Effect of reducing Lu^{3+} content on the fabrication and scintillation

properties of non-stoichiometric $\text{Lu}_{3-x}\text{Al}_5\text{O}_{12}:\text{Ce}$ ceramics^{**}

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Abstract:

$\text{Lu}_{3-x}\text{Al}_5\text{O}_{12}:\text{Ce}$ optical ceramics ($\text{Lu}_{3-x}\text{AG}:\text{Ce}$, $x = 1, 2, 3$ and 4 at. %, respectively) with Lu^{3+} compositions ranging from 1 to 4 at. % below stoichiometry content were fabricated by solid state reaction method and further optimized by an air-annealing process. The effect of Lu^{3+} deficiency on the optical, luminescence and scintillation properties of such a non-stoichiometric $\text{Lu}_{3-x}\text{Al}_5\text{O}_{12}:\text{Ce}$ ceramics was investigated. Significant influence in the material densification was found leading to strong changes in the transparency, radioluminescence (RL) and scintillation response of these ceramics. Within the range of 1 to 4 at. % Lu^{3+} deficiency, Lu_{Al} antisite defects were suppressed effectively and the $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics displayed an extremely

high RL intensity which reaches ~4 times higher than that of the latest commercial LuAG:Ce single crystals while its transparency deteriorated. The microstructure, presence of foreign phases and charge traps acting in scintillation mechanism were also characterized by means of SEM, back scattered electron imaging and thermoluminescence techniques, respectively.

Key words: LuAG:Ce ceramics, Lu^{3+} deficiency, scintillation light yield, non-stoichiometry, antisite defects

1. Introduction

Inorganic scintillating crystals are widely used in ionizing radiation detectors in various modern applications as in medical imaging techniques (X-ray computed tomography CT or positron emission tomography PET), homeland security and high energy physics (LHC electromagnetic calorimeters at CERN) [1-5]. Besides scintillating quality criteria as high light yield, fast scintillation response and low afterglow intensity, good scintillator materials should be fabricated with large size, good chemical stability and material uniformity. Thus a number of new excellent scintillators based on Ce^{3+} and Pr^{3+} -doped materials, together with truly novel nano-scintillator, nano-composite and phase separated material systems, were discovered and studied in depth during the last two decades [6-8]. Optically transparent ceramic materials, which are characterized by lower preparation temperature, more uniform doping and lower cost, are also pushed as an alternative to their single crystal analogs during recent years.

First reported in 2005, Ce^{3+} doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG:Ce) ceramics were fabricated with high transparency by means of solid state sintering technologies [9, 10]. Later on, flame spray pyrolysis for nanoparticle production followed by cold pressing, vacuum sintering and hot isostatic pressing was used for production of ceramics [11]. Also spark plasma sintering method was used for preparation of both undoped LuAG [12] and Ce-doped LuAG [13]. However, many factors affect the radioluminescence (RL) efficiency and scintillation performance of LuAG:Ce ceramics, including the chemical composition, electronic structure, intrinsic and extrinsic defect states, fabrication techniques and also post-preparation treatments. The light yield (LY) of LuAG:Ce ceramics first reported was only 50 % of that of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) reference single crystal. At least 75 % of generated light was released at times longer than 1 μs after excitation and this is due to the occurrence of deep electron traps introduced by using simultaneously traditional sintering aids such as $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ (tetraethyl ortho-silicate, TEOS) and MgO [14]. In 2011, Yanagida et al. accomplished a higher LY in LuAG:Ce ceramics (14800 ph/MeV, 2 μs shaping time) than its single crystal analogous for the first time [15]. In our recent preliminary study, a very high LY (27000 ph/MeV, at 2 μs and higher shaping times) was achieved in LuAG:Ce,Mg ceramics by using a Mg^{2+} ion co-doping strategy. Similarly to what occurs in the Ce-doped orthosilicates (LSO, LYSO), we proposed that the stable Ce^{4+} ions in garnet LuAG:Ce,Mg ceramics can positively participate in the scintillation processes and contribute to fast scintillation response in parallel with stable Ce^{3+} scintillating centers [8,16-18]. Therefore, scintillators based on LuAG garnet structure (both crystals and

ceramics) are presently considered as competitive candidates for advanced scintillation applications.

On the other hand, we have also succeeded in fabricating transparent Lu^{3+} rich non-stoichiometric $\text{Lu}_{3+x}\text{AG}:\text{Ce}$ ceramics without using any traditional sintering aids [19, 20]. The RL efficiency of the best Lu^{3+} rich $\text{Lu}_{3+x}\text{AG}:\text{Ce}$ ceramic is about 2.5 times higher than of that of the $\text{LuAG}:\text{Ce},\text{Mg}$ ceramics above mentioned. Unfortunately, the presence of Lu_{Al} antisite defects (AD)-related shallow electron traps were observed in these ceramics by RL and thermoluminescence (TSL) measurements. As a result, a degraded scintillation performance including higher slow decay components and higher afterglow intensities was obtained. Since the fabrication temperature of $\text{LuAG}:\text{Ce}$ ceramics is lower than that of single crystal analogue and no material melting occurs along the preparation route in the former, it seems easier to suppress the formation of Lu_{Al} AD in ceramics. Thus $\text{LuAG}:\text{Ce}$ ceramic with Lu^{3+} deficiency should be considered as promising material to be AD free with an improved scintillation performance.

Therefore, this paper deals with luminescence (radioluminescence), scintillation properties and also characterization of defects of Lu^{3+} deficient non-stoichiometric $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics. 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 stoichiometric deviation. The discussion on the composition and

properties tailoring includes a comparative study with 1 at. % Lu^{3+} excess $\text{Lu}_{3+1\%}\text{AG:Ce}$ ceramics and the latest commercial LuAG:Ce single crystal.

2. Experimental

We denote the Lu^{3+} deficient non-stoichiometric lutetium garnet ceramics as $\text{Lu}_{3-x}\text{AG:Ce}$ ($x=1, 2, 3$ and 4 at. %). These ceramics 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 weighted according to the chemical stoichiometry of $(\text{Lu}_{1-y}\text{Ce}_y)_3\text{Al}_5\text{O}_{12}$, where $y = 0.003$, while commercial Lu_2O_3 powders of 4N purity were weighted with 1, 2, 3 and 4 wt. % in deficiency accordingly. After being vacuum sintered at 1880°C for 30 h and air-annealed at 1450°C for 20 h, all the samples were double-polished to a thickness of 0.5-1 mm for measurements. In order to clarify the effect of Lu^{3+} content, 1 at. % Lu^{3+} rich $\text{Lu}_{3+1\%}\text{AG:0.5\% Ce}$ non-stoichiometric ceramic sample prepared under the same conditions was used for comparison [19]. The detailed technological route has already been described in our previous works [19, 20]. However, the stoichiometric LuAG:Ce ceramic is lacking in the sample set because high quality stoichiometric LuAG:Ce ceramic could not be fabricated successfully under the same condition without using traditional sintering aids. A 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 either by SICCAS Corp. (Shanghai, China) or obtained from M. Ishii (Shonan Institute of Technology, Japan) 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 fluorometer (Horiba Jobin Yvon, Co., France) equipped with a TXB-04 photon counting detector. For afterglow measurements, samples were irradiated by X-rays with the same X-ray tube (operated at 40 kV) at RT, after which the beam was cut off and the luminescence emitted from samples was recorded immediately 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 yields were measured using hybrid photodetectors (HPMT hybrid photomultipliers DEP PP0470 or PP0475B ones, DEP, Netherlands) [21]. Light yields (LY) as a function of the energy E were evaluated from photoelectron yields $N_{\text{phels}}(E)$ by using of calibrated quantum efficiency (Q.E.) of HPMT's and emission spectra of scintillators. Measured ceramics are characterized by wide emission bands peaking in the green range where Q.E. is around or below 10 % but due to Q.E. calibration and precise measurements of radioluminescence an accuracy of L.Y. 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. Absorption spectra

Fig. 1 shows the absorption spectra of the air-annealed Lu^{3+} -deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics. In the inset there are photographs of selected samples. The broad absorption bands at about 450 and 350 nm are related to the $\text{Ce}^{3+} 4f \rightarrow 5d_1$ and $5d_2$ transitions, respectively. The absorption pattern below 300 nm is composite due to the overlap of higher $4f \rightarrow 5d$ Ce^{3+} absorption bands, Ce^{4+} charge transfer absorption band and various intrinsic and trace-impurity (Fe^{2+} , Yb^{2+}) related absorption [22-24]. The additional absorption band peaking at 240 nm is reported as due to the charge transfer absorption of Ce^{4+} centers [25]. Its occurrence is reasonable because some part of the Ce^{3+} ions would be oxidized to Ce^{4+} state during the air annealing process which was performed to diminish the concentration of oxygen vacancies produced in the vacuum sintering process. Since Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics displayed a poor optical quality, the presence of scattering centers leads to a higher constant absorption in the visible region. When compared to the optical qualities of Lu^{3+} rich $\text{Lu}_{3+x}\text{AG}:\text{Ce}$ ceramics we reported before, it indicates again that excess of Lu^{3+} could act as “self-sintering aid” in the fabrication process of $\text{LuAG}:\text{Ce}$ ceramics [19].

Fig. 1 Optical absorption spectra of Lu^{3+} deficient non-stoichiometric $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics with various Lu^{3+} content (cut-off of the the $4f \rightarrow 5d_1$ absorption band of Ce^{3+} centers peaking at ~ 450 nm is an experimental artifact). In the inset there are photographs of corresponding samples.

3.2. Radioluminescence spectra

In **Fig. 2a**, the RL spectra of the air-annealed Lu^{3+} deficient non-stoichiometric $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics are displayed together with those of the 1 % Lu^{3+} rich $\text{Lu}_{3+1\%}\text{AG}:\text{Ce}$ ceramic and the $\text{LuAG}:\text{Ce}$ reference single crystal. The composition dependent RL intensities (spectrum integrals in the 440-740 nm region related to Ce^{3+} emission) are shown in **Fig. 2b**. Unlike Lu^{3+} rich $\text{Lu}_{3+x}\text{AG}:\text{Ce}$ ceramic and $\text{LuAG}:\text{Ce}$ single crystal, Lu_{Al} AD related luminescence in the UV region can be hardly detected in Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics, see the inset of Fig. 2a. It means that the formation of Lu_{Al} AD can be suppressed effectively as we expected by decreasing the

content of Lu^{3+} in LuAG:Ce ceramics. Therefore, Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics show a remarkable higher RL efficiency than Lu^{3+} rich ones, reaching 4 times of that of the high quality commercial LuAG:Ce single crystal. We note that this quantitative comparison might be influenced by the lowered transparency of the Lu-deficient samples.

Fig. 2 (a) Absolute scale comparison of RL spectra of the Lu^{3+} deficient and Lu^{3+} rich

non-stoichiometric $\text{Lu}_{3\pm x}\text{AG}:\text{Ce}$ ceramics; (b) RL intensity of the ceramics versus Lu^{3+} relative contents. The data of $\text{LuAG}:\text{Ce}$ reference single crystal were also reported as comparison.

3.3. Scintillation properties

Similarly to RL intensity, a clear improved scintillation performance is observed in Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics. As is shown in **Fig. 3** and **Table 1**, the LY of fast parts of decays (below or around 1 μs) of Lu^{3+} deficient $\text{Lu}_{3-1\%}\text{AG}:\text{Ce}$ ceramic is higher than that of 1 % rich Lu^{3+} $\text{Lu}_{3+1\%}\text{AG}:\text{Ce}$ ceramic and the commercial BGO single crystal. LY of ~ 18000 ph/MeV was obtained in 1 % Lu^{3+} deficient $\text{Lu}_{3-1\%}\text{AG}:\text{Ce}$ ceramic (measured with 1 μs shaping time) which is higher than that of the commercial $\text{LuAG}:\text{Ce}$ single crystal where the LY obtained was 16390 ph/MeV (see Table 1). However, the light yield of Lu^{3+} deficient $\text{Lu}_{3-1\%}\text{AG}:\text{Ce}$ ceramic becomes lower than that of the $\text{LuAG}:\text{Ce}$ single crystal when the shaping time is longer than 2 μs (see Fig. 3). **Fig. 4** shows the scintillation decay curves of the ceramics and the $\text{LuAG}:\text{Ce}$ single crystal. The double exponential fit of the decay curves was accomplished and the results are included in Table 1. All the samples show scintillation decays consisting of two components and these ones are due to the prompt and delayed radiative recombination at Ce^{3+} centers. But it is clear that the Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics exhibit faster decays compared to the Lu^{3+} rich one and the $\text{LuAG}:\text{Ce}$ single crystal (between 56-59 ns and around 70 ns, respectively). Furthermore, the relative weight of fast scintillation decay component is

only ~ 41 % in Lu^{3+} rich $\text{Lu}_{3+x}\text{AG:Ce}$ ceramic and ~ 34 % in LuAG:Ce single crystal, while in Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG:Ce}$ ceramic it increases up to ~ 50 %. All the improved scintillation performance could be ascribed to the suppression of Lu_{Al} AD defects and related traps. Consequently, in microsecond time scale, the energy transfer from the host to the Ce^{3+} centers significantly accelerated in Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics [26, 27].

Fig. 3 Light yields of Lu^{3+} deficient and 1% Lu^{3+} rich non-stoichiometric $\text{Lu}_{3\pm x}\text{AG:Ce}$ ceramics and LuAG:Ce single crystal as a function of shaping time in the 0.5 – 10 μs range.

Table 1. Sample characteristics, light yield values and scintillation decay constants (excitation by 662 keV energy of ^{137}Cs of the Lu^{3+} deficient non-stoichiometric $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics, the 1 % Lu^{3+} rich $\text{Lu}_{3+1\%}\text{AG:Ce}$ one 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. The relative intensities of each component $I_i = A_i\tau_i / \sum A_j\tau_j \times 100$ ($i, j = 1, 2$) are also reported.

Samples	Size (mm)	LY _{1μs} (ph/MeV)	LY _{10μs} (ph/MeV)	τ_1 (ns)/ I_1 (%)	τ_2 (ns)/ I_2 (%)
Lu deficient-1 %	Ø15×1	18000	25610	59/48	1230/52
Lu deficient-4 %	Ø15×1	17600	24200	56/50	1140/50
Lu rich-1 %	Ø15×1	14400	22400	69/41	1120/59
LuAG:Ce sc	Ø10×1	16390	27600	70/34	1700/66

Fig. 4. Normalized scintillation decay curves of Lu^{3+} deficient and Lu^{3+} rich non-stoichiometric $\text{Lu}_{3\pm x}\text{AG:Ce}$ ceramics and the reference LuAG:Ce single crystal.

In **Fig. 5**, the afterglow characteristics of Lu^{3+} deficient and Lu^{3+} rich non-stoichiometric $\text{Lu}_{3\pm x}\text{AG:Ce}$ ceramics and LuAG:Ce single crystal are shown together with BGO reference single crystal, which is known by its extremely low afterglow. Apparently, the Lu^{3+} deficient non-stoichiometric $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics show much lower afterglow intensities when compared to the 1 % Lu^{3+} rich one. This result is consistent with the higher RL intensities and light yields in the Lu^{3+} deficient

$\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics in Fig. 2 and Table 1. However, when compared with $\text{LuAG}:\text{Ce}$ single crystal, the $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics show somewhat worse afterglow characteristics which suggests that there should be some deep traps located in the ceramic which play a key role in delaying the carrier transport stage towards Ce^{3+} centers in millisecond time scale during the scintillation process [28].

Fig. 5 Spectrally unresolved afterglow time profiles of Lu^{3+} deficient and Lu^{3+} rich non-stoichiometric $\text{Lu}_{3\pm x}\text{AG}:\text{Ce}$ ceramics, BGO and $\text{LuAG}:\text{Ce}$ single crystals after the 40 kV X-ray excitation cut-off.

3.4. Microstructure and role of defects

As we demonstrated in Fig. 1, the Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics are translucent and the scattering phenomena becomes more severe with decreasing the Lu^{3+} content. To investigate the defects and the effect of Lu^{3+} deviation from stoichiometry on the densification of the ceramics, the SEM and the back scattered electron imaging of the fracture microstructure of the Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG}:\text{Ce}$

ceramics were performed. The back scattered electron imaging of the fracture microstructure of the ceramics with various content of Lu^{3+} are shown in **Fig. 6**. Many residual micropores and the second phase impurities are found, both in the grain boundaries and the host lattice, in all the samples of the Lu^{3+} deficient ceramics. Their concentrations clearly increase with decreasing Lu^{3+} content (see Fig. 6). **Fig. 7** shows the energy dispersive spectra and the analysis results of the second phase impurities in 4 % Lu^{3+} deficient $\text{Lu}_{3-4\%}\text{AG:Ce}$ non-stoichiometric ceramics. It comes out that there are Al_2O_3 or Al-rich compounds which segregated when content of Lu^{3+} ions in LuAG:Ce is lower than its stoichiometric content. This is consistent with the recent finding in the Yttrium-deficient YAG ceramic [29].

Fig. 6. Back scattered electron imaging of the fracture microstructure of the Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics.

Fig. 7. Energy dispersive spectra of the second phase impurities in 4% Lu^{3+} deficient

Lu_{3-4%}AG:Ce non-stoichiometric ceramic.

Finally, TSL measurements were carried out with the aim to visualize the role of shallow and deep traps in the RL, scintillation LY and decays, and afterglow characteristics described above. The TSL glow curves in the 77-500 K temperature range are reported in **Fig. 8**. As seen in Fig. 8, there is relative lack of TSL signal within 150-190 K. It points to the absence of AD-related traps which have TSL signature in this temperature region [30] and is thus consistent with the above described results as for RL spectra, scintillation light yield and decays. The origin of broad TSL band below 150 K is not clear as its shape is different from that observed in TSL characteristics of LuAG:Ce [30] or LuAG:Pr [31] single crystals. It might be related to shallow traps due to disorder in the interface regions with the foreign phase inclusions mentioned above. The dominating peak at about 240 K and another two ones above room temperature reasonably coincide with similar peaks observed in LuAG:Ce and LuAG:Pr single crystals [31,32] and related trap centers probably include oxygen vacancy [33]. TSL peaks above room temperature and related traps usually play the role in radiation damage mechanism [34] and in general can further contribute to LY loss.

Fig. 8. Spectrally unresolved TSL glow curves of the Lu^{3+} deficient $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics. Samples were irradiated for 15 min by X-ray tube at 77K (40 kV, 15 mA) before TSL signal collection.

IV. Conclusions

The Lu^{3+} deficient non-stoichiometric $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics ($x = 1, 2, 3$ and 4 at. %, respectively) were fabricated by solid state reaction method and further optimized by an air-annealing process. We show that such modification of the composition stoichiometry drastically worsen the optical quality and somewhat improves RL intensity and scintillation response of the ceramics. Reported results in this composition range deepen the comprehension of LuAG:Ce ceramic systems. Within 1 to 4 at. % Lu^{3+} deficiency range, the $\text{Lu}_{3-x}\text{AG:Ce}$ ceramics display an extremely high RL intensity which is ~ 4 times higher than that of the high quality commercial LuAG:Ce single crystal and a light yield of about 18000 ph/MeV with short $1\mu\text{s}$

shaping time. By comparing light yield values with different shaping times and scintillation decays, it turns out that $\text{Lu}_{3-x}\text{AG}:\text{Ce}$ ceramics display a more intense and faster scintillation response than isostructural single crystals commercially available. However, due to the occurrence of Al-rich second phase impurities and other materials defects, the optical quality of these ceramics is degraded and further work is needed to improve it.

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