

Phase formation in yttrium aluminum garnet powders synthesized by chemical methods

S.-M. SIM

School of Materials Science & Engineering, Hong-Ik University, Chochiwon 339-701, South Korea

K. A. KELLER*, T.-I. MAH*

Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433-7817, USA
E-mail: smsim@wow.hongik.ac.kr.

Yttrium aluminum garnet (YAG) powders were synthesized by precipitation of hydroxides using three types of precursors: nitrates (nitrate process), isopropoxides (alkoxide process), and isopropoxides chelated with ethyl acetoacetate (modified alkoxide process). The phase development in the powders during heat treatments was investigated with DTA and XRD. An intermediate hexagonal $YAlO_3$ (YAH) phase was formed at 800°C in all powders regardless of the synthesis processes, but its complete transformation to YAG at higher temperatures ($\geq 1000^\circ\text{C}$) occurred only in the powders prepared by the nitrate and modified alkoxide processes. The alkoxide process led to the largest deviation from the bulk composition, producing a single phase of YAH that transformed into YAG plus a stable YAM ($Y_4Al_2O_9$) phase. The modified alkoxide process led to the most homogeneous bulk composition, resulting in the least amount of YAH in the powder. The poor chemical homogeneity in the powders prepared by the nitrate and alkoxide processes was attributed to the segregation of the hydroxides and to the presence of the double alkoxide, respectively. © 2000 Kluwer Academic Publishers

1. Introduction

Three pseudo-binary 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 the cubic form with a garnet structure [2]. YAP has an orthorhombic distorted perovskite structure [3] and YAM is monoclinic [4, 5]. There is another $YAlO_3$ phase, which is a hexagonal modification (YAH) and found only in chemically synthesized powders [6–9].

Among these compounds, YAG has received the most attention due to its good optical properties. Single crystal YAG is best known as a solid-state laser host material. Recently, transparent polycrystalline YAG ceramics have been fabricated for use as solid-state laser materials [10, 11]. It also has been recognized that YAG may be the most creep-resistant oxide [12–14]. YAG ceramics in the form of single crystal and polycrystalline fibers, matrices, and eutectic composites have many potential applications as high-temperature engineering materials.

Synthesis of YAG powder by solid-state reaction requires high temperatures. Heat treatments of mixed oxide powders at temperatures below 1600°C yield YAP

and Al_2O_3 coexisting with YAG [9, 15, 16]. In order to obtain pure YAG at lower temperatures, powders have been synthesized by various chemical methods such as precipitation of hydroxides [7–9, 17–23], thermal decomposition of nitrates [16], sol-gel process [24, 25], and a hydrothermal technique [26]. The literature concerning phase formation in these powders shows conflicting results. Pure YAG was reported by Glushkova *et al.* [17], Vrolijk *et al.* [19, 20], and de With and van Dijk [21], who prepared powders by precipitating nitrate or sulfate solutions. Gowda [24] obtained pure YAG at 810°C from a gel prepared with aluminum tri-*sec*-butoxide and yttrium acetate. Liu *et al.* [25] also obtained pure YAG at 1000°C by pyrolysis of aluminum and yttrium isobutyrate.

Second phases such as YAP, YAM, and YAH, along with YAG, have been reported by many investigators. Apte *et al.* [18] found YAP or YAM by the addition of base into a nitrate solution and claimed that the addition of the solution to base and heat treatment of the hydroxides in a hydrogen atmosphere can consistently yield pure YAG. Bertaut and Mareshal [6] first found YAH by the evaporation of a nitrate solution. Yamaguchi and coworkers [7, 8] reported YAH in the hydrolysis of isopropoxides and found it transformed to YAG at about

* Present address: UES, Inc., Dayton, OH 45432-1894, USA.

1050°C. Kinsman *et al.* [9] obtained YAH by precipitation of a nitrate solution that transformed to YAG at temperatures below 1000°C.

Most literature reports indicate that the occurrence of the second phases might be due to poor chemical homogeneity in the powders, which can result from the synthesis process and the chemical nature of the precursor. In this paper, the effect of the synthesis processes and the precursors on the phase formation in YAG powders was investigated. The powders were synthesized by precipitation of aluminum and yttrium hydroxides using three types of the precursors: nitrates (nitrate process), isopropoxides (alkoxide process), and isopropoxides chelated with ethyl acetoacetate (modified alkoxide process). The phase development of these powders during various heat treatments was examined with differential thermal analysis (DTA) and X-ray powder diffraction (XRD).

2. Experimental procedure

In the nitrate process, YAG powder was prepared by coprecipitation and spray drying of the hydroxides. Aqueous solutions of $Y(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were mixed in a Y:Al molar ratio of 3:5. The hydroxides were precipitated by dropwise addition of excess NH_4OH into the solution under vigorous stirring. A subsequent wash with de-ionized water removed residual ammonia and nitric ions. After washing several times, the hydroxides were dispersed in water and granulated with a spray dryer equipped with a nozzle atomizer (Yamato, Model DL-41). In the alkoxide process, YAG powder was prepared by hydrolysis of aluminum and yttrium isopropoxides, $Al(OC_3H_7)_3$ and $Y(OC_3H_7)_3$, which had been synthesized based on the procedure described by Mazdiyasi [27]. The alkoxides were diluted in 2-propanol, mixed in an appropriate molar ratio, and refluxed for 12 h at 80°C. The mixture was hydrolyzed by the addition of an excess amount of water containing the alcohol, dried under reduced pressure at 80°C, and then ground. In the modified alkoxide process, equimolar amounts of $Y(OC_3H_7)_3$ and ethyl acetoacetate, $CH_3COCH_2CO_2C_2H_5$ (EAA), were mixed and refluxed under 2-propanol for 6 h. The solution was then mixed with a solution of $Al(OC_3H_7)_3$ diluted with the alcohol, refluxed at 80°C for 12 h, and slowly hydrolyzed as in the previous process. The precipitated hydroxides were washed with acetone several times, dried under reduced pressure at 80°C, and then ground.

Thermal behavior of the powders was studied with differential thermal analysis (TA Instruments, Model 1600 DTA) at a heating rate of 10°C/min up to 1500°C in air. For phase analysis, the powders were heated to temperatures between 775 and 1100°C at a heating rate of 10°C/min in air and air quenched to room temperature. Some powders were heated in the DTA furnace under the same conditions as in the thermal analysis in order to identify the phase related to each DTA peak. Phases present in the powders heat-treated at various temperatures were examined by X-ray powder diffraction with $Cu K_\alpha$ radiation (Rigaku Rotaflex Diffractometer). The XRD pattern of YAH was indexed

using a least-squares refinement technique and high purity Si powder (99.999%) was used as an internal standard.

3. Results and discussion

Fig. 1 shows the DTA curves of the powders prepared by the three synthesis processes. The powders prepared by both nitrate and alkoxide processes exhibited two exothermic peaks: a strong, sharp peak and a weak, broad peak, occurring respectively at 925 and 990°C for the nitrate-derived powder (Fig. 1a) and at 920 and 1014°C for the alkoxide-derived powder (Fig. 1b). The first peaks were found to correspond to the crystallization of YAH and the second peaks to the transformation of YAH to YAG. On the other hand, the powder prepared by the modified alkoxide process exhibited only a strong and sharp exothermic peak at 921°C, as shown in Fig. 1c, due to the crystallization of YAG from an amorphous phase. The phase related with each DTA peak was confirmed by XRD of the powders heat-treated in the DTA furnace. Fig. 2 shows the XRD patterns of the powder prepared by the nitrate process. YAG and YAH coexisted at 951°C (Fig. 2a). As the temperature was raised to 1000°C, the amount of YAG increased, while the amount of YAH considerably decreased (Fig. 2b). In the powder obtained by the alkoxide process, only YAH was detected at 951°C and a small amount of YAG appeared at 1000°C. In the powder prepared by the modified alkoxide process, YAG and a very small amount of YAH were present with an amorphous phase at 900°C and only the YAG phase was observed at 1000°C.

DTA peaks similar to Figs 1a and b have been observed in many chemically synthesized powders. Kinsman *et al.* [9] reported peaks at 938 and 1020°C from nitrate-derived powder. Although Glushkova *et al.* [17] and Apte *et al.* [18] observed two exothermic

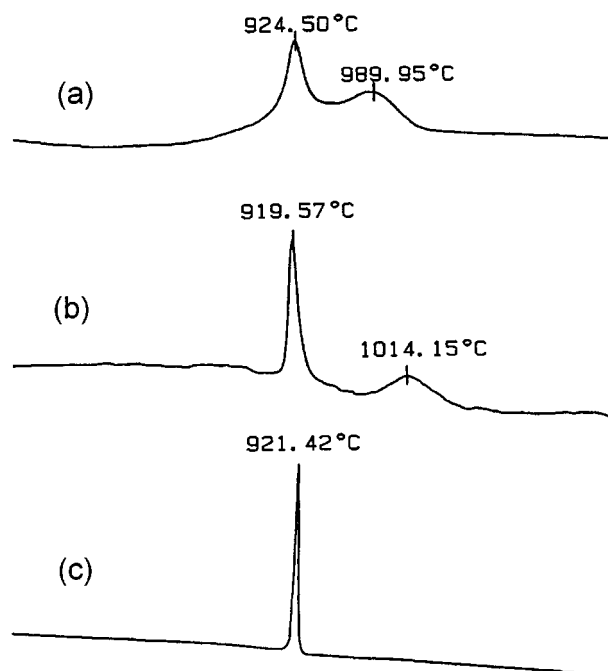


Figure 1 DTA curves for the powder prepared by (a) nitrate process, (b) alkoxide process, and (c) modified alkoxide process.

TABLE I Phases present in the powders heat-treated at various temperatures^a

Temperature (°C)	Nitrate process	Alkoxide process	Modified alkoxide process
775	Am ^b	Am	Am
800	Am + (YAG) ^c + ((YAH) ^d) ^e	Am + ((YAH))	YAG + ((YAH))
825	(YAG) + (YAH)	YAH	YAG + ((YAH))
850	YAG + YAH	YAH	YAG + ((YAH))
900	YAG + (YAH)	YAG + YAH	YAG + ((YAH))
1000	YAG	YAG + ((YAM))	YAG
1100	YAG	YAG + (YAM)	YAG

^aHeated at a heating rate of 10°C/min in air and air quenched.

^bAmorphous phase.

^cA small amount.

^dHexagonal YAlO₃.

^eA very small amount.

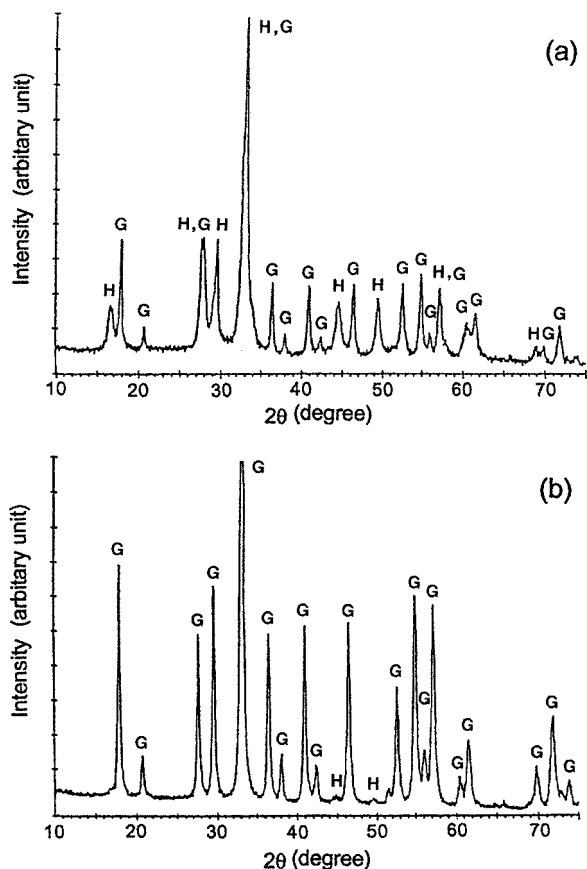


Figure 2 X-ray diffraction patterns of the powder prepared by nitrate process and heated in a DTA furnace at (a) 951°C and (b) 1000°C: G corresponds to YAG and H to YAH.

peaks from nitrate-derived powders, none of these peaks were identified as being associated with the formation of YAH. Yamaguchi *et al.* [7] also found two peaks at about 900 and 1000°C from alkoxide-derived powder. A DTA peak similar to Fig. 1c has been reported in sol-gel derived pure YAG powders by Gowda [24] who found a peak at 905°C, and by Liu *et al.* [25], who found a peak at 930°C.

Heat treatments at various temperatures clearly revealed the sequence of phase development in the powders. Phases present in the powders, heated at a heating rate of 10°C/min and air quenched to room temperature, are listed in Table I. An intermediate YAH

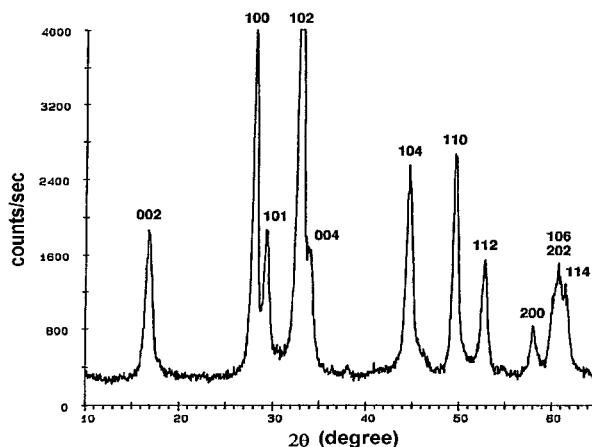


Figure 3 X-ray diffraction pattern for the single YAH phase of the powder prepared by alkoxide process and heated at 850°C.

phase appeared at 800°C regardless of the synthesis processes, and disappeared either at higher temperatures ($\geq 1000^\circ\text{C}$) or after prolonged heat treatments (≥ 2 h) [28].

The complete transformation of YAH to YAG depended on the synthesis processes. The powder prepared by the nitrate process crystallized into a mixture of YAG and a small amount of YAH that persisted up to 900°C and then fully converted to YAG at 1000°C. The powder prepared by the alkoxide process exhibited only YAH upon crystallization. This YAH developed into a well-crystallized single phase before it transformed to YAG. The XRD pattern of this pure YAH phase, obtained at 850°C, has not been previously reported, and is shown in Fig. 3. At higher temperatures ($\geq 1000^\circ\text{C}$), a small amount of YAM appeared in addition to YAG and remained. The powder prepared by the modified alkoxide process crystallized into YAG at a lower temperature compared to the other powders. Concurrently, a very small amount of YAH appeared and completely transformed to YAG at 1000°C. The formation of YAG from YAH has been explained by the reaction of YAH with unreacted Al₂O₃ [9]. If Al₂O₃ remains in the powder, aluminum continues to diffuse into the YAH which then changes into YAG. Although Al₂O₃ was not detected in this study, some studies have shown the presence of Al₂O₃ in solid-state reacted powders [9, 15] and alkoxide-derived powder [23] after insufficient heat treatments.

The formation of second phases in the powders can arise from a deviation in stoichiometry from YAG. This can be seen by the DTA peaks. The occurrence of the second exothermic peaks in Figs 1a and b suggests that the nitrate and alkoxide processes lead to a large deviation from the bulk composition, resulting in the formation of YAH. Such a deviation is indicated by a temperature interval between two exothermic peaks. A large temperature interval between the peaks (920°–1014°C) for the alkoxide-derived powder than (925°–990°C) for the nitrate-derived powder means that the alkoxide process produces the largest deviation from the bulk composition, causing the formation of YAM. The single exothermic peak in Fig. 1c suggests that the modified alkoxide process yields the most homogenous bulk composition.

For the nitrate process, the deviation in stoichiometry may occur as a result of the segregation of aluminum and yttrium hydroxides during coprecipitation. Each hydroxide is known to precipitate at different pH values (pH 3.5 for aluminum and pH 7 for yttrium) [18]. When a droplet of the base contacts the solution, the cations should precipitate in the same ratio as the bulk solution. However, according to Apte *et al.* [18], the ions in the precipitates can be exchanged from the surrounding solution because of the different solubilities of aluminum and yttrium. This can give rise to a non-uniform distribution of the cations in the hydroxides, even if the starting solution has a stoichiometric ratio of YAG.

For the alkoxide process, YAH or YAM is formed due to the presence of a double alkoxide in the solution of the alkoxide mixture. It was confirmed by nuclear magnetic resonance spectroscopy [29] that when the isopropoxides are mixed in a Y:Al molar ratio of 3:5, a stable, hydrolysis-resistant double isopropoxide, $Y\{Al(OPr^i)_4\}_3$, having a Y:Al molar ratio of 1:3, is formed, leaving residual yttrium isopropoxide. The different rates of hydrolysis reactions between these alkoxides can cause an inhomogeneous distribution

of yttrium and aluminum in the precipitates, which makes the crystallization of YAH favorable. The excess yttrium in the powder leads to the formation of the yttrium-rich YAM phase. YAM has been observed in YAG powder that was prepared from a nitrate solution without washing precipitates [30]. The melting of a residual ammonium nitrate in the hydroxides during calcination caused a significant change in the distribution of the cations.

The X-ray diffraction pattern of the pure YAH in Fig. 3 was indexed and the result is presented in Table II. The d-spacings are in good agreement with those reported by previous workers [6, 7, 9]. The values of the lattice parameters were found to be $a = 0.3672$ nm and $c = 1.0522$ nm. The crystallographic data for YAH and other phases are listed in Table III for comparison. Bertaut and Mareschal [6] reported YAH as a single compound, while Yamaguchi and coworkers [7, 8] claimed a YAH solid solution that exists in the range of compositions between 37.5 and 50 mol% Y_2O_3 . The present study could not determine whether YAH is a solid solution or a single compound. However, the lattice parameters for this study show that YAH is formed in a 1:1 molar ratio rather than in a 3:5 molar ratio of Y:Al. This supports the contention that the occurrence of YAH is due to poor chemical homogeneity in the as-prepared powder.

The modified alkoxide process results in the least deviation from the bulk composition. The formation of YAG along with a very small amount of YAH indicates an intimate mixing of the cations in the precipitates. When EAA is added to the solution of yttrium isopropoxide, it replaces alkoxy groups and forms bonds between yttrium ions and acetate groups, yielding $Y(OPr^i)_2(acac)$. The mixing of the chelated yttrium isopropoxide with aluminum isopropoxide forms a double alkoxide, $Y\{Al(OPr^i)_4\}_2\{Al(OPr^i)_3(acac)\}$ [29]. This double alkoxide and the remaining chelated yttrium alkoxide have slow hydrolysis rates and inhibit the segregation of the cations in the hydroxides during hydrolysis. Pure YAG powder has been obtained from aluminum tri-sec-butoxide and yttrium acetate [24]. Yttrium acetate acts in the same manner as EAA does.

TABLE II X-ray diffraction data for YAH^a of powder^b prepared by alkoxide process

<i>hkl</i>	$d_{obs}(nm)$	$d_{cal}(nm)$	<i>I/I₀</i>
002	0.5261	0.5261	27
100	0.3178	0.3180	62
101	0.3045	0.3044	23
102	0.2721	0.2721	100
004	0.2631	0.2631	21
104	0.2027	0.2027	35
110	0.1836	0.1836	40
112	0.1734	0.1733	19
200	0.1589	0.1590	7
106		0.1536	
202		0.1522	
114		0.1506	

^aHexagonal $YAlO_3$ phase with unit cell parameters of $a = 0.3672$ nm and $c = 1.0522$ nm.

^bHeated to 850°C at the same heating rate as in Table I.

TABLE III Crystallographic data of yttrium aluminates

Phase	Structure	Space group	Lattice parameter (nm)	Ref.
YAG($Y_3Al_5O_{12}$)	Cubic	<i>Ia3d</i>	$a = 1.201$	2
YAM($Y_4Al_2O_9$)	Monoclinic		$a = 0.737, b = 1.047,$ $c = 1.112, \beta = 108.5^\circ$	4
YAP($YAlO_3$)	Orthorhombic	<i>Pnma</i>	$a = 0.5179, b = 0.5329,$ $c = 0.7370$	3
YAH($YAlO_3$)	Hexagonal	<i>P6₃/mmc</i>	$a = 0.3678, c = 1.052$ ($c/a = 2.860$)	6
	Hexagonal ^a		$a = 0.3678, c = 1.046$ ($c/a = 2.844$)	7
	Hexagonal ^b		$a = 0.3678, c = 1.054$ ($c/a = 2.866$)	8
	Hexagonal		$a = 0.3672, c = 1.052$ ($c/a = 2.865$)	Present study

^aSolid solution contains 37.5 mol% Y_2O_3 (3:5 = Y:Al).

^bSolid solution contains 50 mol% Y_2O_3 (1:1 = Y:Al).

4. Conclusions

YAG powders were synthesized by three chemical methods: the nitrate process, the alkoxide process, and the modified alkoxide process. An intermediate YAH phase was formed at 800°C regardless of the synthesis processes and disappeared at higher temperatures ($\geq 1000^\circ\text{C}$). Its complete transformation to YAG depended on the synthesis processes. The DTA and the X-ray diffraction analysis showed that the formation of the second phases was due to poor chemical homogeneity in the as-prepared powders. The exothermic peaks of the DTA curves suggested that the alkoxide process led to the largest deviation from the bulk composition, producing a single phase of YAH upon crystallization that transformed to a stable YAM phase coexisting with YAG. The modified alkoxide process resulted in the most homogeneous bulk composition, yielding the least amount of YAH in the powder. The deviation from the bulk composition in the powders prepared by the nitrate and alkoxide processes was attributed to the segregation of the hydroxides during the coprecipitation and to the presence of the yttrium-aluminum double alkoxide, respectively.

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