Novel High Efficiency Microcolumnar LuI$_3$:Ce for Hard X-ray Imaging

Z Marton$^1$, Vivek V. Nagarkar$^1$, Stuart R. Miller$^1$, Charles Brecher$^1$, Harish B. Bhandari$^1$, Peter Kenesei$^2$, Stephen K. Ross$^2$, Jonathan D. Almer$^2$, and Bipin Singh$^1$

$^1$Radiation Monitoring Devices, Inc., Watertown, MA 02472, USA
$^2$X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

E-mail: ZMarton@rmdinc.com

Abstract. We have developed a structured scintillator using a vacuum deposition technique that is suitable for manufacturing large area scintillators in a microcolumnar form. While providing high absorption efficiency, it also allows great temporal and spatial resolution X-ray imaging. Microcolumnar films of extremely fast and bright cerium-doped lutetium iodide (LuI$_3$:Ce) scintillator were synthesized. It has high density (~5.6 g/cm$^3$), high effective atomic number (59.7), bright green emission (540 nm range, well matched to commercial optics and CCD sensors), light yield exceeding 115,000 ph/MeV, and rapid, afterglow-free decay (~28 ns). This new scintillator could resolve the 153 ns bunch structure of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Due to the fast, afterglow-free decay, and high efficiency of LuI$_3$:Ce, during the experiments performed at the 1-ID hard X-ray beamline at the APS, single 65 keV X-ray photons could be resolved with high signal-to-noise ratio and with temporal resolution better than 20 ns. In the future, it will enable a wide range of hard X-ray (20 keV to 100 keV) imaging and/or high frame-rate applications such as dynamic studies of the structural and electrochemical properties of batteries using microtomographic X-ray imaging, internal corrosion in fuel cells, and time-resolved muscle diffraction experiments.

1. Introduction

Recent developments in synchrotron radiation sources have generated an urgent need for high-performance X-ray detectors that offer sub-microsecond to millisecond temporal resolution [1]. The dramatic increase in the brightness of such sources, including ultra-high photon fluence, in conjunction with beam divergence approaching nanometers [2], have made it possible now to conduct experiments that have heretofore been impractical or impossible. However, exploitation of the capabilities of these new sources requires a complementary enhancement of detector performance for hard X-rays, up to 100 keV. This energy is needed to penetrate many state-of-the-art engineering materials such as titanium alloys, aluminum-lithium alloys, and steels, to analyze chemical dynamics in novel devices, batteries and energy storage concepts. Such X-rays are used to investigate labile biological materials as well that withstand higher energies better than the 8-12 keV of conventionally...
used X-rays. Most synchrotron X-ray imaging detectors are based on CCD optical detectors coupled to scintillating phosphor converter screens [3, 4]. The familiar difficulties of slow readout speed and limited imaging area with all such traditional detectors have been addressed by various manufacturers by combining modular designs based on large-area CCDs or scientific-grade CMOS (s-CMOS) sensors with parallel high-speed output architecture sensors bonded to fiberoptic tapers, making it possible to design high frame-rate detectors [5]. Unfortunately, however, CCD/CMOS-based area detectors currently in use have been designed for soft X-rays, and they function poorly when used with hard X-rays.

We developed a process synthesizing structured thin films of a particular interest, cerium-doped lutetium iodide (LuI$_3$:Ce), invented recently at RMD [6, 7, 8], which is well-suited for manufacturing large-area films needed for demanding hard X-ray imaging applications using vacuum deposition technology.

2. Material and method
LuI$_3$:Ce, offers high potential for hard X-ray imaging applications due to its excellent properties. It has one of the highest conversion efficiencies (115,000 photons/MeV), a rapid initial decay (28 ns), an emission in the visible range (540 nm) [7, 8] with virtually no afterglow and can be readily fabricated into microcolumnar films for high resolution imaging applications [9, 10].

We performed co-evaporation runs using separate sources for the host and activator. However, we found that better control of the stoichiometry could be achieved by using doped targets of the desired composition rather than separate targets for dopant and host and trying to balance the respective vapor pressures. This change also substantially simplified the deposition process. We used our hot-wall evaporation concept to synthesize the films. It consisted of a silica crucible placed in a cylinder of wrap-around tantalum heaters. The disc-shaped substrate was placed on the top of the crucible and heated throughout the deposition process by a high-power quartz lamp to 350°C - 500°C. The entire setup was mounted in a vacuum chamber with a typical pressure in the ~10$^{-6}$ Torr range.

3. Results
3.1. Morphology
Our samples were characterized in terms of their morphology using SEM microscopy. The columnarity is evident in Figure 1. The images clearly show the anticipated columnar nature of resulting films, which is crucial for channelling scintillation light to provide the desired high spatial resolution in spite of their thickness. As the data presented below attest, even our 1 mm thick films demonstrated high spatial resolution of 250 µm, confirming our initial premise that the columnar nature of LuI$_3$:Ce films will mitigate the traditional trade-off between spatial resolution and efficiency, which is crucial for hard X-ray imaging.

![Figure 1](Left) Microcolumnar LuI$_3$:Ce film showing the desired columnar structure. (Right) Side view of the same film showing tightly spaced, vertically oriented columns. This columnar structure is responsible to provide excellent spatial resolution in spite of its 1 mm thickness.

3.2 Scintillation properties
We measured afterglow on LuI$_3$:Ce and compared to our thallium-doped CsI standard. As Figure 2 shows, our novel scintillator film displays virtually no afterglow next to CsI:Tl. The X-ray excited emission spectra (Figure 2, inset) of the LuI$_3$:Ce films were measured using the Cu-target X-ray generator (8 keV Cu Kα line) available at RMD. For the required flux at the sample, the X-ray generator was operated at 40 kVp with 20 mA current. The resulting scintillation light was passed through a McPherson model 234/302-0.2m monochromator and detected using an RCA model C31034 photomultiplier tube (PMT).

The typical spectroscopic shape of the scintillation emission from LuI$_3$:Ce crystal was known from work on single crystals before this film program had even begun [6]. The emission, centred at about
540 nm, is broad, but contains at least two incompletely resolved but unquestionably separate components. Although the intensities of these components differ somewhat, the correspondence between their locations demonstrates that our vapor deposition approach allows film growth with stoichiometry similar to that of the crystal.

**Figure 2** Semi-log plot of the scintillation decay of LuI$_3$:Ce (with 5% Ce) and standard CsI:Tl on exposure to a 50 ns X-ray pulse. The measured intensity at ~3 ms after the X-ray exposure has been stopped dropped to ~10$^{-7}$ of the original value (when the X-rays were on). Thus, the afterglow in the LuI$_3$:Ce crystal is ~0.00001%, and is about two orders of magnitude lower than the standard CsI:Tl scintillator. In the inset, mission spectra for a representative LuI$_3$:Ce film under X-ray excitation. The corresponding data for a LuI$_3$ crystal [6] containing 5 mol% Ce confirms that the vapor deposition method can produce scintillation-grade LuI$_3$:Ce and that its emission properties may be adjusted by controlling growth conditions.

3.3 Spatial and temporal resolution

To obtain a quantitative measure of the spatial resolution of a 350 µm thick film, we calculated its modulation transfer function while exposing it to 70kVp X-ray. As it can be seen, this 350 µm thick LuI$_3$:Ce film has a resolution of 5 lp/mm (100 µm) with 10% modulation (Figure 3a). The screen certainly resolves higher line pairs, albeit with reduced contrast. It is important to note that the CCD camera used for these measurements has Nyquist limiting frequency of only 8.6 lp/mm corresponding to its 57 µm effective pixel size. Thus, one would expect to see even better resolution with a higher resolution camera.

The hard X-ray imaging and temporal resolution studies were performed at beamline I-ID of APS at Argonne National Laboratory. For imaging, we used an axially symmetric tungsten pin with flat top measuring ~100 µm in size. The pin was set in front of the scintillator and the images were acquired at strategically selected energies: 62 keV (just below the Lu K-edge); 65 keV (just above the edge); and 82 and 100 keV (considerably higher energies). These data are shown in the inset of Figure 3.

For temporal response measurements the film container was placed in the beam so that the X-rays would impinge on the LuI$_3$:Ce sample through the aluminum base and packaging, and the resulting light was measured on the opposite side by an APD. Two X-ray settings were used during these measurements, 82 keV and 65 keV. The APD output was coupled to a fast digital oscilloscope that stored the data. A representative oscilloscope trace is shown in Figure 3b, and, on an expanded scale, in the bottom image as well. The data shows two 65 keV APS pulses 153 ns apart, which correspond to the bunch structure of the APS. We have confirmed that each of these pulses is a signal from single photon interaction in the scintillator. These data demonstrate that the decay time of our scintillator is <20 ns.
Figure 3 Modulation Transfer Function (MTF) of a 350 µm thick LuI₃:Ce film (a). The inset shows that the 1 mm thick LuI₃:Ce scintillator was able to resolve the 100 µm tungsten pin target. Images taken at energies below and above the Lu K-edge show no difference, indicating efficient and short range absorption of the fluorescence photons. Oscilloscope trace (b) shows fast decay time <20 ns of the LuI₃:Ce film. The inset data show two 65 keV APS pulses 153 ns apart, which corresponds to the bunch structure of the APS. Each pulse is a single X-ray photon, demonstrating the sensitivity and brightness of the scintillator, which permits detection of a single event.

4. Conclusion

While a variety of X-ray detectors satisfy the resolution, efficiency, and large active area needs for imaging with low-energy X-rays (8 keV to 12 keV), none is suitable for the hard X-rays (20 keV to 100 keV) and/or for high frame rate applications that are critical for numerous time resolved studies. We developed a process utilizing hot-wall evaporation that allows us to grow structured cerium doped lutetium iodide (LuI₃:Ce) scintillator, that will extend the applicability of current CCD/CMOS detectors to hard X-ray energies and will facilitate new detector designs with advanced features being sought to support such new studies. Its superior stopping-power, microcolumnar structure, fast decay enhance its brightness, spatial resolution and potential for timing resolution studies at high X-ray energies, respectively, while the low afterglow significantly reduces the required data acquisition time.

Acknowledgements

We thank Dr. Steve K. Ross and Dr. Peter Kenesei and Dr. Jonathan D. Almer at Argonne National Laboratory for carrying out hard X-ray imaging experiments at the 1-ID beamline of APS as well as for valuable discussions. This work was supported in part by the US Department of Energy under Grant DE-SC0007549. Use of the APS was supported by the US Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-ENG-38. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

References

[1] 16th Pan-American Synchrotron Radiation Instrumentation Conference (SRI2010, Sept. 21-24, 2010), held at Argonne National Laboratory (Argonne, IL).
[2] National Synchrotron Light Source II (NSLS II), Brookhaven National Laboratory.
[3] Phillips WC, Stanton M., O’Mara D., Naday I. and Westbrook E. 1993 SPIE 1900
[4] Phillips WC, Stewart A, Stanton M, Naday I, Ingersoll C 2002 J. Synchrotron Rad. 9 36
[5] Nagarkar VV, Singh B, Guo L, Gore D, Irving TC 2007 Nuclear Instruments and Methods in Physics Research Section A 576(1) 38
[6] Shah KS, Glodo J, Klugerman M, Higgins W, Gupta T, Wong P, Moses WW, Derenzo SE, Weber MJ, and Dorenbos 2004 IEEE Trans. Nucl. Sci. 51(5) 2302
[7] Glodo J, Shah KS, Klugerman M, Wong P, Higgins B, and Dorenbos P 2005 Nuclear Instruments and Methods in Physics Research A 537 279
[8] Glodo J., van Loef, EVD., Higgins WH, and Shah KS 2008 IEEE Trans. Nucl. Sci. 55(3) 1496
[9] Rodnyi PA, Physical Processes in Inorganic Scintillators (CRC Press, 1997)
[10] Knoll GF, Radiation Detection and Measurement, Second Edition, (John Wiley & Sons, 1989)