Concentration quenching of photoluminescence in optically transparent Lu$_2$O$_3$:Eu thin films deposited to be used as scintillators

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Abstract
Photoluminescent thin films of europium doped lutetium oxide (Lu$_2$O$_3$:Eu) – an established material for x-ray scintillators – have been grown on glass substrates employing radio-frequency magnetron sputtering deposition technique. Optically transparent, crystalline films were obtained by only controlling the deposition process parameters. Neither any pre-treatment on glass substrate nor any post-deposition treatment on the films was applied. To our knowledge, depositing transparent but crystalline films of Lu$_2$O$_3$:Eu on glass substrates in such a direct way is an achievement that is reported for the first time in the literature. Using separate sputtering targets for the matrix constituent (Lu$_2$O$_3$) and the dopant enabled us to control the doping level of europium atoms in the films. By varying the magnetron power applied to the Eu$_2$O$_3$ target, we produced a series of Lu$_2$O$_3$:Eu thin films with different Eu concentrations. Significant quenching of luminescence by concentration was observed in the films. Detailed chemical and microstructural analyses revealed that europium atoms segregated from the matrix at high concentrations, an important contributor to concentration quenching. Some remarks have been given on finding the europium concentration that will give best scintillator performance.

1. Introduction
Scintillators are instruments that are used to convert the incident beams of electromagnetic radiation (x-rays, γ-rays, etc) with very short wavelengths or energetic particles into visible photons. In medical imaging, they are mostly used for turning x-rays into visible light, which is then imaged by sensitive CCD/CMOS cameras.

Lu$_2$O$_3$:Eu is a proven scintillator material. It yields a light output comparable to CsI:Tl, a widely used scintillator material [1]. It has the highest density among all known scintillator materials, very high x-ray absorption (Zeff = 67.3) cross-section, high light yield of 48 photons/keV [2], and a bright red emission (at around 611 nm) for which CCD/CMOS sensors have high sensitivity. A final important feature of Lu$_2$O$_3$ is that it does not have absorption edges in the energy region of typical medical x-rays (20–60 keV). This feature is mandatory to obtain high-quality images [3].

Lu$_2$O$_3$:Eu is a highly refractory material (melting point > 2400°C). Therefore, the first scintillators from Lu$_2$O$_3$:Eu were produced by sintering its powders. The whole process was quite complex as it involved first synthesis of Lu$_2$O$_3$:Eu powders, and then sintering those powders to obtain flat scintillating screens. 16 cm × 16 cm wide scintillator screens were produced with this technique [4].

However, those screens prepared from sintered lanthanide oxide powders were not optically transparent due to light diffusion by ceramic grains, which also reduce spatial resolution of imaging. This made it necessary to apply hot pressing in order to make the material transparent. Yet, hot pressing is not appropriate for producing a material whose planar dimensions are in centimeters while its thickness is in the sub-millimeter range. Cutting and subsequent polishing could lead to discarding 90% of the original material, which is economically unfeasible.
In this study, we used radio frequency magnetron sputtering for deposition of Lu2O3 and doping with Eu. Thin film deposition techniques were tried by several research groups [2, 5, 6] as well as the same people [7] who introduced sintered Lu2O3:Eu scintillators for the first time.

Physical vapor deposition (PVD) approach, which was already being used for commercial production of micro-columnar films of conventional scintillator materials, was tried for Lu2O3:Eu, too. PVD processes involve the physical vaporization of material from a bulk source of the same chemical composition as the desired film. The high melting point of Lu2O3 makes it extremely difficult to achieve vaporization by conventional thermal means. Therefore, vaporization of this refractory oxide by physical means requires application of focused high power (from an electron beam, laser beam, or plasma) onto the target’s surface.

In this study, we explored the possibility of growing high-quality Lu2O3:Eu thin films on glass substrates using RF (radio frequency)-sputtering technique. Having the scintillator material on glass enables introducing optical lenses between the scintillator and the camera. This, in turn, makes it possible to use smaller camera sensors to grab the photons emitted from the scintillator. A camera sensor that is larger than 5 cm × 5 cm is outrageously costly. Using more than one camera sensors side-by-side for a single scintillator brings its own costs and complications. Focusing the light emitted by the scintillator onto a camera sensor is the most promising way to develop wide-area x-ray imaging systems. Yet, the cost and complication -this time- comes from the transparent substrate on which scintillator film is to be grown. Those transparent substrates are single-crystal sapphire [8] or yttria, both of which is very expensive when it is many centimeters wide.

High-lead glasses would be the ultimate substrate for a scintillator film in terms of availability, cost, and potency to absorb x-rays which may escape from the film scintillator but it isn’t easy to obtain high quality Lu2O3 films on glasses. This is because the amorphous nature of glass makes it very difficult to grow crystalline films on it. This fact, combined with the refractory nature of the film’s material, makes it unlikely to obtain a crystalline Lu2O3:Eu film on glass substrates. As far as we found in the literature, this was succeeded only on highly abraded glass [2]. Abrasion yields an abundance of nucleation sites on the glass surface, which helps to grow micro-columnar structures in the normal direction. Yet, it also diminishes the optical transparency of the glass substrate, which is totally undesirable for our specific application.

High-lead glass substrates also do not permit high temperatures neither during nor after the deposition of the films because of their high susceptibility to thermal shocks. Therefore, the deposited film should have high luminescence efficiency in as-deposited form. We tried and succeeded to grow crystalline Lu2O3:Eu films with high luminescence efficiency on glass by RF-sputtering technique.

We also explored the concentration dependence of luminescence efficiency of Eu ions inside Lu2O3.

2. Materials and methods

In this study, we used radio frequency magnetron sputtering for deposition of Lu2O3 and doping with Eu. The coating process was carried out using two target materials, Lu2O3 and Eu2O3. Coatings with different Eu contents were produced by applying 75 W to the Lu2O3 target and 10 W, 25 W, 30 W, 35 W, and 50 W to the Eu2O3 target during the coating processes.

The substrates were ultrasonically cleaned by using acetone and isopropyl alcohol prior to the deposition process. The cleaned samples were loaded into the deposition chamber, which was then pumped down to 5 × 10⁻⁶ Torr base pressure in order to have a clean deposition environment. Deposition of Lu2O3:Eu coatings were performed by using high purity (99.95%) Lu2O3 and Eu2O3 cylindrical targets (3 inches in diameter). As the target materials are ceramics, extreme care was exerted not to cause breaking or cracking. A small power of 20 W was applied to the magnetrons initially to form the plasma. This power was then increased by 10 W in every 5 min until the desired value. Since the coating speed was very low (0.3 μm h⁻¹) all coating processes were carried out for 5 h.

Morphology of the coatings was examined using a Zeiss - Sigma 300 model scanning electron microscope (SEM). Chemical compositions of the films were investigated using an EDAX Element model, energy-dispersed x-ray (EDX) spectrometer attached to this SEM device.

To examine the crystallinity of the coatings, their x-ray diffraction (XRD) data were acquired using a Panalytical Empyrean model XRD device utilizing 0.154 nm Cu-Kα radiation. In order to minimize the effects that may come from the glass substrate, the coatings were examined in grazing incidence geometry with an x-ray entrance angle of 1°. The step size of the scans was set to 0.1°.

The PL characteristics of Lu2O3:Eu thin films were evaluated using a MAPLE II- Low Temp Macro Photo-Luminescence system from Dongwoo Optron, (S. Korea). Maple-II is a monochromator-based system that employs a photo-multiplier tube as its sensor and microscope lenses with different magnifications to focus the
beam onto the sample. Photoluminescence measurements were made with a 325 nm excitation wavelength at 300 K temperature. Samples were kept under vacuum to minimize optical noise. The signal-to-noise ratio of the measurements was further increased by making phase-locked measurements at 70 Hz.

SPECS FlexPS brand x-ray photoelectron spectroscopy (XPS) system was used to examine the binding status of Eu atoms inside the coatings. This system includes a hemispherical analyzer with a 150 mm diameter and an electron lens analyzer with a 200-channel detector for high precision XPS analysis. Quasi-monochromatic Al Kα radiation (1486.71 eV) was used for analysis. Whole-spectrum analyses were made at 1 eV energy resolution, while high-resolution XPS spectra for individual peaks were recorded with 0.1 eV energy resolution.

3. Results

All Lu₂O₃:Eu films were produced as transparent thin films by using the RF-sputtering technique, as shown in figure 1. This high transparency increases the chance of the films to be scintillator candidates because it enables most of the photons to be released from Eu ions to exit the film without being absorbed inside.

3.1. Chemical composition of films

The chemical composition of the produced coatings was analyzed using the EDX detector, attached to our SEM. An acceleration voltage of 15 KeV was applied during these analyses. Lα peaks of Lu and Eu were used to obtain the elemental results. Almost an exponential increase of Eu molar concentration was recorded after 25 W of magnetron power applied to the Eu₂O₃ target as given in table 1.

3.2. Photoluminescence measurements

The schematic energy level diagram of Eu ions is given in figure 2. Electrons excited to ⁵D levels can transit to ⁷F energy levels by emission of photons. ⁵D₀ → ⁷F₂ transition is typically more dominant than the others. The energy of this transition corresponds to emission of red light at around 611 nm [⁹, ¹⁰].

Figure 3 shows the PL spectra of our Lu₂O₃:Eu thin films, excited by a laser source with a wavelength of 325 nm. These spectra are caused by the transitions of ⁵D₀ → ⁷F₉(J = 0,1,2,4) of europium ions inside our samples at 300 K. The sharp peak seen on every spectrum at 650 nm is an overtone of the excitation wavelength. Two samples with intermediate Eu concentrations of 4.8% and 10.5% exhibited strong luminescence. Broad but small peaks were observed for the transitions of ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ at around 592 nm and 709 nm,

![Figure 1](image_url)

**Figure 1.** Glass substrates coated with Lu₂O₃ films containing 0.6%, 1.0%, 4.8%, and 27% Eu from left to right. The picture showing the transparency of the Lu₂O₃:Eu coatings. The transparency of the coated glass sample is clearly demonstrated by the high visibility of the text below the sample.
respectively. The intense red luminescence at a wavelength of 615 nm originates from the $^5D_0 \rightarrow ^7F_2$ transition, and the last peak centered at 626 nm comes from the $^5D_0 \rightarrow ^7F_2$ transition.

When these two films are compared among themselves, it is striking that their luminescence intensities are close to each other despite the vast difference in their Eu-content. The photoluminescence intensity is proportional to the product of the number of excited Eu ions and the quantum efficiency of the radiative transition. The fact that PL is approximately constant while the Eu concentration is more than doubled indicates that the quantum efficiency of the luminescence decreases at about the same rate. It is well-known that rare-earth ions’ luminescence efficiency drops as their concentration inside a matrix material increases after a threshold value which is reported to be less than 1% for europium atoms inside Lu$_2$O$_3$ matrix [11]. This drop in
quantum efficiency is known as ‘concentration quenching’. Concentration quenching happens due to non-
radiative energy transfer processes between active ions; Eu ions in this case. It is observed in all rare-earth-doped
(or transition-metal-doped) solid, optical gain media such as laser crystals or glasses. Here in our study, it
manifests itself more explicitly in the film with the highest Eu content. Sample-5 with 27.4% Eu concentration,
exhibits only one very small emission band around 615 nm, which is much weaker than Sample — 3 and
Sample-4.

The highest integrated PL intensity was obtained when dopant (Eu) molar concentration was 4.8%. This was
not surprising since a previous study, in which Eu concentration was varied with much smaller steps inside
Lu2O3 powders, demonstrated that maximum PL was obtained when Eu concentration was 5% [12]. 4.8% is
very close to that maximum. However, the photoluminescence intensity of Sample-4 with 10.5% europium was
not much lower. This shows that there is quite a wide range of Eu concentration that gives a sufficient PL
intensity.

3.3. Film morphology
SEM images revealed that the produced coatings have columnar growth with a striking change as Eu content
increases. The film with the lowest Eu content has quite a smooth surface. However, doping with Eu has induced
a granularity with void spaces in between the columns. This is seen as a rough surface when observed from
above, as in figure 4.

Cross-sectional images of the films which show the highest photoluminescence are given in figure 5. Dense
columnar growth is very dominant in these films. The average column width is within 70–80 nm.
This observed columnar microstructure is the most suitable structure for thin film scintillators since
individual needles guide the light that is created upon the absorption of energetic particles. This, in turn,
provides a better spatial resolution of particle detection. Micro-columnar films of Cs:ETI provides submicron
imaging resolution without the need for pixelation [13].

3.4. X-ray diffraction analyses
Figure 6 depicts the XRD data obtained in a grazing incidence scheme. Strong and sharp diffraction peaks, seen
in the low angle part of these graphs indicate that the deposited film is well crystallized. The angular (2θ) positions of the diffraction peaks of the coatings are in agreement with the cubic Lu2O3 structure (JCPDS card no: 043-1021).

One noticeable difference between the JCPDS card is the absence of Lu2O3’s strongest diffraction peak from
(222) planes. However, such discrepancy is common in GI-XRD data since the Bragg condition is rarely satisfied
in grazing incidence geometry for all planes found in JCPDS cards which are all obtained from or calculated for
powder samples. If the film has grown in a highly preferred orientation, the peak intensities may change even
with the lateral orientation of the substrates since this changes the orientation of atomic planes inside the film
with respect to the incident x-rays. This is yet another reason why the intensity ratios of peaks in JCPDS cards are
not preserved in GI-XRD data of thin films. A similar phenomenon was also reported for Lu2O3 films grown on
Si(100) surface in another report [14] where the intensity of (222) planes was much smaller than those of (400)
planes, though it is the other way around in the relevant ICDS card. In our data, lutecia’s (222) planes, whose
vector lie along the body-diagonal of the lattice’s unit cell do not show up. Nevertheless, the strong (400) XRD
peak of Lu2O3 in all the films shows that films are crystalline to a high degree. On the other hand, diminishing of
peaks around 50 and 60 after 4.8%-Eu-doped Lu2O3 manifests some partial amorphization with the increasing
Eu concentration.

In sputter deposition, growing a crystalline film of a refractory, ionic material on glass at ambient
temperature can be succeeded only when the deposition rate is low. For such materials, room temperature PVD
deposition, combined with high deposition rates, produces coatings with very poor crystallinity. This is why we
set the magnetron powers to 1/4 of available power in our system and set the deposition pressure to 10 mTorr.

Indeed, when we had set the process pressure to 20 mTorr in the initial runs, we obtained amorphous films
whose XRD patterns exhibited no peak at all. This is natural since the sputtering system’s total pressure is one of
the most critical parameters that define the deposition rate in sputtering-based PVD. Raising the total pressure
increases the number of ions available for sputtering and enhances the rate of material ejection from the target;
thus, the deposition rate.

(400) peak’s shift to lower 2θ from 34.8 to 33.2 as europium content increases from 1.0 atomic% to 27.4% is
a direct outcome of europium atoms’ causing stress inside the Lu2O3 matrix. Lu2O3 and Eu2O3 have very similar
XRD diffraction data since they crystallize in the same cubic structure with very close inter-planar separations.
Lutetium oxide’s(400) diffraction peak is at 2θ = 34.95, while europium oxide’s same peak is at 2θ = 32.9.
Europium atoms’ causing stress reveals that they are dispersed inside the lutetium oxide matrix. However, (400)
peak of Eu2O3 has also manifested itself in Sample 5, which has the highest Eu concentration. It is apparent that
Eu$_2$O$_3$ has segregated from the Lu$_2$O$_3$ matrix at this high concentration. Such segregation aggravates concentration quenching and may explain why photoluminescence of Lu$_2$O$_3$:27.4%Eu is so low.

3.5. XPS investigation results

X-ray photoelectron spectroscopy (XPS) of samples was also investigated to obtain information on the dispersion of Eu atoms inside the lutetium oxide matrix. XPS is a surface-sensitive spectroscopic technique based on the detection of photoelectrons emitted from a sample due to irradiation of the sample by (quasi) monochromatic x-ray photons. Material properties are deduced from the measurement of the kinetic energy and the number of the ejected electrons. It is a quantitative technique for measuring the elemental composition of the surface of a material, and it also determines the binding states of the elements. XPS not only shows what elements are present but also to what other elements they are bonded.

We carried out XPS analyses to probe the chemical state of Eu atoms inside the films. Eu atoms exhibit stronger XPS peaks from their 4d electronic levels. But, the 4d$_{3/2}$ and 4d$_{5/2}$ doublet peaks are overlapped, making analyses of chemical shift very difficult. Therefore the atom’s 3d$_{3/2}$ peak was selected for chemical shift analyses. This peak is about 10 eV separated from its doublet twin, 3d$_{5/2}$. Thus, shifts due to chemical bonding can be clearly observed from its position in the energy scale. It is centered at 1126 eV for elemental Eu and at 1135 eV for Eu$^{3+}$ ions, bound to oxygen atoms in Eu$_2$O$_3$ [14].

Our films—as depicted in figure 7—exhibited the 3d$_{5/2}$ peak at 1135.1 ± 0.2 eV peak with an accompanying one at around 1126.2 eV. This small XPS peak does not automatically indicate the existence of unbound
Europium atoms though its position is very close to that of elemental Eu. This peak is typical to almost all Lu₂O₃:Eu films which we have seen in the literature [6, 15, 16] and originates from doubly ionized Eu atoms, (Eu²⁺) [16, 17]. It is apparent that not all europium atoms are triply ionized during thin film deposition. Also, the intensity ratio of 1126 eV/1135 eV peaks decreases with increasing Eu concentration. Therefore, it cannot point out to clustering of Eu atoms inside the Lu₂O₃ matrix. Since this Eu²⁺ peak is almost in the same position as that of elemental Eu, it is impossible to distinguish the two and comment beyond that. Indeed, our aim was to

Figure 5. SEM cross-sections of films with 4.8% (a) and 10.5% (b) atomic Eu concentration.

Figure 6. Stacked GI-XRD scans of Lu₂O₃:Eu films with different Eu contents which are given as insets on the individual diffraction curves.
observe whether there was a shift in the 3d_{5/2} peak. Such a shift was not seen up to a concentration of 10.5%. In the sample with the highest concentration, a small, downward shift of 0.3 eV was observed indicating the change in europium atoms’ environment as the Eu/Lu ratio increases.

4. Conclusions

In this paper, we report on the synthesis and characterization of thin Lu₂O₃:Eu films with different Eu-doping levels with a particular focus on photoluminescence quenching of europium ions’ light emission.

We have developed a PVD process based on the co-sputtering of Lu₂O₃ and Eu₂O₃ from different targets. Optically transparent Lu₂O₃:Eu thin films were successfully coated on glass substrates using the RF-sputtering technique. This study was presented to the literature as the first study in which Eu concentration in the final coating was varied by using separate Lu₂O₃ and Eu₂O₃ targets and by changing the power applied to the Eu₂O₃ target.

Introducing the dopant rare-earth ions from a separate target is particularly important as it allows to control their concentration in the film matrix. Because, as also shown in this study, when the concentration of luminescent rare earth elements in the matrix reaches a certain level, their luminescence decreases. An optimum concentration value has to be found. That would be very costly if Eu₂O₃-doped Lu₂O₃ targets with different Eu concentrations were used.

Slow deposition at low magnetron powers and low process pressure made it possible to obtain crystalline films on glass substrates at room temperature without heat treatment or any other post-deposition processing.

The deposited films, which had an Eu concentration of 4.8% and 10.5%, had features that made them good candidates for next-generation scintillators. As sufficient PL intensity can be obtained from a relatively wide concentration range, other parameters -such as the width of micro-columns which affect the spatial resolution may determine the films’ overall performance as a scintillator.

PL intensity at 27.4% Eu was very low as a result of concentration quenching. XPS analyses showed only a small shift of binding energy of Eu atoms, but the XRD spectrum exhibited a noticeable angular shift to Eu₂O₃’s 2θ positions in this sample. The emergence of (400) peak of Eu₂O₃ in this film points to segregation of europium from the Lu₂O₃ matrix. Such segregation enhances concentration quenching and may explain the sharp drop in luminescence level observed in the sample.

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Conflicts of Interest

Authors have no competing interests to declare.

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