Preparation of Cerium-Activated GAG Phosphor Powders
Influence of Co-doping on Crystallinity and Luminescent Properties

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An impure-phase GdAlO₃ usually remains in the product of gadolinium aluminum garnet (GAG) powder as synthesized. In this study, an attempt to prepare a stable GAG pure-phase powder by substituting small cations (Tb³⁺, Y³⁺, or Lu³⁺) at the dodecahedral sites or the substituting the large cation (Ga³⁺) for the Al³⁺ sites of the garnet structure was made. Pure garnet-phase GAG powder was formed by calcining at 1500°C for 2 h. It was found that increasing the Lu³⁺ content in the Gd³⁺ lattice site of the dodecahedral or increasing the Ga³⁺ content in the Al³⁺ site induces a blue shift in the emission wavelength. The color temperature of the pure GAG:Ce (YAG:Ce) phosphor powder (~2000 K) formed was lower than that of yttrium aluminum garnet and terbium aluminum garnet (TAG:Ce) phosphors.

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Garnet crystal is widely used at high temperatures because of its low creep rate and high thermal and chemical stabilities.1,2 It is also used in solid-state laser host materials, refractory coating fillers, magnetic materials, and phosphor powders.3,4

The optical properties of Ce³⁺-activated garnet series phosphor used in white light emitting diodes (WLEDs) have received considerable attention in recent years.5 In some illuminant applications, especially indoor illumination, the light source requires a higher color rendering index (CRI) and a lower color temperature to create a pleasant, relaxing atmosphere. Unfortunately, WLED using yttrium aluminum garnet (YAG:Ce) as a light-conversion layer can create a “stark” or “cold” atmosphere because of their poor color qualities. Blending other red-emitting phosphors into the YAG:Ce phosphor or changing the YAG structure by substituting cations with different radius have been proposed as solutions to this problem.6,7 Recent researches have developed a novel garnet phosphor, cerium-activated terbium aluminum garnet (TAG:Ce), to produce a yellowish phosphor combined with a redder component.8,9 Huh et al. found that the λem of phosphor shifts to a longer wavelength as the doping concentration of Ga³⁺ in the YAG:Ce structure increases.10

The unit cell of the garnet phase ([Al]₃[Ga]₃[Cl]₀₁₂) has a symmetrical cubic structure in which A, B, and C are at the dodecahedral, octahedral, and tetrahedral sites, respectively. In the Re₂O₅–Al₂O₃ garnet system (Re, rare earth), Re ions occupy the 24C (dodecahedral site) (distorted cubic lattice) with coordination number (CN) = 8,11,12. In the Gd₂O₃–Al₂O₃ phase diagram, there are three stable compounds: gadolinium aluminum monoclinic (GAM, Gd₄Al₂O₇), gadolinium aluminum perovskite (GAP, GdAlO₃), and gadolinium aluminum garnet (GAG, Gd₃Al₅O₁₂).13

In previous studies, GAG powder was prepared by quenching the glass-crystallized product from a PbO or PbF₂ flux at a high temperature; however, the purity of the product was not described.14,15 Previous studies, GAG powder was prepared by quenching the glass-crystallized product from a PbO or PbF₂ flux at a high temperature; however, the purity of the product was not described.14,15

Experimental

The starting solution was Al(NO₃)₃, Gd₂O₃, and CeCl₃ at the molar ratio of Gd:Al/Ce = 2.97:5.03 with the total concentration of the cation 0.04 M. A precipitation process, with 0.2 M ammonium hydrogen carbonate (AHC) as the precipitation agent, followed the normal strike method as reported in detail in our previous studies.18,19 The doping concentrations of Tb³⁺, Y³⁺, Lu³⁺, and Ga³⁺ were at 10–30 atom % (the starting materials were Tb₂O₃, Y₂O₃, Lu₂O₃, and Ga₂O₃, respectively). The precipitates were filtered and dried at 100°C for 12 h and were then calcined at the desired temperature for 2 h. The calcined products were heated in an atmosphere of 95 vol % nitrogen and 5 vol % hydrogen at 1500°C for 2 h. The structure of the final products was identified using X-ray diffraction (XRD, Rigaku MultiFlex) with a scan speed of 4°/min and a scan step of 0.01°. Thermal behavior was determined by thermogravimetric-diifferential thermal analysis (Setsys Evolution TGA-DTA) at a heating rate of 10°C/min under a continuous nitrogen flow with 3 vol % hydrogen. The powder morphology was observed using a field emission transmission electron microscope (Hitachi FE2000). Emission and excitation spectra were detected with a Hitachi F-4500 spectrometer using a Xe lamp as the excitation source. In addition, the emission wavelength spectra of the samples were recorded with an MFS230 fluorescence spectrometer, excited at 470 nm.

Results and Discussion

Phase evolution of GAG:Ce phosphors.—Figure 1 shows the changes in the X-ray diffraction peak intensity of the product at different calcination temperatures. Three different phases, hexagonal GAP (H-GAP), orthorhombic GAP (O-GAP), and GAG, initially crystallized and coexisted in products after calcining at 900°C. The hexagonal perovskite structure transformed from the garnet precursor by wet-chemical processes16,17 is easily converted into the garnet phase at higher temperatures. Yamaguchi et al.22 derived a modified sol-gel process and gave the YAG synthesis scheme as:

amorphous precursor → hexagonal YAP → orthorhombic YAP → YAG

As presented in Fig. 1, H-GAP exists only in the temperature range below 1100°C and then transforms to GAP and GAG at higher temperatures. O-GAP is the intermediate phase at 1000–1100°C, which may be phase-transformed to the GAG phase when calcined at 1300–1400°C. Although GAG increased as the calcination temperature increased, it transformed to the O-GAP phase at temperatures above 1500–1600°C. These results indicate that the GAG phase only exists in a temperature region of
Figure 1. Relative intensity of the XRD peak of H-GAP (102), O-GAP (121), and GAG (420) as calcined at various temperatures.

1200–1400°C. In our work, the formation of the GAG mechanism could follow

\[
\text{hexagonal GAP} \rightarrow \text{orthorhombic GAP} \rightarrow \text{GAG}
\]

Figure 2 shows the TGA/DTA results of the as-precipitated powder, in which most of the weight loss occurred below 880°C. The initial endothermic peak located at 150°C would be the result of dehydration of H$_2$O (absorbed moisture and included molecular water) and the decomposition of ammonium dawsonite, which is commonly observed in the AHC precipitation process. Two exothermic peaks at about 910 and 930°C indicate the crystallization of H-GAP and GAP, respectively. The distinct exothermic peak around 1060°C may be attributed to the transformation of the O-GAP to GAG structure.

To prepare the pure garnet structure, four kinds of trivalent cations, Tb$^{3+}$ (104 pm), Y$^{3+}$ (102 pm), Lu$^{3+}$ (97 pm), and Ga$^{3+}$ (CN:4 = 47 pm, CN:6 = 55 pm) were doped to substitute for Gd$^{3+}$ (106 pm) and Al$^{3+}$ (CN:4 = 39 pm, CN:6 = 53 pm), respectively.

Table 1 is the summary of the phases presented by XRD analysis of the products calcined at 1300–1500°C. It was found that a decrease in the average substitutional ionic radius on the dodecahedral site favors a decrease in the diffraction peaks of GAP and the formation of pure GAG powder. Cockayne et al. and Kaminskii et al. reported that a single crystal of the garnet structure can be grown when the average ionic radius on the dodecahedral site is less than 0.103 nm. Kimura et al. obtained pure DyAG by co-doping larger ions, Gd$^{3+}$, and smaller ions, Y$^{3+}$, so that the mean radius of the dodecahedral site was less than 0.103 nm. Because Ga$^{3+}$ was adopted to substitute for the Al$^{3+}$ site, the pure GAG phase was obtained, and it was found that an increase in Ga$^{3+}$ content favors the formation of pure GAG structure. The smaller ions (Tb$^{3+}$, Y$^{3+}$, and Lu$^{3+}$) substituted for the Gd$^{3+}$ site or the bigger ions (Ga$^{3+}$) substituted for the Al$^{3+}$ site led to a decrease in the formation temperature of the pure garnet phase. Increasing the doping concentration also led to a decrease in the formation temperature of the pure garnet phase.

Figure 3 shows the morphology of the as-precipitated powder and the products as heat-treated at the different temperatures. The as-precipitated powder is 10–20 nm agglomerated particles in which the primary particles are uniform and spherical. The product powder had elliptic, dense, submicrometer particles that transformed to an irregular form upon calcining at 1600°C for 2 h.

Photoluminescence properties of GAG:Ce phosphors.— The emission wavelength of products doped with different concentrations of Lu$^{3+}$ is shown in Fig. 4. Upon excitation at 470 nm, the emission band centered at 564.57 nm belongs to the pure GAG:Ce. The emission peak of the phosphor powder shifted to a longer wavelength. The peak position of the emission band depends on the Ce$^{3+}$ in the garnet host environment, which is explained by considering the ionic relationship of Re–O–Ce.

Table 1. Phases of the trivalent ions (Tb$^{3+}$, Y$^{3+}$, Lu$^{3+}$, and Ga$^{3+}$) substituted at the desired concentration (10, 20, and 30%) for calcined product and temperature. a

<table>
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<tr>
<th>Concentration</th>
<th>Temp. (°C)</th>
<th>Lu$^{10%}$</th>
<th>Lu$^{20%}$</th>
<th>Lu$^{30%}$</th>
<th>Y$^{10%}$</th>
<th>Y$^{20%}$</th>
<th>Y$^{30%}$</th>
<th>Th$^{10%}$</th>
<th>Th$^{20%}$</th>
<th>Th$^{30%}$</th>
<th>Gd$^{10%}$</th>
<th>Gd$^{20%}$</th>
<th>Gd$^{30%}$</th>
<th>Ga$^{20%}$</th>
<th>Ga$^{30%}$</th>
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<td>O</td>
<td>G</td>
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<td>G + Pw</td>
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<td>G + Pw</td>
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a “P”: GAP; “G”: GAG; subscripts w and s describe the weak and strong peaks, respectively.
energy gap of O–Ce in Me–O–Ce. Therefore, the blue shift of the emission band of Lu3+ and Ga3+ substituted for GAG powder occurs as shown in Fig. 4, which means a higher energy Ce3+ 4f-5d absorption due to the increase in O–Ce ionicity. The photoluminescence intensity of Lu3+ and Ga3+ doped and undoped GAG phosphor excited at 470 nm is shown in Fig. 5. The phase purity also has an effect on the luminescence properties of the phosphor. Pan26 indicated that the decrease in the luminescence intensity of garnet phosphor in the Gd substituted for the dodecahedral site of YAG phosphor is probably due to the presence of the GAP structure. Our previous report19 concluded that the emission intensity of the pure YAG phase is higher than that of materials with a perovskite structure (YAP). The emission intensity of the undoped product of GAG:Ce is lower than that of the Lu3+ or Ga3+ doped GAG:Ce phosphor. This may be due to the presence of a perovskite structure in the GAG:Ce structure.

When comparing the luminescence property of pure GAG:Ce with that of TAG:Ce and YAG:Ce, an energy schematic diagram for Ce3+ in a garnet-series phosphor including YAG, TAG, and pure GAG can be drawn, as in Fig. 6. The 4f-5d transition of Ce3+ at the ground state is excited to the conduction band and releases to the lowest 5d level. The energy then returns to 4f state and emits light. The Ce3+ in the 4f state (ground state) splits up in a doublet state (2F5/2,2F7/2) due to spin-orbit coupling. The energy difference between these split states is about 2200 cm−1.31,32 In the garnet-series

Figure 3. SEM morphologies of (a) as-precipitated powders, and the products calcined at (b) 900, (c) 1100, (d) 1300, (e) 1400, (f) 1500, and (g) 1600°C.

Figure 4. The maximum emission band of GAG/Ce powders at different substituted concentrations of Lu3+ (solid line) and Ga3+ (dashed line) excited at 470 nm.

Figure 5. The photoluminescence intensity of Lu3+ and Ga3+ doped and undoped GAG phosphor excited at 470 nm.

Figure 6. The energy schematic diagram of the YAG, TAG, and pure GAG phosphor and the energy transfer process in Ce3+ (* Ref. 19, (** Ref. 18, and (***) in this report.
phosphor, the emission spectra of Ce³⁺ are quite similar. The only difference is in the wavelength of the emission peak of the host. The emission wavelength of pure GAG:Ce phosphor powder is longer than that of TAG:Ce and YAG:Ce phosphor powders because the decrease in energy for electron transferring from O²⁻ to Ce³⁺ represents a decrease in the ionicity of the garnet host.

The color properties of a white-light source are described by a CIE chromaticity (x, y) and color temperature for YAG (△), TAG (●), and pure GAG (○) phosphor powders in CIE diagram. The Ga³⁺ substituted for Al³⁺ and the smaller cations, including Y³⁺, Tb³⁺, and Lu³⁺ substituted at the dodecahedral site, enhances the phase stability of GAG:Ce to form a pure garnet structure. The emission wavelength of GAG:Ce was shifted to the blue range by increasing the doping concentration of Lu³⁺ and Ga³⁺. The GAG:Ce phosphor powder shows a lower color temperature when compared with YAG and TAG phosphors and thus is more suitable for warm WLED applications.

**Conclusion**

The GAG:Ce-series phosphor was successfully prepared using the coprecipitation method and calcination at certain temperatures. The Ga³⁺ substituted for Al³⁺ and the smaller cations, including Y³⁺, Tb³⁺, and Lu³⁺ substituted at the dodecahedral site, enhances the phase stability of GAG:Ce to form a pure garnet structure. The emission wavelength of GAG:Ce was shifted to the blue range by increasing the doping concentration of Lu³⁺ and Ga³⁺. The GAG:Ce phosphor powder shows a lower color temperature when compared with YAG and TAG phosphors and thus is more suitable for warm WLED applications.

**References**