Preparation and study of epitaxial Cr^{4+} : GGG films for passive Q switches in neodymium lasers

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Abstract. **The efficient technology is developed for growing Cr- and Ca-doped gadolinium – gallium garnet single-crystal films of thickness up to 100 μm on large substrates (76 mm) by the method of liquid-phase epitaxy from a solution – melt. The dependences of the absorption spectra of films and optical losses at 1 μm on the growth conditions and the solution – melt composition are studied. It is shown that Cr^{4+} ions are formed in the films, and these films can be used as passive Q switches in lasers.**

Keywords: *liquid-phase epitaxy, epitaxial film, gadolinium – gallium garnet, solid-state laser, passive Q-switching.*

1. Introduction

Garnet crystals doped with Cr^{4+} ions attract interest because of their wide applications in Q switches for 1-μm lasers and as active media for lasers tunable in the near-IR region between 1.2 and 1.5 μm. The growth technology of bulk yttrium – aluminium garnet Cr^{4+} : YAG and gadolinium – gallium garnet Cr^{4+} : GGG crystals has been developed already for more than 15 years [1]. At present the investigations aimed at the improvement of the optical characteristics of Cr-doped garnets and the search for a physical model explaining the mechanism of formation of Cr^{4+} ions in crystals are being continued [2–4]. Of special interest is the development of simple and efficient, reliable and low-cost, compact lasers emitting short and stable single-mode pulses [5]. One of the possible designs is a monoblock consisting of a crystalline active element and an epitaxial single-crystal layer grown on its surface as on a substrate, which acts as a Q switch [6, 7]. This is a complicated technological problem, which can be solved in several steps. It is necessary first of all to achieve a high quality of films grown on small-diameter substrates (smaller than 30 mm).

The aim of our study was to find the optimum conditions for growing homogeneous single-crystal GGG films of high optical quality on the surface of GGG

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substrates of large diameters (more than 70 mm) and to determine their spectral characteristics allowing the application of these films as Q switches in compact laser systems.

2. Growth of epitaxial films

To build compact monoblock laser systems, it is necessary to grow high-quality epitaxial films with specified parameters. We have chosen a GGG crystal as a material for a substrate and film because the technology of growing high-quality GGG crystals for substrates is well developed. We have grown earlier Cr-doped single-crystal films on GGG single-crystal plates by the method of liquid-phase epitaxy from a solution – melt with a high concentration of Cr^{4+} ions [8]. In this paper, we developed the technology for growing epitaxial films heavily doped with Cr^{4+} ions with minimal optical losses at a wavelength of 1 μm.

The method of growing epitaxial crystal films from a solution – melt allows one to vary their growth temperature in a certain range to optimise the film parameters. Films were grown at different solution – melt compositions and temperatures in the range from 830 to 1010 °C. Substrates of diameter 76 mm were prepared from pure GGG crystal plates with the (111) orientation maintained with an accuracy of $\pm 2''$ and the same (to the fifth decimal place) crystal lattice parameter $a_s = 12.38254$ Å. A series of 17 Cr, Ca : GGG/GGG samples was grown on a GGG substrate of diameter 76 mm in experiments. The $PbO – B_2O_3$ system was used as a solvent in the solution – melt.

The growth regimes for each composition were worked off by determining the saturation temperature T_s and the dependence of the film growth rate f_g on the supercooling degree ΔT. The saturation temperature, which was determined by extrapolating the experimental temperature dependence of the film growth rate T_g to zero, was equal to the temperature at which the film growth rate was zero.

The dependence of the growth rate on supercooling is the same for all solution – melts: it is linear for small ΔT, then saturates, and decreases due to the spontaneous crystallisation of the garnet on the crucible walls and in the solution – melt volume. Salts containing bivalent Ca ions were added to the solution – melt. In this case, Cr^{4+} centres appeared during the film growth, which provided the charge compensation for doped bivalent ions. The concentration ratio of Ca and Cr ions in films determined by X-ray fluorescence analysis was from 1 : 5 to 1 : 10. Crystal films were formed on both sides of the plate.

The quality of the deposited epitaxial films was controlled by several parameters. First, we measured the lattice

parameter α_f which depended to some extent on the solution–melt supercooling and increased with increasing ΔT. This can be caused first of all by the processes of embedding Pb^{2+} and Pb^{4+} ions into the dodecahedral and octahedral sublattices of a crystal film. Figure 1 shows the typical rocking curves of X-ray diffraction for an A8-15 sample in which the difference $\Delta\alpha$ of lattice parameters of the substrate (α_s) and film (α_f) is relatively large. A small half-width ($\sim 0.03°$) of the curves demonstrates a high crystallographic quality of the epitaxial film. To achieve a coincidence between the lattice parameters of the film and substrate to the third decimal place, we changed the solution–melt composition because otherwise the epitaxial film could crack due to mechanical stresses.
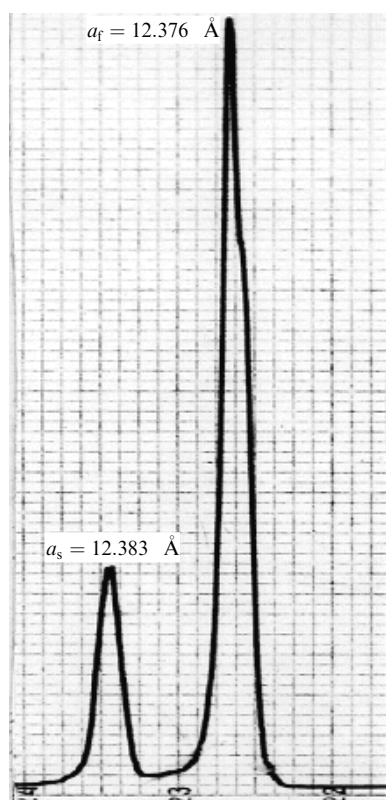

Figure 1. X-ray diffraction (rocking curves) upon reflection from the (888) plane of an A8-15 sample. The half-width of peaks is $\sim 0.03°$.

Second, the microscopic control of the film homogeneity was performed by transmitting light through crossed polarisers, which demonstrated the absence of any block structure and inclusions. The epitaxial film thickness was constant with a high degree of accuracy over the entire substrate surface. The film thickness for different samples was different and lied in the range from 1.5 to 110 µm.

3. Study of optical and lasing characteristics

Cr^{4+} ions have broad absorption bands in the red (600–800 nm) and near-IR (near 1 µm) spectral regions. The annealing of bulk garnet crystals in the oxygen atmosphere results in an increase in the intensity of these bands, the absorption coefficient being dependent on the annealing temperature and atmosphere. To analyse the influence of

growth conditions only, crystals were not annealed at this stage of the study.

Aside from structural studies, we investigated the absorption and luminescence spectra of the grown epitaxial films to determine the oxidation degree of chromium ions. The absorption and luminescence spectra were recorded with a Shimadzu UV-31101PC spectrophotometer and an ARC InSpectrum spectrofluorimeter, respectively. The absorption spectra exhibit structural bands. Measurements of the luminescence excitation spectra showed that the structural spectrum in the 600–800-µm region can be decomposed into the absorption bands of Cr^{3+} and Cr^{4+} ions. In addition, absorption by chromium ions in epitaxial films is summed with absorption by colour centres which appear due to the entering of lead oxides from the solution–melt into the film during the growth process. Thus, the absorption bands of chromium ions in the film are added with the pedestal of the so-called grey losses. During absorption saturation in Cr^{4+}-doped films, this pedestal gives the residual absorption.

The level of grey losses depends on the concentration of weakly controllable impurities Pb^{2+}, Pb^{4+}, and Pt^{4+} entering into the film from the solution–melt and crucible material. The concentration of these impurities is determined to a great extent by the growth temperature and decreases with temperature. Figure 2 shows the absorption spectra of three samples from one series (IV), which were grown at somewhat different temperatures. One can see that even small differences in the growth temperature change the level of grey losses in these samples, whereas the concentrations of Ca and Cr ions remain almost constant. The lowest losses at a wavelength of 1 µm in this series of experiments were 23 cm^{-1} (see curve in the inset in Fig. 2). In this case, the concentration of Cr^{4+} ions was $\sim 4 \times 10^{18}$ cm^{-3}, which is $\sim 1\%$ of the total concentration of chromium ions in the epitaxial film.

In the next series of experiments, the molar ratio of the gallium and gadolinium oxides in the solution–melt was decreased to $\sim 2.5\%$ (compared to $\sim 15\%$ in series IV) in order to reduce the entering of lead ions into the film. The content of calcium and chromium oxides and their ratio in the solution–melt in series V were the same as in series IV.
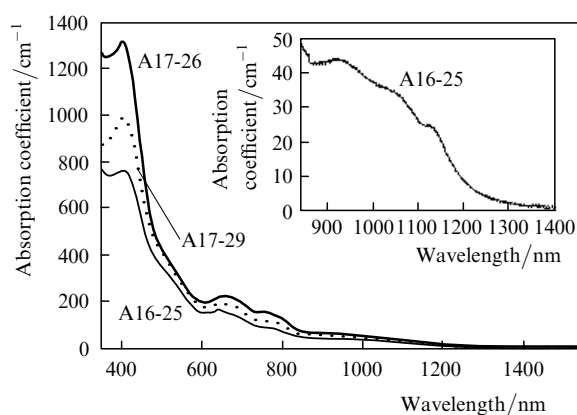

Figure 2. Absorption spectra of epitaxial Cr, Ca : GGG/GGG films (series IV) A17-26 (the film thickness is $2h = 24$ µm, $T_g = 1000\,°C$), A17-29 ($2h = 25$ µm, $T_g = 1005\,°C$), A16-25 ($2h = 65$ µm, $T_g = 1008\,°C$). The inset shows the absorption spectrum of an A16-25 sample in the near-IR region.

As a result, the content of lead in the grown films was reduced by more than an order of magnitude (according to the mass spectral data, from ~ 2000 ppm down to 80 ppm). In this case, losses at a wavelength of 1 μm decreased down to ~ 0.8 cm^{-1} (Fig. 3). Unfortunately, the concentration of Cr^{4+} ions also considerably decreased (down to $\sim 4 \times 10^{17}$ cm^{-3}, which is an order of magnitude lower that in samples of series IV). The concentrations of chromium and calcium ions in the film were the same for both series of experiments.
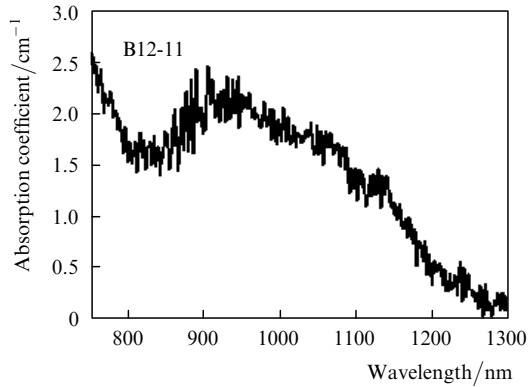

Figure 3. Absorption coefficient of a B12-11 epitaxial Cr, Ca : GGG/GGG film (series V) in the near-IR region.

We measured absorption saturation in the grown films at a wavelength of 1 μm by using a diode-pumped, Q-switched Nd^{3+} : YAG laser. A sample was located on the optical axis behind the waist of the probe laser beam and could be moved along the axis, the pulse energy density on the sample surface being a function of the sample on the optical axis. The laser operated in the multimode regime. The divergence of the probe laser radiation was ~ 3 mrad and the beam diameter was ~ 2 mm. The laser pulse repetition rate was 11.76 kHz and the pump power was 19 W. Because the excited-state lifetime of the Cr^{4+} ion was 1.3 μs and the duration of the probe laser pulse was 50 ns, we measured the dependence of absorption saturation for Cr^{4+} ions in films on the probe pulse energy density. Figure 4 presents the transmission of a Q switch cut out from an A16-25 epitaxial film sample as a function of the probe pulse energy. These data show that the level of residual losses in this film upon absorption saturation is $\sim 8\%$. The type of absorption
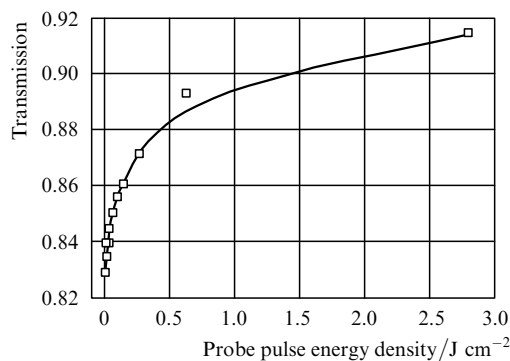

Figure 4. Dependence of the transmission of an A16-25 epitaxial film on the probe pulse energy density.

saturation suggests that this sample can be used as a Q switch.

We analysed the homogeneity of the grown epitaxial films by measuring transmission over the entire plane of the film for low probe pulse powers and for absorption saturation. Figure 5 presents the experimental data obtained for an A15-23 sample. Measurements were performed at several points along the sample diameter, the measurement error being $\sim 1\%$. This study demonstrated a high degree of homogeneity of the grown epitaxial films.
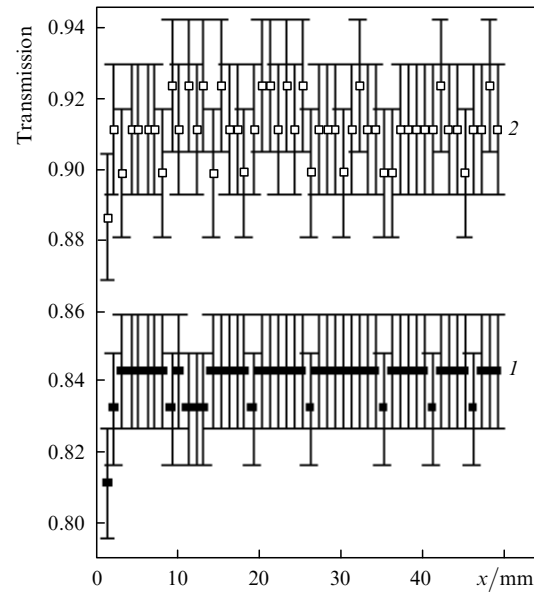

Figure 5. Transmissions of an A15-23 epitaxial film for a low probe beam power (*1*) and upon absorption saturation (*2*) as functions of the transverse scan coordinate x ($x = 0$ and 38 mm corresponds to the film edge and centre, respectively).

The possibility of using Cr-doped epitaxial films as passive Q switches was studied by placing films at the Brewster angle into the resonator of the diode-pumped Nd^{3+} : YAG laser. The films used in these experiments were not processed additionally (after their growth) and had no AR coatings. The duration of laser pulses observed in experiments was $500 - 800$ ns, the pulse repetition rate was ~ 100 kHz, and the output power was ~ 0.5 W for 7 W of pump power. When the lasing threshold was considerably exceeded, other modes appeared which affected the laser pulse shape and its amplitude stability.

4. Conclusions

We have developed the method for liquid-phase epitaxial deposition of Cr^{4+} : GGG single-crystal on pure GGG substrates of large diameter. This technology makes it possible to grow films with the crystal structure and properties that almost completely coincide with those of single crystals grown by the Czochralski method. The growth regimes and compositions of the solution-melt allowing the preparation of epitaxial films heavily doped with Cr^{4+} (up to 5×10^{18} cm^{-3}) and having low losses at 1 μm have been determined. It has been shown that Cr^{4+}-doped GGG films can be used as passive Q switches in 1-μm lasers. The films have an acceptable level of grey

losses, which opens up the possibility to improve their parameters by annealing at different temperatures in different atmospheres.

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