Journal of Alloys and Compounds 502 (2010) 206–210

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effects of aging on the characteristics of Nd:YAG nano-powders

Xiaolin Zhang, Duo Liu*, Yuanhua Sang, Hong Liu, Jiyang Wang

State Key Laboratory of Crystal Materials, Shandong University, 27 South Shanda Road, Jinan, Shandong 250100, PR China

ARTICLE INFO

Article history:
Received 29 January 2010
Received in revised form 15 April 2010
Accepted 17 April 2010
Available online 15 May 2010

Keywords:
Ceramics
Precipitation
X-ray diffraction
Scanning electron microscopy

ABSTRACT

We report here the synthesis of homogeneous and fine Nd:YAG (Nd:$Y_3Al_5O_{12}$) nano-powders via the microwave-assisted precipitation (MAP) method followed by calcination at 1373 K for 2 h. We find that the phase, morphology, and sinterability of the Nd:YAG nano-powders are affected remarkably by the conditions of aging. It is confirmed that aging should be performed in enclosed environment in order to obtain uniform and pure phase Nd:YAG nano-powders. The Nd:YAG nano-powders obtained from the precursors aged in enclosed vessel for 6 days showed better sinterability and finer grains than those aged in air. Transparent Nd:YAG ceramic pellet was obtained by vacuum sintering at 2003 K for 10 h (a transmittance of 75%) from the Nd:YAG nano-powders aged in enclosed vessel for 6 days.

1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) is a synthetic crystal of complex cubic oxide, best known as laser host materials due to its excellent mechanical, thermal, and optical stabilities. As a four level laser medium, neodymium-doped YAG (Nd:YAG) has narrow fluorescence emission and is widely used to realize laser operation with high output and low threshold, which does not need charge compensation due to direct replacement of Nd^{3+} to Y^{3+} in YAG lattices. In 1995, Ikesue et al. [1] reported successful fabrication and laser operation of transparent Nd:YAG ceramics with optical properties nearly the same as those of YAG single crystal. In addition, Nd:YAG ceramics show technical advantages over their single crystal counterparts in ways such as greater Nd^{3+} concentrations, lower processing cost [2], better mechanical and thermal stabilities, and lower processing temperature (~2023 K) [3]. It is also worthy of mention that YAG powders doped with rare earth ions, e.g. Ce^{3+} [4], Eu^{3+} [5,6], Tb^{3+} [7], have recently received considerable interest as phosphors on white light emitting diodes (LEDs).

The processing of transparent YAG ceramics requires high quality ceramic powders with controllable and enhanced sinterability. Nanosized powders of single dispersion and uniform shape without agglomeration are highly demanded to achieve excellent optical and thermal homogeneities. A variety of methods, such as (1) the solvothermal method [8], (2) the spray pyrolysis method [9], (3) the microwave irradiation method [10], (4) the co-precipitation method [5], have been developed for the synthesis of YAG nano-powders. However, it still remains a challenge for the fabrication of the Nd:YAG nano-powders with desired sinterabilities and microstructures. From the fundamental point of view, the improved sinterability of nano-powders is closely linked to the enhanced diffusivity and creep rate of nanocrystalline materials. The boundary diffusivity of nanocrystalline materials is estimated to be $\sim 10^3$ times greater than that of conventional polycrystalline materials [11]. A reduction of grain size from 10 μm to 10 nm increases the creep rate by a factor of 10^9, which in combination with the boundary diffusivity leads to a total enhancement of sintering rate by 10^{12} [12]. As a result, nano-powders usually allow densification of ceramic pellets at much lower temperatures. However, reduced particle sizes also greatly increase the surface areas where impurity ions and chemical species may accumulate, which may eventually lead to the formation of pores and secondary phases during the processing of ceramic products. These microstructural defects would significantly reduce the durability and optical performances of transparent ceramics. Consequently, controlled synthesis of Nd:YAG nano-powders with predictable and stable microstructures is crucially of importance for fabricating high quality transparent Nd:YAG ceramics.

In view of chemical environments, the properties of nano-powders are affected by many factors, including (1) solvents [13,14], (2) precipitants [8], (3) dispersants [15], (4) calcined temperatures [16,17], (5) aging conditions [18,19], and (6) pH values [20]. Transparent Nd:YAG ceramics of excellent performance could be obtained from nano-powders synthesized only if all these factors are precisely controlled. As a result, an in-depth understanding of the chemical and physical processes occurred during the preparation of YAG nano-powders becomes important. In this paper, we report the synthesis of Nd:YAG nano-powders via the

---

* Corresponding author. Tel.: +86 531 88363901.
E-mail address: liuduo@sdu.edu.cn (D. Liu).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.04.144

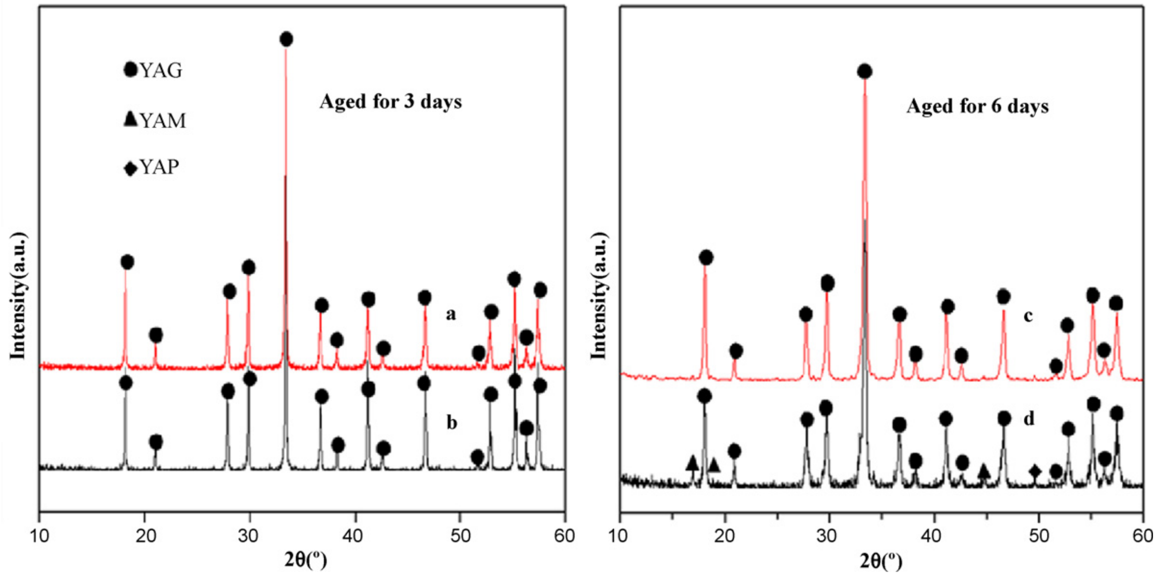

Fig. 1. XRD patterns of the Nd:YAG nano-powders obtained from the precursors aged under different conditions at room temperature (a and c: in enclosed vessel, b and d: in air), followed by calcination at 1373 K for 2 h.

microwave-assisted precipitation (MAP) method by using urea as the precipitant and we find that aging conditions can greatly affect the properties of the Nd:YAG nano-powders.

2. Experimental procedures

High purity Y_2O_3 and Nd_2O_3 powders (99.999%) were dissolved in nitric acids (99.99%) as the yttrium source. Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.999%) was dissolved in distilled water as the aluminum source. The concentrations of Y^{3+}, Nd^{3+} and Al^{3+} were carefully controlled. Urea ($CO(NH_2)_2$, AR) and ammonium sulfate ($(NH_4)_2SO_4$, AR) were used as the precipitant and dispersant, respectively. The ratio of $(NH_4)_2SO_4$ to starting materials was kept at 8 wt%. Urea was dissolved into this solution to achieve a ratio [urea]/[M] ([M]: the sum of mixed metal ions) of 25, and the molar ratio between (Y^{3+} + Nd^{3+}) and Al^{3+} ions was 3:5. The precursors were obtained by microwave treatment of the mixed aqueous solutions. The microwave-assisted reactions were carried out in a microwave oven operating at 2.45 GHz and 800 W for 54 min. Then, the precursors were aged for different time ranged from 1 day up to 26 days in either enclosed vessel or in air. All the experiments were conducted in clean room to avoid possible contaminations. The precursors were washed 3 times with distilled water and ethanol, respectively and then dried at 353 K overnight. The precursors were calcined at 1373 K for 2 h in a computer-controlled furnace. The resultant Nd:YAG nano-powders were examined by a X-ray diffractometer (XRD, D8-Advance, Bruker-AXS, Karlsruhe) and a scanning electron

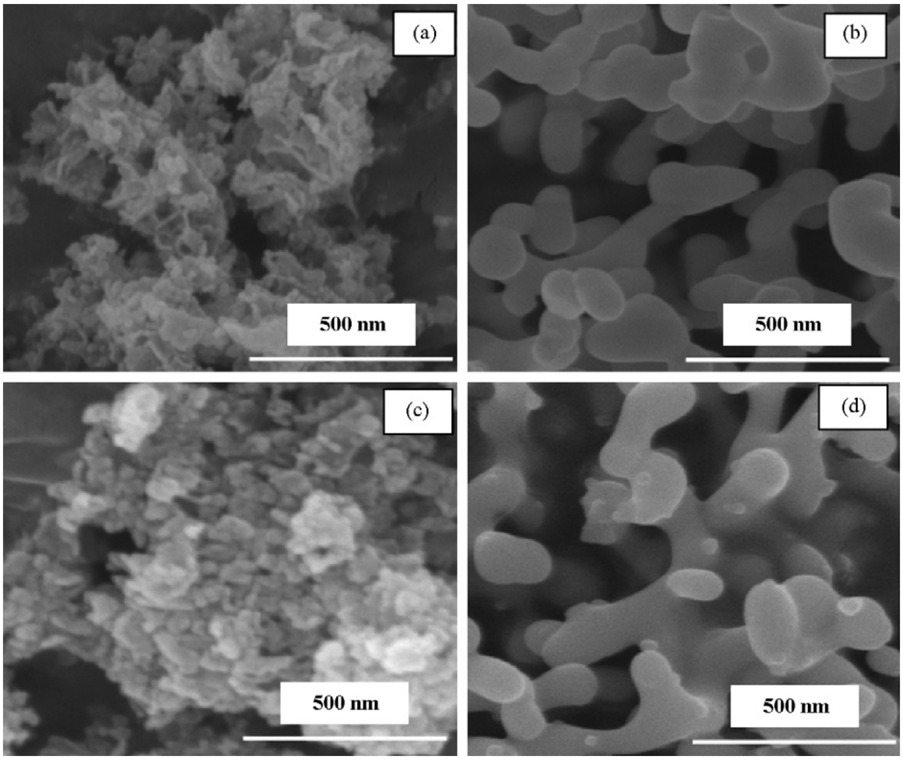

Fig. 2. SEM images of the precursors aged for 3 days at room temperature and the corresponding Nd:YAG nano-powders obtained after calcination at 1373 K for 2 h (a and b: in enclosed vessel, c and d: in air, a and c: the precursors, b and d: the nano-powders).

microscope (SEM, S-4800, Hitachi, Tokyo). The Nd:YAG nano-powders were uniaxially pressed into pellets at 200 MPa. The green compacts were sintered in a vacuum furnace at 2003 K for 10 h. The ceramic pellets were polished on both sides for transmittance measurement in the wavelength range of 300–900 nm by using a spectrophotometer (U-3500, Hitachi, Tokyo). The transmittance of a Nd:YAG single crystal sample was also measured for comparison.

3. Results and discussion

Nd:YAG nano-powders studied here were synthesized by using the microwave-assisted precipitation (MAP) with urea being the precipitant. Microwave irradiation enables dielectric and volumetric heating of the solution and thus facilitates homogeneous synthesis of the precursors in a very short time by simultaneously activating all reaction species. Microwave-assisted synthesis has been extensively used for the synthesis of advanced materials of various forms [21,22]. The reactions involved during the microwave treatment are summarized here. First, urea hydrolyzes at elevated temperature, e.g. above 356 K, to form $NH_3{\cdot}H_2O$ and H_2CO_3 [23], according to the equation:

$$H_2NCONH_2 + H_2O \xrightarrow{>356\,K} 2NH_3 \cdot H_2O + H_2CO_3$$

$NH_3{\cdot}H_2O$ and H_2CO_3 react to form $NH_4{}^+$, OH^-, and $CO_3{}^{2-}$. Al^{3+} and Y^{3+} ions then react with OH^- and $CO_3{}^{2-}$ according to the following equation [16]:

$$Al^{3+} + Y^{3+} + OH^- + CO_3{}^{2-} + H_2O \;\rightarrow\; Y_3Al_5(OH)_{(24-2x)}(CO_3)_x{\cdot}nH_2O$$

As a result, the resultant precursors have OH^- and $CO_3{}^{2-}$ groups exposed on their surfaces, resulting in high sensitivity of the precursors to air.

Previous studies indicated that both the precursors and the powders calcined below 1073 K are amorphous in nature [24]. Pure phase Nd:YAG nano-powders can be obtained when they are calcined at temperature exceeding 1123 K. Fig. 1 shows the XRD patterns of the Nd:YAG nano-powders obtained from the precursors aged under different conditions at room temperature (a and c: in enclosed vessel, b and d: in air), followed by calcination at 1373 K for 2 h. It can be seen that, under the same calcination conditions, the nano-powders obtained from the precursors aged in enclosed vessel are pure phase YAG (Fig. 1a and c). In contrast, although the sample obtained from precursors aged in air for 3 days shows no evidence of other phases (Fig. 1b), the sample obtained from precursors aged in air for 6 days show a small amount of YAM ($Y_4Al_2O_9$) and YAP ($YAlO_3$) phases (Fig. 1d). The results suggest that aging plays an important role for the synthesis of pure phase Nd:YAG nano-powders and the aging environment has to be carefully studied and controlled.

Fig. 2 shows the SEM images of the precursors aged for 3 days at room temperature and the corresponding Nd:YAG nano-powders obtained after calcination at 1373K for 2 h (a and b: in enclosed vessel, c and d: in air, a and c: the precursors, b and d: the nano-powders). It can be clearly seen that the morphologies are quite different for samples aged in enclosed vessel and in air. The precursors aged in enclosed vessel are of floccule in shape and uniformly distributed (Fig. 2a). In comparison, the precursors aged in air are of granule in shape (Fig. 2c). These results show that the effects of aging in enclosed vessel are different from those in air. Uniform Nd:YAG nano-powders of elliptical shape were obtained after aging the precursors in enclosed vessel, as shown in Fig. 2b. In contrast, the nano-powders obtained after aging in air show a lot of tiny grains attached on large ones (Fig. 2d). The presence of these small grains could be deleterious to fabricating Nd:YAG transparent ceramics due to their distinct thermodynamic behaviors during sintering. Our results also indicate that aging behaviors of the precursors rely on the environment. The reason for this lies possibly on the fact that there exists exchange of CO_2 and water between the precursor solution and air if aging was conducted in air. Dissolution of CO_2 into the solution leads to reduction of pH value and the evaporation of water into air will change the concentration of ion species, both of which alternate the local chemical environment to which the precursors are exposed. As a result, the chemical balances between the precursors and the solvent were broken and new balances have to be established, which alternatively leads to rearrangement of ions on the precursor surfaces. Hence, one would expect that the reactivity and sinterability of the precursors aged under different conditions are distinct. Similar observations had been reported for a variety of nanoparticles. For example, it was recently found that addition of a very small amount of water to nanosized amorphous ZnS particles leads to crystallization [25].

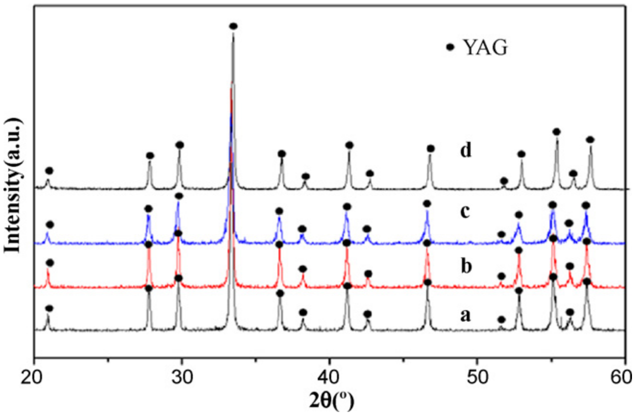

Fig. 3. XRD patterns of the Nd:YAG nano-powders obtained from the precursors aged for different time in enclosed vessel at room temperature followed by calcination at 1373 K for 2 h (a: no aging, b: 3 days, c: 6 days, d: 26 days).

Fig. 3 shows the XRD patterns of the Nd:YAG nano-powders obtained from the precursors aged for different time in enclosed vessel at room temperature followed by calcination at 1373 K for 2 h (a: no aging, b: 3 days, c: 6 days, d: 26 days). It is confirmed that all the nano-powders are pure phase YAG. However, the diffraction peaks of the Nd:YAG nano-powders obtained from the precursors aged for 6 days are broadened, as shown in Fig. 3c. This observation implies that the size of the nano-powders becomes smaller. Our calculations by using the Scherrer equation reveal that the average size of the sample aged for 6 days is 29.8 nm, much smaller than the samples aged for 0, 3, and 26 days, all of which show an average size of ~44 nm. This result is also confirmed by SEM analysis, as shown in Fig. 4. The reason for this abnormal behavior is discussed as follows. Nanoparticles synthesized by wet chemical routes are usually metastable and highly active, because they contain high density of defects, such as vacancies, impurity ions and dislocations, and their surfaces are usually occupied by absorbed ions, molecules, and dangling bonds. As a result of lattice relaxation, time-dependent nucleation and growth have been extensively observed for a variety of nanoparticles, such as those in Ref. [26]. Although the underlying mechanism for the sample aged for 6 days exhibiting smaller grain size still remains unknown, we believe that the competition between the dissolution of the highly strained surface regions and the grain growth of the amorphous precursors should play an important role. A more detailed study is currently in progress.

Fig. 5 shows the XRD patterns of Nd:YAG ceramic pellets sintered under vacuum at 2003 K for 10 h from Nd:YAG nano-powders aged under different conditions at room temperature (a: 3 days in enclosed vessel, b: 3 days in air, c: no aging, d: 6 days in air, e: 6 days in enclosed vessel, f: 26 days in enclosed vessel). It is confirmed that the Nd:YAG ceramic pellet with pure phase YAG (Fig. 5e) obtained from precursors aged for 6 days in enclosed vessel are transparent, with a transmittance close to 75% (Fig. 6). However, if other phases,

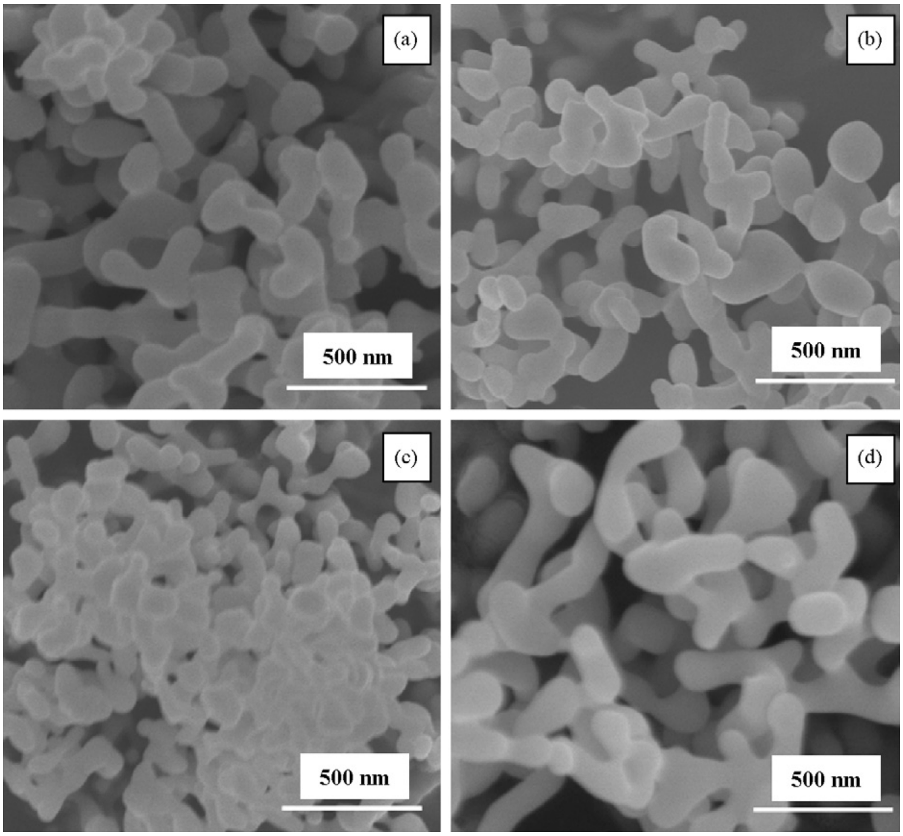

Fig. 4. SEM images of the Nd:YAG nano-powders obtained from the precursors aged for different time in enclosed vessel at room temperature followed by calcination at 1373 K for 2 h (a: no aging, b: 3 days, c: 6 days, d: 26 days).

e.g. YAM and YAP, are present, the Nd:YAG ceramic pellets are either milkiness or translucent. These results further confirm that high quality Nd:YAG nano-powders of single phase is important for the synthesis of transparent Nd:YAG ceramics. Among those transparent ceramic samples, it is found that the sample aged for 6 days in enclosed vessel has the best transmittance, which suggests that the uniform nano-powders with smaller size have better sinterability.

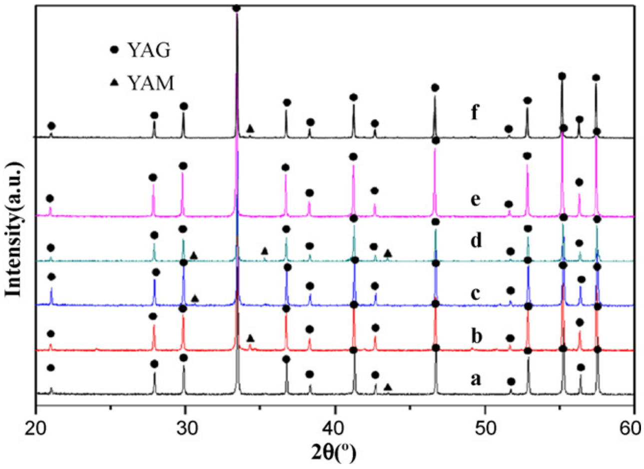

Fig. 5. XRD patterns of Nd:YAG ceramic pellets sintered under vacuum at 2003 K for 10 h from Nd:YAG nano-powders aged under different conditions at room temperature (a: 3 days in enclosed vessel, b: 3 days in air, c: no aging, d: 6 days in air, e: 6 days in enclosed vessel, f: 26 days in enclosed vessel).

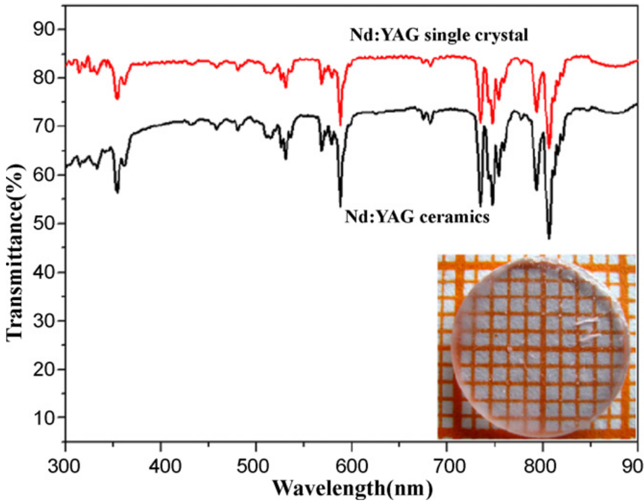

Fig. 6. Optical in-line transmittance spectrum of the transparent Nd:YAG ceramic and Nd:YAG single crystal (inset: a photograph of the transparent ceramic pellet).

4. Conclusions

In summary, we find that aging effects are significant for the synthesis of high quality Nd:YAG nano-powders. It is verified that Nd:YAG nano-powders aged in enclosed vessel exhibits better sinterability than their counterparts obtained in air. Aging time is also an important parameter that needs to be carefully controlled. The Nd:YAG nano-powders obtained from the precursors aged for 6 days in enclosed vessel exhibit the smallest grain size. We also found that the sinterability of Nd:YAG nano-powders is greatly influenced by aging conditions.

Acknowledgements

The authors thank the National Science Foundation of China (Grant Nos. 50702031, 60974117, 50990303, 50872070), 973 Program of China (Grant No. 2009CB930503) for financial support.

References

[1] A. Ikesue, T. Kinoshita, K. Kmata, J. Am. Ceram. Soc. 78 (1995) 1033–1040.
[2] J. Lu, T. Murai, K. Takaichi, Appl. Phys. Lett. 78 (2001) 3586–3588.
[3] A.A. Kaminskii, Laser Photon. Rev. 1 (2007) 93–177.
[4] Z. Wu, X. Zhang, W. He, Y. Du, N. Jia, G. Xu, J. Alloys Compd. 468 (2009) 571–574.
[5] J. Su, Q.L. Zhang, S.F. Shao, W.P. Liu, S.M. Wan, S.T. Yin, J. Alloys Compd. 470 (2009) 306–310.
[6] C. Lu, C. Huang, B. Cheng, J. Alloys Compd. 473 (2009) 376–381.
[7] H. Lee, Y. Cheng, C. Huang, J. Alloys Compd. 479 (2009) 759–763.
[8] Z. Wu, X. Zhang, W. He, Y. Du, N. Jia, P. Liu, F. Bu, J. Alloys Compd. 472 (2009) 576–580.
[9] S. Lee, D. Jung, J. Han, H. Koo, Y. Kang, J. Alloys Compd. 477 (2009) 776–779.
[10] M.L. Saladino, G. Nasillo, D.C. Martino, E. Caponetti, J. Alloys Compd. 491 (2010) 737–741.
[11] J. Horvarth, R. Birringer, H. Gleiter, Solid State Commun. 62 (1987) 319–322.
[12] J. Karch, R. Birringer, H. Gleiter, Nature 330 (1987) 556–558.
[13] H. Chen, R. Yang, Adv. Mater. Res. 11 (2006) 11–14.
[14] S. Tong, T. Lu, W. Guo, Mater. Lett. 87 (2007) 1–3.
[15] K. Takayasu, J.G. Li, I. Sakaguchi, K. Hirota, J. Am. Ceram. Soc. 87 (2004) 517–519.
[16] J. Wang, S. Zheng, J. Am. Ceram. Soc. 92 (2009) 1217–1223.
[17] C.H. Lu, W.T. Hsu, C.H. Hsu, H.C. Lu, B.M. Cheng, J. Alloys Compd. 456 (2008) 57–63.
[18] L. Montanaro, K. Belgacem, P. Llewellyn, F. Rouquero, F. Merlo, P. Palmero, J. Therm. Anal. Calorim. 88 (2007) 789–793.
[19] M.P. Albano, L.B. Garrido, Ceram. Int. 34 (2008) 1279–1284.
[20] M.S. Tsai, W.C. Fu, G.M. Liu, J. Alloys Compd. 440 (2007) 309–314.
[21] B.J. Shen, J.S. Ma, H.C. Wu, C.H. Lu, Mater. Lett. 62 (2008) 4075–4077.
[22] Z. Ni, R.I. Masel, J. Am. Chem. Soc. 128 (2006) 12394–12395.
[23] D.J. Sordelet, M. Akinc, M.L. Panchula, Y. Han, J. Euro. Ceram. Soc. 14 (1994) 123–130.
[24] J. Li, Y. Pan, F. Qiu, Y. Wu, W. Liu, J. Guo, Ceram. Int. 33 (2007) 1047–1052.
[25] H. Zhang, B. Gilbert, F. Huang, J.F. Banfield, Nature 424 (2003) 1022–1025.
[26] T. Sugimoto, J. Colloid Interface Sci. 28 (1987) 65–108.