

# Improved scintillation time response in (Lu0.5Gd0.5)2O3:Eu3+ compared with Lu2O3:Eu3+ transparent ceramics

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1	Improved scintillation time response in
2	$(Lu_{0.5}Gd_{0.5})_2O_3 : Eu^{3+}$ compared to $Lu_2O_3 :$
3	Eu <sup>3+</sup> transparent ceramics
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## 1 Abstract

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The scintillation properties of two sesquioxides ceramics  $Lu_2O_3:Eu^{3+}$  and 3  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  were studied. Both ceramics present comparable transparency 4 and light yield whereas (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> showed an order of magnitude reduced 5 afterglow in the 3-300 ms range. A thorough study of the location and behavior of 6 Eu<sup>3+</sup> dopant ions at C<sub>2</sub> and S<sub>6</sub> sites of Lu<sub>2</sub>O<sub>3</sub> and (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub> structures was carried 7 out with low temperature selective excitation of  $Eu^{3+}$ . This revealed that (i) at both  $C_2$ 8 and S<sub>6</sub> sites,  $Eu^{3+}$  4f-4f lifetime is shorter in  $(Lu_{0.5}Gd_{0.5})_2O_3$ :  $Eu^{3+}$  than in  $Lu_2O_3$ :  $Eu^{3+}$ 9 (ii) the host matrix  $(Lu_{0.5}Gd_{0.5})_2O_3$  as compared to  $Lu_2O_3$  favors the location of Eu<sup>3+</sup> 10 at  $C_2$  site. As decay times of Eu<sup>3+</sup> in  $C_2$  and  $S_6$  sites are 1.0 ms and 3.8 ms 11 respectively, the preferred occupation of  $C_2$  in  $(Lu_{0.5}Gd_{0.5})_2O_3$ : Eu<sup>3+</sup> implies a much 12 shorter decay time for  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  in the 3-20 ms range. Reduction of 13 14 afterglow in the 20-300 ms range is illustrated by thermally stimulated luminescence peaks presenting a highly reduced intensity for (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> compared to 15  $Lu_2O_3:Eu^{3+}$  implying reduced charge trapping defects in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ 16 17 ceramics.

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19 Keywords: ceramics, scintillation, Computed Tomography, luminescence,
20 sesquioxide

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- 22

## 1 Introduction

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A scintillator is a material able to detect ionizing radiation (X,  $\alpha$ ,  $\beta$ ,  $\gamma$ -rays, 3 neutrons...) and convert them into visible light. In order to obtain performant 4 5 scintillators the high energy electron-hole pairs produced after ionisation should be efficiently transferred to the luminescent center. This last stage is very material-6 dependent. One of the most important application fields of scintillation is medical 7 8 imaging. Today the main scintillating materials for medical imaging are 9 Gd<sub>2</sub>O<sub>2</sub>S:Pr,Ce,F [1], (Y,Gd)O<sub>3</sub>:Eu,Pr [2] and CdWO<sub>4</sub> [3,4] for X-ray Computed 10 Tomography (CT) whereas BGO (Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>) [5,6], NaI:Tl [7], LYSO  $((Lu, Y)SiO_5:Ce^{3+})$  [8,9] and LPS  $(Lu_2Si_2O_7)$  [10,11,12] are often used for Positron 11 Emission Tomography (PET). BGO [13], LYSO [14] and CsI:Tl [13] have also been 12 13 shown useful for megavoltage X-Ray imaging (portal imaging and cone-beam CT). In 14 the aim of decreasing the radiation dose received by the patient during a scan, 15 scintillators with enhanced efficiency are being investigated. In the first stage of 16 detection, the ionizing radiation must be stopped by the scintillator within the shortest range of the material in order to produce sharp images. High density and high 17 18 effective atomic number are required for the host material. In that respect lutetium sesquioxide  $Lu_2O_3$  constitutes one of the best possible hosts with a density  $\rho$  of 9.43 19  $g/cm^3$  and an effective atomic number  $Z_{eff}$  of 69. With its cubic structure it can be 20 21 synthesized as a transparent ceramics which is very advantageous to produce 22 scintillators at a lower cost. However obtaining a nanosecond fast response in Lu<sub>2</sub>O<sub>3</sub> from 5d-4f emissions of dopants such as  $Ce^{3+}$ ,  $Pr^{3+}$  or  $Tb^{3+}$  was found impossible due 23 to the location of the 5d levels of  $Ln^{3+}$  (Ln = Ce, Pr, Tb) inside the conduction band 24 [15]. Nevertheless  $Eu^{3+}$  4f-4f luminescence is observed in  $Lu_2O_3:Eu^{3+}$ . It presents a 25

typical red luminescence that matches very well the sensitivity spectrum of 1 2 photodiode detectors and its decay time is in the order of millisecond in most hosts [16]. Lempicki *et al.* in 2002 were the first to claim the use of  $Lu_2O_3$ : Eu<sup>3+</sup> ceramics as 3 a scintillator [17]. While a typical 1-2 ms response time is considered as totally 4 5 acceptable for scintillators in X-rays CT application, longer afterglow should be 6 suppressed so that CT images do not get blurred by delayed signals. Unfortunately afterglow is often a limiting parameter in sesquioxide hosts. An afterglow of some 7 hundreds of milliseconds has been reported by several authors in  $Lu_2O_3$ :Eu<sup>3+</sup> 8 [18,19,20] as well as in  $Lu_2O_3$ :Tb<sup>3+</sup> [21]. The afterglow in sesquioxides could 9 10 originate from Frenkel defects as the structure allows easy displacement of oxygen 11 atoms. However no experimental proof has been brought up till now. Alternatively co-doping was reported as a way to reduce afterglow in some cases.  $Pr^{3+}$  [22] or Ti<sup>4+</sup> 12 [23] co-doping in (Y,Gd)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> for instance were found to reduce persistent 13 luminescence of Eu<sup>3+</sup>. On the contrary Ca<sup>2+</sup> addition in Lu<sub>2</sub>O<sub>3</sub>: Tb<sup>3+</sup> [21] enhanced 14 long-lasting luminescence in the material. 15

In this work an alternate way to improve time response in Eu<sup>3+</sup>-doped 16 sesquioxides is reported. By heavily substituting the lutetium host cation with 17 gadolinium in  $Lu_2O_3$  up to the composition ( $Lu_{0.5}Gd_{0.5}$ )<sub>2</sub>O<sub>3</sub>, the luminescence time 18 19 characteristics of the Eu<sup>3+</sup>-doped scintillating ceramics are very much improved while the density of this latter compound (about 8.4  $g/cm^3$ ) is still very favorable. In the first 20 21 part of the paper the scintillation properties including afterglow measurements of  $Lu_2O_3:Eu^{3+}$  and  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  ceramics are investigated. In the second part, the 22 selective excitation of  $Eu^{3+}$  in the two cationic sites of the structure unravels reasons 23 24 for different luminescence decay behaviors and the time reponse improvement of  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  ceramics is discussed. 25

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## 2 **Experimental Section**

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4 Gobain Crystals. The starting powders were synthesized by an inverse coprecipitation 5 method. A solution pH = 10 of ammonia and oxalic acid was prepared. For the 6 7 synthesis of Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>, lutetium and europium nitrates were dissolved in ionized 8 water and then added dropwise to the ammonia/oxalic acid solution while stirring. A white precipitate of  $Lu_2(C_2O_4)_3:Eu^{3+}$  was formed [17]. The precipitate was washed 9 10 first with water and then with ethanol before being dried for one hour at 100°C. The powder was then fired at about 800°C. For  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  lutetium, gadolinium 11 and europium nitrates were used. The powders structure was checked by X-ray 12 13 diffraction and showed pure bixbyite structure with space group Ia-3 (206). Initial 14 Europium concentration was 6 at% and 7 at% (via Eu<sub>2</sub>O<sub>3</sub>) for Lu<sub>2</sub>O<sub>3</sub> and 15  $(Lu_{0.5}Gd_{0.5})_{2}O_{3}$  ceramics, respectively as this concentration range was found optimum 16 with respect to the light yield of the ceramics [24]. After grinding, pellets were prepared by pressing powders under isostatic conditions at room temperature and then 17 18 at high temperature. Finally the ceramics were pressed under isostatic conditions at 19 high temperature, before being annealed at 1000°C in air. Both ceramics are 1 cm-20 diameter large and 1 mm-thick. A Gd<sub>2</sub>O<sub>2</sub>S:Pr (GOS:Pr) ceramics of 10 mm- diameter 21 and 1 mm-thickness also studied in our laboratory [25] is used as an element of 22 comparison.

Total transmission was measured using a UV-VIS Cary 6000i double beam spectrophotometer. Ceramics samples were placed at the entrance of an integrating sphere. They were excited on their entire surface from the front and light transmitted and emitted in all directions behind the ceramics was collected by the integrating
 sphere.

For radioluminescence measurements the ceramics were excited by X-rays produced by a molybdenum tube operated at 50 KV and 20 mA impinging on the samples surface with a 45° angle. Light was collected at 45° angle from the surface *via* an optical fibre by a Princeton Charge Coupled Device (CCD) camera cooled at -65°C coupled with an Acton SpectraPro monochromator.

8 In thermally stimulated luminescence (TSL) experiments the ceramics were silver 9 glued on a copper sample holder attached to the cold head of a helium closed cycle 10 cryostat. They were first excited for 10 minutes through a beryllium window of the 11 cryostat by a molybdenum X-ray source operated at 50 KV and 20 mA. A Lakeshore 12 temperature controller was then used to apply a 20 K/min heating rate between 10 K 13 and 650 K. Luminescence was collected through a quartz window of the cryostat by 14 the same detection device as the one used in radioluminescence (optical fibre / 15 monochromator / CCD camera).

Afterglow was measured after X-ray excitation provided by a tungsten X-Ray tube operated at 120 kV and 13.3 mA on ceramics placed on a photodiode. Afterglow measurement was carried out with a 1 ms integration time and up to 300 ms.

Laser-excited low temperature luminescence measurements were carried out on ceramics silver glued on a copper sample holder mounted on the cold head of a closed cycle cryogenic refrigerator. The cold head was cooled to 10 K. Fluorescence and decay spectra were recorded using as excitation source an optical parametric oscillator laser (10 Hz, 8 ns) pumped by the third harmonic of a YAG:Nd laser. A Roper/Princeton Intensified Charged Couple Device (ICCD) detector was used to detect the fluorescence with a time delay up to 20 ms.

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## 2 **Results**

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## 1. Scintillation properties of Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> and (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> ceramics

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In-line transmission of Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> and (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> ceramics were 6 measured at the main emission wavelength of  $Eu^{3+}$ , i.e. 612 nm, as 46 % and 38 %, 7 8 respectively. Though these values do not appear very high, the ceramics looked 9 transparent. Light was actually very much scattered as samples had not been polished 10 or coated with any anti-reflection layer. As the refractive index of the material is 11 rather high (1.93 and 1.95 at 612 nm for Lu<sub>2</sub>O<sub>3</sub> and (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub> respectively) a 12 surface treatment is required to avoid light losses. In order to test the ability of the as-13 prepared ceramics to serve as efficient scintillator pixels used for instance in X-ray 14 CT, their total transmission spectrum was measured and is presented in Figure 1. Let 15 us remind that total transmission was measured with an integrating sphere able to 16 collect both transmitted and scattered light at the back of the ceramics. Therefore total 17 transmission corresponds to light potentially used by a photodetector placed at the 18 back of a scintillating element made of the 1 mm-thick ceramics. Figure 1 shows that Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> and (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> ceramics present a total transmission of 81 % 19 and 83 %, respectively at the main emission wavelength of  $Eu^{3+}$  (612 nm), indicating 20 21 that the emitted photons should be efficiently extracted from the materials. Both 1 22 mm-thick ceramics, prepared here by the same procedure, show a similar and 23 satisfying optical quality in terms of total light transmission.

Note that the transmission spectra of Figure 1 show expected intra-configurational 4f-4f transition lines of  $Eu^{3+}$ . The band gaps of  $Lu_2O_3$  and  $(Lu_{0.5}Gd_{0.5})_2O_3$  precursor

1 powders were measured in a previous work as 5.6 eV and 5.4 eV, respectively [24]. 2 These values correspond to the absorption edge observed at the short-wavelength side of the spectra around 220 nm. The spectra also display two absorption bands 3 identified as low transmission dips at 245 nm / 282 nm and at 245 nm / 293 nm for 4  $Lu_2O_3:Eu^{3+}$  and  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ , respectively. However this part of the spectrum 5 is modified by the fact that emitted light is not filtered out in this measurement. In that 6 way, the total transmission spectrum at wavelengths where high absorption also 7 reflects some features of an excitation spectrum of Eu<sup>3+</sup> luminescence. Thus efficient 8 absorption bands for Eu<sup>3+</sup> luminescence may appear as high transmission values since 9 they imply intense luminescence of  $Eu^{3+}$  at 612 nm. Hence the spectrum in that range 10 11 can alternatively be read as two excitation bands at maxima of the transmission curve, at 233 nm / 258 nm and 235 nm / 268 nm for  $Lu_2O_3:Eu^{3+}$  and 12 i.e.  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ , respectively. These values are comparable to what was 13 measured by Chen et al. on Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> ceramics at 245 nm and 266 nm and attributed 14 to charge transfer (CT) absorption bands of  $Eu^{3+}$  [26]. Zych *et al.* also observed a 15 double band at 245 nm and 270 nm for a  $Lu_2O_3$  :Eu<sup>3+</sup> ceramics which they attributed 16 to  $Eu^{3+}$  CT bands in the two sites of  $Lu_2O_3$  [27]. 17

The X-ray excited radioluminescence spectra of Lu<sub>2</sub>O<sub>3</sub>:6%Eu<sup>3+</sup> 18 and  $(Lu_0 _5Gd_{0.5})_2O_3:7\%Eu^{3+}$  are shown in Figure 2 along with the radioluminescence 19 spectrum of a standard  $Gd_2O_2S:Pr^{3+}$  non-transparent ceramics. The sesquioxides 20 spectra are composed of expected 4f-4f emission lines for Eu<sup>3+</sup>. The main line 21 corresponds to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup> at 612 nm and gives a bright red 22 luminescence that perfectly matches silicon photodetectors sensitivity [17]. The other 23  ${}^{5}D_{J} \rightarrow {}^{7}F_{J}$  emission lines are identified on the figure and are very similar for both 24 compounds. The integrated intensities for both  $Lu_2O_3:Eu^{3+}$  and  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ 25

ceramics are in the range of the intensity for the GOS:Pr ceramics and are similar the one to each other. However no absolute light yield value was here inferred from this comparison as the transparency of the standard and the sesquioxides is different. Pulse-height measurement, which was not available in our laboratory, or comparison with an absolute reference should be carried out in order to measure an absolute light output value. Note that the most recent work indicates a light yield as high as 70 000 photons/MeV obtained with a (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>: 10% Eu<sup>3+</sup> ceramics [28].

8 Figure 3 shows afterglow measurements of the two ceramics in part per million of the initial light output. At 300 ms  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  ceramics presents an afterglow 9 about one order of magnitude lower than Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>. Two parts can be distinguished 10 11 in the decays. Within the first milliseconds (up to 20 ms) the ceramics present a time response in the order of the decay time of Eu<sup>3+</sup> excited states. Pseudo decay times 12 13 calculated over the two  $(\tau_1)$  and three  $(\tau_2)$  first points are reported in Table 1 as an element of comparison. They are reported here as "short afterglow". Both  $\tau_1$  and  $\tau_2$  are 14 shorter for  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  than for  $Lu_2O_3:Eu^{3+}$ . A second part of the afterglow 15 curve can be distinguished between 50 ms and 300 ms. This part of the curves allows 16 17 us to evaluate the "long afterglow" decay times  $\tau_3$  reported in Table 1. The long afterglow decay time is again found shorter for (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> than for 18  $Lu_2O_3:Eu^{3+}$ . 19

TSL glow curves of both ceramics between 10 K and 535 K are shown in Figure 4. The glow curve of  $Lu_2O_3:Eu^{3+}$  ceramics presents a main peak at 195 K and two peaks of lower intensity at 54 K and 110 K. The inset of Figure 4 zooms into the 250 K-450 K region. In that region three peaks of much lower intensity can be distinguished at 297 K, 338 K and 375 K. At this point it is difficult to relate with certainty any specific TSL peak to the afterglow observed above. Though of low 1 intensity, the peaks of the 250 K-450 K region might contribute to the afterglow. However the afterglow at some hundred of ms in Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> may most probably be 2 3 related to the main TSL peak at 195 K. This hypothesis is supported by a study of Kostler *et al.* on  $(Y,Gd)_2O_3:Eu^{3+}$  [22] in which the TSL curve of  $(Y,Gd)_2O_3:Eu^{3+}$  was 4 found very similar in shape above 150 K to the one presented here for Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> 5 with a main peak at 180 K similar to our 195 K peak. By comparing the TSL curve 6 with the afterglow at 100 ms at various temperatures, they showed that the afterglow 7 8 at 100 ms was unambiguously related to the TSL peak at 180 K.

In Figure 4 the TSL glow curve of  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  presents very similar 9 10 peaks position to  $Lu_2O_3$ : Eu<sup>3+</sup>. The main peak is slightly widened in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  and its maximum is shifted from 195 K in  $Lu_2O_3:Eu^{3+}$  to 205 K. 11 In the 250 K-450 K range, the same low intensity peaks as for  $Lu_2O_3:Eu^{3+}$  might be 12 13 present too though the sensitivity is too low to detect the two last peaks at 338 K and 375 K. Defects responsible for charge trapping in both compounds are therefore 14 probably of same nature. However all peaks of  $(Lu_0 \,_5Gd_0 \,_5)_2O_3$ : Eu<sup>3+</sup> show a strongly 15 reduced intensity compared to those of Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>. 16

- 17
- 18 **2.** Site selective excitation of Eu<sup>3+</sup>
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A representation of the bixbyite structure of cubic lutetium sesquioxide is shown in Figure 5. It is comparable to fluorine  $CaF_2$  with <sup>1</sup>/<sub>4</sub> anionic vacancy. The oxygen ions constitute a face centered cubic network with oxygen vacancies located on [1 1 1] directions. Two different cationic sites with symmetry  $C_2$  and  $S_6$  exist in a ratio 3:1.  $C_2$  sites are located at the center of the cubes that present two anionic vacancies on a diagonal of a face of the cube. The cations at  $C_2$  occupy 24d Wickoff positions at (u 0 1 1/4). Two oxygen ions are at a medium distance of the C<sub>2</sub> cation (similar to the cation-2 oxygen distances in S<sub>6</sub> sites), two are at a shorter distance and two at a longer distance. The  $C_2$  cationic site is non centro-symmetric.  $S_6$  sites (or  $C_{3i}$ ) are located at 3 4 the center of the cubes that present two anionic vacancies situated on the central diagonal of the cube. The cations occupy 8b Wickoff positions at (1/4 1/4 1/4 ). The six 5 oxygen ions are at equal distance from the central cation. The  $C_2$  cationic site is 6 centro-symmetric. The centro-symmetry character of the site determines the 7 luminescence spectrum of Eu<sup>3+</sup>. 8

9 Up to now contradictory results were published about a possible preferential occupation of  $Eu^{3+}$  in one of the two cationic sites of the Lu<sub>2</sub>O<sub>3</sub> structure. Concas *et* 10 al. [29] showed that  $Eu^{3+}$  occupy mainly C<sub>2</sub> sites in 10%-doped materials whereas a 11 theoretical work from Stanek et al. demonstrated that Eu<sup>3+</sup> should be mainly located 12 at S<sub>6</sub> sites especially at low concentration [30]. Zych et al. also confirmed this 13 14 assertion and furthermore demonstrated that it is impossible to entirely remove 8b emission coming from  $S_6$  sites in Lu<sub>2</sub>O<sub>3</sub> compounds. However this author indicates 15 that 8*b* emission should be minimized in hosts like  $Sc_2O_3$ :Eu<sup>3+</sup> [31]. 16

As a general LaPorte rule, the 4f-4f dipolar electric transitions of Eu<sup>3+</sup> are parity 17 forbidden. When  $Eu^{3+}$  is located at a centro-symmetric site such as S<sub>6</sub> these transitions 18 remain forbidden. The dipolar magnetic transitions which are anyway much weaker 19 are allowed if  $\Delta J = 0, \pm 1$  while  $J=0 \rightarrow J=0$  transitions are forbidden. Hence for Eu<sup>3+</sup> 20 at the S<sub>6</sub> site at 10 K only  ${}^7F_0 \rightarrow {}^5D_1$  transition in absorption and  ${}^5D_0 \rightarrow {}^7F_1$  transition 21 in emission can be observed. Other  ${}^{5}D_{0} \rightarrow {}^{7}F_{i}$  transitions might be observed but with 22 very weak intensity as they originate from vibronic excited states of  ${}^{5}D_{0}$ . On the 23 24 contrary, the C<sub>2</sub> site presents no symmetry inversion so that opposite parity states such 25 as 5d are admixed with 4f states. A relaxation of the selection rule therefore takes

1 place and dipolar electric transitions become partly allowed. Hence for  $Eu^{3+}$  in C<sub>2</sub> site 2 all the  ${}^{5}D_{0} \rightarrow {}^{7}F_{j}$  transitions can be observed. Those for which  $\Delta J = 0, \pm 2$  being 3 "hypersensitive" to this phenomenon are enhanced.

Luminescence spectra of  $Lu_2O_3:Eu^{3+}$  and  $(Lu_0 \cdot Gd_0 \cdot J_2O_3:Eu^{3+})$  ceramics were 4 recorded at 10 K by exciting the ceramics between 525 nm and 530 nm. This 5 excitation wavelength range allows excitation of Eu<sup>3+</sup> via the  ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$  transition 6 which is allowed for  $Eu^{3+}$  at both sites. Laser excitation was used in the aim of 7 selectively exciting  $Eu^{3+}$  in  $C_2$  or  $S_6$  sites. At 10 K a very limited number of vibronic 8 states of  ${}^{5}D_{0}$  are populated. Hence  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transitions will be allowed for Eu<sup>3+</sup> at 9 both sites whereas  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transitions will be allowed (forced dipolar electric) for 10  $Eu^{3+}$  in  $C_2$  sites and forbidden for  $Eu^{3+}$  in  $S_6$  sites. 11

The emission spectra of Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> for four exciting wavelengths  $\lambda_i$  (i = 1, 2, 3, 4) 12 located between 525 nm and 530 nm with  $\lambda_1 > \lambda_2 > \lambda_3 > \lambda_4$  are shown in Figure 6. 13 They display luminescence lines corresponding to intraconfigurational 4f-4f 14 transitions from the excited  ${}^{5}D_{0}$  levels of  $Eu^{3+}$  to the various spin-orbit split states  ${}^{7}F_{i}$ . 15 The dominant emission line at 611 nm originates from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  hypersensitive 16 transition of  $Eu^{3+}$  in C<sub>2</sub>. In order to identify the possible contributions of  $Eu^{3+}$  at both 17 18 sites, the shortest wavelength range (580 nm - 605 nm) was looked upon into detail. 19 Two groups of emission lines have been distinguished : (i) a first group (group 1) of lines are present for  $\lambda_1$  excitation (lowest energy) and their relative intensity decreases 20 when the excitation energy increases ( $\lambda_{exc}$  decreases): they are pointed out on the main 21 22 graph of Figure 6 at 581.1 nm, 587.5 nm, 593.7 nm and 600-601 nm. (ii) the second group (group 2) of lines are absent for  $\lambda_1$  excitation and their relative intensity 23 24 increases when  $\lambda_{exc}$  decreases : they are shown in the insets of Figure 6 at 582.6 nm, 593.1 nm and 596.8 nm. The other emission lines of the 580 nm - 605 nm range are 25

1 of lower intensity and are attributed to transitions to various vibronic states of the  ${}^{7}F_{1}$ 2 level.

As energy transfer is known to happen from  $Eu^{3+}$  in  $S_6$  site to  $Eu^{3+}$  in  $C_2$  site [31,32,33] any exciting wavelength  $\lambda_i$  of Figure 6 would allow the observation of the luminescence of  $Eu^{3+}$  in  $C_2$  sites either by direct excitation of  $Eu^{3+}$  in  $C_2$  or by excitation of  $Eu^{3+}$  in  $S_6$  and subsequent energy transfer to  $Eu^{3+}$  in  $C_2$ . As the lines in group 2 are not observed for  $\lambda_1$  excitation, group 2 is identified as originating from  $Eu^{3+}$  in  $S_6$  whereas group 1 lines are produced by  $Eu^{3+}$  in  $C_2$ .

For  $Eu^{3+}$  in C<sub>2</sub> site the emission line at 581.1 nm being the one at the highest 9 energy is identified as the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition of Eu<sup>3+</sup>. The three other emissions at 10 587.5 nm, 593.7 nm and 600-601 nm were attributed to transitions from  ${}^{5}D_{0}$  to the 11 three Stark components of the  ${}^{7}F_{1}$  level hence leading to a crystal field splitting of 369 12  $cm^{-1}$  for the  ${}^{7}F_{1}$  level. The energy positions of the  ${}^{7}F_{0}$  and the split  ${}^{7}F_{1}$  levels named 13  ${}^{7}F_{1a}$   ${}^{7}F_{1b}$  and  ${}^{7}F_{1c}$  levels are reported in Table 2. In order to verify this attribution the 14  ${}^{5}D_{0}$  energy position and the barycenter of the  ${}^{7}F_{1}$  levels were reported in Figure 7. The 15 figure displays the barycenter law - in that case, for lanthanide cations, only the spin 16 orbit interaction is considered - enounced by Antic-Fidancev [34] corresponding to 17 the position of the  ${}^{7}F_{1}$  level barycenter without any effect of the crystal field in regard 18 to the position of the  ${}^{5}D_{0}$  level. Data for Eu<sup>3+</sup> in C<sub>2</sub> lie right on the line of the 19 barycenter law, which corroborates our attribution. 20

For Eu<sup>3+</sup> in S<sub>6</sub> site, the attribution of the emission lines shown in the insets of Figure 6 is a little bit more delicate. The emission line at 582.6 nm is very close to the  $^{5}D_{0} \rightarrow ^{7}F_{0}$  line of Eu<sup>3+</sup> in C<sub>2</sub> site (581.1 nm) and one could assume that it would correspond to the  $^{5}D_{0} \rightarrow ^{7}F_{0}$  transition of Eu<sup>3+</sup> in S<sub>6</sub> site as it was reported in Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> by Hunt and Pappalardo [35]. However this transition is forbidden and

1 would therefore appear with a somewhat lower intensity. Like several others [32,33] we would rather attribute this line to a  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition. Within this frame two 2 hypotheses can be drawn. In a first hypothesis (hypothesis 1), following Buijs [32], 3 4 Meijerink and Blasse [16], the lines at 582.6 nm and 593.1 nm would correspond to transitions  ${}^{5}D_{0} \rightarrow {}^{7}F_{1a}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{1b}$  whereas the line at 596.8 nm would be a 5 transition from <sup>5</sup>D<sub>0</sub> to a non-fundamental vibronic level of <sup>7</sup>F<sub>1</sub>. According to groups 6 theory the  ${}^{7}F_{1}$  levels may split into only two levels, one of them being degenerated. 7 Depending on which one is degenerated two barycenter points (hypothesis 1A and 8 9 1B) were calculated as shown in Table 2. Their position is reported in Figure 7. Both 10 points seem too low regarding to the barycenter law of Antic-Fidancev. In a second hypothesis (hypothesis 2), we assume a slightly distorted  $S_6$  site which allows the 11 three  ${}^{7}F_{1}$  levels to be non-degenerated. The three lines at 582.6 nm, 593.1 nm and 12 596.8 nm would then correspond to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1a}$ ,  ${}^{7}F_{1b}$ ,  ${}^{7}F_{1c}$  transitions as reported in 13 Table 2. In that case, the barycenter point would be more properly located in Figure 7. 14 15 We therefore adopted this last hypothesis.

The emission spectra of  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  at 10 K excited at three various 16 wavelengths in the 525 nm - 530 nm range are shown in Figure 8. They present 17 similar features to  $Lu_2O_3:Eu^{3+}$  with widened lines. This is explained by the disorder 18 19 created by the substitution of one half of lutetium ions by larger gadolinium ions. By varying the excitation wavelength the spectra vary less than in the case of Lu<sub>2</sub>O<sub>3</sub> 20 :Eu<sup>3+</sup>. One can mainly observe the transition lines of  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  at 581 nm,  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ 21 (587,7 nm, 593,4 nm and 600,2 nm) of  $Eu^{3+}$  in C<sub>2</sub>. The energy positions of the levels 22 are reported in Table 2. They are close to values for C<sub>2</sub> site in Lu<sub>2</sub>O<sub>3</sub>. Note the 23 important fact that for Eu<sup>3+</sup> in S<sub>6</sub> only the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition can be observed at 24 582.2 nm and with a weak intensity. This shows that the occupation ratio of  $\mathrm{Eu}^{^{3+}}$  in  $\mathrm{S}_6$ 25

1 relative to  $C_2$  is smaller in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  than in  $Lu_2O_3:Eu^{3+}$ . This difference 2 between the two compounds will be observed with even more acuity in the following 3 part of the paper (cf. Figure 10).

The decay curves at 10 K of  $Eu^{3+}$  in C<sub>2</sub> and S<sub>6</sub> sites was measured by exciting the 4 samples via the  ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$  line and recording the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1a}$  emission line. They are 5 shown in Figure 9. The decay profiles of  $Eu^{3+}$  in S<sub>6</sub> sites for both sesquioxides were 6 found mono-exponential with a decay time of several milliseconds. For  $Eu^{3+}$  in  $C_2$ 7 8 sites the decays may appear bi-exponential though the second exponential part reaches 9 quickly the background level. Different decay times were calculated depending on the site occupied by  $Eu^{3+}$ . In  $Lu_2O_3:Eu^{3+}$  the trivalent europium at the S<sub>6</sub> site presents a 10 characteristic lifetime of 4.7 ms whereas its main decay time is 1.4 ms at the  $C_2$  site. 11 These results are in line with decay times found by Zych *et al.* in  $Lu_2O_3:1\%Eu^{3+}$  at 12 13 room temperature: 4.4 ms at the  $S_6$  site and 1.4 ms at the  $C_2$  site [31]. In  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ , the lifetimes were measured as 3.8 ms and 1.0 ms for Eu<sup>3+</sup> at the 14 S<sub>6</sub> and C<sub>2</sub> sites, respectively. Hence in both host materials the decay times are much 15 shorter for  $\operatorname{Eu}^{3+}$  at the  $C_2$  than at the  $S_6$  site, due to the much more symmetrical 16 character of  $S_6$  relative to  $C_2$ . On the other hand the  $(Lu_{0.5}Gd_{0.5})_2O_3$  host contributes to 17 reducing the decay times of  $Eu^{3+}$  in both  $C_2$  and  $S_6$  sites which may be explained by a 18 less symmetrical environment in  $(Lu_{0.5}Gd_{0.5})_2O_3$  than in  $Lu_2O_3$ . The decay time for the 19 second part of the curves for  $Eu^{3+}$  in  $C_2$  sites was not calculated as the signal was too 20 21 noisy. However the decay time is in the order of some milliseconds. This most probably corresponds to the energy transfer from  $Eu^{3+}$  at S<sub>6</sub> sites to  $Eu^{3+}$  at C<sub>2</sub> sites as 22 23 it was shown to take place in ref. 31.

Those different time decaying emissions should therefore contribute to the "short afterglow" of the ceramics as defined in the first paragraph. This can be visualized on

time-resolved luminescence spectra presented in Figure 10. Figure 10.A shows 1 spectra of  $Lu_2O_3:Eu^{3+}$ . Over the first microseconds (spectrum (a)), emission from  $Eu^{3+}$ 2 in  $C_2$  and  $S_6$  sites is observed. The  $C_2$  emission dominates with the hypersensitive  ${}^5D_0$ 3  $\rightarrow$  <sup>7</sup>F<sub>2</sub> line. Over the 6-9 ms time range one can mainly observe the contribution of 4  $Eu^{3+}$  is S<sub>6</sub> sites as it corresponds to the decay time period of  $Eu^{3+}$  in S<sub>6</sub> whereas  $Eu^{3+}$ 5 fast emission in C<sub>2</sub> has almost totally vanished. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  hypersensitive 6 transition of  $Eu^{3+}$  in C<sub>2</sub> site is also observed with a weak intensity. Over the 20-25 ms 7 time interval the main part of  $Eu^{3+}$  emission in both sites has decayed. Only residual 8 9 emission from both sites is observed with a similar intensity. Similar features are observed in Figure 10 B for  $(Lu_{0.5}Gd_{0.5})_2O_3$ : Eu<sup>3+</sup> with a different ratio between C<sub>2</sub> and 10  $S_6$  due to different decay times and different repartition of Eu<sup>3+</sup> ions. Most clearly a 11 main difference between  $Lu_2O_3:Eu^{3+}$  and  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  can be underlined in 12 the first microseconds in the zooms of spectra (a) : the intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  line 13 of  $Eu^{3+}$  in S<sub>6</sub> is much less important in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  (B) than in  $Lu_2O_3:Eu^{3+}$ 14 (A). Quantitatively the ratio of the emissions from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  line of Eu<sup>3+</sup> in S<sub>6</sub> 15 over the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1a}$  line of Eu<sup>3+</sup> in C<sub>2</sub> varies from 2.2 in Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> to 0.4 in 16  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ . This shows again very clearly that the population of S<sub>6</sub> site over 17  $C_2$  by  $Eu^{3+}$  is much lower in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  than in  $Lu_2O_3:Eu^{3+}$ . 18

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### 20 Discussion

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Transparent ceramics of  $Lu_2O_3$ : 6%  $Eu^{3+}$  and  $(Lu_{0.5}Gd_{0.5})_2O_3$ : 7%  $Eu^{3+}$  were prepared in a strictly identical way so that the differences between the two samples are limited to the composition. Though it is always difficult to avoid any effect of the microstructure in a ceramics sample, the two ceramics presented similar total
 transmission and light output.

By selectively exciting  $Eu^{3+}$  at the two cationic sites of the sesquioxide structure 3 we could observe emission of the dopant ion at both sites in the  $Lu_2O_3:Eu^{3+}$  and in the 4  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  ceramics though a very different repartition of  $Eu^{3+}$  in the two 5 sites was observed according to the composition. The decay time of the emitting 6 excited  ${}^{5}D_{0}$  state of Eu<sup>3+</sup> was found very different from one site to the other. Light 7 emitted from the europium ions located in the non centro-symmetric  $C_2$  site almost 8 totally decayed within  $3.\tau_{C2}$ , i.e. 4-5 ms in Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> and 3-4 ms in 9  $(Lu_{0.5}Gd_{0.5})_2O_3$ : Europium ions occupying S<sub>6</sub> sites needed  $3.\tau_{S6}$ , i.e. 14-15 ms in 10  $Lu_2O_3$  and 11-12 ms in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  to emit the quasi-totality of their 11 luminescence. Hence the repartition of dopant ions amongst the C2 and S6 sites is of 12 13 great importance as far as the time response of the scintillator is concerned. Even in 14 the hypothesis where no delay is introduced by charge trapping, the sole influence of dopant repartition among the two sites affects what was measured here as the "short 15 afterglow". Indeed the afterglow measured here up to 20 ms was found more 16 important for  $Lu_2O_3:Eu^{3+}$  than for  $(Lu_0 \, {}_5Gd_0 \, {}_5)_2O_3:Eu^{3+}$ . This is directly related with 17 the decay times of  $Eu^{3+}$  which were found shorter in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  than in 18  $Lu_2O_3:Eu^{3+}$  at both sites. This can be understood as the presence of gadolinium 19 20 introduces an asymmetry which may relax the selection rules for 4f-4f transitions and therefore increase the probability in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  of the otherwise forbidden 21 22 transitions.

Moreover, we showed that the population of  $S_6$  sites by  $Eu^{3+}$  is much lower in (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> than in Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>. As the decay of Eu<sup>3+</sup> luminescence is at least 3 times longer in S<sub>6</sub> than in C<sub>2</sub> site, this fact will result in a shorter decay of Eu<sup>3+</sup>

luminescence measured in (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> compared to Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>. The 1 different  $Eu^{3+}$  localization in sites of  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  relative to  $Lu_2O_3:Eu^{3+}$  can 2 be understood by considering the sizes of the  $Lu^{3+}$ ,  $Gd^{3+}$  and  $Eu^{3+}$  cations. Levy *et al.* 3 [36] showed that in cubic sesquioxides, an isovalent cationic dopant such as  $Eu^{3+}$ 4 preferably substitutes the host cation at the  $C_2$  site if it is smaller than the host cation 5 and at the  $S_6$  site otherwise. This would originate from the presence around the cation 6 in C<sub>2</sub> of bonds both shorter and longer than the average distance whereas all the 7 distances are equal in S<sub>6</sub>. The shorter bonds in C<sub>2</sub> would therefore favor the presence 8 of smaller cations. In Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>, Eu<sup>3+</sup> being larger than Lu<sup>3+</sup> would preferentially 9 occupy S<sub>6</sub>. In  $(Lu_{0.5}Gd_{0.5})_2O_3$  the average cationic size is bigger than in  $Lu_2O_3$  so the 10 affinity of  $Eu^{3+}$  for S<sub>6</sub> should decrease. 11

Finally we showed that the "long afterglow" was also higher in  $Lu_2O_3:Eu^{3+}$  than in 12  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ . The TSL glow curves were found consistent with this 13 observation as the TSL intensity was highly reduced in  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  compared 14 to  $Lu_2O_3:Eu^{3+}$  over the whole temperature range. However we showed that the main 15 TSL peak at around 200 K may be more specifically responsible for afterglow at 16 around 100-300 ms. Trojan et al. [20] recently showed that the afterglow in 17  $Lu_2O_3:Eu^{3+}$  was mainly related to  $Eu^{3+}$  at S<sub>6</sub> sites. Either the energetic location of  $Eu^{3+}$ 18 at S<sub>6</sub> site was more favorable to the transfer from the trap to the luminescent center or 19 the traps were located in the vicinity of  $Eu^{3+}$  at S<sub>6</sub> sites [20]. We showed here that 20  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  favored the location of  $Eu^{3+}$  ions more in  $C_2$  sites and less in  $S_6$ 21 22 sites relative to the host Lu<sub>2</sub>O<sub>3</sub>. Following the argument of Trojan et al., this would 23 result in less afterglow, and that is precisely what was observed here (see Figure 3).

Alternatively the decrease of TSL intensity may be explained by a reduction in stress and therefore of defects related to  $Eu^{3+}$  introduction into the host. One can

briefly analyze the induced distortion of the  $Lu_2O_3$  host when introducing  $Eu^{3+}$  as a 1 2 dopant relatively to distortion occurring in the  $(Lu_{0.5}Gd_{0.5})_2O_3$  host. First, one can observe an increase of the measured unit cell parameter from 10.391 Å for Lu<sub>2</sub>O<sub>3</sub> to 3 10.602 Å for  $(Lu_{0.5}Gd_{0.5})_2O_3$ , in good agreement with the variation of the ionic radii 4 of the constituent (0.95 Å, 0.938 Å and 0.848 Å for Eu<sup>3+</sup>, Gd<sup>3+</sup> and Lu<sup>3+</sup>, 5 respectively). The distortion occurring when introducing  $Eu^{3+}$  ions in  $Lu_2O_3$  can be 6 7 estimated by calculating the ratio of the lattice parameters of Eu<sub>2</sub>O<sub>3</sub> (no distortion and a = 10.866 Å) and Lu<sub>2</sub>O<sub>3</sub>. In this case, the ratio is 4.5%. When introducing Eu<sup>3+</sup> in the 8 (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub> host, the ratio becomes 2.5%. This effect indicates that for 9  $(Lu_{0.5}Gd_{0.5})_2O_3$  compounds the introduction of Eu<sup>3+</sup> occurs with limited distortions 10 11 with regard to the  $Lu_2O_3$  host.

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### 13 Conclusion

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15 We propose a transparent ceramics prepared from the mixed sesquioxide  $(Lu_{0.5}Gd_{0.5})_2O_3$  doped with trivalent europium as a potential new scintillator with 16 improved time response characteristics relative to the well-known  $Lu_2O_3:Eu^{3+}$ . 17  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  presents a density of about 8.4 g/cm<sup>3</sup>, which still lies amongst the 18 19 highest densities of existing scintillators and therefore is very favorable for efficient 20 X-rays absorption within a small thickness. The measured total transmission was 21 found close to the maximum value (81 %) while no laser quality polishing of the 22 samples has been done (this is usually the case in the scintillator field where the main 23 purpose is to extract the maximum light output).

With afterglow and TSL measurements we demonstrated the advantages of  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  ceramics over  $Lu_2O_3:Eu^{3+}$ . On the one hand  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$ 

1 presents a faster intrinsic decay time for  $Eu^{3+}$  and on the other hand the ceramics 2 shows a reduced afterglow over the hundreds of milliseconds time range and a 3 reduced TSL intensity over the 10 K - 650 K temperature range.

These improved properties were explained in two terms. First  $Eu^{3+}$  intercalation in (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> most probably leads to less distortion than  $Eu^{3+}$  in Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> as a better cationic size match occurs. Hence less defects in the material may be susceptible to trap charges during irradiation and delay their subsequent transfer and recombination at Eu<sup>3+</sup> ions. This therefore reducesTSL intensity and afterglow.

9 Secondly and most of all we demonstrated that (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub> composition allows a different repartition of  $Eu^{3+}$  ions amongst the  $C_2$  and  $S_6$  cationic sites of the 10 sesquioxide structure.  $\text{Eu}^{3+}$  ions at both sites in  $\text{Lu}_2\text{O}_3$ :  $\text{Eu}^{3+}$  and  $(\text{Lu}_{0.5}\text{Gd}_{0.5})_2\text{O}_3$ :  $\text{Eu}^{3+}$ 11 ceramics have been characterized in terms of energy level positions and kinetics of the 12 fluorescence by selectively exciting  $Eu^{3+}$  at the two cationic sites of the sesquioxide 13 structure. The  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  compound was shown to greatly favor 14 intercalation of  $Eu^{3+}$  in  $C_2$  site over  $S_6$ .  $Eu^{3+}$  at  $C_2$  site presents a fast decay (1 ms and 15 1.4 ms for  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  and  $Lu_2O_3:Eu^{3+}$ ), respectively while the decay 16 constant of  $Eu^{3+}$  at S<sub>6</sub> site is almost 4 times longer (3.8 ms and 4.7 ms respectively for 17  $(Lu_{0.5}Gd_{0.5})_2O_3:Eu^{3+}$  and  $Lu_2O_3:Eu^{3+}$ ). Thus favoring the substitution by  $Eu^{3+}$  at a  $C_2$ 18 site was found to decrease the effective decay time of the ceramics. Additionally the 19 different repartition of  $Eu^{3+}$  at  $C_2$  and  $S_6$  sites in the two different ceramics should also 20 have an effect on afterglow as  $Eu^{3+}$  at S<sub>6</sub> site may be responsible for afterglow. 21 22 Further work is now required to determine with more accuracy the light yield and the 23 energy resolution of these promising scintillators.

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- 1 Tables
- 3 Table 1 Pseudo-decay times distinguished in the afterglow curves of Lu<sub>2</sub>O<sub>3</sub>:Eu and
- $(Lu_{0.5}Gd_{0.5})_2O_3$ : Eu ceramics.

	$\tau_1$ (ms)	$\tau_2$ (ms)	$\tau_3$ (ms)
Lu <sub>2</sub> O <sub>3</sub> :Eu	1.1	3.9	340
(Lu <sub>0.5</sub> Gd <sub>0.5</sub> ) <sub>2</sub> O <sub>3</sub> :Eu	0.9	3.1	210

- **Table 2** Energy position of  $Eu^{3+}$  levels in  $Lu_2O_3$  :Eu and in  $(Lu_{0.5}Gd_{0.5})_2O_3$  :Eu (in
- 9 cm<sup>-1</sup>)

Level energy	$^{7}F_{0}$	${}^{7}F_{1a}$	${}^{7}F_{1b}$	$^{7}F_{1c}$	$^{7}F_{1}$	${}^{5}D_{0}$
(cm <sup>-1</sup> ) Site and compound					barycenter	
$C_2$ in $Lu_2O_3$	0	187	365	556	369	17 208
$S_6$ in Lu <sub>2</sub> O <sub>3</sub> (hyp. 1)	0	139	458	-	245 (hyp. 1A) 352 (hyp. 1B)	17 321 <sup>32</sup>
$S_6$ in Lu <sub>2</sub> O <sub>3</sub> (hyp. 2)	0	139	458	542	380	
C <sub>2</sub> in (Lu <sub>0.5</sub> Gd <sub>0.5</sub> ) <sub>2</sub> O <sub>3</sub>	0	176	349	545	357	17 212

## 1 Figure captions

Figure 1. Total transmission spectra of  $Lu_2O_3$ : 6%  $Eu^{3+}$  and  $(Lu_{0.5}Gd_{0.5})_2O_3$ : 7%  $Eu^{3+}$ ceramics. Main transitions from the fundamental level <sup>7</sup>F<sub>0</sub> towards the indicated excited levels of  $Eu^{3+}$  are given on the figure.

5

Figure 2. X-ray excited luminescence spectra of  $Lu_2O_3$ : 6%  $Eu^{3+}$  and  $(Lu_{0.5}Gd_{0.5})_2O_3$ 7 : 7%  $Eu^{3+}$  ceramics relative to commercial GOS :  $Pr^{3+}$ . The extraction of light 8 between GOS :  $Pr^{3+}$  and sesquioxides should not be compared as sesquioxides are 9 transparent whereas GOS :  $Pr^{3+}$  is only slightly translucent.

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11 Figure 3. Afterglow curves of Lu_2O_3:Eu and (Lu_{0.5}Gd_{0.5})_2O_3:Eu ceramics.
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Figure 4. Thermally Stimulated Luminescence (TSL) glow curves of  $Lu_2O_3$ : Eu and ( $Lu_{0.5}Gd_{0.5})_2O_3$ : Eu ceramics after X-ray irradiation at 10 K. Heating rate : 20 K / minute.

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17 Figure 5. Cristal structure of  $Lu_2O_3$  showing the symmetry of the two cationic sites  $C_2$ 18 and  $S_6$ .

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Figure 6. Laser-excited luminescence spectra of  $Lu_2O_3$ : 6%  $Eu^{3+}$  excited at four different wavelengths between 525 nm and 530 nm with  $\lambda_1 > \lambda_2 > \lambda_3 > \lambda_4$  and recorded at 10 K.

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Figure 7. Position of the  ${}^{7}F_{1}$  barycenter versus  ${}^{5}D_{0}$  level (in red) for Eu $^{3+}$  in the two sites of Lu<sub>2</sub>O<sub>3</sub> compared to the barycenter law (in black) from  ${}^{27}$ . In blue are drawn the two ruled out hypothesis for position of Eu $^{3+}$  in S<sub>6</sub> site.

1 Figure 8. Laser-excited luminescence spectra of  $(Lu_{0.5}Gd_{0.5})_2O_3 : 7\% Eu^{3+}$  excited at 2 three different wavelengths between 525 nm and 530 nm with  $\lambda_1 > \lambda_2 > \lambda_3$  and 3 recorded at 10 K.

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Figure 9. Decay profiles of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1a}$  emission excited at 10K *via* the  ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ transition at 581.2 nm in Lu<sub>2</sub>O<sub>3</sub>:Eu and 581.3 nm in (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu for Eu<sup>3+</sup> in C<sub>2</sub> and at 582.6 nm for Lu<sub>2</sub>O<sub>3</sub>:Eu and 582.9 nm in (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu for Eu<sup>3+</sup> in S<sub>6</sub>. The emission wavelengths are (i) for Lu<sub>2</sub>O<sub>3</sub>:Eu, 582.7 nm and 587.7 nm for Eu<sup>3+</sup> in S<sub>6</sub> and C<sub>2</sub> sites, respectively (ii) for (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu, 582.9 nm and 588.1 nm for Eu<sup>3+</sup> in S<sub>6</sub> and C<sub>2</sub> sites, respectively.

12 Figure 10. Time-resolved luminescence spectra of Lu<sub>2</sub>O<sub>3</sub>:Eu (A) and 13 (Lu<sub>0.5</sub>Gd<sub>0.5</sub>)<sub>2</sub>O<sub>3</sub>:Eu (B) ceramics recorded at 10 K for time intervals indicated on the 14 figure. Ceramics were excited via the  ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$  transition at 525 nm- 530 nm.

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#### Figures

#### Figure 1







# 3 Figure 3









- 2 3

### Figure 5





#### Figure 6













Figure 8





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# **Figure 10**







