

Optical Absorption and Luminescence of $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Cr},\text{Mg}$ Epitaxial Films

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The optical absorption, emission spectra and luminescence decay kinetics under photoexcitation of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) garnet epitaxial films doped with Cr^{3+} ions and co-doped with Cr^{3+} and Mg^{2+} ions have been investigated. Luminescence of the GGG:Cr films due to ${}^4T_2 \rightarrow {}^4A_2$ and ${}^2E \rightarrow {}^4A_2$ transitions in Cr^{3+} ions have been observed. Increase of the activator ions concentration has an influence on the intensity and decay time of Cr^{3+} ions photoluminescence. Introduction of the magnesium ions leads to partial transformation of chromium valence state ($\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$) and to the appearance of a broad absorption band with the maximum at 860 nm. The narrow lines with luminescence maxima at 704 and 706 nm have arisen in the highly doped GGG:Cr,Mg films.

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1. Introduction

Gadolinium-gallium garnet crystals (GGG) are known to be widely used in different areas of science and engineering. The investigation results of the Cr^{3+} -ions optical-luminescent characteristics in GGG:Cr and GGG:Cr,Nd single crystals as a possible matrix for Nd^{3+} -lasers were presented in [1, 2]. The other perspective direction of this material application is creation of simple and effective lasers with Q-switching in the near infra-red spectrum region. The main features of passively Q-switched monolith neodymium microchip lasers development are considered in [3, 4]. The active medium of laser is an epitaxial structure combining an epitaxial layer of absorber $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Cr}^{4+}$ (YAG:Cr) grown on substrate of generating YAG:Nd crystals by liquid phase epitaxy method. On the other hand, the Cr-doped GGG films have some advantages in comparison with YAG films. The main fact is that saturation of phototropic centers absorption take place at the higher emission power level. The possibility of using of GGG:Cr⁴⁺ epitaxial films for modulation of Nd-laser radiation was noted in [5].

The aim of this work was the obtaining of GGG single crystalline films of high optical quality with different content of chromium and magnesium ions and studying of their optical absorption and luminescent properties.

2. Experimental

Single crystalline films of GGG:Cr were grown up on (111)-oriented pure GGG substrate by standard isother-

mal liquid-phase epitaxy (LPE) method from super-cooled solution of garnet-forming components dissolved in flux solvent based on $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$. All technological experiments were carried out on air using five-heating-zone LPE furnace "Garnet-3" (LPAI, France). The growth temperature was in the range of 1000–1040 °C. The MgO was introduced into the melt to obtain quadrivalent state for the chromium ions. The films with thickness of 14–100 μm were grown at growth rate changed from 0.5 to 1.4 $\mu\text{m}/\text{min}$. As-grown GGG:Cr epitaxial films had a green coloring, while the film GGG:Cr,Mg were brown. The concentration ratio of Cr and Mg ions in the GGG:Cr,Mg epitaxial films was 11:1.

Optical absorption spectra were computed from transmission spectra measured by spectrophotometer Shimadzu UV-3600 at room temperature in the spectral region 250–1600 nm. Luminescence spectra as well as decay kinetics were measured on the Nanosecond luminescence spectrometer ("Ekspla", Lithuania) which is based on nanosecond tunable Nd:YAG laser system NT342/UV at room temperature.

Some samples were annealed in vacuum and air at 600 °C and 1000 °C, respectively, for investigation of influence of annealing in the reducing and oxidizing atmosphere on their optical absorption and luminescence. Annealing in air were carried out in furnace Supertherm LHT 04/17 ("Nabertherm") and in vacuum in furnace GSL-1600-80X ("MTI").

3. Results and discussion

The room temperature absorption spectra of Cr-doped GGG single crystalline films for two different chromium concentrations are shown in Fig. 1. Two broad bands associated with well known transitions ${}^4A_2 \rightarrow {}^4T_1$ (U-band) and ${}^4A_2 \rightarrow {}^4T_2$ (Y-band) in the Cr^{3+} ions and located at

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470 and 630 nm, respectively, are observed. The weak line centered at 697 nm is associated with non-phonon $^4A_2 \rightarrow ^4E_2$ transition (*R*-lines). If the chromium content in the films increases from 0.3 to 3 mol.% in the melt, then the intensities of the “blue” and “orange” absorption bands with maxima at 470 and 630 nm increase from 18 to 115 cm^{-1} and from 10 to 56 cm^{-1} , respectively. Thus the main peculiarity of GGG:Cr epitaxial films grown from Bi-solution is possibility to obtain films with large value of absorption in *U*- and *Y*-bands.

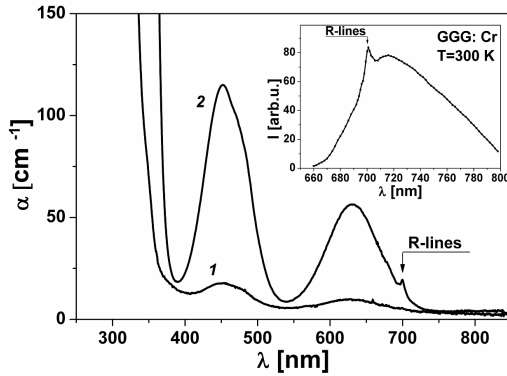


Fig. 1. Absorption spectra of GGG:Cr epitaxial films with Cr_2O_3 content in the melt 0.3 mol.% (1) and 3 mol.% (2). Inset presents luminescence spectra of GGG:Cr.

Luminescence spectrum for GGG:0.3 mol.% Cr film recorded under excitation in the absorption band with maximum at 470 nm is represented in an inset in Fig. 1. A maximum intensity of photoluminescence is observed in the spectral region 700–760 nm at a room temperature. This wide luminescence band, which is typical for Cr^{3+} ions in octahedral position of the garnet structure can be attributed to $^4T_2 \rightarrow ^4A_2$ emission transitions [1, 2]. Besides the broad band with $\lambda_m = 730$ nm, the narrow weak line at $\lambda_m = 697$ nm, which corresponds to *R*-lines (transition $^2E \rightarrow ^4A_2$) is observed in the luminescence spectra of GGG:Cr films under optical excitation. Total intensity of the luminescence in red spectral region decreases twice with growing of chromium impurity content from 0.3 to 3 mol.% in the melt.

The decay of Cr^{3+} emission in single crystalline films was studied with nanosecond tunable YAG:Nd laser system (3–6 ns pulse width) under excitation of the samples in the $^4A_2 \rightarrow ^4T_2$ absorption band. The decay kinetics of Cr^{3+} luminescence in GGG epitaxial films shows (see Fig. 2) single exponential behavior at room temperatures with approximation function $I(t) = A \exp[t/\tau] + \text{background}$. The room-temperature photoluminescence decay time for GGG:0.3 mol.% Cr is equal to 124.6 μs , which is somewhat shorter than decay time of Cr^{3+} ions in GGG single crystals ($\tau_{\text{Cr}} = 164 \mu\text{s}$ [2]). The exponential decay curve with the chromium content in the melt 3 mol.% demonstrates the value of lifetime $\approx 66.7 \mu\text{s}$. Moreover, the decay kinetics of Cr^{3+} ions luminescence

in GGG:Cr epitaxial films under excitation in the absorption band with maximum at 470 nm is slower than under excitation in the region of band-to-band transitions. The decrease of the Cr^{3+} ions lifetime in the high concentrated samples under excitation in the absorption band of Cr^{3+} ions ($\lambda_{\text{exc}} = 470$ nm) indicates that the $\text{Cr}^{3+} \leftrightarrow \text{Cr}^{3+}$ energy transfer occurs. Therefore, decay time constant as well as total intensity of luminescence decreases at the increase of Cr^{3+} emission centers concentration.

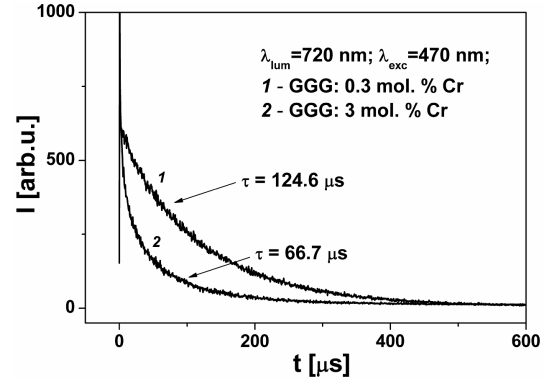


Fig. 2. Decay kinetics of Cr ions luminescence in the GGG:Cr films excited by visible light (in the absorption band of Cr^{3+} ions) at 300 K.

Figure 3 shows absorption spectra of GGG:Cr and GGG:Cr,Mg epitaxial films at room temperature with high concentrations of impurities, which corresponds to 4 mol.% Cr in the melt. The content of magnesium in the melt was equal to 0.36 mol.%. Two characteristic broad absorption bands with maxima at 470 and 630 nm as well as *R*-lines related with the transitions in Cr^{3+} ions occupying octahedral sites in GGG crystals lattice are observed in both GGG:Cr and GGG:Cr,Mg films. Moreover, in the case of chromium and magnesium ions co-doping the strong brownish coloration of the films and broad absorption band with the maximum at 860 nm appeared. Curve 3 presents a difference between absorption for the as-grown GGG:Cr and GGG:Cr, Mg epitaxial films. Besides the broad band with $\lambda_m = 860$ nm, the intensive absorption near 400 nm and two shoulders at 520 and 680 nm are observed in the optical absorption spectra of GGG:Cr, Mg epitaxial films.

Absorption band at about 410 nm was observed previously in GGG:Cr,Mg films obtained from the $\text{PbO-B}_2\text{O}_3$ melt and was associated with the presence of Cr^{4+} ions in the octahedral positions of lattice [6]. Intense absorption in the region at 800–1200 nm, which appears in GGG films with high content of chromium and magnesium, grown from the Bi-solvent, can be attributed to the overlapping transitions in Cr^{4+} ions, which occupied the tetrahedral sites of garnet lattice. It was shown in [7] for the case of YAG:Cr⁴⁺ crystals co-doped by Ca or Mg that the visible absorption band between 600 and 700 nm and intense band in near IR region at about 1000 nm

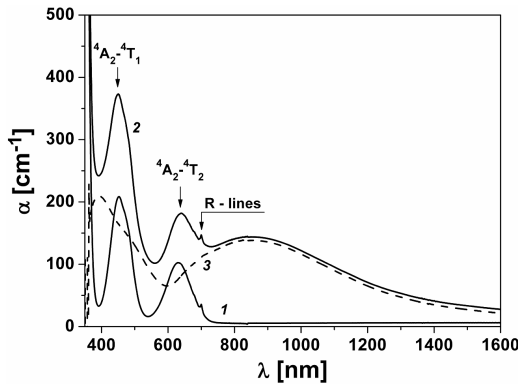


Fig. 3. Absorption spectra of GGG:Cr (1), GGG:Cr,Mg (2) epitaxial films and difference absorption spectra (3) of these films.

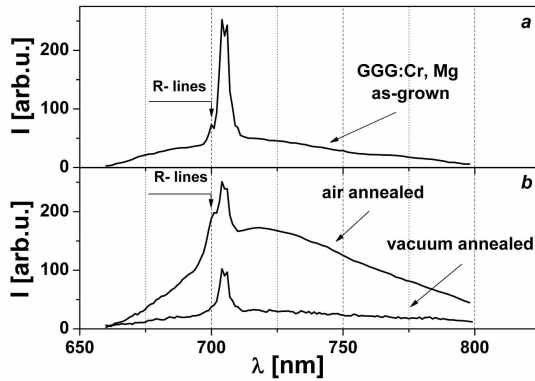


Fig. 4. The luminescence spectra of as-grown GGG:Cr, Mg epitaxial film obtained under 470 nm wavelength excitation at the 300 K (a). Influence of the annealing in the air and vacuum on the luminescence spectra of GGG:Cr,Mg epitaxial film (b).

correspond to the transition from 3B_1 ground state of the tetrahedral coordinated Cr^{4+} ions (D_{2d} symmetry) to the 3E and 3A_2 excited levels, respectively. Due to the lower crystal field strength in GGG garnet we observed a shift of the absorption bands maxima to the region with longer wavelength.

The essential changes are observed in the luminescence spectra of highly doped epitaxial films. Figure 4a shows the luminescence spectra of as-grown GGG film co-doped with chromium (4 mol.% in the melt) and magnesium (0.36 mol.% in the melt) obtained under 470 nm wavelength excitation at the temperature 300 K. Besides a broad band associated with ${}^4T_2 \rightarrow {}^4A_2$ transitions ($\lambda_m = 730$ nm) and *R*-lines associated with ${}^2E \rightarrow {}^4A_2$ transitions ($\lambda_m = 697$ nm), the appearance of two new narrow lines at 704 and 706 nm are observed in these films. Moreover, doping with Mg leads to decrease of total intensity of Cr^{3+} luminescence caused by transformation of valence states $Cr^{3+} \rightarrow Cr^{4+}$.

These narrow lines are observed also in the spectrum of the GGG:Cr,Mg film annealed in air atmosphere at

1000 °C during 1 h (see Fig. 4b). The emission intensity of the broad band at 730 nm and *R*-lines increases after air annealing, too. Vacuum annealing (30 min at 600 °C) leads to a significant decrease of the Cr^{3+} ions luminescence.

Influence of annealing in the oxidizing and reducing atmospheres on the luminescence intensity of GGG:Cr,Mg samples can be partially caused by changing of Cr^{3+} and Cr^{4+} ions ratio in octahedral positions of garnet structure. Moreover, in highly doped GGG:Cr,Mg epitaxial films the transformation of Cr-ions valence can be provided not only by unlocal charge compensation of Mg^{2+} but also by formation of oxygen vacancies (V_O^{2+}) or F^+ -centers which arise on their basis. The elimination of oxygen vacancies at the oxidizing annealing leads to the transformation of Cr^{4+} -octahedra to Cr^{3+} -ions, which enhances the luminescence intensity in the red spectral region.

The existence of new narrow line may indicate that Cr^{3+} ions occupy several different crystals sites in GGG:Cr,Mg films. Thus, it implies the presence of at least two types of Cr^{3+} site in films highly co-doped by magnesium and chromium ions.

4. Conclusions

Optical quality GGG:Cr and GGG:Cr,Mg single crystalline films with high concentration of Cr ions and thickness up to 100 μm were obtained. The single exponential behavior in the Cr^{3+} ions photoluminescence decay indicates that only one type of centers exists in the GGG:Cr epitaxial films. Decrease of the luminescence intensity and decay time at the activator ions content increase is caused by the concentration quenching. The intense absorption band in near IR region with maximum at 860 nm being arised at Mg co-doping is associated with the formation of the tetrahedral coordinated Cr^{4+} ions. The new lines of luminescence at 704 and 706 nm in highly doped GGG:Cr,Mg films can be attributed to chromium ions in garnet lattice distorted by magnesium ions.

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