Journal of Ceramic Processing Research. Vol. 9, No. 2, pp. 111~117 (2008)

JOURNAL OF
Ceramic Processing Research

Synthesis and sintering of YAG powder by a mechanochemical solid reaction of yttria with two types of Aluminum source

Hyun-Gi Jung, Seok-Jun Hong, Gil-Ho Hwang, Won-Kyu Han and Sung-Goon Kang*

Division of Advanced Materials Science and Engineering, Hanyang University, Seoul 133-791, South Korea

YAG (yttrium aluminum garnet, $Y_3Al_5O_{12}$) powders were synthesized by a mechanochemical solid reaction of Y_2O_3 with AlOOH and γ-Al_2O_3. Phase development of the resultant YAG samples during grinding and calcination was compared between two types of aluminum source. The reaction of Y_2O_3 with AlOOH was activated by mechanical energy and the use of fine powder instead of heat energy, leading to the direct formation of YAG without second phases such as YAP (yttrium aluminum perovskite, $YAlO_3$) and YAM (yttrium aluminum monoclinic, $Y_4Al_2O_9$) with calcination at 800°C. However, the sample containing g-Al_2O_3 and Y_2O_3 yielded YAP along with YAM after calcination at 900°C because g-Al_2O_3 transformed into α-Al_2O_3, which made it difficult to diffuse Al^{3+} into Y_2O_3 lattice, and then by increasing temperatures to 1300°C, a well-crystallized phase of pure YAG was obtained. YAG powders showed good sinterability, although the samples were hardly agglomerated after grinding. After the same calcination of two samples at 1000°C, YAG samples containing the AlOOH and γ-Al_2O_3 were densified to ~96.7 and ~92.9% of the theoretical density, respectively, by sintering at 1600°C for 4 h under atmospheric conditions. It is concluded that the use of a fine, type of starting materials and grinding time are believed to be important factors in the mechanochemical synthesis of YAG.

Key words: YAG, Synthesis, Phase formation, Transition alumina, Sintering

Introduction

Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) is attractive in many areas due to its superior creep resistance, excellent thermal stability, corrosion resistance and interesting optical properties. Due to its homogeneous optical properties and lack of birefringence effects, Nd-, Er-, and Ho-doped single crystal YAG are widely used as solid-state laser gain host materials and luminescence materials [1-4]. In the meantime, research studies on polycrystalline YAG have been reported over the past 20 years. Polycrystalline YAG has many potential applications, such as thermal barrier coatings and high-temperature structural materials [5-7]. As part of a U.S. Air Force initiative to develop high-temperature materials for use in future turbine engines, YAG was identified as a potential candidate for an oxide-oxide composite matrix as well as a reinforcement fiber. However, owing to low reactivity between Y_2O_3 and Al_2O_3, the fabrication of polycrystalline YAG by a solid-state reaction requires high sintering temperatures above 1600°C. Heat treatment of mixed oxide powders at temperatures below 1600°C yields intermediate phases, such as YAM (yttrium aluminum monoclinic, $Y_4Al_2O_9$), YAP (yttrium aluminum perovskite, $YAlO_3$), and Al_2O_3 coexisting with YAG [1, 8]. The use of fine and reactive YAG powder with improved sinterability is essential in obtaining YAG ceramics with a full density and transparency at low temperatures [8, 9]. In order to synthesize such powders, various chemical methods have been investigated including co-precipitation [10-11], sol-gel process [12], hydrothermal synthesis [13], spray pyrolysis [14], and a urea method [15]. These methods have reduced the formation temperature of the YAG phase to 900-1200°C. However, the chemical processes have some intrinsic disadvantages against the conventional solid-state reaction. For example, co-precipitation usually uses chloride or nitrate salts. The presence of anions can damage the properties of the synthesized powders and the final products. It is necessary to use a water or ethanol for removing there ions. This makes it difficult to control the stoichiometric composition of the designed compound [16].

Mechanochemical processing or high-energy ball milling was originally developed for the production of alloys and intermetallic compounds in 1966 [17]. The major advantage of this method is that the process is activated by mechanical energy rather than heat energy at elevated temperatures.

Recently, a mechanochemical synthesis that produces reactive and fine YAG powders by grinding the constituent oxides has been used as an alternative to chemical methods [16,18]. Literature concerning the synthesis of YAG powder shows that the mechanochemical reaction depends on the starting materials. Zang and Saito [18], who used Y_2O_3, α-Al_2O_3, $Al(OH)_3$, and AlOOH powders, reported no mechanochemical reaction between Y_2O_3 and á-Al_2O_3 or $Al(OH)_3$. Kong et al. [16] claimed to produce pure YAG powder from

*Corresponding author:
Tel : +82 2 2220 0404
Fax: +82 2 2296 4560
E-mail: sgkang@hanyang.ac.kr

commercially available Y_2O_3 and Al_2O_3 by grinding and calcination at 1000°C and attributed the formation of the YAG phase to reduced particles size resulting from grinding. According to a previous study [24], the phase development of YAG by a solid state reaction is very complex. Several reactions occur at the same time including: the grain growth of Al_2O_3 and Y_2O_3, the diffusion of Al^{3+} into the Y_2O_3 lattice and the phase formation reaction of YAM YAP YAG.

In this study, the characteristics of Y_2O_3 with AlOOH and g-Al_2O_3 during grinding, calcination, and sintering were investigated to obtain further information on the synthesis of YAG ceramics and their applications.

Experimental

Materials

Y_2O_3, AlOOH and γ-Al_2O_3 were used as starting materials. Y_2O_3 was prepared by precipitation of 99.9% yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$). As a precipitant, ammonia water (2M, reagent grade) and ammonia sulfate were used. During the precipitation process, the reaction system was kept at a temperature lower than 5°C and the final pH value of the solution was 8.1. Then, the precipitate slurry was aged for 3 h with mild agitation by a magnetic stirrer. The precipitated slurry was filtrated and washed with deionized water and anhydrous ethyl alcohol to remove the NH_4NO_3 and prevent agglomerations. The precipitate was dried at 80°C for 24 h, and then was calcined at 600°C in an air atmosphere for 4 h to obtain nanocrystalline Y_2O_3 powder [9]. AlOOH was prepared by heating $Al(OH)_3$ (Gibbsite, Aldrich) powder at a rate of 5 K minute^{-1} to 400°C and held for 2 h [18-21].

Powder synthesis and sintering

Y_2O_3 with AlOOH and γ-Al_2O_3 powder was mixed using a mortar and acetone at a 5 : 3 molar ratio of Al to Y, respectively. Then, the sample was dried at 80°C for 8 h. The milling process was carried out using a Spex 8000-D mixer mill consisting of a zirconia vial (50 ml) and balls (10 mm in diameter, 3 EA) in air at room temperature for up to 24 h. To investigate the phase development, the samples ground for 12 h were calcined at temperatures between 600°C and 1300°C for 2 h. After synthesis of the YAG powders, 4 mm thick pellets were formed under a pressure of 200 MPa with a 11 mm diameter mold using powders calcined at 1000°C for 2 h. Then, the pellets were sintered at 1300-1700°C for 4 h under atmospheric conditions in a furnace with a super kanthal heating element.

Characterization

Phase identification in the powders which were ground and calcined was investigated with X-ray powder diffractometry (CuKα radiation, 40 kV, 100 mA, Rigaku). The specific surface area of the ground powder was measured using a nitrogen gas adsorption instrument (Micrometrics) based on the Brunauer-Emmett-Teller (BET) method. The particle size and morphology of the ground powder were examined with a field emission scanning electron microscope (FE-SEM, Hitachi, S-4700). Densities of the sintered samples were measured by the Archimedes method, which used water as the immersion medium. The sintered samples were polished, and thermally etched at a temperature 150°C below the sintering temperatures. Microstructures of the samples were also observed using FE-SEM.

Results and Discussion

Phase identification and powder morphology during grinding process

Fig. 1 shows the X-ray diffraction patterns of the samples ground for different intervals of time. As the grinding time increased, Bragg peaks of Y_2O_3 crystals gradually disappear and a nearly amorphous phase comes

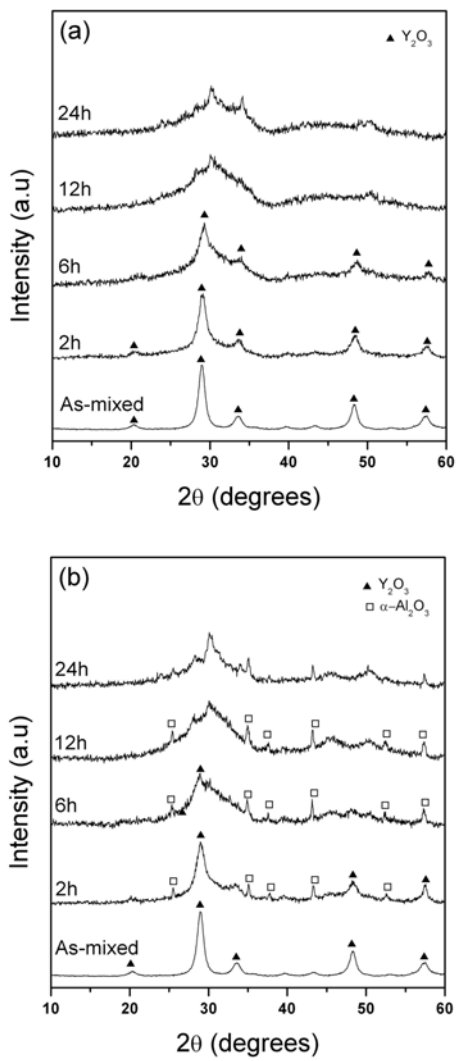

Fig. 1. XRD patterns as a function of grinding time for the samples of synthetic Y_2O_3 with: (a) AlOOH, and (b) γ-Al_2O_3.

to be observed in 12 h. The stability of the crystal structure of the materials against grinding depends on their inherent nature as well as the grinding conditions. Some materials, called soft materials, tend to transform easily into an amorphous states with grinding where as others called hard materials, tend to remain in a crystalline state [18]. In Fig 1(a), Y_2O_3 produced by precipitation and AlOOH is considered as a soft material. Therefore, it was easy to transform into an amorphous state. Unlike a previous study using reagent grade Y_2O_3 and AlOOH [18], which yielded YAP and YAG after grinding for 12 h, an intermediate or YAG (JCPDS #33-0040) phase was not observed in this study up to 24 h. γ-Al_2O_3 in the sample containing Y_2O_3 and γ-Al_2O_3 was converted into α-Al_2O_3 (JCPDS # 46-1212) after grinding for 2 h. γ-Al_2O_3 is produced by the dehydration of AlOOH, which is transformed by thermal energy through a series of metastable transition alumina phases including γ-, δ-, θ-Al_2O_3 and finally forming thermodynamically stable α-Al_2O_3 (corundum). The transformation from θ- to α-Al_2O_3 requires a reconstruction of the structure, involving a change in the oxygen sublattice from cubic to hexagonal and occurs with a large energy difference [19-22]. In this case, the mechanochemical reaction instead of thermal energy resulted in the complete transformation of γ-Al_2O_3 into α-Al_2O_3 during grinding of the powder mixture.

Fig. 2 shows SEM micrographs for the samples of as-mixed and ground for 12 h. The samples before grinding, as shown in Figs. 2(a) and (c), are agglomerated by weak surface forces such as electrostatic, Van der Waals or capillary forces; which can be easily separated. After grinding for 12 h, the sample containing AlOOH and γ-Al_2O_3 became barely agglomerated and consisted of primary particles with sizes of 50 and 200 nm approximately, respectively, as shown in Fig. 2(b), and 2(d). As above, the weak and hard agglomeration can be explained by specific surface areas values, as follows.

Fig. 3 shows specific surface areas for the samples. The as-mixed samples containing AlOOH and γ-Al_2O_3 had specific surface areas of 98.2 and 92.4 m^2/g, respectively, mainly due to the large surface areas of the synthetic Y_2O_3, AlOOH and γ-Al_2O_3 powders. As grinding time increased, the specific surface areas of samples

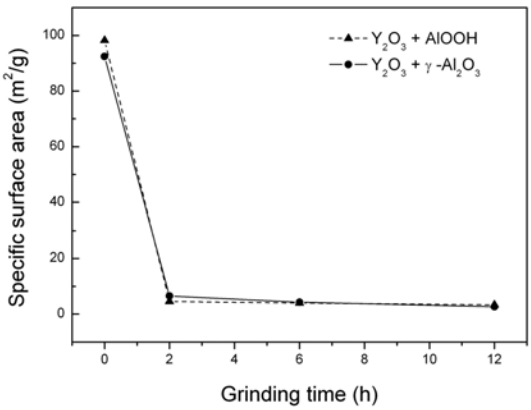

Fig. 3. Specific surface areas of the samples as a function of grinding time.

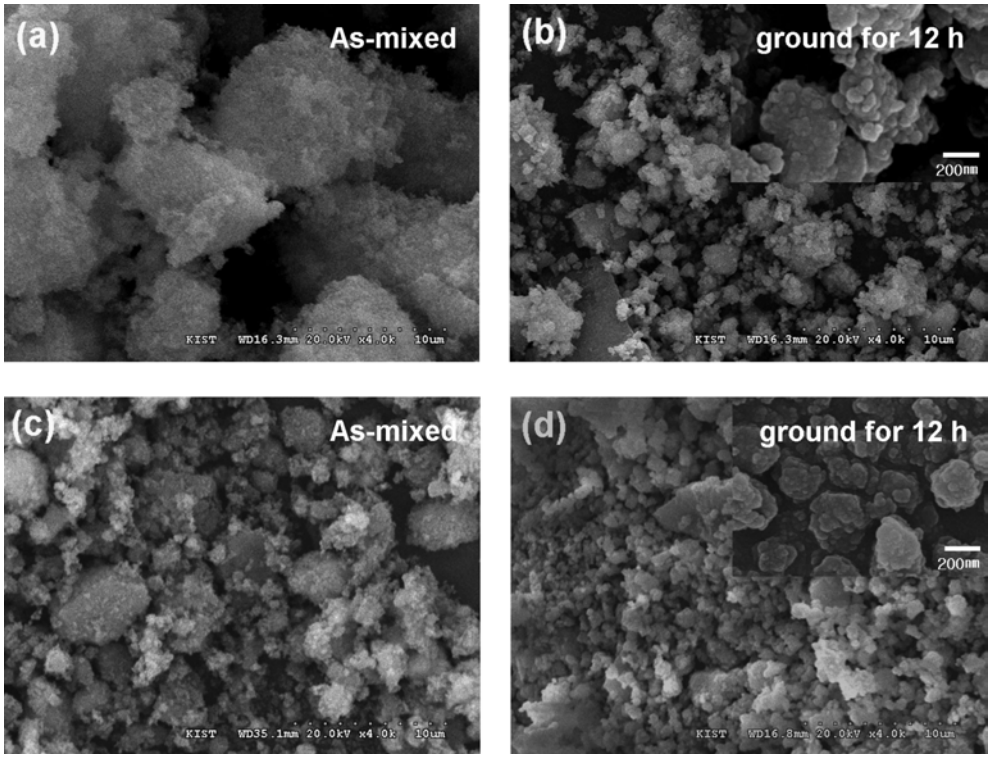

Fig. 2. SEM micrographs for the samples of synthetic Y_2O_3 ; (a) as-mixed with AlOOH, (b) ground with AlOOH for 12 h, (c) as-mixed with γ-Al_2O_3 and (d) ground with γ-$Al_2O_3$for 12 h γ-Al_2O_3.

containing AlOOH and γ-Al_2O_3 decreased rapidly, reaching a value of 3.3 and 2.7 m^2/g after a grinding time of 12 h, respectively, because samples are barely agglomerated by strong chemical bonds from a chemical reaction or diffusion. Agglomeration is generally observed in the dry grinding process, where particles are broken in a fine scale and held together by moisture present or Van der Waals attraction. In this case, it is considered that when the grinding time was increased the decrease of specific surface area values is due to aggregates from the mecanochemical reaction, which makes it difficult for the absorption of nitrogen gas onto the primary particles, resulted in low specific surface areas of samples.

Formation of YAG during calcining the ground powders

It is known that in a solid-state reaction between Y_2O_3 and Al_2O_3, an Al_2O_3-rich YAM phase first is formed and then transformed into YAP, which continues to react with Al_2O_3, producing YAG. A pure phase YAG can be obtained at higher temperatures above 1600°C in a conventional solid-state reaction for Y_2O_3 and Al_2O_3 binary systems. The reaction can also be accelerated if the particle size of the starting powders is reduced [23].

XRD patterns of the samples ground for 12 h and calcined at various temperatures for 2 h are shown in Fig. 4. In the case of the sample containing AlOOH, the YAG phase directly appeared with calcination at 600°C without intermediate phases, and a well-crystallized phase of YAG was easily obtained by calcining the ground sample at 800°C for 2 h. Ther realative intensity of YAG increased with an increasing the calcinations temperature. However, remarkable discrepancies concerning phase development were observed for the sample containing γ-Al_2O_3. In this sample, YAM ($Y_4Al_2O_9$, JCPDS # 34-0368) and YAP ($YAlO_3$, JCPDS # 33-0041) appeared along with small peaks from α-Al_2O_3 at 900°C. When the calcining temperature was increased to 1100°C, YAG ($Y_3Al_5O_{12}$) occurred coexisting with YAP. A pure YAG phase was obtained. When the calcining temperature was increased to 1300°C, which was nearly 500°C higher than the sample containing AlOOH. This phenomenon may be explained in two ways. In the first, the diffusion of Al^{3+} into Y_2O_3 lattice is difficult because a-Al_2O_3 converted from ã-Al_2O_3 during grinding is a stable phase. Also, the sample containing γ-Al_2O_3 has a lower reactivity for YAG formation compared to the AlOOH. Because it has larger primary particles after grinding, as shown in line high magnification images of Fig 2(b) and (d).

If α- or θ-Al_2O_3 is used as the aluminum source to synthesize YAG, the diffusion does not occur at low temperature. When the calcining is performed at higher temperatures, Y_2O_3 and α-Al_2O_3 exhibit a larger grain. This would induce a longer diffusion distance for the solid state reaction [24].

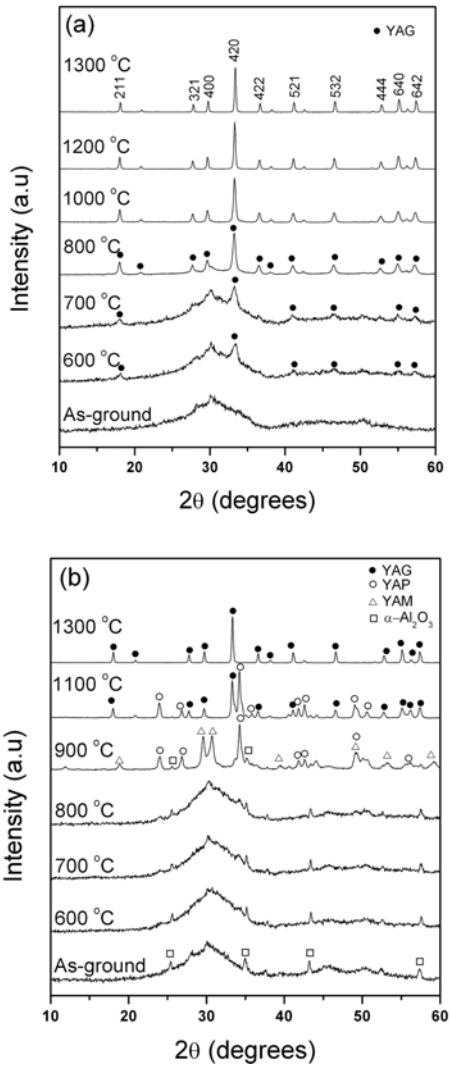

Fig. 4. XRD patterns of the samples ground for 12 h and calcined at various temperatures for 2 h of: (a) Y_2O_3 and AlOOH, (b) Y_2O_3 and γ-Al_2O_3..

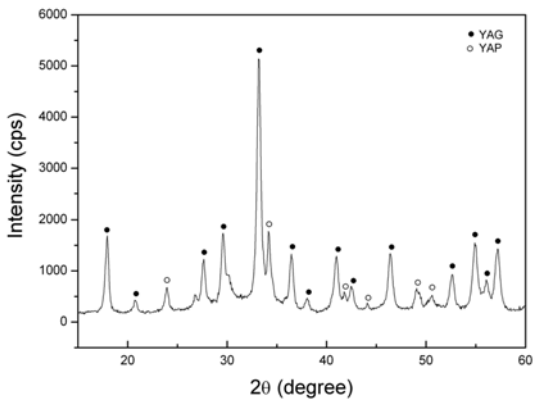

Fig. 5. XRD pattern for the sample of Y_2O_3 and AlOOH ground for 24 h and heated at 800°C for 2 h.

Both of the samples which increased internal energy and elastic distortion [24, 25] of Y_2O_3 by a mechanochemical reaction showed a faster reactivity than by a

conventional solid state reaction at lower temperature.

A long period of grinding time could not improve the reactivity for the phase formation of YAG. Fig. 5 shows the XRD pattern of the Y_2O_3 and AlOOH sample ground for 24 h and calcined at 800°C for 2 h.

While the sample ground for 12 h gave a pure YAG phase, an intermediate YAP phase existed in the sample ground for 24 h, which may be due to severe agglomeration of the sample, as shown in Fig. 6. From these results, it is concluded that the types and grinding time of starting materials are important factors in the mechanochemical synthesis of YAG.

Sintering behavior of YAG powders prepared by mechanochemical process

Fig. 7 shows the relative density of the compact samples sintered from 1300 to 1700°C for 4 h under air atmospheric conditions. The relative density of the YAG samples sintered at 1600°C was 96.7 and 92.9% of the theoretical density, respectively. Between 1550 and 1600°C, the samples showed maximum linear shrinkage rate.

The microstructures of the mirror-polished and thermally-etched samples sintered from 1300 to 1600°C are shown in Fig. 8-9. Both of the samples sintered at 1300°C exhibit a fine grain size distribution of ~200 nm,

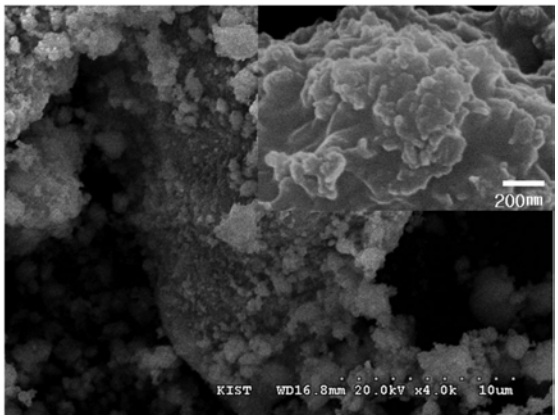

Fig. 6. SEM micrograph for the sample of Y_2O_3 and AlOOH ground for 24 h.

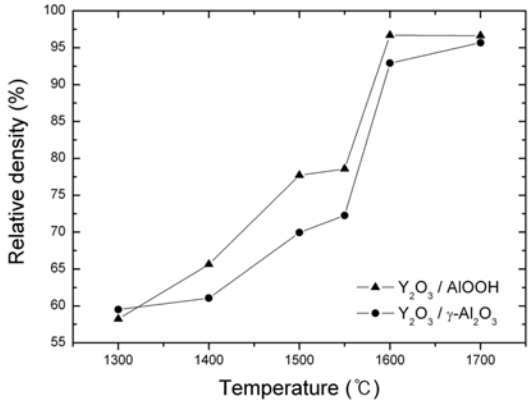

Fig. 7. Relative density of the samples sintered at various temperatures for 4 h.

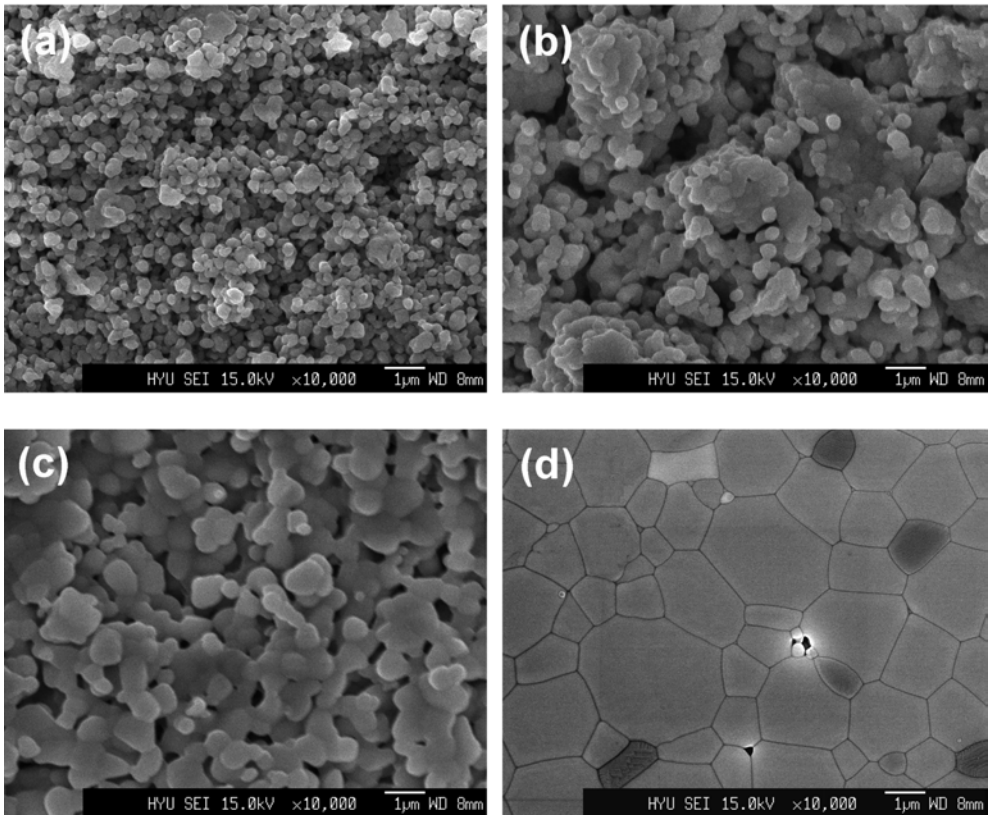

Fig. 8. SEM micrographs of Y_2O_3 and AlOOH samples sintered for 4 h at: (a) 1300°C, (b) 1400°C, (c) 1500°C, and (d) 1600°C.

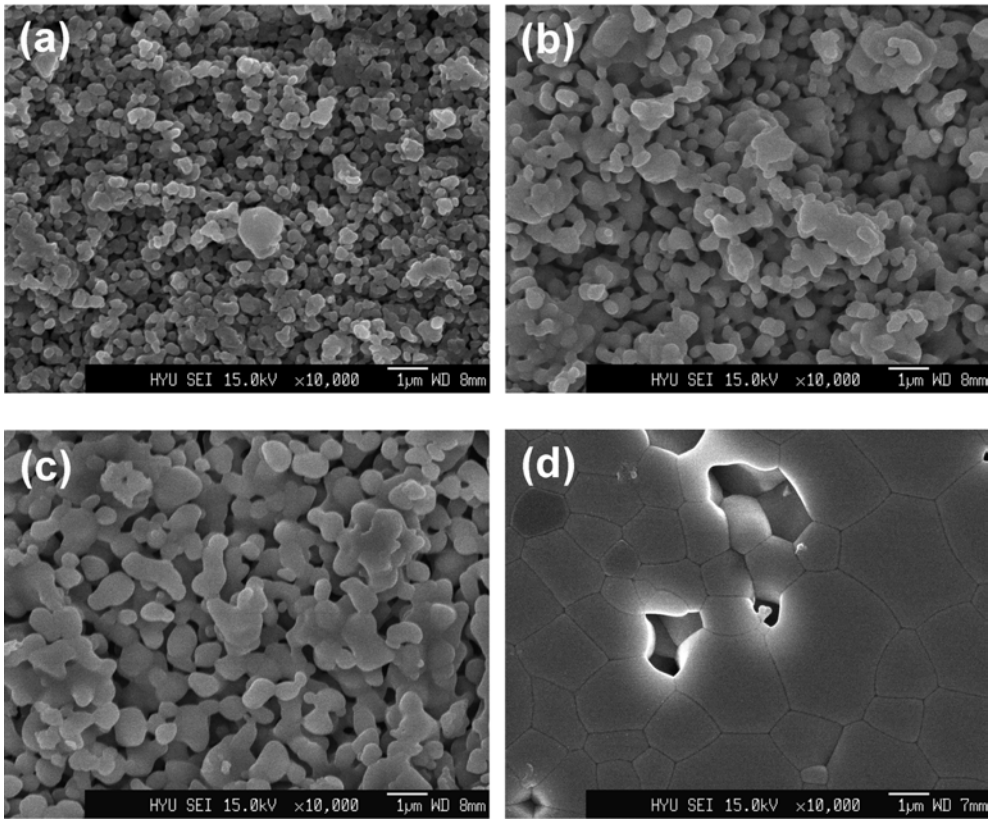

Fig. 9. SEM micrographs of Y_2O_3 and γ-Al_2O_3 samples sintered for 4 h at: (a) 1300°C, (b) 1400°C, (c) 1500°C, and (d) 1600°C.

as shown in Figs. 8(a) and 9(a). The samples containing AlOOH and γ-Al_2O_3 showed similar sintering behavior. As the sintering temperature was increased to 1400°C, the coalescence of particles occured, which formed networks. As the temperature rose to 1500°C, the samples completely transformed and underwent rapid grain coarsening with an increase in grain size at 1600°C. Rapid grain coarsening of the networked microstructure resulted in pore entrapment. The sample containing AlOOH showed a better microstructure than the sample containing γ-Al_2O_3 after sintering at 1600°C for 4 h.

Conclusions

YAG powders were produced via a mechanochemical solid reaction of synthetic Y_2O_3 and two types of aluminum source, AlOOH and γ-Al_2O_3, and their phase formation and sintering behavior were comprised.

The sample containing Y_2O_3 and AlOOH was converted into a nearly amorphous phase after grinding for 12 h. The γ-Al_2O_3 in the sample containing Y_2O_3 and γ-Al_2O_3 was transformed into α-Al_2O_3 by mechanical energy.

Calcining the ground sample containing AlOOH at 800°C directly converted Y_2O_3 and AlOOH into pure YAG phase, whereas the sample containing γ-Al_2O_3 transformed into a pure YAG at 1300°C, accompanied with intermediate phases such as YAP or YAM at lower temperatures. In the case of the sample containing γ-Al_2O_3, the lack of formation of YAG during calcinations is ascribed to lower ionic diffusivity, since γ-Al_2O_3 was transformed into a stable α-Al_2O_3 phase, which severe agglomeration after the grinding process.

The relative density of the samples containing AlOOH and γ-Al_2O_3 which were sintered at 1600°C was 96.7 and ~92.9% of the theoretical density, respectively.

As a result, it is concluded that, in the formation and sintering of YAG powders by the mechanochemical process, the use of a fine particle type of starting materials and grinding time are controlling requirements to achieve pure YAG at a low temperature and give a dense body.

Acknowledgement

This work was supported by the research fund of Hanyang University. (HY-2006-I)

References

1. K. M. Kinsman, and J. McKittrick, J. Am. Ceram. Soc. 77 (1994) 2866-72
2. T. Saiki, K. Imasaki, S. Motokoshi, C. Yamanaka, H. Fujita, M. Nakatsuka, and Y. Izawa, Opt. Commun. 268 (2006) 155-159
3. H. Yagi, J. F. Bisson, K. Ueda, and T. Yanagitani, J. Lumines. 121 (2006) 88-94
4. V. Babin, M. Kink, Y. Maksimov, K. Nejezchleb, M. Nikl,

and S. Zazubovich, J. Lumines. 122-123 (2007) 332-334
5. P. G. Klemens, and M. Gell, Mater. Sci. Eng. A, 245 (1998) 143-149
6. N. P. Padture, and P. G. Klemens, J. Am. Ceram. Soc. 80 (1997) 1018-20
7. T. I. Mah, T. A. Parthasarathy, and H. D. Lee, J. Ceram. Process. Res. 5 (2004) 369-379
8. A. Ikesue, and I. Furusato, J. Am. Ceram. Soc. 78 (1995) 225-28
9. L. Wen, X. Sun, Z. Xiu, S. Chen, and C. T. Tsai, J. Eur. Ceram. Soc. 24 (2004) 2681-2688.
10. J. G. Li, T. Ikegami, J. H. Lee, T. Mori, and Y. Yajima, J. Eur. Ceram. Soc. 20 (2000) 2395-2405
11. F. Yuan, and H. Ryu, Mater. Sci. Eng. B, 107 (2004) 14-18
12. H. M. Wang, M. C. Simmonds, and J. M. Rodenburg, Mater. Chem. Phys. 77 (2002)
13. Y. Hakuta, T. Haganuma, K. Sue, T. Adschiri, and K. Arai, Mater. Res. Bull. 38 (2003) 1257-1265
14. M. Nyman, J. Caruso, and M. J. Hampden-Smith, J. Am. Ceram. Soc. 80 (1997) 1231-38
15. N. Matsushita, N. Tsuchiya, and K. Nakatsuka, J. Am. Ceram. Soc. 82 (1999) 1997-84
16. L. B. Kong, J. Ma, and H. Huang, Mater. Lett. 56 (2002) 344-348
17. L. Lu, and M.O. Lai, Mechanical Alloying, 1998, P. 1, chapter 1.
18. Q. Zhang, and F. Saito, Powder Technol. 129 (2003) 86-91
19. P. Alphonse, and M. Courty, Thermochim. Acta, 425 (2005) 75-89
20. X. Bokhimi, J. A. Toledo-Antonio, M. L. Guzman-Castillo, B. Mar-Mar, F. Hernandez-Beltran, and J. Navarrete, J. Solid State Chem. 161 (2001) 319-326
21. T. Tsukada, H. Segawa, A. Yasumori, and K. Okada, J. Mater. Chem. 9 (1999) 549-553
22. W. C. Wei, and J. W. Halloran, J. Am. Ceram. Soc. 71 (1988) 166-72
23. A. Ikesue, T. Kinoshita, K. Kamata, and K. Yoshida, J. Am. Ceram. Soc. 78 (1995) 1033-40
24. M. S. Tsai, W. C. Fu, W. C. Wu, C. H. Chen, and C. H. Yang, J. Alloys compd. (2007);accepted
25. S. N. Patankar, D. Zhang, G. Adam, and F. H. (Sam) Froes, J. Alloys compd. 353 (2003) 307-309