

Phototropic Centers in Lasers Systems Based on Rare Earth Garnet Crystals

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Abstract—The emission from Cr^{3+} ions at 730 nm is enhanced under the action of the second harmonic radiation of a neodymium laser, while the intensity of emission at 1.54 μm from Cr^{4+} ions in tetrahedral positions remains unchanged. This result casts doubt on the interpretation of absorption bands at 0.775–1.26 μm and the luminescence bands at 1.103–1.67 μm in the spectra of rare earth garnets, which have been previously assigned to electron transitions in Cr^{4+} ions occupying tetrahedral positions in the garnet structure. © 2005 Pleiades Publishing, Inc.

The interest in phototropic centers in garnets is related to the fact that their absorption bands fall within the region of lasing transitions in Nd^{3+} ion, which is one of the most widely used laser ions. Garnet crystals have been successfully used for implementing the regimes of passive mode synchronization and passive Q switching in neodymium lasers and for establishing the possibility of obtaining effective lasers tunable in a wavelength range of 1.4–1.6 μm . Most researchers [1–4] believe that phototropic centers in garnets represent $(\text{Cr}^{4+})_{\text{tet}}$, that is, tetravalent chromium ions replacing Al^{3+} or Ga^{3+} ions in garnet based crystals and occurring in a tetrahedral environment of oxygen ligands. These $(\text{Cr}^{4+})_{\text{tet}}$ centers account for the absorption band peaked at 1.06 μm and for the luminescence in the 1.52–1.56 μm range [5]. Il'ichev *et al.* [6] were the first who expressed doubt in this interpretation and suggested an alternative model of the phototropic center, as Cr^{3+} surrounded by an unidentified defect. According to another standpoint, the phototropic centers are related to Cr^{2+} ions [7].

This study was aimed at obtaining additional information concerning the properties of phototropic centers and the processes involved in the interaction of rare earth (RE) garnets with high-power laser radiation.

The experiments were performed with single crystal RE garnets of two types: gadolinium scandium aluminum garnet (GSAG) doped with Ca^{2+} and Cr^{3+} ions

($\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$) and gadolinium scandium gallium garnet (GSGG) doped with Cr^{3+} and Nd^{3+} ions ($\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$). Impurities uncontrolled in the course of crystal growth were determined by emission spectral analysis (see table). Since we are mostly interested in the nature of optical absorption in the vicinity of 1.06 μm , let us compare the absorption coefficients of GSAG- $\text{Ca}^{2+}, \text{Cr}^{3+}$ ($K = 9.45 \text{ cm}^{-1}$) and GSGG- $\text{Cr}^{3+}, \text{Nd}^{3+}$ ($K = 6.9 \text{ cm}^{-1}$). The concentrations of defects in the two crystals differ insignificantly (by a factor of ~ 1.37). Taking into account that no special preliminary measures (such as intentional Me^{2+} introduction and oxidative annealing in the course of growth) were taken for introducing Cr^{4+} into the GSGG crystal, it is impossible to assign the absorption at 1.06 μm entirely to the presence of Cr^{4+} ions related to the appearance of uncontrolled Me^{2+} impurities. The sample crystals were exposed to the coherent second harmonic (2ω) and fourth harmonic (4ω) radiation of a neodymium laser. The concentration of Cr^{3+} ions was determined using the intensity of photoluminescence (PL) at $\lambda_m = 730 \text{ nm}$ (for $\lambda_{\text{ex}} = 532 \text{ nm}$) at the moment of excitation with the second harmonic of a YAG-Nd laser. Simultaneously, the concentration of Cr^{4+} ions was determined at the moment of laser action (by monitoring a change in the luminescence intensity at 1.54 μm for $\lambda_{\text{ex}} = 532 \text{ nm}$ and in the free lasing regime).

The content of impurities (%) in RE garnet crystals studied (by data of emission spectroscopy)

Crystal	Mg	Ca	Cu	Ti	Si	B
GSAG-Ca,Cr ($\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$)	$<3 \times 10^{-4}$	0.1	2×10^{-4} – 6×10^{-4}	–	$<10^{-3}$	–
GSGG-Cr,Nd ($\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$)	$<10^{-3}$	–	10^{-4} – 3×10^{-4}	$<10^{-3}$	$\approx 10^{-3}$	10^{-3}

Using optical spectroscopy and polarization techniques, we obtained the following experimental results:

(1) The absorption spectra of samples exhibit signals corresponding to the excited states 4T_2 and 4T_1 (630 and 452 nm) of $(Cr^{3+})_{oct}$ ions; 3T_2 (520 nm) of $(Cr^{4+})_{oct}$ ions; and 3T_1 (660 nm), 1A_1 (504 nm), 1T_2 (475 nm), 1T_1 and 3T_1 (410 nm) of $(Cr^{4+})_{tet}$ ions [2]. The PL spectra display a broad emission band at $\lambda = 730$ nm related to the transition from the excited state 4T_2 to the ground state 4A_2 of Cr^{3+} ions and another broad emission band ($\lambda = 1.54 \mu m$) excited in the region of $1.06 \mu m$. An analysis of the spectra shows that chromium ions may occur in both Cr^{3+} and Cr^{4+} states, while no evidence of chromium in the divalent state was found.

(2) Additional information about the structure of phototropic centers was obtained by measuring the spectra of polarized emission from RE garnet crystals. Figure 1 shows the azimuthal dependence of the emission at $\lambda = 1.54 \mu m$ and the degree of polarization for the $GSGG(Cr^{3+}, Nd^{3+})$ sample. These data confirm that the emitting oscillator is oriented along a fourth-order (C_4) axis. As is known, the crystals of cubic symmetry (typical of the garnets studied) contain three such axes parallel to the cube edges. Therefore, three groups of linear oscillators with $\lambda_m = 1.54 \mu m$ can align in these directions. This behavior is most likely for Cr^{3+} ions occurring in an octahedral environment, rather than for Cr^{4+} ions in a tetrahedral environment.

(3) Taking into account the forbidden bandwidths of the RE garnets studied (5.56–6.2 eV) and the photon energies of 4ω (4.66 eV) and 2ω (2.33 eV) modes of the YAG-Nd laser, it was possible to observe recharge of the impurity ions under the action of coherent laser radiation. Figure 2 shows the curves of the Cr^{3+} PL intensity versus time of irradiation with 4ω and 2ω harmonics of the YAG-Nd laser for both garnet crystals studied. In the course of laser action, the emission from Cr^{3+} ions in the $GSAG(Ca^{2+}, Cr^{3+})$ crystal increases. A growth in the concentration of Cr^{3+} ions may take place as a result of the interaction of electrons with Cr^{4+} ions. If this were the case, we would observe a decrease in the concentration of Cr^{4+} ions. However, the curves in Fig. 2 show that the concentration of these ions remains unchanged. Another possible mechanism of the optical conversion is, for example, $Cr^{2+} + h \rightarrow Cr^{3+}$. However, it was noted above that divalent chromium ions were not found in the garnet crystals studied. Therefore, the observed luminescence with a maximum at $1.54 \mu m$ excited in the region of $1.06 \mu m$ is not related to electron transitions in tetravalent chromium ions.

Let us consider the transformations of impurity ions in $GSGG(Cr^{3+}, Nd^{3+})$ in more detail. The ionization potential of Cr^{3+} is 49.0 eV. The laser photon energies for the 4ω and 2ω modes are 4.66 and 2.33 eV, respectively. The multiphoton processes are unlikely, since

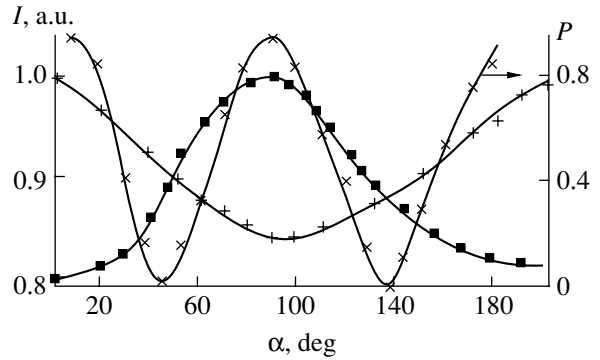


Fig. 1. Azimuthal dependences of the intensity I and the degree of polarization P of the PL at $\lambda = 1.54 \mu m$ for the $GSGG(Cr^{3+}, Nd^{3+})$ crystal.

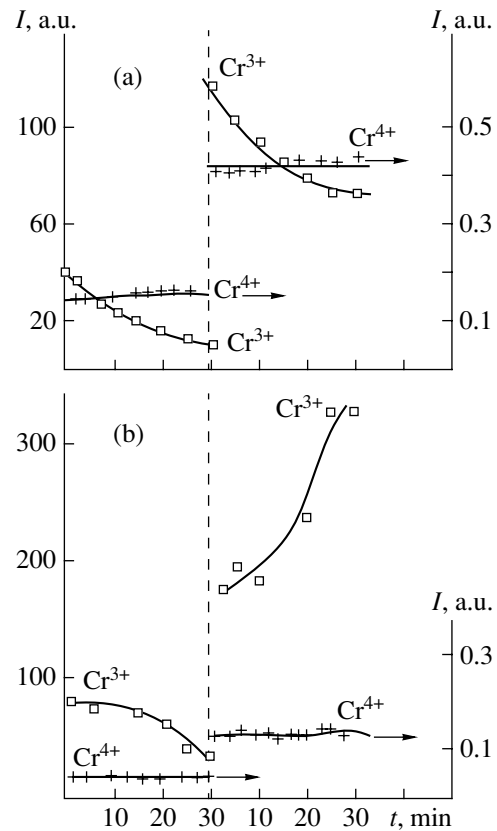


Fig. 2. Time variation of the intensity of PL from Cr^{3+} ($\lambda_m = 730$ nm) and Cr^{4+} ($\lambda_m = 1.54 \mu m$) ions in (a) $GSGG(Cr^{3+}, Nd^{3+})$ and (b) $GSAG(Ca^{2+}, Cr^{3+})$ crystals under the action of fourth (4ω , $t < 30$ min) and second (2ω , $t > 30$ min) harmonics of YAG-Nd laser.

their probabilities drop with an increasing number of photons. Therefore, the decay of Cr^{3+} ions is mediated by a hole jumping over the excited states of these ions. The efficiency of this decay is a quadratic function of the average power of the second harmonic radiation of the YAG-Nd laser. Thus, Cr^{3+} ions decay according to a

two-step mechanism. For Cr^{4+} ions incorporated into the RE garnet crystal lattice in the course of growth (as in GSAG-Ca,Cr crystals) or induced as a result of the laser action (as in GSGG-Cr,Nd crystals), the possible reactions are as follows: (i) $\text{Cr}^{4+} + e(\text{Cr}^{3+})^* \longrightarrow h\nu + \text{Cr}^{3+}$; (ii) $\text{Cr}^{3+} + h \longrightarrow \text{Cr}^{4+}$. The two processes occurring simultaneously lead to the establishment of a balance in the concentration of Cr^{3+} ions. This balance can be violated if the concentration of tetravalent chromium ions in the crystal exceeds that of the trivalent ions. In this case, the emission from Cr^{3+} will increase, as is the case in GSAG($\text{Ca}^{2+}, \text{Cr}^{3+}$) samples (Fig. 2). On the contrary, if the concentration of Cr^{3+} ions in the crystal exceeds that of the photoinduced Cr^{4+} ions, the emission from Cr^{3+} will decrease, as in GSGG($\text{Cr}^{3+}, \text{Nd}^{3+}$) samples (Fig. 2). During the repeated laser action, the balance in enhanced emission from Cr^{3+} is observed already upon a 20-min exposure. This behavior is violated if the sample is exposed to coherent second harmonic radiation of the YAG-Nd laser at a low temperature (77 K). Therefore, an electron under these conditions passes to an excited ion level via the conduction band, rather than exhibiting tunneling from an electron trap to an excited level of Cr^{4+} (otherwise the process would be temperature-independent). An analysis of the curves of the efficacy of the Cr^{3+} PL intensity enhance-

ment at various temperatures allowed us to estimate the thermal energy as $kT = 0.011$ eV. Taking into account the quadratic dependence of the efficacy of the Cr^{3+} PL intensity enhancement on the average laser power, we also estimate the depth of electron traps relative to the valence band bottom as 4.671 eV.

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