Effective lattice stabilization of gadolinium aluminate garnet (GdAG) via Lu\(^{3+}\) doping and development of highly efficient (Gd,Lu)AG:Eu\(^{3+}\) red phosphors

Jinkai Li\(^1\), Ji-Guang Li\(^1,2\), Zhongjie Zhang\(^1\), Xiaoli Wu\(^1\), Shaohong Liu\(^1\), Xiaodong Li\(^1\), Xudong Sun\(^1\) and Yoshio Sakka\(^2\)

\(^1\) Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110004, China
\(^2\) Advanced Materials Processing Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: LJjiguang@nims.go.jp

Received 7 March 2012
Accepted for publication 6 May 2012
Published 27 June 2012
Online at stacks.iop.org/STAM/13/035007

Abstract

The metastable garnet lattice of Gd\(_3\)Al\(_5\)O\(_{12}\) is stabilized by doping with smaller Lu\(^{3+}\), which then allows an effective incorporation of larger Eu\(^{3+}\) activators. The [(Gd\(_{1-x}\)Lu\(_x\))(1-y)Eu\(_y\)]\(_3\)Al\(_5\)O\(_{12}\) (x = 0.1–0.5, y = 0.01–0.09) garnet solid solutions, calcined from their precursors synthesized via carbonate coprecipitation, exhibit strong luminescence at 591 nm (the 5D\(_0\) → 7F\(_1\) magnetic dipole transition of Eu\(^{3+}\)) upon UV excitation into the charge transfer band (CTB) at \(~\)239 nm, with CIE chromaticity coordinates of x = 0.620 and y = 0.380 (orange-red). The quenching concentration of Eu\(^{3+}\) was estimated at \(~\)5 at.\% (y = 0.05), and the quenching was attributed to exchange interactions. Partial replacement of Gd\(^{3+}\) with Lu\(^{3+}\) up to 50 at.\% (x = 0.5) while keeping Eu\(^{3+}\) at the optimal content of 5 at.\% does not significantly alter the peak positions of the CTB and 5D\(_0\) → 7F\(_1\) emission bands but slightly weakens both bands owing to the higher electronegativity of Lu\(^{3+}\).

The effects of processing temperature (1000–1500 °C) and Lu/Eu contents on the intensity, quantum efficiency, lifetime and asymmetry factor of luminescence were thoroughly investigated. The [(Gd\(_{0.7}\)Lu\(_{0.3}\))(0.95Eu\(_{0.05}\))]\(_3\)Al\(_5\)O\(_{12}\) phosphor processed at 1500 °C exhibits a high internal quantum efficiency of \(~\)83.2% under 239 nm excitation, which, in combination with the high theoretical density, favors its use as a new type of photoluminescent and scintillation material.

Keywords: gadolinium aluminate garnet, lattice stabilization, Eu\(^{3+}\) doping, photoluminescence

1. Introduction

Rare-earth aluminate garnets (REAG, RE\(_3\)Al\(_5\)O\(_{12}\)), especially YAG, have been widely studied for optical and high-temperature mechanical applications [1, 2]. When properly activated with luminescent centers, the REAG compounds are important inorganic phosphors (such as YAG:Ce), which find applications in cathode ray tubes (CRTs), field emission displays (FEDs), vacuum fluorescent displays, scintillators, electroluminescent materials and so forth [3–7], owing to their high chemical and radiation stabilities, wide bandgap and excellent radiation conversion efficiency. YAG:Tb is a green phosphor used in FEDs [8–11], while Ce\(^{3+}\)-activated YAG and LuAG yellow phosphors combined with blue light-emitting diodes (LEDs) are efficient white-light sources [12–16]. Eu-activated YAG and LuAG
are also promising red phosphors that may be widely used in optical displays and lighting [16–20].

The [(Gd\(_{1-x}\),Lu\(_x\))\(_{3-y}\),Eu\(_y\)]Al\(_2\)O\(_12\) solid solution system was chosen for this study because of the following three major reasons:

1. Gd\(_2\)Al\(_2\)O\(_12\) (GdAG) is isostructural with YAG and belongs to the cubic space group 1\(\bar{a}\)3\(d\) at room temperature. Compared with Eu\(_{3+}\)-activated YAG, the smaller electronegativity of Gd\(_{3+}\) (1.20) than that of Y\(_{3+}\) (1.22) may result in an easier charge transfer (CT) from the 2p orbital of O\(_{2-}\) to the 4f orbital of Eu\(_{3+}\) and thus higher intensities of the CT/PL bands [21, 22]. In addition, Gd\(_{3+}\) may sensitize the \(5\)D\(_0\) \(\rightarrow\) \(7\)F\(_{1/2}\) red emissions of Eu\(_{3+}\) through an efficient energy transfer from Gd\(_{3+}\) to Eu\(_{3+}\) [23, 24], further improving Eu\(_{3+}\) luminescence.

2. GdAG is stable up to about 1300 °C and decomposes to GdAlO\(_3\) perovskite and Al\(_2\)O\(_3\) at higher temperatures up to 1500 °C [25]. Doping GdAG with larger Eu\(_{3+}\) ions would further destabilize the garnet structure and lower the decomposition temperature. This severely retards the development of (Gd,Eu)AG-based phosphors and transparent ceramics. Our recent results revealed that the crystal structure of GdAG could be effectively stabilized via doping with 10 at% or more of Lu\(_{3+}\) to form (Gd,Lu)AG solid solutions [26], paving the way for the development of highly efficient (Gd,Lu)AG:Eu red phosphors.

3. For scintillation applications, the material should have a high theoretical density to ensure a high x-ray stopping power. In this regard, the (Gd,Lu)AG solid solution is more desirable than YAG as the host lattice because Lu (175) and Gd (157) have much higher atomic weight than Y (89). Therefore, (Gd,Lu)AG:Eu can potentially become a new kind of scintillation material.

REAG powders are traditionally synthesized via solid-state reaction of the component oxides [27, 28], which has the shortcomings of high annealing temperature, lengthy intermittent grinding, contamination, large particle size and significant aggregation of the final product. Therefore, soft chemical processing is currently widely adopted for the synthesis of fluorescent powders [7–15]. In this work, (Gd,Lu)AG:Eu phosphors were calcined from their precursors synthesized via carbonate coprecipitation with ammonium hydrogen carbonate as the precipitant [29]. Phase evolution of the precursors upon calcination and photoluminescence properties of the oxide phosphors were studied by the combination of x-ray diffractometry (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), photoluminescence excitation/photoluminescence (PLE/PL) spectroscopy and fluorescence decay analysis. Luminous properties of the (Gd,Lu)AG:Eu phosphors were correlated with the processing temperature, specific surface area (particle size) of the powder and, particularly, the Lu\(_{3+}\) and Eu\(_{3+}\) contents.

2. Experimental procedure

The starting chemicals used in this work were gadolinium oxide (Gd\(_2\)O\(_3\), 99.99% pure, Huizhou Ruier Rare-Chem. Hi-Tech. Co Ltd. Huizhou, China), lutetium oxide (Lu\(_2\)O\(_3\), 99.99% pure, Huizhou Ruier), europium oxide (Eu\(_2\)O\(_3\), 99.99% pure, Huizhou Ruier), ammonium aluminium sulfate dodecahydrate (alum, NH\(_4\)Al(SO\(_4\))\(_2\)-12H\(_2\)O >99% pure, Zhenxin Chemical Reagent Factory, Shanghai, China), ammonium hydrogen carbonate (AHC, NH\(_4\)HCO\(_3\)), analytical grade, Shenyang Chemical Reagent Factory, Shenyang, China) and nitric acid (HNO\(_3\), excellent grade, Shenyang Chemical Reagent Factory). All the reagents were used as received without further purification.

Concentrated rare-earth nitrates solutions were prepared by dissolving RE\(_2\)O\(_3\) (RE = 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\(_{1-x}\),Lu\(_x\))\(_{3-y}\),Eu\(_y\)]Al\(_2\)O\(_12\). Precursor precipitate was synthesized by adding dropwise 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 solution under mild stirring at room temperature. In all the cases, the total concentration of Gd\(_{3+}\), Lu\(_{3+}\) and Eu\(_{3+}\) was kept constant at 0.09 M so that the (Gd + Lu + Eu):Al atomic ratio would be the 3 : 5 of the garnet formula. The \(x = Lu/(Lu + Gd)\) and \(y = Eu/(Eu + Lu + Gd)\) atomic ratios in \([(Gd\(_{1-x}\),Lu\(_x\))\(_{3-y}\),Eu\(_y\)]Al\(_2\)O\(_12\) were varied to reveal the effects of Lu\(_{3+}\) and Eu\(_{3+}\) contents on characteristics of the resultant REAG (RE = Gd, Lu and Eu) powders. 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 °C for 24 h, lightly crushed and calcined in air at selected temperatures for 4 h to produce oxides.

Phase composition of the powder was characterized by XRD (Model PW3040/60, PANAL YTICAL.B.V, Almelo, the Netherlands) using nickel-filtered CuK\(_\alpha\) radiation at a scanning speed of 4´2θ min\(^{-1}\). Morphology and microstructure of the calcined powders were observed by FE-SEM (Model JSM-7001F, JEOL, Tokyo, Japan) and TEM (Model JSM-3000F, JEOL, Tokyo, Japan). Specific surface areas of the REAG powders were measured with an automatic surface area analyzer (Model TriStar II 3020, Micromeritics Instrument Corp, Norcross, GA) using the Brunauer–Emmett–Teller (BET) method via nitrogen adsorption at 77 K. PL and PLE spectra of the (Gd,Lu)AG:Eu phosphors were acquired at room temperature using an FP-6500 fluorescence spectrophotometer (JASCO, Tokyo, Japan) equipped with a 60 mm-diameter integrating sphere (Model ISF-513, JASCO, Tokyo, Japan) and a 150 W Xe lamp as the excitation source. Monochromatization of the excitation and emission lights was achieved with a Rowland concave grating (1800 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. Spectral responses of the equipment were corrected in the range of 220–850 nm with a Rhodamine-B solution.
Figure 1. XRD patterns of the [(Gd$_{1-x}$Lu$_x$)$_{0.95}$Eu$_{0.05}$]$_3$Al$_5$O$_{12}$ powders with the Lu contents (a) $x = 0$, (b) $x = 0.1$ and (c) $x = 0.2$ calcined at different temperatures; (d) a comparison of the XRD patterns of the powders calcined at 1500 °C. The letters G, P, M and R represent REAG garnet, REAP perovskite, monoclinic REAM and RE$_2$O$_3$ phases, respectively. RE = Gd and Eu for the $x = 0$ sample and RE = Gd, Lu and Eu for the others. All the unlabeled peaks belong to the REAG phase.

3. Results and discussion

Figure 1 shows phase evolution of [(Gd$_{1-x}$Lu$_x$)$_{0.95}$Eu$_{0.05}$]$_3$Al$_5$O$_{12}$ versus ination temperature revealing that the precursors and powders calcined up to 800 °C are essentially amorphous (figures 1(a)–(c)). Crystallization of the amorphous mass started at ∼900 °C, at which point rare-earth sesquioxide RE$_2$O$_3$, monoclinic RE$_3$Al$_5$O$_9$ (REAM), REIO$_3$ perovskite (REAP) and REAG garnet phases emerged simultaneously (figures 1(a)–(c)). The intensity of REAG diffractions increased while the RE$_2$O$_3$, REAM and REAP peaks weakened with increasing temperature (figures 1(a)–(c)), indicating further crystallization of REAG via the reactions among the other three phases and amorphous alumina [26]. Similar crystallization sequences were observed for YAG crystallization via solid-state reaction from powder mixtures of the component oxides [30] and from some types of precursors prepared by wet chemical synthesis [31]. The $x = 0.1$ and $x = 0.2$ samples completely transformed into REAG at 1300 °C (figure 1(b)) and 1150 °C (figure 1(c)), respectively. Sharper and stronger REAG diffractions were observed at even higher temperatures up to 1500 °C, indicating crystal growth.

The garnet structure of these Lu$^{3+}$-containing samples ($x = 0.1$–0.5) persisted up to 1500 °C (figure 1(d)), and no impurity phase was detectable with XRD. The Lu-free sample ($x = 0$), however, remained up to 1500 °C as a phase mixture of REAG, REAP and quasi-amorphous alumina that was undetectable by XRD, and no phase-pure garnet could be obtained (figure 1(a)). However, for the $x = 0$ sample, under identical calcination at 1300 °C, (Gd,Eu)AP crystallized as the major phase in the present work, whereas GdAG was the dominant phase in Eu$^{3+}$-free samples [26]. This result suggests that doping GdAG with the larger Eu$^{3+}$ ion destabilizes the garnet structure and hinders the crystallization of pure garnet. It is also seen from figures 1(a)–(c) that Lu$^{3+}$
Figure 2. Lattice constants and theoretical densities versus the Lu content in the \([\text{[(Gd}_{1-x}\text{Lu}_x)_{0.95}\text{Eu}_{0.05}]}\)\text{Al}_2\text{O}_3\] solid solutions calcined at 1500 °C.

doping lowers the temperature of REAG crystallization, and, for \(y = 0.05\) (5 at.% of Eu), the addition of 10 at.% Lu\(^{3+}\) \((x = 0.1)\) stabilized the garnet structure against its thermal decomposition as \(\text{RE}_2\text{Al}_5\text{O}_{12} \rightarrow 3\text{REAI}_3\text{O}_9 + \text{Al}_2\text{O}_3\).

At the same Eu\(^{3+}\) content of 5 at.% \((y = 0.05)\), XRD peaks of the phase-pure REAG steadily shift toward the high angles with increasing Lu\(^{3+}\) concentration (figure 1(d)), suggesting the contraction of the unit cell dimensions. This shrinking can be explained by the smaller ionic radius of Lu\(^{3+}\) than that of Gd\(^{3+}\) (0.0977 and 0.1053 nm for 8fold coordination, respectively) \([32]\). Figure 2 shows the calculated lattice constants and theoretical densities of the \([\text{[(Gd}_{1-x}\text{Lu}_x)_{0.95}\text{Eu}_{0.05}]}\)AG solid solutions formed at 1500 °C, as a function of the Lu\(^{3+}\) content. Clearly, the cell parameter linearly decreases with Lu\(^{3+}\) concentration and follows Vegard’s law, implying that homogeneous solid solutions have already been formed. The theoretical density calculated from the cell parameters linearly increases with Lu\(^{3+}\) concentration and tends to approach that of LuAG \((6.73 \text{g cm}^{-3})\). The stabilized garnet structure, increased effective atomic number, and improved theoretical density via Lu\(^{3+}\) doping make (GdLu)AG:Eu a promising new scintillation material.

Figure 3 shows the particle morphologies for some typical samples. The oxide crystallites/particles grow significantly with increasing calcination temperature, but relatively good dispersion persists up to 1500 °C owing to the excellent dispersion of the carbonate precursors. BET analysis yielded specific surface areas of \(~8.083, 8.589, 4.009\) and \(0.153 \text{m}^2\text{g}^{-1}\) for the powders shown in figures 3(a)–(d), respectively.

Figure 4 shows PLE and PL spectra of the \([\text{[(Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Eu}_{0.05}]}\)\text{Al}_2\text{O}_3\] sample calcined at 1150 °C for 4h. The broad and strong PLE band with a maximum at \(~239\) nm is ascribed to a CTB, namely, the electronic transition from the 2p orbital of O\(^{2-}\) to the 4f orbital of Eu\(^{3+}\) activators \([33]\). The typical \(8S_7/2 \rightarrow 2I_1\) intra-f-f transition of Gd\(^{3+}\) is clearly observed at 275 nm \([34]\), providing direct evidence of an energy transfer from Gd\(^{3+}\) to the Eu\(^{3+}\) activators. The typical \(8S_7/2 \rightarrow 6P_1\) transition of Gd\(^{3+}\), usually found at \(~311\) nm \([34]\), overlaps with the \(7F_{0,1} \rightarrow 5H_{3/2}\) transition of Eu\(^{3+}\) and is thus not clearly distinguishable. As marked in the figure, other bands were observed corresponding to the \(7F_{0,1} \rightarrow 5D_4\) transition of Eu\(^{3+}\) at \(~363\) nm, \(7F_{0,1} \rightarrow 5D_7\) transition at \(~382\) nm, \(7F_{0,1} \rightarrow 5D_6\) transition at \(~396\) nm and \(7F_{0,1} \rightarrow 5D_2\) transition at \(~414\) nm \([35]\). The emission spectra obtained by excitation into the CTB at 239 nm are composed of \(5D_0 \rightarrow 7F_j\) \((J = 1, 2, 3, 4)\), as labeled in the figure. Emission lines of Eu\(^{3+}\) dominated by the \(5D_0 \rightarrow 7F_1\) magnetic dipole transition at 591 nm. The strongest peak at 591 nm has a full width at half maximum (FWHM) of only \(~6\) nm, indicating high purity and crystallinity of the phosphor particles. In cubic GdAG, Gd\(^{3+}\) is coordinated by eight oxygen ions and possesses D\(_2\) point symmetry \([4]\). 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 slightly perturbed from the highly symmetric D\(_{2h}\) point group, the emission spectrum is 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. The \(5D_0 \rightarrow 7F_2\) transition of Eu\(^{3+}\) (580 nm) is only allowed for C\(_1\), C\(_n\) and C\(_{m\_}\) point groups, and is thus absent from the emission spectra of the well-crystallized (GdLu)AG:Eu phosphor obtained in this work. The 591 nm emission steadily gains intensity with increasing Eu\(^{3+}\) doping up to 5 at.% and then decreases (inset of figure 4), and the optimal Eu\(^{3+}\) content \((5\text{at.})\) determined in this work is close to those widely reported for the Y, Gd\(_{2}\)O\(_3\):Eu phosphor systems \([36]\).

Huang and Lou \([37]\) previously developed a theoretical description on the relationship between the luminescence intensity and the activator concentration, which agrees with the recent experimental results by Dai et al \([38]\), Li et al \([39]\) and Meng et al \([40]\). According to Huang et al, the type of luminescence quenching in solids can be concluded by analyzing the constant \(s\) in the following equation \([37,38]\):

\[
\log(I/c) = (-s/d) \log c + \log f, \tag{3}
\]

where \(I\) is the emission intensity, \(c\) the Eu\(^{3+}\) content, \(d\) the sample dimensionality \((d = 3\) for energy transfer among Eu\(^{3+}\) ions inside particles), \(f\) is independent of the dopant concentration, and \(s\) is the index of the electric multipole. The values of \(s\) are 6, 8 and 10 for the electric dipole–dipole, electric dipole–quadrupole and electric quadrupole–quadrupole interactions, respectively, whereas \(s = 3\) corresponds to the exchange interaction. The \(\log(I/c)−\log(c)\) plot of the 591 nm emission (figure 5) yields a slope \(-s/3 = -0.833 \pm 0.071\), i.e. an \(s\) value of approximately 3. This value indicates that the luminescence quenching is dominated by exchange interactions resulting from the energy transfer among Eu\(^{3+}\) ions. The associated processes can be broadly classified into radiative and non-radiative; the former is dominated by emission and radiative transfer, whereas the latter includes internal relaxation and multipolar interactions between ions \([41]\). With increasing Eu\(^{3+}\) content, the emission intensity first increases because of the larger number of luminous centers. A further increase in the Eu\(^{3+}\) concentration, however, enhances the probability of energy transfer among the Eu\(^{3+}\) activators due to the shortened distances among them.
that ‘phonon-assisted three $\text{Eu}^{3+}$ ion nonresonant interactions’ are responsible for the energy transfer and luminescence quenching [41].

Figure 3. Particle morphologies of the samples with (a) $x = 0.3$ and $y = 0.05$ calcined at 1150$^\circ$C, (b)–(d) $x = 0.5$ and $y = 0.05$ calcined at 1150, 1300 and 1500$^\circ$C, respectively.

Figure 4. PLE and PL spectra of the $x = 0.3$, $y = 0.05$ phosphor calcined at 1150$^\circ$C. The PLE spectrum was obtained by monitoring the 591 nm emission, while the PL spectrum was obtained under UV excitation at 239 nm. Inset shows the relative intensity of the 591 nm emission, normalized to that of the $y = 0.01$ sample, as a function of the $\text{Eu}^{3+}$ content.

Figure 5. Relationship between log($I/c$) and log ($c$) for the $[\{(Gd_{0.7}Lu_{0.3})_{1-y}\text{Eu}_y\}Al_5O_{12}$ phosphors calcined at 1150$^\circ$C for 4 h.

While keeping $\text{Eu}^{3+}$ at the optimal content of 5 at.%, the effects of $\text{Lu}^{3+}$ concentration on the PLE and PL properties of the phosphors were studied and the results are shown in figure 6. Replacing Gd$^{3+}$ with Lu$^{3+}$ up to 50 at.% does not significantly affect the CTB position but tends to blue-shift the
Yields of 71.7, 69.3, 62.4 and 57.7% and external efficiency by Lu primarily due to the decreased covalency of the chemical bond in the bond structure of the Eu\(^{3+}\) ion. The incorporation of Lu\(^{3+}\) also be attributed to the higher electronegativity of Lu\(^{3+}\) as expected from the CTB intensity. This result can also be attributed to the higher electronegativity of Lu\(^{3+}\).

Figure 6. Comparison of the PLE (a) and PL (b) spectra of the \([\text{Gd}_{0.8}\text{Lu}_{0.2}\text{Eu}_{0.05}]\text{Al}_2\text{O}_3\) phosphor powders calcined at 1150°C. The inset in (b) shows the relative intensity of the 591 nm emission, normalized to that of the \([\text{Gd}_{0.5}\text{Lu}_{0.5}\text{Eu}_{0.05}]\text{Al}_2\text{O}_3\) sample, as a function of the Lu content.

Figure 7. Intensity of the 591 nm emission for \([\text{Gd}_{0.5}\text{Lu}_{0.5}\text{Eu}_{0.05}]\text{Al}_2\text{O}_3\), as a function of the calcination temperature (a). Inset in (a) is the temperature-dependent intensity of the 591 nm emission normalized to that of the sample calcined at 1000°C; (b) is the appearance of emission from the 1500°C sample excited at 254 nm with a handheld UV lamp.

The effects of calcination temperature on PL have been investigated in the temperature range of 1000–1500°C on the sample of the \([\text{Gd}_{0.7}\text{Lu}_{0.3}\text{Eu}_{0.05}]\text{Al}_2\text{O}_3\) composition, and the results are shown in figure 7. While the positions of PL bands do not change appreciably, the PL intensity increases with sintering temperature, especially when it is above 1300°C—a 116% increase was recorded at 591 nm between 1000 and 1500°C (inset in figure 7(a)). This is mainly due to the improved crystallinity and increased particle size as revealed by XRD (figure 1) and morphological observations (figure 3). The 1500°C sample has CIE chromaticity coordinates of \(x = 0.620\) and \(y = 0.380\) and thus emits a vivid orange-red color, as also seen from the digital picture (figure 7(b)). It should be noted that all the
samples studied in this work have almost identical color coordinates. The samples processed at 1000, 1150, 1300 and 1500 °C have internal quantum efficiencies of 62.8, 69.3, 67.6 and 83.2% and external quantum yields of 38.1, 44.4, 47.5 and 56.1%, respectively. The high quantum efficiency and theoretical density of the 1500 °C powder make it an efficient luminescent and scintillation material.

Two types of dipole transitions exist in the Eu³⁺ emission spectrum, characterized by the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition and the $^5D_0 \rightarrow ^7F_2$ electric dipole transition. The Judd–Ofelt parity law predicts that the magnetic dipole transition is allowed, whereas the electric dipole transition is forbidden [43, 44]. The latter is allowed only if Eu³⁺ occupies low centrosymmetric points. The cubic Gd₃Al₅O₁₂ lattice, like Y₃Al₅O₁₂, has only one type of crystallographic position for Eu³⁺ substitution, that is, the centrosymmetric D₂ point. Accordingly, the $^5D_0 \rightarrow ^7F_2$ emission should be suppressed and only the $^5D_0 \rightarrow ^7F_1$ emission would occur in an ideal garnet lattice. The occurrence of $^5D_0 \rightarrow ^7F_2$ transition in this work might arise from a slight deviation of the Eu³⁺ site from D₂ symmetry due to the lattice distortion by Eu³⁺ and particularly Lu³⁺ doping and from the Eu³⁺ ions residing on the particle surface. Surface Eu³⁺ ions are not fully coordinated and therefore have lowered symmetries. The intensity ratio $I_{591}/I_{610}$, called asymmetry factor of luminescence, has been widely adopted to probe the local symmetry of Eu³⁺ ions. We analyzed the $I_{591}/I_{610}$ ratio for the powders processed at different temperatures and the results are shown in figure 8. A steady increase in the ratio from 2.06 to 2.85 was observed upon raising the temperature from 1000 to 1500 °C. This increase can be explained by two factors: (i) lattice perfection via interdiffusion of the cations, which allows the Eu³⁺ activators to move towards their crystallographic positions of D₂ symmetry, and (ii) decreased amount of surface Eu³⁺ ions due to the particle growth at higher processing temperatures.

Figure 9 shows decay kinetics of the 591 nm emission from the [Gd₀.₇Lu₀.₃]₃O₉Eu₀.₀₅]Al₂O₃ sample calcined at 1150 °C for 4 h. The decay curve can be fitted by a single exponent according to the equation

$$I = A \exp(-t/\tau_R) + B,$$

where $\tau_R$ is the fluorescence lifetime, $t$ the delay time, $I$ the relative intensity, and $A$ and $B$ are constants. The fitting yields $\tau_R = 7.28 \pm 0.15$ ms, $A = 106.45 \pm 3.77$ and $B = 0.16 \pm 0.06$. The inset in figure 9 is the lifetime of the 591 nm emission plotted against the processing temperature of the sample. A significant lifetime shortening from 8.87 to 4.09 ms was observed from 1000 to 1500 °C, with a drastic decrease starting at 1300 °C. The lifetime of the 1500 °C sample is close to that of the YAG:Eu powder (4.66 ms) synthesized by microwave processing through a sol–gel method [18].

In some Eu³⁺-doped oxides, a shorter luminescence lifetime is observed along with increasing surface area of the material, owing to the enhancement of the nonradiative transition rate by defects [45]. In other oxides, the lifetime decreases at a smaller surface area, as also observed in this work, due to the lowered radiative transition rate arising from the varied effective refractive index [46]. In the latter case, the radiative lifetime can be related to the refractive index using the equation [47]

$$\tau_R \sim \frac{1}{f(\text{ED}) \left[ \frac{1}{2} \left( n_{eff}^2 + 2 \right) \right]^2 n_{med}}.\tag{5}$$

Here, $f(\text{ED})$ is the oscillator strength for dipole transition, $\lambda_0$ is the wavelength in vacuum, $n_{eff}$ is the effective refractive index and $n_{eff} = n_c \cdot x + (1 - x) \cdot n_{med}$, where $x$ is the filling factor, that is, the fraction of space occupied by the particle in the surrounding medium (air in this work), and $n_c$ and $n_{med}$ are the refractive indices of the bulk material and surrounding medium, respectively; $n_{eff}$ roughly equals $n_{med}$ for extremely small particles, for which the $x$ value approaches 0. For the intermediately sized particles of our samples, $n_{eff}$ increases with the particle size. This would account for the decreasing...
lifetime at a higher calcination temperature of the sample. The effects of lattice defects on lifetime, however, can by no means be completely excluded. Deep traps can temporarily arrest electrons resulting in longer lifetimes. The concentration of such deep traps, if present, would decrease with processing temperature thereby shortening the lifetime. A detailed defect analysis is underway.

The effect of Lu$^{3+}$ content on fluorescence lifetime is shown in Figure 10. The lifetime significantly increases with Lu$^{3+}$ doping up to 50 at.%. This phenomenon may also be understood from Equation (5). BET analysis yielded specific surface areas of 8.083, 8.589, 9.001 and 9.844 m$^2$ g$^{-1}$ for the $x = 0.2, \ x = 0.3, \ x = 0.4$ and $x = 0.5$ samples, corresponding to average particle sizes of $\sim 120, 110, 105$ and 95 nm, respectively. The decreasing particle size might be the reason for the observed increasing lifetime at a higher Lu content. Here again, defects cannot be neglected, since Lu$^{3+}$ incorporation should induce lattice distortions.

Figure 11 reveals that the fluorescence lifetime shortens with increasing Eu$^{3+}$ content. As the samples processed at 1150 °C all have similar specific surface areas of $\sim 8.59$ m$^2$ g$^{-1}$, irrespective of the Eu$^{3+}$ content, this phenomenon might be understood as follows. When the Eu$^{3+}$ content is low, the interaction among luminescent centers can be neglected. In such a case, the energy transfer from the interior to surface sites is ineffective due to the long distances among the Eu$^{3+}$ ions, and thus, a relatively long lifetime is observed. A higher Eu$^{3+}$ concentration would lead to the formation of a resonant energy transfer net, which could act as an additional channel to the nonradiative centers on the surface and therefore shorten the lifetime. Compromised from the theoretical density of the material, effectiveness of garnet structure stabilization, fluorescence lifetime and intensity, the optimal composition was deduced in this study as [(Gd$_{0.8}$Lu$_{0.2}$)$_{1-y}$Eu$_y$]Al$_2$O$_3$ ($x = 0.2, \ y = 0.05$).

4. Conclusions

[(Gd$_{1-x}$Lu$_x$)$_{3-y}$Eu$_y$]Al$_2$O$_3$ (REAG:Eu) garnets with an orange-red luminescence have been prepared from carbonate-based precursors by calcination at 1000–1500 °C. The resultant REAG:Eu powders show relatively good dispersion and fairly uniform particle morphologies. Lu$^{3+}$ doping not only stabilizes the garnet structure of (Gd, Eu)AG and lowers the temperature of garnet crystallization, but also raises the effective atomic number and theoretical density of the material. The REAG:Eu particles exhibit strong emission at 591 nm ($^{5}D_{0} \rightarrow ^{7}F_{1}$ magnetic dipole transition) upon UV excitation into the charge transfer band at $\sim 239$ nm, and the quenching concentration of Eu$^{3+}$ is $\sim 5$ at.%. When keeping Eu$^{3+}$ at the optimal content of 5 at.%, the replacement of Gd$^{3+}$ with Lu$^{3+}$ up to 50 at.% weakens the 591 nm emission owing to the higher electronegativity of Lu$^{3+}$. Therefore, to achieve efficient luminescence, the Lu$^{3+}$ content should be minimized provided that the garnet structure is stabilized. Calcination at a higher temperature, particularly above 1300°C, greatly improves the intensity of the 591 nm emission. The lifetime of the 591 nm emission is closely related to the processing temperature of the sample and the Lu$^{3+}$ and Eu$^{3+}$ contents—a higher temperature or Eu$^{3+}$ content shortens whereas a higher Lu$^{3+}$ content increases the lifetime. The materials developed in this work may potentially find numerous applications in luminescence and scintillation fields.

Acknowledgments

This work was supported in part by the National Natural Science Foundation of China (Grants no. 50972025, 50990303, 50172030 and 51172038), the Liaoning BaiQianWan Talents Program, and the Fundamental Research Funds for the Central Universities (Grants no. N110802001, N100702001 and N110602008).
References

[1] Ikesue A and Aung Y L 2006 J. Am. Ceram. Soc. 89 1936
[2] Yagi H, Yanagitani T, Yoshida H, Nakatsuika M and Ueda K 2007 Opt. Laser Technol. 39 1295
[3] Lopez O A, McKittrick J and Shea L E 1997 J. Lumin. 71 1
[4] Ravichandran D, Roy R, Chakhovskoi A G, Hunt C E, White W B and Erdei S 1997 J. Lumin. 71 291
[5] McKittrick J, Shea L E, Bacsals C F and Bosze E J 1999 Displays 19 169
[6] Kang Y C, Lenggoro I W, Park S B and Okuyama K 2000 Mater. Res. Bull. 35 789
[7] Zhou H H, Lin J, Yu M, Han S M, Wang S B and Zhang H J 2003 Mater. Res. Bull. 38 1289
[8] Guo Z, Huang M L, Chen H H, Yang X X and Zhao J T 2012 J. Non-Cryst. Solids 358 88
[9] Choe J Y, Ravichandran D, Blomquist S M, Kirchner K W, Forsythe E W and Morton D C 2011 J. Lumin. 93 119
[10] Zhang J J, Ning J W, Liu X J, Pan Y B and Huang L P 2003 Mater. Res. Bull. 38 1249
[11] Hreniak D, Strezk W, Mazur P, Pazik R and Zazbkowska-Wacławek M 2004 Opt. Mater. 26 117
[12] Alldred A L 1961 J. Inorg. Nucl. Chem. 17 215
[13] Judd B R 1962 Phys. Rev. 127 750
[14] Opelt G S 1962 J. Chem. Phys. 37 511
[15] Peng H, Song H, Chen B, Wang J, Lu S and Yang X S 2002 J. Phys. Chem. B 106 3815
[16] Meltzer R S, Feofilov S P, Tissue B and Yuan H B 1982 Phys. Rev. B 25 1467
[17] Christensen H P, Gabbe D R and Jenssen H P 1982 Phys. Rev. B 25 1467
[18] Meneghetti M, Di Silvio E and Vannini V 2007 Phys. Rev. B 75 094109
[19] Mikheev A S and Seliverstov S 2008 Phys. Rev. B 78 094108