Composition and properties tailoring in Mg^{2+} codoped non-stoichiometric LuAG:Ce,Mg scintillation ceramics

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Abstract:

A comprehensive study of the optical, radioluminescence and scintillation properties of both the Lu^{3+} rich and Lu^{3+} deficient non-stoichiometric $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ($\text{Lu}_{3+x}\text{Al}_5\text{O}_{12}\text{:Ce,Mg}$, $x = -4, -1, +1$ and $+4$ at.%) ceramics are performed, completed further by the microstructure and defects characterization. Small deviation from the stoichiometric composition as well as Mg^{2+} codoping play a crucial role in ceramic transparency, radioluminescence intensity and the timing characteristics of scintillation response. The Lu_{Al} antisite defects could be suppressed efficiently by controlling Lu^{3+} content below stoichiometry of LuAG host. MgO (Mg^{2+} ions) as effective sintering aids, can improve both the optical quality and scintillation performance (light yield, scintillation decay times and the ratio of fast decay components). We generally discuss the composition dependence of defects and properties tailoring. We also performed the systematic comparative study with the

stoichiometric LuAG:Ce,Mg ceramic and the commercial BGO and LuAG:Ce single crystals.

Key words: Non-stoichiometric ceramics, LuAG:Ce,Mg scintillator, Mg^{2+} co-dopant, antisite defects, afterglow

1. Introduction

High R&D activity in the field of inorganic scintillators employed for ionizing radiation detection has very long history, and has been triggered mainly by the pressing needs of modern medical imaging, high energy physics, homeland security and environmental applications during the last two decades [1, 2]. Therefore, a number of new or improved scintillators or phosphors such as Ce and Pr doped single crystals, novel semiconductor composites, metal-organic frameworks and phase-separated materials systems, have been discovered and studied in depth [3-9]. Cerium doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG:Ce) aluminum garnet showed excellent physical and chemical properties and promising scintillation performance among them, e.g. high density of 6.73 g cm^{-3} , suitably positioned emission band peaking at 500–550 nm and short scintillation decay times of $\sim 60 \text{ ns}$ in the dominant component of scintillation response. High theoretical light yield value of $\sim 60000 \text{ photons/MeV}$ was forecasted [10, 11]. However, due to the very high melting point temperature of LuAG garnet and the radius mismatch between the host cations and the Ce^{3+} or Pr^{3+} dopants, the Lu_{Al} antisite defect (AD) related shallow traps and chemical segregation can occur, respectively, during crystal growth [12-14]. As a result, the highest reported light

yield for LuAG:Ce single crystals (~26000 ph/MeV [12]) and those of optical ceramics (~25000 ph/MeV [8,11,14]) are far below the theoretical values. Moreover, high intensity of slower decay components and strong afterglow intensity degrade the scintillation performance further [15, 16].

Recently, “band gap engineering” and “defect engineering” strategies were applied to single crystals of garnet structure for their optimization and an amazingly high light yield up to 58000 ph/MeV has been achieved in $\text{Gd}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}$ (GAGG:Ce) multicomponent garnet crystal [17-20]. We found [20-22] that the off-stoichiometric adjustment was also an efficient approach to influence the densification process and Lu_{Al} AD creation, thus improving the optical quality and/or the scintillation performance of LuAG:Ce optical ceramics [21]. By introducing an excess of Lu^{3+} ions as self-sintering aid, highly transparent $\text{Lu}_{3+x}\text{AG}:\text{Ce}$ ($x = 1, 2, 3$ and 4 at.%) ceramics with good scintillation properties could be fabricated successfully. However, Lu_{Al} AD related shallow electron traps were observed in these ceramics by radioluminescence (RL) and thermoluminescence (TSL) measurements [22]. On the contrary, Lu_{Al} AD could be suppressed effectively by reducing the content of Lu^{3+} content, leading to a great improvement on RL and light yield properties. Unfortunately, the optical quality of Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics was very low [23]. Therefore, sintering aids appear critical in LuAG:Ce ceramics to achieve both high optical transparency and scintillation performance.

In the recent study [8], it was positively demonstrated that divalent Mg^{2+} ions co-dopant could not only improve the optical quality of LuAG:Ce ceramics, but also

drive the partial conversion of Ce^{3+} to Ce^{4+} [24]. These Ce^{4+} ions, although not luminescent under direct photoluminescence excitation, act as precursors of temporary Ce^{3+} centers that are created during irradiation with ionizing radiation and contribute to fast scintillation part in parallel with stable Ce^{3+} centers [9, 25]. The positive outcomes served as our motivation to apply these divalent Mg^{2+} codoping ions to the non-stoichiometric LuAG:Ce ceramics.

Therefore, in this work, Mg^{2+} codoped non-stoichiometric LuAG:Ce,Mg ceramics were designed and fabricated to suppress the formation of Lu_{Al} AD, to improve optical transparency and to act positively on the scintillation response by creation of stable Ce^{4+} centers. Optical absorption, RL spectra, TSL glow curves, scintillation characteristics including light yield, scintillation decay, afterglow intensity and also the microstructure of the ceramics were measured to reveal systematically the influence of simultaneous stoichiometric deviation and Mg^{2+} co-doping. The material composition-defect-scintillation properties relationship was revealed. The discussion on the composition and properties tailoring includes a comparative study with the latest commercial BGO and LuAG:Ce single crystals.

2. Experimental

$\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} deviation from stoichiometry content ($x = -4, -1, +1$ and $+4$ at.%) were fabricated by solid state reaction method and further optimized by an air-annealing process. Commercial powders of 4N purity CeO_2 and $\alpha\text{-Al}_2\text{O}_3$ were weighed according to the chemical stoichiometry of

$(\text{Lu}_{1-y-z}\text{Ce}_y\text{Mg}_z)_3\text{Al}_5\text{O}_{12}$, the concentration of Ce^{3+} and Mg^{2+} was $y = 0.3$ at.% and $z = 0.2$ at.% respectively. Commercial Lu_2O_3 powders of 4N purity were weighed with -4, -1 at% in deficiency and +1, +4 at.% in excess, respectively. The starting materials were mixed and ball-milled by highly pure Al_2O_3 ceramic balls with anhydrous alcohol for 12 h. After stove-dried and mesh-sieved, the powder mixtures were dry-pressed to form a disk with a diameter of 18 mm and subsequently isostatically cold-pressed at 250 MPa. The powder compacts were vacuum sintered in a vacuum tungsten wire furnace at 1860 °C for 10-30 h and then air-annealed at 1450 °C for 20 h. Finally, both faces of the obtained oxide ceramics were polished to achieve sample thickness of 0.5-1 mm which was further used in optical experiments. A stoichiometric LuAG:0.3%Ce,0.2%Mg ceramic [9], commercial LuAG:Ce single crystal grown by Czochralski method (by Crytur Ltd., Turnov, Czech Republic), as well as a Bridgman grown BGO single crystal provided by SICCAS Corp. (Shanghai, China) were used as reference samples.

Absorption spectra in the 200-800 nm range were measured using a Varian Cary 5000 spectrometer (Varian Inc., USA). The microstructure of the ceramics was observed with a S-4800 field emission scanning electron microscope (SEM, Hitachi, Japan). RL spectra were measured under an X-ray tube excitation (Seifert GmbH, Germany, 40 kV, 15 mA) at the custom-made 5000M model Horiba Jobin Yvon spectrofluorometer (Horiba Jobin Yvon, Co., France) equipped with a TXB-04 photon counting detector (IBH Scotland). For afterglow measurements, samples were irradiated for few minutes by X-rays with the same X-ray tube (operated at 40 kV) at

room temperature, after which the X-ray was cut off and the luminescence emitted from samples was recorded continuously as a function of time. TSL measurements were performed in the 77-500 K temperature range in the cryostat Optistat (Oxford Instruments) after X-ray irradiation at 77 K (operated at 40 kV for 15 minutes). A 5 K/min heating rate was adopted.

Scintillation light yield was measured using hybrid photodetectors (HPMT hybrid photomultipliers DEP PP0470 or PP0475B ones, DEP, Netherlands) [21,22]. Measured ceramics are characterized by wide emission bands peaking in the green range where quantum efficiency of HPMT is around or below 10 % and the overall accuracy of light yield measurements is $\pm 5\%$. Scintillation decay curves were obtained by using the Hamamatsu PMT R375 (Hamamatsu Co., Japan) and TDS3052 digital oscilloscope (Tektronix Inc., USA) under excitation by 662 keV γ -ray photons of ^{137}Cs source. To enhance collection of scintillation photons a teflon reflection tape was used to cover the measured samples. Good optical coupling between samples and HPMT photocathode window was ensured by Q2-3067 optical grease (Dow Corning Co., USA).

3. Results and discussion

3.1 Optical properties

The photographs of non-stoichiometric $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} deviation from stoichiometry are shown in **Fig. 1** (from left to right, $x = -1, -4, +1$ and $+4$ at.%, respectively). When compared with the non-stoichiometric $\text{Lu}_{3\pm x}\text{AG:Ce}$

ceramics reported before [23], the optical quality of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics are significantly improved after introducing the MgO sintering aid.

Absorption spectra of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics ($x = -4, -1, 0, +1, \text{ and } +4$ at.%) are shown in **Fig. 2**. The absorption peaks related to the Ce^{3+} and Ce^{4+} centers were affected remarkably by various Lu^{3+} deviation. Therefore, the relative concentrations of stable Ce^{3+} and Ce^{4+} centres, oxygen vacancies and O^- centres introduced by Mg^{2+} codopant and Lu^{3+} deviation may play a key role in the RL intensity of the ceramics. Furthermore, it is reasonable to assume that some other unknown defect may come out in Lu^{3+} rich or Lu^{3+} deficient $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics due to the complex garnet structure.

Fig. 1. Photographs of non-stoichiometric $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics. From left (a) to right (d), the deviation of Lu^{3+} from stoichiometry content (x value) is -1, -4, +1, and +4 at.%, respectively.

Fig.2. Optical absorption spectra of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, 0, +1, and +4 at.%.

3.2 Radioluminescence spectra

Fig. 3 (a) shows the RL spectra of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} deviation from stoichiometric content ($x = -4, -1, +1, \text{ and } +4$ at.%) and those of the commercial BGO and LuAG:Ce reference single crystals. The emission transitions $5d_1 \rightarrow 4f$ ($^2F_{7/2, 5/2}$ doublet) of Ce^{3+} centers are peaking at ~ 520 nm and were observed in all LuAG:Ce ceramic samples and in LuAG:Ce single crystal (see Fig. 3(a)). Moreover, the Lu_{Al} AD related luminescence could be also detected in the UV region. This radioluminescence is very strong in the LuAG:Ce single crystal and much weaker in ceramic analogues, as shown in the inset of Fig 3(a). Dependence of RL integrated intensity of emission band corresponding to the Ce^{3+} centers (440 - 740 nm) and Lu_{Al} AD (250 - 430 nm) on the relative content of Lu^{3+} is shown in Fig. 3(b). It is observed that the RL intensity of Ce^{3+} emission centers decreases and that of Lu_{Al} AD related luminescence increases as the content of Lu^{3+} (x values) in $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ increases. This indicates that the formation of Lu_{Al} AD can be suppressed effectively by decreasing the fabrication temperatures and the content of Lu^{3+} in $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics. However, the RL intensity of Ce^{3+} centers of stoichiometric LuAG:Ce,Mg ceramic was higher than that of the non-stoichiometric ones. The exact reasons and their clarification need further study.

Fig. 3. (a) RL spectra of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} content; (b) dependence of RL integrated intensity of the Ce^{3+} centers and Lu_{Al} AD on the relative content of Lu^{3+} , the values of stoichiometric LuAG:Ce,Mg optical ceramic and LuAG:Ce single crystal are also given.

3.3. Scintillation properties

In **Fig. 4**, the light yield values (part a) and their relative ratios (part b) of Lu^{3+} rich and Lu^{3+} deficient $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics are given as a function of shaping time from 0.5 μs to 10 μs . Here, the values for the best stoichiometric LuAG:Ce,Mg ceramic and the commercial LuAG:Ce single crystal are also reported. Similar to the trend of RL intensity, the light yield values tend to decrease as the amount of Lu^{3+} ions increases. Light yield values of the Lu^{3+} deficient ceramics are much higher than that of LuAG:Ce single crystal in the whole shaping time range, thanks to the suppression of Lu_{Al} AD. Specifically, the 4 at.% Lu^{3+} deficient $\text{Lu}_{3-4\%}\text{AG:Ce,Mg}$ ceramic displays the highest light yield among all the non-stoichiometric samples. It reaches ~24200 ph/MeV when using a short shaping time of 1 μs and this value is

1.48 times higher than that of the LuAG:Ce single crystal (~ 16390 ph/MeV). It is worth noting that although the light yield value of Lu^{3+} deficient $\text{Lu}_{3-4\%}\text{AG:Ce,Mg}$ ceramic are lower than that of the best stoichiometric LuAG:Ce,Mg ceramics when measured at short shaping times, it becomes higher at shaping time longer than $4\ \mu\text{s}$. Following Fig. 4(b) showing the relative light yield values measured with different shaping times, the scintillation response can be classified clearly into 4 groups for all the measured samples. The difference of light yield values between the shortest $0.5\ \mu\text{s}$ and the longest $10\ \mu\text{s}$ shaping time value in stoichiometric LuAG:Ce,Mg ceramics, Lu^{3+} rich $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ones ($x = +1, +4$ at.%), Lu^{3+} deficient ones ($x = -1, -4$ at.%) and the LuAG:Ce single crystal is $\sim 15\%$, $\sim 50\%$, 75% and $\sim 110\%$, respectively. Such phenomenon may be explained by the influence of Lu^{3+} content on the defect creation and the distinct role of these defects on RL and light yield characteristics, as it will be discussed below.

Fig. 4. (a) Light yield values of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} deviation from stoichiometric content and the commercial LuAG:Ce reference single crystal as a function of shaping time in the range 0.5 – 10 μs ; (b) Relative light yield of samples from (a) obtained by normalizing curves in (a) by the LY for 0.5 μs shaping time.

Fig. 5 shows the scintillation decay curves of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, 0, +1, and +4 at.%. The double exponential fits of the decay curves were accomplished and the results are included in Table 1. All the samples show scintillation decays consisting of the fast and slow components corresponding to the prompt and delayed radiative recombination at stable Ce^{3+} and Ce^{4+} centers, respectively. It is observed that the effect of Lu^{3+} non-stoichiometry on the scintillation decay time of fast component is relatively weak, since all the non-stoichiometric samples show a value of ~58 ns. The stoichiometric LuAG:Ce,Mg ceramic, by contrast, shows somewhat faster decay time of ~52 ns while the commercial LuAG:Ce single crystal shows a slower decay time of ~70 ns. However, the relative intensity of fast component are $I_1 = 60\%$ and 68% for 1 at.%

and 4 at.% Lu^{3+} rich ceramic, respectively. These values are much higher than that of the Lu^{3+} deficient ones where $I_1 \sim 50\%$. For the stoichiometric LuAG:Ce,Mg ceramic $I_1 = 49\%$ and for the LuAG:Ce single crystal $I_1 = 34\%$ (see Table 1). This clearly shows that less “slow scintillation light” is generated in all ceramic samples compared to single crystal and it can be further tuned by adjusting the Lu^{3+} content in $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics.

Fig. 5. Normalized scintillation decay curves of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, 0, +1, and +4 at.% and the LuAG:Ce single crystal samples (excitation ^{137}Cs , 662 keV).

3.4. Afterglow time properties

Afterglow is also an important scintillation parameter for medical imaging applications, such as CT and many high-speed imaging. The afterglow characteristics of $\text{Lu}_{3+x}\text{AG:Ce}$ ceramics with various Lu^{3+} deviation from stoichiometry and that of the reference LuAG:Ce single crystal are also measured together with that of BGO single crystal which is characterized by extremely low afterglow. Apparently, the

afterglow intensity is significantly reduced by the combination of Mg^{2+} codoping and the Lu^{3+} deviation. Stoichiometric LuAG:Ce,Mg ceramic and Lu^{3+} deficient $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics ($x = -1, -4$ at.%) show much lower afterglow intensities when compared to the LuAG:Ce single crystal. Surprisingly, an ultralow signal level, approaching that of the BGO standard sample, was obtained in Lu^{3+} rich $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ($x = +1, +4$ at.%) ceramics. The results are displayed in **Fig. 6** and the relative values of afterglow intensity at 4 ms after X-ray cut off (the signal level with X-rays ON is normalized to 1) are reported in Table 1.

Fig. 6. Spectrally unresolved afterglow time profiles of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} deviation content from stoichiometry, BGO and LuAG:Ce single crystals. Visually higher level of afterglow signal in few channels of BGO crystal is due to the counting detection technique and lower intensity of BGO scintillation before the X-ray cutoff.

Table 1. Sample characteristics, light yield values (with shaping time of 1 μs) and scintillation decay times (excitation by 662 keV of ^{137}Cs) of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$

ceramics and the LuAG:Ce single crystal. A double-exponential function $I(t) = \sum A_i \exp [-t/\tau_i]$ $i=1, 2$ is used to fit the scintillation decay curves and the relative intensity of each component $I_i = A_i \tau_i / \sum A_j \tau_j \times 100$ ($i, j = 1, 2$) is reported as well.

Lu deviation	Size (mm)	LY(ph/MeV)	τ_1 (ns)/ I_1 (%)	τ_2 (ns)/ I_2 (%)	Afterglow at 4 ms (%)
-1%	Ø15×1	21900	58/51	870/49	1.52
-4%	Ø15×1	24200	59/50	910/50	0.93
+1%	Ø15×1	16100	57/60	700/40	0.41
+4%	Ø15×1	16900	56/68	570/32	0.37
0	Ø15×0.5	24550	52/49	1100/50	0.54
LuAG:Ce sc	Ø10×1	16390	70/34	1700/66	1.26

3.5. Microstructure and role of defects

Theoretically, there is a number of defect mechanisms that help to conserve site balance, charge, and mass while facilitating deviations from the stoichiometric LuAG composition. However, the lowest energy mechanisms for Y_2O_3 and Al_2O_3 excess were reported as follows [26]:

The nonstoichiometry is compensated only by cation antisites, the simplest defect structure in YAG garnet. Furthermore, it was reported that the Eq. (1) was valid for higher Y_2O_3 concentration (>1 mol%) while Eq.(2) was valid only for low Al_2O_3 concentrations (< 0.2 mol%).

To investigate the defects and the effect of Lu^{3+} deviation from stoichiometry on

the densification of the ceramics, the SEM image of the fracture microstructure of both Lu^{3+} deficient and Lu^{3+} rich $\text{Lu}_{3+x}\text{AG}:\text{Ce},\text{Mg}$ ceramics were performed, as shown in **Fig. 7**. As compared to the Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics which we reported before [23], very dense, almost pore-free microstructures with much less of Al_2O_3 or Al-rich second phase compounds are obtained after Mg^{2+} codoping. This result verifies the positive role of MgO as sintering aids during the fabrication process. As these second phases work as scattering centers, it is consistent with higher level of absorbance measured at the $\text{Lu}_{3-4\%}\text{AG}:\text{Ce},\text{Mg}$ ceramic in Fig.2. In the Lu^{3+} rich $\text{Lu}_{3+x}\text{AG}:\text{Ce},\text{Mg}$ ceramics, no obvious secondary phase is observed. This result coincides with the defect status of nonstoichiometric YAG we mentioned above, in which Y_2O_3 has a broader nonstoichiometric range than Al_2O_3 .

Fig. 7. SEM imaging of the fracture microstructure of the $\text{Lu}_{3+x}\text{AG}:\text{Ce},\text{Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, +1, and +4 at.%.

Finally, TSL measurements were performed with the aim to monitor the role of shallow and deep traps in the RL, light yield and afterglow characteristics of the samples above described. The TSL glow curves in the 77-500 K temperature range are given in **Fig. 8**. First of all, a monotonically decreasing signal is observed in all the ceramics, accompanied by three dominant peaks located at 230 K, 280 K and 320

K. Some weak peaks at around 430 K and 470 K can be also observed, see the TSL glow curves in logarithmic scales in the inset of the **Fig. 8**. Besides, the TSL signals below 190 K are very broad, which point to the existence of large variety of different defects including Lu_{Al} AD giving rise to a broad distribution of trap levels [27] where also tunneling recombination processes may exist [28]. Furthermore, a surprisingly lower TSL signal was observed in Lu^{3+} rich $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics when compared to the Lu^{3+} deficient ones. This result is consistent with the improved afterglow characteristics of Lu^{3+} rich ceramics shown in Fig.6. Due to the much lower RL intensity and light yield values of Lu^{3+} rich $\text{Lu}_{3-x}\text{AG:Lu,Mg}$ ceramics, we speculate that very deep traps which could not be observed in the inspected temperature range of TSL (their T_{max} could be above the measurement limit) may exist in these ceramics. Other non-radiative channels could also exist competing with luminescent centers in the scintillation process. In addition, TSL signal peaking at 320 K, which is dominating in most of the ceramics including the stoichiometric LuAG:Ce,Mg ceramics we reported before [9], seems quite weak in Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG:Ce,Mg}$ ceramics. The changes of defect-related traps acting in this temperature range may be the reason that the light yield of these Lu^{3+} deficient ceramics at longer shaping times is even higher than that of best stoichiometric LuAG:Ce,Mg ceramics.

Fig. 8. TSL glow curves of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, +1, and +4 at.%. In the inset there are the same glow curves displayed in logarithmic scales.

4. Conclusions

In this contribution, the Lu^{3+} deficient and Lu^{3+} rich non-stoichiometric $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ($x = -4, -1, +1$ and $+4$ at.%) transparent ceramics codoped with Mg are fabricated successfully by solid state reaction method. We have shown that the optical quality, radioluminescence intensity and the scintillation response of LuAG:Ce,Mg ceramics are drastically influenced by the Mg^{2+} codopant and LuAG stoichiometry. In the case of Lu^{3+} deficiency, Lu_{Al} antisite defect could be suppressed efficiently. The Lu-defficient non-stoichiometric $\text{Lu}_{3-x}\text{AG:Ce,Mg}$ ceramic displays a higher light yield up to 24200 ph/MeV, together with an improved optical transparency after Mg^{2+} codoping. In the case of Lu^{3+} excess, a relative lower light yield of 16900 ph/MeV, which is comparable with the commercial LuAG:Ce single crystal, was obtained. As another advantage an extremely reduced afterglow intensity was obtained in these ceramics. By comparing light yield values with different

shaping times and scintillation decays, it turns out that both the Lu^{3+} rich and Lu^{3+} deficient $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics display a more intense and faster scintillation response than the commercial LuAG:Ce single crystal. A broader comprehension about Lu_{Al} antisite defect and chemical-physical modification was achieved in ceramics after studying their microstructure and the defect-related traps. However, these results also suggest that full optimization in these ceramic scintillators has not yet been reached despite excellent performance already obtained.

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Figure Captions

Fig. 1. Photographs of non-stoichiometric $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics. From left (a) to right (d), the deviation of Lu^{3+} from stoichiometry content (x value) is -1, -4, +1, and +4 at.%, respectively.

Fig.2. Optical absorption spectra of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, 0, +1, and +4 at.%.

Fig. 3. (a) RL spectra of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} content; (b) dependence of RL integrated intensity of the Ce^{3+} centers and Lu_{Al} AD on the relative content of Lu^{3+} , the values of stoichiometric LuAG:Ce,Mg optical ceramic and LuAG:Ce single crystal are also given.

Fig. 4. (a) Light yield values of $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} deviation from stoichiometric content and the commercial LuAG:Ce reference single crystal as a function of shaping time in the range 0.5 – 10 μs ; (b) Relative light yield of samples from (a) obtained by normalizing curves in (a) by the LY for 0.5 μs shaping time.

Fig. 5. Normalized scintillation decay curves of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, 0, +1, and +4 at.% and the LuAG:Ce single crystal samples (excitation ^{137}Cs , 662 keV).

Fig. 6. Spectrally unresolved afterglow time profiles of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with various Lu^{3+} deviation content from stoichiometry, BGO and LuAG:Ce single crystals. Visually higher level of afterglow signal in few channels of BGO crystal is due to the counting detection technique and lower intensity of BGO scintillation before the X-ray cutoff.

Fig. 7. SEM imaging of the fracture microstructure of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, +1, and +4 at.%.

Fig. 8. TSL glow curves of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics with Lu^{3+} deviation from stoichiometric content of -4, -1, +1, and +4 at.%. In the inset there are the same glow curves displayed in logarithmic scales.

Tables

Table 1. Sample characteristics, light yield values (with shaping time of 1 μs) and scintillation decay times (excitation by 662 keV of ^{137}Cs) of the $\text{Lu}_{3+x}\text{AG:Ce,Mg}$ ceramics and the LuAG:Ce single crystal. A double-exponential function $I(t) = \sum A_i \exp[-t/\tau_i]$ $i=1, 2$ is used to fit the scintillation decay curves and the relative intensity of each component $I_i = A_i \tau_i / \sum A_j \tau_j \times 100$ ($i, j = 1, 2$) is reported as well.