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Production of phosphor (YAG : Tb) fine particles by hydrothermal synthesis in supercritical water

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Rapid and continuous production of phosphor (YAG : Tb) fine particles by hydrothermal synthesis in supercritical water was studied. At temperatures higher than the critical temperature of water, continuous and rapid (<60 s) production of YAG : Tb fine particles was achieved. Emission spectra obtained by UV excitation of the particles were in agreement with the typical spectral pattern of YAG : Tb. Single phase YAG : Tb was produced by using stoichiometric mixtures of metal salts [$Al(NO_3)_3$, $Y(NO_3)_3$, and $TbCl_3$] as aqueous solutions with an alkali molar ratio $\{[OH^-]/([NO_3^-]+[Cl^-])\}$ of 1 and a rapid heating method. No additional thermal treatment was necessary to obtain crystalline products.

1 Introduction

Aluminium yttrium garnet ($Al_5Y_3O_{12}$, YAG) based phosphors, such as YAG : Cr, YAG : Tb, YAG : Ce and YAG : Tm, are used for cathode ray tube applications because they are thermally stable and resist saturation at high current excitations.[1] The commercial method for YAG phosphor synthesis is *via* solid-state reaction of stoichiometric mixtures of the component oxides at high temperature (2000–2200 °C).[2] However, in this method two phases ($YAlO_3$ and $Y_4Al_2O_7$) form as intermediates during the heating period. Long reaction times of 10–20 h are required to completely transform the two phase system into $Y_3Al_5O_{12}$.

Other methods for producing YAG phosphors include precipitation,[3,4] sol–gel,[5] combustion[6] and hydrothermal syntheses.[7] Using these methods,[3–6] compositionally homogeneous products can be obtained, however, they require an additional thermal treatment at high temperature (>1000 °C) to obtain well crystallized products with good luminescence properties. Takamori and David[7] have reported the hydrothermal synthesis of YAG : Tb particles at 400–700 °C and 100 MPa over 20 h using powders of the component citrates prepared by a spray-drying method. This method also requires long reaction times, in the order of a day to obtain well crystallized particles.

We have developed a method for the rapid production of fine metal oxide particles by hydrothermal synthesis in supercritical water ($T_c = 374$ °C; $P_c = 22.4$ MPa).[8–10] This method has the following attractive features: (i) rapid reaction times (<1 min), (ii) continuous production of products, (iii) highly crystalline products without the need for further thermal treatments, and (iv) low solvent (water) contents in the products. Furthermore, this method can be applied to produce complex metal oxides.[10] The objective of this study was to develop a system to rapidly and continuously produce phosphor (YAG : Tb) fine particles by hydrothermal synthesis in supercritical water. We investigated the effects of variations in the following reaction conditions: (i) concentrations of the precursor metal salt solutions, (ii) reaction temperature, and (iii) heating rate. Based on these experiments, we report herein the optimum conditions required to obtain single phase YAG in supercritical water.

2 Experimental

2.1 Materials

Precursor solutions were prepared by dissolving aluminium nitrate [$Al(NO_3)_3\cdot 9H_2O$, Wako Chemicals), yttrium nitrate [$Y(NO_3)_3\cdot 6H_2O$, Wako Chemicals] and terbium chloride [$TbCl_3\cdot nH_2O$; $n = 6$–8, Wako Chemicals] in deionized water. The aluminium nitrate concentration of the feed solution was set at 0.05 M. The total Y + Tb concentration was varied over the range 0.03 to 0.10 M, while the Tb concentration was set at 5 mol% of that of Y. Aqueous potassium hydroxide solution (0.24 M) was used to adjust the pH. The addition of KOH was evaluated by monitoring the alkali molar ratio, $R = [OH^-]/([NO_3^-]+[Cl^-])$.

2.2 Experimental apparatus

Fig. 1 shows a diagram of the experimental apparatus employed. A premixed aqueous metal salt solution was fed into the apparatus by a high pressure pump at a rate of 2 cm^3 min^{-1}. Aqueous potassium hydroxide solution was introduced by another pump, also at a rate of 2 cm^3 min^{-1}. These two aqueous solutions were combined at a mixing point (MP1) at room temperature. This solution was then added to

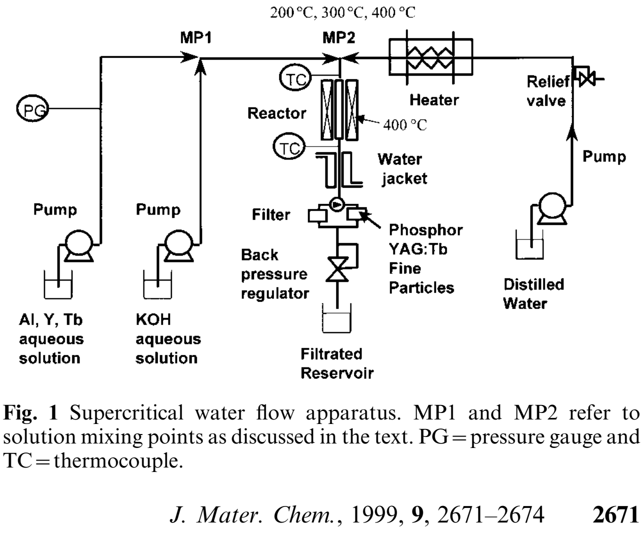

Fig. 1 Supercritical water flow apparatus. MP1 and MP2 refer to solution mixing points as discussed in the text. PG = pressure gauge and TC = thermocouple.

supercritical water (450–550 °C, 8 cm^3 min^{-1}) at mixing point MP2, and thus the solution was rapidly heated to the reaction temperature. The solution was passed through a tube reactor and then cooled by an external water jacket at the end of the reactor. Particles produced were collected by an inline filter. The pressure of the system was maintained at 30 MPa by a back-pressure regulator (Model 26-1722-24, Tescom Corp., MN, USA). The reaction temperatures employed were 350, 385, 400 and 420 °C. Reaction times were evaluated by total flow rate, reactor volume and density of pure water at the reaction temperature and pressure. Reaction times were in the range 40 to 120 s.

Using the apparatus described above, further experiments were also conducted to investigate the effect of varying the heating rate. As shown in Fig. 2, the temperature at MP2 was set at either 200 or 300 °C and then the solution was heated to 400 °C in the reactor.

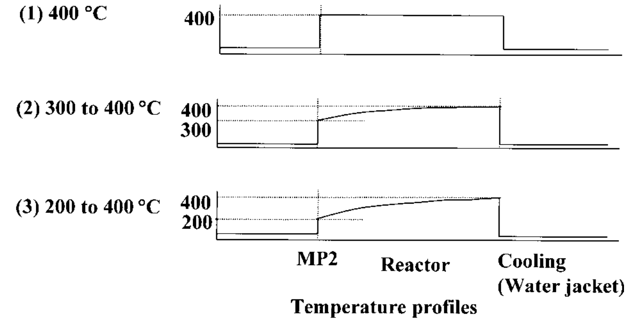

Fig. 2 The various reactor temperature profiles investigated.

2.3 Analyses

The concentrations of remaining metals in the recovered solution were measured by inductively coupled plasma (ICP) emission spectroscopy (SPS-1200, Seiko, Tokyo). The extent of conversion of each metal ion to solid product was calculated as follows:

$$X_i = 1 - \frac{C_i}{C_{i,0}} \tag{1}$$

where, C_i and $C_{i,0}$ are concentrations of the i species (i = Al, Y, Tb) in the recovered and feed solutions, respectively. The selectivity of YAG in the solid products, S_{YAG} wt%, was evaluated as follows:

$$S_{YAG} = \frac{1/3(C_{Y,0}X_Y + C_{Tb,0}X_{Tb})M_{YAG}}{1/3(C_{Y,0}X_Y + C_{Tb,0}X_{Tb})M_{YAG} + \{C_{Al,0}X_{Al} - 5/3(C_{Y,0}X_Y + C_{Tb,0}X_{Tb})\}M_{AlOOH}} \tag{2}$$

where, M_{YAG} and M_{AlOOH} represent the molecular weight of $Al_5Y_3O_{12}$ (YAG) and AlOOH, respectively. In these analyses, we made the following assumptions: (i) the products were AlOOH or YAG or a mixture of these compounds, and (ii) both yttrium and terbium ions react to form YAG only. These assumptions were only necessary for the comparison of results between the various runs.

Powders recovered were washed with distilled water and dried in an oven at 60 °C for 24 h. The structure of the product was analyzed by X-ray powder diffraction (XRD) (Model M18XHF-SRA, Mac Science, Yokohama) with Mo-Kα radiation and a scan speed of 2° (2θ) min^{-1}). Observation of particle morphology and size was performed on a transmission electron microscope (TEM) (Model H-8010, Hitachi, Tokyo). Specimens for TEM were prepared by collecting the solution–particle suspensions and applying them to a copper mesh fitted with a collodion membrane, followed by drying.

3 Results and discussion

3.1 Rapid and continuous production of YAG phosphor fine particles

Fig. 3(a) shows a typical X-ray diffraction pattern of the products. The reaction conditions were 400 °C, 30 MPa and 60 s of residence time, with the starting material having a (Y + Tb)/Al molar ratio of 0.6 and an alkali molar ratio of 1.0. All the peaks could be assigned to the XRD pattern of cubic YAG. A high background level was observed in the XRD profile. For comparison Fig. 3(b) shows the X-ray diffraction pattern of products synthesised by conventional solid state reactions according to methods reported in the literature.[2] The products were found to be mixtures of YAG and YAM ($Y_4Al_2O_7$). By comparing Fig. 3(a) and 3(b), it was found that the high background signal was not due to amorphous products, since the product of the solid state reaction is effectively 100% crystalline. The high background levels in the XRD spectra are apparently due to the lack of a monochromater in our XRD system.

Fig. 4 shows a TEM photograph of the particles obtained. Since the particles of around 100 nm had a well developed plane, they appeared to be single crystals. Fig. 5 shows the emission spectrum of the product at 420 °C and 30 MPa. The spectrum obtained agreed with that of a typical YAG : Tb phosphor. The maximum emission intensity of the products was comparable with that of particles produced by the conventional solid state reaction method.

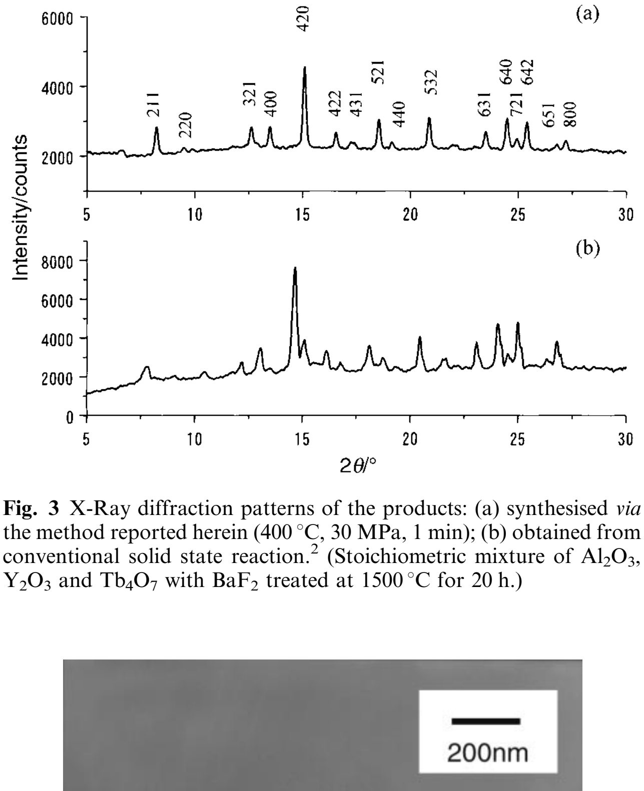

Fig. 3 X-Ray diffraction patterns of the products: (a) synthesised *via* the method reported herein (400 °C, 30 MPa, 1 min); (b) obtained from conventional solid state reaction.[2] (Stoichiometric mixture of Al_2O_3, Y_2O_3 and Tb_4O_7 with BaF_2 treated at 1500 °C for 20 h.)

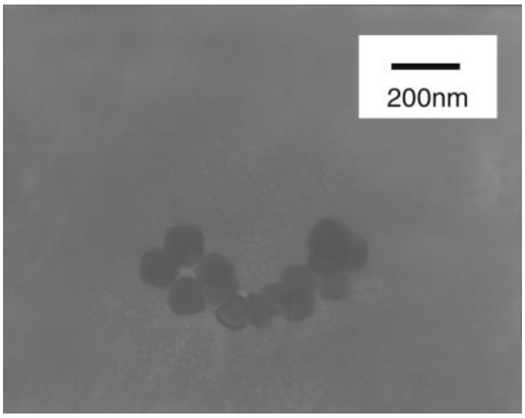

Fig. 4 TEM photograph of the YAG particles obtained.

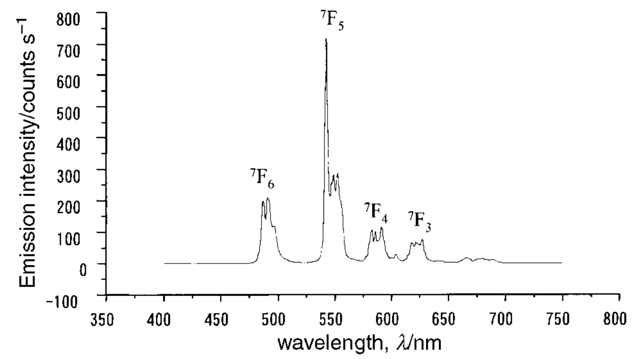

Fig. 5 Emission spectra of the products formed at 420 °C under 30 MPa excited by UV (273 nm) radiation.

3.2 Determination of optimum conditions for producing single phase YAG phosphors

The effect of the reaction conditions on the particles produced was investigated to determine the optimum conditions for the production of single phase YAG. Variables examined in this study were (Y + Tb)/Al molar ratio, alkali molar ratio, temperature and heating rate. Table 1 summarizes the experimental conditions and results which are discussed below.

3.2.1 (Y + Tb)/Al molar ratio. The (Y + Tb)/Al molar ratios of the starting solutions employed to obtain single phase YAG are shown in runs 1–3 (Table 1). The reaction temperature and pressure were 400 °C and 30 MPa. In run 1, single phase YAG formed at the stoichiometric molar ratio for YAG, *i.e.* (Y + Tb)/Al = 0.6. In runs 2 and 3, the excess Al or Y formed elemental oxyhydroxides, AlOOH and YOOH, respectively.

3.2.2 Alkali molar ratio. In runs 4–6 (Table 1), the effect of the alkali molar ratio on the products and the extent of conversion can be seen. At higher alkali molar ratios YOOH formed with YAG. Although the conversions of Y and Tb were around 100%, the conversion of Al was low. On the other hand, at lower alkali molar ratios, the products were mixtures of AlOOH and YAG. Conversion of Y and Tb decreased with decreasing alkali molar ratio.

It has been reported that aluminium ions become more soluble in aqueous solutions at high pH and the negatively charged species $Al(OH)_4^-$ becomes prevalent at high temperatures.[11] Thus a greater number of aluminium ions can probably dissolve in the higher alkali molar ratio solutions, and the excess yttrium ions probably form the elemental oxyhydroxide YOOH stoichiometrically. At lower alkali molar ratios, Y and Tb ions most likely become more soluble and thus an excess of aluminium ions leads to the formation of AlOOH.

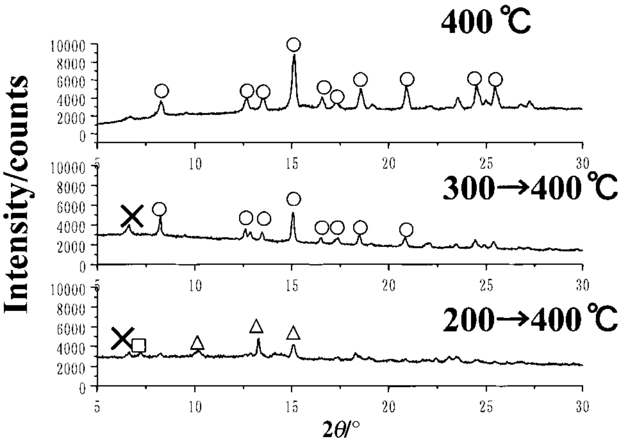

Fig. 6 X-Ray diffraction patterns for products prepared using various heating patterns. (△: $AlYO_3$, □: YOOH, ×: AlOOH; ○ :YAG).

3.2.3 Reaction temperature. In runs 7–9 (Table 1), the effect of the reaction temperature on the conversion extent and YAG selectivity is shown. At 350 °C the main product was AlOOH and the conversions of both Y and Tb were low, especially for Y which was only 16%. With increasing reaction temperature both the conversion of Y(Tb) and the selectivity of YAG increased. At 420 °C, the main product was YAG. From these results it can be seen that temperatures higher than the critical temperature of water lead to higher conversions (>98%) of yttrium and terbium ions and a higher selectivity of YAG (>98 wt%).

The lower conversion of Y at 350 °C can be explained by considering the dissolution of yttrium species in hydrothermal solutions. Since our experiments were performed under a constant pressure of 30 MPa, the density of the solution decreased with increasing reaction temperature. Around the critical temperature the density of water decreases drastically and thus water soluble yttrium species probably became insoluble and were deposited as oxides of YAG : Tb.

3.2.4 Heating rate. Fig. 6 shows the X-ray diffraction patterns of products prepared with the various heating patterns shown in Fig. 2. When the temperature at MP2 was set at 200 °C, the products were mixtures of hexagonal $AlYO_3$, AlOOH and YOOH. When this was increased to 300 °C, the products were mixtures of AlOOH and YAG, while at 400 °C single phase YAG was formed.

We conducted other experiments to study whether the

Table 1 Experimental conditions and results

Run	T/°C	P/MPa	(Y + Tb)/ Al molar ratio	Alkali molar ratio	Heating rate[a]	Conversion Al	Y	Tb	YAG selectivity	Products[b]
1	400	30	0.6	1.0	Direct	0.99	0.96	0.97	0.98	YAG
2	400	30	0.3	1.0	Direct	—	—	—	—	YAG, AlOOH
3	400	30	1.2	1.0	Direct	—	—	—	—	YAG, YOOH
4	400	30	0.6	0.5	Direct	0.99	0.78	0.79	0.88	YAG, (AlOOH)
5	400	30	0.6	0.7	Direct	0.99	0.88	0.90	0.94	YAG, (AlOOH)
6	400	30	0.6	1.2	Direct	0.72	0.99	1.00		YAG, (YOOH)
7	350	30	0.6	1.0	Direct	1.00	0.16	0.58	0.30	AlOOH, YAG
8	385	30	0.6	1.0	Direct	1.00	0.81	0.84	0.90	YAG, (AlOOH)
9	420	30	0.6	1.0	Direct	1.00	1.00	1.00	1.00	YAG
10	400	30	0.6	1.0	Gradient 200 to 400 °C	—	—	—	—	AlOOH, YOOH, $AlYO_3$
11	400	30	0.6	1.0	Gradient 300 to 400 °C	—	—	—	—	AlOOH, YAG

[a] 'Direct' means that the metal salt solution was heated to the reaction temperature at MP2 (Fig. 1). 'Gradient' means that the metal salt solution was heated gradually in the reactor as described in the text. [b] Species within parentheses indicate minor products.

products formed at the mixing point or during the heating period in the reactor (Table 1). When the temperature at MP2 was set at 200 °C or 300 °C with no heating in the reactor, the product was AlOOH. Thus we concluded that hexagonal $AlYO_3$, YOOH and YAG formed during the heating period.

From these results, slower heating seems to lead to the formation of various intermediates. As reported in our previous study,[10] these products transform into stoichiometric YAG after longer reaction times. However, rapid heating seems to prevent the formation of these intermediates, and thus, in our experiments, single phase YAG can be obtained within 1 min.

The hydrothermal synthesis of YAG phosphor by Takamori and David[7] was performed at higher temperatures and pressures than those that we used. During hydrothermal synthesis using an autoclave type reactor, elemental oxyhydroxides (AlOOH) or other complex oxides ($Y_4Al_2O_7$) would form during heating periods. Thus, dissolving these oxides is required to produce YAG. To increase the solubility of these oxides in hydrothermal solution, Takamori and David used high temperatures and pressures. Since the oxides' solubility was low under these conditions, long reaction times were required.

As described in the results of experiments using varying heating patterns in this study, when oxides other than YAG formed during heating periods single phase YAG could not be obtained after short reaction times. Rapid heating with appropriate concentrations of precursors inhibits the formation of elemental oxides/oxyhydroxides (AlOOH, YOOH, $YAlO_3$).

4 Conclusion

Phosphor (YAG:Tb) fine particles have been produced continuously and rapidly (< 1 min) *via* hydrothermal synthesis in supercritical water with the system developed in this study. The emission spectra of the particles obtained agreed with a typical spectrum of YAG:Tb. Single phase YAG has been produced by using stoichiometric mixtures of metal salt [$Al(NO_3)_3$, $Y(NO_3)_3$, and $TbCl_3$] solutions with an alkali molar ratio $\{[OH^-]/([NO_3^-]+[Cl^-])\}$ of 1. Temperatures higher than the critical temperature of water were required to produce single phase YAG. This is probably due to the high stability of yttrium species in the hydrothermal solution. Rapid heating was found to be very important for producing single phase YAG.

Acknowledgement

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