Fabrication of yttrium aluminum garnet transparent ceramics from yttria nanopowders synthesized by carbonate precipitation

Hua Gong · Dingyuan Tang · Hui Huang · Jan Ma

Abstract Nanocrystalline yttria powders have been successfully synthesized by using yttrium nitrate as starting salt and ammonium hydrogen carbonate as precipitant. It was found that a small amount of ammonia sulfate in the yttrium nitrate solution can effectively reduce the agglomeration and the resultant powders display good dispersion. Pure cubic phase yttria powders were prepared by calcining the precipitate at 1100 °C for 4 h. The size of the as-prepared yttria powders was about 60 nm in diameter and showed excellent sintering activity. The as-prepared yttria nanopowders and commercial ultrafine alumina powders were used to fabricate YAG ceramics by solid-state reaction method and transparent YAG ceramics have been obtained by vacuum sintering at 1760 °C for 6 h.

1 Introduction

Transparent polycrystalline yttrium aluminum garnet (YAG) ceramics forms in cubic crystal structure and belongs to the isometric crystal system [1]. Owing to its high thermal stability, chemical properties and unique homogenous optical properties, transparent YAG ceramic is not only an important high-temperature structure material, but also an excellent host material for fluorescence material and high-power solid-state lasers [2–4]. Compared to its single-crystal form, polycrystalline YAG ceramics have the advantages of low cost, ease fabrication of large size, high dopant concentration, mass-production and multifunctionality. However, how to fabricate high-performance transparent YAG ceramic used for solid-state laser to satisfy the extremely severe requirements of laser materials is the biggest challenge.

The first transparent polycrystalline Nd:YAG ceramics for laser media was a significant milestone developed by Ikesue et al. [5, 6] using solid-state reaction in 1995. Since then, more and more attentions have been attracted on the fabrication of YAG [7, 8]. Translucent or fully transparent YAG ceramics have been fabricated by various techniques. Li et al. [9] fabricated translucent YAG ceramics at 1700 °C for 1 h under vacuum-sintering from YAG powders synthesized via co-precipitation using ammonium hydrogen carbonate as the precipitant. Lu et al. [10] produced large-scale Nd:YAG ceramic rod with diameter of 8 mm and length of 203 mm and the performance of the laser ceramics was comparable to that of conventional YAG single crystals. Zych et al. [11] prepared YAG transparent optical ceramics using the mixture of Y_2O_3 and Al_2O_3 powders by hot-press at 1750 °C for 4 h under a pressure of about 300 atm. Spark plasma sintering was applied by Chaim et al. [12] to fabricate YAG transparent ceramics at 1400 °C for 3 min using nanocrystalline YAG powders as source materials.

No matter what techniques were applied to fabricate YAG transparent ceramics, the synthesis of high-quality powders are extremely vital. In this work, Y_2O_3 nanosized powders

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with good sinterability were synthesized by wet chemical precipitation process. YAG transparent ceramics were fabricated by a solid-state reaction method using the as-prepared Y_2O_3 powders and commercial ultrafine Al_2O_3 powders as starting materials. The morphologies and microstructure of the Y_2O_3 nanopowders and YAG ceramics were investigated. The optical properties of the transparent ceramics were also studied.

2 Experimental

Yttrium nitrate hexahydrate ($Y(NO_3)_3.6H_2O$), ammonium hydrogen carbonate (NH_4HCO_3), and ammonium sulfate (($NH_4)_2SO_4$)) was used as source material, precipitant and dispersant, respectively. ($NH_4)_2SO_4$ aqueous solution was added into 0.5 mol/l $Y(NO_3)_3$ aqueous solution. Then, 2.5 mol/l NH_4HCO_3 aqueous solution was dripped into the mixed solution of ($NH_4)_2SO_4$ and $Y(NO_3)_3$ and white yttrium carbonate precipitate was formed. After aging at room temperature for 2 days with continuously stirring, the yttrium carbonate precipitate slurry was filtered and washed repeatedly with deionized water in order to remove the impurities. Finally, the precipitate was calcined at 500–1200 °C for 4 h with a heating rate of 5 °C/min.

The as-prepared Y_2O_3 powders were used to fabricate YAG ceramics. The Y_2O_3 powders and commercial Al_2O_3 powders (AKP-30, Sumitomo Chemical Co., Ltd.) were blended together according to the stoichiometric ratio of YAG and were ball-milled in ethanol for 5 h. Tetraethyl orthosilicate (TEOS, 0.5 wt.%) was added as sintering aid. The powder mixtures were dried and pressed into pellets in a stainless steel die at ~30 MPa. The green body was further cold-isostatically pressed at 200 MPa. The compacted pellets were sintered at 1760 °C for 6 h under vacuum of around 10^{-3} Pa in a furnace with molybdenum heating element and then annealed at 1550 °C for 10 h in air.

The as-synthesized Y_2O_3 nanopowders were used to fabricate YAG ceramics. Phase identification of the Y_2O_3 powders and YAG ceramics was performed by a Shimadzu X-ray diffractometer (XRD) with CuK_α radiation. The morphologies and microstructures of the Y_2O_3 powders were observed by a Leo 1550 field emission type scanning electron microscope (SEM) and JEOL JEM-2010 transmission electron microscopy (TEM). Densities of the sintered YAG ceramics were measured by the Archimedes method and H_2O was used as the immersion medium. Microstructure of the polished surface of the transparent YAG ceramics was observed by SEM after thermally etched at 1600 °C for 1 h in air furnace. Transmittance of the transparent ceramics was measured over the wavelength region from 200 to 900 nm using a UV–vis spectrometer (Shimadzu, 2501 PC, Kyoto, Japan).

3 Results and discussions

Figure 1 shows XRD patterns of the yttrium carbonate precursor calcined at various temperatures. The yttrium carbonate precursor exhibits low crystallinity after aging for 2 days. The precursor was partly decomposed at 500 °C and some yttria phase was formed [Fig. 1(b)]. After calcined at 700 °C, the precursor was almost completely decomposed and crystallized. With the increase of calcination temperature, continued refinements in peak shapes and intensities indicated the growth of grains in the yttria powders [Fig. 1(c–f)]. All the peaks of the powders calcined at 1100°C can be indexed by cubic yttria (PDF, 41–1105).

Figure 2 shows the SEM images of the Y_2O_3 powders calcined at 1000 °C and 1100 °C for 4 h with and without sulphate dispersant. The as-prepared Y_2O_3 powders obtained with sulphate dispersant are uniform with a narrow particle size distribution and fairly well-dispersed [Fig. 2(a–b)]. The particle size increases with the increasing calcination temperature. The average particle size of the Y_2O_3 powders calcined at 1100 °C is ~60 nm in diameter [Fig. 2(b)], which is a little smaller than that of the AKP-30 Al_2O_3 [Fig. 2(d)]. However, the Y_2O_3 powders synthesized without sulphate dispersant, exhibit severe agglomeration [shown in Fig. 2(c)], which results to poor sintering reactivity of the powders.

One of the reasons for the good dispersion of the as-synthesized Y_2O_3 powders is the fineness of the yttrium carbonate precursor, of which the pseudomorph does not remain after calcination [13]. Another predominant reason for the good dispersion is the presence of sulfate as dispersant. The yttrium carbonate ($Y_2(CO_3)_3\cdot2H_2O$) precipitation has a positive ζ potential in aqueous solution. SO_4^{2-} can adsorb onto the $Y_2(CO_3)_3\cdot2H_2O$ particles according to the electrostatic force. The SO_4^{2-} has a higher decomposition temperature than carbonate, and its existence at comparatively high temperature can reduce the element diffusion between particles, resulting in a smaller particle size. Furthermore, the
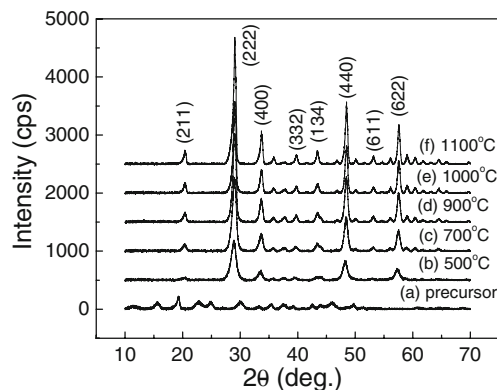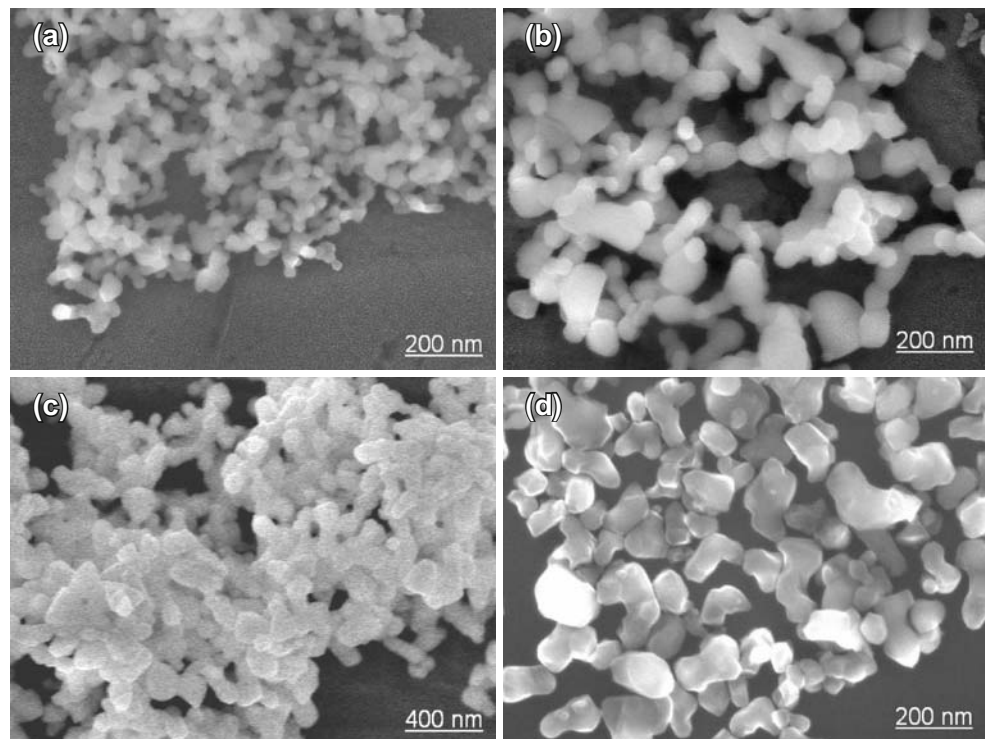

Fig. 1 XRD patterns of (a) yttrium carbonate precursor calcined at (b) 500 °C, (c) 700 °C, (d) 900 °C, (e) 1000 °C and (f) 1100 °C for 4 h

Fig. 2 SEM images of the Y_2O_3 powders calcined at (**a**) 1000 °C and (**b**) 1100 °C with sulphate dispersant, (**c**) 1100 °C without dispersant for 4 h and (**d**) AKP-30 Al_2O_3 powders

decomposition of SO_4^{2-} at high temperatures also contributes to the dispersion of powders [14]. Our experiments also show that the sulfate-ion-modified Y_2O_3 powders obtained at 1100 °C display good sinterability, and Y_2O_3 ceramics with over 98% of its theoretical density have been obtained by sintering Y_2O_3 pellets in air at 1650 °C for 2 h. Thus, the Y_2O_3 powders synthesized by us are ideal starting materials of Y to fabricate YAG transparent ceramics.

Figure 3 shows the TEM micrograph of the Y_2O_3 grains calcined at 1100 °C for 4 h. It was found that some particles were single crystals while others were formed by conglomeration of several single crystals [Fig. 3(a)]. The result indicates that the precursor formed primary particles after calcination. Figure 3(b) shows HRTEM micrograph of a

typical yttria grain. Three Y_2O_3 grains were connected together to form a chain-like particles. The clear lattice fringes indicated a single crystal structure of the Y_2O_3 grains. The interfacial spacing was 3.2 and 2.4 Å, corresponding to (222) and (420) plane of cubic crystal structure of yttria (a=9.183 Å), respectively.

The synthesized Y_2O_3 and commercial Al_2O_3 powders were used to fabricate YAG ceramics. Transparent YAG ceramics were obtained by sintering the pellets at 1760 °C for 6 h under vacuum of around 10^{-3} Pa followed by annealing at 1550 °C for 10 h in air. Figure 4 shows the photograph of mirror-polished transparent YAG ceramics with Ø11 mm in diameter and 1.5 mm in thickness. The letters can be clearly read through the sample. The relative density of the

Fig. 3 (**a**) TEM and (**b**) HRTEM images of Y_2O_3 grains calcined at 1100 °C for 4 h
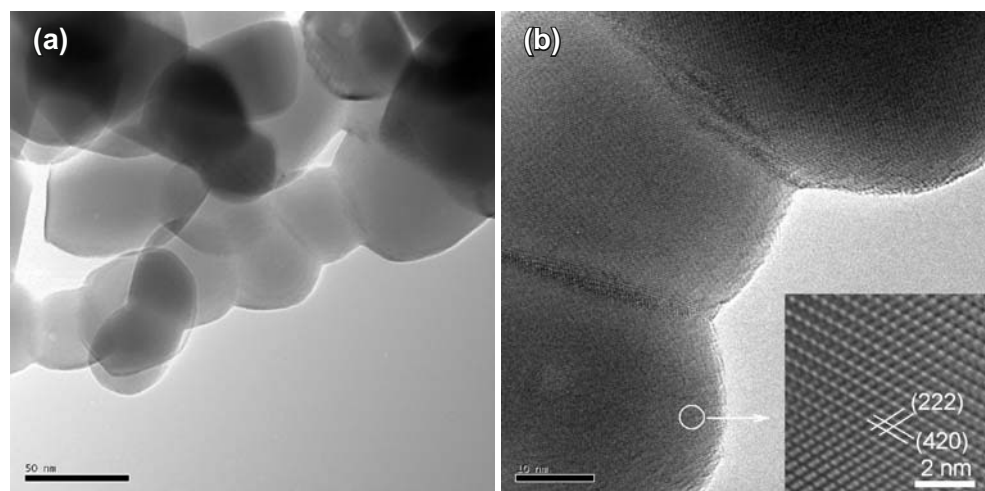
Fig. 4 Photograph of mirror-polished YAG transparent ceramics on the logo of our university

transparent YAG ceramics reached 99.8% of the theoretical. XRD pattern of the YAG ceramics is shown in Fig. 5. Wen et al. [14, 15] indicated that there would be many inclusions in the sintered body if the mixture powders were not sintered at high temperature to yield pure YAG phase at first. However, in our works, all of the observed peaks are characteristic of cubic YAG and no other phases are detected. This attributed to the high-quality Y_2O_3 powders. The well-dispersed Y_2O_3 powders could mix with the commercial Al_2O_3 powders homogenously and thus the mixture powders could react completely during sintering. Figure 6 shows the SEM morphology of the polished surface of the transparent YAG ceramics after thermal etching at 1600 °C for 1 h. The ceramics was very dense and no pinholes or other defects were observed.

Figure 7 shows the optical transmission spectra of the YAG transparent ceramics with the thickness of 1.5 mm in the wavelength range from 200 to 900 nm. In the measured wavelength region, the transmittance is about 75% in the
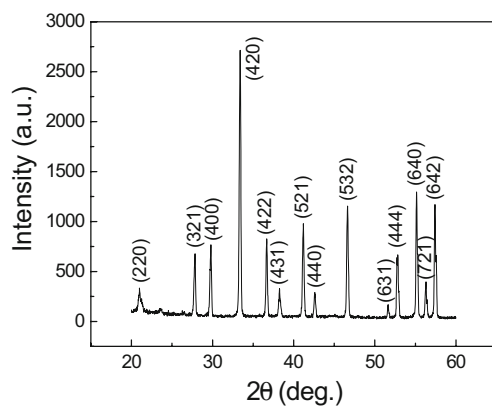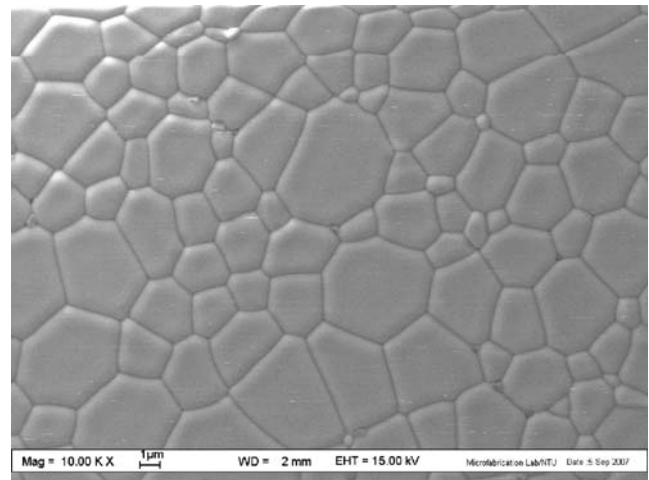

Fig. 6 SEM image of the YAG transparent ceramics

visible region and the in-line optical transmittance increases with increasing wavelength. The drop-off in transmittance at <350 nm means the presence of some smaller pores, or impurities located in the sample. In order to improve the optical properties, further work is focus on more precise control of the precursor preparation and formation techniques to compact the powders more homogenously.

4 Conclusion

Well-dispersed nanocrystalline Y_2O_3 powders were synthesized by carbonate precipitation process. The addition of a small amount of ammonia sulfate to the yttrium nitrate solution benefits to yield highly reactive Y_2O_3 powders. With the increase of calcination temperature, the grain size of yttria increased obviously. Our results suggested that the optimum calcination temperature of the yttrium carbonate precursor was 1100 °C. The Y_2O_3 powders are fine with 60 nm in diameter, narrow in size distribution and loosely agglomerated. Using the Y_2O_3 powders and commercial
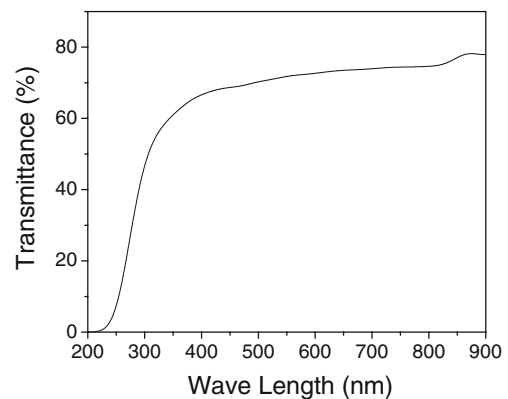

Fig. 5 XRD patterns of the YAG transparent ceramics

Fig. 7 The transmittance spectrum of the YAG transparent ceramics

Al$_2$O$_3$ powders as starting materials, transparent YAG ceramics were successfully fabricated by vacuum sintering at 1760 °C for 6 h through solid-state reaction method by one-step sintering.

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