

Synthesis of yttrium aluminum garnet powder by a citrate gel method

Byung-Joo Chung, Joon-Young Park and Soo-Man Sim*

School of Materials Science & Engineering, Hongik University, Jochiwon, Chungnam 330-701, Korea

Yttrium aluminum garnet (YAG) powder was synthesized by a citrate gel method using nitrates and citric acid. The citrate gel almost decomposed at $\sim 600^{\circ}\text{C}$ and began to crystallize into YAG at 800°C with concurrent formation of a very small amount of an intermediate hexagonal YAlO_3 (YAH) phase, which completely transformed to YAG after prolonged heating (≥ 2 h) or at higher temperatures ($\geq 1000^{\circ}\text{C}$). Well-crystallized, phase-pure YAG powder could be obtained after calcination at 900°C for 6 h. Attrition milling of the powder for 2 h resulted in an average particle size of $0.55\text{ }\mu\text{m}$. However, during the milling process, ZrO_2 (652 ppm Zr) was introduced into the powder containing SiO_2 (131 ppm Si) as a sintering aid and found to retard densification of YAG. Despite the presence of ZrO_2 , sintering the powder compacts for 6 h in air exhibited a considerable densification at temperatures above 1400°C , resulting in a relative density of 95.2% at 1600°C .

Key words: YAG, Powder synthesis, Citrate gel, Decomposition, Sintering.

Introduction

Yttrium aluminum garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$), existing in a cubic form with a garnet structure, has received much attention because of its interesting optical and mechanical properties. Single crystal YAG is widely used in solid-state lasers. Rare-earth doped YAG powders are promising phosphor candidates for displays due to their excellent stability to high intensity irradiation by electron beams [1-3]. Since YAG is known as the most creep-resistant oxide [4, 5], polycrystalline YAG in a pure form or in the form of composites has many potential applications as high-temperature engineering materials. Transparent polycrystalline YAG is also considered as an alternative to single crystal YAG [6].

Synthesis of polycrystalline YAG by solid-state reaction requires prolonged heating at high temperatures and sintering aids such as SiO_2 . Heat treatments at temperatures below 1600°C do not yield a single phase YAG but yttrium aluminum perovskite (YAP, YAlO_3), yttrium aluminum monoclinic (YAM, $\text{Y}_4\text{Al}_2\text{O}_9$), or Al_2O_3 co-existing with YAG [1, 6]. Therefore, a fine, agglomerate-free powder with phase-pure YAG is essential to achieve a full density and transparency at lower temperatures and for a shorter sintering time. In order to obtain such powders, various chemical methods have been employed including precipitation of hydroxides [1, 7-9], sol-gel processes [10-14], urea method [15], spray pyrolysis [16], and combustion synthesis [17]. However, most methods still require temperatures above 1000°C and prolonged heating to completely transform the second

phases into YAG. This can result in severe agglomeration in the powders, which may lead to poor sinterability.

Recent studies have been focused on the fabrication of transparent polycrystalline YAG by using fine, reactive powders. Ikesue and coworkers [6, 18], who prepared high purity fine powders of Al_2O_3 and Y_2O_3 by a precipitation method, obtained transparent Nd:YAG with optical properties equivalent to the single crystal form by vacuum sintering for 20 h at 1750°C . Li *et al.* [19] claimed that transparent YAG could be obtained without sintering aids at 1700°C from the powder produced by a precipitation method using ammonium hydrogen carbonate as a precipitant. Tachiwaki *et al.* [13] reported transparent YAG at 1600°C from the powder synthesized from chlorides and hydrazine.

The citrate gel method has advantages of a tight control of stoichiometry and incorporation of low-level dopants. In this method, a citrate solution containing metal ions is heated to convert into a gel, which is decomposed and subsequently calcined to form oxide powders. The uniform distribution of metal ions in the precursor solution can be maintained throughout the whole process. Previous work has demonstrated that Y-doped SrZrO_3 powder with a single perovskite phase can be produced at a lower temperature and have better sinterability as compared to the powder prepared by a solid-state reaction [20]. Roy *et al.* [17] obtained phase-pure YAG powder at 900°C by a citrate-nitrate combustion technique. Cinibulk [21] also reported phase-pure YAG powder at 800°C from a citrate precursor. However, neither has reported the detailed characteristics of the powders. In the present study, YAG powder was synthesized by a citrate gel method using Al and Y nitrates and citric acid. The thermal behavior of the gel

*Corresponding author:
Tel : +82-41-860-2518
Fax: +82-41-863-6561
E-mail: smsim@wow.hongik.ac.kr

and characteristics and sinterability of the powder were investigated.

Experimental Procedure

Aqueous solutions of 1.93M $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich) and 2.12M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%, Junsei) were mixed in a 3:5 molar ratio of Y:Al. The mixture was added to a solution of 2M citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 99.5%, Kanto) in a 3:1 molar ratio of citric acid:nitrates, heated to 80°C to remove water, and then dried for 24 h at 80°C under vacuum.

The thermal behavior of the gel was studied with TG/DTA (TG-DTA 2000, MAC Science) at a heating rate of $3^\circ\text{C} \cdot \text{min}^{-1}$ up to 1500°C in air. For phase analysis, the gel was heated up to 1500°C and air quenched to room temperature. Some gels were heated at 800, 860, and 900°C for 0, 2, and 4 h under the same conditions as in the thermal analysis in order to identify the phase related to each DTA peak. Phases present in the heat-treated samples were examined by X-ray powder diffraction with $\text{CuK}\alpha$ radiation (M03XHF, MAC Science).

The powder for the sintering experiment was prepared by decomposing the gel at 600°C for 6 h, followed by calcination at 900°C for 6 h in air. The calcined powder was attrition-milled with ZrO_2 balls (3 mm in diameter) at 600 rpm for 2 h. SiO_2 as a sintering aid was introduced into the milled powder by hydrolysis of TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$, Acros). The powder containing 0.5 wt% TEOS solution diluted in a mixture of ethanol and water was ball-milled with ZrO_2 balls and dried. The powder was then mixed with 0.5 wt% polyvinyl butyral as a binder and isostatically pressed into pellets (1 cm in diameter) at 200 MPa. The pellets were heated for 4 h at 600°C to remove the binder and sintered for 6 h at temperatures between 1300°C and 1600°C in air.

The particle size and apparent density of the powder were measured with a laser diffraction particle size analyzer (SALD-2001, Shimadzu) and a He gas pycnometer (AccuPyc 1330, Micromeritics), respectively. Bulk densities of the sintered samples were determined by the Archimedes method and the relative densities were calculated from the bulk densities and the theoretical density of YAG (4.55 g/cm³). Powder morphology and the microstructure of the sintered samples were examined with scanning electron microscopy (JSM-5410, JEOL). The concentrations of the starting solutions and impurity contents in the powder were determined by inductively coupled plasma analysis.

Results and Discussion

TG/DTA curves of the citrate gel are presented in Fig. 1, showing that the gel decomposes in the following stages: dehydration, decomposition of the citrate, and oxidation of the decomposition products. A small weight loss up to ~150°C is due to dehydration of the

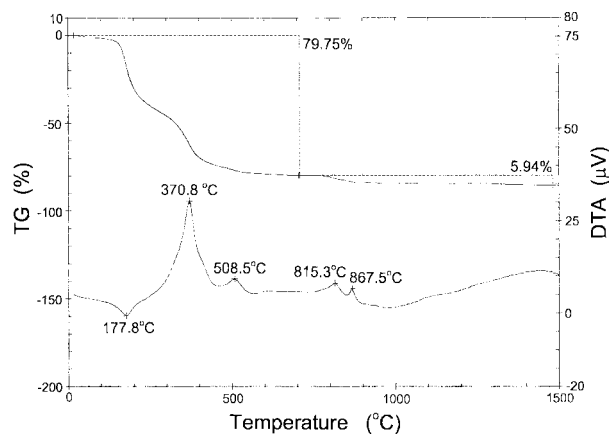


Fig. 1. TG/DTA curves of the gel at a heating rate of $3^\circ\text{C} \cdot \text{min}^{-1}$ in air.

gel. The initial decomposition occurs up to ~200°C as shown by a weak endothermic peak at 178°C. A strong exothermic peak at 371°C and a weak exothermic peak at 509°C indicate the oxidation of the decomposition products. The decomposition of the gel was nearly completed at ~600°C, resulting in a weight loss of 80%. An exothermic peak at 815°C, accompanied by a weight loss of 6%, is attributed to the oxidation of the carbon residue. An exothermic peak at 868°C was found to correspond to the crystallization of YAG.

Figure 2 shows XRD patterns of the gel heated to various temperatures and cooled to room temperature without being held. The gel, which remains amorphous up to 800°C, exhibits only the YAG phase at 1000°C. As the temperature is raised to 1200°C, the YAG phase becomes well crystallized with an increase in its peak

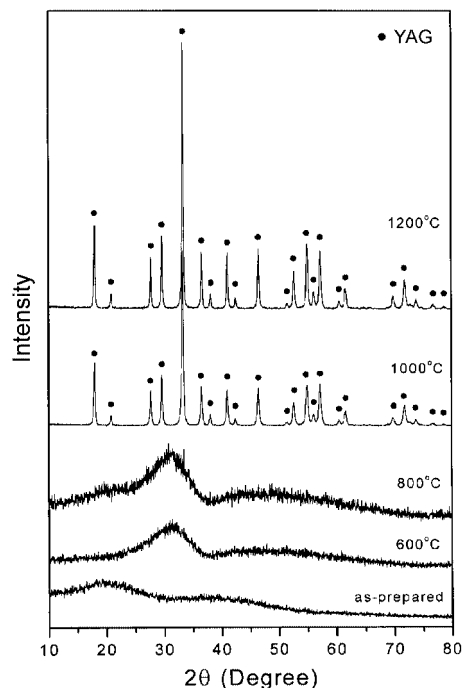


Fig. 2. XRD patterns of the gel heated at various temperatures.

intensity. The phase development at temperatures between 800°C and 900°C is illustrated in Fig. 3, showing XRD patterns of the gel that was heated at the same heating rate as in the thermal analysis and held for various times. At 800°C, the amorphous gel was almost crystallized into YAG after 2 h and the crystallization of YAG continued with a further heating up to 4 h, as shown in Fig. 3(a). No other phases were detected at 800°C. However, a very small amount of hexagonal YAlO_3 (YAH) phase in addition to YAG appeared at 860°C and 900°C, as shown in Fig. 3(b). The YAH phase disappeared and completely transformed to YAG after 2 h heating at both temperatures. Calcination at 900°C for 6 h resulted in a well-crystallized, phase-pure YAG powder and its XRD pattern was found to be identical to that for 1200°C in Fig. 2.

The YAH phase has been reported in many chemically synthesized powders [8, 10-13, 15, 16, 21]. Most literature reports indicate that the YAH phase appears in the temperature range between 800°C and 1000°C regardless of the synthesis methods. Recently, the powder prepared from a citrate precursor showed YAH at 900°C when heated under an argon atmosphere [21]. However, the powder prepared from the same precursors as in this study was reported to contain a small amount of YAM along with YAG between 850°C and 900°C [17].

The very small amount of an intermediate YAH phase observed in the powder, as shown in Fig. 3, suggests that the citrate gel method can yield a powder with the smallest deviation from the YAG composition. It has been proposed that the occurrence of the second phases is related with chemical homogeneity in the

YAG powder [12]. A small deviation from the YAG composition results in the formation of the YAH phase and its amount depends on the extent of the deviation. A large deviation in stoichiometry results in the YAM phase. Such a deviation can be also seen in DTA peaks. Two exothermic peaks arising from a large deviation have been observed in the powders synthesized by precipitation of hydroxides using nitrates and alkoxides [11, 12] and by a sol-gel process using chlorides and hydrazine [13]. The first peak was attributed to the crystallization of YAH and the second peak to the transformation of YAH to YAG. In Fig. 1, a single exothermic peak due to the crystallization of YAH could not be observed, since the peak intensity for the YAH phase was very weak or the peak might overlap with the strong peak corresponding to the crystallization of YAG. Therefore, the peak at 868°C in Fig. 1 could be assigned to the crystallization of YAG.

The crystallization temperature for the pure YAG phase was found to be consistent with those reported in the powders prepared from citrate precursors [17, 21]. From the results of TG/DTA and XRD, the crystallization of YAG in the present powder began at 800°C with concurrent formation of YAH, which then transformed to YAG after prolonged heat-treatments (≥ 2 h) or at higher temperatures ($\geq 1000^\circ\text{C}$). Roy *et al.* [17] reported that the crystallization of YAG began at 800°C and was completed below 900°C. Cinibulk [21] obtained a well-crystallized YAG powder after 1 h heating at 800°C.

The calcined YAG powder exhibited good milling characteristics because of macroscopic pores present in the powder and a weak agglomeration between the particles. The pores arise from the evolution of large

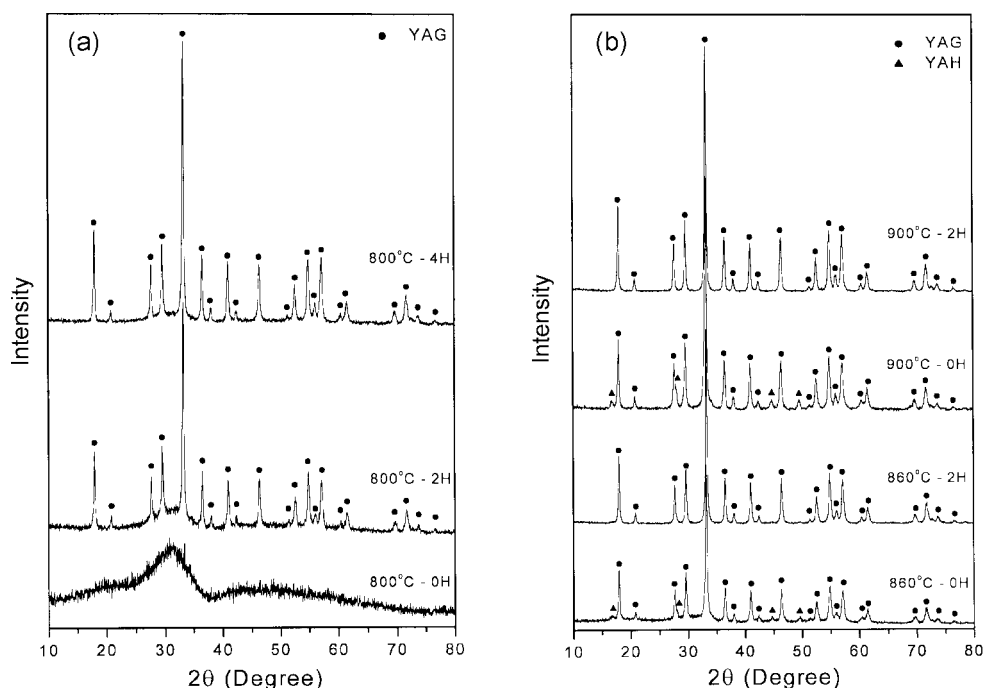


Fig. 3. XRD patterns of the powder heated at (a) 800°C for 0, 2 and 4 h and (b) 860°C and 900°C for 0 and 2 h.

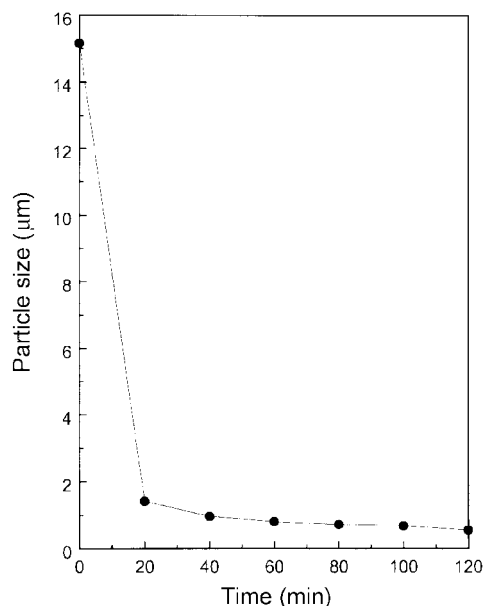


Fig. 4. Average particle size of the powder as a function of milling time.

amounts of gases during decomposition of the citrate [20]. The low calcination temperature can reduce agglomeration between the particles. Fig. 4 shows the average particle size of the powder calcined at 900°C as a function of attrition milling time. Milling for 20 minutes significantly decreased the average particle size from 15.56 μm to 1.41 μm. However, a further milling up to 2 h gradually decreased the particle size to 0.55 μm. The powder before milling had a broad size distribution ranging from 100 μm to 0.3 μm, whereas the powder after milling for 2 h had a much narrower size distribution ranging from 2 μm to 0.3 μm, as shown in Fig. 5.

The morphology of the powder milled for 2 h in Fig. 6 shows the particles consisting of strongly agglomerated primary particles in ~0.1 μm size. The strong agglomeration resulted from the high reactivity of the powder

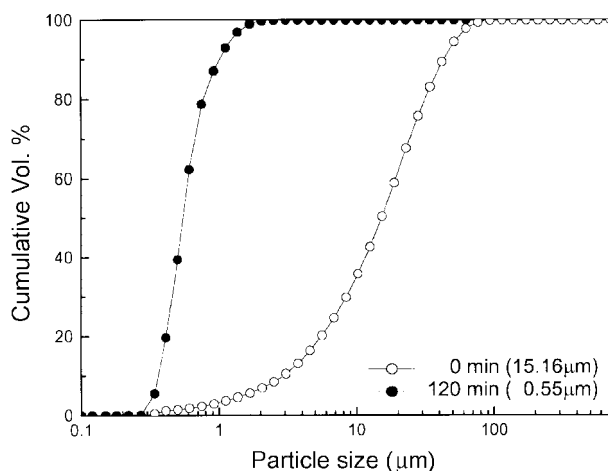


Fig. 5. Particle size distributions of the powders calcined and attrition-milled for 2 h.

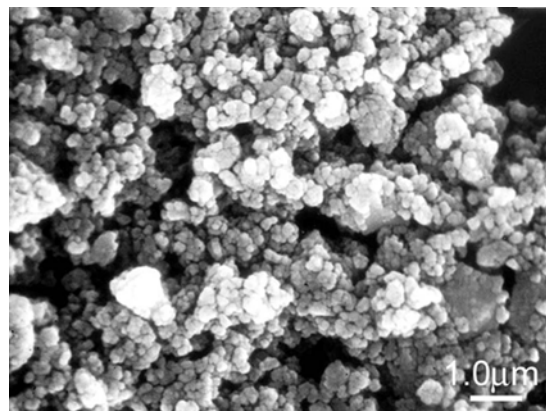


Fig. 6. SEM micrograph of the powder attrition-milled for 2 h.

that led to particle sintering during the calcination. These particles remained in the milling process, as indicated by the particle size distribution (Fig. 5) that the powder contained 10% of large particles (>1 μm). The milled powder had a slightly larger apparent density of 4.20 g/cm³ (92.3% of the theoretical density) compared with that of the calcined powder (4.16 g/cm³).

Fig. 7 exhibits the relative densities of the samples sintered between 1300°C and 1600°C for 6 h in an ambient atmosphere. The green compact with a relative density of 51.6% showed a small densification at 1300°C, resulting in a slight increase in density (58.7%). A considerable densification occurred at temperatures above 1400°C with an increase in the relative density from 68.1% at 1400°C to 88.6% at 1500°C. As the densification continued to higher temperatures, the density reached 95.2% at 1600°C.

It has been reported that the addition of SiO₂ enhances densification as well as grain growth of YAG [6, 18]. SiO₂ is also known to improve the microstructure by inhibiting abnormal grain growth and

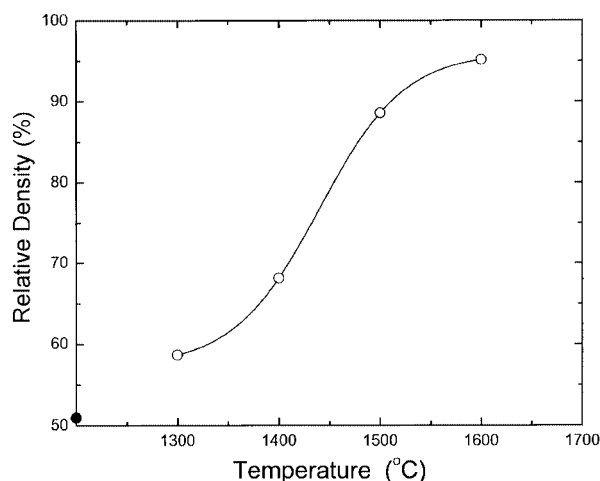


Fig. 7. Relative densities of the samples sintered at various temperatures for 6 h (●: green density).

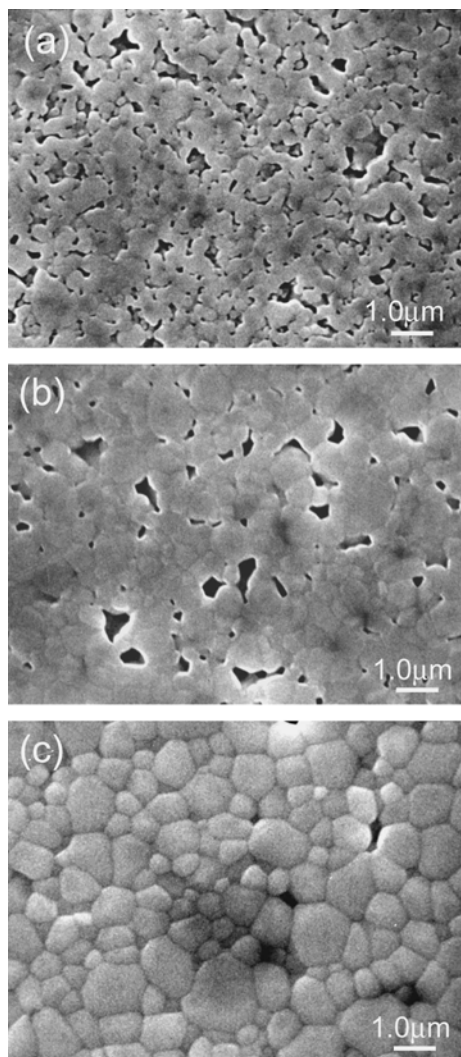


Fig. 8. SEM micrographs of the samples sintered at (a) 1400°C, (b) 1500°C, and (c) 1600°C.

precipitation of impurity phases at grain boundaries. Ikesue and coworkers [6, 18] reported that a full density and transparency could be achieved by adding SiO_2 (320 ppm Si) and vacuum sintering at 1750°C. In the present study, the Si content detected by ICP was only 131 ppm. Therefore, any notable improvement in the sintered densities was not obtained due to the insufficient amount of SiO_2 . The ICP analysis revealed that the milled powder contained 652 ppm Zr as a major impurity. It was confirmed that the ZrO_2 had been incorporated from the ZrO_2 balls used in the milling process. In addition, the powder, which had not been attrition-milled, with the same SiO_2 content could be densified to 97% at 1600°C. This implies that ZrO_2 retards the densification of YAG and suppresses the effect of the sintering aid present in the powder.

However, despite the presence of ZrO_2 , the powder prepared by the citrate gel method showed better sinterability than the powders prepared by other chemical methods. The powder obtained from nitrates exhibited a relative density of 89% at 1600°C and an appreciable

densification above 1500°C [8]. The powder synthesized from nitrates also revealed a relative density of 63% at 1500°C in air and 81.2% at 1500°C in vacuum [19]. The powder obtained by a sol-gel process showed a relative density of 95% at 1650°C and a considerable densification above 1500°C [14].

Figure 8 shows microstructure of the sintered samples. In Fig. 8(a), necks formed between particles and open pores indicate that the densification at 1400°C is in an initial stage. Although grain boundaries were barely seen in Fig. 8(b), grains grew by coalescence of the particles and large pores observed at 1400°C still persisted at 1500°C. At 1600°C, the grains grew to $\sim 1.5 \mu\text{m}$ size and most of the small pores present at 1500°C disappeared, as shown in Fig. 8(c). The grain sizes at 1600°C seemed to be smaller than those reported for the powders without impurities, probably due to the presence of ZrO_2 [13, 14]. It is expected that a higher density and better microstructure can be achieved if the incorporation of impurities such as ZrO_2 can be avoided in the milling process and a proper amount of SiO_2 is added to the powder.

Conclusions

YAG powder was synthesized by a citrate gel method using Al and Y nitrates and citric acid. The TG/DTA and X-ray diffraction analysis showed that the amorphous citrate gel almost decomposed at $\sim 600^\circ\text{C}$ and began to crystallize into YAG at 800°C. Upon crystallization of YAG, a very small amount of an intermediate YAH phase formed and disappeared after prolonged heating (≥ 2 h) or at higher temperatures ($\geq 1000^\circ\text{C}$). Well-crystallized, phase-pure YAG powder could be obtained after calcination at 900°C for 6 h.

Attrition milling of the calcined powder for 2 h produced fine YAG powder having an average particle size of $0.55 \mu\text{m}$. However, during the milling, ZrO_2 (652 ppm Zr) was introduced into the powder and found to retard the densification of YAG and suppress the effect of SiO_2 (131 ppm Si) as a sintering aid. Despite the presence of ZrO_2 , the powder showed good sinterability. Sintering the powder compacts for 6 h in air exhibited a considerable densification at temperatures above 1400°C, resulting in a relative density of 95.2% at 1600°C.

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