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## The development of Ce<sup>3+</sup>-activated (Gd, Lu)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> garnet solid solutions as efficient yellow-emitting phosphors

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#### Abstract

Ce<sup>3+</sup>-activated Gd<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> garnet, effectively stabilized by Lu<sup>3+</sup> doping, has been developed for new yellow-emitting phosphors. The powder processing of  $[(Gd_{1-x}Lu_x)_{1-y}Ce_y]_3Al_5O_{12}$ solid solutions was achieved through precursor synthesis via carbonate precipitation, followed by annealing. The resultant (Gd, Lu)AG : Ce<sup>3+</sup> phosphor particles exhibit typical yellow emission at ~ 570 nm (5d–4f transition of Ce<sup>3+</sup>) upon blue-light excitation at ~ 457 nm (the <sup>2</sup>F<sub>5/2</sub>–5d transition of Ce<sup>3+</sup>). The quenching concentration of Ce<sup>3+</sup> was determined to be ~ 1.0 at% (y = 0.01) and the quenching mechanism was suggested to be driven by exchange interactions. The best luminescent [(Gd<sub>0.9</sub>Lu<sub>0.1</sub>)<sub>0.99</sub>Ce<sub>0.01</sub>]AG phosphor is comparative to the well-known YAG : Ce<sup>3+</sup> in emission intensity but has a substantially red-shifted emission band that is desired for warm-white lighting. The effects of processing temperature (1000–1500 °C) on the spectroscopic properties of the phosphors, especially those of Lu<sup>3+</sup>/Ce<sup>3+</sup>, were thoroughly investigated and discussed from the centroid position and crystal field splitting of the Ce<sup>3+</sup> 5d energy levels.

Keywords: gadolinium aluminate garnet, lattice stabilization, Ce<sup>3+</sup> doping, yellow phosphor, photoluminescence behavior

#### 1. Introduction

Rare-earth aluminate garnets ( $Ln_3Al_5O_{12}$ , LnAG), exemplified by yttrium aluminate garnet  $Y_3Al_5O_{12}$  (YAG) and lutetium aluminate garnet  $Lu_3Al_5O_{12}$  (LuAG), are a group of multifunctional ceramic materials, owing to their wide bandgaps, excellent chemical and thermal stabilities, and high light-transmittance in a wide spectral region [1–8]. In the phosphor field,  $Ce^{3+}$ -doped YAG is a widely used phosphor for the conversion of blue to yellow light in the rapidly expanding market of white light emitting diodes (LEDs) [9–11], though low color rendering and high correlated color temperature are frequently deemed as drawbacks due to the lack of sufficient red spectral intensity. In the scintillation family, transparent YAG :  $Ce^{3+}$  ceramics show extremely high luminescence efficiencies and a short decay times (tens of nanoseconds) and thus might be used as advanced scintillators for medical x-ray detectors [12,13]. A scintillation material should have a high theoretical density to assure high x-ray-stopping power. Unfortunately, YAG itself is lacking in stopping power due to its low density (4.54 g cm<sup>-3</sup>). In this regard, iso-structural LuAG is more attractive than YAG, since Lu has a much higher atomic

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weight (175) than Y (89). The high price of Lu<sub>2</sub>O<sub>3</sub>, however, makes the LuAG ceramic nearly unaffordable for practical use. In the market,  $Gd_2O_3$  and  $Y_2O_3$  are similar in price but  $Gd^{3+}$  has an atomic weight (157, close to the 175 of Lu) significantly higher than  $Y^{3+}$ . Therefore, GdAG-based transparent ceramics could be ideal scintillator materials, after  $Ce^{3+}$  doping. As a result, new yellow-emitting phosphors from  $Ce^{3+}$ -doped GdAG-based powders are expected to compete with YAG :  $Ce^{3+}$  in lighting applications.

The LnAG compounds crystallize in a bcc structure and the cubic cell consists of eight formula units with a single type of Ln-site (24c, eight-fold coordination,  $D_2$  point symmetry). The crystal structure of an ideal aluminate garnet can be viewed as a framework built up via corner sharing of Al-O polyhedra, with the Ln atoms residing in the dodecahedral interstices [14]. The dodecahedra have a fixed geometric shape and dimension, and thus a critical size exists for the Ln<sup>3+</sup> cations to enter these interstitial spaces. Gd is the boundary element for the garnet structure to be formed and GdAG was reported to be stable up to  $\sim 1300$  °C, followed by a thermal decomposition to GdAlO<sub>3</sub> perovskite and Al<sub>2</sub>O<sub>3</sub> up to 1500 °C (Gd<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>  $\rightarrow$  3GdAlO<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>) [15]. Since Ce<sup>3+</sup> is larger in size than Gd<sup>3+</sup>, doping GdAG with Ce<sup>3+</sup> activators would further destabilize the garnet structure and lower the decomposition temperature. This decomposition behavior makes the development of highly efficient (Gd,Ce)AG phosphors and transparent ceramics almost impossible; this might be the reason why optical properties of the (Gd,Ce)AG compounds have rarely been reported up to date. To suppress the thermal decomposition, we proposed in this work the doping of  $GdAG : Ce^{3+}$  with significantly smaller  $Lu^{3+}$  to reduce the average  $Ln^{3+}$  size for structure stabilization. This strategy raises the theoretical density of the material at the same time as retaining the favorable luminescence performance of Ce<sup>3+</sup>, and thus may yield a new yellow phosphor and scintillation material for optical and medical imaging applications.

It is well-known that the luminescence behavior of a phosphor heavily depends on particle morphology, which in turn relies on the synthesis route used [16]. Many synthesis processes have thus been developed to obtain luminescent LnAG materials, such as solid-state reaction [17], co-precipitation [18], spray pyrolysis [19], sol-gel [20], combustion [21] and so on. Co-precipitation generally yields powders of good purity, high degree of homogeneity, low phase formation temperature and narrow particle size distribution. We employed in this work a carbonate co-precipitation route [22], with ammonium bicarbonate as the precipitant, to prepare (Gd, Lu)AG : Ce<sup>3+</sup> phosphor powders of low aggregation. The resultant materials were systematically investigated in terms of the phase evolution of the precursor upon calcination and the photoluminescence (PL) properties of the resultant oxides via the combined techniques of x-ray diffractometry (XRD), Brunauer-Emmett-Teller (BET), field-emission scanning electron microscopy (FE-SEM) and photoluminescence spectroscopy. The observed luminescent properties were then correlated with the processing temperature and particularly

the  $Lu^{3+}/Ce^{3+}$  contents. In the following sections, we report the synthesis, phase evolution and photoluminescent properties of the (Gd, Lu)AG :  $Ce^{3+}$  yellow phosphors.

#### 2. Experimental procedure

The rare earth and aluminum sources for powder synthesis are  $Ln_2O_3$  (Ln = Gd, Lu and Y, 99.99% pure, Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd, Huizhou, China), Ce(NO<sub>3</sub>)<sub>3</sub> ·  $6H_2O$  (99.99% pure, Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd) and alum (NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O, > 99% pure, Zhenxin chemical Reagent Factory, Shanghai, China). Ethanol and concentrated nitric acid (~ 63 wt%) are of analytical grade and were purchased from Shenyang Chemical Reagent Factory (Shenyang, China). The stock solution of  $Ln(NO_3)_3$  was prepared by dissolving the corresponding oxide with a proper amount of nitric acid.

Aqueous salt solutions for precipitation were made from the nitrate solutions and alum according to the formulae of  $[(Gd_{1-x}Lu_x)_{1-y}Ce_y]_3Al_5O_{12}$  (x = 0.1–1.0, y = 0–0.03). Carbonate precursor was precipitated by drop-wise addition of 200 ml of a  $0.125 \text{ mol } l^{-1}$  (for Al<sup>3+</sup>) mixed cation solution into 320 ml of a 1.5 mol l<sup>-1</sup> ammonium bicarbonate solution under mild stirring at room temperature. The x and y in  $[(Gd_{1-x}Lu_x)_{1-y}Ce_y]_3AG$  were varied to reveal the effects of Lu<sup>3+</sup> and Ce<sup>3+</sup> contents on the characteristics of the resultant phosphors. The precipitate was homogenized for 30 min after the completion of precipitation, centrifuged and washed repeatedly with distilled water and alcohol to remove by-products. The wet precipitate was then dried in the air at 100 °C for 24 h, lightly crushed and calcined in the air at 600 °C for 4 h for thermal decomposition. The samples were finally heat-treated at elevated temperatures in a reducing atmosphere of Ar/H<sub>2</sub> (5 vol.% of H<sub>2</sub>) to suppress  $Ce^{3+}$  oxidation, using a heating rate of  $10 \circ C/min^{-1}$  and a duration time of 4 h, followed by cooling at  $10 \,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$  to 500 °C and then natural cooling to room temperature. For comparison, a  $(Y_{0.99}Ce_{0.01})AG$   $(YAG: Ce^{3+})$  phosphor was also made according to the above synthetic procedures.

Phase identification was performed via XRD (Model PW3040/60, PANALYTICAL B.V, Almelo, the Netherlands) using nickel-filtered CuK $\alpha$  radiation and a scanning speed of  $4^{\circ} 2\theta \min^{-1}$ . The morphology and microstructure of the calcination products were observed by FE-SEM, (Model JSM-7001F, JEOL, Tokyo, Japan). Specific surface areas of the oxide powders were analyzed on an automatic analyzer (Model TriStar II 3020, Micrometritics Instrument Corp., Norcross, GA, USA) using the BET method via nitrogen adsorption at 77 K. Photoluminescence spectra (wavelength accuracy:  $\pm 1 \text{ nm}$ ) of the phosphors were collected at room temperature using an FP-6500 fluorospectrophotometer (JASCO, Tokyo) equipped with a 60 mm diameter integrating sphere (Model ISF-513, JASCO) and a 150W Xe-lamp as the excitation source. Monochromatization of the excitation and emission lights was achieved with a Rowland concave grating  $(1800 \text{ grooves mm}^{-1})$ . Optical measurements were conducted under identical conditions for all the samples, with slit widths of 5 nm for both the excitation and emission sides.



**Figure 1.** XRD patterns of the  $[(Gd_{0.9}Lu_{0.1})_{0.99}Ce_{0.01}]AG$  precursor calcined at various temperatures (a) and a comparison of the XRD patterns of the  $[(Gd_{1-x}Lu_x)_{0.99}Ce_{0.01}]AG$  phosphors calcined at 1500 °C (b). The processing temperatures and Lu contents (the *x* value) are indicated in the figures. Letters G, P, M and R represent LnAG garnet, LnAP perovskite, LnAM monoclinic and Ln<sub>2</sub>O<sub>3</sub> phases, respectively, Ln = Gd, Lu and Ce. All the unlabeled peaks belong to the LnAG phase. The standard diffractions of Gd<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>(GdAG) garnet are included in (a) as bars.

Spectral responses of the equipment were corrected in the range 220–850 nm with a Rhodamine-B solution (5.5 g  $1^{-1}$  in ethylene glycol) and a standard light source unit (ECS-333, JASCO) as references.

#### 3. Results and discussion

XRD analysis has been performed to investigate the temperature-course phase evolution of the precursor (the precipitate dried at 100 °C) upon calcination, with the  $[(Gd_{0.9}Lu_{0.1})_{0.99}Ce_{0.01}]AG$  sample as an example (figure 1(a)). Except for the precursor, the other samples shown in figure 1(a) were obtained by calcining the  $600 \,^{\circ}\text{C}$ pretreated powder at the different temperatures indicated in the figure. It can be seen that the precursor and the powders calcined up to 800 °C are essentially amorphous and crystallization started at 900 °C, yielding a mixture of the rare-earth sesquioxide Ln<sub>2</sub>O<sub>3</sub>, Ln<sub>4</sub>Al<sub>2</sub>O<sub>9</sub> monoclinic (LnAM), LnAlO<sub>3</sub> perovskite (LnAP) and LnAG garnet phases (figure 1(a)). With increasing annealing temperature, the diffraction intensity becomes successively stronger for LnAG while weaker for Ln<sub>2</sub>O<sub>3</sub>, LnAM and LnAP, indicating further crystallization of LnAG via reactions among these three phases and alumina. A pure LnAG phase was produced at 1300 °C and its XRD pattern can be well-indexed with the cubic structure of GdAG (space group: $Ia\bar{3}d$ , JCPDS: 1-73-1371). Annealing at the even higher temperature of 1500 °C only yielded stronger and sharper XRD peaks, without any change in phase purity of the product, indicating crystallite (an individual particle or a part of a particle) growth and a full stabilization of the garnet lattice with the incorporated Lu<sup>3+</sup> even in the presence of 1 at.% (y = 0.01) of much bigger Ce<sup>3+</sup> (for eight-fold coordination, Ce<sup>3+</sup>, Gd<sup>3+</sup> and Lu<sup>3+</sup> have their respective ionic radii of 0.1143, 0.1053 and 0.0977 nm) [23]. In addition, the x = 0.2 and 0.3–0.5 samples have all completely transformed into pure LnAG at the lowered temperatures of 1150 and 1000 °C, respectively, revealing that  $Lu^{3+}$  doping appreciably promotes LnAG crystallization. Similar results were previously reported by us in a work dealing with the effects of Lu content on GdAG crystallization [24] and thus the results obtained in that work are not shown. The crystallization temperature is appreciably lower than those (up to  $1500 \,^{\circ}$ C) needed for the solid reaction [25], owing to the improved cation homogeneity in the co-precipitated carbonate precursor.

The structure stabilization and promoted crystallization of (Gd,Ce)AG by Lu<sup>3+</sup> doping can be understood from the ionic radius of Ln<sup>3+</sup> in LnAG. The average lanthanide size in the combination  $[(Gd_{0.9}Lu_{0.1})_{0.99}Ce_{0.01}]^{3+}$  is 0.1046 nm, which is very close to the 0.1040 nm of  $\text{Tb}^{3+}$  in  $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (TbAG). Tb<sup>3+</sup> is known as the largest single lanthanide for a thermodynamically stable garnet to be formed. The average  $Ln^{3+}$  size is equal to that in  $[(Gd_{0.9}Lu_{0.1})_{0.95}Eu_{0.05}]AG$ , which was developed in our previous work as a thermodynamically stable garnet phosphor for efficient red emission [26]. The average Ln<sup>3+</sup> size decreases with more Lu<sup>3+</sup> incorporation, making it easier for the lanthanides to enter the dodecahedral interstices and thus further lowers the crystallization temperature of LnAG. Al<sub>2</sub>O<sub>3</sub> was not unambiguously detected with XRD at any calcination temperature, though definitely needed for aluminate crystallization, which was ascribed to the poor crystallinity of transition Al<sub>2</sub>O<sub>3</sub> ( $\gamma$ -,  $\delta$ - and  $\theta$ -type) [22, 26–28].

At the fixed Ce<sup>3+</sup> content of 1 at.% (y = 0.01), XRD peaks of the phase-pure LnAG steadily shift toward the high angle side along with more Lu<sup>3+</sup> incorporation (figure 1(b)), suggesting a gradually contracted unit cell of the crystal structure. This is understandable from the significantly smaller ionic radius of Lu<sup>3+</sup> than Gd<sup>3+</sup>. Figure 2 exhibits the calculated lattice constants and theoretical densities of the [(Gd<sub>1-x</sub>Lu<sub>x</sub>)<sub>0.99</sub>Ce<sub>0.01</sub>]AG solid solutions formed at 1500 °C. Clearly, the cell parameter linearly decreases with increasing Lu<sup>3+</sup> incorporation and observes Vegard's law, implying that homogeneous solid solutions have already been formed.



**Figure 2.** Lattice constants and theoretical densities of the  $[(Gd_{1-x}Lu_x)_{0.99}Ce_{0.01}]AG$  garnet solid solutions calcined at 1500 °C, as a function of the Lu content (the *x* value).

The theoretical densities are much higher than that of YAG  $(4.54 \text{ g cm}^{-3})$ , owing to the larger atomic weight of Gd (157) and Lu (175). The stabilized garnet structure, the increased effective atomic number and the significantly improved theoretical density may thus allow (Gd, Lu)AG : Ce<sup>3+</sup> to be a promising scintillation material.

Figure 3 shows FE-SEM morphologies of the  $[(Gd_{0.7}Lu_{0.3})_{0.99}Ce_{0.01}]AG \quad powders \quad processed$ in the temperature range of 1000-1500 °C, from which it can be seen that the originally rounded oxide crystallites/particles undergo considerable growth and tend to be somewhat elongated and branched due to the neck formation via sintering among the adjacent particles at temperatures above 1000 °C. Relatively good particle dispersion, however, persisted up to the high temperature of 1500°C owing to the excellent dispersion of the carbonate precursor. BET analysis found specific surface areas of  $\sim 19.61$ , 9.68, 4.17 and  $0.21 \text{ m}^2 \text{ g}^{-1}$  for the powders shown in figures 3(a)-(d), respectively. With the theoretical density values shown in figure 2 and by applying the equation  $D_{\text{BET}} = 6000/(\rho_{\text{th}} \times S_{\text{BET}})$ , where  $D_{\text{BET}}$  is the average particle size (nm),  $\rho_{\text{th}}$  the theoretical density (6.28 g cm<sup>-3</sup>) and  $S_{\text{BET}}$  the specific surface area (m<sup>2</sup> g<sup>-1</sup>), the average particle sizes were calculated to be  $\sim 49$  nm, 100 nm, 229 nm and 4.55  $\mu$ m for the powders processed at 1000, 1150, 1300 and 1500 °C, respectively.

Photoluminescence spectra of the  $[(Gd_{0.9}Lu_{0.1})_{1-y}$ Ce<sub>y</sub>]AG samples made at 1300 °C are depicted in figure 4 with the key results summarized in table 1. Two excitation bands centered around 338 and 457 nm are identified on the photoluminescence excitation (PLE) spectra (figure 4(a)), with the latter being significantly stronger, which is in good agreement with the observations reported in the literature [29, 30]. The first band (~ 340 nm) is the transition from the ground state (<sup>2</sup>F<sub>5/2</sub>) of Ce<sup>3+</sup> to the T<sub>2g</sub> state composed of three individual bands, and the second band (~ 460 nm) is the transition from the ground state to the E<sub>2g</sub> state composed of two individual bands. The weak peak observed at ~ 275 nm, which is absent from the YAG : Ce<sup>3+</sup> and LuAG : Ce<sup>3+</sup> samples shown later, is owing to the typical <sup>8</sup>S<sub>7/2</sub>  $\rightarrow$  <sup>6</sup>I<sub>J</sub> intra f-f transition of Gd<sup>3+</sup> [31]. The intensity ratio ( $I_b/I_a$ ) of the J Li et al

 $\sim$  460 to 340 nm excitation peaks remains almost constant at  $4.8 \pm 0.5$  up to y = 0.01, which then rapidly increases to ~9.0 at y = 0.02 and further to  $\sim 12$  at y = 0.03 (table 1). This may indicate that substantial non-radiative absorption takes places when the Ce<sup>3+</sup> content is above 1 at.% (y = 0.01). The PL spectra recorded under  $\lambda_{ex} = \sim 457$  nm display apparently strong and broad emission bands covering the region from about 475 to 650 nm. The bands have similar full width at half maximum (FWHM) values of  $\sim 110$  nm, suggesting similar crystallinity of the powders. Gaussian fitting of the PL band yielded two components in each case (figure 4(b), the inset), which are the characteristic double peak emissions of Ce<sup>3+</sup> ascribed to the electron transitions from the lowest crystal-splitting component (<sup>2</sup>D<sub>3/2</sub>) of the 4f<sup>0</sup>5d<sup>1</sup> excited level to the  $4f^15d^0$  ground states of  ${}^2F_{5/2}$  (shorter  $\lambda'_{em}$ , table 1) and  ${}^{2}F_{7/2}$  (longer  $\lambda'_{em}$ , table 1) [32]. The breaking of the  $4f^{1}5d^{0}$ degeneracy into the two levels of  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$  is known as the result of spin-orbit coupling. Raising the Ce<sup>3+</sup> content from y = 0.002 to 0.03 brings about significantly varied emission intensities, as seen from figure 4(b). Peak intensity of the emission band significantly improves up to  $\sim 1.0$  at.% of  $Ce^{3+}$  (y = 0.01) and then deteriorates owing to concentration quenching. The optimal  $Ce^{3+}$  content (1.0 at.%) determined in this work is the same as those widely reported for the YAG : Ce<sup>3+</sup> phosphor systems [19]. Further observation found that the emission spectra tend to slightly red-shift with increasing Ce3+ doping. Though non-radiative energy transfer among the  $Ce^{3+}$  activators has been proposed as one possible reason [10], it may also be due to crystal field effects. It is commonly known that the emission wavelength of  $Ce^{3+}$  depends on both the overall 4f–5d separation and the ligand field splitting of the 5d levels [33,34]. It is also widely accepted that the 5d energy level is significantly more sensitive to the crystal field relative to the 4f ground state. Increasing Ce<sup>3+</sup> doping would distort the ligand field, leading to more splitting of the 5d level and a shifting of the lowest excited state to slightly lower energies. This would account for the red-drifting of the emission band and also the generally slightly larger Stokes shift ( $\Delta S$ , table 1). Enhanced crystal field splitting with more Ce<sup>3+</sup> incorporation is also evidenced by the increasing  $\delta$  values shown in table 1. That is, the energy difference between the two lowest lying 5d-states of Ce<sup>3+</sup> tends to increase owing to the crystal field splitting.

 $\lambda_{ex}$  and  $\lambda_{em}$  are the excitation and emission wavelengths (accuracy :  $\pm 1$  nm), while  $\lambda'_{em}$  is the two emissions deconvoluted via Gaussian fitting;  $I_b/I_a$  is the intensity ratio of the longer to shorter  $\lambda_{ex}$ ; FWHM is the full width at half maximum of  $\lambda_{em}$ ;  $\delta$  is the energy difference between the two lowest lying 5d-states of Ce<sup>3+</sup>, which is calculated from the peak wavelengths of the two excitation bands ( $\lambda_{ex}$ );  $\Delta S$  is the Stokes shift, calculated as the difference between the maximum of the blue excitation band ( $\lambda_{ex} \sim 457$  nm) and the first emission (shorter  $\lambda'_{em}$ ). The blue excitation band was used for  $\Delta S$  calculation since it is the strongest for each sample and its peak wavelength is close to the emission wavelength of (Ga,In)N-based commercial blue LED chips. The maximum error estimated from the wavelength accuracy is  $\pm 135$  cm<sup>-1</sup> for  $\delta$  and  $\pm 80$  cm<sup>-1</sup> for  $\Delta S$ .



**Figure 3.** FE-SEM morphologies of the  $[(Gd_{0.7}Lu_{0.3})_{0.99}Ce_{0.01}]AG$  powders (x = 0.3, y = 0.01) calcined at 1000 °C (a), 1150 °C (b), 1300 °C (c) and 1500 °C (d).



**Figure 4.** PLE (a) and PL (b) spectra of the  $[(Gd_{0.9}Lu_{0.1})_{1-y}Ce_y]AG$  phosphors calcined at 1300 °C. The emission wavelength ( $\lambda_{em}$ ) and excitation wavelength ( $\lambda_{ex}$ , blue light ~ 457 nm) used for the measurements are indicated in table 1. The inset in part (b) is the Gaussian fitting of the PL spectra.

The mutual interaction type of luminescence quenching in solid-state phosphors can be concluded by analyzing the constant s according to the equation [35, 36]

$$\log(I/c) = (-s/d)\log c + \log f,$$
(1)

where I is the emission intensity, c the activator content, dthe sample dimension (d = 3 for energy transfer among the activators inside particles), f is a constant independent of activator concentration and s is the index of electric multipole. The s values of 6, 8 and 10 are for the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole electric interactions, respectively whereas s = 3 corresponds to the mechanism of exchange interaction. The  $\log(I/c) - \log(c)$ plot is given in figure 5, from which a slope (-s/3) of  $-0.842 \pm 0.099$  is derived, yielding an s value of around 3 for the Ce<sup>3+</sup>-doped (Gd,Lu)AG system. This indicates that the observed luminescence quenching is dominantly resulted from exchange interactions for the energy transfer among Ce<sup>3+</sup> ions, possibly via a 'phonon assisted three activated ions nonresonant interaction' mechanism [37]. That is, an energy transfer network is formed by at least three Ce<sup>3+</sup> ions and the energy exchange among the Ce<sup>3+</sup> ions occurs via phonon-photon interactions and not via resonant vibrations of the  $Ce^{3+}$  ions themselves.

Keeping Ce<sup>3+</sup> at the optimal content of 1.0 at.%, the effects of  $Lu^{3+}$  concentration (the x value) on PLE and PL properties of the  $[(Gd_{1-x}Lu_x)_{0.99}Ce_{0.01}]AG$  phosphors are studied in figure 6, with the YAG :  $Ce^{3+}$  sample included for comparison. The key spectroscopic parameters derived from figure 6 are summarized in table 2. It can be seen that the  $I_{\rm b}/I_{\rm a}$  ratio varies in the limited range of  $4\pm 1$  for all the samples and the FWHM values remain almost constant at 110 nm except for LuAG :  $Ce^{3+}(x = 1.0)$ . The smaller FWHM (~100 nm) of LuAG :  $Ce^{3+}$  may imply a better crystallinity of this phosphor. It is also seen from figure 6(b)and table 2 that the  $[(Gd_{1-x}Lu_x)_{0.99}Ce_{0.01}]AG$  solid solutions (x = 0.1-0.5) all emit at substantially longer wavelengths than their YAG :  $Ce^{3+}$  and particularly LuAG :  $Ce^{3+}(x = 1.0)$ counterparts and have much larger Stokes shifts  $\Delta S$ . The emissions thus have more red spectral intensities, which are desired for warm-white lighting. If one assumes that the 4f ground state of Ce<sup>3+</sup> is not appreciably affected by the host lattice, as commonly believed, the observed red shifting of PL bands may thus be discussed as follows by considering the overall 4f-5d separation and ligand field splitting of the  $Ce^{3+}5d$  energy levels [33, 34]. The centroid of the  $Ce^{3+}$ 

**Table 1.** Spectroscopic properties of the  $[(Gd_{0.9}Lu_{0.1})_{1-y}Ce_y]AG$  garnet compounds, as a function of the Ce<sup>3+</sup> content.

Sample	$\lambda_{ex}(nm)$	$I_{\rm b}/I_{\rm a}$	$\lambda_{em}(nm)$	FWHM (nm)	$\lambda_{em}^\prime(nm)$	$\delta(\mathrm{cm}^{-1})$	$\Delta S(\text{cm}^{-1})$		
y = 0.002	2 338, 457	5.3	567	112	554, 602	7704	3831		
y = 0.00	5 338, 457	4.4	569	110	557, 605	7704	3929		
y = 0.01	338, 457	4.2	569	108	558, 607	7704	3961		
y = 0.02	337, 457	9.0	571	110	558, 608	7792	3961		
y = 0.03	337, 458	12.1	571	110	558, 608	7840	3913		

**Table 2.** Spectroscopic properties of the  $[(Gd_{1-x}Lu_x)_{0.99}Ce_{0.01}]AG$  garnet compounds, as a function of the  $Lu^{3+}$  content, with samples  $(Y_{0.99}Ce_{0.01})AG$  and  $(Lu_{0.99}Ce_{0.01})AG$  (x = 1.0) included for comparison.

Sample	$\lambda_{ex}(nm)$	$I_{\rm b}/I_{\rm a}$	$\lambda_{em}(nm)$	FWHM (nm)	$\lambda_{em}^\prime(nm)$	$\delta(\mathrm{cm}^{-1})$	$\Delta S(\text{cm}^{-1})$
$     \begin{array}{r}         x = 0.1 \\         x = 0.2 \\         x = 0.3 \\         x = 0.4 \\         x = 0.5 \\         x = 1.0 \\         YAG \cdot Ce^{3+}     \end{array} $	338, 457	4.21	569	108	558, 607	7704	3961
	338, 457	4.82	569	110	558, 607	7704	3961
	339, 457	4.73	570	111	558, 602	7569	3961
	340, 456	4.88	567	112	558, 602	7434	4009
	342, 454	4.66	565	116	541, 591	7213	3542
	348, 448	3.39	510	100	500, 544	6414	2321
	341, 454	4.46	534	106	520, 566	7299	2796

5d state, which determines the overall 4f-5d separation, is affected by the polarizability of the surrounding anion ligands and the covalency of the host crystal [38]. For LnAG :  $Ce^{3+}$ , the centroid would shift to lower energies with decreasing electronegativity ( $\chi$ ) of Ln<sup>3+</sup>. Lu<sup>3+</sup>, Y<sup>3+</sup> and Gd<sup>3+</sup> have their respective  $\chi$  values of 1.27, 1.22 and 1.20 [39], and the values calculated for the  $(Gd_{1-x}Lu_x)^{3+}$  combinations are 1.207, 1.214, 1.221, 1.228 and 1.235 for x = 0.1, 0.2, 0.3, 0.4 and 0.5, respectively. The materials may thus be placed in the order (Gd<sub>0.9</sub>Lu<sub>0.1</sub>)AG, (Gd<sub>0.8</sub>Lu<sub>0.2</sub>)AG, YAG, (Gd<sub>0.7</sub>Lu<sub>0.3</sub>)AG, (Gd<sub>0.6</sub>Lu<sub>0.4</sub>)AG, (Gd<sub>0.5</sub>Lu<sub>0.5</sub>)AG and LuAG with increasing  $\chi$  of Ln<sup>3+</sup>. The  $\chi$  values seem to be able to account for the successively longer emissions observed for the garnets in the order LuAG, YAG, (Gd<sub>0.8</sub>Lu<sub>0.2</sub>)AG and (Gd<sub>0.9</sub>Lu<sub>0.1</sub>)AG, but cannot explain the emission behaviors of the x = 0.3-0.5 samples. This is because Ce<sup>3+</sup> emission is also significantly affected by the crystal field splitting of the 5d energy levels and more splitting would push the lowest excited state of Ce<sup>3+</sup> to lower energies to emit lights of longer wavelengths. If one assumes that the phosphors studied in this work all have an ideal garnet structure, the extent of field splitting is thus dominantly affected by the Ce-O bond length (lattice constant), the molecular orbital overlap between  $Ce^{3+}$ and  $O^{2-}$ , and the  $\chi$  value. The effects of the lattice constant on splitting can be reflected with the equation

$$D_q = \frac{Ze^2r^4}{6R^5},\tag{2}$$

where *Z* is the charge of the anion (Z = 2 for  $O^{2-}$ ), *e* is the charge of an electron, *r* is the radius of the d wave function and *R* is the bond length [40]. The equation has been successfully used to explain the effects of bond length on the emission wavelength of  $Y_3Al_{5-x}Ga_xO_{12}$ :  $Ce^{3+}(x = 0-5)$  garnet phosphors [34] and would predict increasing crystal field splitting (successively longer emission wavelength) in the order (Gd\_{0.9}Lu\_{0.1})AG, (Gd\_{0.8}Lu\_{0.2})AG, YAG, (Gd\_{0.7}Lu\_{0.3})AG, (Gd\_{0.6}Lu\_{0.4})AG, (Gd\_{0.5}Lu\_{0.5})AG and LuAG, according to the results of



**Figure 5.** The relationship between  $\log(I/c)$  and  $\log(c)$  for the  $[(Gd_{0.9}Lu_{0.1})_{1-y}Ce_y]AG$  phosphors calcined at 1300 °C.

figure 2 and the lattice constants of YAG (1.2010 nm, JCPDS: 1-72-1315) and LuAG (1.1906 nm, JCPDS: 1-73-1368). Apparently, bond length (lattice parameter) alone cannot explain the observed emission behaviors. The crystal field spitting of Ce<sup>3+</sup> is actually rather complicated and is yet significantly influenced by other factors. For example, both the bonding and anti-bonding orbitals of Ce<sup>3+</sup> would be displaced to lower energies with increasing  $\chi$ , but not necessarily by the same amount [41]. This may cause field splitting to either increase or decrease [41]. Besides, non-uniform distortion of the Ce<sup>3+</sup> site is expected to increase with increasing Lu3+ doping, which may also significantly affect field splitting, as experimentally shown for the inverse-garnet of Mg<sub>3</sub>Y<sub>2-v</sub>Gd<sub>v</sub>Ge<sub>3-z</sub>Si<sub>z</sub>O<sub>12</sub>: Ce<sup>3+</sup>(y = 0-2) [34]. It may thus be safer to say that the observed luminescence properties (figure 6(b) and table 2) are the results of the combined contributions from the centroid position and crystal field splitting of Ce<sup>3+</sup> 5d energy levels.



**Figure 6.** PLE (a) and PL (b) behaviors of the  $[(Gd_{1-x}Lu_x)_{0.99}Ce_{0.01}]AG$  phosphors calcined at 1300 °C, with the  $(Y_{0.99}Ce_{0.01})AG$  sample included for comparison. The emission  $(\lambda_{em})$  and excitation  $(\lambda_{ex}$ , blue light ~ 457 nm) wavelengths used for the measurements are indicated in table 2. Part (c) are the results of Gaussian fitting of the PL spectra shown in part (b).

It is observed that both the PLE and PL band intensities steadily decrease with increasing Lu<sup>3+</sup> doping. More Lu<sup>3+</sup> incorporation reduces the lattice parameter (figure 2) and would thus produce a stiffer host lattice, from which increased phonon energy and thus improved luminescence might be

7



**Figure 7.** Photoluminescence behaviors of the  $[(Gd_{0.7}Lu_{0.3})_{0.99}Ce_{0.01}]AG$  phosphors processed at the different temperatures indicated in the figure. The inset is the temperature-dependence intensity of the 570 nm emission, where the relative intensity was obtained by normalizing the observed 570 nm emission intensity to that of the sample calcined at 1000 °C.

expected [42, 43]. The reverse observation suggests that increasing the doping of significantly smaller Lu<sup>3+</sup> may have brought about more lattice defects, such as interstitial ions and even anti-site cations, though further analysis is needed to clarify their type and occurrence. Compared with YAG :  $Ce^{3+}$  and LuAG :  $Ce^{3+}$ , the (Gd, Lu):  $Ce^{3+}$  solid solutions have appreciably diffuse and broadened PLE bands in the > 400 nm region (figure 6(a)), which appear as doublets with the right-hand tail tends extended to a longer wavelength at a higher Lu<sup>3+</sup> content. The defects thus seem to create a less defined quasi energy level in the lower 5d state of  $Ce^{3+}$  that corresponds to the PLE side-band centered at  $\sim$  490 nm. Interactions of the excited electrons with these defect states may have also led to the observed luminescence deterioration at a higher Lu<sup>3+</sup> content. Nonetheless, it is a delight for us to see that the best luminescent [(Gd<sub>0.9</sub>Lu<sub>0.1</sub>)<sub>0.99</sub>Ce<sub>0.01</sub>]AG phosphor has an emission intensity comparable to (Y<sub>0.99</sub>Ce<sub>0.01</sub>)AG and is higher than (Lu<sub>0.99</sub>Ce<sub>0.01</sub>)AG (figure 6(b)). Further analysis indicated that, under the blue-light excitations indicated in table 2, the  $[(Gd_{1-x}Lu_x)_{0.99}Ce_{0.01}]AG$  phosphors have integrated emission intensities (in the 475-800 nm range) being  $\sim 0.97, 0.87, 0.77, 0.55, 0.51$  and 0.76 times that of  $(Y_{0.99}Ce_{0.01})AG$  for x = 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0, respectively.

 $\lambda_{\rm ex}$ ,  $\lambda_{\rm em}$ ,  $\lambda'_{\rm em}$ ,  $I_{\rm b}/I_{\rm a}$ , FWHM,  $\delta$  and  $\Delta S$  have the same meanings as given in table 1. Wavelength accuracy is  $\pm 1$  nm. The maximum error estimated from the wavelength accuracy is  $\pm 135 \text{ cm}^{-1}$  for  $\delta$  and  $\pm 85 \text{ cm}^{-1}$  for  $\Delta S$ .

The PL spectra shown in figure 7 were studied as a function of sample synthesis temperature from 1000 to  $1500 \,^{\circ}$ C, with the composition [(Gd<sub>0.7</sub>Lu<sub>0.3</sub>)<sub>0.99</sub>Ce<sub>0.01</sub>]AG as an example. This composition was chosen since its higher Lu content allows the garnet to be crystallized as a pure phase at the low temperature of  $1000 \,^{\circ}$ C and thus the effects of processing temperature can be investigated

in a wider range. It can be seen from figure 7 that raising the processing temperature from 1000 to 1500 °C did not bring about any appreciable change to the peak position of the 5d-4f transition but yielded a 153% increment in the 570 nm emission intensity (figure 7, the inset). Meanwhile, the phosphors processed at 1150, 1300 and 1500 °C show integrated emission intensities about 1.35, 1.52 and 2.41 times that of the 1000 °C sample, respectively. FWHM analysis of the emission bands found successively decreasing values of  $\sim 118$ , 114, 111 and 109 nm for the phosphors processed at 1000, 1150, 1300 and 1500 °C, respectively. The enhanced luminescence is primarily owing to the improved crystallinity of the sample. CIE chromaticity analysis found that the  $[(Gd_{0.9}Lu_{0.1})_{0.99}Ce_{0.01}]AG$ ,  $(Y_{0.99}Ce_{0.01})AG$  and (Lu<sub>0.99</sub>Ce<sub>0.01</sub>)AG phosphors have color coordinates of around (0.48,0.51), (0.39,0.57) and (0.31,0.58), corresponding to color temperatures of  $\sim 3044$ , 4612 and 6010 K, respectively. The Gd-containing phosphors all have similar color coordinates, despite the spectral shifting observed in figure 6(b). The chromaticity data further confirm that the  $(Gd_{1-x}Lu_x)AG: Ce^{3+}$  yellow phosphors developed in this work have more red portions in their emission than (Y<sub>0.99</sub>Ce<sub>0.01</sub>)AG and particularly (Lu<sub>0.99</sub>Ce<sub>0.01</sub>)AG, and are more desired for application in LEDs for warm-white lighting.

#### 4. Conclusions

 $[(Gd_{1-x}Lu_x)_{1-y}Ce_y]_3Al_5O_{12}$  garnet phosphors have been calcined from their respective carbonate precursors co-precipitated with ammonium bicarbonate. Detailed characterizations with the combined techniques of XRD, FE-SEM, BET and PLE/PL have yielded the following main conclusions:

- Lu<sup>3+</sup> doping not only effectively stabilizes the garnet lattice of (Gd,Ce)AG and lowers the temperature of garnet crystallization but also raises the effective atomic number and theoretical density of the material, which are important for scintillation applications.
- (2) The resultant (Gd, Lu)AG : Ce<sup>3+</sup> phosphors, with relatively good dispersion and fairly uniform particle morphologies, exhibit strong yellow emissions centered at  $\sim$  570 nm (5d–4f transition of Ce<sup>3+</sup>) under blue-light excitation at  $\sim$  457 nm (<sup>2</sup>F<sub>5/2</sub>–5d transition of Ce<sup>3+</sup>). The luminescence quenching concentration of Ce<sup>3+</sup> was determined to be  $\sim$  1.0 at.% and the quenching mechanism was proposed to be driven by exchange interactions. Increasing Ce<sup>3+</sup> doping tends to red-shift the emission spectra.
- (3) At the optimal  $Ce^{3+}$  content of 1.0 at.%, the  $Gd^{3+}$ -based garnet phosphors display substantially red-shifted emissions when compared with  $(Y_{0.99}Ce_{0.01})AG$ which and  $(Lu_{0.99}Ce_{0.01})AG$ , are desired for lighting. The warm-white most luminescent  $[(Gd_{0.9}Lu_{0.1})_{0.99}Ce_{0.01}]AG (x = 0.1, y = 0.01)$  phosphor is comparable to  $(Y_{0.99}Ce_{0.01})AG$  and higher than (Lu<sub>0.99</sub>Ce<sub>0.01</sub>)AG in emission intensity and is thus

expected to be a new yellow phosphor. More  $Lu^{3+}$  in (Gd, Lu)AG : Ce<sup>3+</sup> tends to deteriorate the luminescent performance, and thus its content should be minimized.

(4) A higher processing temperature from 1000 to 1500 °C yields a steadily improved emission intensity but also larger particles of the phosphor at the same time. For practical applications, the optimal processing temperature should be determined by considering the luminescence intensity and particle size.

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