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Effect of microstructural features on the laser efficiency of $Nd^{3+}:Y_3Al_5O_{12}$ ceramics

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Abstract. **The optical properties and microstructure of transparent $Nd^{3+}:Y_3Al_5O_{12}$ ceramics synthesised by different reactive sintering routes are studied. It is found that the residual porosity of optical ceramics is directly related to the homogeneity of the microstructure of initial compacts, which can be estimated by the existence of particle agglomerates larger than 1 μm in initial nanopowders. A qualitative correlation is established between the residual porosity, the optical losses and the lasing slope efficiency of $Nd^{3+}:Y_3Al_5O_{12}$ ceramics. The maximum laser efficiency (η = 49 %) was observed in the samples with the lowest porosity (2.3×10^{-3} vol %).**

Keywords: *Nd:YAG laser ceramics, porosity, optical losses, lasing efficiency.*

1. Introduction

In recent years, considerable attention is paid to transparent neodymium-doped yttrium aluminium garnet ceramics $Nd^{3+}:Y_3Al_5O_{12}$ (Nd:YAG), which is used as an active medium of compact lasers with high average and peak powers [1, 2]. Compared to single crystals of the same composition, Nd:YAG ceramics has a number of advantages, such as a low production cost, the possibility of doping with higher concentrations of neodymium (typical concentrations of neodymium ions are 1–3 at % in YAG crystals [3] and up to 10 at % in ceramics [4, 5]), and a comparatively simple preparation of composite elements.

The development of solid-state microlasers capable to operate without active cooling requires the creation of active media with high structural perfection and low optical losses. However, the synthesis of optically homogeneous transparent YAG ceramics is a complex technological problem. The defects formed at different stages of ceramics production (residual porosity, impurity phases, etc.) inevitably decrease the ceramics transparency due to light refraction at the interface between two phases, i.e., between matrix and defect (pores, impurity phase). The optical transmission and laser properties of ceramics also depend on the grain size, the concentration of dopant ions and the impurity composition [6–8] and are to a large extend determined by the technological route of ceramics production.

Recently [9], we reported on the synthesis of transparent single-phase Nd:YAG ceramics which demonstrated a slope lasing efficiency of 33%, while the efficiency of the best ceramic samples exceeds 50% [10–12]. In this connection, it seems interesting to study the influence of the microstructure of YAG ceramics on its optical and laser properties. Previously, it was found that the residual porosity affects the optical properties [13] and lasing efficiency [14] of Nd:YAG ceramics, while the relation between the optical and laser properties of this ceramics was studied in [15]. In the present work, we study the influence of the structural and optical inhomogeneity of Nd:YAG ceramics on the laser parameters. The knowledge of these dependences will allow one to optimise the synthesis of highly efficient laser ceramics.

2. Experimental technique

The Nd:YAG ceramics was synthesised by solid-phase reactive sintering according to [16]. We used Y_2O_3, Nd_2O_3 (99.999%, d = 3–5 μm), and Al_2O_3 (99.99%, $d \approx$ 0.25 μm) powders as initial components and tetraethyl orthosilicate (TEOS, > 99.999%) as a sintering additive. The powder mixtures of initial oxides were ground in a ball mill in isopropyl alcohol for 15 h, dried at 70 °C, and granulated by sieving. The compacts were prepared by isostatic pressing at P = 250 MPa. Prior to vacuum sintering, they were annealed in air for two hours at 800 °C. The ceramics was obtained by vacuum sintering at a temperature of 1750 °C for 10 h. To restore the stoichiometry with respect to oxygen, the ceramic samples were annealed in air at 1300 °C for 15 h, after which they were polished. As a result, we obtained cylindrical samples of transparent Nd:YAG ceramics with a diameter of 15 mm and a thickness of 1.75 mm (samples 1 and 2).

Ceramic sample 3 was synthesised at the Shanghai Institute of Ceramics, Chinese Academy of Sciences, by a similar method [17]. As sintering additives, the authors of [17] used TEOS and magnesium oxide. The initial powders were milled in ethanol for 10 h. After drying and granulation, the powders were annealed at a temperature of 800 °C for one hour. The ceramics was sintered at a temperature of 1760 °C for 30 h, and the sintered samples were annealed in air at 1450 °C for 10 h. The samples were 10 mm in diameter and 1.55 mm thick.

The ceramics morphology was studied using a JEOL JSM-6390LV scanning electron microscope, and the existence of optical anisotropy in the ceramic samples was revealed

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using a polarising optical microscope. The linear optical transmission spectra of Nd:YAG ceramics were measured with a PerkinElmer Lambda-35 spectrophotometer within the range 250–1100 nm. Since the thickness of the samples was different, as a criterion of their optical homogeneity we used the linear optical loss coefficient k calculated according to the Lambert–Beer law taking into account a single Fresnel reflection from the sample–air interface by the formula

$$k = \frac{1}{h}\ln\left[\frac{(1-R)^2}{T}\right], \quad (1)$$

where h is the ceramic sample thickness, R is the reflection coefficient dependent on the wavelength, and T is the linear light transmission coefficient.

To determine the size of pores and the residual porosity, we used the optical microscopy method described in [13]. The slope efficiency of the samples was measured under pumping by a fibre-coupled laser diode (λ_p = 808 nm). The pump beam diameter was 105 μm. The laser cavity was formed by two separate mirrors, namely, by highly reflecting (R = 100%) and output (R = 80%) mirrors. To minimise the reflection losses, the samples were positioned at the Brewster angle to the optical axis.

The emission spectral linewidth was measured with an S150-3648 (SolarLS JSC, Belarus) spectrometer with a linear dispersion of 5 nm mm^{-1}. The laser characteristics were studied under pulsed excitation with a pulse repetition rate of 1 kHz. The signal off-duty ratio necessary to minimise sample heating was 25%; in addition, the samples were mounted on a copper heat-sink plate.

3. Results and discussion

The surface morphology of Nd:YAG ceramic samples obtained using different sintering routes is shown in Fig. 1. The average size of grains was about 11.0 μm in samples 1 and 2 and 8.5 μm in sample 3. Despite a difference in the sintering duration, all the three ceramic samples have a homogeneous microstructure and similar grain sizes. The observation of samples in a polarising microscope revealed no changes in the polarisation of transmitted light, which indicates that the ceramic samples are optically isotropic. X-ray diffraction analysis showed no phases except for yttrium aluminium garnet. Thus, the main mechanism of the appearance of optical losses in the studied ceramics is light scattering by residual pores.

Figure 2 shows the linear optical transmission spectra of Nd:YAG ceramics. The groups of absorption lines in the wavelength range 300–900 nm corresponds to the transitions from the ground $^4I_{9/2}$ level to the excited levels of Nd^{3+} ions. The wavelength dependence of the linear optical loss coefficient k calculated by (1) is presented in Fig. 2b. Attention is drawn to the high absorption and scattering losses in the short-wavelength part of the spectrum for samples 1 and 2. A sharp increase in k with decreasing wavelength of propagating light in the range 300–700 nm is caused by scattering from small pores with diameters not exceeding 100 nm [18]. In turn, sample 3 demonstrates a high transparency in the entire studied spectral range, which points to negligibly low concentration of nanosized pores in this ceramic sample.

The residual porosity of the Nd:YAG ceramics is shown in Fig. 3a. The existence of small (not exceeding 500 nm) pores in samples 1 and 2 introduces a slight error in the aver-

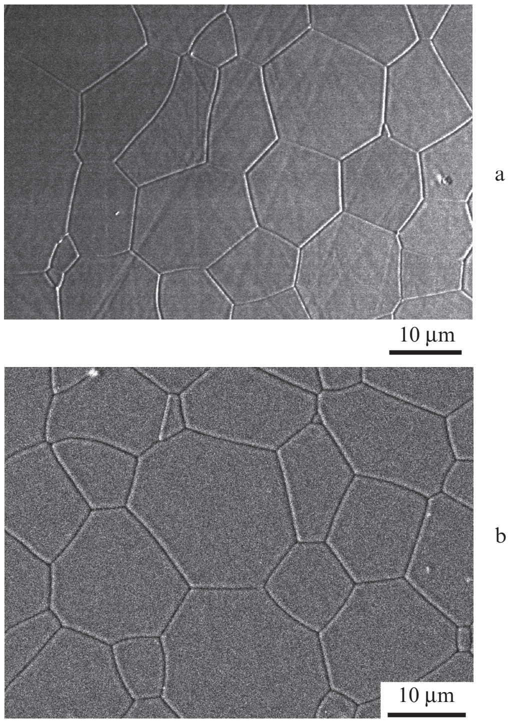

Figure 1. Surface morphology of Nd:YAG ceramic samples (a) 1 and (b) 3 after thermal etching.

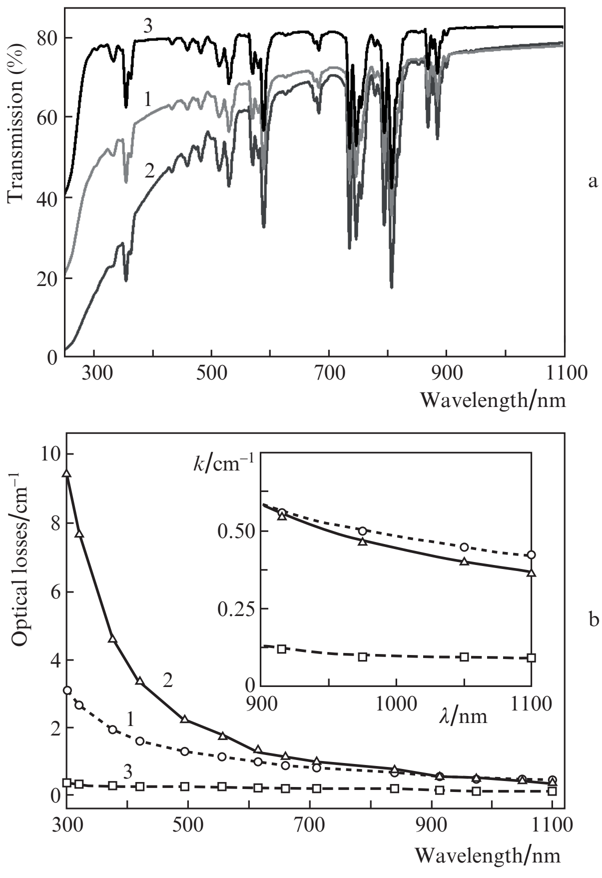

Figure 2. (a) Linear optical absorption spectrum and (b) linear optical loss coefficient for Nd:YAG ceramic samples 1, 2 and 3. The inset shows the optical loss coefficient in the region of lasing wavelength of neodymium ion.

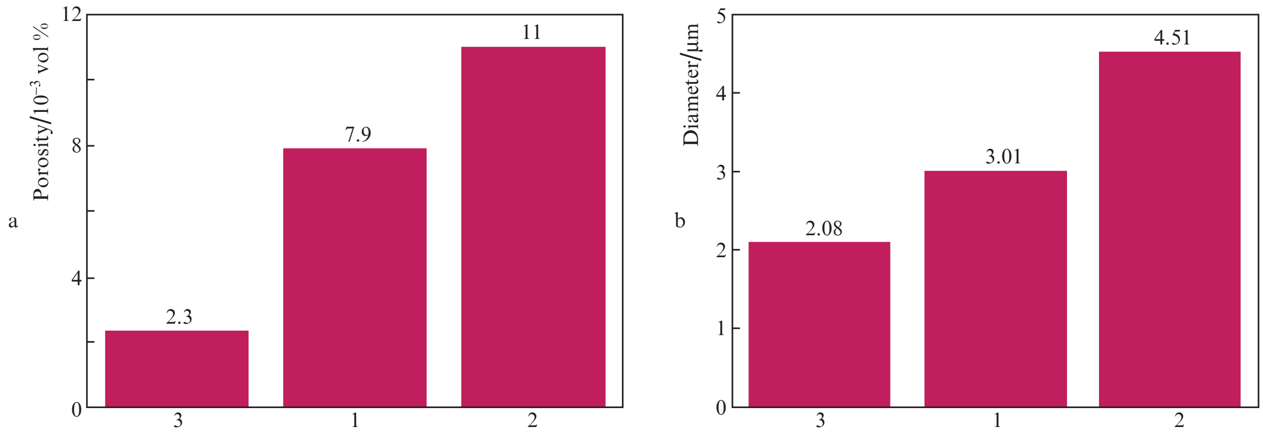

Figure 3. (a) Residual porosity and (b) average pore diameter of Nd : YAG ceramic samples 1, 2 and 3.

age diameter of pores, because of which the calculated residual porosity is underestimated [13]. Nevertheless, the volume fraction of pores in sample 3 synthesised according to [17] (2.3×10^{-3} vol %) is considerably smaller than in samples 1 and 2 obtained by the method of [16] (7.9×10^{-3} and 11×10^{-3} vol %, respectively). The average diameter of pores in samples 1 and 2 (3.0 and 4.5 μm) is also larger than in sample 3 (2.1 μm) (Fig. 3b).

Figure 4 shows the size distribution of pores in Nd : YAG ceramics. Samples 1 and 2 contain pores with sizes reaching 25–40 μm, which are stable to sintering. It is natural to relate the formation of large pores to agglomeration (aggregation) of initial powders, which manifests itself in the inhomogeneous microstructure of initial compacts [19]. As a result, the aggregates that survive after compaction significantly affect the compaction kinetics [20]. Thus, it is the compact microstructure homogeneity (which can be measured in percentage of agglomerates with sizes exceeding 1 μm in initial powders) that to a large extent determines the optical homogeneity and the concentration of scattering centres in laser ceramics. It was found that nanopowders $2.97Y_2O_3-0.03Nd_2O_3-5Al_2O_3$ prepared according to [16] contain a fraction of large, more than 1 μm in size, particles with a weight content exceeding 10%. As a result, ceramic samples 1 and 2 have a comparatively low optical homogeneity. A higher homogeneity of initial powders used to synthesise sample 3 [17, 21, 22] made it possible to avoid formation of large pores and obtain a much lower residual porosity. In additions, longer sintering (30 h) used in the case of sample 3, due to the vacancy-by-vacancy dissolution of pores, led to a decrease in their dimensions compared to samples 1 and 2, which were sintered for 10 h.

The threshold average pump powers and the differential efficiencies η_{dif} of Nd : YAG ceramics obtained by different reaction sintering routes are listed in Table 1. The output laser power of the samples under study as a function of pump power is shown in Fig. 5. One can see that samples 1 and 2, which have different concentrations of neodymium ions (1 and 2 at %, respectively), demonstrate close efficiencies η_{dif} (27%). The differential efficiency of sample 3 (1 at %) reaches 49%. Thus, the amplification efficiency of samples 1 and 2 is limited by their optical inhomogeneity rather than by the concentration of active centres.

Let us consider the relation between the microstructural properties of ceramics with its laser characteristics. Sample 3, which demonstrates a high differential efficiency ($\eta_{dif} = 49\%$),

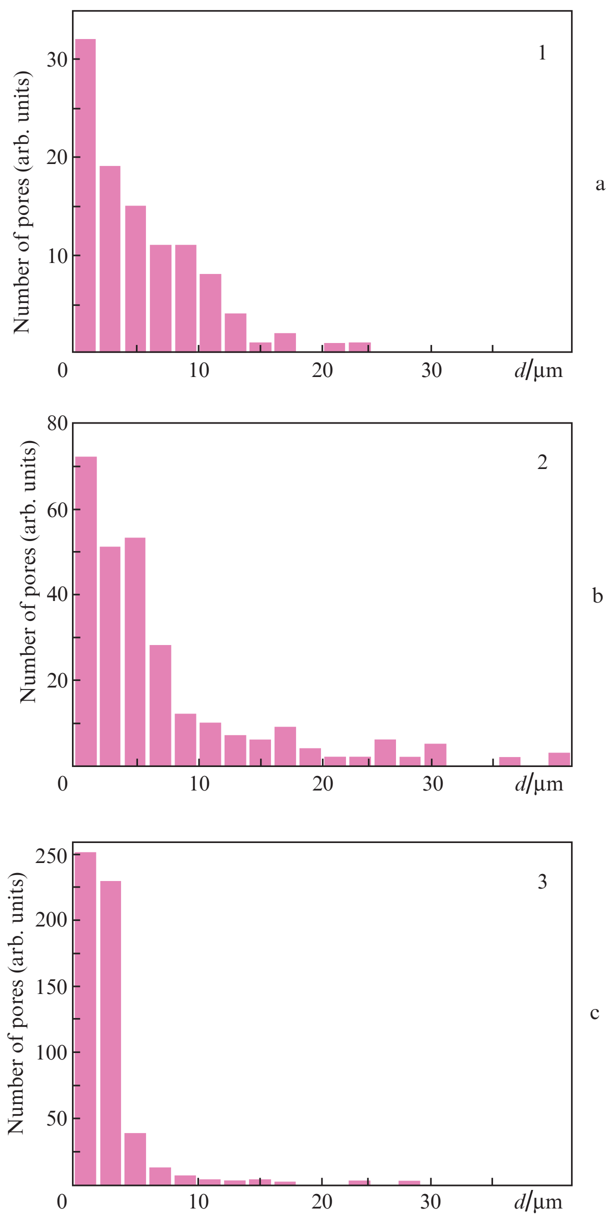

Figure 4. Size distribution of pores in Nd : YAG laser ceramic samples (a) 1, (b) 2 and (c) 3.

Table 1. Laser parameters of Nd : YAG ceramic samples 1, 2 and 3.

Sample	Nd^{3+} concentration/at %	Threshold average pump power/W	η_{dif} (%)
1	1	0.9	27
2	2	0.97	27
3	1	0.6	49

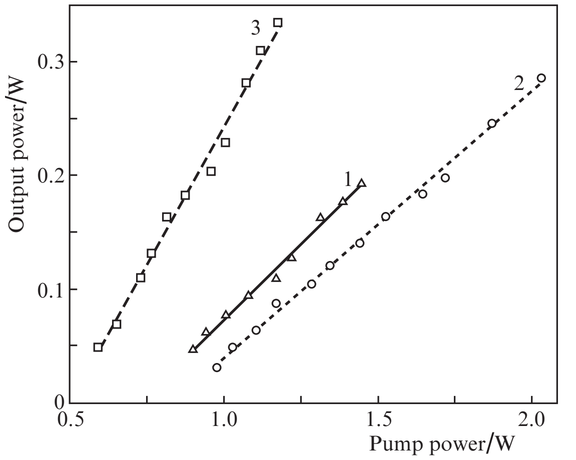

Figure 5. Dependence of the output laser power on the pump power for Nd : YAG ceramic samples 1, 2 and 3.

has a residual porosity at a level of 2.3×10^{-3} vol %, while the linear optical loss coefficient of this ceramics at the laser wavelength (1064 nm) does not exceed 0.1 cm^{-1}. Samples 1 and 2 are characterised by a much higher porosity and contain pores with diameters up to 40 μm with an insignificant difference in their average size. The low residual porosity is a key requirement for achieving a high laser efficiency of Nd : YAG ceramics. Further progress in improving the optical quality of laser ceramics can be achieved by optimisation of the granulometric composition of initial powders and by improving the microstructural homogeneity of initial compacts.

Thus, it is established that the optical homogeneity and laser properties of $Nd^{3+}:Y_3Al_5O_{12}$ ceramics are to a large extent determined by the microstructural homogeneity of initial compacts, as well as by the technological route of consolidation of nanopowder. It is shown that light scattering by residual pores is the main mechanism of optical losses in the studied transparent $Nd^{3+}:Y_3Al_5O_{12}$ ceramics. The key parameters necessary for high differential laser efficiency (about 50%) are monophasity, low porosity (2.3×10^{-3} vol %) and the absence of nanosized pores, which are responsible for optical losses in the short-wavelength spectral region.

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References

1. Li Jiang, Pan Yubai, Zeng Yanping, et al. *Int. J. Refract. Met. Hard Mater*., **39**, 44 (2013).
2. Bagaev S.N., Kaminskii A.A., Kopylov Yu.L., et al. *Kvantovaya Elektron*., **43** (3), 271 (2013) [*Quantum Electron*., **43** (3), 271 (2013)].
3. Mao Y.-L., Deng P.-Z., Zhang Y.-H., et al. *Chin. Phys. Lett*., **19** (9), 1293 (2002).
4. Merkle L.D., Dubinskii M., Schepler K.L., Hegde S.M. *Opt. Express*, **14** (9), 3893 (2006).
5. Springer R.M., Thomas M.E., Hahn D.V., Narducci F.A. *Proc. SPIE Int. Soc. Opt. Eng*., **7302**, 730212 (2009).
6. Ohtomo T., Kamikariya K., Otsuka K. *Jpn. J. Appl. Phys*., **46** (42), L1013 (2007).
7. Aschauer U., Bowen P. *J. Am. Ceram. Soc*., **93** (3), 814 (2010).
8. Osipov V.V., Solomonov V.I., Orlov A.N., et al. *Kvantovaya Elektron*., **43** (3), 276 (2013) [*Quantum Electron*., **43** (3), 276 (2013)].
9. Kosyanov D.Yu., Baumer V.N., Tolmachev A.V., et al. *Crystallogr. Rep*., **60** (2), 299 (2015).
10. Qi Y., Lou Q., Ma H., Dong J. *Chin. Opt. Lett*., **3** (2), 89 (2005).
11. Ikesue A., Aung Y.L., Yoda T., et al. *Opt. Mater*., **29** (10), 1289 (2007).
12. Zhu H.Y., Xu C.W., et al. *Laser Phys. Lett*., **10** (7), 075802 (2013).
13. Vorona I.O., Yavetskiy R.P., Shpilinskaya O.L., et al. *Pis'ma Zh. Tekh. Fiz*., **41** (10), 72 (2015) [*Tech. Phys. Lett*., **41** (5), 496 (2015)].
14. Boulesteix R., Maitre A., et al. *Opt. Express*, **18** (14), 14992 (2010).
15. Vatnik S.M., Osipov V.V., Luk'yashin K.E., et al. *Kvantovaya Elektron*., **44** (6), 585 (2014) [*Quantum Electron*., **44** (6), 585 (2014)].
16. Yavetskiy R.P., Baumer V.N., Doroshenko A.G., et al. *J. Cryst. Growth*., **401**, 839 (2014).
17. Li J., Liu J., Liu B., et al. *J. Eur. Ceram. Soc*., **34** (10), 2497 (2014).
18. Yavetskiy R.P., Shpilinskaya O.L., Baumer V.N., et al. *Funct. Mater*., **20** (4), 445 (2013).
19. Krell A., Klimke J. *J. Am. Ceram. Soc*., **89** (6), 1985 (2006).
20. Balakrishnan A., Pizette P., et al. *Acta Mater*., **58** (3), 802 (2010).
21. Liu J., Lin L., Li J., et al. *Ceram. Int*., **40** (7A), 9841 (2014).
22. Liu B., Li J., Ivanov M., et al. *Opt. Mater*., **36** (9), 1591 (2014).