

Synthesis of nanocrystalline yttria powder and fabrication of transparent YAG ceramics

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Abstract

Synthesis of nanocrystalline yttria powder from $Y(NO_3)_3$ solution and ammonia water was investigated. It was found that the precursor precipitate is $Y_2(OH)_5(NO_3) \cdot H_2O$. The addition of small amount of ammonia sulfate in yttrium nitrate solution can reduce the agglomeration and particle size of the produced yttria powders. Nanocrystalline yttria powder (60 nm in average size) was obtained by calcining the precursor at 1100 °C for 4 h. Using this yttria powder and a commercial ultrafine Al_2O_3 powder, fully transparent YAG ceramics was fabricated by vacuum sintering at 1700 °C for 4 h through a solid-state reaction method. It was found that the addition of 0.5 wt.% tetraethyl orthosilicate (TEOS) is suitable for the fabrication of transparent YAG ceramics. If the amount of TEOS is less than 0.05 wt.%, abnormal grain growth occurs, and pores are entrapped in the grains. If the amount of TEOS is more than 3 wt.%, large amount of liquid phase is yielded, leaving some residual inclusions at grain boundaries. These are detrimental for the transparency of YAG ceramics.

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1. Introduction

Crystalline yttrium aluminum garnet ($Y_3Al_5O_{12}$) exists in the cubic form and has a garnet structure.¹ YAG is not only a very important laser material, but also a high-temperature structural material and a fluorescence material, and Nd-doped YAG single crystal has been the most widely used solid-state laser material.^{2,3} YAG single crystals are normally synthesized by the Czochralski method. However, YAG single crystals are very expensive, and it is difficult to produce large size YAG single crystals. In recent years, a lot of efforts have been made for synthesizing transparent polycrystalline YAG ceramics.^{3–5} Transparent polycrystalline YAG ceramics have the advantages of low price, ease of manufacture and mass-production, the possibility of making large sized crystals, and the possibility of the incorporation of Q-switching and Raman shifting within the source. The synthesis of highly transparent YAG ceramics is technically quite difficult since the

application of optical materials in a solid-state laser must face extremely severe conditions.

Translucent YAG specimens have been fabricated via vacuum sintering at 1850 °C for 4 h using YAG powders synthesized by a sulfate co-pyrolysis method.⁴ Li et al. produced YAG powders from carbonate precursors synthesized via co-precipitation using ammonium hydrogen carbonate as the precipitant.^{5–7} The YAG powder can be densified to translucency without sintering aids by vacuum sintering at 1700 °C for 1 h. The first Nd: YAG ceramic laser was developed by Ikesue and colleagues at Japan's Krosaki Corporation in 1995. The transparent YAG ceramics maintained high efficiency conversion and good optical characteristics, and it was equivalent or superior to a 0.9 at.%Nd: YAG single crystal.^{8–13}

Fabrication of fully transparent YAG ceramics using solid-reaction method needs highly sinterable Y_2O_3 and Al_2O_3 powders. As reported by Ikesue et al.,³ Y_2O_3 and Al_2O_3 was synthesized by the pyrolysis of $Y_2OHCl_5 \cdot nH_2O$ and $Al(OH)_3$, respectively. Ikegami et al. synthesized thin flakes of yttrium hydroxide that has a cardhouse structure. When calcined at 1100 °C for 4 h,

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highly sinterable yttria powder was obtained, and the powder can be sintered to transparency under vacuum.¹⁴

The present work attempts to produce highly sinterable nanometric yttria powder using a wet chemical method. Then using the nano yttria powder and a commercial ultrafine Al_2O_3 powder as starting materials, fabrication of transparent YAG ceramics by a solid-state reaction method was investigated systematically.

2. Experimental

2.1. Synthesis of ultrafine Y_2O_3 powder

Yttria powder (99.99%, Changchun, China) was dissolved in a high-purity nitric acid, and then was diluted with deionized water to the concentration of 0.26 M. To investigate the effect of ammonia sulfate, for some specimens, 0.9 g ammonia sulfate was added to a 500 ml yttrium nitrate solution. 2 M ammonia water (reagent grade) was used as the precipitant solution. The precursor precipitate was synthesized by dripping the ammonia water to the mother salt solution at a speed of 3 ml/min. The reaction system was kept at a temperature lower than 4 °C. The final pH value of the solution was 7.9. Then, the precipitate slurry was aged for 3 h with mild agitation by a magnetic stirrer. The precipitate slurry was filtrated and washed with deionized water for four times to remove the NH_4NO_3 by-products. After washing, the precipitate slurry was dried at 60 °C for 24 h. After drying, the precipitate was ground using an alumina mortar and pestle, and then was calcined at selected temperatures in a flowing oxygen atmosphere to obtain nanocrystalline yttria powder.

2.2. Synthesis of ultrafine YAG powder

The alumina powder (Taimicron TM-D, Taimei Chemical Co. Ltd.) used is 220 nm in average particle diameter and 99.99% in purity. For the fabrication of YAG ceramics, the ultrafine yttria powder and alumina powder were weighted accurately in order to ensure a Y:Al ratio of 3:5. Tetraethyl orthosilicate (TEOS) was added as the sintering aid (0.5 wt.% in ethyl alcohol). The procedure for the synthesis of ultrafine YAG powder is as follows:

Weighing and mixing of starting materials → ball milling → drying → high temperature (1200 °C) calcinations → addition of sintering aid TEOS → ball milling → drying → low temperature (800 °C) calcination in flowing oxygen.

The first ball milling aims at mixing the Y_2O_3 and Al_2O_3 starting materials. The powder mixture was

milled in a 95% ethanol for 24 h with high purity zirconia balls. The second ball milling attempts to crash the agglomerates formed during the high temperature calcination and to hydrolyze the TEOS with the water contained in the ethanol to yield SiO_2 . High temperature calcination is a key step in the experiment. If the starting powders are not calcined at high temperature to yield YAG phase, there will be many inclusions in the sintered body. The purpose of calcination in flowing oxygen is to burn out the residue organic materials in the powder.

2.3. Compaction and sintering of the YAG powder

After synthesis of the YAG powder, 3 mm thick pellets were formed under a pressure of 200 MPa with a 13 mm diameter mold. Then the pellets were sintered at 1700 °C for 5 h under vacuum of 1.3×10^{-3} Pa in a furnace with molybdenum heating element (VSF-7, Shenyang, China).

2.4. Characterizations

Phase identification was performed via X-ray diffractometry (XRD) (model D/MAX-RB, Japan), using nickel-filtered CuK_α radiation and a scanning speed of $2\theta = 8^\circ$ per minute. A transmission electron microscope (TEM, Philips EM420) was used to observe the morphologies of the precursor precipitate and the Y_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ powders. Densities of the sintered specimens were measured by the Archimedes method, which used water as the immersion medium. The sintered specimens were thermally etched at 1500 °C for 2 h in air. Microstructures of the polished surface of the specimens were observed using electron probe micro-analysis (EPMA) and scanning electron microscopy (SEM, EPM-810Q). Fracture surfaces of the specimens were also observed using SEM.

Specimens for transmittance measurement were cut into 1.5-mm thick slices and both surfaces were mirror-polished using 0.5 μm diamond slurries. Transmittance of the transparent YAG ceramics was measured over the wavelength region from 200 to 1200 nm using a spectrometer with an aperture of 8.5 mm (DMR-22, Germany).

3. Results and discussions

3.1. Effect of ammonia sulfate on morphology of the yttria powders

TEM observation indicates that the precursor precipitate has a thin flake structure in a manner similar to a house of cards (Fig. 1). The addition of ammonia sulfate has no effect on the morphology of the precursor precipitate.

If ammonia water is added to a rare earth salt solution, rare earth hydroxide precipitates will be produced, and the ratio of $\text{OH}^-/\text{Ln}^{3+}$ changes from 2.5 to 3.0 depending on the cations. Thus, the composition of the precursor is most likely to be $\text{Y}_2(\text{OH})_5(\text{NO}_3)\cdot\text{H}_2\text{O}$, as proved by the XRD analysis (Fig. 2). After calcining at temperatures $\geq 700^\circ\text{C}$ for 2 h, the precursor transforms to yttria phase (Fig. 2).

Fig. 3 shows the morphology of the Y_2O_3 powders after calcining at 1100°C for 4 h. It can be seen that the

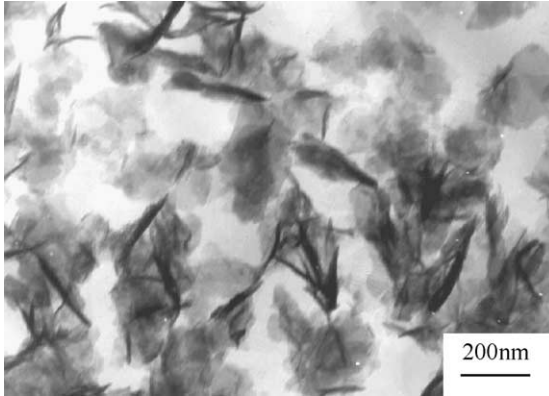


Fig. 1. TEM morphology of the precursor precipitate.

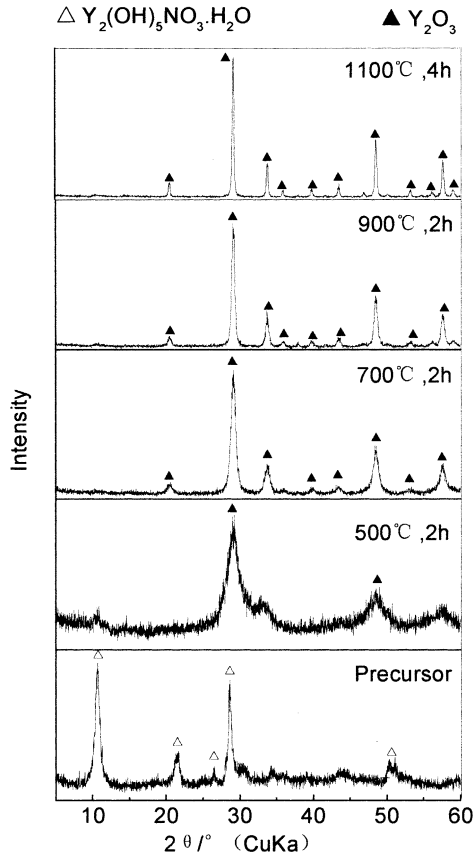


Fig. 2. XRD spectra of the precursor and the calcined powders.

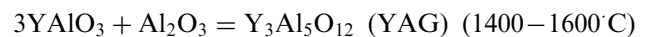
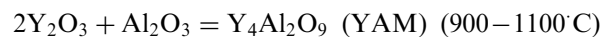
Y_2O_3 powder without the doping of ammonia sulfate is agglomerated and has a larger particle size (about 200 nm). On the other hand, the sulfate-doped yttria powder is well dispersed and has a smaller particle diameter (about 60 nm). $\text{Y}_2(\text{OH})_5(\text{NO}_3)\cdot\text{H}_2\text{O}$ has a positive ζ potential in aqueous solution.¹⁵ SO_4^{2-} can adsorb onto the $\text{Y}_2(\text{OH})_5(\text{NO}_3)\cdot\text{H}_2\text{O}$ particles due to the electrostatic force. The SO_4^{2-} has a higher decomposition temperature than hydroxides, and its existence at comparatively high temperature may reduce the element diffusion between particles, resulting in a smaller particle size. Its decomposition at high temperatures is also beneficial for the dispersion of powder.

The sulfate-doped yttria powder also has good sinterability, and it can be sintered to transparent body by vacuum sintering at 1700°C . Thus, this yttria powder was used as one of the starting materials for fabricating YAG.

3.2. Formation of YAG during heating the powder mixtures

Fig. 4 shows the morphology of the commercial Al_2O_3 powder used for making YAG ceramics. The primary particle diameter of the Al_2O_3 is about 220 nm.

Fig. 5 shows the XRD spectra of powder mixture heated at 1000, 1100, 1200, and 1300°C for 2 h. $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM) forms at 1000°C . At 1100°C hexagonal YAlO_3 (YAP) crystallizes, with small peaks of YAG. At 1300°C or beyond, YAG is the only phase detected. Conventionally, YAG powder processing involves extensive mixing and lengthy high temperature reaction between the starting powders. Early researchers found that the reaction sequence proceeds by a series of steps of reactions as follows:¹⁶



The reaction between alumina and yttria occurs by the diffusion of Al^{3+} into yttria. The first phase to be developed during heat treatment is the yttrium-rich YAM phase. This reaction begins at about 900°C . At about 1100°C , the Al^{3+} not only continues to react with the yttria, but also diffuses into YAM to form YAP phase. Finally, the alumina reacts with YAP at approximately 1400°C to yield YAG phase. A single YAG phase can only be achieved when the temperature is higher than 1600°C . Some researchers have reported that YAP and Al_2O_3 will remain unless the starting powders are heated at 1600°C for 20 h or heated to 1700°C .¹⁶ However, we found that the YAG formation temperature in the present work is much lower than the one in the conventional solid-state reaction method.

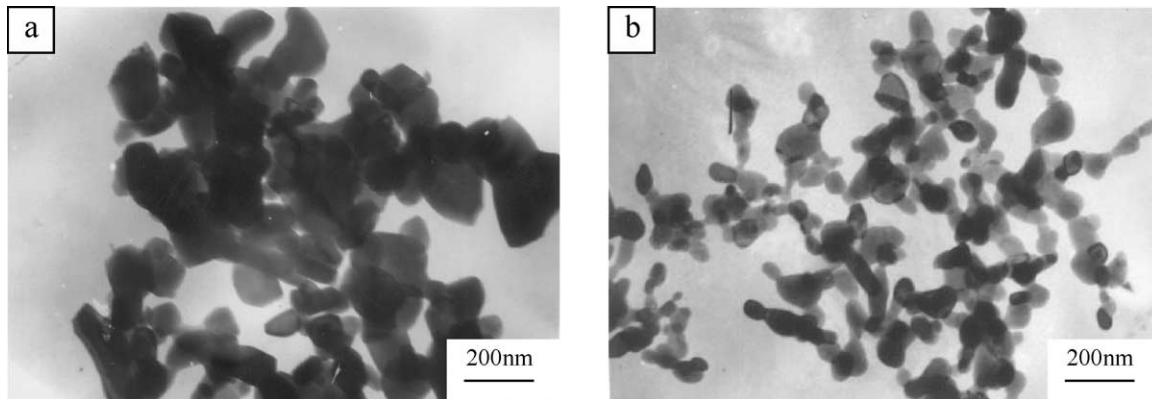


Fig. 3. TEM micrographs showing the morphology of the yttria powder (a) without the addition of SO_4^{2-} and (b) with the addition of SO_4^{2-} .

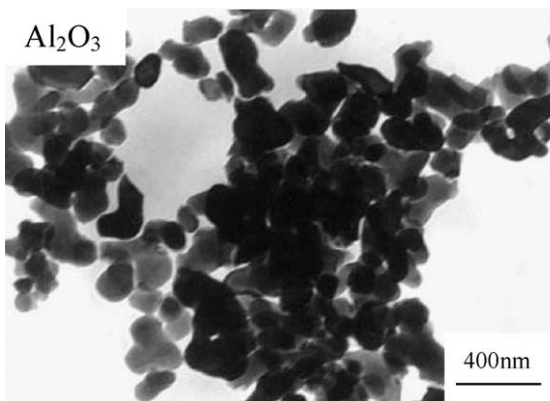


Fig. 4. Morphology of the Al_2O_3 powder (TEM).

Therefore, good mixing, well dispersion and high activity of the starting materials account for the low temperature formation of YAG.

3.3. Effect of TEOS doping on microstructures of the sintered YAG specimens

The TEOS additives can enhance the sintering of YAG ceramics, and is indispensable to obtain high quality transparent YAG ceramics. However, if the addition of TEOS is less than 0.05 wt.% or more than 3 wt.%, the sintered ceramics are opaque. Normally, when sintering oxide ceramics, if there is no sintering aid, translucent or transparent ceramics cannot be obtained. This is because abnormal grain growth always occurs at the final stage of sintering, resulting in a breakaway of grain boundary-pores. As demonstrated by the YAG ceramic with 0.05 wt.% TEOS, the pores were entrapped in the grains [as shown in Fig. 6(a)]. If this happens, the sintering process is nearly ceased in fact, since the lattice diffusion coefficient is much smaller

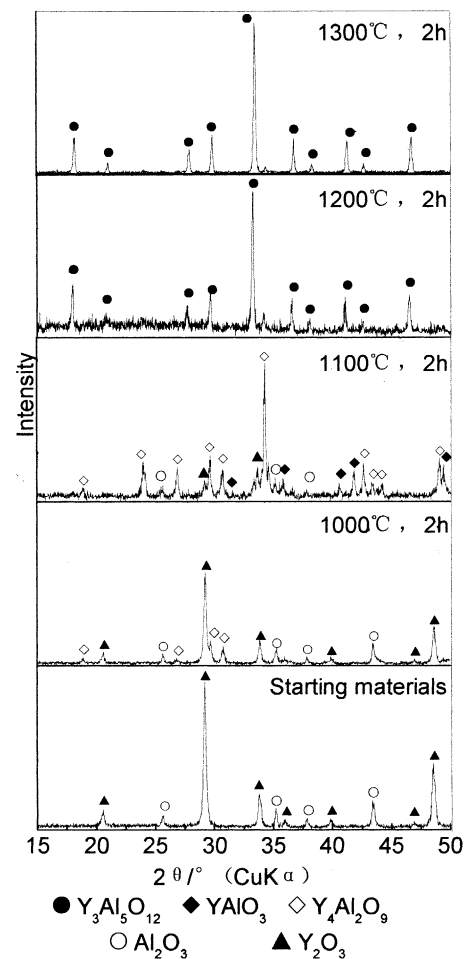


Fig. 5. X-ray diffraction profiles of the specimens heated at different temperatures.

than that of the grain-boundary. According to the Al_2O_3 – Y_2O_3 – SiO_2 phase diagram, SiO_2 can react with Y_2O_3 and Al_2O_3 to yield an intergranular liquid phase during the sintering of YAG. The second phase and

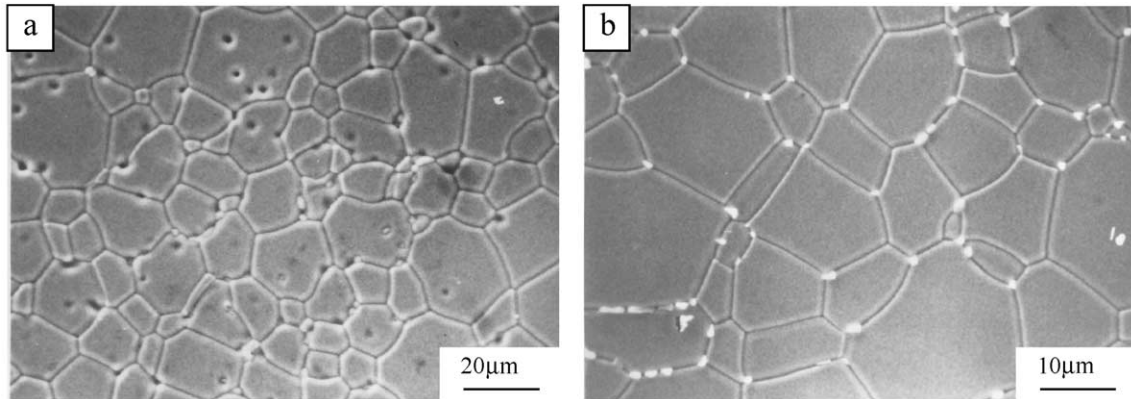


Fig. 6. SEM morphologies of the YAG ceramics with (a) 0.05 wt.% TEOS and (b) 3 wt.% TEOS as sintering aid.

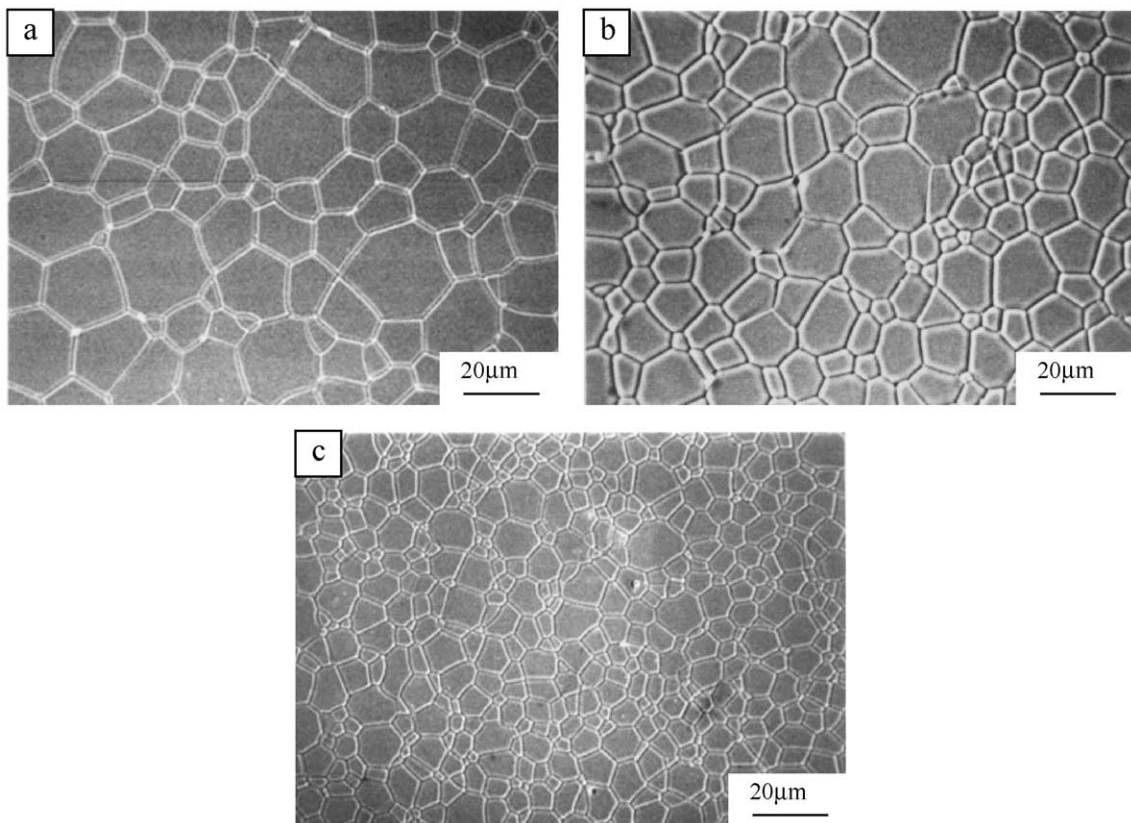


Fig. 7. Microstructure of the YAG ceramics with 0.5 wt.% TEOS (a) sintered at 1700 °C; (b) sintered at 1650 °C; (c) sintered at 1600 °C.

impurity (silicon) enhance the early stage of the sintering process. On the other hand, TEOS can act as grain growth inhibitor, avoiding the abnormal grain growth. As proved by the specimens with 0.5 wt.% TEOS, pores have been removed completely and the ceramics have uniform microstructures (as shown in Fig. 7), and a fully transparent YAG ceramic can be obtained. If the addition of TEOS is more than 3 wt.%, large amount of liquid phase will be yielded, leaving some residual inclusions at grain boundaries [as shown in Fig. 6(b)].

This is detrimental for the transparency of the YAG ceramics.

3.4. Effect of sintering temperature on microstructure and optical properties of YAG ceramics

Fig. 8 shows the relative density of the compact bodies sintered from 1300 to 1700 °C for 5 h under vacuum. The relative density of the YAG sintered at 1600 °C is 99.2%, and the specimen sintered at 1700 °C reaches

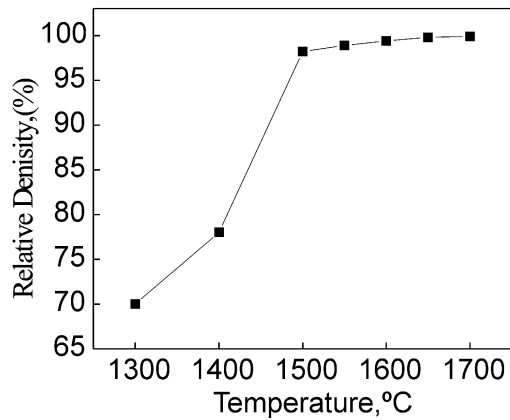


Fig. 8. Relationship between relative density and sintering temperature.

the theoretical value. Between 1400 and 1500 °C the specimen shows maximum linear shrinkage rate.

Fig. 9 shows the fracture surface of the sintered specimens. It can be seen that grain size increases with increasing temperature. Obvious grain growth occurs between 1500 and 1600 °C. A dense and nearly pore-free microstructure was observed at 1600 °C or above (Figs. 7 and 9).

Fig. 10 shows the line profile of YAG polycrystal obtained by EPMA. The Al, Y, and Si contents remain unchanged across the grain boundary, indicative of an even distribution of the elements.

Fig. 11 shows a photograph of the mirror-polished specimens sintered from 1600 to 1700 °C. Each pellet is

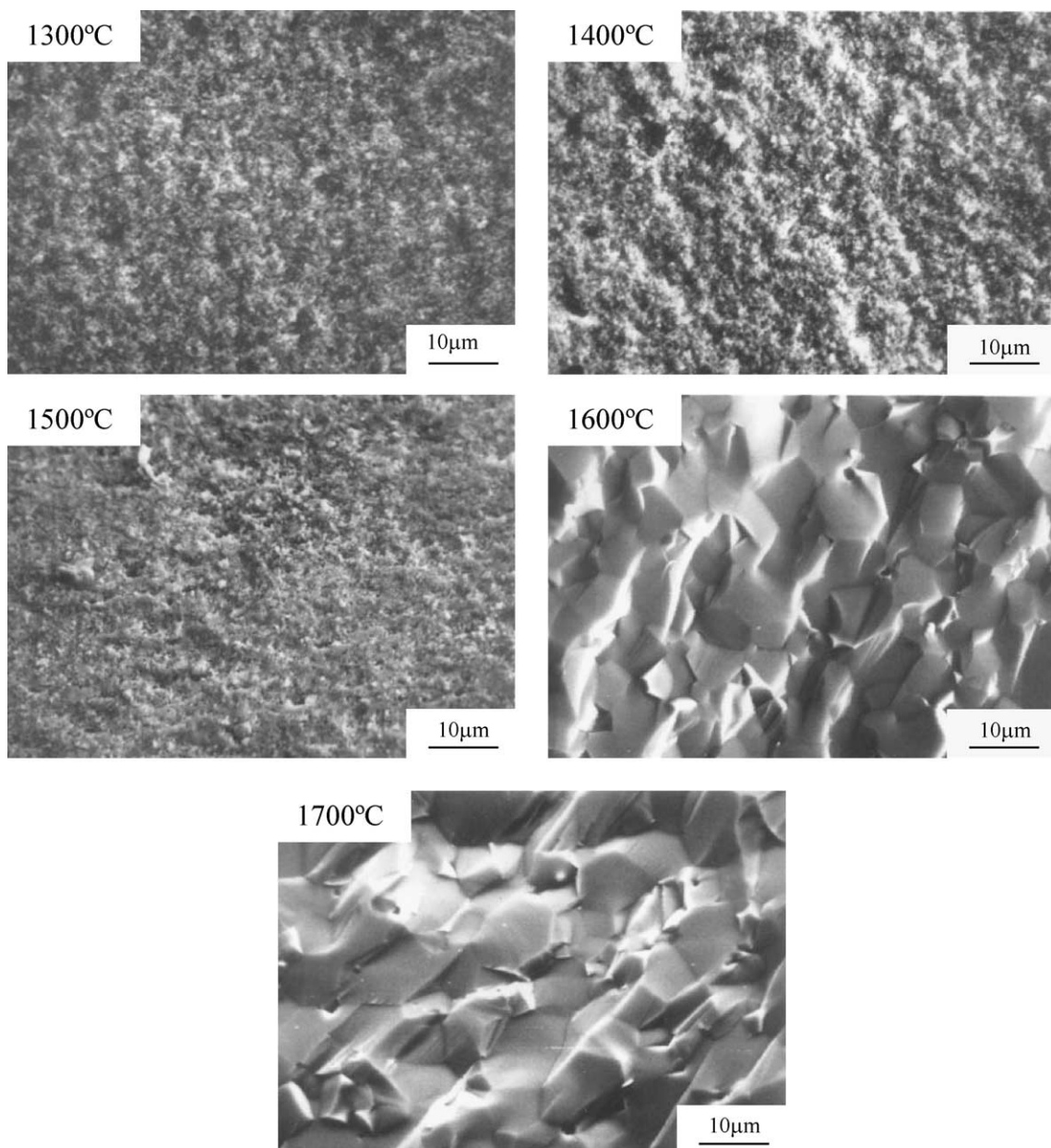


Fig. 9. Fracture surfaces of specimens sintered at various temperatures (SEM).

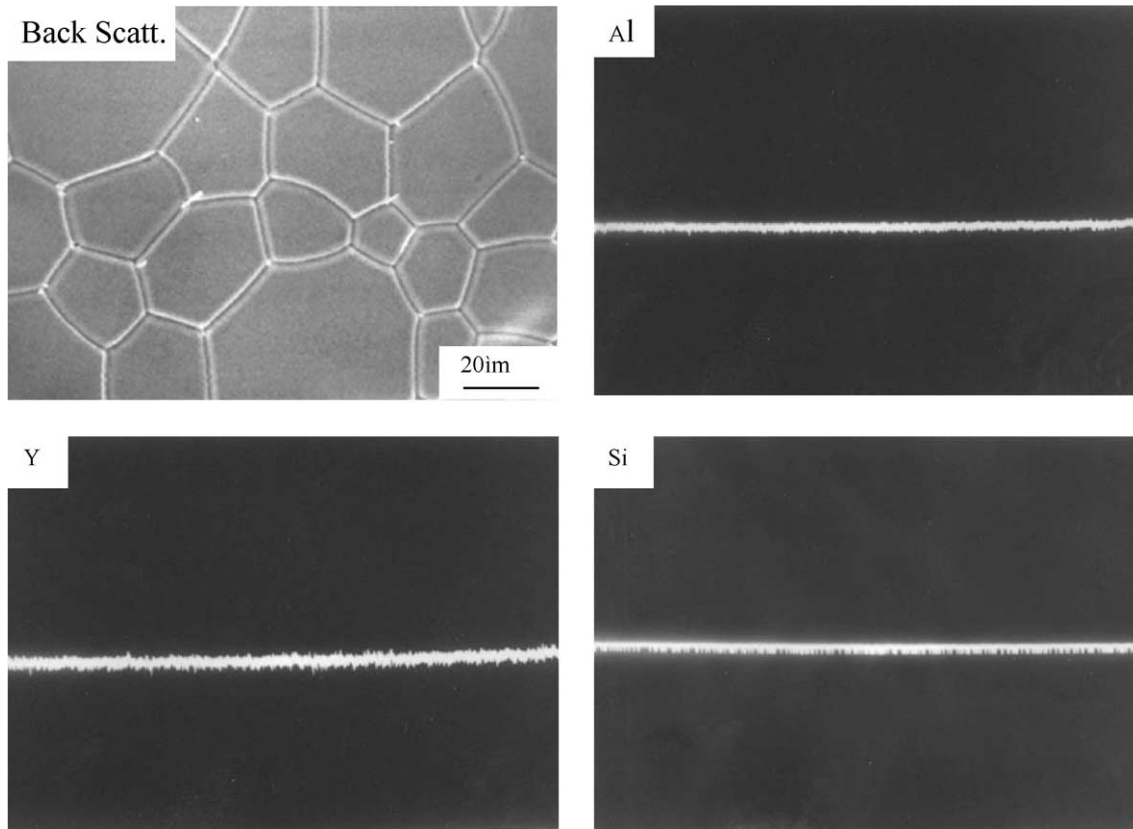


Fig. 10. Backscattered photographs with line profiles for Y, Al, and Si elements across grain boundaries (EPMA).



Fig. 11. Appearance of mirror-polished specimens sintered from 1600 to 1700 °C.

~10.5 mm in diameter and ~1.5 mm thick. The pellet sintered at 1700 °C exhibits the best transparency, whereas the one sintered at 1600 °C is somewhat cloudy in the center.

Light transmittance is the main parameter for evaluating the optical properties of transparent ceramics. Fig. 12 shows the in-line transmittance spectra in the wavelength ranging from 200 to 1200 nm for the specimens sintered at 1700 and 1600 °C for 5 h. The data of single-crystal and transparent YAG ceramics sintered by Ikesue et al.⁸ are also shown. The in-line transmittance increases with increasing wavelength. This can be attributed to the difference between single crystal and polycrystalline ceramics. There are some scattering centers in the ceramics. When the optical scattering center is significantly smaller than the wavelengths, the scattering intensity can be determined by Rayleigh's equation,¹⁷ i.e., the scattering intensity increases proportionally with λ^{-4} where λ is the wavelength. Thus, the scattering intensity increases with the decrease

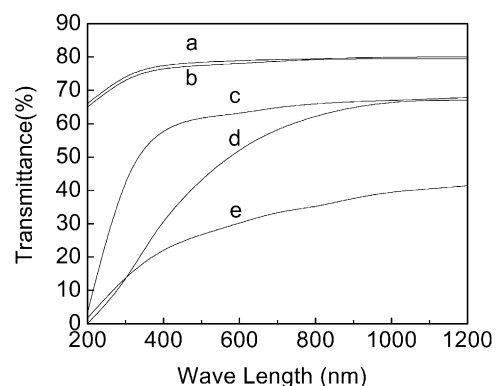


Fig. 12. Optical transmission spectra of YAG single crystal and some polycrystalline YAG ceramics (a) single crystal;⁸ (b) ceramics sintered at 1800 °C (1 mm thick)⁸ (c) ceramics sintered at 1700 °C (present work 1.5 mm thick); (d) ceramics sintered at 1700 °C (1 mm thick);⁸ (e) ceramics sintered at 1600 °C (present work 1.5 mm thick).

of wavelength.¹³ When the specimen is sintered at 1700 °C, optical transmittance is 63% in the visible light wavelengths, and reaches almost 70% in the infrared wavelengths. The transmittance is higher than the result of Ikesue et al. under the same sintering condition (as shown in Fig. 12), but lower than that of the ceramics sintered at 1800 °C. The transmittance increases with the increase of average grain size.⁸ If the average grain size exceeds 20 μm , the in-line transmittance will

become a constant. Thus, for the present fabrication process, if the sintering temperature is increased to 1800 °C, it may be possible to obtain a YAG ceramic with optical properties very close to those of a single crystal.

4. Conclusions

1. Nanocrystalline yttria powder with 60 nm in average primary particle size was synthesized from $Y(NO_3)_3$ solution and ammonia water. The precursor precipitate is $Y_2(OH)_5(NO_3) \cdot H_2O$. The addition of small amount of ammonia sulfate in yttrium nitrate solution can reduce the agglomeration and particle size of the produced nanocrystalline yttria powders.
2. The amount of TEOS is crucial for the transparency of YAG ceramics fabricated from the solid-state reaction method. If the amount of TEOS is less than 0.05 wt.%, abnormal grain growth occurs, and pores are entrapped in the grains. If the amount of TEOS is more than 3 wt.%, large amount of liquid phase is yielded, leaving some residual inclusions at grain boundaries. These are detrimental for the transparency of the YAG ceramics. It was found that the addition of 0.5 wt.% TEOS is suitable for the fabrication of transparent YAG ceramics.
3. Using the nanocrystalline yttria powder and a commercial Al_2O_3 ultrafine powder, fully transparent YAG ceramics was fabricated by vacuum sintering at 1700 °C for 4 h through solid-state reaction method. Optical transmittance of the YAG ceramic is 63% in the visible light wavelengths and 70% in the infrared wavelengths.

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