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Scintillation properties of semiconducting $^{6}LiInSe_2$ crystals to ionizing radiation

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ABSTRACT

$^{6}LiInSe_2$ has gained attention recently as a semiconducting thermal neutron detector. As presented herein, the chalcogenide compound semiconductor also detects incident neutrons via scintillation, making $^{6}LiInSe_2$ the only lithium containing semiconductor to respond to neutrons via both detection mechanisms. Both yellow and red crystals, which appear in the literature, were investigated. Only the yellow crystal responded favorably to ionizing radiation, similar to the semiconducting operation utilizing electrodes. The obtained light yield for yellow crystals is 4400 photons/MeV, referenced to $Bi_4Ge_3O_{12}$ (BGO).The estimated thermal neutron light yield was 21,000 photons/thermal neutron. The two measured decay time components were found to be 31 ± 1 ns (49%) and 143 ± 9 ns (51%).This crystal provides efficient, robust detection of neutrons via scintillation with respectable light yield and rapid response, enabling its use for a broad array of neutron detection applications.

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1. Introduction

Thermal neutron detectors are important for the search for water and life in asteroids and planetary terrain, illicit nuclear material detection, neutron radiography, as well as to monitor nuclear power plant fuel processes [1–4]. A worldwide shortage of ^{3}He, currently the primary neutron detection medium, has led to great interest in solid state materials as alternative neutron detectors [1]. These alternative materials respond to incident radiation either through scintillation, where incident radiation produces visible light, or as a semiconductor, in which incident radiation produces an electric current [4]. The difficulty with most bulk materials is the competing interactions with incident gamma photons and static background induced by neutrons interacting with the surrounding environment, resulting in low neutron detection efficiency and/or poor neutron/gamma discrimination, generating the need to use multi-parameter analysis to distinguish detector response events.

Neutrons have no intrinsic charge, and therefore must be indirectly detected by converting the neutron into detectable ionizing radiation utilizing a neutron capturing isotope. The most commonly used isotopes are ^{6}Li, ^{10}B, ^{199}Hg, ^{113}Cd or ^{157}Gd [3–6]. While both ^{6}Li and ^{10}B can produce charged products via neutron capture, ^{6}Li based materials have the additive bonus of the elimination of gamma ray interactions associated with the neutron capture process of interest. ^{6}Li is within a special subset where its unique reaction products include an alpha particle and a triton, symbolically written as $^{6}Li(n,\alpha)^{3}H$, as opposed to a prompt gamma photon generated by the latter isotopes. As such, a smaller material volume is required to absorb the energy of the products.

Lithium selenoindate is a member of the $LiB^{III}C_2^{VI}$ chalcogenide family. First reported to structurally exist by Hoppe, $LiInSe_2$ crystal growth has been extensively studied for applications in photonics [7–11]. The technical procedure for crystal growth incorporating uniform media requirements is demanding due to the corrosive nature of lithium and relatively high vapor pressure of its constituents at high temperatures, introducing purity and secondary phase production concerns [12,13]. In addition, these crystals often exhibit distinguishable variations in color and impurity content; previously published efforts have also demonstrated this common observation in $LiInSe_2$ samples [14–16]. Despite these difficulties, significant progress has been made concerning crystal growth and the understanding of the optical–electrical properties of this material for radiation detection [17–19].

$LiInSe_2$ has the ability to respond to ionizing radiation through direct charge carrier transport; however, charge carrier trapping is demonstrated in crystals affecting the overall charge collection

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efficiency [18,19]. In more recent years, radiation detection viability has been investigated with the incorporation of isotopically enriched lithium-6. Due to its direct gap characteristics, this material should undergo charge carrier recombination, producing visible light by external excitation [4,20]. Here, neutron detection is explored through scintillation. While all scintillators can suffer from energy transfer to non-radiative channels, most traditional scintillator materials suffer from non-proportional energy response, which degrades the energy resolution due to the mobility of the charge carriers in the bulk; these observations are not significantly pronounced in semiconductor detectors [21–24]. In both applications, the forbidden energy gap is a key parameter since this parameter determines the number of electron–hole pairs generated due to energy deposition and potentially available pairs for recombination. In principle, narrowing the gap provides the framework to both improving the light yield in the visible spectral range and tuning the response of scintillating materials. This makes scintillating semiconductors excellent detection material templates of study. The absorption edge for $LiInSe_2$ at room temperature is reported to be around 2.8 eV, introducing the opportunity to explore nonproportionality in selenides and in a forbidden energy gap regime that has not yet been explored [17,25].

Indeed, due to its unique composition as a solid state material structurally incorporating lithium-6, $^6LiInSe_2$ should provide the capability for neutron capture events to be observed and cleanly separated from the natural radioactivity of its neighboring constituents in the host in natural abundance, because of its large Q-value of 4.78 MeV, for the thermal neutron capture event. The next most probable thermal neutron capture process in $^6LiInSe_2$ is indium-115 which most frequently produces low energy prompt gammas. The transition percentages and gamma emissions of lithium-6 and indium-115 are well tabulated in the national nuclear data center website [26]. Neutron capture within the $^6LiInSe_2$ crystal by ^{115}In, assuming natural abundance, may account for as much as 18% of the interactions. These ^{115}In captured neutrons would not contribute to the $^6LiInSe_2$ detection response and would therefore limit the overall neutron detection efficiency.

This material can also support detection capabilities within small geometric constraints. The thermal neutron mean free path in $^6LiInSe_2$ is 0.09 cm. Due to the high density of the converter isotope (^6Li), the crystal can achieve an excellent thermal neutron capture efficiency of 99% at a crystal thickness of approximately 0.5 cm. In addition, when coupled with a Si photo detector (such as a silicon photomultiplier). $LiInSe_2$ will have the advantage of being compact, low power and therefore attractive for handheld instruments. The research presented herein demonstrates that neutron capture in $^6LiInSe_2$ produces a rapid scintillation response with modest light yield.

2. Experimental

$^6LiInSe_2$ crystals were grown under synthesis conditions incorporating the two step recipe explained in Tupitsyn et al. utilizing 95% isotopically enriched lithium-6 [19]. Growth of the ternary compound was executed with a two zone furnace by the vertical Bridgman technique. The furnace utilized resistive coils, in temperature controlled zones, in a practically thermally isolated enclosure. The hot zone was set at a temperature of 940 °C and the cold zone was set at 760 °C. The vertical growth translation rate was 0.7 cm/day. After cooling down, the ingot was sectioned and wafers were fabricated by polishing and chemical etching in 5% Bromine–Methanol solution. The dimensions of the fabricated samples were measured to be $0.45 \times 0.41 \times 0.10\ cm^3$ for the yellow crystal and the red crystal was measured to be $0.60 \times 0.60 \times 0.06\ cm^3$. Representative crystals are shown in Fig. 1.

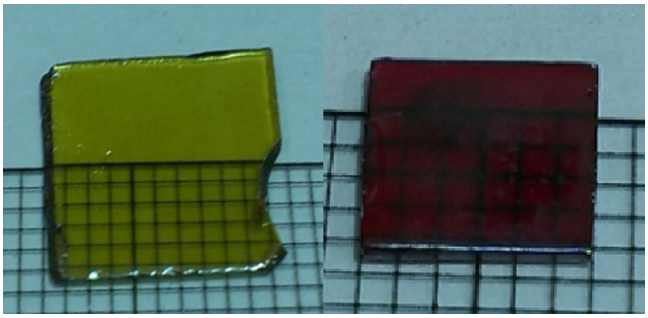

Fig. 1. Image of representative $^6LiInSe_2$ crystals, illustrating the differences in color from numerous growth and fabrication observations. The yellow color is attributed to stoichiometric crystals while the red color is caused by defects related to lithium deficiency.

To explore the scintillation characteristics of $^6LiInSe_2$, the detection system was constructed by optically coupling the $^6LiInSe_2$ crystal to the window of a Hamamatsu 6231-100 PMT, securing a reflective surrounding and covered by an opaque enclosure to ensure the collection of the scintillated light. The luminous flux, induced by incident radiation, is converted into an electrical signal and conditioned using a pre-amplifier, processed using an Ortec 671 shaping amplifier, supplied to a Canberra Multi-Channel Analyzer (MCA) and graphically displayed utilizing Canberra Genie software. From the irradiation of alpha particles, the timing characteristics of the scintillation event were also measured; this task was achieved by feeding the output of the PMT to a digital oscilloscope. Characteristic pulse decay times were determined by fitting the output of the pre-amplifier to a weighted linear sum of exponentially decaying terms.

To analyze the material response to ionizing radiation from different colored crystals through scintillation, X-ray Excited Optical Luminescence (XEOL) was conducted to observe allowed charge carrier transitions with a relatively high density of states. One of the advantages, exploited in this technique, is that the source photon will experience a greater mean free path as opposed to direct band edge excitation. This allows one to observe more of the bulk response to external excitation. The samples were irradiated with a Cu Kα source and the induced photoluminescence was collected through an optical fiber and process utilizing an Ocean Optics USB2000 spectrometer. In addition, these measurements were taken at room temperature (25.4 °C) for complementary correlation of the absorbance spectra. The room temperature absorbance spectrum was taken with a UV–vis–NIR spectrometer (Varian Cary 500 Scan).

In order to evaluate neutron induced scintillation response, the crystal was exposed to a moderated 2 Ci PuBe source using a similar pulse height spectra acquisition system. The thermal neutron flux was provided by the source enclosed in a high density polyethylene block to reduce the kinetic energy of the neutrons emitted by the source. The source was placed at the center of the $30.5 \times 45.7 \times 25.4\ cm^3$ block. Taking the source characteristics and moderator dimensions into account, only a fraction of the neutrons incident on the crystal are thermal neutrons [27]. It should be noted that the moderated source emits a mixed field of both thermal neutrons and gamma rays.

For the neutron experiment, the detection system was constructed by optically coupling the $^6LiInSe_2$ crystal to the window of a Hamamatsu 6533 PMT securing a reflective surrounding and covered by an opaque enclosure. The scintillation response is converted into an electrical signal where an Ortec 623 spectroscopy amplifier and gated integrator collected the electrical signal