The Czochralski growth of $SrLaGa_3O_7$ single crystals and their optical and lasing properties

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Abstract

Single crystals of $SrLaGa_3O_7$ undoped and doped with 5 and 10 at. % of neodymium were grown by the Czochralski technique. Their composition and dopant distribution were checked by X-ray microprobe.

The Nd-doped crystals were investigated for their lasing and spectral properties. Absorption spectra in the range 180-8000 nm and the luminescence spectra in the range 200-800 nm were measured Throughout the whole spectrum differential changes of the absorption coefficient were found. Optical transitions corresponding to this effect are indicated.

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1. Introduction

Single crystals of $SrLaGa_3O_7$ (SLG) belong to a large family of compounds of the general formula ABC_3O_7 where A=Ca, Sr, Ba; B=La, Gd; and C=Ga, Al. These compounds crystallize in the tetragonal melilite structure which belongs to point group 42m and to space group $P42_1m$. The structure of ABC_3O_7 exhibits many distortions which is a result of the disordered occupancy of neighboring sites by ions with significant differences in ionic radii and valence. Some of them were obtained in the polycrystalline state through high temperature synthesis of a stoichiometric mixture [1-6]. Single crystals of some ABC_3O_7 compounds were obtained by the laser-heated pedestal growth method [7, 8].

The most suitable conditions for growth of ABC_3O_7 single crystals were obtained by the Czochralski method. This method was used for the growth of $BaLaGa_3O_7$:Nd single crystals which were some of the most extensively investigated among ABC_3O_7 materials with lasing properties. However, it was found that, owing to the high degree of structural inhomogeneities, connected with the large difference in the ionic radii of Ba^{2+} and La^{3+}, the material exhibits a high energy threshold for laser action (about 90 J) [9]. Therefore $BaLaGa_3O_7$: Nd cannot be treated as a potential new material for use in laser techniques.

Another compound was obtained in which Sr atoms were substituted for Ba. Single crystals of $SrLaGa_3O_7$:Nd exhibit much better lasing properties [10-12], probably due to higher structural homogeneity. In this case the difference in the ionic radii of Sr^{2+} and La^{3+} is negligible.

Single crystals of $SrLaGa_3O_7$ have the following properties: melting point, 1760°C; unit cell parameters a=0.806 nm and c=0.534 nm; density, 5.24 g cm^{-3} [4]. The thermal conductivity is relatively high (11 W mK^{-1}) in comparison to that for neodymium-doped yttrium-aluminum-garnet (YAG:Nd) (13 W mK^{-1}) which is very important for application in laser techniques.

In this work undoped and Nd-doped SLG single crystals were obtained by the Czochralski method. All crystals were of good quality. Undoped single crystals were successfully used as substrates for high temperature superconducting (HTSC) layers, e.g. $YBa_2Cu_3O_{7-\delta}$ (YBCO). Nd-doped crystals were investigated for their optical and generation properties.

2. Experiments and results

To prepare the SLG charge the following starting materials of purity 99.99% were used: $SrCO_3$ from the Research and Development Center for Vacuum Technique, Poland; La_2O_3 from the Research Center of Lublin University, Poland; and Ga_2O_3 and Nd_2O_3 from Johnson Matthey, UK. They were annealed or dried before weighing. The charge was prepared according to the formula: $Sr_{1.1}La_{1.0}Ga_{3.1}O_7$. After careful mixing the material was put in an alumina container into a resistivity furnace and the following schedule of heating was realized: 400°C for 2h, 800°C for 2h and 1200°C for 3h.

Fig.1. Photographs of SLG single crystals (a) Nd-doped crystals, one as grown and the other cut perpendicularly to the growth direction [0001]; (b) Nd-doped crystal with two opposite plates parallel to the [0001] direction polished (left) and a plate out from an undoped crystal perpendicularl to the [0001] direction (right).

For melting of the charge material and single-crystal growth an MSR-2 system made by Metals Research Ltd., England, was used. The system is equipped with an r.f. generator and a device for automatic diameter control that requires weighing of the growing crystal. Apart from the iridium crucible and passive afterheater a set of ceramic insulation (sintered, grog and felt) was used to obtain, during growth, appropriate axial and radial temperature gradients which are necessary for high quality single crystals.

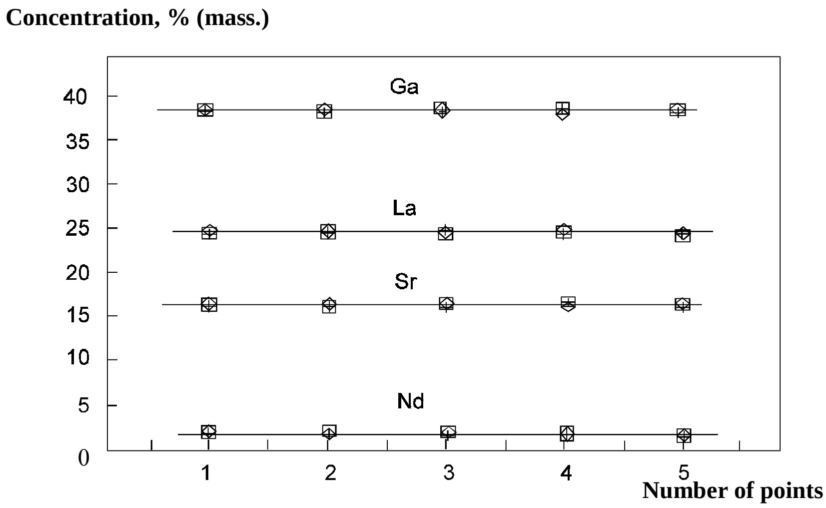
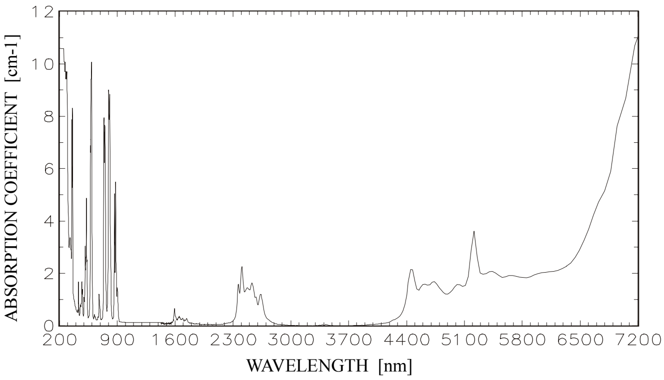


Fig. 2. The X-ray-measured distribution of the base elements and of the dopant along the crystal and across the diameter: -----, stoichiometric composition; ◊, results of measurements along 80 mm crystals of composition $Sr_{1.1}La_{0.95}Nd_{0.05}Ga_{3.1}O_7$; , results for an 80 mm crystal of composition $Sr_{1.4}La_{0.89}Nd_{0.05}Ga_{3.02}O_7$; +, measurements across a 25 mm diameter for a crystal of composition $Sr_{1.4}La_{0.89}Nd_{0.05}Ga_{3.02}O_7$.

Crystals were pulled by the Czochralski method from the iridium crucible 50 mm in diameter and 50 mm in height. The pulling speed was about 3 mm h^{-1} and the rotation rate 50 rev min^{-1}. The crystals were pulled in a pure nitrogen atmosphere. All SLG single crystals were grown in the [001] direction After completing the growing run crystals were cooled down for 20 h.



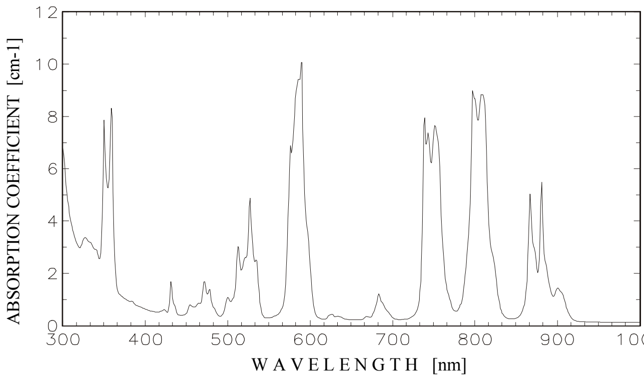


Fig. 3. Photographs of SLG single crystals, (a) Nd-doped crystals, one as grown and the other cut perpendicularly to the growth direction [001]; (b) Nd-doped crystal with two opposite planes parallel to the [001] direction polished (left) and a plate cut from an undoped crystal perpendicularly to the [001] direction (right).
Fig. 4. Absorption coefficient spectrum for an $SrLaGa_3O_7$ plate in the wavelength range 300-1100 nm.

The dopant was introduced into the undoped SLG charge by adding $SrNdGa_3O_7$ or the components were mixing according to the following formulae: $Sr_{1.04}La_{0.89}Nd_{0.05}Ga_{3.02}O_7$ for 5 at.% of Nd; $Sr_{1.04}La_{0.84}Nd_{0.1}Ga_{3.02}O_7$ for 10 at.% of Nd. Nd atoms were substituted for La.

The conditions of growth of Nd-doped crystals were analogous to those in the case of undoped crystals.

Single crystals of SLG and SLG:Nd of diameter up to 20 mm and length up to 80 mm were obtained. They are shown in Fig. 1. In Fig. 1(a) there is an Nd-doped as-grown boule with seed and boules with planes perpendicular to the [001] direction and polished (one of them rounded). In Fig. 1(b) there is an Nd-doped boule with two opposite planes parallel to the [001] direction polished and plate cut from an undoped SLG crystal for use as a substrate for epitaxial HTSC layers.

Undoped SLG crystals were colourless and Nd-doped crystals were of lilac tint. All the single crystals obtained were transparent and free of cracks, iridium inclusions and other macroscopic defects. The cross-section of a crystal was approximately circular and the outer surface was corrugated as in the case of $Ga_3Gd_5O_{12}$ single crystals.

The solid-liquid interface in the cone part was convex towards the melt and in the cylindrical part was planar. In some crystals there were striations in the cone.

All crystals were annealed in the resistivity furnace at 1200^{o}C for 50 h in an atmosphere of oxygen and then cooled down to room temperature for 24 h. In this way thermal stresses were reduced and crystals were more resistant to mechanical treatment. They could be easily cut, lapped and polished without cracking.

The composition of single crystals and the neodymium distribution were examined by use of an X-ray microprobe. The distribution of the base elements of he compound and of the dopant along the crystal and across the diameter of the cross-section are depicted in Fig. 2. For comparison, data for a stoichiometric composition are also depicted.

The chemical composition of the good quality single crystals obtained differs from the stoichiometric composition but it is uniform along the crystal axis and also the neodymium distribution is homogeneous along the crystals. Plates cut from the cone and from the tail of boules were of the same composition.

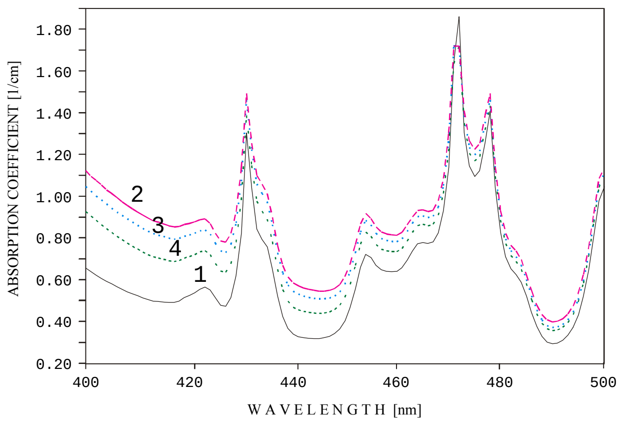
Therefore starting from a charge of a certain deviation from the stoichiometric composition homogeneous single crystals (in the limits of the measurement's accuracy) were obtained. Their composition also differs from the stoichiometric composition.

All the single crystals obtained were without macroscopic defects and of good optical quality.

3. Optical investigations

Samples approximately 6 mm in thickness, with both sides optically polished, were cut out from undoped and Nd^{3+} - doped crystals in the direction perpendicular to the optical c axis. From crystals doped with 10 at. % Nd^{3+}, laser rods 4 mm in diameter and of lengths 48.5 mm (SLG1), 48.8 mm (SLG2), 35.0 mm (SLG3) and 36.8 mm (SLG4) were also cut out.

The spectrophotometers used to measure the characteristics were a UV-visible LAMBDA 2 and Fourier transform IR 1705 device from Perkin Elmer.



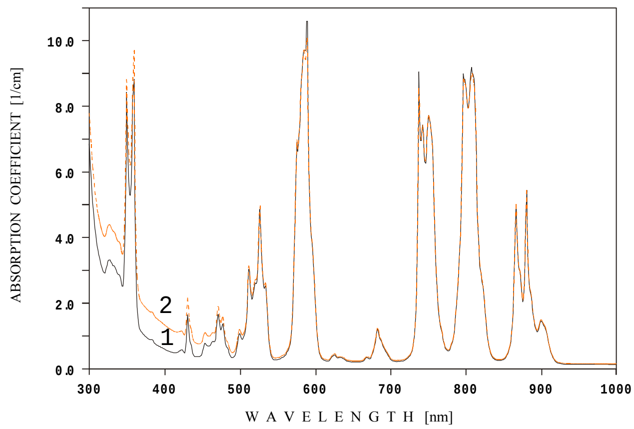
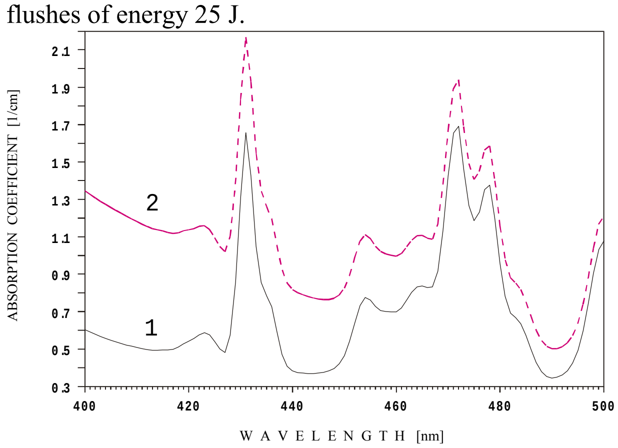


Fig. 5. Changes of absorption for the excited SLG rod: curve 1, before excitation; curve 2, 1 h after excitation without any UV-removing filter; curve 3, 1 h after excitation with GG-5 filter; curve 4, 24 h after excitation.

Fig. 6. Changes of absorption coefficient for the excited SLG plate: curve 1, before excitation; curve 2, after excitation by 40 flushes of energy 25 J.



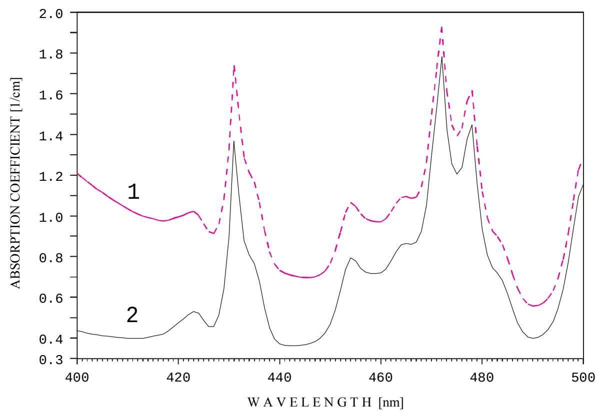
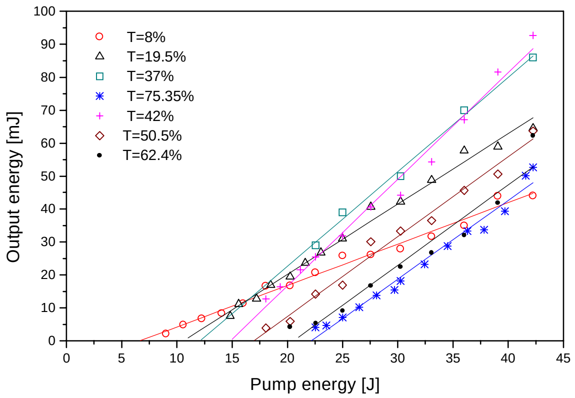
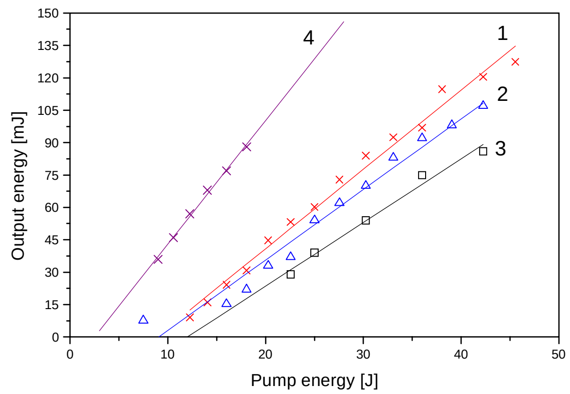


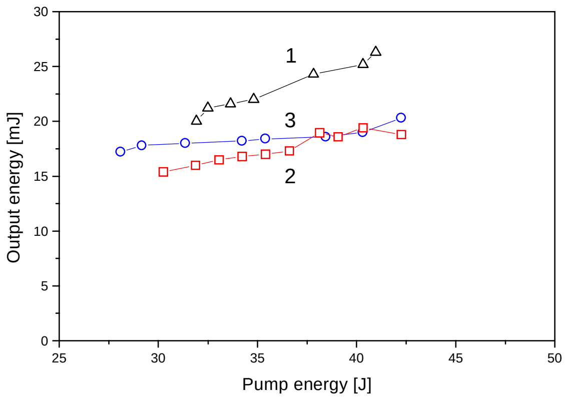
Fig. 7. Details of changes of absorption for the excited SLG plate: curve 1, before excitation; curve 2, after excitation by 40 flushes of energy 25 J.

Fig. 8. Changes of absorption for the annealed and excited SLG rod: curve 1, 1 h after excitation; curve 2, after annealing and excitation.

The absorption spectra in the range 200-7200 nm, and in the specific range of 300-1000 nm for pumping, are presented for 10 at. % Nd-doped crystal in Fig. 3 and Fig. 4, respectively. The absorption threshold is at 250 nm and lattice absorption is observed above 6200 nm. Two narrow and sharp peaks in the vicinity of 870 and 890 nm should be noted corresponding to the $^4I_{9/2}$ - $^4F_{3/2}$ transition of the Nd^{3+} ion.







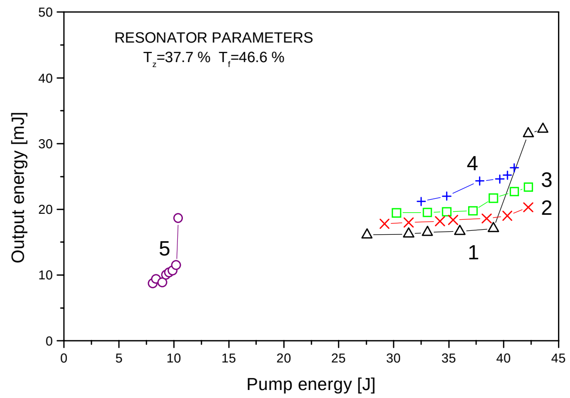


Fig. 9. Outut energy of the free running laser with SLG1 rod and different output mirrors

Fig. 10. Efficiency of SLG for the SLG1 rod and YAG lasers line 1, SLG, first measurement efficiency, 0.37%, threshold 8.842J; line 2, SLG, second measurement efficiency 0.33% threshold, 0.075J; line 3, SLG, with a GG5 filter efficiency 0.29%, threshold, 11.995J; line 4, YAG, efficiency 0.57%, threshold, 2.848J.

Fig. 11. Generation of a single pulse by the SLG1 rod (output mirror transmission equal to 37.7%; Δ, with a GG-5 filter, , with antireflex coatings; o, without a filter.

Fig. 12. Comparison of the single pulse generation for SLG and YAG rods; Δ – first measurement, * - second measurement, and + measurements with a GG-5 filter; o – YAG rod.

Some of the samples underwent optical excitation after measurements, and these were repeatedly continued in order to investigate changes in the absorption coefficient and the relaxation phenomena associated with these changes. The essential changes in absorption spectrum were observed within ranges 346-368 nm, 429-441 nm and 450-490 nm. To determine whether these changes are durable, the next series of measurements were carried out. The results are shown in Figs. 5-8.

The changes of the absorption of the investigated rods and plate are given there as a function of time elapsed from the moment of their excitation by 40 pulses from the pumping flashlamp, each of energy 24 J. Within 24 hours the characteristics do not return to the form observed before the excitation; hence the changes are stable. To determine the reasons why the above changes take place, the investigated rods and plates were then annealed in an oxidizing atmosphere. The spectral characteristics of absorption confirm the disappearance of these newly created absorption bands in annealed specimens. However, these bands appear again when the annealed crystals are excited by flashlamp radiation (see Fig.8). The probable reason for such changes in absorption spectra is the presence of colour centres in the crystal lattice.

The relaxation rate of colour centres induced by flashlamp irradiation measured immediately after the irradiation process is equal to approximately 1% per 1000 s.

From our measurements it is clear, that changes in the absorption coefficient are insignificant for wavelengths greater than 500 nm.

For more detailed studies of this phenomenon laser rods were used in the giant-pulse configuration of a laser head and the measurements were carried out without filtering or with the use of GG-5 filter (λ_{cut} = 450nm) or sodium glass (λ_{cut} = 350nm) in order to remove UV radiation.

4. Lasing properties

Laser rods were put into the plane-parallel laser cavity 24 cm long, made of messing covered with gold. A single xenon lamp with a diameter of 4 mm was excited with energies of 7-100 Joules. The pulse width was 120 µs, and the output mirror transmissions were 8%, 20%, 37%, 42%, 51%, 62% and 75% (Fig. 9). UV radiation was eliminated by either a GG5 or sodium glass filters (Fig. 10). The pulse energies were measured using an ED-200 "Gentec" measuring head and the pulses were also recorded by a Tectronix oscilloscope.

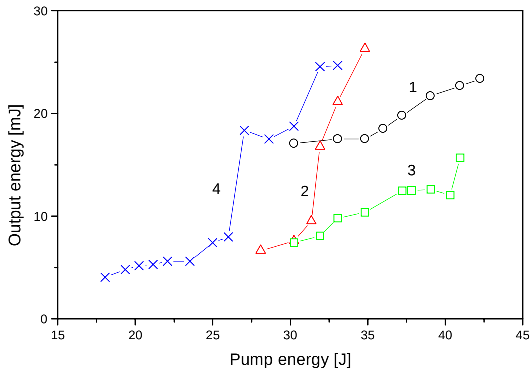


Fig. 13. Generation of a single pulse for all manufactured SLG rods (with a GG-5 filter); o – SLG1 rod with an AR coating; Δ – SLG2 rod without a coating;   – SLG3 rod without a coating; * - SLG4 rod without a coating.

The giant-pulse measurements were carried out in a Q-switch mode type of resonator using an optimized non-linear absorber with a transmission of 46,6 % and the optimized output mirror.

The results of free-running laser emission of the four rods are shown in Figs. 9 and 10. The differential efficiency of the SLG1 laser rod, compared to the efficiency of YAG:Nd^{3+} rod is shown in Fig. 10. The higher efficiency of the YAG:Nd^{3+} rod is clearly visible.

The dependences of the generation thresholds and laser efficiency on the transmission of the output mirrors are shown in Fig. 9. The characteristics given there define also the value of the dynamic loss coefficient (ρ=0.0523 cm^{-1}). This value is small if we consider the presence of defects in the crystal, but is large in comparison to the value of the dynamic loss coefficient for YAG:Nd^{3+} rods (ρ = 0.005 cm^{-1}).

The optimized value of the output mirror transmission is equal to 37.7% for the SLG1 rod.

The generation of a single pulse obtained for an SLG1 laser rod is shown in Fig. 11. The generation was measured without and with UV-removing plates in the resonator. As can be observed, the deeper UV cut-off (GG-5 glass plate) improves essentially the generation characteristics of the laser, i.e. the laser pulse energies are higher and the generation threshold is lower. The UV cut-off obtained with the plate made of sodium glass has practically no influence on the laser generation.

The increase of output energy of the laser pulse observed when the GG-5 glass plate was present in the resonator is a contrary effect, compared to the appropriate changes of energy during free-running generation (see Fig. 11).

The comparison of a single-laser-pulse generation for SLG and YAG rods is shown in Fig.12. The rods cut from the same $SrLaGa_3O_7$:Nd^{3+} crystal have different threshold energies for pulse generation, as can be seen in Fig.13.

5. Conclusions

With the use of the Czochralski method single crystals of $SrLaGa_3O_7$ undoped and doped with 5 an 10 at.% of Nd^{3+} were obtained. The crystals were of good quality and the dopants distribution was uniform. The optical characteristics were measured; then laser rods were cut and their generation properties were evaluated.

It was found, that optical pumping leads to degradation of the optical parameters (longer absorbance, greater thresholds and lower efficiencies in laser actions) and that thermal annealing of laser rods may limit these phenomena to a certain extent. A detailed study of lasing properties in a free-running mode indicated that optimization of laser head and especially of the transmission of the output mirror is necessary for comparison of an SLG laser to Nd:YAG rods, for example.

It was also found that in the free-running mode laser thresholds are a few times larger for SLG compared to good quality YAG rods, but the shape efficiency is lower only by several per cent compared with YAG rods and may be comparable to that of a rod of average quality [4].

From the giant-pulse mode generation in the passive Q-switch modulation measurements it is evident that for SLG laser rods the output energy is twice that of the corresponding YAG rods. This phenomenon can be utilized practically in laser pulsed systems which require high energies, e.g. surgery, stomatology, or laser marking.

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