High efficiency microcolumnar Lu₂O₃:Eu scintillator thin film for hard X-ray microtomography

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Abstract. We have developed microstructured Lu₂O₃:Eu scintillator films capable of providing spatial resolution on the order of micrometers for hard X-ray imaging. In addition to their extraordinary resolution, Lu₂O₃:Eu films simultaneously provide high absorption efficiency for 20 to 100 keV X-rays, and bright 610 nm emission, with intensity rivalling that of the brightest known scintillators. At present, high spatial resolution of such a magnitude is achieved using ultra-thin scintillators measuring only about 1 to 5 µm in thickness, which limits absorption efficiency to ~3% for 12 keV X-rays and less than 0.1% for 20 to 100 keV X-rays, resulting in excessive measurement time and exposure to the specimen. Lu₂O₃:Eu would significantly improve that (99.9% @12 keV and 30% @ 70 keV). Important properties and features of our Lu₂O₃:Eu scintillator material, fabricated by our electron-beam physical vapour deposition (EB-PVD) process, combines superior density of 9.5 g/cm³, microcolumnar structure emitting 48000 photons/MeV whose wavelength is an ideal match for the underlying CCD detector array. We grew thin films measuring 5–50µm in thickness as well as covering areas up to 5 x 5 cm² which can be a suitable basis for microtomography, digital radiography as well as CT and hard X-ray Micro-Tomography (XMT).

1. Introduction
Recently, the availability of synchrotron and microfocus X-ray sources to the scientific community has generated new developments in the field of CT on the micron scale, leading to a new generation of X-ray microtomography (XMT) instrumentation [1]. In essence, XMT inherits CT techniques pushed to their intrinsic limits in spatial resolution and contrast sensitivity, enabling ultra-precise X-ray attenuation measurements on tiny volumes. With the increasing computational power to manage and process the large data sets it produces [2], XMT is becoming an influential research technique.

Furthermore, commercial developments in detector arrays, parallel architecture computing and 3D visualization schemes have made XMT an attractive tool for researchers; newly possible studies include, for example, the microscopic investigation of wood and other plant structures [3], and even fossilized structures for paleobotany [4]. Likewise, XMT is having a profound effect on fields of high immediate importance, modelling complex systems such as the fluid exchange interactions that occur at the micron level within the 3D porous rock matrix, thereby enabling prediction of oil field extraction potential [5] and the behaviour of CO₂ injected into rock layers [6]. To be more specific, soft X-rays in the energy range of 8-20 keV are lacking the ability of penetrating many contemporary...
engineering materials, such as titanium alloys, aluminum-lithium alloys, and steels. Thus there is a high demand to use hard X-rays, with energies ranging from 35 keV to as high as 100 keV. On the other hand, current detectors have been designed for soft X-rays, and function very poorly with hard X-rays due to the nature of the scintillators used to convert the incident X-ray beam into visible photons. For example, a YAG:Ce scintillator commonly used in XMT detectors is only 5 µm thick so as to achieve the desired high spatial resolution. However, due to its ultra-thin nature, low density (4.6 g/cm$^3$), and low effective atomic number ($Z=29$), it stops only 5.2% of the X-rays at 12 keV, and only 0.3% at 70 keV. Furthermore, its low light yield (20 photons/keV) seriously limits image quality, unless data acquisition times are excessively long. It is apparent that these scintillators are clearly insufficient for hard XMT, providing poor image quality and requiring long acquisition times. In order to address these matters, a high-yield scintillator was synthesized with adequate stopping power for hard X-rays. It was fabricated as 9 µm thick microcolumnar-structured forms to achieve submicron resolution after incorporated into lens coupled systems for maximum absorption at high X-ray energies.

2. Material and Methods
Lu$_2$O$_3$:Eu has earlier been established as a scintillator [7]. It has the highest density among all known scintillators, very high X-ray absorption ($Z_{\text{eff}}=67.3$), high light yield of 48 photons/keV and a bright red emission (610 nm) that matches well to CCD sensitivity to yield high overall quantum efficiency. A structured film of this material will stop significantly more of the incident high- and low-energy X-rays than any scintillator now in use or under investigation, without sacrificing spatial resolution. It would improve the detection efficiency and would have a dramatic effect on XMT research.

Our approach for depositing films of the highly refractory ($T_m=2400^\circ$C) Lu$_2$O$_3$:Eu with the desired columnar morphology was electron-beam physical vapour deposition (EBPVD). The growths were carried out at ambient substrate temperature and in high vacuum of about 10$^{-6}$ Torr. Several different substrates were explored, including optically transparent silica, silicon, and low-Z graphite for reduced X-ray absorption.

3. Results
3.1. Morphology
The microstructure and the thickness of the films were examined using scanning electron microscopy (SEM). A variety of substrates and thicknesses were probed. The most columnar-like microstructure was accomplished on abraded silica substrates. The microscopic irregularity of this surface provides an abundance of nucleation sites for growth in the normal direction, which is a critical condition to grow microcolumnar structures [8]. This is illustrated in figure 1a.

![Figure 1](image-url)

Figure 1. SEM micrograph of a 9 µm thick microcolumnar Lu$_2$O$_3$:Eu film grown on highly abraded silica substrate (a), as well as the thickest film grown measuring 55 µm (b).

The thickest and brightest layer that we have successfully grown so far was 55 µm (figure 1b) and took 8 hours to grow. Although the bottom “seed layer” of about 5 µm appears to have started as
columnar, most of the interior of the deposited material does not display such well-defined structure. But the textured nature of the outer surface suggests that some degree of directionality may persist throughout the entire thickness. So far, the thickest columnar sample we were able to grow is 9 µm in thickness. In order to grow highly ordered columnar film with such a thickness needs further experimentation as follows: the growth of columnar microstructure can be promoted through off-axis setup (the incoming plume of the evaporated substance is not perpendicular to the substrate surface) and also the substrate temperature and degree of crystallinity have a big impact on the thin film growth mode and can be used to engineer the growth process. Also the growth speed is a factor one has to take into account. Slower growth rate helps form columnar structure as well.

3.2. Scintillation properties
We characterized the spectral distribution and decay properties of the emitted light. The results (figure 2a) demonstrate that the synthesized doped oxide coating scintillates just like its transparent optical ceramic (TOC) counterpart and it effectively utilizes the spectral sensitivity of the CCD arrays.

![Figure 2](image-url)

**Figure 2.** (a) Radioluminescence of Lu$_2$O$_3$:Eu film, whose spectral structure is indistinguishable from that of the transparent optical ceramic, not shown here. (The resolution of the monochromator is no better than 20 nm, and consequently unable to fully resolve the fine structure.) The relative quantum efficiency of a typical inline CCD (dashed line, right axis) is more than 60% at the main emission wavelength of 610 nm. A photograph of the bright red scintillating film under UV excitation is included in the inset. The temporal decay of this light, shown in (b), is by nature fairly slow (an f-f transition), with the slight differences in shape from that of the ceramic (somewhat faster initially, but more persistent later, as shown in the inset) clearly attributable to a greater abundance of lattice defects, which act both to quench the prompt emission and to enhance the delayed afterglow.

The decay measurement was conducted by irradiating the specimens with a pulsed X-ray beam with energy adjustable from 40 kVp to 160 kVp. The duration of the X-ray excitation was varied from 0.1 to 1 second to quantify the decay performance under the exposures expected during imaging using synchrotron sources. These decay measurements revealed a small but consistent difference between film and ceramic (figure 2b, inset), with the film decay being slightly faster initially but slower at later times. This can be due to more severe and abundant defects present in the film, which can provide sites for non-radiative quenching of the emitting (Eu$^{3+}$) ion along with others that can serve as traps for the electron-hole excitation carriers to give rise to afterglow.

3.3. Spatial resolution and X-ray imaging
A line-pair phantom with frequencies from 15 to 20 lp/mm was used to reconstruct the contrast transfer function (CTF) in order to quantify spatial resolution. From these results (presented in figure 3a) it is clearly evident that 20 line-pairs can be resolved with 10% modulation, which corresponds to a spatial resolution of 25 µm. As the inset of figure 3a depicts, a Lu$_2$O$_3$:Eu TOC and a
single crystalline YAG:Ce of comparable thicknesses (200 µm and 250 µm, respectively, synthesized in-house) have very similar spatial resolution of 9 lp/mm at 10% contrast. However, the radiation detection index of Lu$_2$O$_3$:Eu, scaling with $\rho Z_{eff}^4$, is superior to that of a doped YAG crystal by a factor of 60, which means a considerable drop of data acquisition time.

We also performed two tests that involved imaging of real objects. In the first, an IC chip with 25 µm bond wires was imaged using the same in-house facilities. The clarity and sharpness of the image of these wires is clearly evident in figure 3b. For these images, we used a Photometrics XR-250 camera with 57 µm effective pixel size. The X-rays were from a Gendex dental X-ray source operating with a 300 µm focal spot and 70 kVp with 10 mA, as well as 2 seconds exposure settings.

Figure 3. (a) Contrast transfer function (CTF) calculated from a line profile on a line-pair phantom pictured above the graph. It clearly shows superior spatial resolution of about 20 lp/mm produced by a 7 µm thick film. The inset shows the comparison of CTFs coming from a 250 µm thick single crystal YAG:Ce and a 200 µm Lu$_2$O$_3$:Eu TOC. The same kind of performance is demonstrated by in-house imaging of an (b) IC chip (25µm wires) and a (c) synchrotron-based image of a 30µm-pitch micro-mesh taken at Argonne National Laboratory. The inset shows the zoomed image proving the resolution. (a) and (b) images were taken by a Photometrics XR-250 CCD camera (57 µm pixel size) and a Gendex dental X-ray source (300 µm focal spot, 70 kVp, 10 mA) while (c) was generated by 52 keV synchrotron beam and recorded with a 4008x2672 pixel Cooke PCO 4000 CCD camera (7.4 µm pixel size).

Another test on these scintillators was conducted at the Advanced Photon Source (APS) hard X-ray beam line 1-ID-C at Argonne National Laboratory. An image of a micro-mesh resolution target with gold “wires” 20 µm deep and 5 µm wide on a 30 µm pitch was acquired using a 9 µm thick Lu$_2$O$_3$:Eu film. The incident energy was 52 keV. The image was magnified through a 7.5x Mitutoyo objective and relayed onto a 4008x2672 pixel CCD camera (Cooke PCO 4000). Since the CCD pixel size was 7.4 µm, the resulting image resolution was 1 µm. The measured depth of focus was found to be 6 µm. As seen in figure 3c and the inset, the Lu$_2$O$_3$:Eu scintillator film was able to fully resolve the structure of this 5 µm mesh.

4. Conclusion
In this paper, we report on the synthesis and testing of thin Lu$_2$O$_3$:Eu films for the purposes of XMT measurements. Such films have four distinct advantages: they have high effective atomic number; they are non-hygrosopic; they have a bright red emission; and they can be formed with a microcolumnar structure providing high spatial resolution. We have developed a process, based on electron-beam physical vapour deposition (EBPVD), by which polycrystalline microcolumnar layers can be grown on a wide variety of substrates. We have characterized these films and demonstrated their superior...
performance capabilities. And, finally, we have confirmed their suitability to XMT applications and their potential for reducing data acquisition time.

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