Synthesis of Ce\(^{3+}\)-doped Y\(_3\)Al\(_5\)O\(_{12}\) phosphor particles by precipitation method with diamine molecules as precipitating agent

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An aqueous solution of aluminum nitrate and yttrium nitrate was prepared and ethylenediamine molecules were added into the aqueous solution. The obtained precipitated precursor particles were fired and oxide particles were obtained. When ethylenediamine was used for the precipitation, the single phase of YAG was obtained by firing the precursor particles at more than 1073 K. On the other hand, when hexamethylenediamine was used for the precipitation, the YAG phase was not able to be obtained by firing the precursor at 1373 K. Formation behavior of YAG phase greatly depended on the used diamine molecules. Furthermore, Ce\(^{3+}\)-doped YAG phosphor particles were prepared by firing precipitated particles from the aqueous solution in which the nitrates of Al\(^{3+}\), Y\(^{3+}\), and Ce\(^{3+}\) were dissolved with ethylenediamine as precipitating agent. The PL spectra of the obtained particles had the photoluminescence (PL) peak at 535 nm even though the firing temperature was 1073 K.

Key-words : Precipitation method, Ethylenediamine, Y\(_3\)Al\(_5\)O\(_{12}\), Phosphor, Firing temperature

[Received August 27, 2013; Accepted November 11, 2013]

1. Introduction

Importance of inorganic phosphor materials for display devices has been increasing in recent years.\(^1,2\) In particular, development of appropriate phosphor particles for white light emitting diode (WLED) is also a very important issue. Furthermore, low energy and high yield synthesis method of the phosphor materials for LED devices have been intensively investigated.\(^3,4\)

Yttrium aluminum garnet (Y\(_3\)Al\(_5\)O\(_{12}\), YAG) is one of the base oxides for phosphor materials for their chemical and physical stability. Doping with a small amount of rare earth cations, Eu, Tb, Ce, enables to control YAG fluorescence characteristics.\(^4,5\) In particular, Ce\(^{3+}\)-doped YAG particles have the broad band emission with the central emission peak at 550 nm when they were excited by blue light diode. Therefore, it is key material for development of WLEDs. In general, when a solid-state reaction method was employed to obtain YAG:Ce particles, high temperature heat treatments above 1723 K are required.\(^5,7\) Accordingly, development of low energy and environmental friendly synthesis process became an important issue.

In recent years, various kinds of solution processes to obtain YAG phosphor particles have been reported. The solution processes suit to prepare the phosphor particles with environmentally friendly and low energy process since the precursors with homogeneous dispersion of cations can be easily obtained by the solution synthetic processes. Various kinds of solution processes for Ce\(^{3+}\)-doped YAG particle preparation have been reported such as solvothermal synthesis, co-precipitation method, sol–gel method, and combustion method.\(^9,10\) The precipitation methods are simple but also effective methods so that particularly numerous researches have been studied.

In this study, we specifically examined diamine molecules as a precipitating agent.\(^12\) A diamine molecule has two amino groups that can coordinate to metal ions. Furthermore, diamine molecules can act as a base in aqueous solution, making them useful as a precipitation agent.\(^13\) Therefore, when diamine molecules are added to an aqueous solution containing metal cations, a hydroxide precipitate with homogeneous dispersion of cations can be obtained easily since the coordination of diamines will adjust the concentration of free cations without ligands. This homogeneity of dispersion of cations is essentially important for low temperature formation of Ce\(^{3+}\)-doped YAG phase and high efficient luminescence. Therefore, relations between the formation condition of Ce\(^{3+}\)-doped YAG phosphor particles and the used alkyl diamine molecules were examined and the appropriate diamine molecules for YAG formation were investigated.

2. Experiments

2.1 Preparation of YAG particles

Y(NO\(_3\))\(_3\)·6H\(_2\)O and Al(NO\(_3\))\(_3\)·9H\(_2\)O were dissolved in deionized H\(_2\)O and 50 mL of the solution was obtained. The concentration of the cations (Y\(^{3+}\)+Al\(^{3+}\)) of the solution was adjusted to 0.1 mol/L. The molar ratio of [Y\(^{3+}\)]/[Al\(^{3+}\)] in the aqueous solution was 3.5. Ethylenediamine (en) was added to the aqueous solution. The molar ratio of [en]/[Y\(^{3+}\)]+ [Al\(^{3+}\)] was adjusted to 2.0. This solution with precipitate was then heated at 348 K for 24 h in a closed glass vessel. The precipitate was then separated by centrifugation at 3000 rpm for 5 min. The obtained precipitate was again dispersed in 100 mL of deionized H\(_2\)O and the solution was centrifuged again. These dispersion in H\(_2\)O and centrifuge process were repeated 3 times. The obtained precipitate was dried at 348 K for 12 h to obtain powders. This synthesis procedure was also conducted using 1,3-propanediamine, 1,4-butanediamine, and hexamethylenediamine substituted for ethylenediamine. The obtained powders were fired at one of 973, 1073, 1173, 1273, and 1373 K for 1 h under air atmosphere to obtain oxide powders. All chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries Ltd.).
2.2 Preparation of Ce$^{3+}$-doped YAG particles

Ce$^{3+}$-doped YAG particles were also prepared by using diamine molecules as precipitating agent. Y(NO$_3$)$_3$$\cdot$6H$_2$O, Al(NO$_3$)$_3$$\cdot$9H$_2$O, and Ce(NO$_3$)$_3$$\cdot$6H$_2$O were dissolved in deionized H$_2$O. Then 50 mL of the solution was obtained. The cation (Y$^{3+}$ : Al$^{3+}$ : Ce$^{3+}$) concentration of the solution was adjusted to 0.1 mol/L. The molar ratio of [Y$^{3+}$] : [Al$^{3+}$] : [Ce$^{3+}$] in the aqueous solution was adjusted to 2.95 : 5 : 0.05. The reagent grade of Ce(NO$_3$)$_3$$\cdot$6H$_2$O produced by Wako Pure Chemical Industries Ltd. was also used in this preparation. Furthermore, the aqueous solutions in which the cation molar ratios of [Y$^{3+}$] : [Al$^{3+}$] : [Ce$^{3+}$] was 2.975 : 5 : 0.025 and 2.9 : 5 : 0.1 were also prepared. The same diamine molecules used for the preparation of YAG particles were also used. The heating condition of the solution with a precipitate and the separation process were same as described in the YAG preparation method. The obtained precipitated powders were fired at one of 973, 1073, 1173, 1273, and 1373 K for 1 h under reduction atmosphere. The reduction atmosphere was created as follows: charcoal powder was put on bottom in a larger crucible. A smaller crucible contained the precipitated powder was put in the crucible. The reduction atmosphere was created as follows: charcoal powder was put on bottom in a larger crucible. A smaller crucible contained the precipitated powder was put in the larger crucible. The larger crucible was covered with a cap and fired in a furnace.

2.3 Characterization

The obtained powders were characterized using X-ray diffraction (XRD) (Cu Kα 40 kV, 30 mA, MXP-18; Bruker AXS). The particle shape was observed using field emission scanning electron microscopy (FE-SEM, JSM-6330; JEOL). The photoluminescence (PL) spectra were measured with excitation light at 465 nm (λex) (RF-5300PC, Shimazu Co. Ltd.).

3. Results and discussion

3.1 Characterization of YAG particles obtained by precipitation method with diamine molecules

Figure 1 shows the XRD patterns of the particles obtained by firing precursor particles precipitated from the aqueous solution by using ethylenediamine as a precipitating agent. As shown in Figs. 1(a) and 1(b), the precipitated precursor particles and the particles fired at 973 K for 1 h showed no clear XRD peak. This indicated that the obtained particles were amorphous. On the other hand, when the firing temperature was at above 1073 K, all peaks in the XRD patterns shown in the Figs. 1(c)–1(e) can be assigned to yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$, YAG). Accordingly, the particles obtained by firing the precursor particles precipitated with ethylenediamine were single phase of YAG when the firing temperatures were more than 1073 K.

To examine effect of the precipitating agent on formation of YAG phase, the XRD patterns of the particles obtained by firing precursor particles precipitated with hexamethylenediamine were shown in the Fig. 2. In the XRD pattern of the precursor particles, the peaks which can be assigned to aluminum hydroxide appeared as shown in the Fig. 2(a). This result indicated that the precursor particles precipitated with hexamethylenediamine consisted with aluminum hydroxide (bayerite) and amorphous phase. When the firing temperatures are 1073 and 1173 K, the peaks in the XRD patterns can be assigned to Y$_3$Al$_5$O$_{12}$ (YAM, yttrium aluminum monocrystalline) as shown in the Figs. 2(c) and 2(d). The excess aluminum oxide particles should be included as amorphous phase. When the firing temperature is 1373 K, the XRD peaks can be assigned to Y$_3$Al$_5$O$_{12}$ and YAM. As shown in the Fig. 2(e), in the case that hexamethylenediamine was used as a precipitating agent, YAG single phase was not able to be obtained. The masking effect of ethylenediamine for Al$^{3+}$ ions and Y$^{3+}$ ions made the concentration of the cations without ligands in the solution quite low since ethylenediamine is a chelate ligand. Slow rate of formation of aluminum hydroxide and yttrium hydroxide under quite low concentrations of cations enabled to inhibit segregation on the precipitating process. Therefore, the homogeneous dispersion of cations in the obtained precursor particles enabled to obtain YAG phase at 1073 K. On the other hand, in the case that hexamethylenediamine was used as a precipitating agent, it is not a chelate ligand so precipitate with homogeneous composition of cations was not able to be obtained. Therefore, the formation of YAG did not occur.

Figure 3 illustrates the XRD patterns of the fired precursor particles at 1073 K for 1 h, which were prepared by using some diamine molecules. As shown in the Figs. 3(b) and 3(c), when 1,3-propanediamine and 1,4-butanediame were used, the XRD patterns had no peaks and it indicated that the amorphous phase was obtained. Furthermore, only when ethylene diamine was used as precipitating agent, a single phase of YAG was obtained. This result would indicate that a chelate effect of precipitating agent was important for formation of YAG. The inhabitation of segregation in the precipitated precursor enabled to obtain the YAG single phase at 1073 K.

It is also an important issue to investigate formation process...
of oxide particles from the precursor particles. TG-DTA curves of the precursor particles were measured. The Fig. 4(a) illustrates the TG-DTA curves of the precursor precipitated by using ethylenediamine. The weight decreased slowly below 700 K. Furthermore, a clear exothermic peak in the DTA curve did not appear. The ethylenediamine molecules coordinated to the cations were removed during the precipitation process. This result means that the ethylenediamine molecules which coordinated to Al$^{3+}$ and Y$^{3+}$ ions were simultaneously substituted for hydroxide ions. Therefore, the obtained hydroxide precipitate had the homogeneous dispersion of Al$^{3+}$ and Y$^{3+}$ ions at atomic level as in the aqueous solution. Figure 4(b) shows the TG-DTA curves of the precursor precipitated by using hexamethylenediamine. The DTA curve has a sharp exothermic peak at 547 K. At this temperature, a steep decrease of weight was observed in the TG curve. The weight loss corresponded to the decomposition of hexamethylenediamine molecules which coordinated to the cations. As mentioned above, hexamethylenediamine is not a chelate ligand. Strength of coordination of hexamethylenediamine molecules depends on the cations. Therefore, hydroxide including Al$^{3+}$ ions and that including Y$^{3+}$ ions precipitated separately and the strongly coordinated diamine molecules were included in the precipitated particles. This TG-DTA result of hexamethylenediamine also indicated that the dispersed state of the cations in the precipitated precursor was not homogeneous. When the diamine molecules were used as the precipitating agents, dehydration of hydroxides and oxidation of coordinated diamine molecules had finished until 800 K. The obtained particles fired at 800 K had low crystallinity and the temperature at which the crystallized oxide phase was formed depends on the dispersed state of the cations. The cation arrangement in the precipitate obtained with ethylenediamine suited for formation of the YAG phase.

The relation between morphology of the obtained particles and the used diamine molecules were examined by FE-SEM observations. Figure 5 shows the FE-SEM images of the particles obtained by firing the precursor particles at 1373 K for 1 h. When ethylenediamine was used as precipitating agent as shown in the Fig. 5(a), strongly aggregated structure of YAG particles whose average diameter was 90 nm was observed. Furthermore, the particle sizes varied a little. This result seems to be related to the obtained particles were a single phase of YAG. Figure 5(b) shows the FE-SEM image of the particles obtained by firing the precipitated precursor particles with hexamethylenediamine as precipitating agent. The aggregated structure of particles with plate like morphology was observed. This particle morphology is specific to bayerite.

3.2 Effect of diamine molecules on photoluminescence characteristics of Ce$^{3+}$-doped YAG particles

The photoluminescence (PL) characteristics of the particles obtained by firing the precursor precipitated from the aqueous solution with Ce$^{3+}$, Y$^{3+}$, and Al$^{3+}$ were examined. Figure 6 shows the PL spectra of the obtained particles with ethylenediamine as a precipitating agent. The PL spectra of the fired particles whose compositional formula was $\text{Ce}_{0.05} \text{Y}_{2.95} \text{Al}_3\text{O}_{12}$ were shown in the Figs. 6(a)–6(d). When the firing temperature was 973 K as...
shown in the Fig. 6(a), a PL peak did not appear. When the firing temperature increased from 1073 to 1373 K, intensity of the PL peak at 535 nm increased. This phenomenon corresponded to improvement of crystallinity of the obtained Ce$^{3+}$-doped YAG particles. The Figs. 6(e) and 6(f) show PL spectra of the particles fired at 1373 K whose compositional formulas were Ce$_{0.05}$Y$_{2.95}$Al$_{5}$O$_{12}$ and Ce$_{0.02}$Y$_{3}$Al$_{5}$O$_{12}$, respectively. The PL peak intensities were weaker than that of Ce$_{0.05}$Y$_{2.95}$Al$_{5}$O$_{12}$. Accordingly, the Ce$^{3+}$-doped YAG whose compositional formula was Ce$_{0.02}$Y$_{3}$Al$_{5}$O$_{12}$ for strong PL intensity. When the doped amount of Ce$^{3+}$ in the YAG phase increased from Ce$_{0.05}$Y$_{2.95}$Al$_{5}$O$_{12}$ to Ce$_{0.10}$Y$_{2.9}$Al$_{5}$O$_{12}$, the decrease of the PL intensity which corresponded to concentration extinction occurred. This phenomenon indicated that the doped Ce$^{3+}$ ions were closely placed in the lattice of Ce$_{0.05}$Y$_{2.95}$Al$_{5}$O$_{12}$. Furthermore, these results indicated that the homogeneous dispersion of Ce$^{3+}$ ions in the YAG lattice was established with aid of ethylenediamine as the precipitating agent.

In order to examine effect of diamine molecules on the PL characteristics of the obtained particles, Fig. 7 shows the PL spectra of the particles obtained by firing the precursor precipitated with hexamethylenediamine. The PL curves described as Figs. 7(a)–7(c) were almost same and had no PL peak. This result agreed with the XRD patterns shown in the Figs. 2(a)–2(c), which has no XRD peak of YAG. When the firing temperature was 1373 K, the weak PL peak at 535 nm appeared as shown in the Fig. 7(d). This indicated that a small amount of Ce$^{3+}$-doped YAG phase was included in the obtained particles. Accordingly, the precursor particles precipitated by using ethylenediamine suited for preparation of Ce$^{3+}$-doped YAG particles.

4. Conclusion

YAG particles were prepared by firing the precursor particles precipitated from the aqueous solution including nitrates of Al$^{3+}$ and Y$^{3+}$ with aid of a diamine molecule as a precipitating agent. Formation behavior of YAG phase greatly depended on the used diamine molecules. When ethylenediamine was used for the precipitation, the single phase of YAG was obtained by firing the precursor particles at above 1073 K. On the other hand, when hexamethylenediamine was used for the precipitation, the YAG phase was not able to be obtained by firing the precursor at 1373 K. Homogenous dispersion of the cations in the precursor particles is essentially important for the formation of YAG. Coor-