New Structured Scintillators for Neutron Radiography

V.V. Nagarkar* a, E.E. Ovechkina a, H.B. Bhandari a, L. Soundara-Pandian a, M.J. More a, R.A. Riedel b, and S.R. Miller a

a Radiation Monitoring Devices, Inc., 44 Hunt Street, Watertown, MA, 02472, USA
b Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

Abstract

We report on the development of novel neutron scintillators fabricated in microcolumnar formats using the physical vapour deposition (PVD) method. Such structures mitigate the conventional trade-off between spatial resolution and detection efficiency by channelling the scintillation light towards the detector while minimizing lateral spread in the film. Consequently, high resolution and high contrast neutron images can be acquired in a time efficient manner. In this paper, we discuss methods and characterization for scintillator films made from three distinct compositions, Thallium (Tl) or Europium (Eu) doped Lithium Cesium Iodide (Li 3 Cs 2 I 5 :Tl,Eu, referred to as LCI), Tl or Eu doped Lithium Sodium Iodide (Li x Na 1-x I:Tl,Eu, referred to as LNI), and Cerium (Ce)-doped Gadolinium Iodide (GdI 3 :Ce, referred to as GDI).

LCI and LNI scintillators are derived from the well-known CsI and NaI scintillators by the incorporation of 6 Li into their lattice. Based on our measurements reported here, LCI/LNI scintillators have shown to exhibit bright emissions, fast, sub-microsecond decay, and an ability to effectively discriminate between neutron and gamma interactions using pulse shape (PSD) and/or pulse height (PHD) discrimination. LCI has a density of 4.5 g/cm 3 , a measured peak emission wavelength of 460 nm (doped with Eu), and a light yield of ~50,000 photons/thermal neutron. LNI has a density of 3.6 g/cm 3 , an emission peak measured at 420 nm, and a light yield of ~100,000 photons/thermal neutron.

The recently discovered GDI exhibits excellent scintillation properties including a bright emission of up to 5,000 photons/thermal neutron interaction, 550 nm green emission, a rise time of ~0.5 ns and a primary decay time of ~38 ns (Glodo et al., 2006). Its high thermal neutron cross-section of ~255 kb makes it an attractive candidate for neutron detection and imaging. Although it has high density of 5.2 gm/cm 3 and effective atomic number of 57, its gamma sensitivity can be minimized by lowering the film thickness and its neutron sensitivity can be maximized through the use of enriched Gd.

The fabrication of micro-structured films of these materials using an evaporation technique permits the cost-effective volume synthesis of high-quality neutron scintillators over large areas (20 cm x 20 cm) in short time. In addition, the vapour deposition permits stoichiometry and dopant control not possible using conventional crystal growth.

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* Corresponding author. Tel.: +1-617-668-6937; fax: +1-617-926-9980.
E-mail address: vnagarkar@rmdinc.com
1. Introduction

Neutron radiography is a valuable diagnostic technique used in a wide range of industrial and scientific applications, providing complementary information to X-ray imaging. Currently, scintillation detectors employing \(^{6}\text{LiF}/\text{ZnS}:\text{Ag}\) in conjunction with a digital readout (such as CCD or CMOS) are widely used. Thick coating layers ensure good efficiencies due to the high probability of neutron interaction with Li nuclei. However, increasing the layer thickness results in reduced light output due to self-absorption and impairs spatial resolution as light is scattered in the granular structure. A reduction of scintillator layer thickness is, therefore, an obvious way to improve resolution. Thus, the high efficiency has to be sacrificed in favor of higher spatial resolution.

At RMD, we have synthesized several new high resolution scintillators for neutron imaging. These materials are vapor deposited in a microcolumnar form which addresses the conventional spatial resolution–efficiency tradeoff. The deposition process allows control of the material stoichiometry, morphology, and film thickness to produce scintillator films tailored for a wide range of applications in large area formats.

Scintillators containing \(^{6}\text{Li}\) are attractive because interaction with thermal neutrons produces an alpha particle and triton totaling 4.78 MeV which can be readily absorbed and converted to scintillation light. Also several Li containing scintillators (such as \(\text{Cs}_2\text{LiYCl}_6 – \text{CLYC}\)) and other elpasolites (Gloodo et al., 2012) allow for n-\(\gamma\) discrimination based on PHD or PSD and hence are of particular interest to the neutron diffraction detector community (Riedel et al., 2010). Elpasolites, however, are difficult to synthesize in a film form needed for large area coverage. Here we report on the synthesis and characterization of two new Li based scintillators, \(\text{Li}_3\text{Cs}_2\text{I}_5\) (LCI) and \(\text{Li}_x\text{Na}_{1-x}\text{I}\) (LNI) which address this issue. These new compounds have shown excellent initial results and demonstrate a strong potential for future neutron detectors. Fig. 1a and b show pictures of hermetically sealed LCI and LNI films.

In addition, gadolinium-containing scintillators are excellent thermal neutron detectors due to the \(^{157}\text{Gd}\) isotope which provides a very high cross-section of ~255 kb (kilobarns) for thermal neutrons. Using natural Gd, a 200 µm \(\text{GdI}_3:\text{Ce}\) film can absorb up to 95% of thermal neutrons. The same absorption efficiency can be achieved with only 50 µm thick film when using enriched \(^{157}\text{Gd}\) material. By fabricating in thin film format, this scintillator provides excellent neutron sensitivity while minimizing gamma interactions. A hermetically sealed GDI film is shown in Fig. 1c and d.

2. Fabrication of Scintillator Films

2.1. Hot Wall Evaporation

The Hot Wall Evaporation (HWE) technique was used to fabricate films of varying thickness of LCI, LNI, and GDI scintillators. HWE is a vacuum-based PVD technique derived from epitaxial growth techniques. The main characteristic of HWE is the vapor-growth of robust, uniform epitaxial layers under conditions of thermodynamic equilibrium, while minimizing the loss of material. The HWE apparatus used for making these films has been described in greater detail previously (Nagarkar et al., Bhandari et al., 2011). The apparatus consists of a hollow cylinder positioned upright in a vacuum, heated under close temperature control, with an evaporation source “crucible” at one end and a cooled substrate at the other. The heated cylinder wall serves to enclose, deflect and effectively direct the vapours from the sources to the substrate where molecules are deposited with a shallow impinging angle. With the substrate being the coolest part in the system, molecules adhere to the substrate alone and do not accumulate on the hot walls, making efficient use of the source material. We found that excellent control of film stoichiometry could be achieved by using doped...
targets of the desired composition rather than separate targets for dopant and host and attempting to balance the respective vapour pressures. This method of fabrication provides high growth rates that allow fabrication in hours rather than the months required for conventional crystal growth. Films grown by this method are polycrystalline but their physical properties can be controlled as explained by the Movchan & Demchishin’s Structure-Zone (SZ) model (Movchan & Demchishin, 1969). Precise control of the deposition parameters such as increasing the substrate temperature results in films with wider columns that are more transparent and more crystalline in nature.

2.2. Film Morphology

Selected films were imaged with our in-house scanning electron microscope (SEM) (ISI SS40). Because of the hygroscopic nature of the materials, the cross-section of the films appear to have reacted with the ambient moisture despite taking great care to limit exposure to the environmental humidity. Fig. 2. shows SEM micrographs of both GDI and LCI films demonstrating the cross-sectional texture that is indicative of the microcolumnar growth. GDI has layered crystal structure that is unstable and hence it is very challenging to grow them via melt-grown methods. However, growing them in a vapor-deposition mode renders some lattice relaxation owing to large surface area and this can be exploited to fabricate textured films, as is evident in the figure.

3. Film Characterization

For neutron radiography, the key performance parameters are light output and spatial resolution. Hermetically sealed films were evaluated with X-rays, gamma-rays and neutrons. The emission spectra and spatial resolution were measured under X-ray excitation, as described in more detail in the following sections. The decay times were recorded for both gammas and neutrons, and in the case of LCI/LNI samples PSD analysis was performed. The LCI/LNI samples were then coupled to an EMCCD camera and neutron images were acquired at the High Flux Isotope Reactor (HFIR) located at Oak Ridge National Laboratory (ORNL).

Fig. 2. a) Scanning Electron Micrograph (SEM) of the as-deposited GdI₃:Ce film measuring 350 µm thick, showing microcolumnar cross-section. The cross-section appears dendritic owing to the low substrate temperature (200 C) and b) a 210 µm thick LCI film showing a different structure evident of a higher substrate temperature. Both films show the surface damage (due to its hygroscopic nature) caused during its transfer to the SEM chamber in air.

3.1. Spectral Emission

Emission spectra of LCI, LNI and GDI films under continuous X-ray excitation were measured using a Cu target X-ray generator (8 keV Cu Kα line) operated at 40 kVp with 20 mA current. The resulting scintillation light was passed through a McPherson model 234/302-0.2m monochromator and measured at each wavelength with an RCA model C31034 photomultiplier tube (PMT). The operation of the whole instrument, including the X-ray trigger, the rotation of the monochromator to select the wavelength, data acquisition and analysis were computer driven.

Fig. 3 shows the resulting emission spectra for several compositions compared to a standard NaI:Tl crystal. The LCI:Eu emission peak is at 460 nm, which is an advantage as blue emissions generally have a faster decay time, and most of the optical detectors used in scintillation counters and spectrometers use PMTs, which have excellent spectral sensitivity at 460 nm. The corresponding spectra
for LNI:Eu and LNI:Tl demonstrate similar behaviour to that of the NaI:Tl crystal, with a small red shift. As such, their emissions are an excellent match to most photosensors.

In the case of GDI, the film was doped with 2% Ce. The emission shows a relatively broad peak from 450 to 700 nm as a result of the $5d \rightarrow 4f$ transition of Ce$^{3+}$. The peak emission is located at ~540 nm and is very close to 550 nm reported for single-crystal GdI$_3$:Ce (Glodo et al., 2006). These films have an excellent match for CCDs or large area a-Si flat panel detectors, both of which possess 65 – 90% quantum efficiency for green light.

LCI and LNI films produced bright emissions measuring from 10,000-25,000 ph/MeV for gammas and 65,000-100,000 ph/neutron interaction. The GDI film provided 63,000 ph/MeV light output for gammas, and 5,000 ph/neutron.

3.2. Spatial Resolution

The spatial resolution for selected films was measured under x-ray exposure in terms of the pre-sampling MTF($f$) according to the technique described by Fujita et al., 1992. The films were coupled to a Photometrics CCD via a 3:1 fiber optic taper. A Gendex dental X-ray generator was used at a source-to-detector distance of 45 cm with 70 kVp X-rays and images were flat-field corrected to reduce noise. An image of a 10 µm wide slit made of 1.5 mm thick tantalum placed at a slight angle (< 4°) to the pixel matrix at the center of the detector was obtained. The area around the slit was covered with 0.5 cm thick lead. The slit was placed in contact with the surface of the imager so that the spreading of the Line Spread Function (LSF) due to the finite size of the focal spot did not pose a significant limitation. The Fourier Transform (FT) of the finely sampled LSF was performed to provide the presampling MTF.

Fig. 4 shows the MTF($f$) curves for a 180 µm thick LNI film and a 30 µm thick GDI film. The LNI film was deposited on a reflective white BeO substrate and coupled to a fiber optic faceplate. This configuration optimizes it for higher light output rather than spatial resolution, however it still shows 4 lp/mm spatial resolution at 10% MTF. The thinner GDI film was deposited on quartz and hermetically sealed. The actual MTF can be higher than what’s shown here because some of the spatial information in the scintillation light is lost during its propagation from the microcolumnar film to the detector due to the scattering nature of quartz substrate. This suggests that with improved sample preparation, the microcolumnar GdI$_3$:Ce is capable of superior MTF performance owing to its structured cross-section.

3.3. Gamma and Neutron Response

Previous work has shown excellent gamma and neutron response from polycrystalline and crystalline forms of LCI, LNI, and GDI materials (Nagarkar, 2013, Glodo, 2006). Here we report on gamma and neutron response in films of these materials. In the case of LCI and LNI, the key parameters are the decay times which make it possible for PSD, similar to what has been observed in CLYC crystals (Glodo, 2012). The GDI films, on the other hand, provide a very fast decay of 38 ns for both gammas and neutrons, and consequently do not provide the possibility of PSD, since the decay characteristics are the same for both. A summary of the properties of LCI/LNI crystals, along with those for CLYC are shown in Table 1. Both LCI and LNI compositions show comparable performance to CLYC in terms of light yields along with pulse shape discrimination capabilities, which make them ideally suited for neutron detectors in a wide range of applications.
The key parameter for effective PHD is Gamma Equivalent Energy (GEE), which was measured by exposing the specimens to a mixed neutron and gamma field from $^{137}$Cs and $^{252}$Cf sources. The position of neutron peak relative to the gamma peak yields GEE. GEE values for LCI and LNI are shown to be on par with or even exceeding those for CLYC. The LNI film in particular with a 4.1 MeV GEE value means that it is an excellent candidate for PHD.

Table 1. Measured properties of LCI and LNI scintillation crystals.

<table>
<thead>
<tr>
<th>Property</th>
<th>CLYC</th>
<th>LCI</th>
<th>LNI</th>
<th>GDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{em}$, nm</td>
<td>373</td>
<td>450</td>
<td>420</td>
<td>540</td>
</tr>
<tr>
<td>Light yield, photons per:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Neutron</td>
<td>73,000</td>
<td>57,400</td>
<td>102,500</td>
<td>5,000</td>
</tr>
<tr>
<td>1 MeV</td>
<td>22,000</td>
<td>19,800</td>
<td>25,100</td>
<td>63,000</td>
</tr>
<tr>
<td>GEE (MeV)</td>
<td>3.31</td>
<td>2.90</td>
<td>4.1</td>
<td>0.078</td>
</tr>
<tr>
<td>Decay times (ns), $\gamma$ and n</td>
<td>$\tau_\gamma = 1,50,1000$</td>
<td>$\tau_\gamma = 943$</td>
<td>$\tau_\gamma = 181,295,1530$</td>
<td>$\tau_\gamma = 38$</td>
</tr>
<tr>
<td>$\tau_n = 1000$</td>
<td>$\tau_n = 323$</td>
<td>$\tau_n = 207,486,1900$</td>
<td>$\tau_n = 38$</td>
<td></td>
</tr>
<tr>
<td>n-γ PSD/PHD</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

The LNI and LCI films were evaluated for their neutron detection properties under neutron excitation from $^{241}$Am/Be source. Standard NIM spectroscopy electronics were used to acquire data from the films which were coupled to a 3-inch Hamamatsu R6233-100 SBA photo tube. To verify the neutron detection capabilities, spectra were obtained with and without a Boron absorber placed in between the source and the detector. Fig. 5a and b show the spectra measured with a 180 µm LNI and a 270 µm LCI film. Fig. 5b also shows the neutron response for a 200 µm thick GDI film.

The gamma and neutron discrimination properties of the LNI/LCI films were measured by digitizing the waveforms and analysing them offline. Charge integration method was used to obtain the PSD ratios using both LNI and LCI. Pulse shape discrimination scatter plot measured for the LNI film is shown in Fig. 6, and as can be seen a good separation was achieved between the gamma-rays and the thermal neutrons.

3.4. Efficiency Tests Using PMT

Efficiency measurements were carried out at the CG1a beam line at HFIR using 4.1 Å neutrons. The standard for comparison was a 1” diameter tube filled with 10 bars of $^3$He. Efficiency of the $^3$He tube is close to 99% at 4.1Å. A 5 mm thick piece of borated
aluminum plate with a 1cm x 1cm aperture was used to define a count area on the 3He tube and scintillators. Counts were acquired for 100 seconds with the aperture open (signal) and covered with a 2 mm thick piece of borated aluminum plate (background). Measurements with the 3He tube used a standard commercial preamplifier PDT-20A whose output is fed directly into a counter. To measure the LNI scintillators the output from the Electron tube PMT was fed into the counter via an integrating amplifier and a discriminator. The 440 µm thick LNI demonstrated 64% efficiency, consistent with the expected value of ~70% for 4.1 Å neutrons, given the 0.53 Li mole fraction in the film.

3.5. Neutron Imaging Evaluations

The imaging performance of the LCI & LNI scintillator films was evaluated using a fiberoptic coupled EMCCD camera consisting of an Andor back-illuminated, thermoelectrically cooled, 1024x1024 pixel EMCCD with 13 µm pixels as a readout sensor coupled to the scintillator via a detachable 3:1 fiberoptic taper. With the taper in place, the detector has an effective pixel size of 39 µm. The camera has a 10 MHz readout and provides a data acquisition rate of 10-frames-per-second (fps) at full pixel resolution and more than 1000 fps with pixel binning. The EMCCD detector was used in imaging studies using phantoms at HFIR which supplied 4.1 Å cold neutrons, and the beam flux, after attenuation, was 10^7 n/cm²/sec for all the data reported below. Both LNI and LCI films performed well; here we describe results from LNI films which provided the highest efficiency, brightness, and therefore relatively best radiographic image quality.

Flood images were obtained under uniform illumination using the different scintillator materials for 30 secs at a gain setting of 0. The average counts (ADUs) and noise (σ) in the images was measured and the signal to noise ratio (SNR) was computed. Table 2 compares the SNR measured for the different films with the current state-of-the-art 6LiF/ZnS:Ag film. The average counts are adjusted to compensate for the emission wavelength dependent quantum efficiency of the detector. Although the low signal yield per neutron for LCI and LNI films is high, the signal measured in the images was lower, possibly due to the attenuation in the fiber optic window and light losses in the coupling. The images acquired with LNI films produced much less noise, and resulted in higher SNR values. This is indicative of the higher stopping power for neutrons in the LNI material.

Table 2. Average signal and noise measured in images from LCI and LNI films. The average counts are adjusted to compensate for the emission wavelength dependent quantum efficiency of the detector. The low signal counts is possibly due to the attenuation in the fiber optic window and light losses in the coupling.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LiFZnS</th>
<th>LCI (340 µm)</th>
<th>LNI (180 µm)</th>
<th>LNI (440 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Counts (ADUs)</td>
<td>3013.8</td>
<td>192</td>
<td>573</td>
<td>418</td>
</tr>
<tr>
<td>Noise (σ)</td>
<td>289.5</td>
<td>24.1</td>
<td>25.5</td>
<td>20.7</td>
</tr>
<tr>
<td>Signal-to-noise ratio (SNR)</td>
<td>10.4</td>
<td>8</td>
<td>22.5</td>
<td>20</td>
</tr>
</tbody>
</table>

As per the ASTM standard E 545-99, we used the beam purity indicator (BPI) phantom described in ASTM E2003 application note, and an image sensitivity indicator (SI) described in ASTM E2023 to determine the image quality. The phantoms were imaged for 15 sec at a gain set to 100. The BPI is a Teflon block with two lead disks, two boron nitride disks and two cadmium wires, shown in Fig. 7a. By comparing the densities of these regions in the acquired neutron radiograph, the relative contributions to the image from thermal neutrons (N), gamma-rays (γ) and scattered neutrons (S) can be estimated. The image is shown in Fig. 7b.

The SI is a stepped wedge of acrylic resin separated by aluminum shims of varying thicknesses and a base of methyl-methacrylate strips with holes drilled through (Fig. 7c). The image quality is determined by the smallest numbered visible aluminum shim (G) and the highest consecutively numbered hole (H) visible in the methyl-methacrylate strips. Although not evident from Fig. 7d due to limited display dynamic range, G equals 7 and H equals 3 for the 180 µm thick LNI sample. Thus, these images are classified to fall under Category-I radiographs, which is the highest Category as per the ASTM E 545 standard. Note that the low H number is likely due to the 4 Å neutrons strongly scattered by the plastic in the phantom.

To estimate the spatial resolution of the LNI film with neutrons, a Gd test phantom was used that consists of 30 line groups each with 4 periods ranging from 0.25 lp/mm to 25 lp/mm corresponding to periods of 4 mm down to 0.04 mm. Image of the phantom was acquired for 15 sec at a gain of 100. Fig. 8 shows the phantom image in the line-pair region from 4-11 lp/mm. A line profile taken through the image was used to estimate the resolution in lp/mm as shown in Fig. 8b. The 180 µm LNI film demonstrates a resolution of 11 lp/mm @ 10% contrast which is actually a higher spatial resolution than predicted from the previous MTF measurements acquired with X-rays (see Fig. 4). Note that the measurements were performed on two different detector systems and varying imaging conditions. The Gd test mask was also imaged using a 250 µm thick LiF/ZnS:Ag screen for comparison as shown in Fig. 8c under similar imaging conditions. The resolution measured was 12 lp/mm @ 10% contrast, slightly better than the LNI film.
Fig. 7. Schematic of the beam purity indicator phantom (a) and the corresponding image acquired with a 180 µm thick LNI specimen (b). A schematic of the sensitivity indicator phantom (c) used in ASTM standard E-545 for determining the image quality and the image of the phantom acquired with the same LNI film.

Fig. 8. Image of the Gd test object obtained using the (a) 180 µm thick LNI sample (c) 250 µm thick LiF/ZnS:Ag sample coupled to the EMCCD camera. The numbers marked in red indicate the lp/mm. Line profiles through the image are shown on the right for (b) 180 µm thick LNI sample demonstrating a resolution of 11 lp/mm at 10% modulation and (d) 250 µm thick LiF/ZnS:Ag sample demonstrating a resolution of 12 lp/mm at 10% modulation.
4. Conclusions

We have successfully developed films for neutron imaging from two new families of scintillators derived from the well-known CsI and NaI scintillators by the incorporating $^6$Li into their lattice. The LCI/LNI films deposited by the highly efficient HWE technique exhibited scintillation properties similar to crystalline counterparts, and have demonstrated the capability of PSD. Furthermore selected films were integrated into an EMCCD imaging system demonstrating excellent SNR and spatial resolution in thermal neutron imaging. Due to their high efficiency for stopping neutrons, they have an excellent potential in neutron detection and imaging applications.

In addition, we have fabricated GDI films using the HWE deposition technique. These films have demonstrated high light signal and very high cross-section for thermal neutrons with an ultra-fast 30 ns decay time.

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