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Preparation of transparent yttrium aluminum garnet ceramics by relatively low temperature solid-state reaction①

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Abstract: A new preparation method for a highly sinterable Y_2O_3 powder was developed, using the mixture of the powder with Al_2O_3 powder, a transparent yttrium aluminum garnet(YAG) ceramic was prepared at relatively low temperature by a solid-state reaction method. Yttrium nitrate was used as a mother salt, and aqueous ammonia was used as a precipitant reagent, the fine and dendritic precursor crystalline was prepared by adding 0.5% ammonium sulfate into the precipitation reaction system. The highly pure and low-agglomerated Y_2O_3 powders were obtained by calcinating the precursor at 1 100 ℃, the primary particles are spherical and 60 nm in diameter. The mixture of Y_2O_3 and Al_2O_3 powders was calcinated, and the resulting mixture compact pressed in mold could be sintered to transparency under vacuum at 1 700 ℃. The sintered transparent YAG polycrystalline exhibits a homogeneous microstructure and its transmittance reaches 45% in the visible light region and 70% in the near-infrared wavelength region.

Key words: low temperature; yttria; sulfate ions; solid-state reaction; YAG; transparent ceramics

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1 INTRODUCTION

Yttrium aluminum garnet (YAG) is a kind of complex oxide resulted from the reaction of Y_2O_3 and Al_2O_3. Its chemical formula is $Y_3Al_5O_{12}$. It has a garnet crystal structure and belongs to hexagonal system. YAG ceramics hold promise for certain optical applications such as high temperature windows used to detect infrared waves or devices used to record nuclear radiation. Because of its thermal stability, high hardness, physical and chemical stability, and excellent transparency in a wide wavelength region from visible light to infrared light, the crystal field of YAG ceramics favors its use as an excellent host material in laser crystals[1-3]. The conventional YAG transparent polycrystalline was fabricated at high sintering temperature (above 1 700 ℃) and long sintering time (more than 10 h) by a solid-state reaction method in many studies[4-7]. Therefore, its cost is very high.

The transparency of ceramics strongly depends not only on its intrinsic properties such as chemical composition and crystal system, but also on its microstructure including inclusions, pores, grain boundaries, grain size and homogeneity[8]. Many theoretically transparent ceramics could not be sintered to transparency by the normal sintering method, because of the large scattering and reflecting loss to lights resulted from all kinds of defects in the sintered body. Since the property of sintered body is a direct consequence of sintering technique, it is important to prepare a high-purity and well-sinterable powder for a new high-performance and inexpensive ceramics.

Ceramic powders are usually prepared by pyrolysis of the precipitant precursor synthesized by wet-chemical method. Various factors in the preparing process, such as anions in the reaction solution system, have great influence on the crystallization of precursor[9]. In this paper, yttria powder was prepared using yttrium nitrate as a mother salt, aqueous ammonia as a precipitant solution. The results show that sulfate ions have an obvious influence on the morphology and agglomeration of crystallized precursor. A YAG ceramics with excellent transmittance was obtained using the self-prepared yttria powder and commercial alumina powder as starting materials at relatively low temperature, above 1 600 ℃.

2 EXPERIMENTAL

Commercial Y_2O_3 powders with size about 5 μm (99.99%, made in Zibo, China) were dissolved in

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reagent grade nitric acid, and 0.26 mol·L^{-1} yttrium nitrate solution was used as a mother salt solution by adding deionized water. 1 mol·L^{-1} aqueous ammonia solution was dripped into the mother solution with agitation by a magnetic stirrer at a dripping speed of 2 mL·min^{-1}. The temperature of reaction system was maintained at about 0 ℃. The aqueous ammonia solution stopped dripping when pH value of the reaction system reached 8.5. The precipitate slurry was aged with agitation at 0 ℃ for 5 h. The precursor was filtered and washed twice with ion-exchange water, then washed twice with acetone. The precursor after the final washing was dried at room temperature in flowing N_2 gas. The resulting powder was poured into a quartz boat and calcined in flowing O_2 gas. While preparing the mother salt solution, 0.5% ammonium sulfate was added into the solution, in order to compare with the sulfate ion undoped into the mother solution.

The thermal decomposition of the precursor was analyzed by DTA (Model DT30, SHIMADZU, Japan) in flowing O_2 gas at a heating rate of 10 ℃·min^{-1}. The precursor and its calcination result were identified by X-ray diffraction (XRD, Model D/MAX-RB, RIKEN, Japan) analysis, and their morphologies were observed by transmission electron microscopy (TEM, Model EM420, Philips).

Al_2O_3 powder used as one of raw materials was commercially produced (99.99%, DESING Co, Japan). After the Al_2O_3 and Y_2O_3 powders had been mixed with 0.5% ethyl silicate (TEOS)[10] as a sintering aid, the mixture was milled with high-purity ZrO_2 balls in ethanol for 12 h. Then, the milled slurry was dried and calcined in flowing O_2 gas. The resultant was identified by XRD analysis. For the sintering studies, the mixture calcined at 1 200 ℃ was pressed in steel mold at 200 MPa into disks which are 13 mm in diameter and 2-3 mm in height. The powder compact was sintered at 1 500-1 700 ℃ in a vacuum furnace with a molybdenum mesh heater at a heating rate of 250 ℃·h^{-1}. The vacuum in the furnace was less than 1×10^{-3} Pa at the holding temperature.

The sintered specimens were polished into ones with thickness of 1 mm and average micro-roughness (R_a) of less than 1 μm on both surfaces. The densities of the resulting specimens were measured by the Archimedes method. The inline transmittance of the transparent specimens was measured in the wavelength range from 200 to 3 000 nm using an auto-recording spectrophotometer (Model DMR-22, Germany). For observing the microstructure of the specimen surface, the polished specimens were thermally etched by annealing at 1 500 ℃ for 1.5 h in air, and the surface of etched specimen was sprayed with fine gold powders. After that, the surface microstructures of specimens were observed by scanning electron microscopy (SEM, Model EPM-810Q, SHIMADZU, Japan).

3 RESULTS AND DISCUSSION

3.1 Preparation of Y_2O_3 powder

The yttria powders prepared under different conditions were abbreviated to YNA and YNAS, respectively. Among others, YNA means that the yttria powder was obtained by using yttrium nitrate as a mother salt, aqueous ammonia as a precipitant solution; YNAS means that the yttria powder was obtained by yttrium nitrate as a mother salt, aqueous ammonia as a precipitant solution, adding 0.5% ammonium sulfate.

Fig. 1 shows TEM photographs of YNA and YNAS precursors. Although the compositions of YNA and YNAS precursors are the same according to the XRD results, their morphologies are different obviously. In Fig. 1(a), the YNA precursor particles are spherical and 60 nm in diameter, but highly agglomerated. In Fig. 1(b), the crystalline of YNAS precursor is dendritic and 150 to 300 nm in length and 50 nm in diameter, the bifurcated and dendritic shapes make the precursor bulk large, indicating that sulfate ions have a great influence on the synthesis of precursors. Uninduced by sulfate ions, the precursor crystallizes in the all directions, so the resultant is spherical. Induced by sulfate ions, the precursor crystallizes preferentially along some certain directions, so the resultant was dendritic. Other scholars[11, 12] also found that sulfate ions had an approximate influence on preparing nanopowders by the wet-chemical method.

Fig. 2 shows the result of DTA measurement of the precursor. The thermal decomposition of YNA or YNAS precursor was almost ended above 600 ℃. Fig. 3 shows XRD patterns of the precursor and its resultants calcined at 600, 800 and 1 100 ℃. More and more intensified XRD peaks of yttria obtained at 800 and 1 100 ℃ indicate that a further but little decomposition occurs at higher temperatures. The crystallized and highly pure yttria powder was obtained by calcining the precursor at 1 100 ℃. Few sulfate ions mainly affect the crystallization process and agglomeration of precursors, after being washed, the influence on the purity of yttria is negligible.

Fig. 4 shows TEM photographs of YNA and YNAS obtained by calcining the precursor at 1 100 ℃. In Fig. 4(a), the morphology of YNA is irregular and different in size, because the pyrolysis product of the agglomerated precursor is sintered during the calcination. In Fig. 4(b), the primary crystallites of YNAS are spherical, and 60 nm in diameter. In com-

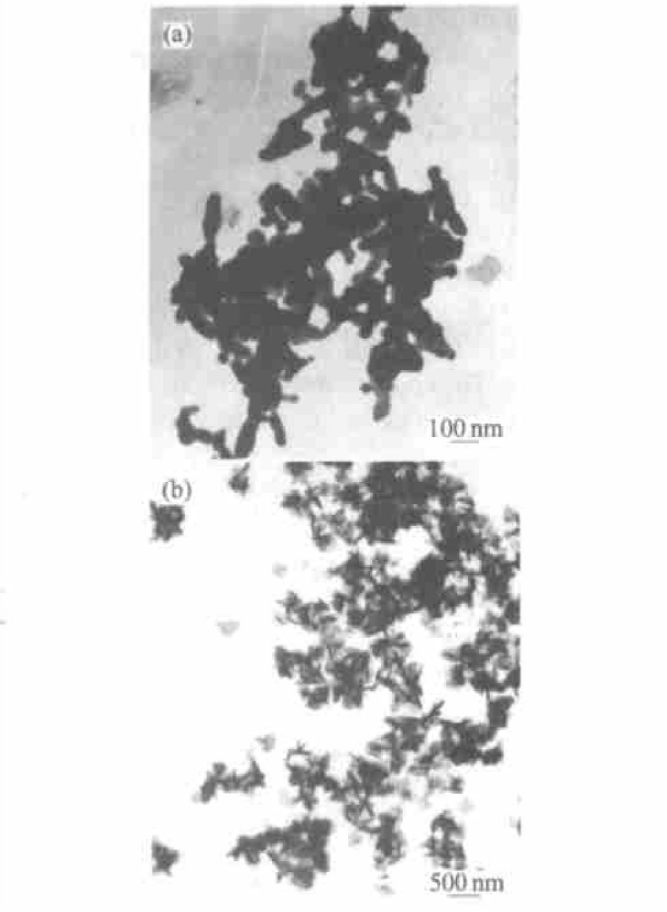

Fig. 1 TEM photographs of precursors obtained by different methods
(a) —YNA; (b) —YNAS

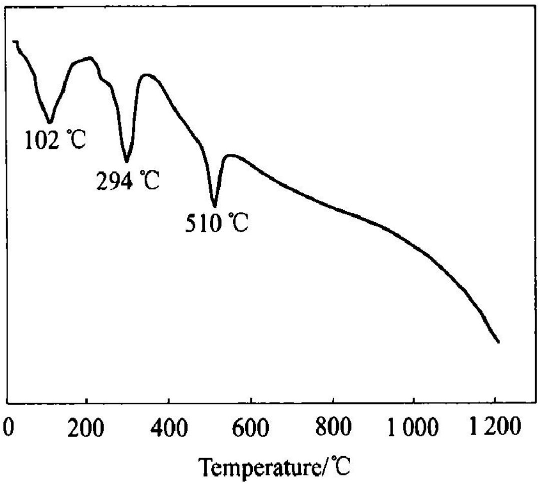

Fig. 2 DTA curve of precursors at heating rate of 10 ℃·min^{-1}

parison with the YNA powder, the YNAS powder is fine and with a narrow size distribution. The dendritic precursor is decomposed into globular oxide particles, not being sintered during the calcination.

3.2 Sintering of YAG

Fig. 5 shows TEM photographs of two different

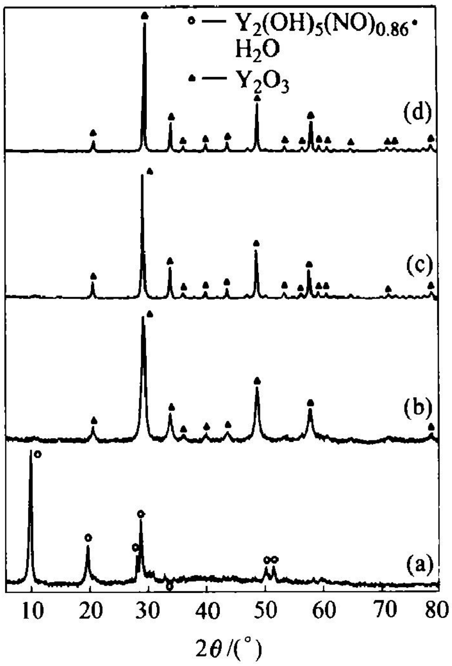

Fig. 3 XRD curves of precursors and their calcination resultants
(a) —Precursor;
(b) —Precursor calcined at 600 ℃ for 1 h;
(c) —Precursor calcined at 800 ℃ for 2 h;
(d) —Precursor calcined al 1 100 ℃ for 3 h

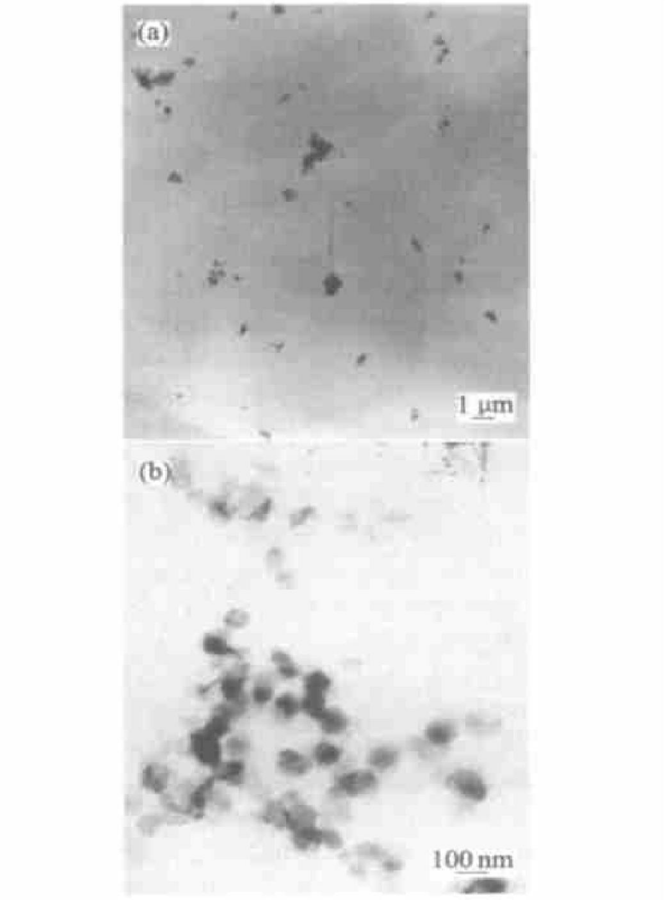

Fig. 4 TEM photographs of Y_2O_3 powder prepared by different methods
(a) —YNA; (b) —YNAS

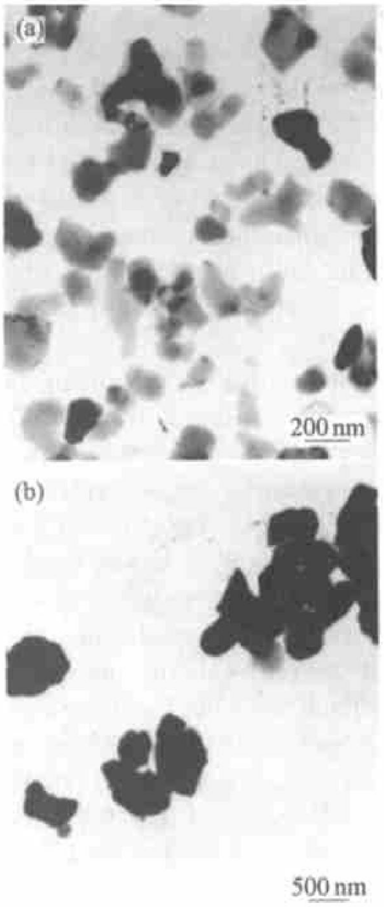

Fig. 5 TEM photographs of two different α-Al_2O_3 raw powders
(a) —Fine Al_2O_3; (b) —Coarse Al_2O_3

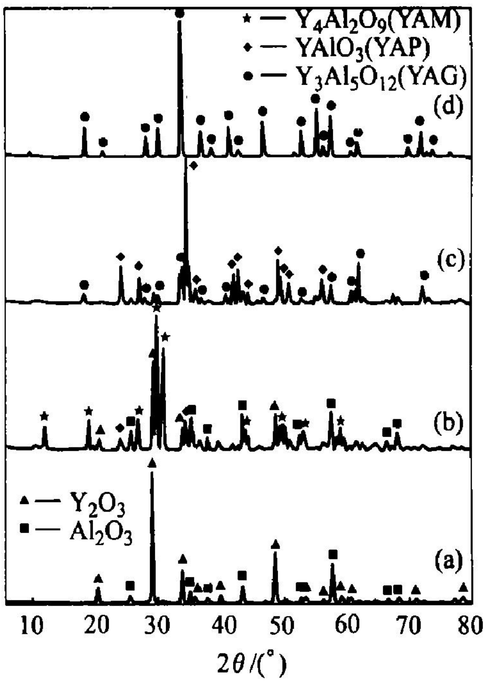

Fig. 6 XRD patterns of mixed powders calcined at different temperatures
(a) —1 000 ℃ for 2 h; (b) —1 200 ℃ for 2 h; (c) —1 200 ℃ for 2.5 h; (d) —1 300 ℃ for 2 h;

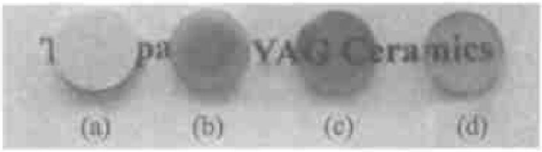

Fig. 7 Appearance of YAG ceramics sintered at 1 700 ℃ for 4 h with various starting mixture
(a) —YNA and fine Al_2O_3; (b) —YNA and coarse Al_2O_3; (c) —YNAS and coarse Al_2O_3; (d) —YNAS and fine Al_2O_3

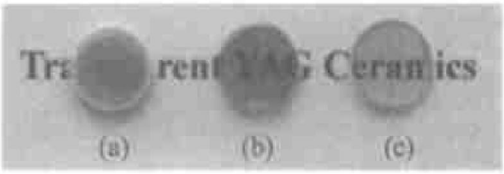

Fig. 8 Appearance of mirror-polished YAG specimens sintered at various temperatures
(a) —1 500 ℃ for 2.5 h; (b) —1 600 ℃ for 3 h; (c) —1 700 ℃ for 4 h

size Al_2O_3 powders commercially produced as raw materials. The primary particle diameters of Al_2O_3 in Fig. 5(a) and Fig. 5(b) are about 140 nm and 400 nm, respectively.

Fig. 6 shows XRD patterns of the Y_2O_3 and Al_2O_3 mixed powders calcined at different temperatures. Y_2O_3 and Al_2O_3 almost do not react below 1 000 ℃. The calcined resultant was transformed into YAM → YAP → YAG with raising the calcining temperature and prolonging the heating time. The pure YAG phase can be obtained by calcining the mixed powders at 1 300 ℃ for 2 h.

Fig. 7 shows the YAG ceramics sintered at 1 700 ℃ for 4 h with various raw mixtures. The specimens in Figs. 7(a) and (b) are opaque, of which one of the raw materials is YNA. While the specimens using YNAS as one of the raw materials in Figs. 7(c) and (d) have an excellent transparency. Y_2O_3 powder has stronger influence on the transparency of YAG ceramics fabricated by the solid-state reaction method than Al_2O_3 powder has. YNAS powder represents much higher sinterability.

Fig. 8 shows the YAG specimens sintered at 1 500-1 700 ℃ using YNAS yttria powder and coarse alumina powder as raw materials. By sintering the YAG specimens above 1 600 ℃, the transparent YAG ceramics was obtained. Fig. 9 shows the relative densities of YAG specimens sintered at 1 500-1 700 ℃. The YANS yittria powder has a very high sinterability, so that almost fully dense bodies were obtained at relatively low temperatures, over 1 600 ℃.

Fig. 10 shows SEM photographs of the surfaces of the specimens sintered at 1 500-1 700 ℃. Fig. 10 shows that the microstructure develops as the grains

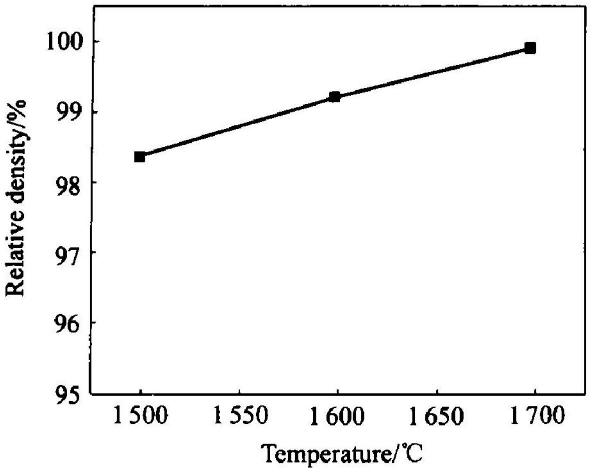

Fig. 9 Dependence of YAG relative density on sintering temperature

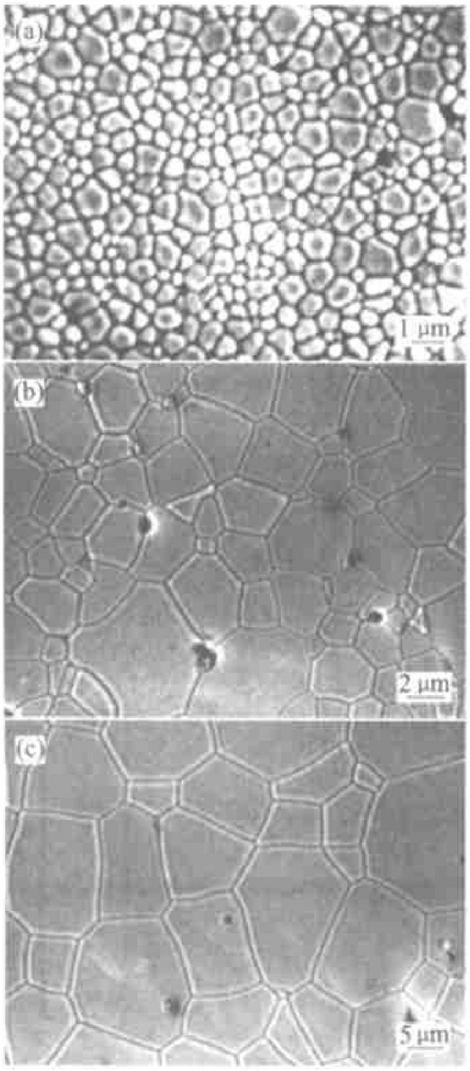

Fig. 10 SEM photographs of polishing and thermal etched surface of YAG

(a) —Sintered at 1 500 ℃ for 2.5 h;
(b) —Sintered at 1 600 ℃ for 3 h;
(c) —Sintered at 1 700 ℃ for 4 h

grow and the pores migrate. In Fig. 10(a), the YAG specimen sintered at 1 500 ℃ has fine grains and many pores at grain boundaries. The reflecting and scattering loss of pores and grain boundaries to lights made the specimen opaque[13]. However, by sintering above 1 600 ℃, the pores remained at grain boundaries are easily eliminated as the grains grow. It is essentially different from the cases of using YNA or conventional yttria powders as raw material in which many pores remain within grains and can not be eliminated. Fig. 10(c) shows that the sintered body obtained at 1 700 ℃ has an almost pore-free and homogeneous microstructure with grains about 7 μm. Because the sintering temperature is relatively low, abnormal grain growth is not observed. The specimen has a typical microstructure of transparent polycrystalline[14].

Fig. 11 shows the inline transmittance spectra of the specimens sintered at 1 700 ℃ using the mixtures of YNAS with fine alumina powder and coarse alumina powder respectively. For comparison, the data of the single-crystal YAG (Osaka, Japan) are also shown. Both the single crystal and the polycrystalline have a strong absorption to ultraviolet lights. The transmittance of YAG polycrystalline increases with the increase of the incident wave length. The lower transmittance of YAG polycrystalline than that of the single crystal level in the visible wavelength region is not only due to the difference of crystal microstructure, surface roughness and thickness, but also the few retained pores. The optical transmittance of YAG polycrystalline in the infrared wavelength region is almost equal to that of the single crystal. The highest transmittance of YAG polycrystalline is 45% in the visible wavelength region(360~800 nm) and 70% in the near-infrared wavelength region(1~3 μm).

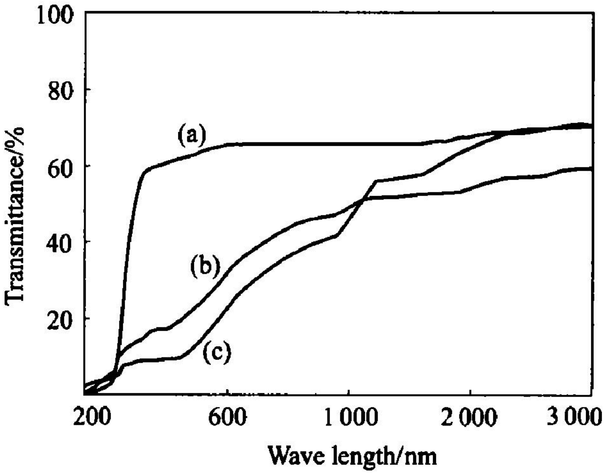

Fig. 11 Optical transmittance spectra of YAG single crystal and YAG polycrystalline ceramics

(a) —0.25 mm thick single crystal;
(b) —1 mm thick polycrystalline YAG sintered with fine Al_2O_3 and YNAS mixture;
(c) —1 mm thick polycrystalline YAG sintered with coarse Al_2O_3 and YNAS mixture

4 CONCLUSIONS

1) The properties of yttria powder have a great influence on the transparence of YAG ceramics fabricated by a solid-state reaction method.

2) The dendritic precursor crystalline can be obtained using yttrium nitrate as a mother salt solution with 0.5% ammonium sulfate, aqueous ammonia as a precipitant solution.

3) The precursor decomposes into the low-agglomerated and high-purity yttria powder by being calcined at 1 100 ℃. The primary particles of yttria are spherical and 60 nm in diameter with a narrow size distribution.

4) The transparent YAG ceramic is fabricated at 1 700 ℃ under vacuum by the solid-state reaction using self-prepared yttria and commercial alumina as raw materials. The highest transmittance of the sintered body is 45% in the visible wavelength region and 70% in the near-infrared wavelength region.

5) The transparent YAG polycrystalline sintered at 1 700 ℃ has an almost pore-free and homogeneous microstructure. No abnormal grain growth occurs.

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