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Synthesis of Y–Al–O compounds by a polymer complex method

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Abstract

Three Y–Al–O compounds, $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), $Y_4Al_2O_9$ (YAM), are all useful materials for optical applications. Polycrystalline powders of Y–Al–O compounds were synthesized by a polymer complex method and all compounds were obtained in a single phase by maintaining the stoichiometry during the process. Thermal analysis showed that the crystallization temperatures were 900 °C for YAG and YAM, and 1100 °C for YAP, which was 300 °C lower than that reported by sol–gel process. Phase development of each compound with temperature was also reported.

Keywords: Phosphors; Chemical synthesis; X-ray diffraction; Thermal analysis

1. Introduction

It is well known that yttrium aluminum double oxides include three compounds: $Y_3Al_5O_{12}$ (yttrium aluminum garnet, YAG), $YAlO_3$ (yttrium aluminum perovskite, YAP), and $Y_4Al_2O_9$ (yttrium aluminum monoclinic, YAM) and that they are all useful host materials in lasers [1] and scintillators [2]. For example, YAP doped with Ce is a promising fast scintillator for synchrotron X-ray experiments [3]. The polycrystalline powders of these materials are usually synthesized by a solid-state reaction between yttria and alumina at high temperatures, but it is difficult to prepare fine powders in a single phase due to aggregation of particles and simultaneous formation of other phases. To obtain fine powders, a sol–gel and related chemical techniques were investigated from a viewpoint of low-temperature powder preparation [4–7]. Synthesizing single-phase YAP, however, is still difficult because of preferential formation of other phases, even with the wet chemical process [8,9].

We have reported the first successful formation of single-phase YAP fine powders by a polymer complex method [10]. A polymer complex method using a citric acid was invented by Pechini [11] and successfully applied for powder preparation of many kinds of ceramics [12]. The advantages of this method including small particle size, second phase suppression, and low heat treatment temperature were reported earlier [10,13]. In this study we applied this method to the stoichiometric synthesis of three Y–Al–O compounds, and also discussed the results with an emphasis on the temperature dependence of their phases.

2. Experimental details

Three Y–Al–O powders were synthesized by the polymer complex method in the same procedure as previously reported [10]. In this study, yttrium nitrate ($Y(NO_3)_3$, Nippon Yttrium Co., Ltd., 99.9%) and aluminum nitrate ($Al(NO_3)_3$, Kojundo Chemical Laboratory Co., Ltd., 99.9%), were used as starting materials after cation concentrations of each solution were determined by ethylenediaminetetraacetic acid chelatometry. Both solutions were mixed with a stoichiometric ratio for three compounds. An ethylene glycol ($C_2H_6O_2$, Wako Pure Chemical Industries Ltd., 99.5%) and a citric acid ($C_6H_8O_7$, Wako Pure Chemical Industries Ltd., 98.0%) were added in a molar ratio of 40 and 10 to the metals, respectively, and stirred at 130–140 °C till the transparent brown resin was formed.

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Charring the resin at 300 °C for 2 h in an electric furnace (Denken Co., Ltd., KDF-S70) resulted in a black solid mass called precursor. The precursor was lightly ground with a mortar and pestle, and heat-treated for crystallization.

The polycrystalline powders obtained were identified by X-ray diffraction (XRD) technique (MAC Science Co., Ltd., MXP-3). Measuring conditions were as follows; anticathode of Cu, Ni filter, tube voltage of 40 kV, tube current of 30 mA. Thermal analyses were done with thermogravimetry/differential thermal analyzer (TGD9600, ULVAC-RIKO Inc.). An elevating temperature rate was set at 10 °C/min.

3. Results and discussion

Precursors obtained from a mixture of Y:Al = 3:5, 1:1, and 4:2 were all heat-treated at 1100 °C for 2 h. The XRD patterns of the obtained powders are shown in Fig. 1, where a top (A), a middle (B), and a bottom (C) represent a mixture of 3:5, 1:1, and 4:2, respectively. The patterns are in good agreement with those of YAG, YAP, and YAM reported on the International Centre for Diffraction Data (ICDD) database (33-0040, 33-0041, and 34-0368, respectively) and so it was confirmed that the three compounds obtained were all in a single phase.

Then the phase development of the three compounds with temperature was investigated. The phase development of the YAG is shown in Fig. 2. The precursor of Y:Al = 3:5 mixture was heat-treated at 700 °C for 2 h, and the XRD was measured not in situ but after cooling down to room temperature. Then the same sample was fed to next heat treatment at 800 °C for 2 h. This procedure was repeated up to 1100 °C. Below 800 °C the sample was still amorphous, but at 850 °C it started to crystallize. It is also supported by the result of thermogravimetric/differential thermal analysis (TG/DTA) in Fig. 3(A), where the exothermic peak of crystallization is observed around 850 °C. And YAG remains to be stable in a single phase up to 1100 °C. Heat treatment of 2 h at 900 °C seems to be enough to obtain a single-phase YAG.

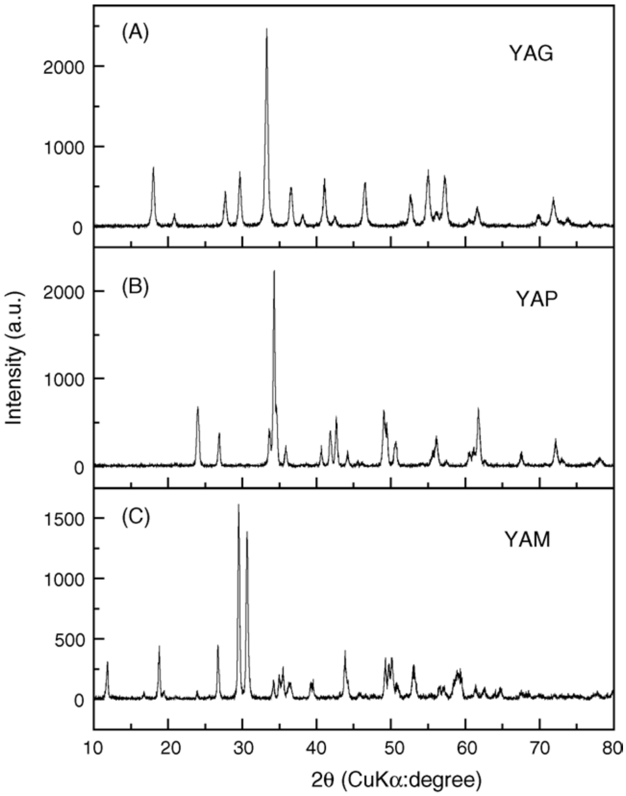

Fig. 1. The XRD patterns of the three powders obtained from the precursors of Y:Al = (A) 3:5, (B) 1:1, and (C) 4:2.

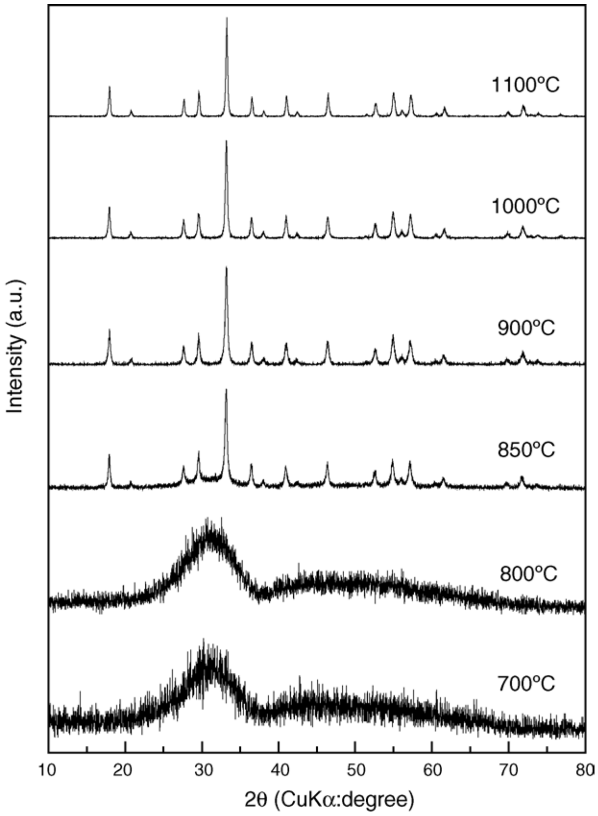

Fig. 2. The phase changes of YAG precursor as a function of heat-treatment temperature.

The phase development of the YAM was also investigated. The precursor from the Y:Al = 4:2 mixture was heat-treated and the XRD patters were measured, in the same manner as YAG. Below 800 °C the sample was still amorphous, but above 850 °C it began to crystallize. The crystallization temperature was a little higher than that of YAG. It was also supported by the TG/DTA result (Fig. 3(B)), where a little exothermic peak of crystallization is observed around 890 °C. And the YAM phase remained to be stable till 1100 °C. Heat treatment of 2 h at 900 °C seems to be enough to obtain a single-phase YAM. Phase development of YAM was proved to be almost the same with that of YAG.

On the other hand, the phase development of YAP is shown in Fig. 4. The precursor from the Y:Al = 1:1 mixture was heat-treated and the XRD patters were measured, in the same manner as YAG and YAM. Below 800 °C the sample was still

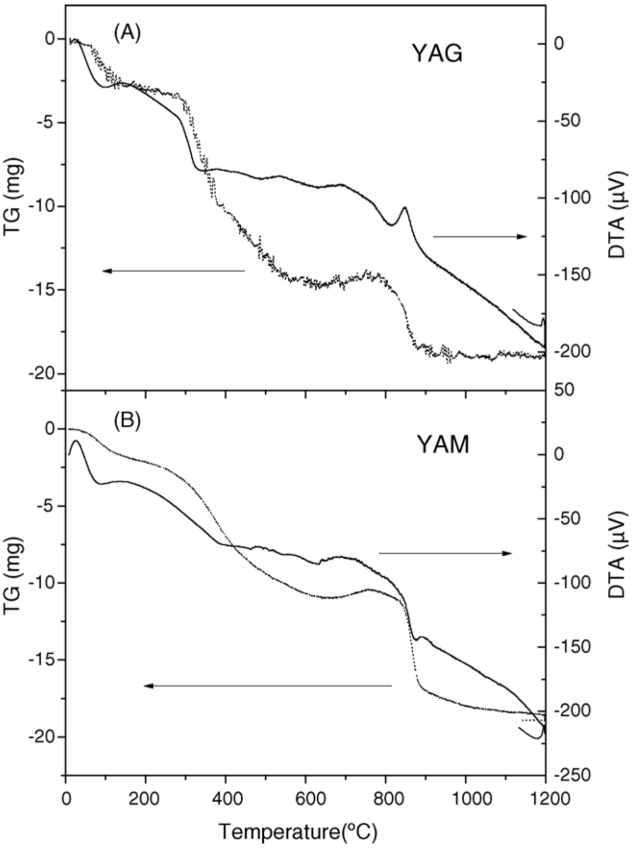

Fig. 3. The TG/DTA results of the (A) YAG and (B) YAM precursors.

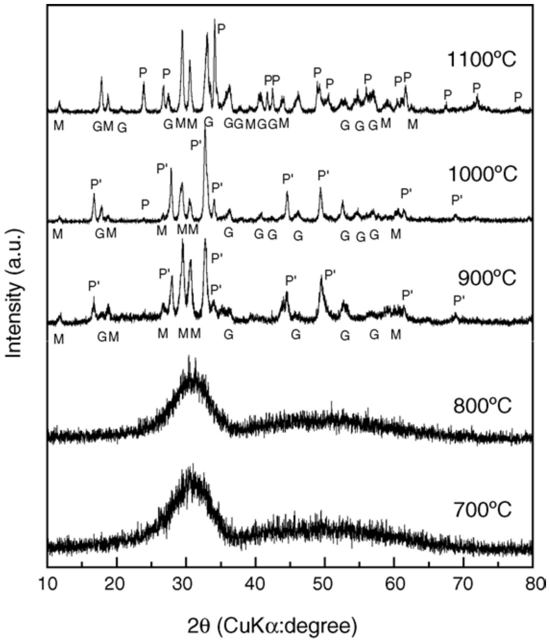

Fig. 4. The phase changes of YAP precursor as a function of heat-treatment temperature: the symbols G, M, P, and P′ represent YAG, YAM, YAP, and hexagonal YAP, respectively.

amorphous, but at 900 °C it began to crystallize. Phases of YAG, YAM, and hexagonal YAP were formed, and hexagonal YAP transformed to orthorhombic YAP at 1100 °C, but single-phase YAP was never obtained. It means that once the sample was cooled down to room temperature before single-phase YAP was formed firmly, stable YAG and YAM phases were preferentially generated and never disappeared even at the temperature for YAP crystallization. Therefore, it is proved that rapidly elevating the temperature up to 1100 °C without cooling process and treating the precursor at the same temperature for 2 h is necessary to obtain a single-phase YAP.

4. Conclusions

The polymer complex method was successfully applied for the synthesis of YAG, YAM, and YAP in a single phase. The crystallization temperatures are 900 °C for YAG and YAM, and 1100 °C for YAP, and the latter is 300 °C lower than that reported by the sol–gel method [14]. Between 900 and 1100 °C, both YAG and YAM remained stable in a single phase, while YAP was always formed with other phases. The result revealed that rapidly elevating the temperature up to 1100 °C without cooling process and treating the precursor at the same temperature for 2 h is necessary to obtain a single-phase YAP.

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