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Influence of pH values on (Nd + Y):Al molar ratio of Nd:YAG nanopowders and preparation of transparent ceramics

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ABSTRACT

The Nd:YAG ceramics were fabricated by vacuum sintering at 1750 °C for 20 h, where the raw nanopowders were synthesized by the co-precipitation method, and calcined at 1050 °C for 2 h. The effect of the pH values of reaction solution on the (Nd + Y):Al mole ratio of the powders was discussed here. It was found that the pH value range of 7.9–8.2 was suitable for the preparation of the Nd:YAG nanopowders. Secondary phases and pores appeared in and between the grains of Nd:YAG ceramic with the (Nd + Y):Al mole ratio of 0.576. The specimens with the (Nd + Y):Al mole ratio range of 0.598–0.603 had fine microstructures, and their transmissions were both over 80% at the near infrared wavelength. If the (Nd + Y):Al mole ratio reached 0.648, many secondary phases occurred along the grain boundaries.

1. Introduction

Neodymium-doped yttrium aluminium garnet (Nd:YAG) single crystal has been widely used in medicine, scientific research, and various industries [1,2]. But its fabrication requires expensive equipment and crucible material. Moreover, it is extremely difficult to fabricate homogenous Nd:YAG single crystals with high neodymium doping concentration because of the segregation in the host materials [3]. Nd:YAG transparent ceramics has attracted much attention as a substitute for Nd:YAG single crystal because of its excellent laser performance, low cost, short preparation period, large size and high concentrations doped [4].

Recently, a lot of methods have been adopted to try to fabricate YAG transparent ceramics, such as solid-state reaction [5,6], sol–gel process [7–9], hydrothermal [10], co-precipitation [11–15]. The composition of the ceramics synthesized by the solid-state reaction was not homogenous. The Nd:YAG powders synthesized by sol–gel process and hydrothermal methods have general advantages like high purity, homogeneity, but it is hard to control the size of these powders. Compared with other chemical methods, co-precipitation is a unique and useful method for obtaining well-dispersed Nd:YAG nanopowder with very good chemical homogeneity and narrow particle size distribution, which helps to obtain Nd:YAG transparent ceramics of large size and high-power output [16]. However, there are several obvious shortcomings in the co-precipitation process, both concentrations of Y^{3+}, Al^{3+} and Nd^{3+} for producing precipitations and their depositing velocities are different, it is quite possible that molar ratio of (Nd + Y):Al will deviate from 3:5 in local areas [17]. The pH values need to be controlled strictly to guarantee the stoichiometric proportion of Nd, Y and Al in calcined nanopowders without any secondary phases.

In this paper, The Nd:YAG nanopowders with high sintering activity were synthesized by co-precipitation method. The relation of (Nd + Y):Al molar ratio of the calcined nanopowders versus pH values of slurries was discussed systematically. The optical properties, microstructures of the resultant Nd:YAG ceramics with different (Nd + Y):Al mole ratios were studied.

2. Experimental

Nd_2O_3 (99.99%, Alfa Aesar Company, USA), $Al(NO_3)\cdot 9H_2O$ (99.99%, Tianjin Fine Chemicals, China) and $Y(NO_3)_3\cdot 6H_2O$ (99.99%, Tianjin Fine Chemicals, China) were used as starting materials. The $Nd(NO_3)_3$ was prepared by dissolving Nd_2O_3 in nitric acid (HNO_3) and diluting with deionized water under stirring. The aqueous solutions of $Al(NO_3)_3$, $Y(NO_3)_3$ and $Nd(NO_3)_3$ were mixed together according to the stoichiometric proportion of Nd, Y and Al in 1 at.% Nd:YAG compound, in which the concentration of Al was 0.05 M. The $(NH_4)_2SO_4$ (Analytical Grade, Shanghai Ling

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Feng Reagent Factory, China) was added in the mixed nitrate solutions as a dispersant. The precipitated slurries with different pH values of 7.6, 7.9, 8.2 and 8.5 were performed by drop-wise addition of 1 M NH_4HCO_3 (99.99%, Tianjin Fine Chemicals, China) solution into nitrates, under rapid stirring. The precipitated slurries were aged for 24 h to make the reaction sufficient, and then the suspensions were filtered and washed repeatedly with deionized water and alcohol to remove residual ammonia and nitrate ions. After washing, the Nd:YAG precursors were dried at 80 °C for 24 h in the oven, and the Nd:YAG nanopowders at a heating rate of 5 °C/min, named as samples 1, 2, 3 and 4, respectively.

The four Nd:YAG nanopowders were blended with the high-purity Al_2O_3 balls for 10 h in ethanol using TEOS as a sintering aid, respectively. The milled slurries were dried, and calcined at 800 °C in the air to remove residual organic components. After this, the Nd:YAG nanopowders were uniaxially pressed into pellets and then isostatically cold pressed at 250 MPa. Green compacts were sintered at 1750 °C for 20 h under vacuum and then annealed at 1450 °C for 20 h in the air. The Nd:YAG ceramics were obtained, and named as specimens A, B, C and D, respectively.

The (Nd + Y):Al molar ratios of the calcined nanopowders were analyzed by chemical analysis and inductively coupled plasma atomic emission spectrometer (ICP-AES, Vista AX CCD, Varian, USA). Thermal behaviors of the Nd:YAG precursors were studied using the thermogravimetry analysis and differential thermal analysis (TG-DTA, STA 449C, Netzsch, Germany) from room temperature to 1200 °C at a heating rate of 5 °C/min in air. The phase compositions of specimens were identified by X-ray diffraction (XRD, Model D/MAX-2550V, Rigaku, Japan). Microstructures of the Nd:YAG ceramics were observed by electron microprobe analysis (EPMA, Model JXA-8100, JEOL, Japan). Mirror-polished samples (Ø 23 × 4 mm^2) on both surfaces were used to measure optical transmittance (Model U-2800 Spectrophotometer, Hitachi, Japan).

3. Result and discussion

TG-DTA curves of the precursor powder for the sample 3 are presented in Fig. 1. The TG-DTA results of the other three samples are similar to that of the sample 3. The endothermal peaks at 109.4 °C and 192.2 °C are caused by the evaporation of chemically absorbed water and crystal water. At temperature range of 200–800 °C, the weight loss of about 17% appears in the TG curve, and a large exothermic peak is detected in the DTA, corresponding to the decomposition of $CO_3{}^{2-}$, OH^- and $NO_3{}^-$ in the precursor. There is no weight loss in the TG curve at around 937.6–1029.5 °C. The sharp exothermic peak at 937.6 °C was attributed to the crystallization of intermediate phases (YAM and YAP). Exothermic peak at around 1029.5 °C corresponds to the formation of YAG. According to this, the calcining temperature should be above 1029.5 °C. In this paper, a calcining temperature of 1050 °C was chosen to obtain the nanopowders with a pure YAG phase and high sintering activity.

The Nd:YAG precursors are carbonate and hydroxide mixed precipitates, and the partial Al hydroxide dissolved as $Al(OH)^{4-}$ ions at pH value above its isoelectric point range of ~8.5–9.5 in the slurries, while the isoelectric points of Y hydroxide is between 10.5 and 11.5 [18]. This conclusion indicates that it is impossible to guarantee the complete precipitation of Y, Al and Nd at the same pH value during the preparation process of Nd:YAG precursors.

Table 1
The (Nd + Y):Al molar ratio of the calcined powders versus pH values of reaction.

Atom%	Sample 1	Sample 2	Sample 3	Sample 4
Y	24.06	24.26	24.53	25.12
Al	42.06	40.87	41.02	39.08
Nd	0.198	0.2	0.211	0.231
(Nd+Y):Al (molar ratio)	0.576	0.598	0.603	0.648
pH value of reaction	7.6	7.9	8.2	8.5

The relation of (Nd + Y):Al molar ratio of the calcined powder versus pH values of reaction solution is investigated systematically in Table 1. The (Nd + Y):Al molar ratio increases with the increase of the pH values of slurries. Obviously, a proper pH value plays a very important role in controlling the molar ratio of (Nd + Y):Al in the nanopowder. As shown in Table 1, the molar ratio of (Nd + Y):Al in the nanopowder is 0.576 lower than 0.6 at pH 7.6. This is because that the partial Al ions begin to precipitate from the nitrate solutions at pH 3.6, while the production of Y precipitates require higher pH value [19]. The nanopowder of the (Nd + Y):Al molar ratio of 0.598 is obtained by adjusting the pH value to 7.9. When the pH value of the slurry is increased to 8.2, the (Nd + Y):Al molar ratio becomes 0.603. The higher pH value of 8.5 leads to the dissolution of partial Al hydroxides in the slurries and the molar ratio of (Nd + Y):Al becomes 0.648, which seriously deviates from 0.6. Thus for present fabrication process of Nd:YAG precursors, the pH values of the slurries should be controlled in the range of ~7.9–8.2. In this case, the obtained powders are very suitable for the preparation of the Nd:YAG ceramics whose optical properties also will be very close to those of Nd:YAG single crystal.

Fig. 2 shows the XRD patterns of specimens A, B, C and D. Although the (Nd + Y):Al molar ratio of the specimens A and D seriously deviates from theoretical value (0.6) of pure YAG, YAG is the only phase detected in them. Maybe the amount of secondary phases (Al_2O_3, YAM and YAP) is too few to be detected by the XRD equipment. But the reason for the fairly small amount of secondary phases in polycrystalline ceramics must be considered [20]. This conclusion is strongly supported by EPMA micrographs shown in Fig. 3(a) and (d).

Compared to the other three specimens, the specimen A, as shown in Fig. 3(a), consists of the average grain size of ~5 μm.

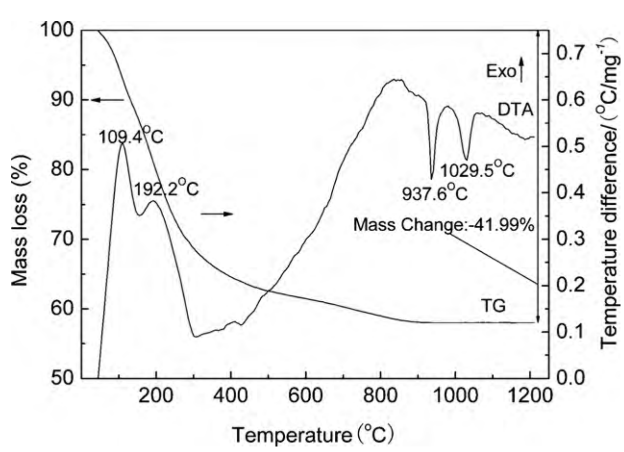

Fig. 1. TG-DTA curve of the sample 3 at molar ratio of the (Nd + Y):Al of 0.603.

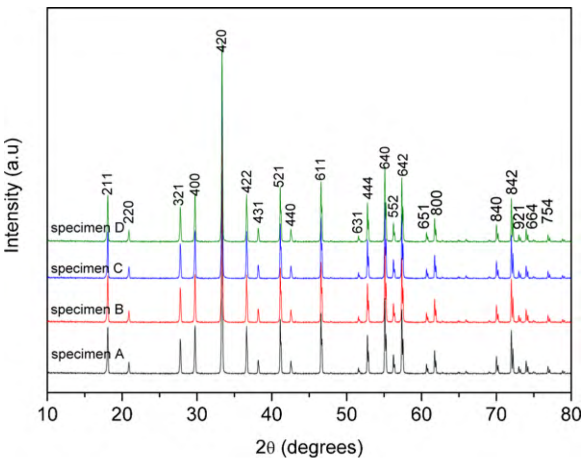

Fig. 2. XRD patterns of four specimens at various molar ratio of the (Nd + Y):Al: (A) 0.576, (B) 0.598, (C) 0.603, (D) 0.648.

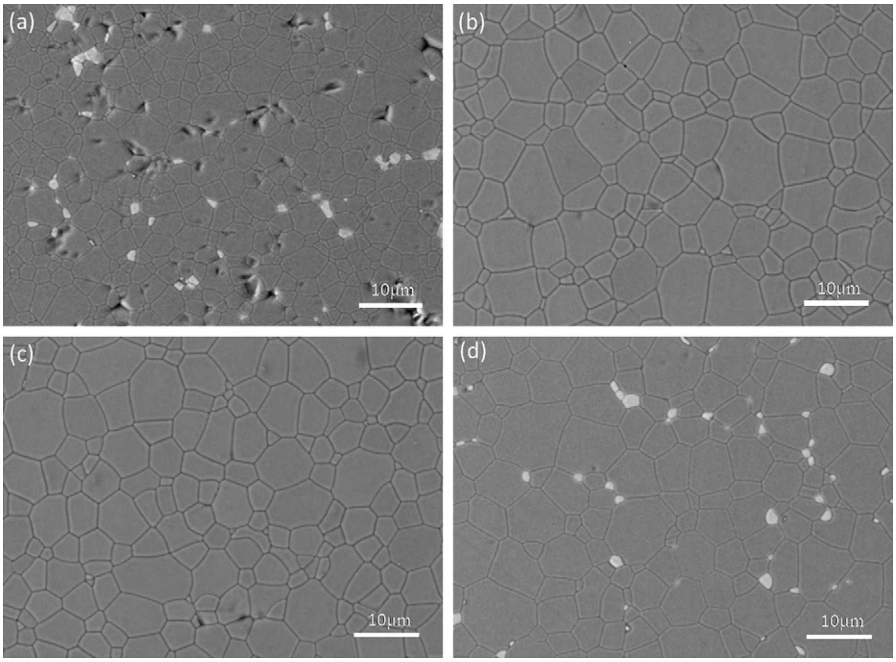

Fig. 3. EPMA micrographs of the Nd:YAG ceramics at various molar ratio of the (Nd + Y):Al: (a) 0.576, (b) 0.598, (c) 0.603, (d) 0.648.

Because the (Nd + Y):Al molar ratio of specimen A is much lower than 0.6, many superfluous Al_2O_3 remains in the calcined powders. During the sintering process, residual Al_2O_3 is prone to diffuse along the YAG grain boundaries, and obstructs normal growth act as grain growth inhibitor, which leads to production of many pores in the specimen A. This is because the decrease of pores depends on grain growth [21]. When the (Nd + Y):Al molar ratio is 0.598 (specimen B) and 0.603 (specimen C), which is very close to 0.6, no secondary phases are observed along the grain boundaries, and pores have been removed completely. The fully dense Nd:YAG ceramics with uniform microstructures (as shown in Fig. 3(b) and (c)) are obtained. Although the (Nd + Y):Al molar ratios of specimen B and C slightly deviate from 0.6, it has almost no effect on the microstructure of Nd:YAG ceramics. This phenomenon suggests that the pH value range of 7.9–8.2 is suitable for the preparation of the Nd:YAG nanopowders. When the (Nd + Y):Al molar ratio is 0.648 in specimen D, superfluous Y_2O_3 can react with Al_2O_3 to yield intermediate phases (YAP and YAM) which can be distincly observed in Fig. 3(d).

Fig. 4 shows the photographs of specimens A, B, C and D with the thickness of 4 mm. Specimen A is translucent, the other three specimens are transparent. In-line transmittance as shown in Fig. 5 is the main parameter for evaluating the optical properties of Nd:YAG transparent ceramics. The specimen A is only translucent as the result of the residual pores and superfluous Al_2O_3 after sintering which act as scattering centers. Both specimens B and C have over 80% transmission at the wavelength of 1064 nm. However, at the wavelength of 400 nm, the transmission of specimens B and C are both lower than 80%, the reason is that the scattering intensity increases with the decrease of wavelength according to the Rayleigh's equation [21]. Maybe small amount of scattering centers still exist in the specimens only cannot be detected by instruments. The optical tranmission of the specimen D is 55% in the visible wavelength, and increases about 60% in the infrared, and seriously lower than those of the specimens B and C. This can be attributed to scattering centers caused by secondary phases and pores.

Fig. 6 shows the fracture surfaces of specimens A, B, C and D. The fracture styles of specimens A and D are both intracrystalline fracture because secondary phases and pores in them enhance strength of grain boundaries. However, both specimens B and C have pore-free microstructure and clean grain boundaries, so their fracture styles are both intergranular fracture.

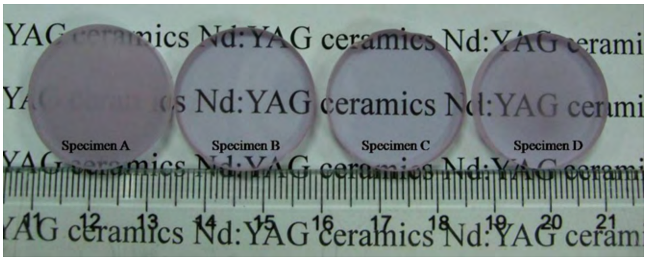

Fig. 4. Photo of four specimens (4 mm thickness) at various molar ratio of the (Nd + Y):Al: (A) 0.576, (B) 0.598, (C) 0.603, (D) 0.648.

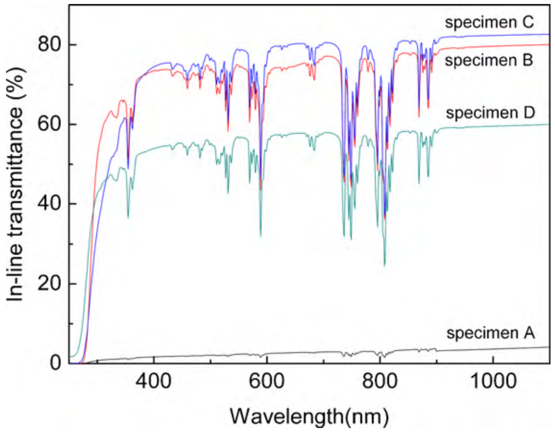

Fig. 5. In-line transmittances of four specimens (4 mm thickness) at various molar ratio of the (Nd + Y):Al: (A) 0.576, (B) 0.598, (C) 0.603, (D) 0.648.

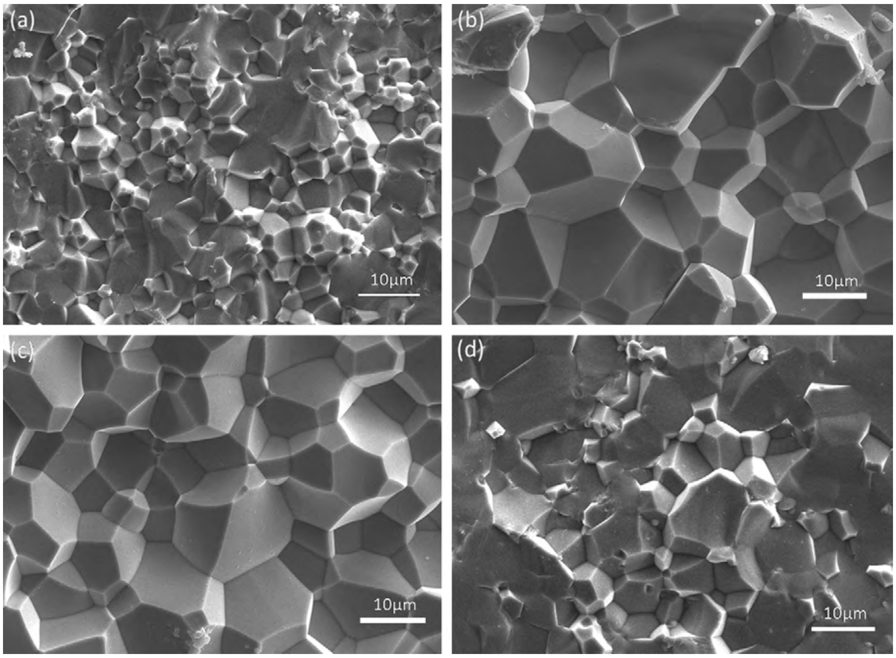

Fig. 6. EPMA micrographs of fracture surfaces of the Nd:YAG ceramics at various molar ratio of the (Nd + Y):Al: (a) 0.576, (b) 0.598, (c) 0.603, (d) 0.648.

4. Conclusions

The Nd:YAG nanopowders with high sintering activity were synthesized by co-precipitation method. The pH value range of 7.9–8.2 is suitable for the preparation of Nd:YAG nanopowders. Both specimens B and C with average grain size of ∼10 μm have fine microstructures. No secondary phases and pores appear in or between the grains. The transmissions of the specimens B and C are both over 80% at the wavelength of 1064 nm. If the pH value is lower than 7.9 or higher than 8.2, residual secondary phases remain in the calcined powders, which leads to the decrease of the transmissions of specimens.

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