Reactive sintering of highly-doped YAG/Nd³⁺:YAG/YAG composite ceramics ☆

Ihor O. Vorona[1,*], Roman P. Yavetskiy[1], Andrey G. Doroshenko[1], Sergey V. Parkhomenko[1], Ekaterina G. Chernomorets[1], Alexander V. Tolmachev[1], Sergey V. Frolov[2], Viktor B. Taranenko[2], Ruslan A. Limarenko[2], Denis Yu. Kosyanov[3]

[1]*Institute for Single Crystals of NAS of Ukraine, 60 Nauky Ave., Kharkiv 61072, Ukraine*
[2]*International Center "Institute of Applied Optics", NAS of Ukraine, 10-G Kudryavska Str., Kyiv 04053, Ukraine*
[3]*Far Eastern Federal University, 8 Sukhanova Str., Vladivostok 690950, Russian Federation*

Abstract

Multilayer YAG/Nd³⁺:YAG/YAG composite laser ceramics were obtained by the reactive sintering in vacuum. The effect of the neodymium ion concentration (1–4 at.%) on the formation of defects and optical quality of composite ceramics was studied. It was found that neodymium ions modify densification kinetics during solid-state reactive sintering of the highly-doped Nd³⁺:YAG ceramics by decreasing shrinkage rate in the temperature range 1320–1350 °C. Differences in phase transformation kinetics during reactive sintering lead to generation of pores at the interface of adjacent layers which decrease the optical homogeneity of fabricated YAG/Nd³⁺:YAG/YAG composite ceramics. The influence of layered structure on the laser performance of optical ceramics was investigated. It was shown that the ceramics with multilayer composite architecture have slope efficiency almost twice as the single-layer ceramics with the same composition (22% and 12.5%, respectively).

Keywords: Nd³⁺:YAG, pressing, sintering, microstructure, optical properties, lasers

I. Introduction

Yttrium-aluminium garnet doped with neodymium ions Nd³⁺:Y₃Al₅O₁₂ (Nd³⁺:YAG) is widely used as an active medium of solid-state near-IR lasers due to its high mechanical and laser strength, transparency in a wide wavelength range, and high thermal conductivity. Optically isotropic cubic structure of YAG makes it possible to obtain transparent polycrystalline ceramics which have the key functional characteristics similar to that of corresponding single crystals [1,2]. In contrast to the melt methods of single crystal growth the ceramic technology ensures formation of the homogeneous highly-doped Nd³⁺:YAG solid solutions.

The trend to decrease the size of the active medium in modern solid-state lasers could be achieved by short-ening the resonator length in order to obtain ultra-short pulses duration in the Q-switching operation. Simultaneously, this indicates a number of technical problems affecting the efficiency of laser generation and the laser beam quality. In particular, a small volume of the active medium at high concentration of laser ions and a use of the laser diode pumping with high radiation density lead to significant dispersion of the refractive index due to the inhomogeneous heating of the medium (the so-called thermal lensing). The use of a combined active medium consisting of a core doped with laser ions and surrounded by optically passive transparent layers makes it possible to inhibit negative effects of the thermal lensing significantly [3]. Several methods were proposed to create composite active media based on the YAG/Nd³⁺:YAG ceramics by diffusion bonding of layers [4] or by tape casting [5]. The ceramic technology combined with reactive sintering makes it possible to form a multilayer structure during moulding of the starting nanopowders. There are several reports on the ob-

taining the composite ceramics by such method [6,7]. However, optical quality of the produced samples is significantly lower in comparison with single-layer ceramics. The reason is the difference in the optimal sintering temperatures and kinetics of the solid-phase reactions during initial and intermediate sintering stages of layers having different chemical compositions.

The aim of the present work is to determine the influence of Nd^{3+} ion concentrations on the kinetics of solid-state reaction during processing of multilayer transparent ceramics. In addition, the goals are to identify the features of multilayer $YAG/Nd^{3+}:YAG/YAG$ composite laser ceramics obtained by the reactive sintering, and to study functional characteristics of the fabricated ceramics.

II. Experimental procedure

Al_2O_3 (>99.99%, Baikowski, France, $d \approx 150–250$ nm), Y_2O_3 (99.999%, Alfa Aesar, $d \approx 3–5 \mu m$), and Nd_2O_3 (>99.99%, Alfa Aesar, $d \approx 3–5 \mu m$) powders were used as starting materials. Tetraethyl orthosilicate (TEOS) (≥99.999%, Alfa Aesar) in amount of 0.5 wt.% (corresponding to 0.14 wt.% of SiO_2) was used as the sintering aid. The powder mixtures, taken according to the garnet stoichiometry $(3-x)Y_2O_3 \cdot xNd_2O_3 \cdot 5 Al_2O_3$ (where $x = 0.03–0.12$), were ground in a planetary ball mill in isopropyl alcohol using 5 mm alumina balls at 140 rpm rotation speed during 15 hours. The obtained suspension was dried and sieved through a 200 mesh screen. The neodymium concentration in the powder mixtures (in comparison to Y^{3+} content) was varied in the range from 0 to 4 at.%.

Moulding of the ceramic composite with layer-by-layer configuration $(YAG/Nd^{3+}:YAG/YAG)$ was carried out as follows. The powder mixtures with composition corresponding to the undoped YAG as outer layers and $Nd^{3+}:YAG$ as the inner layer were charged in metal mould and pressed uniaxially at 30 MPa. Then the composite green body was isostatically pressed at 250 MPa. The single-layer compacts with different compositions were prepared under the same conditions for the comparison. The pressed green bodies were annealed in air at 800 °C during 4 hours in order to remove organic impurities. Reactive sintering was carried out in tungsten crucibles in a vacuum furnace with tungsten heaters at 1750 °C for 10 hours. In order to retain oxygen stoichiometry and to relax microstructural stresses, ceramic samples were annealed in air at 1300 °C for 15 hours. Finally, the ceramics was ground and polished. The typical 2 at.% $Nd^{3+}:YAG$ and YAG/2 at.% $Nd^{3+}:YAG/YAG$ samples obtained after sintering and polishing are shown in Fig. 1.

The densification kinetics of powder compacts was studied by the dilatometric analysis on NETZSCH-402 ED dilatometer. Measurements were carried out in vacuum in the temperature range of 20–1470 °C at a heating rate of 5 °C/min. Microstructure of ceramics was studied using transmission optical microscope Zeiss axioscop 40 with 100×-magnification. The concentration of neodymium ions in composite ceramics was measured using the electron-probe microanalysis by scanning electron microscope JSM-6390LV equipped with energy-dispersive spectrometer AZtecEnergy X-max^N 50. In-line optical transmission spectra of the $Nd^{3+}:YAG$ ceramics were measured on Perkin-Elmer Lambda-35 spectrophotometer in the range of 250–1100 nm. The phase composition was investigated by X-ray diffraction (XRD) with Siemens D-500 diffractometer (Siemens AG, Germany) with $CuK\alpha$ radiation. Phases were identified using the PDF-1 JCPDS X-ray database of the EVA survey system. Laser generation in the uncoated ceramic samples was obtained under the semiconductor laser diode pumping with the wavelength $\lambda = 808$ nm. The resonator with the length of $L = 9$ mm consisted of a plane high-reflectivity mirror ($R_{1064} > 0.999$) and a translucent out-coupling mirror with a transmittance $T_{1064} = 0.06$. The samples were fixed in a copper holder.

III. Results and discussion

3.1. Characterization

The prepared samples were characterized by XRD and a typical pattern of the YAG doped with 2 at.% Nd^{3+} (2 at.% $Nd^{3+}:YAG$) ceramics was shown in Fig. 2.

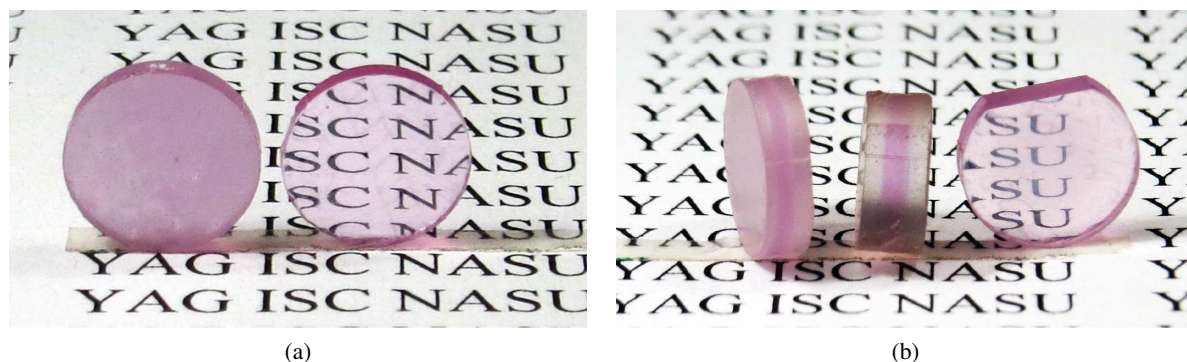(a)   (b)

Figure 1. Appearance of the single-layer 2 at.% Nd^{3+}:YAG ceramics before (left) and after (right) polishing (a) and polished composite YAG/2 at.% Nd^{3+}:YAG/YAG ceramics (b)
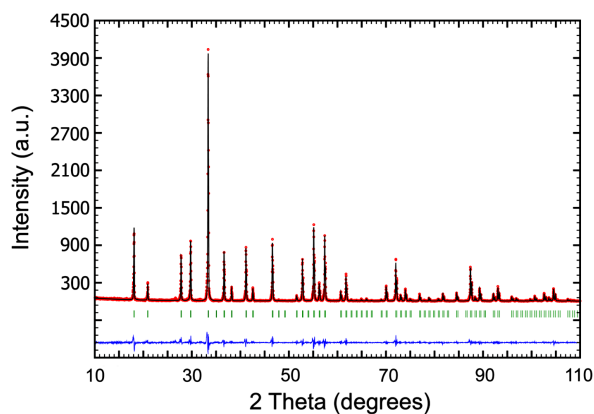
Figure 2. XRD pattern of 2 at.% Nd³⁺:YAG sintered ceramics

According to the Rietveld refinement results, the obtained ceramics is single phase and has pure garnet structure, no secondary phases were found. The unit cell parameter of ceramics increases linearly from 12.008 Å to 12.019 Å with increasing Nd^{3+} ions concentration from 0 to 4 at.%. This indicates the formation of the isomorphic $(Y_{1-x}Nd_x)_3Al_5O_{12}$ substitutional solid solutions. XRD analysis of the composite ceramics also confirms their phase purity.

In-line optical transmission spectra of the single-layer 0, 2, and 4 at.% Nd^{3+}:YAG ceramics are shown in Fig. 3a. The measured samples had a thickness of 1.5 mm. All analysed ceramics is transparent, and the in-line optical transmission value relative to the background line is virtually independent on the concentration of Nd^{3+} ions. Transmittances of the samples at the wavelength $\lambda = 1064$ nm were 83–83.2%, which are very close to the theoretical limit of ~83.9% determined by Fresnel reflection.

Transmission spectra of the multilayer ceramics with a thickness of 3 mm are shown in Fig. 3b. A significant decrease in the optical quality is observed with the increase of Nd^{3+} concentration. The in-line optical trans-

mission at the wavelength $\lambda = 1064$ nm for YAG/2 at.% Nd^{3+}:YAG/YAG ceramics was 80.5%, while it decreases to 74.5% for YAG/4 at.% Nd^{3+}:YAG/YAG sample. The transmittance of highly-doped samples with composite architecture decreases significantly in the short-wavelength spectral range due to the light scattering on the nanosized and submicron residual pores [8, 9].

Figure 4 shows a typical microstructure of YAG/Nd^{3+}:YAG/YAG ceramics observed by a transmission optical microscopy and by SEM. The observed dark defects in the optical images of ceramics are residual pores that appear also on SEM images. Left (Fig. 4a,c) and right (Fig. 4b,d) pairs of images correspond to the samples with 2 at.% and 4 at.% of Nd in doped layer, respectively. The highly-doped composite ceramics contains a significant amount of residual pores which cause transmission decrease. According to the optical microscopy data, the increase of the optical losses in highly-doped composite ceramics is caused by the rising concentration of residual pores. An increase in the neodymium concentration up to 4 at.% does not affect the pore concentration and optical quality of the single-layer samples (Fig. 3a), while the typical porosity of Nd^{3+}:YAG ceramics obtained by the reactive sintering method is $\sim 10^{-3}$–10^{-4} vol.% [10]. Thus, defect formation in the ceramics with "sandwich" structure was caused by pore formation on the interfaces of doped and undoped layers during sintering.

3.2. Effect of Nd³⁺ concentration on densification

The influence of neodymium ions concentration on densification peculiarities of Nd^{3+}:YAG ceramics was studied by dilatometric analysis method performed for $(3-x)Y_2O_3 \cdot xNd_2O_3 \cdot 5Al_2O_3$ ($x = 0.03$–0.12) powder mixtures. The shrinkage curves of green bodies as a function of doping concentration are shown in Fig. 5. The solid-state reactive sintering of Nd^{3+}:YAG ce-
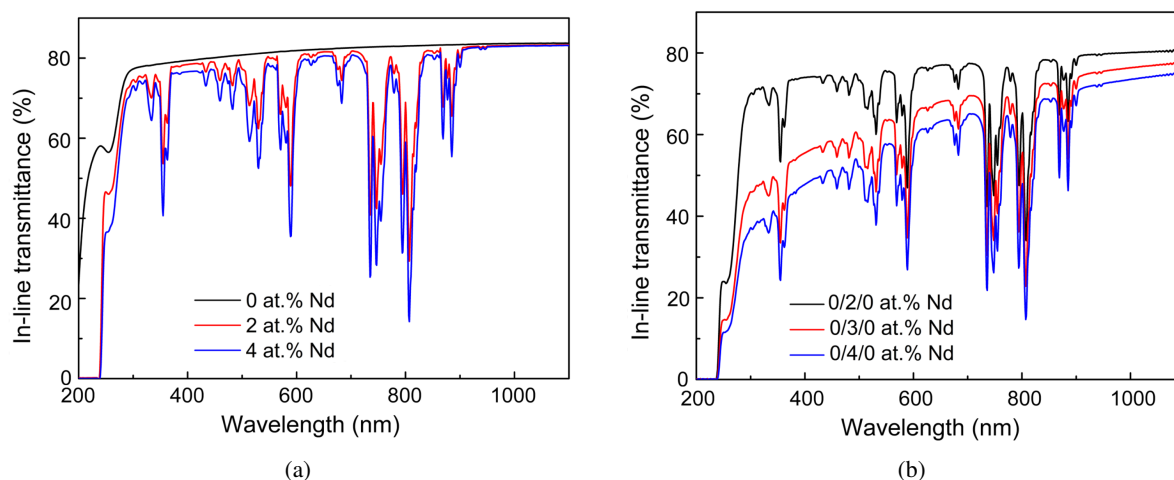

(a)

(b)

Figure 3. In-line optical transmission spectra of the single-layer Nd³⁺:YAG ceramics (a) and multilayer YAG/Nd³⁺:YAG/YAG ceramics (b)
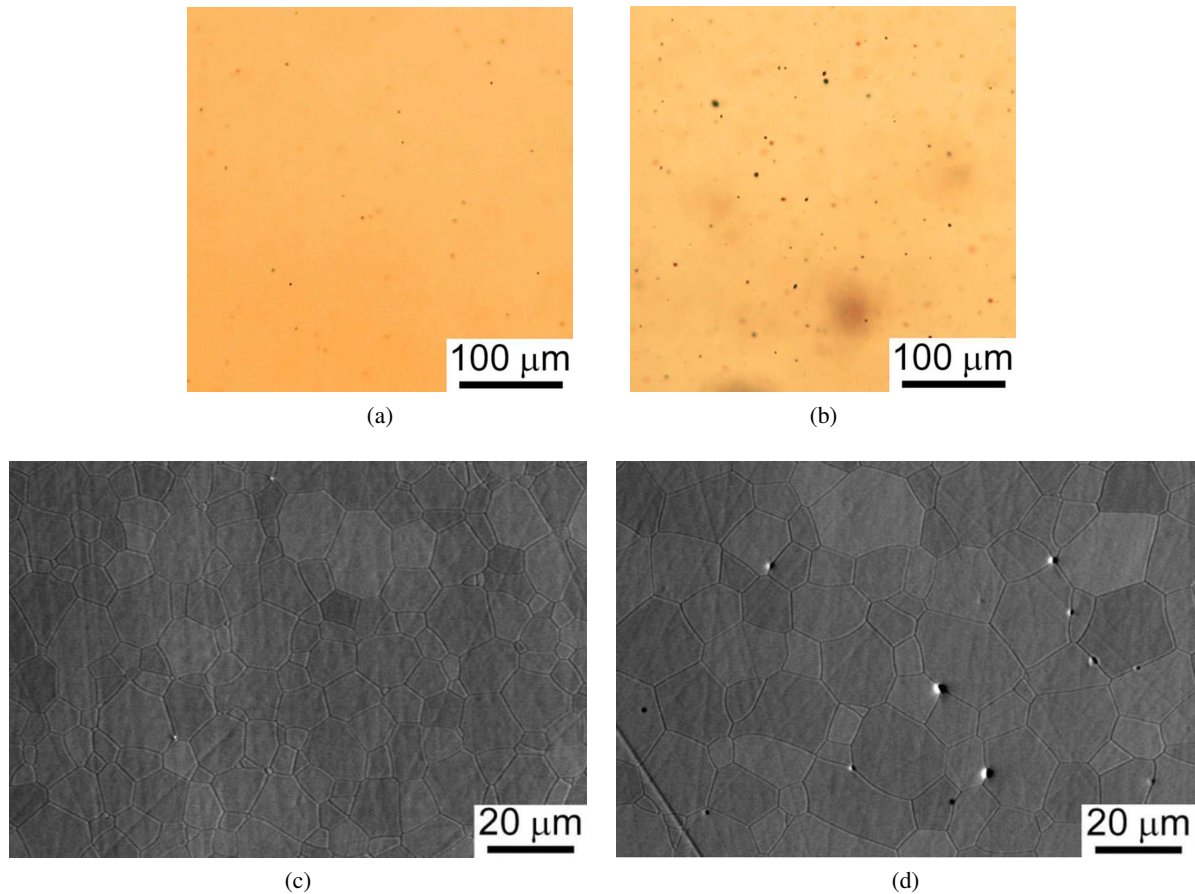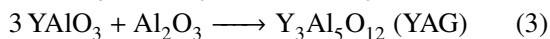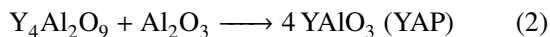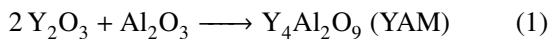
Figure 4. Microstructure of YAG/2 at.% Nd³⁺:YAG/YAG (a, c) and YAG/4 at.% Nd³⁺:YAG/YAG (b, d) ceramics, observed by optical microscopy (a, b) and by SEM (c, d)

ramics and preparation of the polycrystalline yttrium-aluminium garnet from a mixture of submicron or nano-sized powders of starting oxides (Al_2O_3, Y_2O_3, Nd_2O_3) have been usually performed by isothermal holding in vacuum at $T \approx 0.9T_m$ (1750 °C) for several hours. The garnet phase formation is a stepwise process that proceeds through the formation of intermediate yttrium aluminates [11]:

$$2\,Y_2O_3 + Al_2O_3 \longrightarrow Y_4Al_2O_9 \text{ (YAM)} \qquad (1)$$

$$Y_4Al_2O_9 + Al_2O_3 \longrightarrow 4\,YAlO_3 \text{ (YAP)} \qquad (2)$$

$$3\,YAlO_3 + Al_2O_3 \longrightarrow Y_3Al_5O_{12} \text{ (YAG)} \qquad (3)$$

The shrinkage of green bodies at various temperatures is mainly determined by these reactions (1–3). The smaller specific volume of YAP phase relative to that of starting oxides (approximately by 13%) leads to a sharp increase in density of green body during the reaction (2) (T = 1100–1250 °C in Fig. 5a). In the 1250–1350 °C temperature range, densification of the green body is determined by the competition of sintering of powder mixture and YAG formation reaction (3). The sintering process is aimed at densification of a porous green body by removal of pores out of the volume and approaching of particle centres. The reaction (3) is accompanied by an increase in the specific volume by 11%. As a result,

a significant reduction in the shrinkage rate of ceramics is observed at this stage.

The neodymium ion concentration affects significantly the densification rate of the prepared ceramics. Fig. 5b shows that the compaction rate decreases with increasing neodymium concentration, and for the compositions with $C_{Nd} > 2$ at.% it becomes negative resulting in volume expansion. The observed effect can be caused by formation of $NdAlO_3$ (NdAP) intermediate phase in the step (2) which partially replaces YAP phase [11]. This changes the garnet formation kinetics via reaction (3). Heating of green body above the temperature of 1400 °C causes transformation of intermediate phases and promotes neodymium ions to enter the garnet structure as substitutional ones. Moreover, neodymium ions have an impact on the sintering kinetics by forming compounds with sintering aid (silica) [12], which determines largely the shrinkage rate.

Thus, during sintering of the composite ceramics in the temperature range of 1320–1350 °C the undoped YAG layers retain a positive sintering dynamics, while the central doped layer undergoes swelling. The appearing mechanical stresses can be relaxed by generating pores at the interface of adjacent layers, which are responsible for the increased optical losses of ceramics with composite architecture.
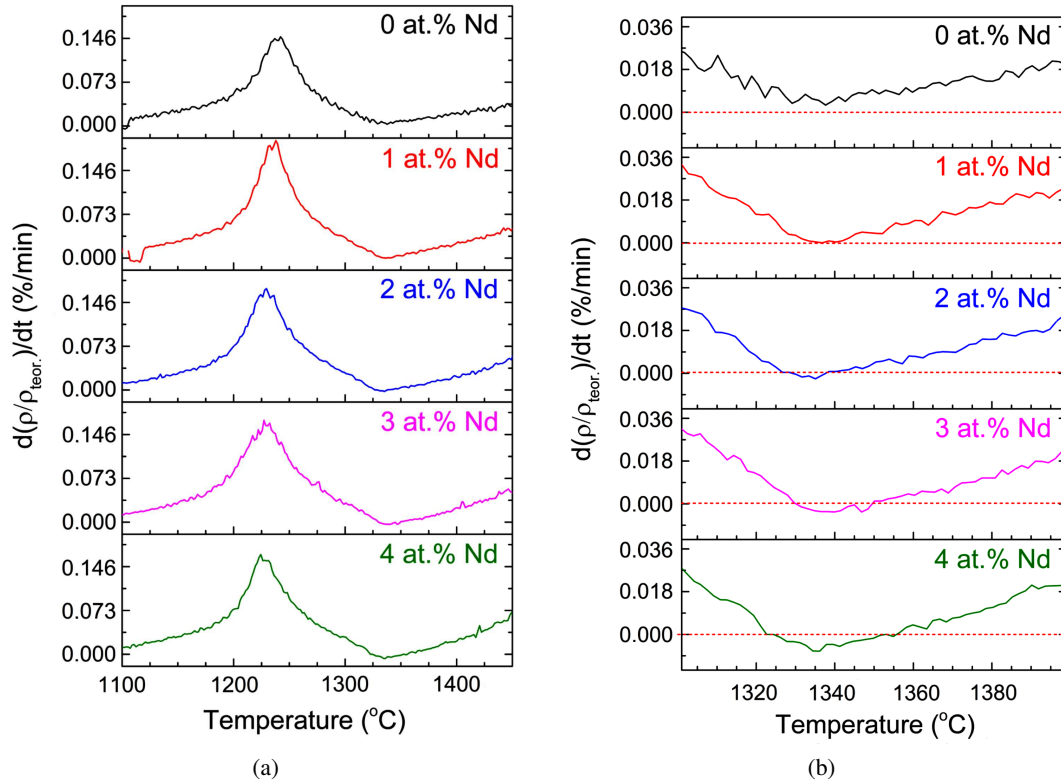
Figure 5. Densification rate of Nd³⁺:YAG ceramics vs. concentration of neodymium ions (a) and enlarged curves in temperature range 1300–1400 °C (b)
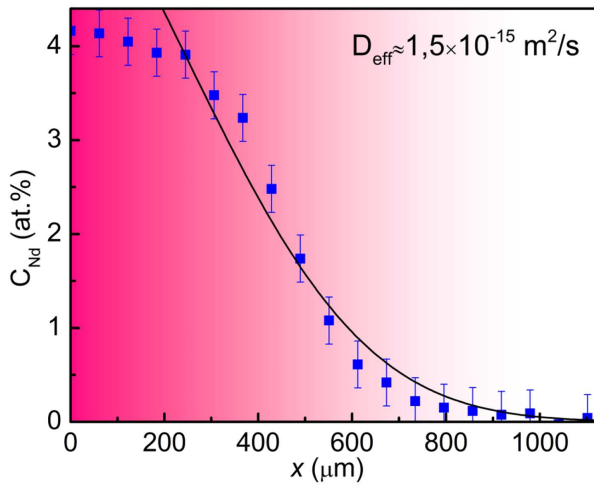

Figure 6. Neodymium ion concentration in multilayer YAG/4 at.% Nd³⁺:YAG/YAG ceramics as a function of the distance in a direction perpendicular to the interface

3.3. Nd³⁺ ions diffusion during sintering

Sintering of YAG/Nd³⁺:YAG ceramics is accompanied by the diffusion of activator ions towards the undoped layer. The neodymium ions concentration distribution in YAG/4 at.% Nd³⁺:YAG/YAG ceramics is shown in Fig. 6. In order to describe the diffusion process, the first Fick's law was applied for the one-dimensional diffusion through a flat boundary. According to this law, the concentration C_{Nd} in the undoped layer at the point x after some time t can be approxi-

mately described by the equation:

$$C_{av} = C_0 \left(1 - \mathrm{erf} \left(\frac{x - x_0}{\sqrt{4 D_{eff} \cdot t}} \right) \right) \qquad (4)$$

where C_0 is the impurity concentration at the interface, erf(x, t) is the error function, x_0 is the coordinate of the interface (we used coordinates for $x = 0$), and D_{eff} is the effective diffusion coefficient.

The effective diffusion coefficient was determined by approximating the experimental data by Eq. (4) (Fig. 6, solid line). It was found that $D_{eff} \approx 1.5 \cdot 10^{-15}$ m²/s which corresponds to an actual diffusion rate of approximately 50 μm/h.

3.4. Laser performance

The effect of structure of ceramic active media on the laser characteristics was studied using the multi-layer sample doped with 2 at.% of Nd³⁺. The single-layer 2 at.% Nd³⁺:YAG ceramics was used as reference. Figure 7 shows CW laser output at the wavelength of 1064 nm as a function of the absorbed pump power for the single-layer 2 at.% YAG:Nd³⁺ and composite YAG/2 at.% Nd³⁺:YAG/YAG ceramics. Solid lines correspond to the linear fits of the experimental data. The slope efficiencies of the composite ceramics and the reference sample were 22% and 12.6%, respectively. Thus, the multilayer structure allows one to almost double the slope efficiency of ceramic laser. It should be noted that a threshold of laser emission for the single-layer ceram-

ics is significantly lower than that for composite ceramics (0.75 and 1.1 W, respectively). This difference arises due to the lower optical quality of the latter (Fig. 7). The laser characteristics of ceramics could be substantially improved by optimizing the measurement conditions, applying anti-reflective coatings on the samples, and using an active cooling of samples.
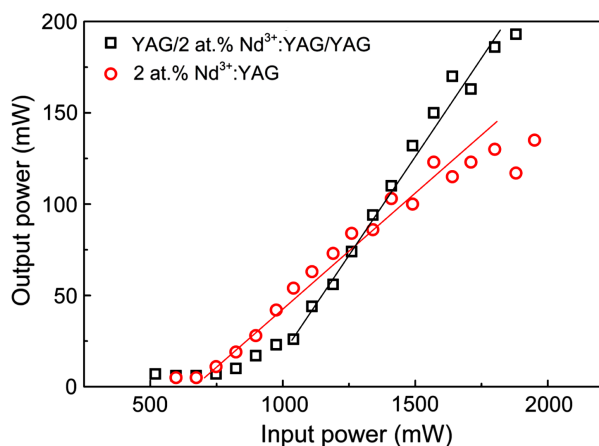

Figure 7. Laser output as a function of the pumping power of the single-layer 2 at.% Nd³⁺:YAG and composite YAG/2 at.% Nd³⁺:YAG/YAG ceramics

IV. Conclusions

YAG/Nd³⁺:YAG/YAG composite laser ceramics was obtained from corresponding oxides by reactive sintering in vacuum. The effect of the neodymium ion concentration on the defect formation and optical quality of composite ceramics was studied.

It has been found that the shrinkage rate of Nd³⁺:YAG ceramics decreases with an increase of concentration of neodymium ions in the starting mixture, and it becomes negative at the Nd³⁺ content higher than 2 at.%. This extreme on the sintering trajectory of ceramics was connected with competition of the densification processes and the garnet phase formation, since the latter results in specific volume decrease. The change in the shrinkage rate could be explained by the partial substitution of YAlO₃ by NdAlO₃ that influence the kinetics of the solid-state reaction $3\,YAlO_3 + Al_2O_3 \longrightarrow Y_3Al_5O_{12}$. The local swelling effects observed at the interface of adjacent layers during reactive sintering of highly-doped YAG/Nd³⁺:YAG/YAG composite ceramics lead to the generation of structural defects and decrease optical quality of synthesized samples.

The structure of the ceramic gain media has significant effect on their laser performance. It has been determined that the presence of cladding layers on the neodymium-doped active layer decreases the thermal lensing effect and doubles the slope efficiency of ceramic laser.

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