Epitaxial growth of LuAG:Ce and LuAG:Ce,Pr films and their scintillation properties

Paul-Antoine Douissard, Thierry Martin, Federica Riva, Yurii Zorenko, Tetiana Zorenko, Kazimierz Paprocki, Alexander Fedorov, Pawel Bilski, Anna Twardak

Abstract—We performed the growth by Liquid Phase Epitaxy (LPE) of Ce and Ce-Pr doped Lu$_2$Al$_5$O$_{12}$ (LuAG) Single Crystalline Films (SCFs) onto LuAG and Y$_2$Al$_5$O$_{12}$ (YAG) substrates. The structural properties of LuAG:Ce and LuAG:Ce,Pr SCFs were examined by X-ray diffraction. The optical properties of the SCFs were studied through cathodoluminescence (CL) spectra, scintillation Light Yield (LY), decay kinetic under $\alpha$-particle (Pu$^{239}$) excitation, X-ray excited luminescence, thermostimulated luminescence (TSL) and afterglow measurements. The SCFs grown on LuAG substrates displayed good surface quality and structural perfection, whereas the SCFs grown on YAG substrates showed a rough surface and poorer crystalline quality, due to a large lattice mismatch between the film and the substrate (0.82\%). Under $\alpha$-particle excitation, the LY of LuAG:Ce SCF exceeded by 2 times that of the best YAG:Ce SCF sample used as reference. Under X-ray excitation, the LuAG:Ce SCF with optimized Ce concentration showed LY close (77\%) to a reference YAG:Ce Single Crystal (SC) scintillator. The afterglow of LuAG:Ce and LuAG:Ce,Pr SCFs was lower (by 1 decade) than that of the tested reference LuAG:Ce SC. However there is not a complete suppression of the afterglow at room temperature (RT), despite the fact that the SCFs present much lower concentration of antisite and vacancy type defects than their SC counterparts. This can be explained by the presence in the films of other trap centers responsible for TSL above RT.

Index Terms—Single Crystal Films, garnet, Liquid Phase Epitaxy, scintillator, X-ray imaging detector, microtomography, lattice mismatch, energy transfer, afterglow.

I. INTRODUCTION

Scintillating screens based on single crystalline films of different oxide compounds are key-components of high-resolution 2D X-ray detectors used at synchrotron facilities for X-ray micro-imaging applications [1-3]. Lu$_2$Al$_5$O$_{12}$ is a good SCF material candidate [4] to complement the currently used Gd$_3$Ga$_5$O$_{12}$:Eu (GGG:Eu), GGG:Tb and Lu$_2$SiO$_{5}$:Tb (LSO:Tb) SCFs [1-3] or thinned LuAG:Ce bulk SCs [5]. At the same time, bulk LuAG:Ce SCs suffer generally from high level of afterglow [6], due to the presence of vacancy and antisite defects, inherent to the solidification process at high temperature [7-9]. The idea that this effect could be strongly reduced in LuAG:Ce films grown by LPE at lower temperatures (\textasciitilde 900 °C–1000 °C) motivated our research. Comparative investigation of the afterglow in LuAG:Ce SCF and SC is not yet reported in literature.

The first LPE growth of LuAG:Ce SCFs onto YAG substrates was realized in 1999 [9]. Later growth of LuAG:Ce SCFs was accomplished several times with either PbO, BaO, or MoO based solvent onto YAG and LuAG substrates [10-19]. Growth of LuAG:Pr SCFs and their application for micro-imaging is considered in [4] but the growth of double Ce,Pr doped LuAG:Ce,Pr SCFs as scintillation screens was never considered yet. Such a SCF scintillator, simultaneously emitting in two emission bands, i.e. UV and visible, could improve the conversion efficiency.

In our study the PbO-B$_2$O$_3$ solvent was used due to its low viscosity, to ensure the best structural and surface quality of the films, which is important for high-resolution X-ray imaging.

II. METHODS

A. Film growth

LuAG:Ce and LuAG:Ce,Pr SCFs were grown by the standard dipping LPE method from supercooled melt-solution based on the PbO+B$_2$O$_3$ solvent [20-22]. Undoped YAG plates with (111) orientation and undoped LuAG plates with (100) orientation served as substrate for the LPE growth. The layers were grown in the temperature range 1040-1090 °C with growth rates comprised between 0.2 and 2 \( \mu \)m/min. The thickness of the epi-layers ranged from 5 \( \mu \)m to 80 \( \mu \)m (Fig. 1).

The CeO$_2$ concentration in the melt-solution was varied in the 5-10 mol. \% range. At 10 mol. \% CeO$_2$ content, Pr$_2$O$_3$ was added in the melt-solution and its concentration varied in the 1.5-3 mol. \% range. The content of films was measured by microprobe analysis and the segregation coefficients of Ce and Pr ions in LuAG SCFs were found to be equal to 0.008 and 0.14, respectively.
B. Structural characterization

Measurements of the lattice constant, SCF/substrate mismatch and structural quality of the LuAG SCFs grown onto LuAG and YAG substrates were performed using X-ray diffraction (spectrometer DRON 4, CuKα X-ray source). Rocking curve measurements were performed to estimate the structural quality of SCFs grown on YAG and LuAG substrates.

In the case of LuAG:Ce SCFs grown on undoped LuAG substrates, this X-ray diffractometer could not resolve the two diffraction peaks of the layer and the substrate, due to very close lattice mismatch. In this case, high resolution diffraction was performed at the ESRF on the BM05 beamline. The beam energy was set to 15 keV (ΔE/E~10^{-4}) through a Si 111 monochromator and 20 % detuning was applied in order to reject high order harmonics. A Si-PIN diode was used to register the diffraction signal.

C. Optical and Luminescence properties

For LY measurements of Ce and Ce-Pr doped LuAG SCF screens, both alpha-particles and X-ray excitations were used.

The scintillation LY of LuAG:Ce and LuAG:Ce, Pr SCFs was measured under excitation by α-particles from a Pu^{239} source (5.15 MeV) using a setup based on a Hamamatsu H6521 photomultiplier and multi-channel analyzer working with a 12 µs shaping time. All the measurements were compared to a standard YAG:Ce SCF sample with LY of 360 phls/MeV [23].

LY under X-ray excitation was measured at 8 keV (Cu-Kα) with a CCD camera, an X-ray generator equipped with a Copper anode and a 25 µm thick copper filter. In this case, a YAG:Ce SC was used as a reference for the conversion efficiency measurement (conversion efficiency of bulk YAG:Ce is equal to 100 %). The scintillators were coupled to microscope optics equipped with an Olympus 2x (NA = 0.08) magnification and a PCO Sensicam SVGa camera. The conversion efficiency was calculated from the flat field image (dark image corrected) obtained under 30 s exposure. The mean ADU signal extracted from a Region Of Interest (ROI) of the image was measured and corrected by the crystal absorption efficiency (crystal thickness and material) and the CCD - camera spectral matching factor (convolution of scintillator emission spectrum and CCD sensor quantum efficiency).

We also studied the scintillation decay kinetics under α-particle excitation using a setup based on the Hamamatsu H6521 photomultiplier and TDS3052 digital oscilloscope.

Afterglow of X-ray excited luminescence of LuAG:Ce SCFs was also evaluated in comparison to their SC analogues. The afterglow of the scintillators down to relative amplitudes of 10^(-5) - 10^{-4} was studied since a dynamic range of up to 14 bits for successive images is required in some X-ray imaging applications. The afterglow decay depends on the exposure time and more slightly on the X-ray photon flux. Typical exposure times on synchrotron sources for X-ray tomography are now 0.1–1 s (monochromatic X-ray beam up to 10^{16} photons/ (s.mm^2)). The afterglow was measured at 8 keV with an X-ray tube equipped with a copper anode and copper filter. This corresponds to an X-ray photon flux of 10^{6} photons/(s.mm^2). The signal decay was measured with a Philips 2020Q photomultiplier coupled to a SR445 Stanford Research amplifier and a SR400 gated photon counter from Stanford Research Instrument working in counting mode and sampled at intervals of 4 ms.

For further investigation of LuAG:Ce SCFs luminescent properties, we used cathodoluminescence spectra (CL) and thermoluminescence (TSL) measurements. Registration of TSL glow curves were performed after α-particle excitation by Am^{241} source in the 300-800 K temperature range using a commercial Risoe DA-20 TL/OSL reader (Denmark).

III. RESULTS

A. Lattice mismatch

LuAG:Ce SCFs grown on YAG substrates displayed as expected a high lattice mismatch of ~ 0.8-1 % (Fig.2a) while LuAG:Ce SCFs grown on LuAG substrates showed very low lattice mismatch below 0.1 %.

The diffraction peaks of the LuAG:Ce SCF and LuAG substrate could not be separated with our laboratory diffractometer (Fig.2b) but could be resolved with the high-resolution setup at the ESRF BM05 beamline (Fig.3). The measured lattice mismatch for LuAG:Ce film grown on LuAG substrate was 0.06 % (Fig. 3), which is 13 times better than in the case of LuAG:Ce grown on YAG substrate (Fig.2a).

Fig.2c exhibits the rocking curves of LuAG:Ce SCFs grown on YAG and LuAG substrates. The Full Width Half Maximum (FWHM) corresponding to the LuAG:Ce SCF grown on YAG substrate is significantly larger than that of the films grown on LuAG substrates. The structural quality of the films grown on YAG substrate is affected by the high lattice mismatch between the YAG substrate and the LuAG:Ce SCF (Fig.2a and 2c). LuAG:Ce SCF grown on LuAG substrate show however a much higher structural perfection, similar to that of the LuAG substrate, as it can be seen from the reduced rocking curve FWHM (Fig. 2c).
Fig. 2: (a) (888) reflection XRD pattern of LuAG:Ce SCF grown onto YAG substrate and (b) (1200) reflection XRD pattern of LuAG:Ce SCF grown onto LuAG substrate. (c) Rocking curve of LuAG:Ce grown on YAG substrate (1) and LuAG substrate (2).

Fig. 3: (800) reflection XRD pattern of the LuAG:Ce (10 mol. %) SCF grown onto undoped LuAG substrate measured with a monochromatic X-ray beam at 15 keV. The lattice mismatch is ~0.06 %.

B. Cathodoluminescence spectra

The CL spectrum of LuAG:Ce SCFs (Fig. 4) presents the characteristic emission band in the green range related to the 5d¹-4f (F⁵/₂;7/₂) transitions of Ce³⁺ ions in LuAG host. The intensity of CL was maximal in the LuAG:Ce SCF grown with 5 mol. % CeO₂ in the melt and steeply decreased with increasing concentration of activator oxide up to 10 %. In Ce, Pr co-doped SCF samples, the CL spectrum (Fig. 4) shows the superposition of wide Ce³⁺ emission band and Pr³⁺ emission bands at 308 and 380 nm (d-f transitions) as well as narrow lines at 610 nm and 663 nm (f-f transitions). It indicates that the excitation energy can be effectively transferred from the LuAG host both to Ce³⁺ and Pr³⁺ ions under high energy radiation. It is interesting to note that the intensity of Ce³⁺ emission band is significantly increased in co-doped LuAG:Ce(10%),Pr(1.5%) SCF (Fig. 4, curve 4) in comparison with LuAG:Ce(10%) sample. This effect is explained by the presence of an effective energy transfer from Pr³⁺ to Ce³⁺ ions due to overlapping of the Pr³⁺ emission band and the Ce³⁺ 4f-5d absorption band in the UV range. The investigation of this energy transfer process in LuAG:Ce,Pr SCFs is detailed in separate papers [24, 25].

Fig. 4. RT CL spectra of LuAG:Ce (1-3) and LuAG:Ce,Pr (4) SCFs grown with different content of Ce and Pr ions (see legend of figure).
C. Light yield and decay kinetic under α-particle and X-ray excitations

Under α-particle excitation, the LuAG:Ce (5 %) SCF showed much higher LY (195-205 %) than the reference YAG:Ce SCF (100 %) sample with LY of 360 phels/MeV [19] in a time window of 12 µs (Table 1). The LY of LuAG:Ce SCFs show strong dependence on Ce concentration. Namely, the LY of these SCFs decreased from 205 % to 120 % for Ce doped samples grown with 5 to 10 mol. % CeO$_2$ in the melt (Table 1). The LY is then slightly increased to 125 % when adding 1.5 mol. % Pr$_{2}$O$_3$ oxide to the melt.

<table>
<thead>
<tr>
<th>Type of scintillator</th>
<th>CeO$_2$/Pr$_2$O$_3$ content, mol. %</th>
<th>Decay time $t_{1/e}/t_{1/2}$, ns</th>
<th>LY, %</th>
</tr>
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<td>5</td>
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<td>205</td>
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<td>195</td>
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<td>130</td>
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<td>120</td>
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<td>100</td>
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<tr>
<td>LuAG:Ce SC</td>
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Table 1. Decay times $t_{1/e}$ and $t_{1/2}$ (scintillation intensity decrease to 1/e and 1/2 levels, respectively) and relative LY of LuAG:Ce and LuAG:Ce,Pr SCFs under excitation by α-particles (Pr$^{3+}$ source, 5.15 MeV), measured with a 12 µs shaping time in comparison with standard YAG:Ce: #42-6 SCF with LY of 360 phels/MeV [19].

Under 8 keV X-ray irradiation, the light output of the LuAG:Ce SCFs was also compared to a reference 6 µm thick LSO:Th,Ce SCF. Similarly to the LY under α–particle excitation, the maximum light output of 77 % under X-ray excitation was found in LuAG:Ce (5 %) SCFs. The light output decreased respectively to 54 % for LuAG:Ce (8%) SCFs and to 40 % for LuAG:Ce (10 %) SCFs. The light output slightly increased to 49 % when adding 1.5 mol. % Pr$_2$O$_3$ in the melt and then decreased to 40 % for SCFs grown at 3 % Pr$_2$O$_3$ (Table 2).

The scintillation decay kinetics of LuAG:Ce and LuAG:Ce,Pr SCFs under α–particle excitation is shown in Fig.5 and Table 1. The decay time of Ce$^{3+}$ luminescence in LuAG:Ce lies in the 33-53 ns range and strongly increase with increasing Ce$^{3+}$ concentration in the melt from 5 to 10 mol. %, most probably due to concentration quenching (Table 1). The fast component of the scintillation decay becomes much shorter in LuAG:Ce,Pr SCFs in comparison with LuAG:Ce SCFs (Fig.5). However both SCFs still showed some long second decay component, suggesting the presence of trap centers above RT in these SCFs.

D. Thermoluminescence glow curves

For investigation of trap related phenomena, the TSL glow curves of LuAG:Ce SCFs were recorded between 50 °C and 500 °C in comparison with a standard LuAG:Ce SC sample. Similarly to LuAG:Ce SC, the glow curves confirmed the presence of deep trap centers in LuAG:Ce SCFs above RT (Fig.6 and 7). The nature of these traps is not determined yet, but due to the absence of antisite defect related centers [27] and expected low concentration of oxygen vacancies in these garnet SCFs [28] grown in oxygen containing atmosphere (air), we assume that these traps could be attributed mainly to the entrance of unwanted impurities in the LPE grown films. Possible impurities can be Pb$^{2+}$ ions, coming from the PbO-B$_2$O$_3$ solvent, or Pt$^{4+}$ ions coming from the Pt crucible and other Pt equipment used in the growth process. As a consequence, various locally non-compensated lattice defects can be created, for instance oxygen or cation vacancies around mentioned impurities [15, 16]. This may result in the formation of trap levels in the forbidden gap, and therefore the appearance of slow component in the luminescence decay kinetics of Ce$^{3+}$ ions as well as the decrease of scintillation efficiency [6, 26].

At the same time, the TSL glow curve of LuAG:Ce SCFs, LuAG:Ce,Pr SCF and LuAG:Ce SC registered both in the UV and visible ranges (Fig.6 and 7) revealed a much higher concentration of traps for the SC than for the SCF counterparts. It can be explained by the very high concentration of Lu$_{3+}$ antisite defects (ADs) [29] and charged oxygen vacancies ($F^-$ centers) coupled with Lu$_{4+}$ ADs [30], in the LuAG:Ce SC grown at high temperature (~2030 °C). These ADs and vacancy related centers, acting as luminescence centers, emit in the UV range in the bands peaking at 300 nm and 400 nm, respectively [29, 30].
E. Afterglow of X-ray excited luminescence

The afterglow in LuAG:Ce SC is most probably caused by antisite defects and oxygen vacancies, working as electronic traps [25, 26]. In SCFs, grown from melt-solution, with negligible concentration of ADs [7-9] and lower concentration of oxygen vacancies [27], the afterglow is reduced by one order of magnitude compared to the LuAG:Ce SC used as reference (Fig. 8). However the afterglow in SCF is not totally suppressed and is relatively strong at RT. It shows the presence of another type of trapping centers responsible for delayed energy transfer to Ce\textsuperscript{3+} centers. As mentioned above, in LPE grown SCF samples, Pb\textsuperscript{2+} and Pt\textsuperscript{4+} ions are always incorporated in the layer and could play a significant role in the appearance of afterglow. This assumption is in good agreement with the presence of trap centers in the TSL glow curve above RT (Fig.6).

The presence of afterglow in the LuAG:Ce SCFs can be a problem in some X-ray imaging applications, as it will limit the available dynamic range in time-resolved experiments. In comparison we plotted the afterglow curve of LSO:Tb SCF: the signal reaches almost $10^{-5}$ in less than 10 ms, whereas in the case of LuAG:Ce SCFs, the signal reaches only $10^{-3}$ after 1 s.

F. X-ray imaging capability

X-ray images were recorded at 8 keV (CuKα). The images were not flat field corrected. A 10 µm thick LuAG:Ce film was coupled to microscope optics and the images were acquired with a PCO Sensicam SVGA CCD camera (1024x1080 pixels, 6.7 µm pixel size). Fig. 9 shows the image of X-ray gold targets (G2480A, from Oxford Instruments) acquired with a 2x (NA = 0.08) magnification microscope objective, resulting in a 3.4 mmx4.2 mm Field of View (FOV) and a ~7 µm spatial resolution. The image is uniform and shows very few point defects. Fig. 10 is a zoom in the image of Fig. 9 obtained with a 10x (NA=0.3) microscope objective. The smallest 25 µm details are clearly visible with high contrast.
investigation at lower CeO$_2$ coming from the PbO based solvent. However, further
the LPE method in a PbO-B$_2$O$_3$ thickness range 5 µm to 80 µm were successfully grown by
concentration in the melt should

IV. CONCLUSIONS

LuAG:Ce and LuAG:Ce,Pr single crystalline films in the thickness range 5 µm to 80 µm were successfully grown by
the LPE method in a PbO-B$_2$O$_3$ solvent. LuAG SCFs grown on undoped (100)-oriented LuAG substrates gave promising results in terms of structural quality and transparency. LuAG films grown on undoped (111)-oriented YAG substrates presented a rough surface and lower structural quality, due to the high lattice mismatch between the substrate and the film.

The light output under alpha-particle excitation is slightly lower (less than 20 %) in the LuAG:Ce SCFs than in the SC counterpart, due to incorporation of unwanted Pb$^{2+}$ ions coming from the PbO based solvent. However, further investigation at lower CeO$_2$ concentration in the melt should be performed, where maximum light output was found in our case (5 mol. % CeO$_2$).

LuAG:Ce SCFs still show some slow components in their scintillation decay under α-particle excitation and afterglow after X-ray excitation. Due to absence of Lu$_{48}^{3+}$ antisite defects and low concentration of oxygen vacancies, we assume that Pb$^{2+}$ and Pr$^{3+}$ contamination in the LuAG:Ce layers could play a significant role in formation of trap centers. This point is confirmed by the presence of TSL peaks above RT in these SCFs.

In the case of LuAG:Ce,Pr films, the simultaneous energy transfer from LuAG host both to Pr$^{3+}$ and to Ce$^{3+}$ was observed. Under X-ray excitation the emission of these films is composed of both Pr$^{3+}$ and Ce$^{3+}$ emission lines.

Finally, LuAG:Ce and LuAG:Ce,Pr SCFs display very interesting properties for X-ray imaging with µm spatial resolution: fast luminescence kinetics, competing LY (~ 80 % of YAG:Ce SC). The X-ray imaging ability of the LuAG:Ce films was checked with a laboratory X-ray generator (Cu anode) by acquiring some X-ray target images (smallest details 30 µm). The images revealed good image uniformity.

The films optical quality will further be tested at much higher spatial resolution by using higher magnification microscope objectives.

The afterglow level should still be reduced, as it can limit the usage in X-ray micro-tomography. More work should be performed to understand the nature of the traps above RT in the TSL glow curves of these SCFs. Optimization of the LY and reduction of the afterglow intensity are needed in LuAG:Ce SCF, for instance by using Gd-Ga co-doping for suppression of high-temperature TSL peaks [31, 32].

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