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Characterization of Spray-Dried Yttrium Aluminum Garnet Powder

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Yttrium aluminum garnet (YAG) powders were synthesized by spray-drying of the hydroxides coprecipitated from a mixture of aqueous solutions of $Al(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$. Phase formation in the powders during heat treatments and their sintering characteristics were investigated. In the powder obtained by washing the hydroxides before spray-drying, a metastable yttrium aluminum hexagonal (YAH) phase was first crystallized and then transformed into YAG as temperature was increased. The formation of YAH was attributed to a deviation in compositions of the particles from the starting composition of YAG. However, the powder prepared without a washing step contained a stable yttrium aluminum monoclinic (YAM) phase in addition to YAG due to a large deviation from the starting composition. A powder compact of a single phase YAG was pressureless-sintered for 4 hrs at 1700°C and the density was 93% of the theoretical density.

Key words : YAG, YAH, YAM, Spray-drying, Powder, Phase formation, Sintering

I. Introduction

Three intermediate compounds are known to exist in the system Al_2O_3-Y_2O_3 : yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$), yttrium aluminum perovskite (YAP, $YAlO_3$), and yttrium aluminum monoclinic (YAM, $Y_4Al_2O_9$).[1] YAG exists in a cubic form with a garnet structure.[2] YAP has an orthorhombic distorted perovskite structure,[3] and YAM is monoclinic.[4] There is another phase, hexagonal $YAlO_3$ phase (YAH), which is found only in pow- ders synthesized by chemical methods.[5,6] YAH phase is the modification of YAP with a hexagonal structure. Among these compounds, doped single crystals of YAG are widely used in solid state lasers. YAG powders are used as phosphors for CRT and translucent YAG ceramics as optical materials. Recently, it has been recognized that YAG may be the most creep-resistant oxide.[7,8] YAG ceramics in the forms of single crytal and polycrystalline fibers, matrices, and eutectic composites have many potential applications as high-temperature structural materials (>1500°C) in oxidizing atmosphere.

The preparation of pure YAG powder by solid state reaction between Al_2O_3 and Y_2O_3 powders requires high temperatures. When the powder mixture is heated below 1600°C, a single phase YAG does not form, but YAP and Al_2O_3 coexist.[9,10] Since heat treatments at high temperatures increase particle sizes, the size should be reduced through a milling process. Thus, impurities are often introduced into the resulting powders. Alternatively, chemical methods such as a sol-gel method and solution coprecipitation not only permit low-temperature synthesis, but also allow the control of chemical homogeneity, particle size and shape, and agglomeration. YAG powders have been prepared by coprecipitation or spray-drying of solutions of nitrates,[11,12] chlorides,[13] and sulfates,[13,14] by hydrolysis of alkoxides,[6,15-17] or by the hydrothermal technique.[18] However, the synthesis of pure YAG powder by the chemical methods is quite difficult. Undesirable phases are almost inevitably formed and can persist after calcination.

In the present study, YAG powder was prepared from the solutions of $Al(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ by coprecipitation and spray-drying. Phase formation in the powder during heat treatments and its sintering characteristics were investigated.

II. Experimental Procedure

Aqueous solutions of nitrates, $Al(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$, were mixed in 5 : 3 molar ratio of Al and Y. The hydroxides were coprecipitated by dropwise addition of excess NH_4OH into the solution under vigorous stirring and washed with de-ionized water in order to remove residual ammonium and nitric ions. After washing was repeated several times, the hydroxides were dispersed in water and spray-dried (Yamato Spray Drier, Model DL-41) under the conditions listed in Table 1. Some of the precipitates were spray-dried without a washing step in order to investigate the washing effect on phase formation during calcination.

Thermal behavior of the powders was studied with differential thermal analysis (DTA) at a heating rate of 10°C/min up to 1500°C in air. Some samples were heated in the DTA furnace under the same conditions as in the thermal analysis for the purpose of identification of the

Table 1. Spray Drying Conditions

Concentration (wt%)	pH	Inlet temperature(°C)	Outlet temperature(°C)	Drying air flow rate (m^3/min)	Atomizing air pressure(kg/cm^2)	Nozzle diameter(μm)
8.0	6.9	160	70	0.4	2	1530

phase related to each DTA peak. Calcination was carried out by heating the powders to temperatures between 800° and 1200°C in air at a heating rate of 3°C/min and holding for 2 hrs. Phases present in the powders were investigated using room-temperature X-ray powder diffraction (Rigaku Rotaflex Diffractometer, CuKα). Densities and size distributions of the powders were measured with a helium gas pycnometer (Micromeritics, AccuPyc 1330) and X-ray sedimentation (Micromeritics, SediGraph), respectively.

The calcined powders were dry-pressed into pellets in 1/4 inch diameter using polyvinyl alcohol as a binder. The pellets were fired for 4 hrs at 600°C to decompose the binder and pressureless-sintered at various temperatures between 1400° and 1700°C for 4 hrs in air. Bulk densities of the sintered samples were determined by the Archimedes method and relative (or percentage of theoretical) densities were calculated using 4.55 g/cm^3 as the theoretical density for YAG. Microstructures of the sintered samples and the powders were observed with SEM.

III. Results and Discussion

Fig. 1 is an SEM micrograph of the powder, prepared with washing prior to spray-drying, after calcination at 900°C. The powder consisted of spherical particles in the size range of approximately 1~20 μm. As-spray dried powder showed the similar particle shapes and its density was increased from 2.43 g/cm^3 to 3.95 g/cm^3 after calcination. The calcination decreased the mean particle diameter from 6.6 μm to 4.6 μm, but did not change the trend of the size distribution, as shown in Fig. 2. On the other hand, the powder prepared without a washing step showed a morphology of porous, bulky shapes due to the melting of ammonium nitrate (NH_4NO_3), which was formed from the residual ammonium and nitric ions during spray-drying. This powder was not used in evaluating sintering characteristics.

The DTA result of the powder prepared with washing is shown in Fig. 3. A strong exothermic peak at 925°C corresponds to the crystallization of YAH from the amorphous powder and a weak exothermic peak at 990°C to the transformation of YAH into YAG. These exothermic peaks have been reported in the powder prepared from Al and Y alkoxides[6,17]. YAH phase has not been found by Glushkova et al[11]. and Apte et al.,[12] who obtained powder from coprecipitation of nitrates. Although they observed the DTA peaks similar to Fig. 3, neither of these peaks were identified. Fig. 4. shows the X-ray diffraction

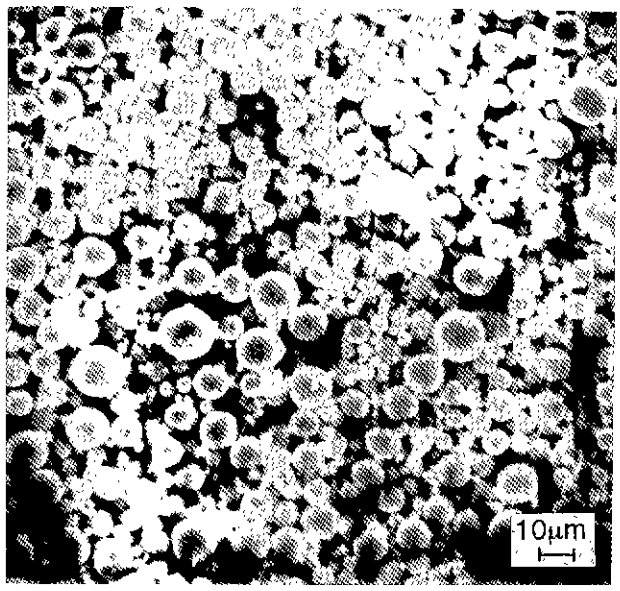

Fig. 1. SEM photograph of spray-dried YAG powder after calcination at 900°C for 2 hrs.

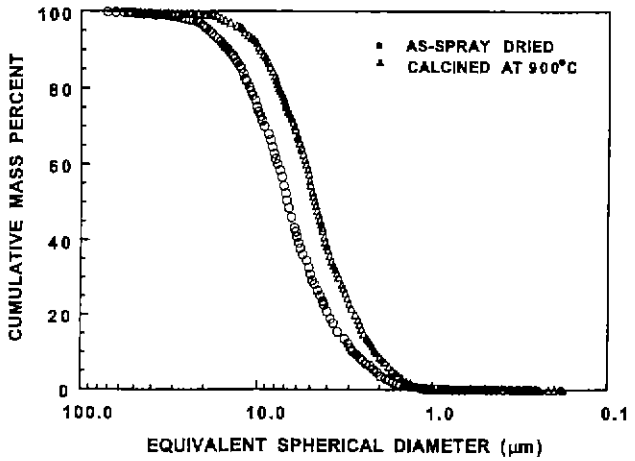

Fig. 2. Particle size distributions of as-spray dried and calcined powders. The powders were prepared with washing before spray-drying.

patterns of the powder heated in the DTA furnace. YAG and YAH coexist at 951°C (Fig. 4(a)). As the temperature is raised to 1000°C, the amount of YAG increases, while the amount of YAH decreases (Fig. 4(b)).

The formation of YAH phase can be attributed to a small deviation in the compositions of individual particles from the starting composition of YAG. The deviation may occur as a result of the segregation of Al and Y hydroxides when the solution is coprecipitated. Al and Y hydroxides are known to precipitate at different

pH values (pH 3.5 for Al and pH 7 for Y).[12] In order to avoid this, an excess amount of NH_4OH is added to the solution. When a droplet of NH_4OH contacts the solution, the metal ions precipitate in the same ratio as the bulk solution. However, according to Apte et al.,[12] the ions in the precipitates can be exchanged from the surrounding solution because of the different solubilities of Al and Y. This can give rise to an inhomogeneity in the hydroxides even if the starting solution has a stoichiometric ratio of the cations to YAG.

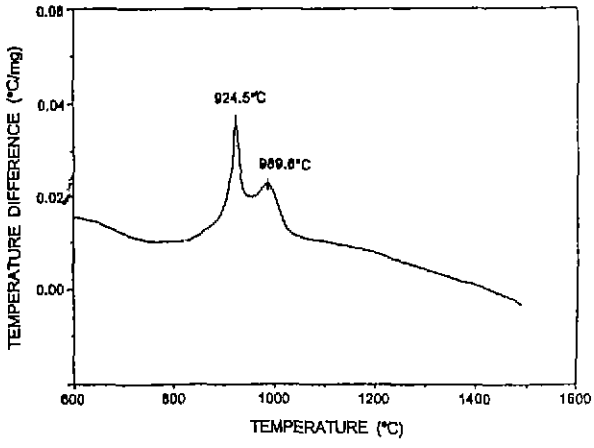

Fig. 3. DTA result of powder prepared with washing before spray-drying.

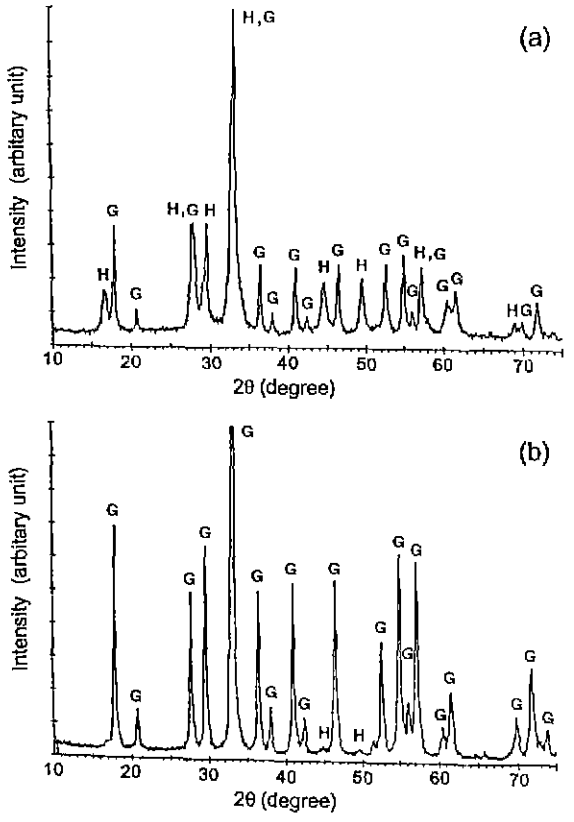

Fig. 4. X-ray diffraction patterns of powder heated in a DTA furnace at (a) 951° and (b) 1000°C. G corresponds to YAG and H to YAH.

The extent of the compositional deviation is illustrated by a temperature interval between two DTA peaks. If the peaks are slightly overlapped as shown in Fig. 3, a single YAH phase cannot be obtained. A larger temperature interval between the peaks (920~1014°C) has been reported in the alkoxide-derived powders.[17,19] When Al and Y alkoxides were mixed, Y-Al double alkoxide, $Y\{Al(OPr^i)_4\}_3$, was formed in the solution, whose hydrolysis reaction was much slower than the individual Al and Y alkoxides. The hydrolysis of such a solution led to a large compositional deviation, resulting in a pure YAH phase at 850°C. On the other hand, a single exothermic peak and a pure YAG phase have been observed in the powder prepared using a chelating agent to suppress the formation of the double alkoxide and to control the hydrolysis rate.[18,20]

In order to examine the stability of YAH, the powders were calcined at temperatures between 800° and 1200°C. The phases present are listed in Table 2. YAH phase was found to be metastable and transformed into either YAG or partially into YAM at all calcination temperatures. In the powder prepared with washing (powder A), only YAG was detected. In the powder prepared without a washing step (powder B), however, a small amount of YAM was detected as a stable phase. Figs. 5 and 6 show the X-ray diffraction patterns of the powders calcined at 800° and 1200°C. For the powder A in Figs. 5(a) and (b), the YAH peaks disappeared at 800°C and the YAG peaks increased their intensity at 1200°C, suggesting a well-crystallized YAG. Whereas, the powder B was crystallized at higher temperature than the powder A as indicated by the weak peaks corresponding to YAG and YAM at 800°C in Fig. 6(a). Fig. 6(b) shows the presence of a small amount of YAM in addition to YAG at 1200°C.

The occurrence of YAM in the powder B is due to a large deviation from the starting composition. As water is evaporated during spray-drying, the residual ammonium and nitric ions are converted into an ammonium nitrate. This ammonium nitrate in the powder melts at low temperature (170°C), thus making the distribution of Al and Y ions non-uniform. Therefore, washing is an important process to produce a single phase YAG powder by coprecipitation of nitric solutions. YAM

Table 2. Phases Present in YAG Powders After Calcination*

Temperature(°C)	Powder A&	Powder B#
800	YAG	Am+(YAG)+((YAM))$
900	YAG	Am+(YAG)+((YAM))
950	YAG	YAG+((YAM))
1050	YAG	YAG+((YAM))
1200	YAG	YAG+(YAM)

* Heated in air at a heating rate of 3°C/min and held for 2 hours.
& Washed before spray-drying.
# Not washed before spray-drying.
$ Am: amorphous, ( ): minor amount, and (( )): trace amount.

or YAP has been reported to exist with YAG in the calcined nitrate-derived powder by Apte et al.,[12] who could not observe YAH. Since YAH is an intermediate phase, it cannot be detected in normal calcination processes. YAM has been also found in the calcined alkoxide-derived powder.[17]

Fabrication of dense polycrystalline YAG ceramics requires high sintering temperatures and pressure. In order to obtain a sample with full density and translucency, SiO_2 and MgO are used as sintering aids. Without the sintering aids, an alkoxide-derived sample prepared by hot-pressing at 1800°C has exhibited 96% of the theoretical density.[16] With the addition of the sintering aids, a fully dense and translucent YAG has been obtained at 1850°C using the powder prepared by spray-drying a sulfate solution.[14]

A compact of the powder A calcined at 900°C was pressureless-sintered without using the sintering aids and its sintering characteristics were evaluated. Fig. 7 shows the relative densities and open porosities of the samples sintered for 4 hrs. Significant densification occurred above 1500°C and concurrently the open porosity decreased. The sample exhibited 89% and 93% of the theoretical density after sintering at 1600° and 1700°C, respectively.

Included in Fig. 7 are de With's data[14] obtained by sintering for 24 hrs compacts of the alkoxide-derived powder calcined at 900°C, since there exists little information regarding the sintering of polycrystalline YAG. Despite the prolonged sintering and the addition of 500ppm of MgO, the densification occured slowly and the density reached about 78% of the theoretical density at 1600°C. The same density as for the sample prepared from the nitrate-derived powder was obtained after sintering for 24 hrs at 1700°C. This suggests that the powder prepared in this work has better sintering characterics than the alkoxide-derived powder. Fig. 8 is an SEM micrograph of the polished surface of the sample sintered at 1600°C, showing the presence of open and closed pores. It is expected that a higher density and better microstructure can be achieved if the green density is improved by other forming processes.

IV. Conclusions

YAG powder was prepared from solutions of Al and Y nitrates, $Al(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ by coprecipitation and spray-drying. The DTA result of the powder prepared with washing showed that an intermediate YAH was first crystallized and then transformed into YAG. The occurrence of YAH was attributed to a deviation in compositions of the particles from the starting composition. YAH was found to be metastable and dis-

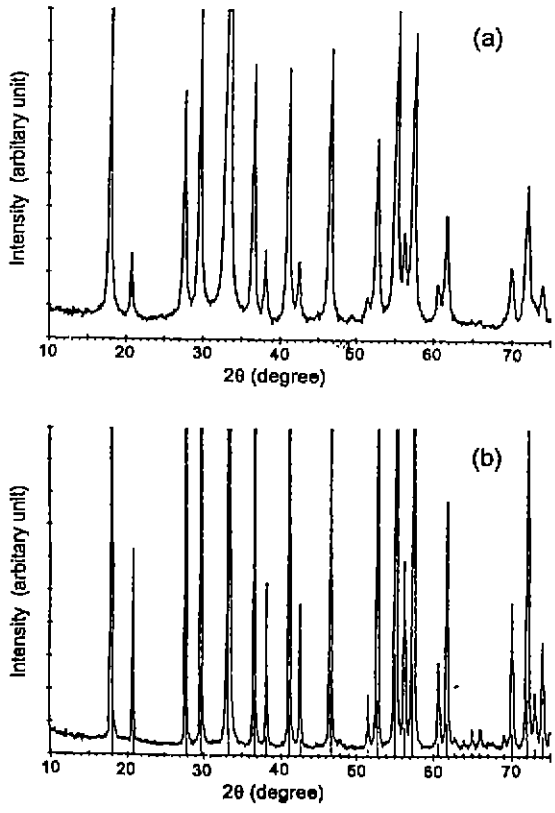

Fig. 5. X-ray diffraction patterns of powder calcined for 2 hrs at (a) 800° and (b) 1200°C. The powder was prepared with washing (powder A).

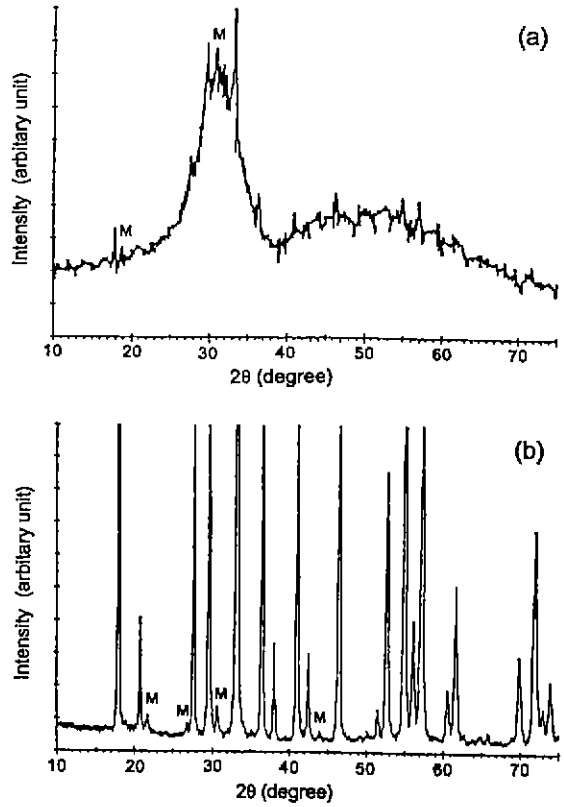

Fig. 6. X-ray diffraction patterns of powder calcined for 2 hrs at (a) 800° and (b) 1200°C. The powder was prepared without a washing step (powder B). M corresponds to YAM.

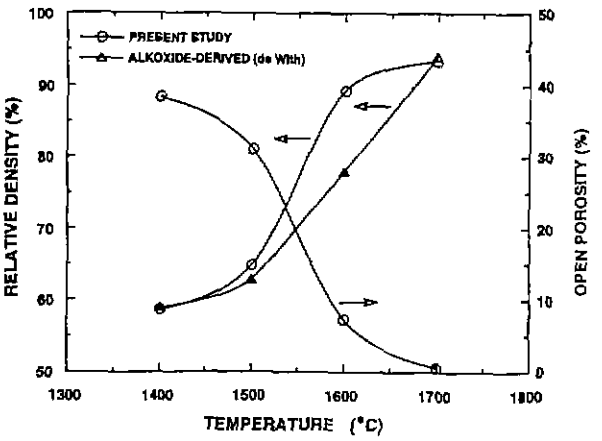

Fig. 7. Relative density and open porosity of sample sintered for 4 hrs as a function of temperature. De With's data[14] are included for comparison.

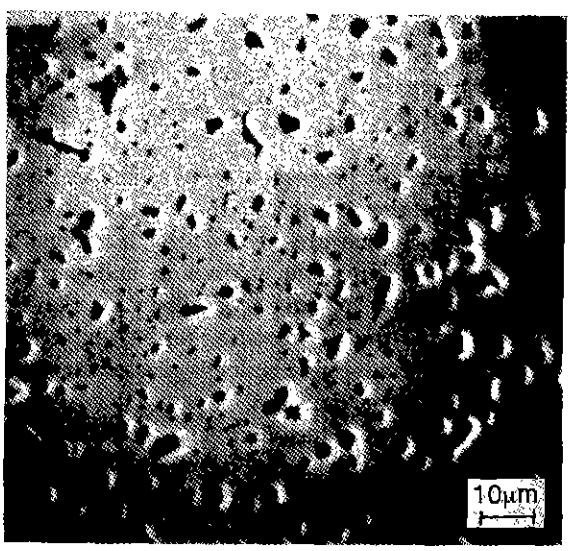

Fig. 8. SEM micrograph of sample sintered for 4 hrs at 1600°C.

appeared after calcination at the temperature range of 800°-1200°C for 2 hrs, resulting in a single phase YAG powder. However, the powder prepared without a washing step exhibited a stable YAM phase in addition to YAG due to a large deviation in compositions. A powder compact of a single phase YAG was pressureless-sintered without a sintering aid for 4 hrs at 1700°C and the density was 93% of the theoretical density.

Acknowledgement

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