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Investigation of New Red Phosphors of Eu^{3+} Activated (Gd, Lu) $_3Al_5O_{12}$ Garnet

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***Abstract*—The metastable garnet lattice of $Gd_3Al_5O_{12}$ (GdAG) has been effectively stabilized by doping smaller Lu^{3+}, which then allows an effective incorporation of rare earth ions Eu^{3+} activators for opto-functionality explorations. Detailed characterizations of the products were achieved by combined means of FT-IR, DTA/TG, XRD, FE-SEM, BET, PL/PLE. The $[(Gd_{0.5}Lu_{0.5})_{1-x}Eu_x]_3Al_5O_{12}$ (LnAG, x=0.01-0.09) garnet solid-solutions with good dispersion and a fairly uniform particle morphology were obtained by calcining their precursors with a general formula of $(NH_4)_xLn_3Al_5(OH)_y(CO_3)_z\ nH_2O$ (Ln=Gd, Lu and Eu), synthesized via carbonate coprecipitation. The LnAG exhibit strong 591 nm emissions (the $^5D_0\rightarrow{}^7F_1$ magnetic dipole transitions of Eu^{3+}) upon UV excitation into the charge transfer band (CTB) at ~238 nm with CIE chromaticity coordinates of x=0.62 and y=0.38 (orange red), and the quenching concentration of Eu^{3+} was found to be 5at% (x=0.05). Owing to the improved crystallization of LnAG at a higher temperature, luminescence emission intensity increases significantly, especially above 1300 ^oC. The Eu^{3+} doped (Gd,Lu)AG phosphors are expected to be a new type of photoluminescent and scintillation material.**

***Index Terms*—gadolinium aluminate garnet, Eu3+ doping, photoluminescence, lattice structure stabilization**

I. INTRODUCTION

Rare-earth aluminate garnets ($Ln_3Al_5O_{12}$, LnAG), especially YAG, are well-known inorganic compounds which have been widely studied for optical and high-temperature mechanical applications [1]. When properly activated with luminescent centers, the LnAG compounds are important inorganic phosphors (such as YAG:Ce) finding wide applications in cathode-ray tubes (CRTs), field emission displays (FEDs), scintillation, vacuum fluorescent displays (VFDs), electroluminescence (EL), and so forth [2], because of their high chemical and radiation stabilities, wide bandgap and excellent radiation conversion efficiency.

The $Gd_3Al_5O_{12}$ (GdAG) based phosphor, though it has higher density than YAG and the Gd^{3+} in this system can Sensitize the $^5D_0\rightarrow{}^7F_{1,2}$ red emissions of Eu^{3+} through an efficient energy transfer [3], has been rarely reported. This is mainly because the GdAG compound is stable up to about 1300 ℃, followed by a thermal decomposition to $GdAlO_3$ perovskite and Al_2O_3 at the even higher temperature up to 1500 ℃ [4]. Doping GdAG with larger Eu^{3+} ions would further destabilize the garnet structure and lower the decomposition temperature. This severely retards the development of GdAG-based phosphors and transparent ceramics.

To suppress the thermal decomposition of GdAG: Eu, doping GdAG: Eu with significantly smaller Lu^{3+} to form (Gd, Lu) AG: Eu solid solutions was proposed in the present work. With this, a new type of red phosphor of the (Gd, Lu) AG: Eu system was synthesized via a well-established carbonate coprecipitation methodology [5]. Phase evolution of the as-synthesized precursors upon calcination and luminescence behaviors of the oxide phosphors were studied in detail via the combined techniques of FT-IR, DTA/TG, XRD, FE-SEM, BET and PL/PLE luminescence spectroscopy. In the following sections, we report the synthesis, characterization, and luminescent performance of the (Gd, Lu) AG: Eu garnet phosphors.

II. EXPERIMENT PROCEDURE

The starting chemicals used in this work are rare earth oxide Ln_2O_3 (Ln=Gd, Lu and Eu, respectively, 99.99% pure, Huizhou Ruier Rare-Chem. Hi-Tech. Co. Ltd., Huizhou, China), ammonium aluminum sulfate dodecahydrate (alum, $NH_4Al(SO_4)_2\cdot 12H_2O$, >99% pure, Zhenxin chemical Reagent Factory, Shanghai, China), ammonium hydrogen carbonate (AHC, NH_4HCO_3, analytical grade, Shenyang Chemical Reagent Factory, Shenyang, China), and nitric acid (HNO_3, excellent grade, Shenyang Chemical Reagent Factory). All the reagents are used as received without further purification.

Concentrated rare-earth nitrate solutions were prepared by dissolving Ln_2O_3 (Ln=Gd, Lu and Eu) in proper amounts of hot nitric acid. Aqueous solutions for precipitation were then made from the nitrate solutions and alum according to the formula $[(Gd_{0.5}Lu_{0.5})_{1-x}Eu_x]_3Al_5O_{12}$. Precursor precipitate was synthesized by dropwise adding 200 mL of a 0.15 M (for Al^{3+}) mixed solution of the mother salts into 320 mL of a 1.5 M AHC

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solution under mild stirring at room temperature. The precipitate was aged for 30 min at room temperature after the completion of precipitation, centrifuged, and washed repeatedly with distilled water and alcohol to remove by-products. The wet precipitate was dried in air at 100 ^{o}C for 24 h, lightly crushed, and was finally calcined in air at the selected temperatures for 4 h to produce oxides.

Phase structure of the powder was identified via XRD (Model PW3040/60, PANAL YTICAL.B.V, Almelo, the Netherlands) using nickel-filtered Cu*K*α radiation at a scanning speed of 4° 2θ/min. Morphology and microstructure of the calcined powders were observed by FE-SEM (Model JSM-7001F, JEOL, Tokyo, Japan). Specific surface areas of the LnAG powders were analyzed on an automatic surface area analyzer (Model TriStar II 3020, Micrometritics Instrument Corp., Norcross, GA) using the Brunauer-Emmett-Teller (BET) method via nitrogen adsorption at 77 K. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the (Gd,Lu)AG:Eu phosphors were collected at room temperature using an FP-6500 fluorescence spectrophotometer (JASCO, Tokyo, Japan) equipped with a Φ60-mm intergating sphere (Model ISF-513, JASCO, Tokyo, Japan) and a 150-W Xe-lamp as the excitation source.

III. RESULTS AND DISCUSSION

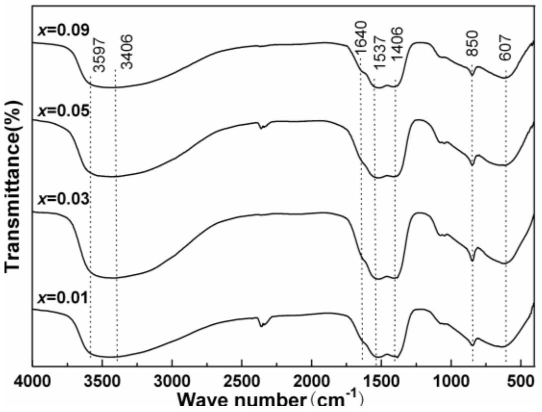

Figure 1. Spectra for the four typical precursors of x =0.01, 0.03, 0.05 and 0.09 respectively.

The functional groups built in the precursors were investigated via FT-IR spectroscopy shown in Fig. 1, using the four typical samples as examples. It is observed that the four samples have similar IR absorption behaviors, suggesting their similar chemical compositions, regardless their different Eu content.

The absorption band at ~3597 cm^{-1} is indicative of hydroxyl (OH^{-}) groups [6], [7]. The broad absorption band at ~3406 cm^{-1} and the shallow shoulder near 1645 cm^{-1} provide evidence of water of hydration in the molecule or surface adsorbed water and are assignable to the O-H stretching vibrations and the H-O-H bending mode, respectively [6], [7]. NH_4^+ usually exhibits absorptions in the region ~3000-3500 cm^{-1}, overlapping with water absorptions, and is thus difficult to distinguish. The shallow absorptions near 2344 cm^{-1} come from surface adsorbed CO_2 and are assignable to the C=O vibrations. The weak absorptions at ~1537, ~1387 and ~850 cm^{-1} may correspond to the characteristic vibrations of carbonate ions The absorption at ~600 cm^{-1} arises from M-O vibrations (M: metallic elements). The results of FT-IR suggest that the precursors have a general formula of $(NH_4)_xLn_3Al_5(OH)_y(CO_3)_z\ nH_2O$ (Ln=Gd, Lu and Eu), in agreement with the results of Li et al [5] with the YAG precursors synthesized similarly.

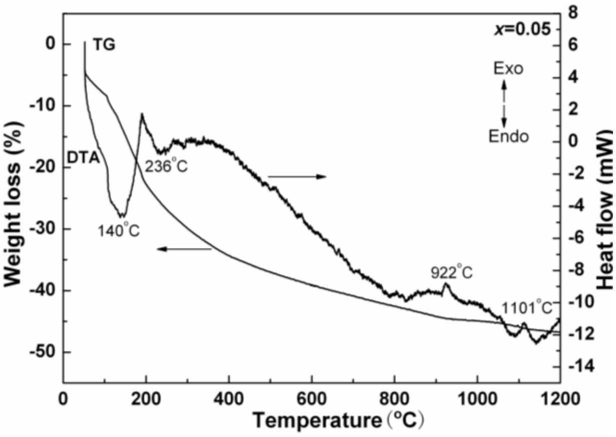

Figure 2. DTA/TG curves of the [(Gd0.5Lu0.5)2.95Eu0.05]Al5O12 precursor

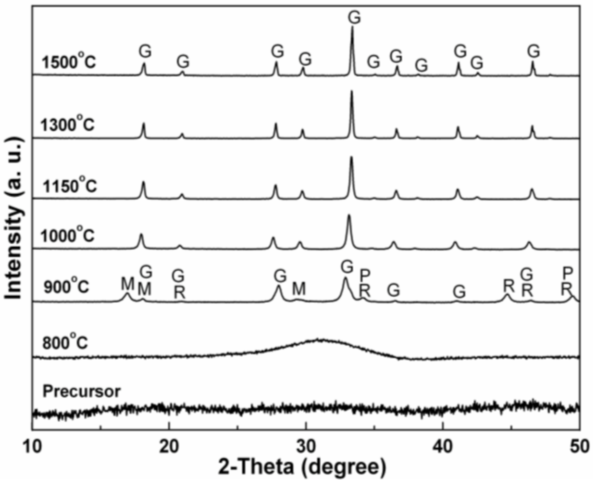

Figure 3. XRD patterns of the [(Gd0.5Lu0.5)0.95Eu0.05]3Al5O12 (x=0.05) powders calcined at various temperatures.

DTA/TG has been performed to study the thermal behaviors of the precursors, and the results are given in Fig. 2 with the x=0.05 as an example. Two endothermic and two exothermic peaks are identified on the DTA/TG curves up to 1200 ℃ with a total weight loss of ~46.92%. The relative larger endothermic peak centered at ~140 ℃, is primarily assigned to the removal of molecular water. The smaller endotherm located at ~236 ℃ is attributable to the decomposition of the ammonium component in the molecule and the release of ammonia. The exotherm peaking at ~922 ℃ is caused by the simultaneous crystallization of rare-earth sesquioxide Ln_2O_3, $Ln_4Al_2O_9$ monoclinic (LnAM, Ln=(Gd, Lu and Eu), $LnAlO_3$ perovskite (LnAP), and LnAG garnet phases, while that at

~1101 ℃ is due to the further crystallization of LnAG via the reactions between LnAP/LnAM and alumina, as evidenced by the XRD results given in Fig. 3.

Fig. 3 displays temperature-course phase evolution of the precursor upon calcination using x=0.05 sample as an example. It is seen that the precursor and the powders calcined up to 800 ^{o}C are essentially amorphous. Crystallization of the amorphous precursor started at 900 ℃ yielding a mixture of rare-earth sesquioxide Ln_2O_3, $Ln_4Al_2O_9$ monoclinic (LnAM), $LnAlO_3$ perovskite (LnAP), and LnAG garnet phases. Stronger diffractions from LnAG while weaker ones from the other phases were observed as the calcination temperature increases, indicating further crystallization of LnAG via the reactions among the other three phases and amorphous alumina [8]. Similar crystallization sequences were also widely observed for YAG crystallization via solid reaction from powder mixtures of the component oxides [9] and from some types of wet-chemically synthesized precursors [5]. The x=0.05 sample completely transformed into LnAG at 1000 ℃. The crystallization temperature is appreciably lower than those (up to 1500 ℃) needed for solid reaction, owing to the improved cation homogeneity in the coprecipitated carbonate precursor. Annealing at the even higher temperature up to 1500 ^{o}C only yielded stronger and sharper XRD peaks of the product but no change in phase purity, indicating that the garnet lattice of GdAG:Eu has been fully stabilized with the incorporated Lu^{3+}. Based upon the XRD analysis shown in Fig. 3, a cell constant of 1.1953 nm was obtained for the x=0.05 sample after calcination at 1500 ^{o}C for 4 h, from which the density was calculated to be 6.41 g/cm^3, approaching that of LuAG (6.73 g/cm^3). The stabilized garnet structure, the increased effective atomic number and the improved theoretical density via Lu^{3+} doping thus allow (Gd,Lu)AG:Eu to be a new type of promising scintillation material.

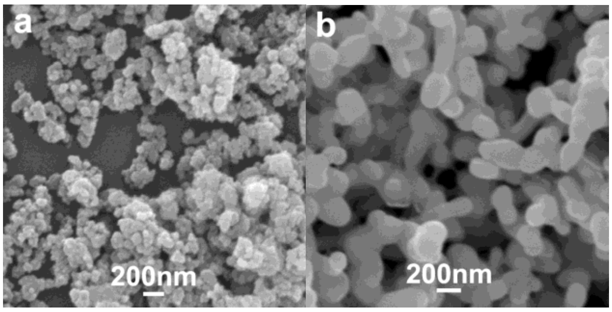

Figure 4. FE-SEM micrographs showing the particle morphology of (a) the [(Gd0.5Lu0.5)0.95Eu0.05] AG precursor and (b) the powder produced at 1300 ℃.

FE-SEM analysis of particle morphology (Fig. 4) indicated that all the precursors obtained in this work are loosely agglomerated and composed of much finer primary particles, as seen from the sample x = 0.05 for example (Fig. 4a). The oxide crystallites/particles for x=0.05 sample grow significantly with increasing calcination temperature, but relatively good dispersion persists up to 1300 ℃ owing to the excellent dispersion of the carbonate precursors (Fig. 4b). BET analysis found specific areas of ~20, ~10, and ~4.5 m^2/g for the powders obtained at 1000, 1150 and 1300 ℃, from which the average particle sizes were calculated to be ~45, 90 and 230 nm, respectively. These size values are close to those observed from the FE-SEM micrographs.

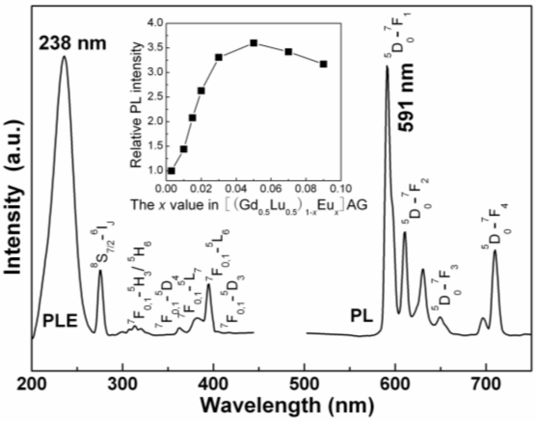

Figure 5. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the x=0.05 phosphor calcined at 1300 ℃. The PLE spectrum was obtained by monitoring the 591 nm emission, while the PL spectrum was obtained under UV excitation at 238 nm. Inset is the relative intensity of the 591 nm emission as a function of the Eu3+ content, where the relative intensities were obtained by normalizing the observed 591 nm PL intensities of the samples to that of the x=0.003 sample.

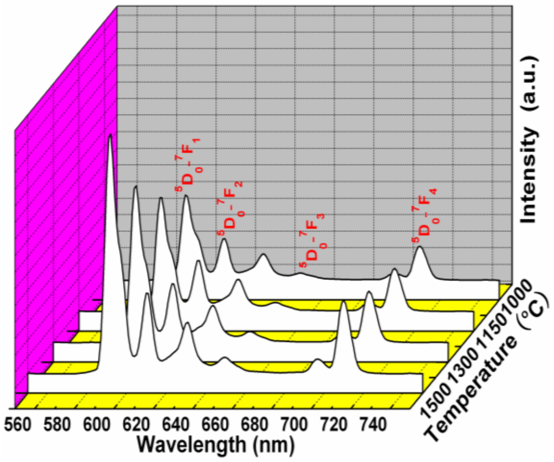

Figure 6. PL spectra of sample [(Gd0.5Lu0.5)0.95Eu0.05]3Al5O12 as a function of the calcination temperature.

Fig. 5 depicts the PLE and PL spectra of sample $[(Gd_{0.5}Lu_{0.5})_{0.95}Eu_{0.05}]$ AG calcined at 1300 ℃ for 4 h. A general observation is that the PLE spectrum is composed of a strong CTB band located at ~238 nm [3] and a series of much weaker intra-4f^6 electronic transitions of Eu^{3+} in the longer wavelength region [10] as marked in the figure. It should be noted that the typical $^8S_{7/2}\rightarrow{}^6I_J$ intra f-f transition of Gd^{3+} is clearly observed at 275 nm [3], providing direct evidence of an energy transfer from Gd^{3+} to the Eu^{3+} activators. Upon UV excitation at ~238 nm, the phosphors exhibit the typical $^5D_0\rightarrow{}^7F_J$ (J = 1, 2, 3, 4, as labeled in the figure) transitions of Eu^{3+} in the 500-750 region, with the PL spectra dominated by the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition at 591 nm. In cubic GdAG, Gd^{3+} is coordinated by eight oxygen ions and possesses D_2 point symmetry [10]. The Lu^{3+} and Eu^{3+} dopant ions would substitute for Gd^{3+} and thus inherit the D_2 symmetry. As the exact local symmetry is only a small distortion of the highly centro-symmetric D_{2h} point symmetry, the emission spectrum is thus dominated by the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition at 591 nm rather than the $^5D_0 \rightarrow ^7F_2$ forced electric dipole transition at 610 nm. Varying the Eu^{3+} content from $x = 0.003$ to 0.09 does not alter peak positions of the emission bands but induces significantly varied emission intensities. The inset in Fig. 5 shows relative intensity of the 591 nm emission as a function of the Eu^{3+} content, from which it can be seen that the emission significantly improves up to ~5 at% of Eu^{3+} (x=0.05) and then deteriorates owing to concentration quenching.

The effects of annealing temperature on PL properties were studied with the optimal composition $[(Gd_{0.5}Lu_{0.5})_{0.95}Eu_{0.05}]$ AG as an example and the results are shown in Fig. 6. Though the PL bands do not show any appreciable change in the peak position of each $^5D_0 \rightarrow ^7F_J$ transition, significantly improved luminescent intensity was observed at a higher temperature, especially when it is above 1300 ℃. A 176% increase in the intensity of the 591 nm emission was yielded with a 500 ℃ temperature increase from 1000 to 1500 ℃. This is mainly due to the improved crystallinity and the increased particle size as revealed by XRD (Fig. 3). The 1500 ℃ sample has CIE chromaticity coordinates of x=0.62 and y=0.38 and thus emits a vivid orange-red color.

IV. CONCLUSIONS

Orange red emitting $[(Gd_{0.5}Lu_{0.5})_{1-x}Eu_x]_3Al_5O_{12}$ (LnAG) garnets have been calcined from their carbonate-based precursors synthesized via coprecipitation in the temperature range of 1000-1500 ℃. The resultant LnAG powders show relatively good dispersion and fairly uniform particle morphologies. Lu^{3+} doping not only stabilizes the garnet structure of (Gd, Eu) AG, but also raises the effective atomic number and theoretical density of the material. The LnAG particles exhibit strong emissions at 591 nm ($^5D_0 \rightarrow ^7F_1$ magnetic dipole transition) upon UV excitation into the charge transfer band at ~238 nm, and the quenching concentration of Eu^{3+} is ~5 at%. A higher calcination temperature, particularly above 1300 ^{o}C, greatly improves the intensity of the 591 nm emission. The materials developed in this work may potentially find wide applications in luminescence and scintillation areas.

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Jinkai Li was born in Weifang city, Shandong province, China on Dec. 1st 1985. In 2003, Jinkai Li studied in the University of Jinan which is located in Jinan city, Shandong province, China, engaged in non-crystal materials research, and got a four-year bachelor's degree in Materials Physics in 2007. In the same year, Jinkai Li studied in the University of Jinan as well in Materials Science. His major research filed was focused on nanofluid materials research and got a three-year master's degree in 2010. In 2010 until now, He entered in Northeastern University located at Shenyang city, Liaoning province, China for achieving a doctor's degree. His major is Materials Science. His published articles are listed as follows: (1) Li JK, Li J-G, Zhang Z J, Wu XL, Liu SH, Li XD, Sun XD, Sakka Y. Gadolinium Aluminate Garnet $(Gd_3Al_5O_{12})$: Crystal Structure Stabilization via Lutetium Doping and Properties of the $(Gd_{1-x}Lu_x)_3Al_5O_{12}$ Solid Solutions (x=0-0.5). Journal of the American Ceramic Society 2012, 95(3):931-936; (2) Li JK, Li J-G, Li J, Liu SH, Li XD, Sun XD, Sakka Y. Development of Eu^{3+} activated monoclinic, perovskite, and garnet compounds in the Gd_2O_3-Al_2O_3 phase diagram as efficient red-emitting phosphors. Journal of Solid

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