Sensitized Photoluminescence of Eu^{3+} and Gd^{3+}-Doped $Y_3Al_5O_{12}$ Phosphors Prepared via a Reverse Microemulsion Process

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Europium-ion and gadolinium-ion codoped $Y_3Al_5O_{12}$ phosphors were synthesized via a reverse microemulsion process. The emission intensity and quantum yield of $Y_3Al_5O_{12}$: Eu^{3+} depend on the codoping concentration of gadolinium ions. The significant enhancement in the luminance and quantum yield via codoping of Gd^{3+} ions imply efficient energy transfer from Gd^{3+} ions to Eu^{3+} activators. The microemulsion-derived $Y_3Al_5O_{12}$: Eu^{3+}, Gd^{3+} phosphors with small particle sizes and enhanced luminescence efficiency are demonstrated to hold application potential for flat panel displays.

Plasma display panels and field emission displays have attracted much attention because of their thin thickness, wide viewing angle, and high resolution. It is necessary to develop phosphors having high emission efficiency for the application in flat panel displays.[1–3] Europium-ion doped yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG: Eu^{3+}) has been considered as a potential red phosphor used in flat panel displays. Various techniques[4–6] have been employed to synthesize this phosphor. However, most of these adopted processes require prolonged high-temperature heating. The obtained particles exhibit irregular and aggregated morphology, resulting in low luminescence efficiency.

In the present investigation, a new microemulsion process was employed to synthesize YAG: Eu^{3+}, Gd^{3+} particles. The obtained powders were found to exhibit small particle size, narrow particle size distribution, and high luminance. The formation processes of the microemulsion-derived powders were examined for determining the appropriate heating conditions. The codoping effects of gadolinium ions on the luminescent properties were also investigated.

$(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$ phosphors were prepared via the reverse microemulsion process. Yttrium nitrate, aluminum nitrate, europium oxide, and gadolinium nitrate were used as starting materials. Europium oxide was initially dissolved in nitric acid. The dispersed aqueous solution was prepared by dissolving stoichiometric amounts of the starting materials in deionized water to form water phase. The overall concentration of yttrium, aluminum, europium, and gadolinium ions was set to 0.1 M. Cyclohexane was used as the oil phase, and poly(oxyethylene) (10) octylphenyl ether (OP-10) and 1-hexanol were adopted as surfactant and cosurfactant, respectively. The aqueous solution was mixed with the oil phase and surfactants at a water-to-oil volume ratio of 5:95 to form water-in-oil microemulsion. The prepared microemulsion was dripped into hot kerosene at 180 °C. The obtained materials were dried at 500 °C for 2 h to prepare the precursors, and the precursors were calcined at 1000–1400 °C for 4 h.

X-ray diffraction (XRD) analysis employing Cu Kα radiation was performed to identify the crystal structure of the heated samples. A scanning electron microscope was used to examine the morphology of the obtained powders. The photoluminescence characteristics of the prepared phosphors were recorded using a fluorescence spectrophotometer. The quantum yield was measured for all samples subjected to excitation at 238 nm. Magnesium oxide and sodium salicylate were used as the reference for measuring the reflectance and the standard for determining the quantum yield, respectively.[7,8]

According to the XRD patterns, single-phased YAG: Eu^{3+} is exclusively formed upon heating at 1100 °C. All diffraction peaks are consistent with the data reported in the ICDD file (No. 33-0040). Attributing to the improved homogeneity of the reactants, the calcination temperature for obtaining phase-pure YAG via the microemulsion process is 500 °C lower than that required for the conventional solid-state reaction process. After heat treatment at 1400 °C, all $(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$ samples exhibit well-characterized XRD patterns corresponding to YAG phase. The 1400 °C-heated powders with a nearly spherical shape and uniform morphology are successfully prepared. The mean particle size of the obtained powders is within the range of 150–200 nm. With increasing the concentration of Gd^{3+} ions, the morphology of the powders maintains a spherical shape, while the particle size is increased slightly.

Figure 1 illustrates the excitation spectra of 1400 °C-heated

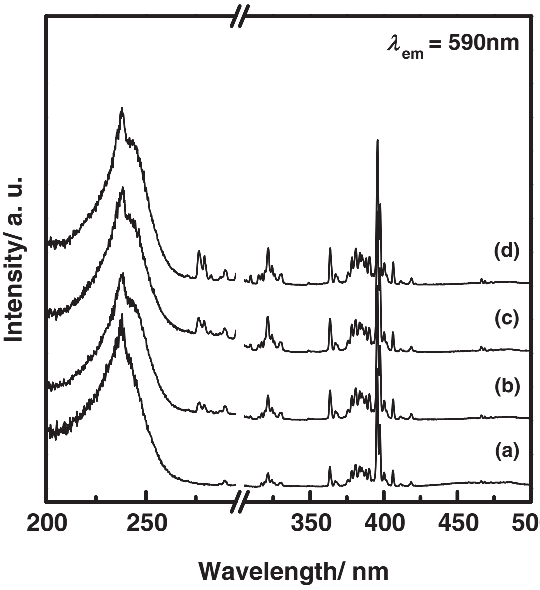

Figure 1. Photoluminescence excitation spectra of 1400 °C-heated $(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$. (a) $m = 0\%$, (b) $m = 3\%$, (c) $m = 5\%$, and (d) $m = 7\%$.

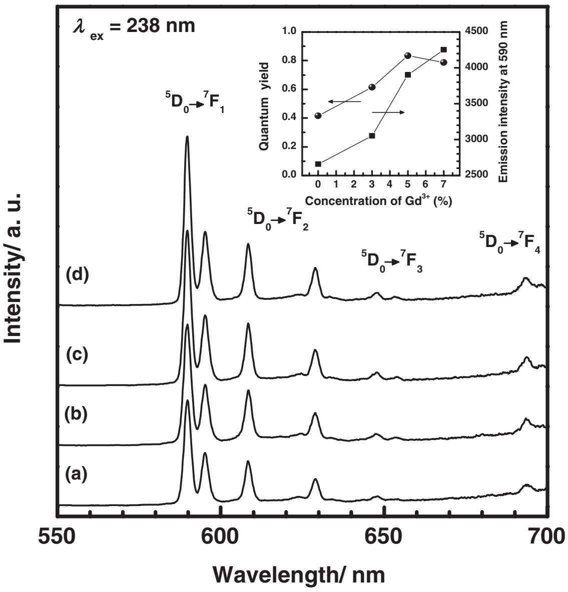

Figure 2. Emission spectra of $(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$ after calcination at 1400 °C. (a) $m = 0\%$, (b) $m = 3\%$, (c) $m = 5\%$, and (d) $m = 7\%$. The inset depicts the relation of the codoping concentration of Gd^{3+} ions to the emission intensity at 590 nm as well as the quantum yield in $(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$.

$(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$ monitored upon 590 nm emission. It reveals a broad band peaking at 238 nm and several sharp peaks in the 300–425 nm region. The broad band is assigned to the charge-transfer band of Eu^{3+}–O^{2-} caused by single electron transfer from the orbital of ligand O^{2-} ($2p^6$) to the empty states of Eu^{3+} configuration ($4f^6$).[9] The intensity of the charge-transfer band enhances with increasing the concentration of Gd^{3+} ions. Furthermore, Gd^{3+} excitation peak at 276 nm ($^8S_{7/2} \rightarrow {}^6I_J$)[10] is observed in the excitation spectra of Eu^{3+} ions monitored at 590 nm in the Eu^{3+}–Gd^{3+} codoped YAG samples. Its intensity is found to increase with increasing Gd^{3+} codoping concentration. These results indicate that the codoping of Gd^{3+} ions sensitizes the Eu^{3+} emission. On the other hand, weak peaks in the 300–500 nm region are due to the intraconfigurational $4f^6$ transitions of Eu^{3+}.[11,12]

The emission spectra of $(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$ heated at 1400 °C upon excitation at 238 nm is illustrated in Figure 2. A number of emission peaks in the range of 580–720 nm are observed, which are associated with the transitions from the excited $^5D_0$ level to ^7F_j ($j = 1$, 2, 3, and 4) levels of Eu^{3+}.[11] The emission peak observed at 590 nm in all the samples corresponds to the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}. On the other hand, the hypersensitive emission at 609 nm corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition, which is influenced by the local symmetry of Eu^{3+} activators.[12] The appearance of emission at 609 nm implies that Eu^{3+} ions substitute at Y^{3+} sites in YAG with a slight deviation from inversion symmetry.

The inset of Figure 2 illustrates the dependence of emission intensity at 590 nm and the quantum yield on the concentration of Gd^{3+} ions in $(Y_{0.95-m}Eu_{0.05}Gd_m)_3Al_5O_{12}$. A remarkable increase in the emission intensity is observed with increasing concentration of Gd^{3+} ions. This indicates efficient energy transfer from Gd^{3+} to Eu^{3+} in the prepared phosphors. The quantum yield of $(Y_{0.9}Eu_{0.05}Gd_{0.05})_3Al_5O_{12}$ is found to be 84%, which is about two times that of $(Y_{0.95}Eu_{0.05})_3Al_5O_{12}$. The above results demonstrate that codoping of Gd^{3+} ions in YAG: Eu^{3+} not only increases the luminescence intensity, but also raises the quantum yield of the prepared phosphors.

The obtained results in this study demonstrate that europium-ion and gadolinium-ion codoped $Y_3Al_5O_{12}$ phosphors were successfully prepared via the reverse microemulsion process. This developed process substantially lowered the required temperature for synthesizing pure garnet phase. The emission of Eu^{3+} ions in the host of YAG strongly depends on the concentration of Gd^{3+} ions. Both the emission intensity and quantum yield increase with increasing concentration of Gd^{3+} ions, implying the occurrence of efficient energy transfer from Gd^{3+} ions to Eu^{3+} ions. The developed YAG: Eu^{3+}, Gd^{3+} phosphors are considered to hold great application potential for flat panel displays.

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