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Optical properties of the polycrystalline transparent Nd: YAG ceramics prepared by two-step sintering

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Abstract

Nd-doped YAG ceramics were fabricated by the solid-state reaction and two-step vacuum sintering method. It is found that the samples exhibit pore-free and homogeneous microstructures and their transparency is up to 84.98% at the visible and near-infrared band and 87% in the mid-infrared wave range. The absorption cross section of 0.3% Nd:YAG at 808 nm is 5.47×10^{-20} cm^2, while the emission cross section at 1064 nm is 4.66×10^{-19} cm^2. The different transmittances of the samples depending on the sintering conditions were also discussed.

Keywords: A. Sintering; C. Optical properties; Nd:YAG; Transparent ceramics

1. Introduction

In recent years, yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) laser ceramics have been fabricated by nanometer technology and vacuum sintering method [1,2]. YAG-based ceramics have got some prominent advantages in cost, performance, composition control, homogeneity and ease of fabrication, while no strict limit in size and geometry, high doping concentration of activator ions. More recently, a number of studies have shown that the optical properties of transparent Nd:YAG ceramics are equivalent or better than YAG single crystals [3–6]. Nd:YAG ceramics with high transmittance could be easily used as high-power solid-state laser materials because high transmittance means smaller absorptivity and higher fluorescence emissivity.

Usually, the fabrication of YAG transparent ceramics were fulfilled by sintering in vacuum at a high temperature and holding a long time, therefore abnormal grain growth could easily happen. A two-step sintering technique was first introduced by Wei and Wang [7], in which the sample was first heated to a higher temperature, and then cooled down to a lower temperature to suppress grain-boundary migration, and held at the lower temperature until the ceramics were full dense. Chen et al. [8] first adopted this concept for sintering of transparent YAG ceramics.

In this work, a facile strategy for fabrication of Nd:YAG ceramics with high optical transmittance was demonstrated. For the preparation of Nd:YAG ceramics, co-precipitant was not used, and high purity expensive precursors were replaced by inexpensive commercial Al_2O_3,Y_2O_3, and Nd_2O_3 powders. This strategy provides a simple, cost-effective, lower sintering temperature route to achieve ceramics with high optical transmittance. And the effects of different sintering conditions on the optical properties of Nd:YAG transparent ceramics were investigated.

2. Experimental procedures

Commercial Al_2O_3, Y_2O_3, Nd_2O_3 (99.99% purity) powders were used as raw materials. Tetraethoxysilane (TEOS, A.R.) was used as sintering aid in all samples. The powders were ball milled, dried, uniaxially pressed and then cold-isostatically pressed in sequence, detailed experimental procedure has been published in our previous work [9]. And then the pellets were sintered using a two-step sintering method, that means the furnace temperature first arises to a higher temperature T_1 (1800 °C), according to the heating rate of 10 °C/min, and then the temperature rapidly decreases to a suitable sintering temperature T_2 (1550–1750 °C) for 1–8 h in a vacuum graphite

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tube furnace under 1.0×10^{-3} Pa during holding process. The sintering temperatures mentioned next in this paper are all indicated T_2 instead of T_1–T_2.

The phase structure of the Nd:YAG ceramics were identified by X-ray diffraction (XRD, DX-1000, Dandong, China). The cross section morphology of Nd:YAG specimens was observed using scanning electron microscopy (SEM, Hitachi JSM-5900, Japan). Specimens were mirror-polished on both surfaces for transmittance measurement (Lambda 900, Perkin Elmer, USA and Spectrum GX, Perkin Elmer, USA). The fluorescence spectra of the specimens excited by an 808 nm laser diode (LD) were measured by a spectrograph (EPP2000/EPP2000C, StellarNet, USA). All the optical spectrums were measured at room temperature.

3. Results and discussion

The XRD patterns of the Nd:YAG ceramics sintered at 1680 °C is shown in Fig. 1. It can be seen that all characteristic peaks of the diffraction patterns are consistent with that of pure YAG crystal structure (JCPDS No. 33-0040). Fig. 2 shows the cross section morphology of Nd:YAG samples sintered at 1700 °C for different holding hours. The specimens are very compact and almost without pores. The corresponding grain size of the samples (a) and (b) is 5 μm and 7 μm, respectively. That means the longer the sintering time, the larger the grain sizes. In the first-step sintering, the grain size increase is entirely due to coarsening. In the second-step sintering, the feasibility of densification without grain growth relies on the suppression of grain-boundary migration while keeping grain-boundary diffusion active. The longer holding time is effective to promote further densification, which would be reflected at the optical properties of the ceramics.

The optical transmittance between 200 nm and 2500 nm of the Nd:YAG ceramics are shown in Fig. 3(a). It appears that the optical transmittance of Nd:YAG ceramics increases with the holding time at the same sintering temperatures. Depending on the pore-free microstructures, the specimen sintered at 1680 °C for 8 h possesses excellent transmittance up to 84.98% at the lasing wavelength of 1064 nm. As reported by Messing and Stevenson [10], pores scatter light and reduce optical transmission in laser ceramics. Therefore, the longer holding time at the reactive temperature is a very important process to remove large pores and to achieve high transparency YAG ceramics [5,11]. The optical transmittance of the specimens sintered at 1680 °C for 4 h with different Nd concentration—0.3, 1, and 1.5% were shown in Fig. 3(b). With the increasing Nd concentration, the absorption peaks of the samples are enlarged and amplified comparatively,

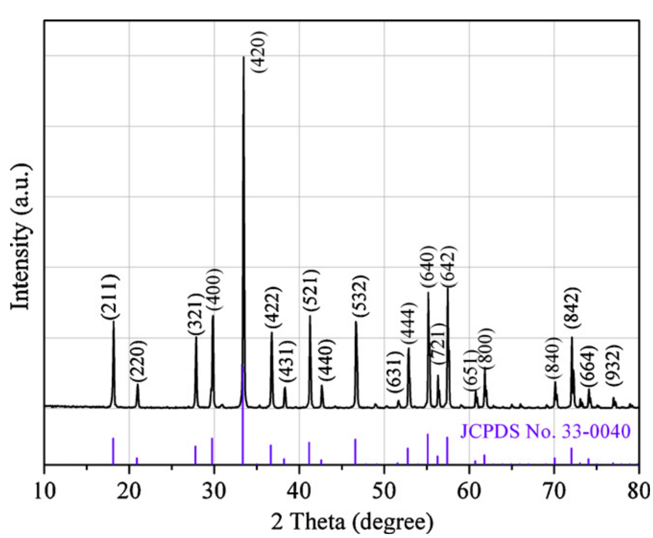

Fig. 1. XRD patterns of Nd:YAG transparent ceramics sintered at 1680 °C.

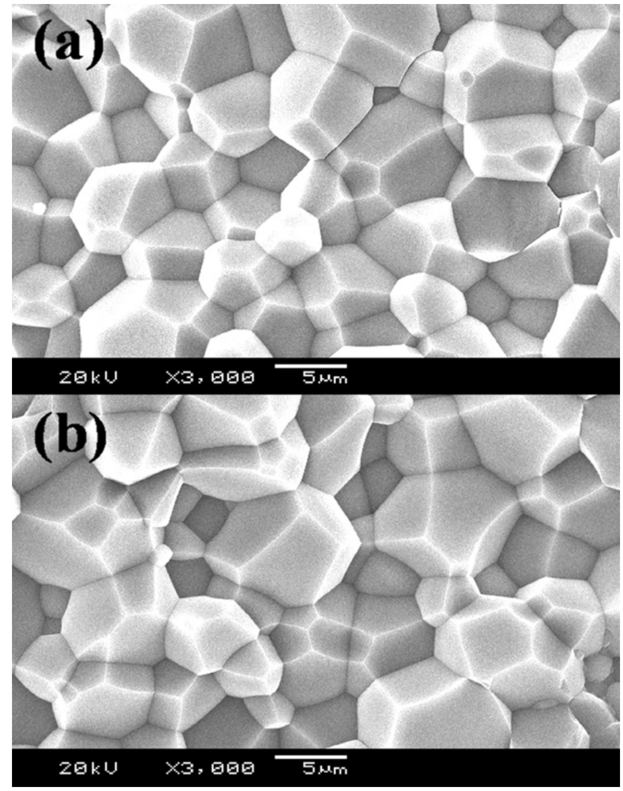

Fig. 2. Cross section morphology of YAG samples sintered at 1700 °C for (a) 5 h and (b) 8 h.

Fig. 4 shows the IR transmittance between 2 μm and 12 μm of 0.3% Nd:YAG ceramics sintered at 1680 °C for 8 h. It is appeared that the IR transmittance of the sample was more than 87% from 2 μm to 4 μm, and the cut-off wavelength is about 6.4 μm. The rather wide transparency range with high transmittance means the Nd:YAG ceramics could become one of the important laser based materials in mid-IR application.

According to the absorption spectrum shown in Fig. 5, it was found that all absorption peaks of Nd:YAG ceramics are broadened, of which the full width at half maximum (FWHM) of the peak centered at 808 nm is 4.24 nm, and this is two to four times of Nd:YAG single crystal [12].

Fig. 6(a) shows the room-temperature fluorescence spectrum of the 0.3% Nd:YAG ceramics. The observed luminescence bands were assigned to the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4I_{11/2}$ transitions. The energy transfer of Nd^{3+} contrast with the fluorescence

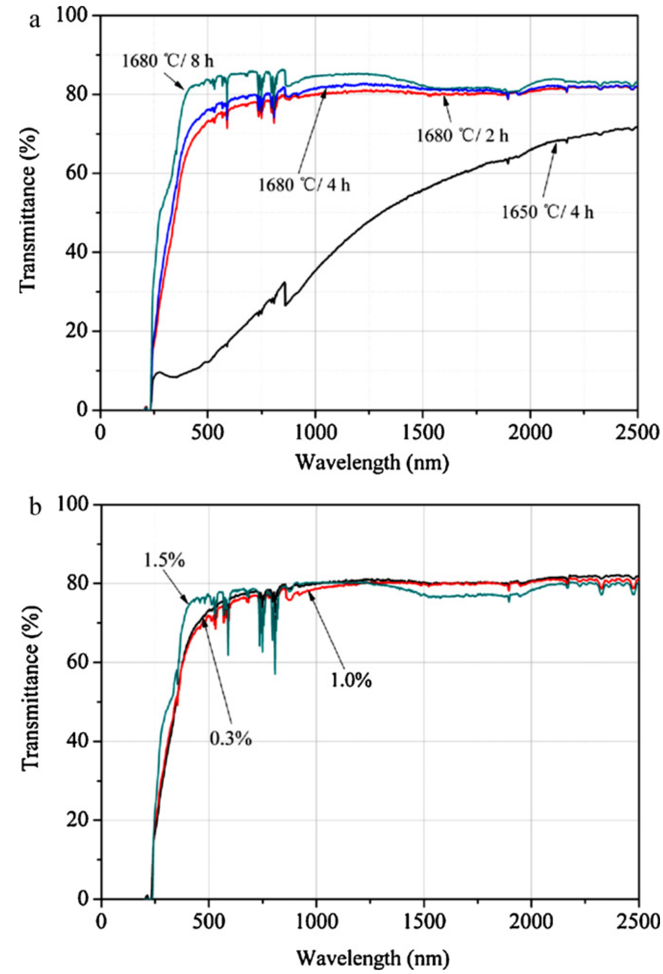

Fig. 3. Optical transmittance of the Nd:YAG ceramics between 200 nm and 2500 nm. (a) Specimens sintered under different temperature/time conditions; (b) Specimens sintered at 1680 °C for 4 h with different Nd concentration—0.3, 1, and 1.5%.

peaks was also shown in Fig. 6(b). The energies of the fluorescence transitions correspond to those reported for Nd^{3+} doped YAG crystals [13]. The strongest emission peak is at 1064.25 nm, corresponding to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+}, of which the FWHM is 1.81 nm. Optical parameters were

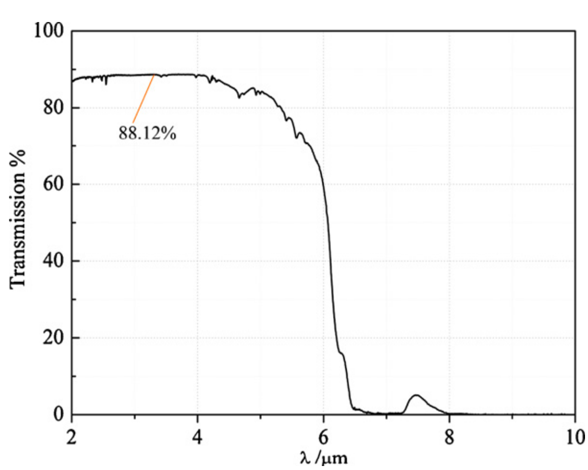

Fig. 4. IR transmittance of 0.3% Nd:YAG ceramics sintered at 1680 °C for 8 h.

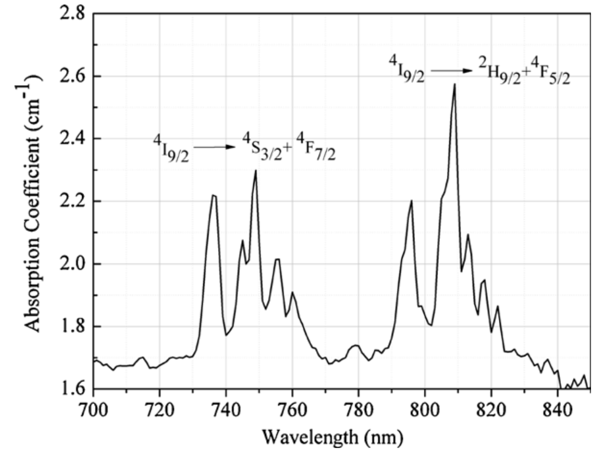

Fig. 5. Absorption spectrum of 0.3% Nd:YAG transparent ceramics at room temperature.

calculated with Judd–Ofelt (J–O) theory [14]. The integrated absorption cross section of 808 nm and the emission cross section of 1064 nm are $5.47 \times 10^{-20}\,cm^2$ and $4.66 \times 10^{-19}\,cm^2$, respectively. The Nd:YAG transparent ceramics with large absorption cross section and emission

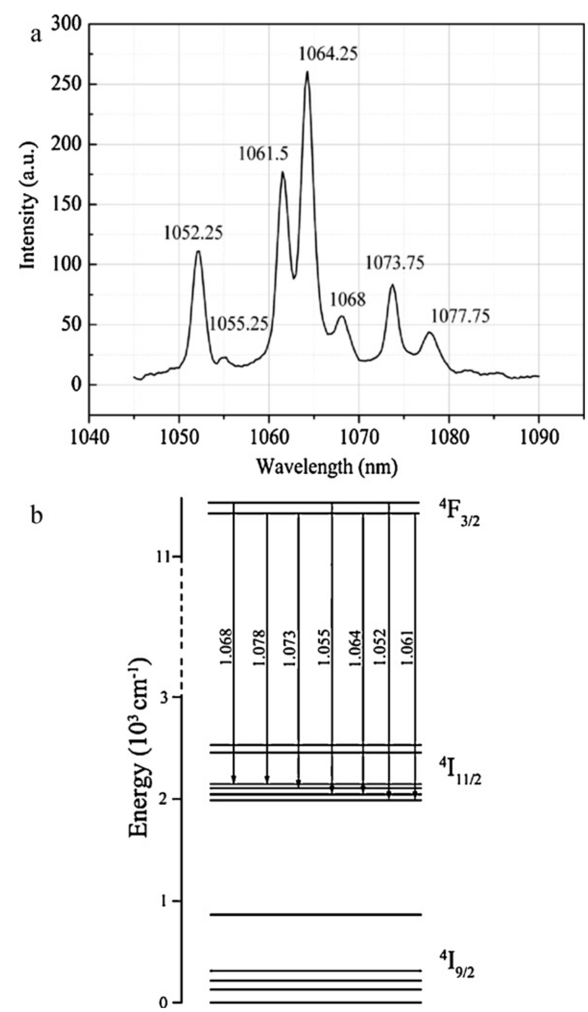

Fig. 6. (a) Fluorescence spectra of 0.3% Nd:YAG ceramics at room temperature and (b) the energy transfer of Nd^{3+} contrast with the fluorescence peaks.

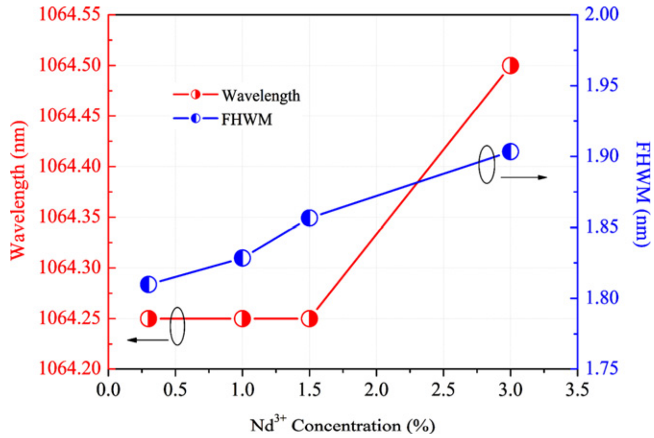

Fig. 7. Fluorescence red shift and FHWM properties of Nd:YAG ceramics as a function of Nd^{3+} concentration.

cross section could be as one kind of good candidate laser materials for high-power solid-state laser.

Emission spectrum for 0.3, 1, 1.5 and 3% Nd:YAG ceramics have also been measured in our previous work [9]. A little wavelength red shift due to a bit change in the crystal field has been observed in Fig. 7, with the increasing of the concentration. The emission peaks are centered at 1064.25 nm and 1064.50 nm for 0.3 and 3% Nd:YAG ceramics, respectively. Because of the fluorescent quenching effect, the fluorescent emission line width at 1064 nm is also a little broadened with Nd concentration increases greater than 1%. Fig. 7 also shows the FWHM of the 1064 nm fluorescent peak. The FWHMs are 1.81 nm, 1.83 nm, 1.87 nm and 1.90 nm for 0.3, 1, 1.5 and 3% Nd:YAG ceramics, respectively. It means that the fluorescent quenching effect is very weak for neodymium concentration less than 1%, which is similar to that of YAG single crystal.

4. Conclusions

High transparent Nd:YAG ceramics were successfully fabricated by two-step sintering method using commercial high-purity oxide powders as the starting materials and TEOS as a sintering additive. In particular the effect of sintering conditions on preparation of transparent YAG ceramics was studied. 0.3% Nd:YAG ceramics sintered at 1800–1680 °C for 8 h possesses dense, pore-free microstructure, and exhibit excellent optical properties—the optical-transmittance is 84.98% at 1064 nm, the absorption cross section at 808 nm is 5.47×10^{-20} cm^2, while the emission cross section at 1064 nm is 4.66×10^{-19} cm^2. The optical transmittance of the samples is more than 87% from 2 μm to 4 μm in infrared wave range.

Acknowledgements

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References

[1] A. Ikesue, T. Kinoshita, K. Kamata, K. Yoshida, Fabrication and optical properties of high-performance polycrystalline Nd:YAG ceramics for solid-state lasers, Journal of the American Ceramic Society 78 (1995) 1033–1040.
[2] J. Li, Y.B. Pan, F.G. Qiu, Y.S. Wu, J.K. Guo, Nanostructured Nd:YAG powders via gel combustion: the influence of citrate-to-nitrate ratio, Ceramics International 34 (2008) 141–149.
[3] I. Shoji, S. Kurimura, Y. Sato, T. Taira, A. Ikesue, K. Yoshida, Optical properties and laser characteristics of highly Nd^{3+}-doped $Y_3Al_5O_{12}$ ceramics, Applied Physics Letter 77 (2000) 939–941.
[4] J.R. Lu, T. Murai, K. Takaichi, T. Uematsu, K. Misiwa, M. Prabhu, J. Xu, K. Ueda, H. Yagi, T. Yanagitani, A.A. Kaminskii, 72 W Nd:$Y_3Al_5O_{12}$ ceramic laser, Applied Physics Letter 78 (2001) 3586–3588.
[5] S.H. Lee, S. Kochawattana, G.L. Messing, Solid-state reactive sintering of transparent polycrystalline Nd:YAG ceramics, Journal of the American Ceramic Society 89 (2006) 1945–1950.
[6] J. Li, Y.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, Optical Materials 31 (2008) 6–17.
[7] C.I Wei, X.H. Wang, Sintering dense nanocrystalline ceramics without final-stage grain growth, Nature 404 (2000) 168–171.
[8] Z.H. Chen, J.T. Li, J.J. Xu, Z.G. Hu, Fabrication of YAG transparent ceramics by two-step sintering, Ceramics International 34 (2008) 1709–1712.
[9] J. Li, Q. Chen, L.L. Yang, G.Y. Feng, W.J. Wu, F.S. Zheng, D.Q. Xiao, J.G. Zhu, High transmittance of Nd-doped YAG transparent ceramics prepared by solid-state reaction method, Ferroelectrics 411 (2011) 62–68.
[10] G.L. Messing, A.J. Stevenson, Toward pore-free ceramics, Science 322 (2008) 383–384.
[11] W.D. Kingery, B. Francois, Grain growth in porous compacts, Journal of the American Ceramic Society 48 (1965) 546–547.
[12] G.A. Kumar, J.R. Lu, A.A. Kaminskii, K. Ueda, H. Yagi, T. Yanagitani, Spectroscopic and stimulated emission characteristics of Nd^{3+} in transparent Y_2O_3 ceramics, IEEE Journal of Quantum Electronics 42 (2006) 643–650.
[13] A.A. Kaminskii, Laser Crystals: Their Physics and Properties, Springer, Berlin, Heidelberg, New York, 1981.
[14] W.F. Krupke, Radiative transition probabilities within the $4f^3$ ground configuration of Nd:YAG, IEEE Journal of Quantum Electronics 7 (1971) 153–159.