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Yb:$(YLa)_2O_3$ laser ceramics produced by microwave sintering

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Abstract. **The possibility of using microwave heating for sintering of optical oxide ceramics and the advantages of this method are considered. Sintering of $Yb_{0.1}:(YLa)_{1.9}O_3$ ceramics by heating with 24-GHz radiation is studied. The compacts for sintering are prepared from nanosized powders obtained by high-temperature synthesis from acetate-nitrates of rare-earth metals. The effect of addition of lanthanum oxide and of the uniaxial pressing conditions on the microstructure and optical transmission of ceramics is studied. Lasing at a wavelength of 1030 nm with an efficiency of 7.5% is achieved in ceramic samples of the $(Yb_{0.05}Y_{0.1}La_{0.85})_2O_3$ composition under pumping by a laser diode at a wavelength of 940 nm.**

Keywords: *laser ceramics, microwave sintering, millimetre radiation, yttrium oxide, lanthanides.*

1. Introduction

Optically transparent ceramics based on Y_2O_3 doped with rare-earth elements is one of the most promising materials for fabricating high-power solid-state lasers. At present, the methods of synthesis of Y_2O_3 optical ceramics doped with Nd^{3+} and Yb^{3+} ions are extensively studied. In the last decade, the development of high-power diode lasers emitting at a wavelength falling into the ytterbium absorption band made it possible to realise the advantages of ytterbium-doped laser materials. The Yb^{3+} ions can be pumped by diode lasers with wavelengths near 940 and 976 nm, which ensures laser oscillation of $Yb:Y_2O_3$ in the region of 1030–1080 nm with a low quantum defect. The low quantum defect in combination with a high thermal conductivity of yttrium oxide reduces the heat load and makes it possible to achieve stable operation of high-average-power lasers. In addition, the wide absorption band of ytterbium allows one to obtain ultrashort laser pulses.

The conventional technology of laser ceramics is the sintering of the compacts in resistance furnaces under high-vacuum conditions (~1×10^{-3} Pa). As a rule, the temperature of sintering of optically transparent yttrium oxide (without applying an external pressure) is about 1750–1800 °C, and the duration of the high-temperature sintering stage is about 20 h. Sintering under these conditions leads to a considerable growth of grains (up to tens of microns) and, as a result, to deterioration of thermomechanical properties of ceramics. The methods of sintering under pressure (hot pressing and hot isostatic pressing) allow one to decrease the sintering temperature and duration. However, the high cost of equipment and significant operational expenses restrict the application of pressure for sintering.

One of the methods for sintering of optically transparent Y_2O_3 ceramics at lower temperatures and suppressed grain growth is the use of La_2O_3 as a sintering additive [1]. This method was used to produce Y_2O_3 laser ceramics doped by both ytterbium and neodymium. For example, ceramics of the 1.5 at% $Nd:(Y_{1.8}La_{0.2})O_3$ composition was obtained by sintering in hydrogen atmosphere at a temperature of 1650–1700 °C during 40–50 h [2]. In this work, the laser power at a wavelength of 1079 nm achieved under diode pumping at 808 nm was 62 mW. Sintering in a hydrogen atmosphere at a temperature of 1650 °C for 50 h was also used in [3] to synthesise 5 at% $Yb:(Y_{1.8}La_{0.2})O_3$ ceramics, which allowed the authors to obtain laser power of 2.1 W with a slope efficiency of 52%.

In the present paper, we study the self-propagating high-temperature synthesis (SHS) of yttrium oxide nanopowder doped with rare-earth ions and the sintering of $Y_{(1.9-x)}La_xYb_{0.1}O_3$ ceramics with $0 < x < 0.35$ under conditions of microwave heating. The prospects of application of microwave heating for production of laser ceramics are determined by the following factors.

(i) The absence of heating elements in the working chambers, owing to which sintering occurs under clean vacuum conditions, which is one of the necessary prerequisites for obtaining optically transparent ceramics. The contamination of ceramic grain boundaries with evaporating heater material (tungsten, molybdenum, carbon) is one of the main problems of sintering of optical ceramics in traditional high-vacuum furnaces.

(ii) The volumetric absorption of microwave radiation, which leads to an inverse (compared to traditional) temperature distribution inside the sample being sintered. As a result, the pores near the sample surface remain open to a later sintering stage, which facilitates their disappearance and increases the compaction rate.

Note also that the use of microwave energy for high-temperature sintering eliminates the problem of service life of heaters and screens used in resistance furnaces. An additional feature important from the practical viewpoint is a high energy efficiency of microwave heating, which allows one to

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save up to 90% of specific energy consumption in high-temperature sintering processes [4].

Today, most processes of microwave sintering of structural and functional ceramics of different compositions are performed using radiation at the standard frequencies of 0.915 and 2.45 GHz. In particular, the 2.45-GHz microwave radiation was used in [5] for synthesis of yttrium aluminum garnet powder and sintering of compacts pressed from this powder. The transmission coefficient of the sintered samples 0.86 mm thick at a wavelength of 520 nm was 45%.

The spectrum of studied high-temperature processes and materials can be considerably extended by using radiation with millimetre wavelengths (with 24-GHz and higher frequencies) [6]. The considerably higher radiation frequency provides the following advantages, which are most important for applications.

(i) The specific absorbed power increases at least proportionally to the radiation frequency, which makes it possible to heat so-called weakly absorbing materials by millimetre radiation without using additional heaters required in the case of standard frequencies.

(ii) In the millimetre wavelength region, the size of applicators (working chambers) exceeds the radiation wavelength by many times. In these applicators, due to the superposition of electromagnetic fields of several hundreds of simultaneously excited modes, the spatial homogeneity of the radiation intensity distribution is high, which provides the possibility of homogeneous heating of large samples.

(iii) For most materials, the temperature dependence of the absorption coefficient becomes weaker with increasing radiation frequency, which decreases the thermal runaway probability.

The first publication on the use of millimetre radiation for sintering of optical ceramics appeared in 2005 [7]. In [8], radiation with a frequency of 83 GHz was used for sintering of Nd:YAG ceramics. The density of the sintered samples was 99% of the theoretical value, but the transparency was insufficient for lasing. Nd:Y_2O_3 ceramics with an extinction coefficient of 0.045 cm^{-1} at a wavelength of 1.06 μm was made by microwave (24 GHz) sintering from compacts of powders synthesised by laser ablation of a target [9]. Lasing in this ceramics was achieved later [10]. In [11], optically transparent Yb:YAG ceramics was produced by reaction synthesis of commercial powders upon heating by 24-GHz radiation.

2. Experimental

Yttrium oxide powder doped with rare earth ions was synthesised by the SHS method from acetate-nitrate metal complexes. As initial materials, commercial yttrium oxide (high purity grade, 99.99%), lanthanum oxide (99.99%), and ytterbium oxide (99.99%) powders, as well as nitric acid (high purity grade, 27-4) and acetic acid (reagent grade) were used. To perform SHS, the mixtures of powders were dissolved in a mixture of nitric and acetic acids with the molar proportion $Ln^{3+}:NO_3^-:CH_3COO = 1:2:1$. The solution was evaporated at a temperature of 110 °C, which resulted in the formation of lanthanide acetate-nitrates in the form of a white crystalline mass. This substance was divided into portions with a weight of about 2 g, which were placed into a quartz crucible and in a furnace preliminarily heated to 700 °C, where acetate–nitrates of metals were ignited and formed a foam-like product after combustion. To complete the oxidation of organic compounds, this substance was annealed at a temperature of 750 °C during ten minutes.

The phase composition of the SHS product obtained from lanthanide acetate–nitrate salts was determines by X-ray diffraction analysis within the angular range $2\theta = 20° - 70°$ with a step of 0.05° using a DRON-3M diffractometer (Russia). The size of crystallites was calculated from line broadening taking into account the instrumental broadening determined with a silicon standard.

The powder morphology was studied by transmission electron microscopy with a JEM 2100 (Japan) microscope. The sizes of powder particles were found from scanning electron microscopy images obtained with a Carl Zeiss Supra 50VP (Germany) and a JEOL-6490LV (Japan) microscopes. The size distribution of powder particles was determined by laser beam diffraction using an Analysette 22 NanoTec (Fritsch, Germany) laser analyser. The specific surface of particles was measured by BET nitrogen adsorption–desorption on a Sorbi-M (Russia) analyser. The element analysis of the synthesised powder was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an iCAP 6300 (US) spectrometer.

The powder was uniaxially pressed with a pressure from 100 to 900 MPa into compacts in the form of disks 18 mm in diameter and ~1 mm thick. To study the effect of plasticiser on the homogeneity of density in compacts, we added to the powder stearic acid (analytical grade) with a concentration varied from 0 to 10 wt%.

The disks were sintered in the working chamber of a gyrotron complex operating with a power up to 6 kW at a frequency of 24 GHz with a feedback computer control of the microwave power entering the chamber [12]. To remove possible residues of plasticiser and adsorbents, the disks were heated in air by microwave radiation up to $T = 700$ °C, after which the chamber was evacuated and further heating to the sintering temperature occurred in vacuum under a pressure of 10 Pa. The disks were placed in the centre of a cylindrical fused quartz crucible with a diameter of 100 mm and a height of 100 mm. Granulated Y_2O_3 powder (99.95%) was used for thermal insulation of the samples. The sample temperature was measured by a Pt ÷ Pt–Rh thermocouple, whose head touched the centre of the lower surface of the disk. The absence of a sharp drop of the thermocouple signal at the instant of switching off of microwave radiation testified to the absence of interference with the thermocouple measurements. The temperature measurement error was determined by verification with the data of an Luxtron M10 (Accufiber Corp.) optical thermometer calibrated by black body radiation and did not exceed 0.5% at the high-temperature stage of sintering. In most experiments, a pile of two disks positioned directly on the thermocouple head was sintered. The sample heating rate was varied within the range of 2–6 K min^{-1}, and the high-temperature exposure time was 2–10 h. After completion of a given temperature–time regime, microwave radiation was automatically switched off, and the thermally insulated samples were cooled with a rate of ~25 K min^{-1} (at the initial stage).

The sintered samples were polished with a submicron diamond paste. The transmission coefficient of the samples in the wavelength range of 200–1100 nm was measured on an SF-256 spectrophotometer. To study the microstructure of the samples, their surface was etched with an 1M nitric acid solution.

3. Results and discussion

Figure 1 shows a scanning electron microscope (SEM) image of the surface of a compacted sample of the $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ composition. One can see that the average size of particles does not exceed 100 nm. Transmission electron microscopy investigations showed that the particles have mainly a plate-like shape and consist of randomly oriented nanocrystallites with sizes of 10–20 nm [13]. According to the X-ray diffraction analysis, the average size of crystallites is 26 ± 1 nm in the as-synthesised powder and 50 ± 3 nm after annealing at a temperature of 1100 °C. The specific surface of particles is 13.4 m^2g^{-1} in as-synthesised powder and 8.1 m^2g^{-1} after annealing at $T = 1100$ °C (equivalent diameter of particles is 89 and 148 nm, respectively).

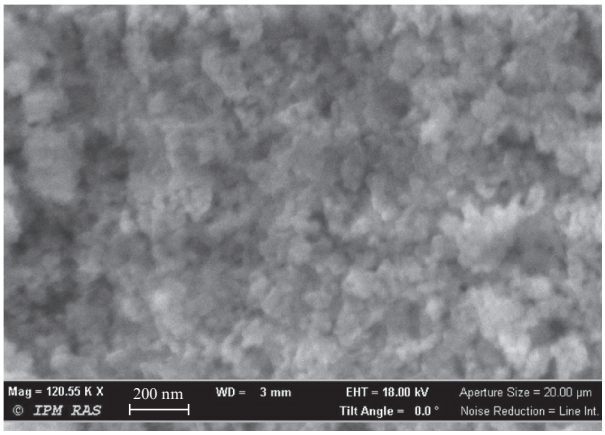

Figure 1. SEM image of the surface of an $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ compact.

Analysis of the size distribution of particles showed that the synthesised powder is agglomerated with an average agglomerate size of ~15 μm. However, the most part of agglomerates is destroyed upon ultrasound treatment. After dispersion during 40 min, the fraction of particles with a size smaller than 300 nm comprises more than 90%. The other 10% of powder consisted of agglomerates with a size of 3–15 μm [13].

The concentrations of the main impurities in the synthesised powder, determined by element analysis and are listed in Table 1, demonstrate that the used SHS method allows one to produce ultradispersed powder of the required $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ composition with a purity grade higher than 99.99%, which consists mainly of soft agglomerates breakable by ultrasound dispersion.

It is known that the addition of lanthanum oxide to yttrium oxide strongly affects the sintering ability and transparency of Y_2O_3 ceramics. The improvement of sintering is explained by the formation of a solid solution in the mixture of Y_2O_3 and La_2O_3 powders at high temperatures, which enhances the grain boundary diffusion in yttrium oxide [14] and, at the same time, restrict the grain growth [15]. In the case of sintering under the conditions of standard resistance heating in hydrogen atmosphere, the highest transparency was achieved for Y_2O_3 ceramics containing from 8 to 12 mol% of La_2O_3 [1, 16]. In order to determine the optimum concentration of La_2O_3 for microwave sintering, the samples with La_2O_3 concentrations varying from 0 to 17.5% were heated to a temperature of 1770 °C and kept at this temperature during two hours.

Table 1. Content of main impurities in the $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ powder synthesised by the SHS method.

Impurity	Concentration /10^{-4} wt%	Impurity	Concentration /10^{-4} wt %
Na	34 ± 4	Ca	21 ± 1
Mg	1.0 ± 0.1	Ti	3.0 ± 0.34
Si	26 ± 3	Fe	0.6 ± 0.1
K	2.8 ± 0.3	Zn	2.5 ± 0.1

Figure 2 presents the photographs of the sintered samples, and Fig. 3 shows the transmittance of $Y_{(1.9-x)}La_xYb_{0.1}O_3$ ($0 \leqslant x \leqslant 0.35$) ceramics at a wavelength of 1.1 μm as a function of La_2O_3 concentration.

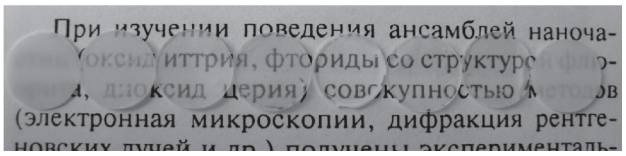

Figure 2. Photograph of sintered disks with lanthanum oxide concentrations from 0 to 17.5 mol% (concentration increases from left to right by 2.5 mol% from one sample to another).

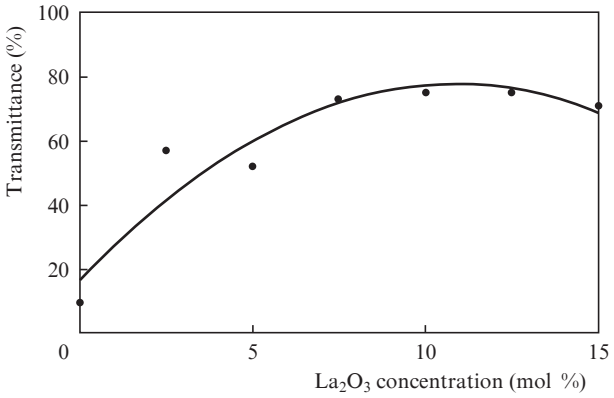

Figure 3. Dependence of the transmission of an $Y_{(1.9-x)}La_xYb_{0.1}O_3$ ceramic sample at a wavelength of 1.1 μm on the lanthanum oxide concentration. The sample thickness is 0.6 mm.

The optical characteristics of 0.6-mm thick samples of yttrium oxide ceramics with different contents of La_2O_3 were measured in [13]. The measurements were performed at a laser wavelength of 1075 nm. The scheme used in [13] allowed the reflection, absorption, and scattering coefficients to be measured. The measurements showed that the reflection coefficient (~9%) almost does not depend on the La_2O_3 concentration. The minimal absorption and scattering coefficients are observed in the La_2O_3 concentration range of 10.0–12.5 mol %. An increase in the La_2O_3 concentration (to higher than 15 mol%) leads to an increase in the absorption and scattering coefficients presumably due to the formation of the $YLaO_3$ phase [17].

The entire set of the our results leads to the conclusion that, upon microwave sintering at a residual air pressure of

10 Pa, the maximum transmittance of the $Y_{(1.9-x)}La_xYb_{0.1}O_3$ ceramics is also achieved at the La_2O_3 concentration of about 10 mol%. Note that, as follows from investigations of the microstructure, the average size of grains in the $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ ceramics is 10 μm (Fig. 4), while the grain size in the Y_2O_3 ceramics obtained under similar conditions is ~40 μm [13].

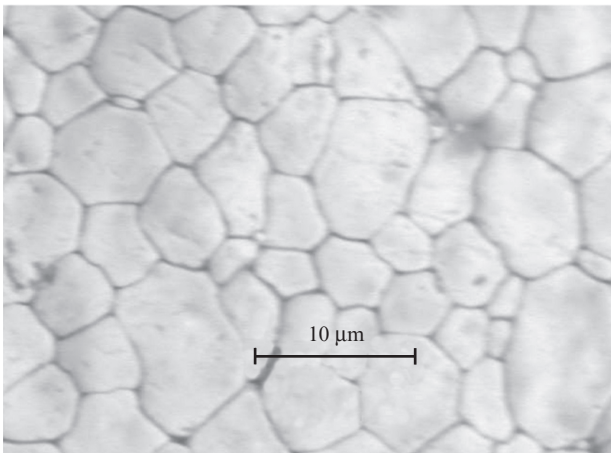

Figure 4. SEM image of a polished and etched surface of an $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ ceramic sample.

A high density of compacts is one of the conditions of sintering of poreless ceramics. However, an increase in the uniaxial pressure may lead to 'overpressing' and stratification in the sample material. The optimal pressure was determined from the results of microwave sintering of samples compacted at different pressures under the same temperature-time conditions. From Fig. 5, which shows the photographs of $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ ceramic samples produced at different pressures, one can see that the best optical transmission belongs to the sample compacted at a pressure of 5 t cm^{-2}.

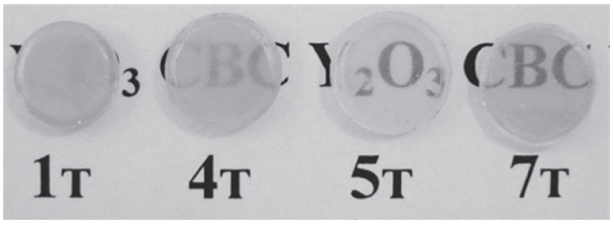

Figure 5. Photographs of samples compacted under different pressuring forces.

This result is confirmed by the porosity both determined by the density estimated by weight and geometric size of the sample and measured by the BET method on a Sorbi-M analyser. With increasing the compaction pressure from one to seven tons, the total porosity decreases from 400 to 180 mm^3 g^{-1}. Simultaneously, the relative amount of large (larger than 50 nm) pores decreases. Obviously, the increase in the transmittance of the sintered ceramic samples with increasing compaction pressure is caused by a decrease in the fraction of large pores. However, as is seen from the photographs shown in Fig. 5, as the pressuring force increases from 5 to 7 t, the transparency of the samples becomes worse due to partial stratification of the material. Our investigations of the density distribution in compacts by optical microscopy with a contrast agent showed that the large 'overpressing' defects can be avoided by using ultrasonic dispersion of powders before compaction and by applying stearic acid as a plasticiser.

The joint effect of plasticiser and compaction pressure on transparency was studied for a series of $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ ceramic samples sintered at a temperature of 1770 °C during two hours. As is seen from the spectra shown in Fig. 6, the highest transmittance was demonstrated by the sample pressed from a powder with addition of 2.5 wt% of stearic acid at a pressure of 7 t cm^{-2}. A lower concentration or absence of plasticiser, as well as a higher compaction pressure, led to stratification and cracking of the compacted material.

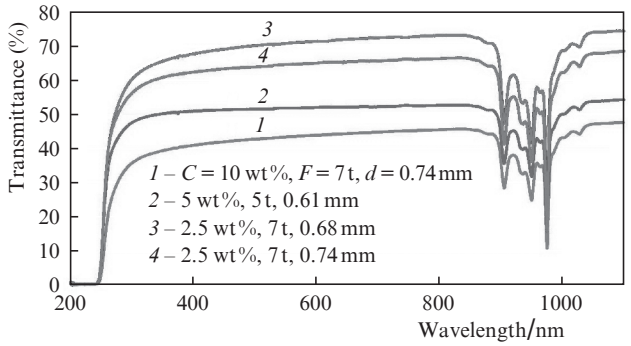

Figure 6. Transmission spectra of $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ ceramic disks with different thicknesses d compacted form initial powders with different stearic acid concentrations C under different pressuring forces F.

The best optical characteristics were demonstrated by the sample produced under the following conditions: pressuring force 7 t, stearic acid concentration 2.5 wt%, La_2O_3 concentration 10 mol%, microwave heating rate ~ 4 °C min^{-1}, sintering temperature 1770 °C, exposure time 10 h, cooling rate ~25 °C min^{-1}. This ceramic sample was used in laser experiments in the free-running regime. After polishing of the sample, its front and rear surfaces were, respectively, antireflection- and reflection-coated.

The sample was pumped by a Laserline LDM 2000 diode module (wavelength 940 nm, pulse duration 2 ms, pulse repetition rate 0.5 Hz, beam spot diameter on the sample 1 mm). The scheme of the experimental laser setup is shown in Fig. 7. The cavity was ~ 10 cm long and was formed by two mirrors

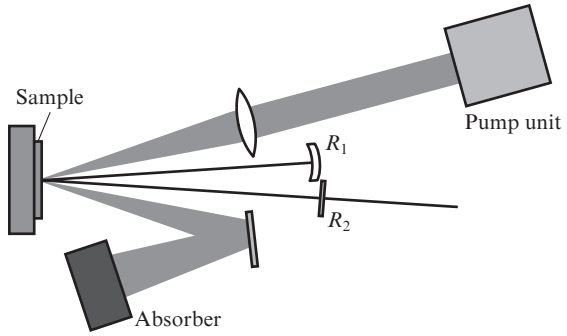

Figure 7. Scheme of the experimental laser setup.

with the following curvature radii r and reflection coefficients R: $r_1 = 30$ cm, $R_1 \simeq 100\,\%$ and $r_2 = \infty$, $R_2 \simeq 95.5\%$. The spectrum of observed free-running lasing had a clear peak at a wavelength of 1030 nm (Fig. 8), which corresponds to the peak in the luminescence spectrum. The laser beam intensity profile was close to Gaussian. The measured dependence of the free-running power on the pump power absorbed in the sample is shown in Fig. 9. This linear dependence shows a slope efficiency of 7.5%.

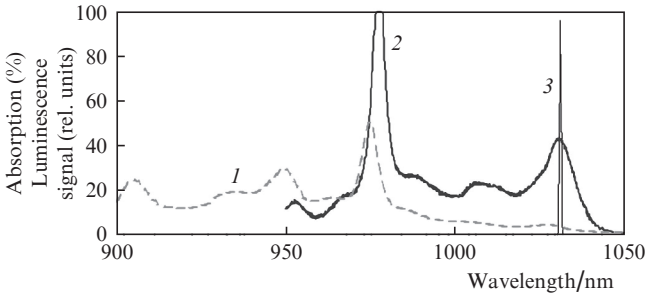

Figure 8. Absorption (*1*), luminescence (*2*), and lasing (*3*) spectra of $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ ceramics.

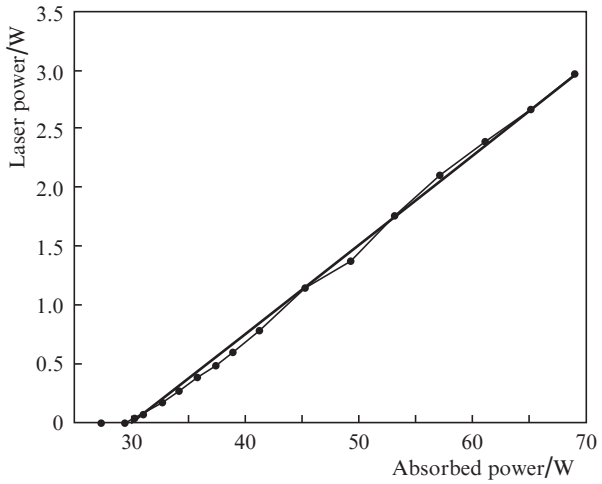

Figure 9. Dependence of the laser power on the absorbed pump power.

4. Conclusions

It is shown that 24-GHz microwave heating is promising for sintering highly transparent $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ceramics from powders produced by self-propagating high-temperature synthesis. The fine $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$powder synthesised by this method had a purity higher than 99.99% and consisted mainly of soft agglomerates breakable by ultrasonic dispersion. The sintering regimes were studied and optimised using a 24-GHz gyrotron complex for high-temperature treatment of materials. The effect of lanthanum oxide as sintering aid on the optical transmission of ceramics is determined in the La_2O_3 concentration range from 0 to 17.5 mol%. The optimal La_2O_3 concentration is 10 mol%. The optical properties of the obtained ceramics are studied depending on the conditions of preparation of initial materials (compaction pressure and plasticiser concentration). Lasing of a produced $(Yb_{0.05}Y_{0.85}La_{0.1})_2O_3$ ceramic disk was demonstrated in a linear cavity at a wavelength of 1.03 μm with an efficiency of 7.5%.

It is expected that the optical properties of ceramics can be improved by using such compaction methods as cold isostatic pressing and slip casting, which allow production of high-density samples with a more homogeneous density distribution, and by detailed optimisation of microwave sintering regimes.

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