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Preparation of spray-dried powders leading to Nd:YAG ceramics: The effect of PVB adhesive

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Abstract

The mixed powders were obtained with Al_2O_3, Y_2O_3 and Nd_2O_3 powders as starting materials using spray drying technology. The main purpose of introducing polyvinyl butyral (PVB) is to contribute to spray granulation of the powders and inhibition of the compositions segregation. The effect of the addition of PVB (0, 1, 2, and 3 wt%) on the morphologies and compositions of the spray-dried powders is discussed. When calcined at 1000 °C for 2 h, the powders with PVB as an adhesive show sphericity and better dispersion. No compositions segregation can be detected. It is found that the powders with 2 wt% PVB after calcinations are suitable for the fabrication of Nd:YAG transparent ceramics. The corresponding ceramics consists of a well-defined microstructure, and no pores or other defects are observed.

Keywords: C. Optical properties; PVB adhesive; Powder technology; Nd:YAG ceramics

1. Introduction

Nd:YAG ceramics are considered to be an alternative to single crystal as laser material because of low price, ease of manufacture, mass-production, high concentration doping, and better homogeneity of the doping ions [1]. Thus, in recent years, various techniques have been made to synthesize Nd:YAG materials. The synthesis methods of the Nd:YAG nanopowders by wet-chemical process require great skills [2–8]. Both concentrations of Y^{3+} and Al^{3+} for producing precipitations and their depositing velocities are different, it is quite possible that molar ratio of Y:Al will deviate from 3:5 in local areas [9]. Nevertheless, agglomeration of the Nd:YAG nanopowders still remains as the most common concern for wet-chemical methods. Nd:YAG ceramics have been fabricated by solid-state reaction method using Al_2O_3, Y_2O_3 and Nd_2O_3 powders as starting materials [10,11]. The stoichiometric proportions of the samples can be controlled easily. Meanwhile, the repeated mechanical mixing also contributes to reduce the agglomeration of the powders.

It is well known that the properties of Nd:YAG ceramics are closely related with the mixed powders characteristics, including size distribution, particle shape, degree of agglomeration, chemical composition. The drying techniques of the mixed slurries are also the main factor in the characteristics of the powders. The conventional oven drying easily causes severe agglomeration and poor sinterability of the powders. Spray drying technology is a unique and simple method for the obtained powders with good dispersibility and sinterability [12]. PVB is a kind of cheap and common adhesive which has been widely used during spray drying process. The addition of PVB as an adhesive helps to inhibit compositions segregation and promote spray granulation, and then improve the properties of the spray dried powders.

In our work, the spherical powders with very good chemical homogeneity were obtained using PVB as an adhesive during spray drying process. The effect of PVB on morphologies and compositions of the spray-dried powders was investigated. The microstructures and optical properties of Nd:YAG ceramics were also studied.

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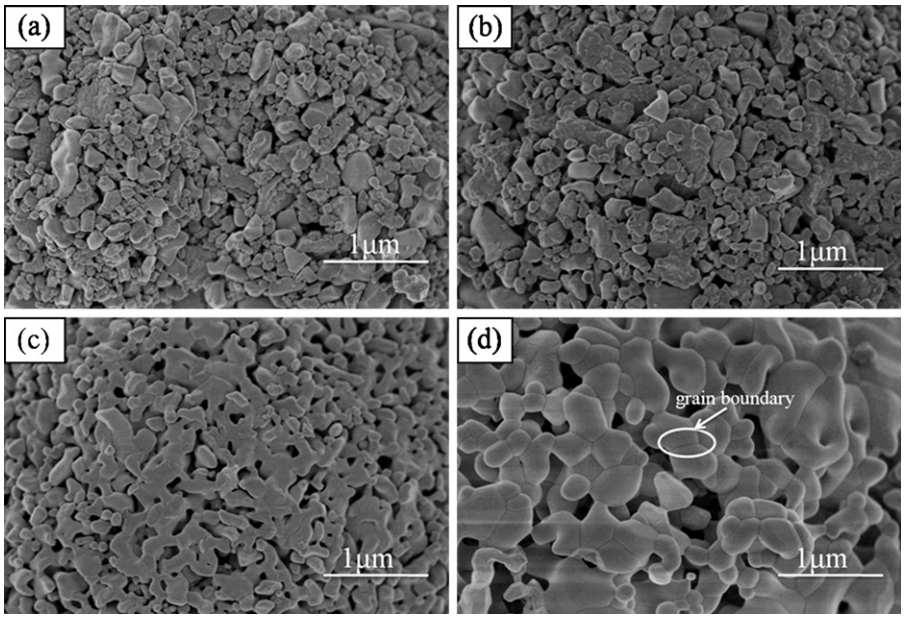

Fig. 1. SEM images of the powders with 3 wt% PVB calcined at (a) 800 °C, (b) 1000 °C, (c) 1200 °C and (d) 1400 °C for 2 h.

2. Experimental procedure

High-purity Al_2O_3 (99.99%), Y_2O_3 (99.99%), and Nd_2O_3 (99.99%) powders were used as staring materials. These powders were blended together according to the stoichiometric ratio of 0.8 at% Nd:YAG and were ball-milled with high-purity Al_2O_3 balls for 12 h in anhydrous alcohol, with 0.5 wt% TEOS as a sintering aid and (0, 1, 2 and 3 wt%) polyvinyl butyral (PVB) as an adhesive. The solid content of the all slurries maintain 46.43 wt%. The milled slurries were dried using spray drying technology, and then calcined in the air to remove the residual organic components. The four calcined powders were dry-pressed under 100 MPa into Φ30 disks and finally cold isostatically pressed under 250 MPa. Green compacts were sintered at 1750 °C for 20 h under vacuum (1.0×10^{-3} Pa) 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.

Fourier transform infrared spectra of the calcined powders were measured in the range of 4000–400 cm^{-1} by a Nicolet IR200 spectrometer (FTIR, Nexus470, Nicolet, MA, USA). The mass ratio of Y_2O_3, Al_2O_3 and Nd_2O_3 of the spray-dried powders were analyzed by chemical analysis and inductively coupled plasma atomic emission spectrometer (ICP-AES, Vista AX CCD, Varian, Santa Clara, USA). The morphologies of the spray-dried powders were examined using scanning electron microscopy (SEM, JSM-6700, JEOL, Tokyo, Japan). The particle size distributions were measured by light through sedimentation method using particle-size analyzer (Sedigraph III 5120, Micromeritics, Norcross, USA). Microstructures of the polishing surfaces of the Nd:YAG ceramics were observed by electron probe microprobe analysis (EPMA, Model JXA-8100, JEOL, Tokyo, Japan). Mirror-polished specimens on both surfaces were used to measure optical transmittance (Model U-2800 Spectrophotometer, Hitachi, Tokyo, Japan).

3. Results and discussion

Fig. 1 shows SEM images of the spray-dried powders with 3 wt% PVB calcined at different temperatures (800, 1000, 1200 and 1400 °C) for 4 h. The same SEM results of the other three samples are also obtained. The morphologies of the mixed powders remain unchanged when the calcination temperature is below 1000 °C. After calcinations at 1200 °C for 2 h, the solid state reaction between Y_2O_3 and Al_2O_3 powders happens. Intermediate phases, like $Y_4Al_2O_9$ (YAM) and $YAlO_3$ (YAP) are commonly found during reaction [13]. Further heating of the powders to 1400 °C, many grain boundaries appear in the calcined powders (shown in Fig. 1(d)), the particle sizes become large, which lead to decreasing of the sintering activity of the powders.

Fig. 2 shows the FTIR spectra of the spray-dried powders without PVB (a) and with 3 wt% PVB (b) after calcinations at

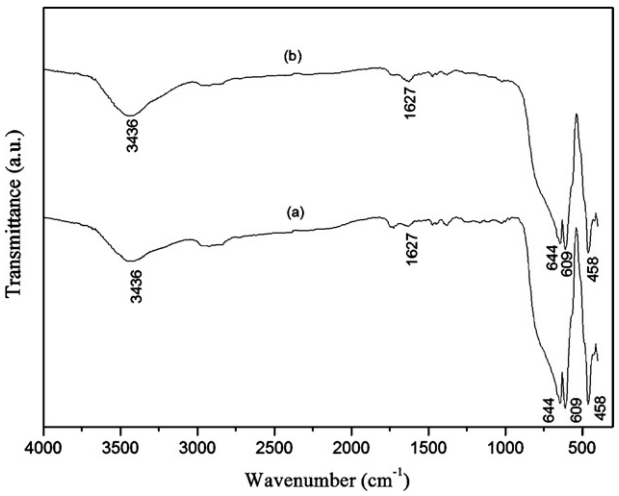

Fig. 2. FTIR spectra of the powders with various weight ratios of PVB: (a) without PVB and (b) 3 wt%.

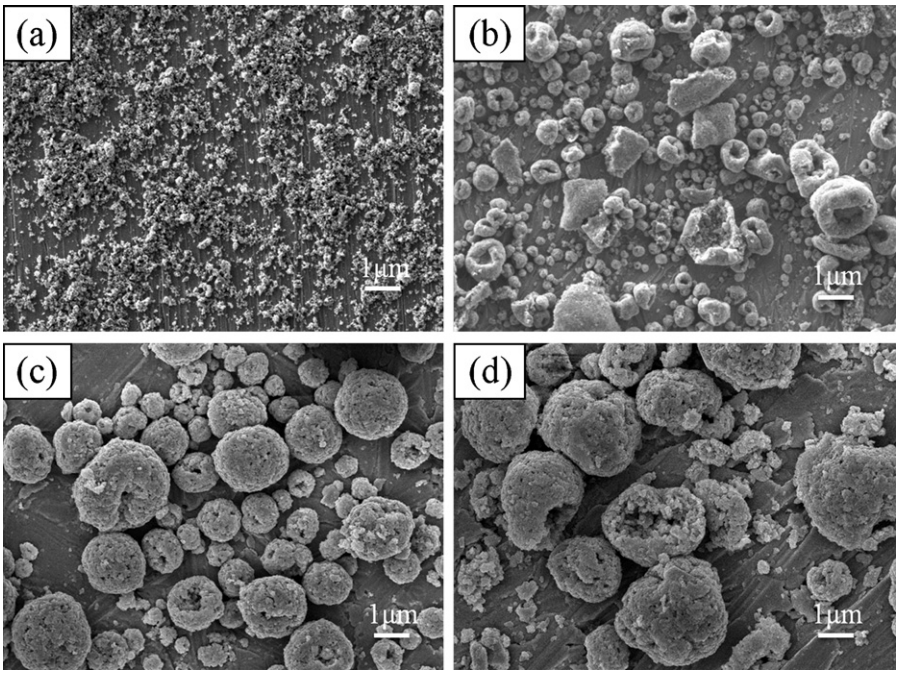

Fig. 3. SEM images of the spray-dried powders with various weight ratios of PVB calcined at 1000 °C for 2 h: (a) without PVB, (b) 1 wt%, (c) 2 wt% and (d) 3 wt%.

1000 °C for 2 h. The wide peaks around 3436 cm^{-1} can be assigned to stretching vibration of O–H and 1627 cm^{-1} to O–H bands of absorbed water [14]. Furthermore, in the 800–400 cm^{-1} (at 458, 609, and 644 cm^{-1}) region of the IR spectra the observed specific peaks may be attributed to characteristic metal–oxygen vibrations of the mixed powders [15]. There are no any characteristic vibrations of the PVB in Fig. 2(b), indicating the PVB is completely removed from the spray-dried powder calcined at 1000 °C for 2 h. It is very important to ensure the optical properties of the subsequent Nd:YAG ceramics.

Fig. 3 shows SEM micrographs of the spray-dried powders with different PVB contents calcined at 1000 °C for 2 h, respectively. The powders without PVB are mainly composed of small, loose aggregates of around 0.28 μm (Figs. 3(a) and 4(a)).

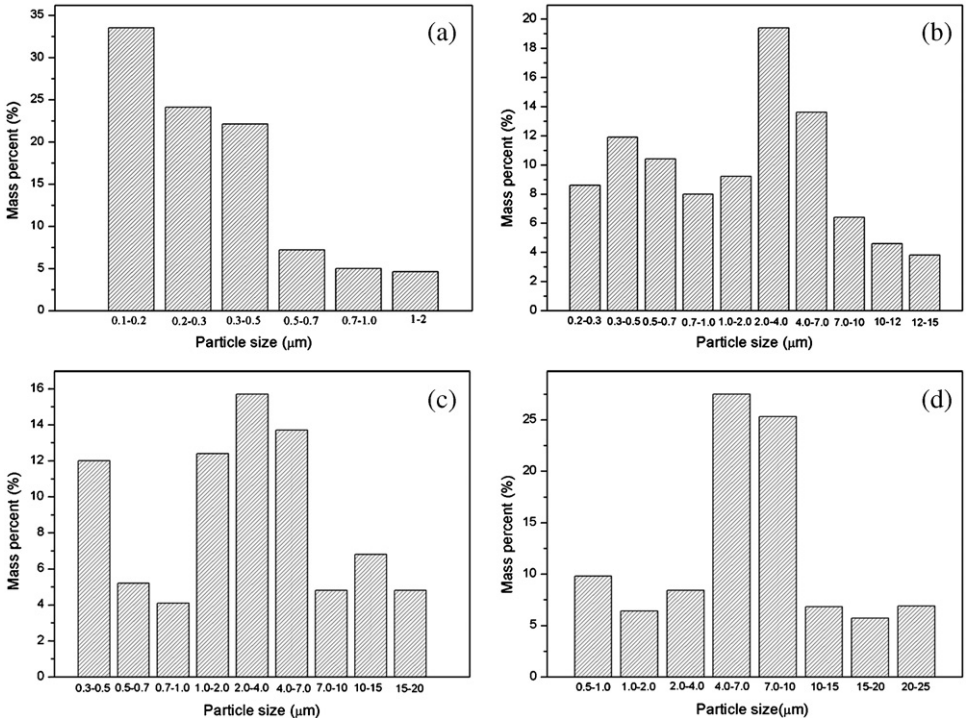

Fig. 4. Particle size distributions of the spray-dried powders with various weight ratios of PVB calcined at 1000 °C for 2 h: (a) without PVB, (b) 1 wt%, (c) 2 wt% and (d) 3 wt%.

The content of PVB is 1 wt%, the particles of around 1.8 μm diameter (Fig. 4(b)) show shriveled surfaces and irregular shapes (Fig. 3(b)). For PVB dopant of 2 wt%, the sample, with best powders flowability, shows relatively big spherical particles with smooth surfaces (Fig. 3(c)), the average size of the aggregates is 2.8 μm (Fig. 4(c)). In contrast, if the amount of PVB increases to 3 wt%, the average particle size of the powders is 3.7 μm, which is the largest than those of the four samples (Fig. 3(d)). These results can be understood by considering that PVB can increase bonding among the oxides powders, which contributes to spray granulation of the powders. On the other hand, the fast flow rate of the high-pressure nitrogen produces strong shear stress during spray drying process, if there is no PVB as an adhesive, the weak bonding among the oxides powders will lead to excessive loss of the Al_2O_3 through the exhaust port of the spray-dried device under shear stress, for the reason that the specific gravity of Al_2O_3 is the lowest among the three oxide powders (Al_2O_3, Nd_2O_3 and Y_2O_3). The molar ratio of (Nd + Y):Al of the powders is 0.65, which seriously deviates from the theoretical value (0.6) (shown in Table 1). If using PVB as an adhesive enhances bonding between the oxides powders, the composition segregation will be controlled. The (Nd + Y):Al of molar ratios of the powders are all very close to 0.6 (shown in Table 1), which is vital for the following sintering process.

Fig. 5 shows SEM micrographs of the four specimens. Many secondary phases can be found in the specimen A (shown in Fig. 5(a)). This is because that superfluous Y_2O_3 is prone to diffuse along the YAG grain boundaries during the sintering process. When the (Nd + Y):Al molar ratio of the powders is very close to 0.6, No grain boundary phases exit in the corresponding ceramics. However, several pores are trapped into grain which can be observed in Fig. 5(b), because the sizes of a portion of particles are too small (Fig. 3(b)), it is easy to cause the insufficient grain growth, compared with the particle of large sizes. These pores are sometimes the main reason for low transparency. Fig. 5(c) reveals that the specimen C has a homogenous microstructure, and no pores or other defects can be observed. The fine microstructure of ceramics may be attributed to well-dispersed and high sintering-active powders. If using more PVB result in further enlargement of the mean particle size of spray-dried powders (Fig. 4(d)), severe abnormal grain growth will appear in the specimen D (shown in Fig. 5(d)). In general,

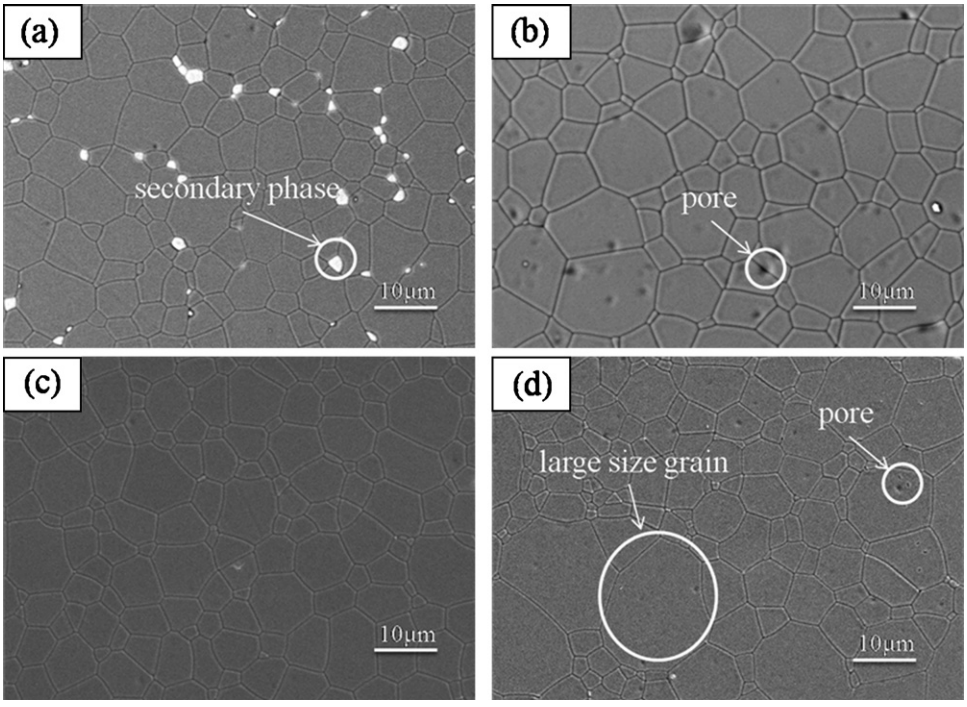

Fig. 5. EPMA images of the Nd:YAG ceramics fabricated from the calcined powders with various weight ratios of PVB: (a) without PVB, (b) 1 wt%, (c) 2 wt% and (d) 3 wt%.

Table 1
Mass ratio of Y_2O_3, Al_2O_3 and Nd_2O_3 of the spray-dried powders with various weight ratios of PVB calcined at 1000 °C for 2 h: (a) without PVB, (b) 1 wt%, (c) 2 wt%, and (d) 3 wt%.

Mass (%)	*a*	*b*	*c*	*d*	Theoretical values
Y_2O_3	58.34	56.93	56.79	56.76	56.47
Al_2O_3	41.24	42.50	42.70	42.80	42.84
Nd_2O_3	0.72	0.66	0.67	0.66	0.68
(Nd + Y):Al (molar ratio)	0.65	0.609	0.603	0.603	0.60

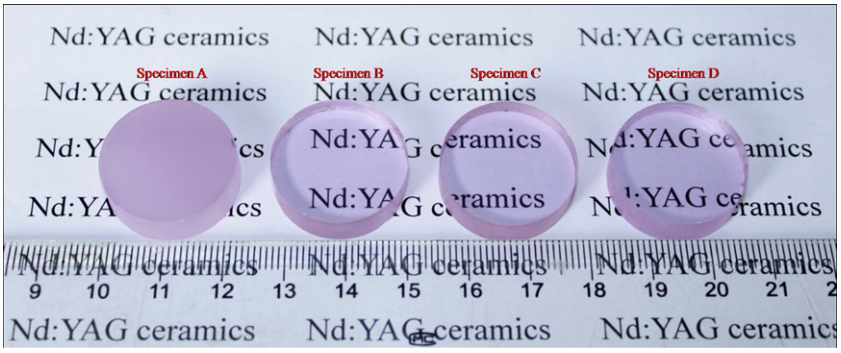

Fig. 6. Photographs of the specimens A, B, C and D with the thickness of 3 mm.

PVB adhesive is used mainly for the purpose of spray granulation of the powders and control of composition segregation, and therefore will be no more added once such suppressing effects have been attained, which can be confirmed by Fig. 6(d).

Fig. 6 shows the photographs of the specimens A, B, C and D with the thickness of 3 mm. The specimen A is opaque as the result of the secondary phases which act as scattering centers. But the other three specimens are transparent. The result shows that the composition segregation has significant effect on the optical qualities of Nd:YAG ceramics. The transmission of specimen C from 300 to 1100 nm is the best of all (shown in Fig. 7). It indicates that the control of the powder qualities, including the particle size, size distribution, morphology, and distribution of element, contributes to refine the microstructure of the sintered body, and then improves the optical properties of the Nd:YAG ceramics [16]. According to the Rayleigh's equation, the scattering intensity increases proportionally with λ^{-4}, where λ is the wavelength [17]. The transmission of the specimen C decreases with the decreasing of wavelength. It can be hypothesized that some scattering centers exit in the ceramics only cannot be detected, such as pores, inclusions. Furthermore, the surface roughness of the Nd:YAG ceramics is not well because of inhibition of the manual polishing technology, which also make the transmittance decrease.

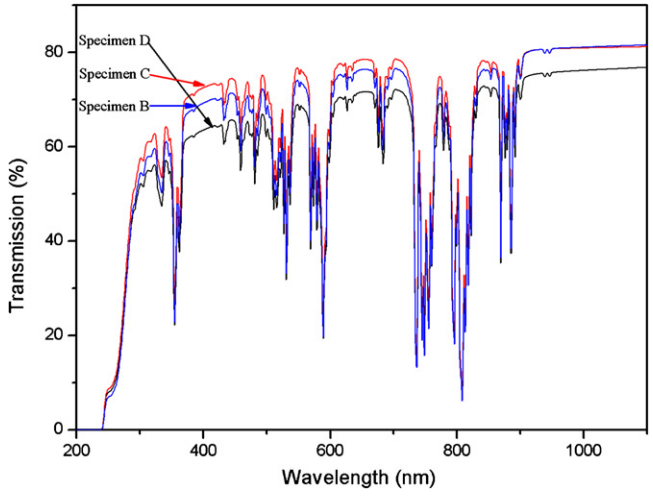

Fig. 7. Transmission of the specimens B, C and D.

4. Conclusion

In the present study, the addition of PVB is helpful for spray granulation of the powders and control of compositions segregation during spray drying process. If there is no PVB, the composition segregation will occur in the spray-dried powders, the subsequent ceramics is opaque. The powders with PVB as an adhesive after calcinations at 1000 °C for 2 h show good dispersion and sintering activity. The optimum amount of PVB for preparation of spray-dried powders is 2 wt%, the corresponding ceramics exhibits the best transparency, no pores, abnormal grains growth or other defects can be observed.

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References

[1] J. Lu, K. Ueda, H. Yagi, T. Yanagitani, A. Kudryashov, A.A. Kaminskii, Potential of ceramic YAG lasers, Laser Phys. 11 (10) (2001) 1053–1057.
[2] W.B. Liu, W.X. Zhang, J. Li, H.M. Kou, Y.Q. Shen, L. Wang, Y. Shi, Influence of pH values on (Nd + Y):Al molar ratio of Nd:YAG nanopowders and preparation of transparent ceramics, J. Alloys Compd. 503 (2010) 525–528.
[3] R. Singh, R.K. Khardekar, A. Kumar, D.K. Kohli, Preparation and characterization of nanocrystalline Nd-YAG powder, Mater. Lett. 61 (2007) 921–924.
[4] M. Suárez, A. Fernández, J.L. Menéndez, M. Nygren, R. Torrecillas, Z. Zhao, Hot isostatic pressing of optically active Nd:YAG powders doped by a colloidal processing route, J. Eur. Ceram. Soc. 30 (2010) 1489–1494.
[5] M.L. Saladino, G. Nasillo, D.C. Martino, E. Caponetti, Synthesis of Nd:YAG nanopowder using the citrate method with microwave irradiation, J. Alloys Compd. 491 (2010) 737–741.
[6] J. Li, Y.B. Pan, F.G. Qiu, Y.S. Wu, W.B. Liu, J.K. Guo, Synthesis of nanosized Nd:YAG powders via gel combustion, Ceram. Int. 33 (2007) 1047–1052.
[7] H. Gong, D.Y. Tang, H. Huang, J. Ma, Agglomeration control of Nd:YAG nanoparticles via freeze drying for transparent Nd:YAG ceramics, J. Am. Ceram. Soc. 92 (2009) 812–817.
[8] X. Li, Q. Li, J.Y. Wang, S.L. Yang, H. Liu, Synthesis of Nd^{3+} doped nanocrystalline yttrium aluminum garnet (YAG) powders leading to transparent ceramic, Opt. Mater. 29 (2007) 528–531.
[9] S.H. Tong, T.C. Lu, W. Guo, Synthesis of YAG powder by alcohol–water co-precipitation method, Mater. Lett. 61 (2007) 4287–4289.

[10] W.B. Liu, B.X. Jiang, W.X. Zhang, J. Li, J. Zhou, D. Zhang, Y.B. Pan, et al., Influence of heating rate on optical properties of Nd:YAG laser ceramic, Ceram. Int. 36 (2010) 2197–2201.
[11] J. Li, W.S. Wu, Y.B. Pan, W.B. Liu, L.P. Huang, J.K. Guo, Fabrication, microstructure and properties of highly transparent Nd:YAG laser ceramics, Opt. Mater. 31 (2008) 6–17.
[12] A. Ikesue, K. Yoshida, Influence of pore volume on laser performance of Nd:YAG ceramics, J. Mater. Sci. 34 (1999) 1189–1195.
[13] S.H. Lee, S. Kochawattana, G.L. Messing, J.Q. Dumm, G. Quarles, V. Castillo, Three-dimensional grain boundary spectroscopy in transparent high power ceramic laser materials, J. Am. Ceram. Soc. 89 (2006) 1945–1950.
[14] J. Su, Q.L. Zhang, C.J. Gu, D.L. Sun, Z.B. Wang, H.L. Qiu, Preparation and characterization of $Y_3Al_5O_{12}$ (YAG) nano-powder by co-precipitation method, Mater. Res. Bull. 40 (2005) 1279–1285.
[15] X. Li, H. Liu, J.X. Wang, H.M. Cui, F. Han, Production of nanosized YAG powders with spherical morphology and nanoaggregation via a solvothermal method, J. Am. Ceram. Soc. 87 (2004) 2288–2290.
[16] J.Q. Wang, S.H. Zheng, R. Zeng, S.X. Dou, X.D. Sun, Microwave synthesis of homogeneous YAG nanopowder leading to a transparent ceramic, J. Am. Ceram. Soc. 92 (2009) 1217–1223.
[17] A. Ikesue, K. Kamata, T. Yamamoto, I. Yamaga, Optical scattering centers in polycrystalline Nd:YAG laser, J. Am. Ceram. Soc. 80 (1997) 1517–1522.