

Technical note

# Synthesis of Nd:YAG powders leading to transparent ceramics: The effect of MgO dopant

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## Abstract

Neodymium doped yttrium aluminum garnet (Nd:YAG) ultrafine powders were synthesized by co-precipitation method using MgO as dopant. The addition of small amount of MgO can reduce the agglomeration and particle size of the produced Nd:YAG powders. The results show that pure phase YAG powders can be achieved by calcining of the precursors at 1000 °C for 2 h. The MgO doped Nd:YAG powders show better dispersion compared with the undoped powders. When the MgO content is 0.01 wt.%, well-dispersed Nd:YAG powders with spherical particles of 100 nm diameter were obtained. The transmission of the corresponding Nd:YAG ceramics is 82.6% at the wavelength of 1064 nm, which is comparable to Nd:YAG single crystals.

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## 1. Introduction

Neodymium-doped yttrium aluminum garnet (Nd:YAG) single crystals have the garnet structure, excellent chemical stability, good optical and good temperature creep resistance.<sup>1</sup> In the recent years, Nd:YAG single crystals has been widely used in medicine, scientific research, and various industries (laser cutting, laser ranging and so on).<sup>2</sup> The Nd:YAG transparent ceramics are considered to be an alternative to single crystal because of its excellent performance, low-cost, ease of manufacture and mass-production and comparatively shorter times of preparation.<sup>3,4</sup>

Owing to such application potential of Nd:YAG ceramics, a lot of efforts have been made to try to synthesize transparent polycrystalline Nd:YAG ceramics, such as solid-state reaction,<sup>5,6</sup> sol-gel,<sup>7,8</sup> hydrothermal,<sup>9</sup> and co-precipitation.<sup>10–13</sup> Among these, co-precipitation is a unique and useful method for obtaining well-dispersed Nd:YAG nanopowders with very good chemical homogeneity and high purity.

However, the dispersion-state and the particle size can be only poorly controlled. Although some studies have proved that pure-phase YAG powders can be easily obtained at relatively low calcination temperature (below 1000 °C) via co-precipitation method,<sup>14,15</sup> the agglomeration problem is hard to avoid during the preparation of the Nd:YAG powders.

In this study, well-dispersed Nd:YAG powders were synthesized via co-precipitation using MgO as additive. The effect of various amount of MgO on preparation of the Nd:YAG powders was studied. Using the Nd:YAG powders as starting material, the corresponding Nd:YAG ceramics were fabricated by vacuum sintering, and the optical properties of them were investigated.

## 2. Experimental

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99.99%, Tianjin Fine Chemicals, China), Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.99%, Tianjin Fine Chemicals, China), Nd<sub>2</sub>O<sub>3</sub> (99.99%, Alfa Aesar Company, USA) and MgO (99.99%, Alfa Aesar Company, USA) were used as starting materials. Aqueous nitrate solutions of Mg<sup>2+</sup> and Nd<sup>3+</sup> were prepared by dissolving MgO and Nd<sub>2</sub>O<sub>3</sub> in diluted nitric acid under stirring and heating. The mixed solutions were prepared by dissolving required amount of the metal nitrates in

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a molar ratio of Nd:Y:Al = 0.03:2.97:5, and the amount of MgO to Nd<sub>0.03</sub>Y<sub>2.97</sub>Al<sub>5</sub>O<sub>12</sub> was controlled to 0 wt.%, 0.008 wt.%, 0.01 wt.% and 0.012 wt.%, respectively. The precipitates were synthesized by drop-wise addition of 1 M NH<sub>4</sub>HCO<sub>3</sub> into the nitrate solution under constant stirring, until a pH equal to 8.2 was obtained. After titration, the suspensions were aged for 24 h, and then filtered and washed with distilled water and ethanol in sequence. After washing, the resulting products were dried at 60 °C for 24 h. The obtained Nd:YAG precursors were calcined at different temperatures for 2 h in air.

TEOS (0.5 wt.%) was added to the calcination Nd:YAG powders. The mixture was blended with the high-purity Al<sub>2</sub>O<sub>3</sub> balls for 10 h in ethanol. The milled slurries were dried and calcined at 800 °C in air. The purpose of calcinations was to remove the residual organic components, and to hydrolyze TEOS to yield SiO<sub>2</sub>, which is a true sintering aid during the sintering. After this, calcination powders were uniaxially pressed into pellet and then isostatically cold pressed at 250 MPa. Green compacts were sintered at 1750 °C for 20 h under vacuum. After sintering, the specimens were annealed at 1450 °C for 20 h in air to eliminate oxygen vacancies formed during vacuum sintering. These defects resulted in the distortion of the lattice, and then lead to a different index of refraction and decrease the optical properties of the specimens. The annealed specimens were mirror polished on both surfaces.

Thermal behaviors of the Nd:YAG precursors were studied using 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 formation process of the Nd:YAG powders was identified by X-ray diffraction (XRD, Model D/MAX-2550V, Rigaku, Japan). Dispersion state and morphologies of the Nd:YAG powders were examined using scanning electron microscopy (SEM, JSM-6700, JEOL, Japan). The optical transmittance was measured using mirror-polished samples (Model U-2800 Spectrophotometer, Hitachi, Japan).

### 3. Results and discussion

TG–DTA curves of the original precursor with 0.01 wt.% MgO are presented in Fig. 1. In the temperature range of 100–200 °C, endothermic peak appears which is attributed to the evaporation of molecular water. Major mass loss of the precursor takes place below 800 °C, corresponding to about 95% of the total weight loss. The broad endothermic peak appears in the range of 250–800 °C, due to the decomposition of carbonate, nitrate and hydroxyl ion. There is no weight loss in the TG curve above 900 °C. A distinct exothermic peak at 949 °C in the DTA curve indicates the crystallization of YAG phase. The latter exothermic peak at 1050 °C is only attributed to the further decomposition and oxidization of the intermediate phase of carbonates.<sup>16</sup> The XRD (Fig. 2) results do not allow relating it to a new phase appearance.<sup>17</sup>

Fig. 2 shows XRD patterns of the Nd:YAG powders with 0.01 wt.% MgO and calcined at various temperatures for 2 h. The powders remain amorphous when the calcination temperature is below 800 °C. After calcinations at 900 °C for 2 h, phase-pure

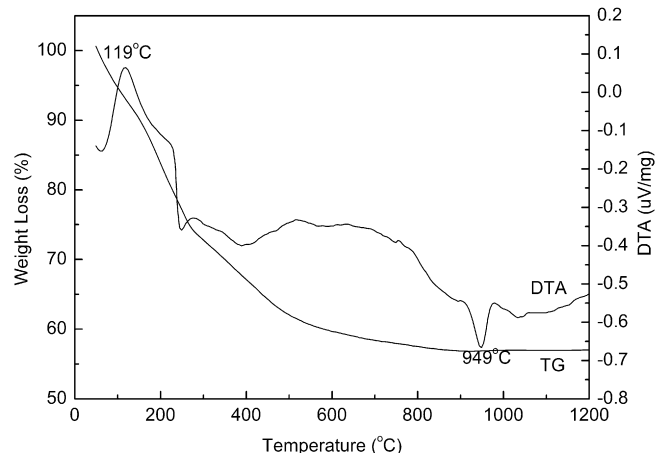


Fig. 1. TG–DTA curves of the original precursor.

cubic YAG containing no other phase is obtained. This crystallization temperature is lower than that detected by DTA, because the exothermic peak in the DTA often lags behind crystallization as a result of the hysteresis of temperature.<sup>15</sup> Further heating of the powders to 1000 °C, continued refinement of peak shapes and intensities is detected, indicating crystalline growth of the Nd:YAG powders as the temperature increases, meanwhile there is no appearance of phase transformation.

The dispersion state of the Nd:YAG powders calcined at 1000 °C changes significantly with MgO content (Fig. 3). The powders without MgO are mainly composed of larger, hard aggregates of around 500 nm size (Fig. 3(a)). For MgO dopant of 0.008 wt.%, the agglomerate size is 300 nm, and for 0.01 wt.%, elliptical particles of around 100 nm diameter are observed (shown in Fig. 3(b) and (c)). These results can be understood by considering that MgO can react with Al<sub>2</sub>O<sub>3</sub> to yield an intergranular phase (MgAl<sub>2</sub>O<sub>4</sub>) during the calcinations of precipitate precursors.<sup>18,19</sup> MgAl<sub>2</sub>O<sub>4</sub> can increase the surface energy of the grain boundary, thus decrease sintering activity of Nd:YAG particles at a relatively lower temperature stage (1000 °C), which contribute to better dispersion of the Nd:YAG powders.

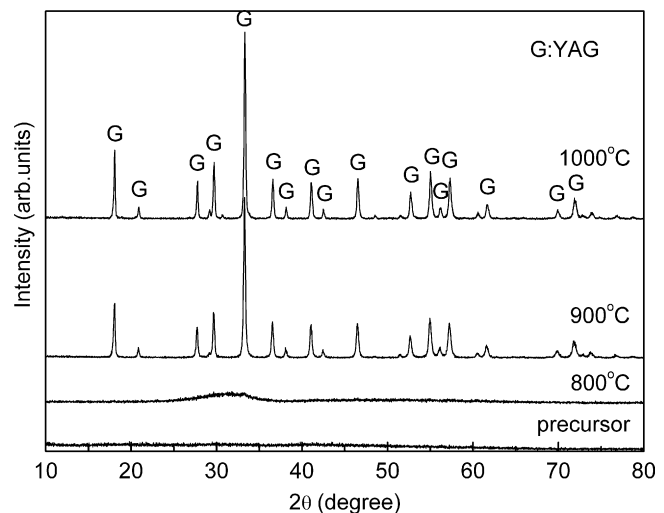


Fig. 2. XRD patterns of the Nd:YAG powders calcined at different temperatures.

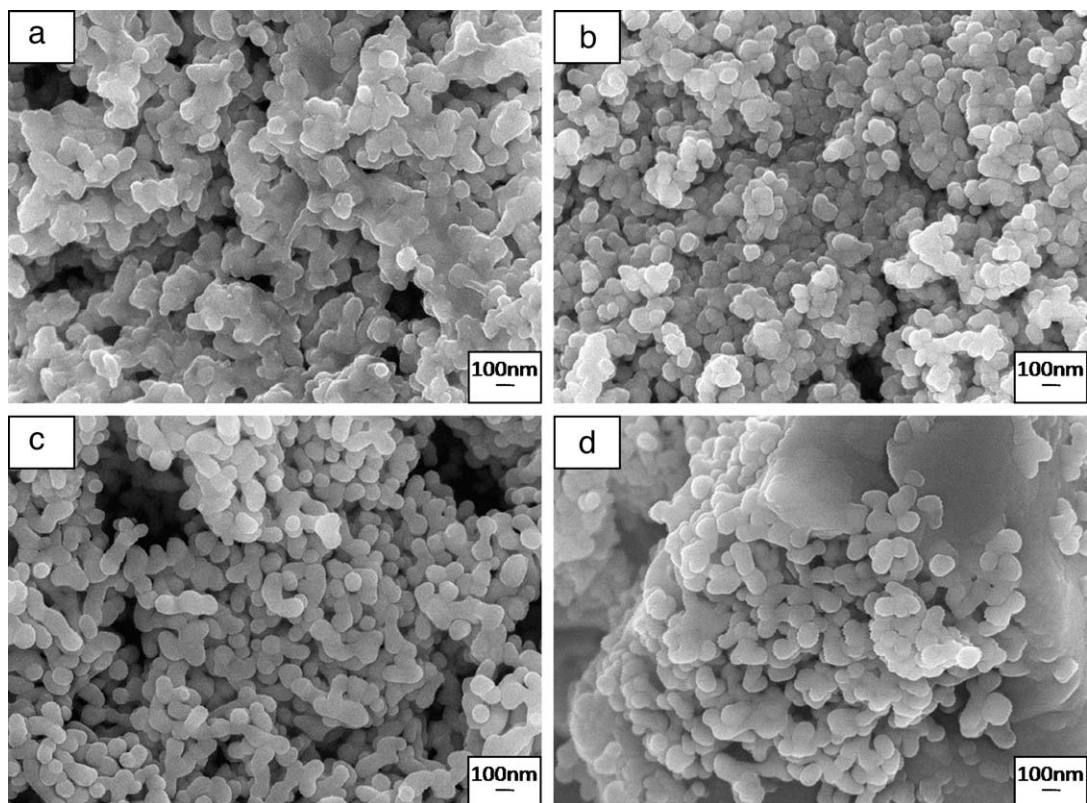


Fig. 3. SEM images of the Nd:YAG powders with various weight ratios of MgO. (a) Without MgO; (b) 0.008 wt.%; (c) 0.01 wt.%; and (d) 0.012 wt.%.

However, the amount of MgO increases to 0.012 wt.%, excess  $\text{MgAl}_2\text{O}_4$  will be yielded, leaving some residual inclusions in the Nd:YAG powders, and then a relatively severe agglomeration appears again (Fig. 3(d)). In general, MgO doping is used mainly for the purpose of suppressing agglomeration of ultra-fine Nd:YAG particles, and therefore will be no more added once such suppressing effects have been attained, which has been confirmed by Fig. 3(d).

Fig. 4 shows TEM images of the Nd:YAG particles with various MgO content calcined at 1000 °C for 2 h. The addition of MgO has a significant effect on the morphology of the Nd:YAG

powders. The Nd:YAG powders without MgO are agglomerated hard, and their averaged size is 500 nm (Fig. 4(a)). In contrast, the powders with 0.01 wt.% MgO are well dispersed, as shown in Fig. 4(b). The average grain size of the spherical particles is 100 nm. The results indicate that MgO dopant can effectively suppress the abnormal growth of the Nd:YAG grains during the calcinations process. The high-quality powders can be synthesized, which is vital for the following sintering process.

Fig. 5(a) shows a photograph of the mirror polished Nd:YAG ceramics sintered at 1750 °C for 20 h after annealing at 1450 °C for 20 h. The specimen with MgO of 0.01 wt.% exhibits a good

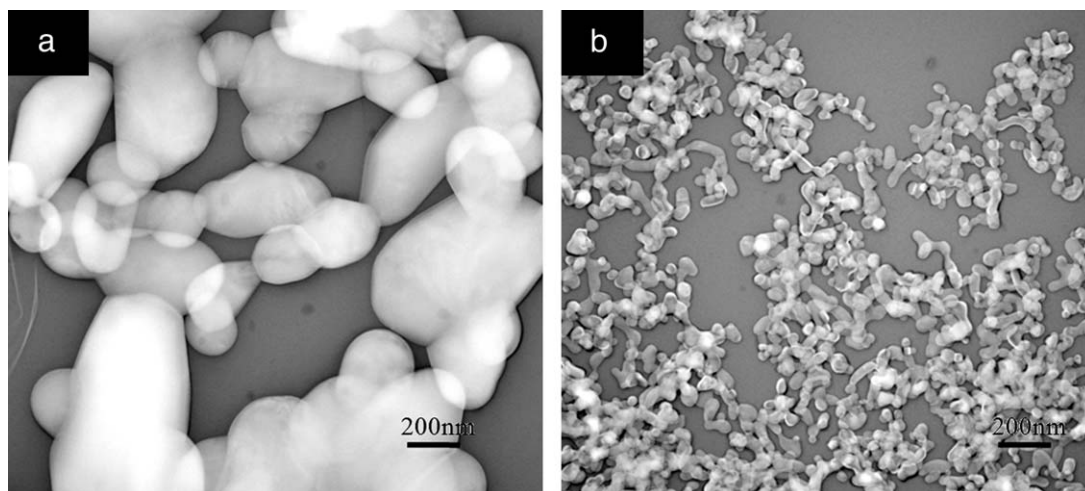


Fig. 4. TEM images of the Nd:YAG powders with various weight ratios of MgO. (a) Without MgO and (b) 0.01 wt.%.

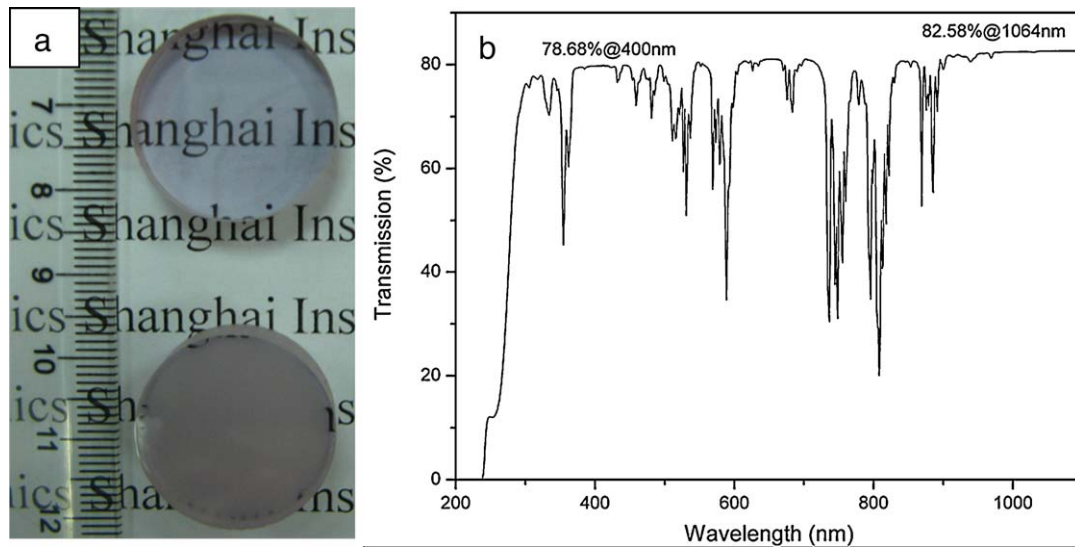


Fig. 5. Photo and transmission of Nd:YAG ceramics ( $\text{\O}20 \times 3$  mm) with various weight ratios of MgO. (a) 0.01 wt.% (upper); without MgO (lower); and (b) 0.01 wt.%.

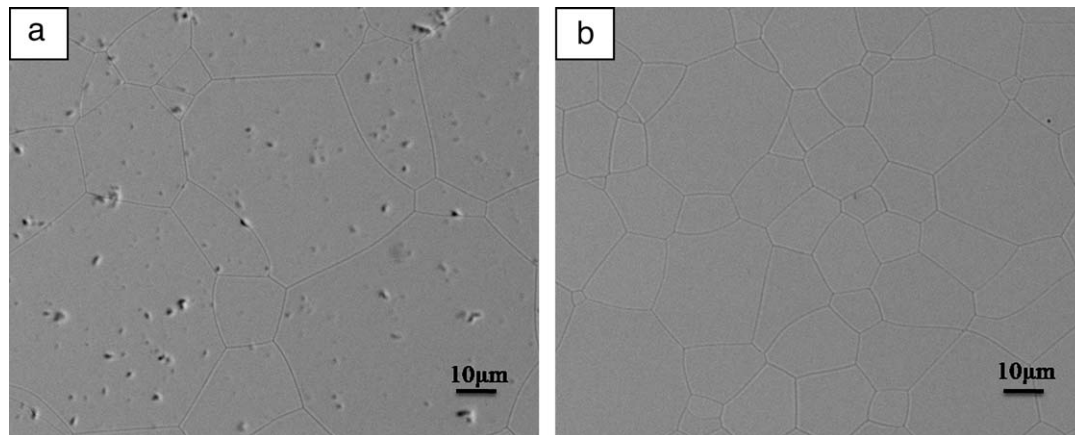


Fig. 6. EPMA images of the Nd:YAG ceramics with various weight ratios of MgO. (a) Without MgO and (b) 0.01 wt.%.

transparency than the undoped specimen (Fig. 5(a)). SEM observation (Fig. 6(b)) of the doped ceramics reveals that the sample has a homogenous microstructure and no pores or other phases can be observed. The fine microstructure of ceramics can be attributed to well-dispersed and high sintering-active powders. The undoped Nd:YAG ceramics is opaque (lower in Fig. 5(a)). This is because of scattering centers in the ceramics such as pores and inclusions (shown in Fig. 6(a)), which can result in a different index of refraction. The powders without MgO present some hard agglomeration (Fig. 3(a)). Large pores are difficult to remove during sintering and are entrapped in the ceramics.

Light transmission is the main parameter for measuring the optical properties of transparent ceramics. The transmission of the Nd:YAG ceramic with 0.01 wt.% MgO over the wavelength range of 200–1100 nm is shown in Fig. 5(b). The optical transmission is 82.6% at the wavelength of 1064 nm. The optical properties of the Nd:YAG ceramic are very close to those of single crystal.<sup>3,20</sup> The result indicates that proper MgO doping can improve the optical properties of the Nd:YAG ceramics.

#### 4. Conclusion

In the present study, high sintering-active Nd:YAG powders can be prepared with the addition of MgO by co-precipitation method. The precursors are converted directly to phase-pure cubic YAG at about 900 °C. The results show that different MgO additions have a significant impact on the dispersion state of the final Nd:YAG powders. The optimum amount of MgO for the preparation of well-dispersed spherical Nd:YAG powders with an average particle size of 100 nm is 0.01 wt.%. The corresponding transparent ceramic is obtained under vacuum sintering, and its transmission is 82.6% at the wavelength of 1064 nm.

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