter et al that was issued in 1973 [11]. Thallium was the principal activator ion for these scintillators - although other activator ions were investigated – including divalent europium in the case of the isovalent alkaline-earth CaI₂ and SrI₂ hosts. In some cases, scintillation was also observed in so-called “intrinsic” scintillators (e.g., CsI, CaI₂) that did not contain any activator ions. It should be noted that all of the alkali halide scintillators delineated above are still widely used in a variety of radiation detection applications - with the exception of KI that was abandoned early on due to the background signal arising from the natural radioactivity of potassium. Additionally, while CaI₂:Eu²⁺ appeared to show early promise, its potential was never realized due, among other things, to severe crystal-growth problems that were linked to the layered structure of this compound. These CaI₂ crystal-growth issues have been examined recently in some detail as described in Ref. [12].

In contrast to the case of Eu²⁺-activated CaI₂, there has been a recent resurgence of interest in divalent-europium-activated SrI₂. The performance of this scintillator, as originally described by Hofstadter, was only 93% of that of Tl-activated NaI - i.e., 35,300 photons/MeV. This material was essentially “rediscovered” circa 2008 [13] when it was found that when SrI₂ is activated using Eu²⁺ levels that were significantly higher than those originally utilized by Hofstadter, and with the application of modern crystal-growth methods and high-purity materials [14], relatively large Eu²⁺-activated scintillator crystals with light yields of 90,000 photons/MeV and with an energy resolution of ~2.6% could be obtained. This development has led to the current commercial availability of SrI₂:Eu²⁺ scintillators.

Subsequent to the initial work of Hofstadter et al [6] on the use of Tl-doped LiI as a scintillator for the detection of “slow” (i.e. thermal neutrons), a number of ensuing

studies of LiI activated with a variety of dopants, including Eu^{2+} , have been carried out [15-20]. These investigations have included the use of crystals grown with naturally abundant Li or by using isotopically enriched ^6LiI in order to exploit the 940 barn cross-section of the ^6Li neutron converter with its ^3H (2.73 MeV) and ^4He (2.05 MeV) reaction products that stimulate scintillator luminescence.

While the monovalent alkali halide hosts: NaI, CsI, or LiI can be activated via the addition of Eu^{2+} , the activator concentrations used for this divalent ion have historically been quite low (e.g., nominally in the range of 0.01 to 0.1 wt%) [17,18] due to the incompatibility of the incorporation of divalent activator ions at relatively high levels into the monovalent alkali halide hosts. Specifically, when divalent ions such as Eu^{2+} are added to single crystals of monovalent-cation alkali halides at a level of between ~0.5 and 5.0 %, the resulting single crystals are effectively white and opaque due to the formation of so-called Suzuki Phase precipitates [21-23]. These Suzuki-phase precipitates scatter the scintillator light thereby adversely affecting the light transmission and reducing the overall radiation detection performance (e.g. light yield and energy resolution) of the scintillator crystals – for either gamma-ray detection (or in the case of LiI:Eu^{2+} crystals containing preferably isotopically enriched ^6Li as the neutron converter) for thermal neutron detection.

Here, we describe the crystal growth and post-growth treatment and preparation of heavily Eu-doped alkali halide single crystals for which the Suzuki Phase precipitates are eliminated by a post-growth treatment process - thereby rendering the otherwise effectively opaque (or significantly optically absorbing) crystals highly transparent to radiation-induced scintillation light resulting from gamma-ray or neutron excitation. The ability to realize significant improvements in the optical transparency of a divalent-ion-doped alkali halide is described in the present work for the specific case of the neutron scintillator LiI:Eu^{2+} . It should be noted, however, that the method of combining high-concentration divalent-ion doping of alkali halides during crystal growth with the post-growth thermal treatment described here is not limited to divalent europium ions - but is applicable to any divalent rare-earth, iron-group ion, or other divalent dopant ions at additive concentrations that result in the formation of Suzuki Phase precipitates. Additionally the combined crystal-growth and post-crystal growth treatment detailed here

is not restricted to the formation of scintillator materials for radiation detection applications – but it is, in fact, applicable to optical materials in general - including lasers, infrared detectors, phosphors, optical amplifiers, filters, and other optical applications for which a heavy divalent-ion doping of alkali halide crystals would be beneficial.

2. Experimental

2.1. Single crystal growth

The Eu^{2+} -activated LiI single crystals employed in this work were grown using the vertical Bridgman technique. The starting growth charge consisted of either naturally abundant LiI (99.995 % purity, APL, Inc.) or isotopically enriched (95.5%) ^6Li lithium iodide (99.999% purity, Sigma Aldrich, Inc., combined with the addition of varying amounts of the EuI_2 activator, 99.995% purity, APL, Inc.). Originally, conventional quartz Bridgman growth ampoules (20 mm I.D.) were used, but we found that if the growth charge was fully melted under vacuum in the ampoule, subsequent cracking of the quartz occurred episodically during the Bridgman growth process - resulting in a loss of the growth run. This was minimized initially by pre-melting the growth charge under vacuum and then breaking the solidified boule into pieces that were small enough to be added to the growth ampoule through the restricted neck used to seal the growth crucible – again under vacuum.

While these steps improved the yield of the LiI crystals, some episodic cracking of the quartz ampoule still occurred. (Similar ampoule cracking problems were encountered and addressed in early work on the growth of LiI single crystals using quartz crucibles as described in Ref. [15].) Given the unpredictable nature of these ampoule-cracking problems, the quartz Bridgman growth crucibles were replaced by vitreous (glassy) carbon crucibles supplied by Sigradur (Hochtemperatur-Werkstoffe GmbH, Thierhaupten, Germany). The vitreous carbon crucibles were then encapsulated in a quartz envelope assembly similar to that illustrated and described in Figs. 2a,b in Ref. [12]. The quartz frit filter shown in Ref. [12] was, however, not used for the growth of LiI, since its use required melting of the growth charge in filling the Bridgman crucible. The LiI:Eu^{2+} crystals were then grown at a translation rate of 0.3 mm/h using a two-

zone Mellen, Inc. tube furnace with a 50 mm-diameter bore and with an upper zone temperature of 550°C and a lower zone set at $T = 425^{\circ}\text{C}$. This approach eliminated interactions between the molten LiI:Eu^{2+} growth charge, adherence of the solidified single crystal boule to the crucible wall, and subsequent crystal cracking due to adhesion and differential thermal contraction effects. As noted previously, significant zoning due to segregation of the Eu activator takes place in the course of the directional solidification that is inherent in the Bridgman crystal-growth process. This generally results in a crystal boule that is initially clear, but that abruptly becomes cloudy with the segregation-induced increase in the Eu content. Accordingly, the upper region of the crystal that contains the Suzuki-Phase precipitates is readily identifiable by simple visual inspection. These segregation phenomena will be treated in detail in our subsequent report of the effects of the removal of Suzuki Phase particles on the gamma-ray-induced scintillation of Eu-activated NaI, LiI, and CsI single crystals.

2.2. Post-Growth Crystal Processing

An as-grown single crystal of naturally abundant LiI:Eu^{2+} produced as described above is shown in Fig. 1a. The Suzuki Phase precipitates [21-23] formed during the crystal growth process in the case of the 3% Eu^{2+} -doped LiI crystal shown here render the ~5 mm-thick as-grown crystal white and essentially opaque. A two-step post-growth thermal treatment after being applied to the crystal shown in Fig. 1a removes the precipitated particles and increases the optical transmission of this material as shown in Fig. 1b. The subject two-step thermal treatment process is generally described as follows: A divalent Eu-doped LiI single crystal that initially contains the Suzuki Phase precipitates is first heated in a dry atmosphere (e.g., dry high-purity argon or another dry noble gas – or as will be discussed later, $\text{Ar} + 4\% \text{H}_2$) at a temperature and for a time period at which point the Suzuki Phase precipitates dissolve, and the associated particulate components are dispersed by diffusion into the alkali halide single-crystal host matrix. The developing increased transparency of the material during heating can be monitored visually or by optical transmission methods until optical clarity is achieved. At this point, the crystal is rapidly cooled (i.e., quenched) at a cooling rate that prevents the re-formation of the Suzuki phase precipitates. In the absence of this rapid cooling

process, the material will simply revert to the original opaque/white state on slow cooling. Once the material is heated to the temperature and for the time required to remove the precipitates and thereby clarify the material, further heating of the crystal has no additional beneficial effects, and the material can be stabilized in the transparent state at that point by the rapid quenching process described here. The quenching/cooling process can be achieved by subjecting the hot crystal to a stream of cool flowing helium gas, by placing the crystal in thermal contact with a cold copper (or other metal) block, or by immersing the crystal in a liquid bath (e.g. mineral oil). The latter two methods were found to yield the least-controlled and less-reproducible results, and in fact, quenching in a liquid medium frequently resulted in fracturing of the crystal. The cooling rate used to prevent the re-formation of the Suzuki Phase precipitates must be adjusted so that it is sufficiently rapid to prevent re-precipitation – but not so rapid that it induces mechanical fracturing of the crystal due to thermal stresses associated with the rapid cooling process. This cooling rate can be determined experimentally, and it will vary depending on the physical size of the crystal to be cooled and, in general, on the specific alkali halide host -i.e., depending on, for example, whether a divalent-ion-doped LiI, NaI, or CsI crystal - or some other alkali halide host is utilized. We have found the helium-gas-flow quenching method, using the system illustrated schematically in Fig. 2, to give the most effective and reproducible results.

In the present specific case of a Bridgman-grown single crystal of LiI doped with 3 wt% Eu^{2+} , the crystal shown in Fig. 1b was heated in an argon atmosphere to a temperature of 400°C and held for 4 hours at that temperature. The crystal was then quenched in flowing He gas with an initial cooling rate of ~100°C/min. This cooling rate did not result in any thermally induced fracturing of the single crystal. A comparison of heated and quenched material, as shown on the right-hand side of Fig. 1b with that shown in Fig. 1a, clearly illustrates the increased optical transparency produced by the removal of the Suzuki Phase particles as a result of the heating and quenching process.

In pursuing the goal of this work of removing the light-scattering Suzuki Phase precipitates and thereby increasing the scintillator optical quality and thermal neutron detection performance of LiI activated with increased levels of Eu^{2+} , we also evaluated thermal treatments using an Ar + 4% H_2 atmosphere. Figure 3 shows the thermal

neutron (AmLi source) photopeak response for an as-grown, untreated naturally abundant LiI:3%Eu²⁺ sample, for a sample treated for 4 h in Ar alone, and for a twin ”book-matched” sample treated for 4 h in Ar + 4%H₂. For the case of the as-grown crystal the photopeak is essentially not discernable, while a distinct photopeak is observed for the sample treated in Ar. An even more intense neutron photopeak (that is also slightly shifted to higher channel numbers) is shown in Fig. 3 for a “twin” (i.e., “book-matched”) sample that was treated in the Ar + 4%H₂ (i.e., forming gas) atmosphere.

Following our observation of the beneficial effect of using the reactive Ar + 4% H₂ atmosphere rather than pure inert Ar, the utilization of an increased thermal processing time prior to the quenching process was also investigated. Figure 4 shows the thermal neutron photopeak for a 3%Eu-activated naturally abundant LiI crystal that was heated for a 4 h period along with the photopeak for an adjacent (i.e., “book-matched”) slice of the crystal that was heated for a 16 h time period. The extended 16 h thermal processing time has clearly resulted in a sharper, more intense neutron photopeak – and one that has now been shifted to a significantly higher channel number.

3. Results

The optical transmission results for a naturally abundant lithium LiI single crystal (3%Eu²⁺ activated) are shown in Fig. 5 - both before and after the thermal processing treatment in Ar as described previously. These optical transmission curves are plotted along with the X-ray-excited (150 keV) photoluminescence spectrum of a thermally processed transparent single-crystal scintillator like that illustrated in Fig. 1b. These results show that the peak of the X-ray-excited luminescence spectrum lies in the high transmission region of the Eu-activated LiI host crystal i.e., in the region that begins near 450 nm and extends up to 800 nm in this plot. These fortuitous optical compatibility results indicate that self-absorption of the radiation-induced scintillation emission due to the LiI host will be low.

The full pulse-height spectrum for a naturally abundant lithium LiI 3%Eu-activated single crystal is shown in Fig. 6a for a crystal that has been heated in Ar for 4 h and then quenched in flowing He gas as described previously in *Section 2.2* to yield a

level of transparency equivalent to that illustrated in Fig. 1b. The AmLi-source thermal neutron peak lying between channel numbers 4,000 and 4,500 is well defined and symmetric in this naturally abundant LiI :3%Eu²⁺-activated scintillator. The pulse-height spectrum for the 662 keV gamma rays emitted by ¹³⁷Cs is also plotted in Fig. 6a along with the thermal neutron response of the crystal. The large difference in channel numbers between the ¹³⁷Cs 662 keV gamma-ray peak and the neutron photopeak in Fig. 6a indicates that pulse-height gamma-ray/neutron discrimination (rather than pulse-shape discrimination) can be utilized over a wide range of gamma-ray energies – including those of interest for many gamma-ray spectroscopy applications. Figure 6b shows the pulse-height spectrum before the thermal processing protocol described previously for the crystal whose post-processing pulse-height spectrum is shown in Fig. 6a. The thermal neutron response in the un-processed crystal is very weak and broad. The spectrum obtained with a Cd shield in place to absorb the neutrons is also plotted in Fig. 6b, and, as expected, it is featureless in the absence of neutrons. A comparison of Figs. 6a and 6b shows the remarkable improvement in scintillator performance that can be realized in a 3% Eu²⁺-activated single crystal of naturally abundant LiI by using the combined thermal heating and quenching process described here.

Figure 7 shows the pulse-height spectrum for a naturally abundant lithium LiI crystal plus a 3%Eu²⁺ activator where the crystal has been thermally processed to remove the Suzuki Phase particles as described in *Section 2.2*. This spectrum is plotted along with the pulse height spectrum of the widely used commercial neutron scintillating glass GS20. A comparison of the two spectra illustrates the superior light yield for thermal neutron detection (~11,000 photons/MeV) of the naturally abundant LiI:3%Eu²⁺ scintillator single crystal versus that of the GS20 glass standard.

The identification and development of the processing parameters described above for the removal of Suzuki Phase precipitates from LiI host crystals containing several percent of Eu²⁺ required extensive experimental studies. Accordingly, the subject serial crystal-growth, sample-treatment, and characterization investigations were carried out using naturally abundant rather than isotopically enriched ⁶Li for economic reasons. However, in practical applications of LiI:3%Eu²⁺ scintillators for neutron detection, the use of isotopically enriched ⁶Li is desirable or necessary. The 940 barn thermal neutron

cross section of ^6Li enriched LiI results in a reduced-thickness detector that still absorbs all or most (e.g., 80% for a 1.5 mm-thick ^6Li crystal) of the neutrons while reducing the detector sensitivity to gamma rays. The crystal-growth and thermal-processing parameters identified here using naturally abundant Li in LiI have subsequently been applied to the growth and thermal processing of crystals incorporating 95.5% isotopically enriched ^6Li . Figure 8 shows the X-ray-excited (150 keV) luminescence spectrum of a 95.5% isotopically enriched $^6\text{LiI:3\%Eu}$ crystal after thermal processing. For comparison purposes, this spectrum is plotted along with the X-ray-excited luminescence result for a commercial NaI:Tl scintillator crystal. The $^6\text{LiI:3\%Eu}$ luminescence emission is significantly sharper than that of the NaI:Tl scintillator, and its peak is located at 466 nm versus the 416 nm peak location of NaI:Tl. The peak emission at 466 nm is advantageous since it falls well within the maximum sensitivity range of current silicon photomultipliers.

An AmLi neutron-source-excited pulse height spectrum for a 95.5% ^6Li enriched LiI:3%Eu crystal is shown in Fig. 9 for a sample that was thermally treated for 16 h at 400°C. A pulse-height spectrum is also plotted in Fig. 9 where a Cd shield has been inserted between the AmLi neutron source and the $^6\text{LiI:Eu}$ scintillator crystal in order to confirm the detection of neutrons by blocking almost all of the AmLi source output. In a manner similar to that illustrated in Figs. 6a,b for the case of a naturally abundant LiI host activated with 3% Eu^{2+} , the thermal heating and quenching process resulted in the well-defined neutron peak shown in Fig. 9 - whereas the neutron signal was barely discernable in the ^6LiI host scintillator prior to the thermal treatment.

4. Discussion and Summary

The initial reports of the discovery of Suzuki Phase precipitates by Suzuki [21-23] and Miyake and Suzuki [24] centered on the monovalent-divalent cation systems: NaCl-CaCl₂ and NaCl-CdCl₂, and in the case of the NaCl-CdCl₂ system, Suzuki [23] used X-ray methods to identify the precipitated phase as having the composition CdCl₂•6NaCl that was present in the form of a super unit cell with a volume 8 times that of the NaCl host matrix. Subsequent to these initial early reports, numerous fundamental

investigations of the optical and physical properties of Suzuki Phase systems have been carried out. These studies included transmission electron microscopy (TEM) investigations of the $\text{NaCl}:\text{Cd}^{2+}$ and $\text{NaCl}:\text{Mg}^{2+}$ systems by Guerrero et al [25] and TEM investigations by Yacaman, Hobbs, and Goringe [26] who observed $6\text{NaCl}:\text{MnCl}_2$ Suzuki Phase particles with sizes on the order of 1 micron. Several basic optical absorption and photoluminescence investigations have also been carried out for Suzuki Phase precipitate systems formed by the presence of Eu^{2+} (the ion of interest here as an activator in LiI for thermal neutron detection) in: several alkali chlorides, bromides and KI [27], in NaCl and KCl [28,29], and in KBr [30,31]. These studies also included investigations of the effects of thermal treatments on the optical spectra. More recently Clemens and Barth have carried out high-resolution scanning force microscopy investigations of the properties of Suzuki Phase precipitates in $\text{NaCl}:\text{Mg}^{2+}$ [32] and $\text{NaCl}:\text{Cd}^{2+}$ [33] where $400 \times 400 \text{ nm}^2$ precipitates were observed on cleaved surfaces of the crystal. This latter reference also includes a useful comprehensive list of pertinent Suzuki Particle references.

The goal of the present work is to improve the performance of $\text{LiI}:\text{Eu}^{2+}$ neutron scintillators by eliminating the deleterious effects of Suzuki Phase precipitates that form specifically in LiI at Eu^{2+} concentrations nominally above ~0.5%. These Suzuki phase particles have previously limited the amount of the Eu^{2+} activator that can be used in LiI crystals (e.g., 0.05 mol per cent, Ref. [34]) since they scatter the scintillator luminescence and significantly reduce the optical transmission characteristics. In realizing this goal, we have combined the Bridgman growth of LiI single crystals containing several percent of Eu^{2+} with a two-stage heating and quenching process that transforms the cloudy, essentially opaque material shown in Fig 1a to the scintillator crystal shown in Fig. 1b. This increased transparency is of particular interest for use in active neutron interrogation detection/imaging systems and in neutron imaging in general. The significant difference in neutron detection achieved in a 3%Eu-activated LiI scintillator as a result of the heating and quenching process described here is clearly shown by a comparison of Figs. 6a and 6b. The large channel number difference between the neutron photopeak and the photopeak of the 662 keV gamma ray emitted by ^{137}Cs in Fig 6a indicates that pulse-height discrimination can be used rather than pulse-shape

discrimination over a wide range of gamma-ray energies. Fig. 7 illustrates the superior light yield of a naturally abundant LiI:3%Eu²⁺ scintillator after thermal processing compared to that of a standard and widely used GS20 glass scintillator. While the results presented here have concentrated on the example of a LiI crystal grown with the addition of 3%EuI₂, other Eu concentrations in the range of 1 to 5% were investigated that yielded equivalent results up to the 5% EuI₂ level - a concentration that apparently represents the limit at or above which an additional bulk phase forms. Finally, as noted previously, large single crystals of LiI can be readily grown using well-established commercial methods so that many of the crystal growth issues that plague some other modern inorganic scintillators are not applicable.

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FIGURE CAPTIONS:

Fig. 1. (a). Suzuki Phase precipitates that form during the crystal growth process in the example of the 3%Eu²⁺-activated, ~ 5 mm-thick naturally abundant LiI crystal shown here render the as-grown material essentially opaque. (b). The two-step thermal treatment described here in *Section 2.2* removes the precipitated particles to produce the scintillator clarity shown in this post-growth-processed crystal photograph.

Fig. 2. The post-growth thermal-processing system used to remove the Suzuki Phase particles is schematically shown here. (Top) A temperature-controlled clamshell resistance-heated furnace is used to heat the as-grown single-crystal sample that is held on a quartz sample support inside a surrounding quartz tube. The sample is initially heated in high-purity Ar or in Ar + 4% H₂, and the crystal is visually monitored by briefly opening the clamshell furnace as the sample temperature is slowly increased. Once the sample becomes initially clarified, the heating process continues for several hours to allow for diffusion away from the initial “source” Suzuki precipitates to stabilize the material. (Bottom) Subsequent to the heating process, the clamshell furnace is opened, the quartz assembly is lifted from the hot furnace, and the scintillator is rapidly cooled (~100°C/min) by using a control valve and flow meter to flow helium gas through a quartz gas tube and diffuser and directly onto the crystal positioned as shown in the drawing.

Fig. 3. A comparison of the pulse height spectra is shown for an untreated naturally abundant LiI:3%Eu²⁺ single-crystal sample, along with that for the sample treated in pure argon, and for a “book-matched” sample treated in Ar + 4%H₂. For the untreated sample, there is no clearly identifiable photo peak, while for the crystal subjected to the two-step thermal process, an intense and clearly defined photopeak is present. For the case of thermal processing in Ar + 4% H₂, the photopeak has become even more intense and has now been shifted to higher channel numbers.

Fig. 4. The effect of thermal processing time on the evolution of the photopeak for a naturally abundant $\text{LiI:3\%Eu}^{2+}$ activated scintillator crystal is shown. The photopeak for a sample heated for 4 h at 400°C and then quenched is shown along with that obtained for a twin sample that was also heated in pure Ar at 400°C - but for a 16 h time period prior to quenching. The photopeak for the sample heated for 16 h is sharper, more intense, and shifted to significantly higher channel numbers.

Fig. 5. The X-ray-excited luminescence spectrum (150 keV) for a naturally abundant $\text{LiI:3\%Eu}^{2+}$ crystal is plotted versus wavelength along with the optical transmission spectra for a heat-treated and non-heat-treated $\text{LiI:3\%Eu}^{2+}$ sample. A comparison of the X-ray and optical transmission results shows that self-absorption effects due to the LiI host material will be low since the X-ray luminescence peak lies in the high-optical-transmission region of the LiI host.

Fig. 6. (a). The pulse-height spectrum is shown for a naturally abundant $\text{LiI:3\%Eu}^{2+}$ crystal after heating at 400°C for 4 h and then rapidly cooling in flowing He gas to produce a transparency like that shown in Fig. 1b. The scintillator was excited using thermal neutrons from an AmLi source. The neutron spectrum with the photopeak above channel number 4000 is not present upon the insertion of a Cd shield between the neutron source and the scintillator crystal. Plotted along with the neutron spectrum is the pulse height spectrum for 662 keV gamma rays from a ^{137}Cs source. A comparison of the neutron and gamma ray spectra shows that pulse height discrimination rather than pulse shape discrimination can be used over a wide range of gamma-ray energies. (b). The thermal neutron response is shown before the two-stage thermal treatment for the crystal whose spectrum is shown in Fig. 6a after thermal processing. The pulse-height response is also shown after the insertion of a Cd neutron shield.

Fig. 7. The pulse-height spectrum for a naturally abundant LiI:3%Eu²⁺ scintillator following the two-stage thermal treatment described in *Section 2.2* is plotted along with the spectrum for a GS20 glass neutron scintillator standard – illustrating the significantly higher response of the 3%Eu-activated LiI scintillator. A ²⁵²Cf neutron source was used for excitation in both cases.

Fig. 8. The X-ray-excited luminescence spectrum (150 keV X-rays) for a 95.5% ⁶Li-enriched ⁶LiI:3%Eu²⁺ scintillator crystal is plotted along with the spectrum for a commercial NaI:Tl scintillator. The spectrum for the ⁶LiI host is both significantly sharper and peaks at a higher wavelength relative to that of the NaI:Tl scintillator. The ⁶LiI:3%Eu emission peaks at 466 nm – a value that is well into the high-response range of solid state Si photomultipliers.

Fig. 9. The AmLi source thermal-neutron-excited pulse-height photopeak spectrum is shown for a 95.5% enriched ⁶LiI:3%Eu²⁺ scintillator crystal after thermal processing. The spectrum of the same crystal taken with a Cd shield in place that removes the majority of the neutrons is also shown. Again, prior to the two-stage thermal processing treatment, the neutron photopeak was barely discernable.

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**Lil: 3%Eu Heat Treatments
16 h vs. 4 h**

Light Yield (GS20 vs. Lil)

^6LiI : 3%Eu After Heat Treatment