

Co²⁺ : GGG nonlinear optical crystal for the 1.3–1.7- μ m spectral range

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Abstract. A cobalt-doped GGG crystal is grown and its properties are studied. The absorption and fluorescence spectra in the visible and IR regions are measured. The absorption cross sections of the Co²⁺ ion in the GGG crystal at a wavelength of 1535 nm are determined for transitions from the ground ($\sigma_{gs} = 4.8 \times 10^{-20}$ cm²) and metastable states ($\sigma_{es} = 1.4 \times 10^{-20}$ cm²). Preliminary experimental results on *Q*-switching of erbium laser radiation by a Co²⁺ : GGG passive *Q*-switch are presented.

Keywords: passive *Q*-switch, GGG crystal, erbium laser.

1. Introduction

In recent years, the number of publications devoted to the creation of materials for saturable absorbers at a wavelength of 1540 nm and to the investigation of their properties has considerably increased [1–3]. Until recently, short pulses of eye-safe rangefinders based on erbium glasses were obtained using solely active *Q*-switches. The use of passive *Q*-switches instead of electro-optic switches, frustrated total internal reflection prisms, or rotating prisms allows one to simplify such devices and reduce their size, weight, and cost.

Despite a wide range of materials proposed as saturable absorbers for erbium lasers, the search for a material optimal from the viewpoint of both the synthesis technique and the *Q*-switching properties is still an urgent problem. Some materials can be comparatively simply synthesised but have functional drawbacks. For example, the absorption spectrum of magnesium- and zinc-aluminosilicate glass ceramics with nanocrystals of spinels doped with divalent cobalt ions is shifted to shorter wavelengths [3]. Because the wavelength 1535 nm lies at the edge of their absorption bands, the transmittance of such passive *Q*-switches strongly depends on the temperature of the environment: the output laser energy at the positive and negative edges of the

operating temperature range can differ by two times simultaneously with the required pump energy. Therefore, the need to adjust the pump energy complicates the electronic scheme and increases the energy consumption. In addition, it cannot be asserted that the problem of obtaining glass ceramic samples with a good optical quality and a high refractive index homogeneity is completely solved. The cobalt-doped LaMgAl₁₁O₁₉ crystals [4] are anisotropic and their application as passive *Q*-switches requires the presence of an additional element (polariser) in the cavity. Due to an induced birefringence in the active element, which causes depolarisation of the radiation, the lasers with LaMgAl₁₁O₁₉ *Q*-switches are usually used only in the single-pulse or low-repetition-rate (up to 1 Hz) regimes.

At present, the requirements imposed on passive *Q*-switches are most completely satisfied by single crystals of magnesium aluminate spinel MgAl₂O₄ doped with divalent cobalt ions Co²⁺ positioned in the tetrahedron vertexes [5]. The large absorption cross sections at the wavelength 1535 nm (the absorption cross section from the ground level is $\sigma_{gs} = 3 \times 10^{-19}$ cm²) and the bleaching relaxation time of 200–400 ns [6] ensure good energy parameters of the *Q*-switched radiation of erbium glass lasers (the gain cross section is $\sigma_g = 7.5 \times 10^{-21}$ cm²). However, the high (2130 °C) melting temperature of the MgAl₂O₄ crystal makes the process of producing these crystals doped with divalent cobalt rather laborious.

In [7, 8], it was shown that the introduction of silicon or germanium oxides into the solution–melt mixture can stabilise the cobalt ions in the divalent state owing to the charge compensation. In the absorption spectra of YAG and YGG crystals grown with addition of a small amount of SiO₂, the cobalt ions showed intense wide bands in the visible (600 nm) and IR (1360 nm) regions and a hardly noticeable band at 2150 nm [7]. The authors of [7] analysed the obtained spectrum based on the ligand field theory and made an unambiguous conclusion that the cobalt ions in these crystals exist in the divalent state in the tetrahedral sublattice of the garnet structure. The fine structure of the spectra measured at 77 K points to a lower symmetry (S4) and spin–orbit splitting. Similar conclusions on the valence and sites of cobalt ions were made by the authors of [8], who studied cobalt-doped epitaxial single crystalline GGG films. The absorption spectrum of Co²⁺ in these films was shifted to longer wavelengths compared to the YAG and YGG crystals, while its IR band was well overlapped with the erbium glass laser wavelength. Unfortunately, the absorption cross sections were not estimated in

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those papers; however, taken into account that cobalt is in the tetrahedral field, the absorption cross sections could be expected to be large. In the present work, we study the characteristics of a $\text{Co}^{2+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$ ($\text{Co}^{2+}:\text{GGG}$) crystal synthesised at the V.A. Kotel'nikov Institute of Radio Engineering and Electronics.

2. Crystal growth

A 2-cm-long $\text{Co}^{2+}:\text{GGG}$ crystal 1 cm in diameter was grown by the standard Czochralski method. The weight concentration of Co_3O_4 in the charge was 0.6%. Since cobalt enters the GGG crystal in the trivalent state, then, in order to convert cobalt to the divalent state, we added SiO_2 for charge compensation. The stoichiometric mixture (200 g) in an iridium crucible was placed into a vacuum chamber with an induction heater. The atmosphere in the chamber consisted of nitrogen with admixture of 1500 ppm of oxygen. As a seed crystal, we used an undoped GGG crystal oriented along the $\langle 111 \rangle$ axis. The crystal growth rate was 1 mm h^{-1} ; the rotation rate was 10 rpm. The crystal quality was fairly good. The distribution of cobalt ions over the boule cross section was inhomogeneous, namely, due to the face effect, the cobalt concentration in the centre was higher than in the periphery.

3. Measurement results and discussion

Figure 1 shows the absorption spectrum of the grown GGG crystal. The spectrum consists of two wide bands at 500–730 and 1000–1700 nm and is identical to the spectra of cobalt-doped GGG films [8] (except for a slight shift to longer wavelengths) and to the spectrum of cobalt in YAG and YGG crystals [7]. Therefore, by analogy, the absorption peaks at 613 and 1423 nm can be identified as the electronic transitions ${}^4\text{A}_2 - {}^4\text{T}_1({}^4\text{P})$ and ${}^4\text{A}_2 - {}^4\text{T}_1({}^4\text{F})$ between the levels of Co^{2+} ions in the tetrahedral lattice. An absorption band peaked at 2350 nm is also observed in the IR region of 2000–2500 nm; this band corresponds to the ${}^4\text{A}_2 - {}^4\text{T}_2({}^4\text{F})$ transition.

For comparison, Fig. 1 also presents the absorption spectrum of a cobalt-doped magnesium aluminate spinel

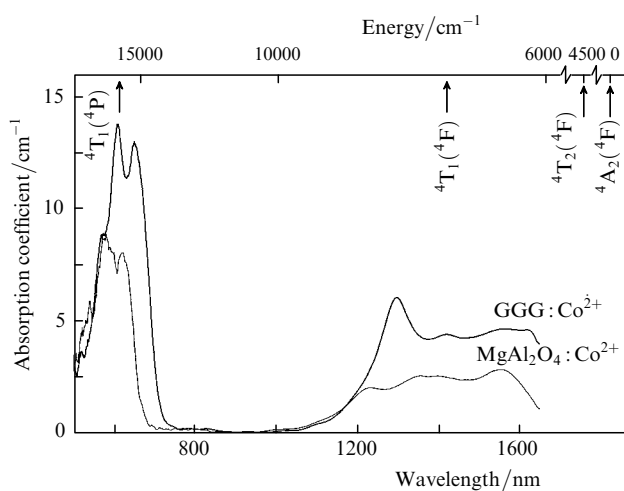


Figure 1. Absorption spectra of cobalt-doped GGG and magnesium aluminate spinel crystals; the arrows show the levels of Co^{2+} ions in the tetrahedral sublattice.

single crystal. One can see that the IR spectrum of cobalt in GGG compares favourably with the spinel absorption spectrum because it is shifted to longer wavelengths. The absorption coefficient almost does not change in the range of 1530–1630 nm, which, as was mentioned above, is positive for practical use of the crystal as a passive Q -switch for erbium glass lasers. The new material can be also promising for modulation of radiation of various crystalline matrices near 1600 nm. On the other hand, the edge of the absorption band corresponding to the ${}^4\text{A}_2 - {}^4\text{T}_1({}^4\text{P})$ transition is also shifted to longer wavelengths by almost 60 nm. This fact should result in an undesirable increase in the cross section of the transition from the metastable ${}^4\text{T}_2({}^4\text{F})$ level to the higher-lying ${}^4\text{T}_1({}^4\text{P})$ level compared to the absorption cross section in $\text{Co}^{2+}:\text{MgAl}_2\text{O}_4$. Recall that the induced absorption cross section σ_{es} (from the metastable level) in $\text{Co}^{2+}:\text{MgAl}_2\text{O}_4$ is 0.07 of the absorption cross section from the ground state [6].

Figure 2 presents the fluorescence spectra of the crystals. Upon excitation by a helium–neon laser (630 nm), the cobalt spinel shows a strong fluorescence band peaked near 660 nm, which corresponds to the ${}^4\text{T}_1({}^4\text{P}) - {}^4\text{A}_2$ transition of Co^{2+} ions in the tetrahedral sublattice. The similar fluorescence band of Co^{2+} ions in the GGG crystal confirms the reliability of conclusions on the sites occupied by these ions in the crystal lattice, which were made based on the absorption spectra. The fluorescence spectrum of Co^{2+} ions in the GGG crystals, as it should be for a material with a weaker crystal field, is wider and its maximum, similar to the maximum of the absorption spectrum, is shifted by 60 nm to longer wavelengths compared to the spectrum of Co^{2+} in the MgAl_2O_4 crystal.

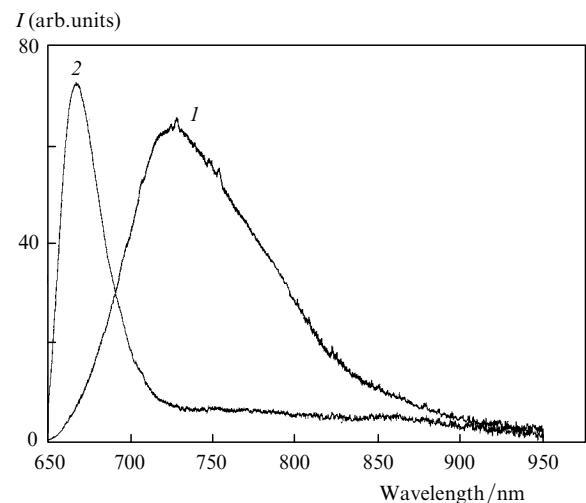


Figure 2. Fluorescence spectra of cobalt ions in GGG (1) and magnesium aluminate spinel (2) crystals.

We tried to determine the lifetime of the ${}^4\text{T}_1({}^4\text{P})$ level of Co^{2+} ions from the e-fold decrease in the 720-nm fluorescence intensity after excitation of the sample by the second harmonic of a $\text{Nd}^{3+}:\text{YAG}$ laser (pulse duration 20 ns). The photomultiplier response time did not exceed 3 ns. However, the observed fluorescence response almost completely replicated the excitation pulse shape. Thus, although we failed to determine the exact lifetime of the ${}^4\text{T}_1({}^4\text{P})$ level, our results allow us to conclude that this lifetime does not

exceed 20 ns. Such a short lifetime of the ${}^4\text{T}_1({}^4\text{P})$ level can be explained by a decrease in the energy gap between the ${}^4\text{T}_1({}^4\text{P})$ and ${}^4\text{A}_2 - {}^4\text{T}_1({}^4\text{F})$ levels. For comparison, the corresponding lifetime for the Co²⁺:MgAl₂O₄ crystal is 140 ns [6].

The absorption saturation of the crystal was measured using a passively *Q*-switched erbium glass laser. A 20-mm-long LGS-KhM phosphate glass active element 1.4 mm in diameter was placed together with a pulsed pump lamp in a diffusion reflector made of Al₂O₃ optical ceramics. The cavity formed of a highly reflecting ($r = 2$ m) and an output ($R = 85\%$) mirrors was 100 mm long. Between the active element and the output mirror, we placed a passive *Q*-switch with a transmittance of 93%, which was made of a cobalt-doped magnesium aluminate spinel single crystal. This design of the laser head allowed generation of low-repetition-rate ($f = 0.2$ Hz) pulses with a 38-ns half-height duration in the TEM₀₀ mode. The output energy spread was $\pm 5\%$. The output energy averaged over 20 measurements was 3 mJ.

The laser radiation was focused by a lens with AR coatings at a wavelength of 1535 nm to a spot 200 μm in diameter (at the level e^{-2}). The maximum energy density in the focal spot was 10 J cm⁻². A 1-mm-thick polished plate cut of the grown Co²⁺:GGG crystal was moved to the focus along the z axis of the focusing lens, which allowed us to change the incident energy density on the sample. The energy passed through the plate was measured with an UP 19K-50F-W5 (Gentec) calorimeter placed at a distance of 10 cm behind the plate. The internal absorption of the plate in the small-signal approximation was $T_0 = 63\%$. The small thickness (1 mm) of the plate ensured a constant transverse size of the focused beam over the plate thickness. The laser beam was incident on the plate at a right angle parallel to the $\langle 111 \rangle$ crystallographic axis.

The experimental dependence of the transmittance on the incident energy density is shown in Fig. 3. One sees that the transmittance increases from 63% to 85% with increasing the energy density. Note that the GGG crystal has a high laser breakdown threshold. We observed no damages in the crystal up to the incident energy density of 10 J cm⁻². Moreover, when the focusing lens was replaced by a lens with a shorter focal length, destructions appeared only at an energy density exceeding 30 J cm⁻².

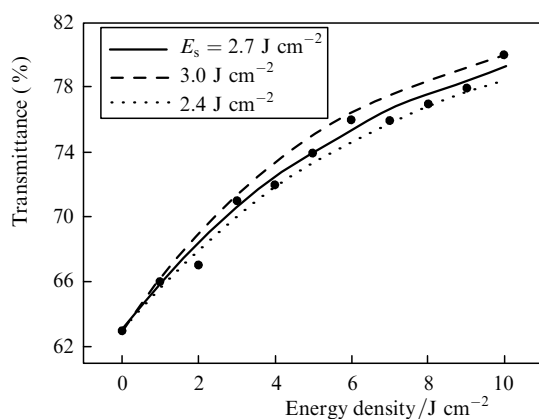


Figure 3. Absorption saturation in the Co²⁺:GGG crystal: the points correspond to the experimental data and the curves show the approximations for different saturation energies E_s ($\sigma_{\text{es}}/\sigma_{\text{gs}} = 0.3$).

In [9], the lifetime of the metastable ${}^4\text{T}_2({}^4\text{F})$ level of cobalt ions in the cobalt-doped yttrium–scandium–gallium garnet Co²⁺:YSGG was measured to be 1 μs . Based on the similarity of the Co²⁺ absorption spectra in the GGG and YSGG crystals, we can assume with a high degree of reliability that the lifetime of this level in Co²⁺:GGG will be only slightly different from the lifetime determined for Co²⁺:YSGG.

Taking into account that the laser pulse duration in our experiment (38 ns) is much shorter than the lifetime of the ${}^4\text{T}_2({}^4\text{F})$ level of cobalt ions, we analysed the obtained results using the Frantz–Nodvik formula [10], which is applicable for the case of a slowly relaxing saturable absorber. In [11], this formula was adapted for a medium with induced absorption from the metastable level:

$$\frac{dE}{dz} = -E_s k_0 \left(1 - \frac{\sigma_{\text{es}}}{\sigma_{\text{gs}}} \right) \left[1 - \exp\left(-\frac{E(z)}{E_s} \right) \right] - k_0 E(z) \frac{\sigma_{\text{es}}}{\sigma_{\text{gs}}}, \quad (1)$$

where E is the radiation energy density; z is the longitudinal coordinate; k_0 is the absorption coefficient in the small-signal approximation; and $E_s = hv/\sigma_{\text{gs}}$. It is assumed that the inactive losses in the crystal are insignificant. The best coincidence with the experimental data is observed at $E_s = 2.7 \pm 0.3$ J cm⁻², $\sigma_{\text{gs}} = (4.8 \pm 0.5) \times 10^{-20}$ cm², and $\sigma_{\text{es}} = 1.4 \times 10^{-20}$ cm². Thus, as was expected from the absorption spectra of the Co²⁺:GGG crystal, the excited-state absorption cross section in this crystal is much higher than in the Co²⁺:MgAl₂O₄ crystal, the cross section ratio being $\sigma_{\text{es}}/\sigma_{\text{gs}} = 0.3$. This factor in combination with the short lifetime of the ${}^4\text{T}_1({}^4\text{P})$ level of Co²⁺ ions can exert a decisive effect on the efficiency of Co²⁺:GGG passive *Q*-switches.

The authors of [12] managed to extrapolate the obtained experimental results for the Co²⁺:YSGG crystal by formula (1) with $\sigma_{\text{gs}} = 5.2 \times 10^{-20}$ cm² and $\sigma_{\text{es}} = 0$, i.e., without taking into account the absorption from the metastable level. The calculations performed in that study showed the possibility of *Q*-switching of the erbium laser radiation using a Co²⁺:YSGG passive *Q*-switch, but this was disproved by experiments. The authors attempted to explain this failure by the short lifetime of the metastable level of the Co²⁺ ion, which makes the Frantz–Nodvik formula inapplicable for calculations. However, this is the absorption from the metastable level that did not allow the authors of [12] to achieve *Q*-switching of the erbium laser. The authors of [9] observed this absorption in the Co²⁺:YSGG crystal and measured its cross section to be $\sigma_{\text{es}} = 1.8 \times 10^{-20}$ cm², which comprises almost 35% of the cross section from the ground level $\sigma_{\text{gs}} = 5.2 \times 10^{-20}$ cm² (this value coincides with the results of [12]).

For lasing experiments, we prepared a 140- μm -thick plane-parallel plate from the grown Co²⁺:GGG crystal. The initial internal transmittance of this plate at the wavelength 1535 nm was 93.5%. The plate had no AR coating. The plate quality cannot be considered as satisfactory due to the presence of pronounced inhomogeneities visible in a microscope. The *Q*-switching ability of the plate [Fig. 4, curve (3)] was examined in the above-described erbium glass laser cavity. One can see that, in the case of Co²⁺:GGG passive *Q*-switch, the output energy monotonically increases with increasing the pump energy. For comparison, Fig. 4 also shows the corresponding dependence for the same laser cavity with a

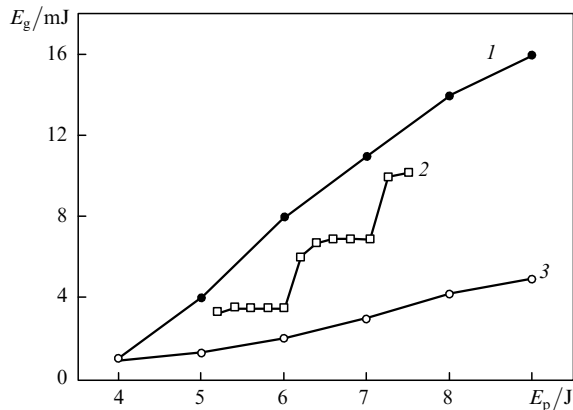


Figure 4. Dependences of the output energy on the pump energy in the free-running regime (1) and in the Q -switching regime with the $Co^{2+}:MgAl_2O_4$ (2) and $Co^{2+}:GGG$ (3) crystals.

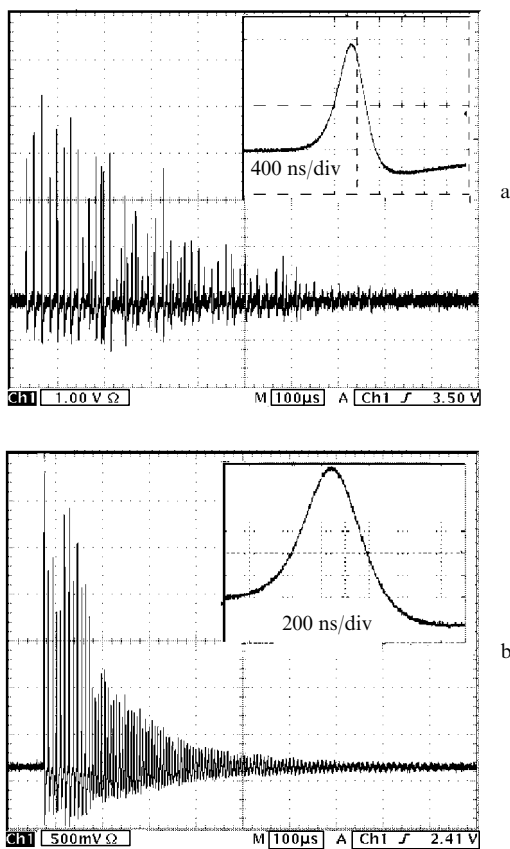


Figure 5. Typical pulse train shape in the case of Q -switching by a $Co^{2+}:GGG$ Q -switch (a) and in the free-running regime (b); the insets show the shape of a single spike of the train.

$Co^{2+}:MgAl_2O_4$ passive Q -switch [curve (2)]. The Q -switched pulse energy was 80% of the free-running energy. The step-wise dependence indicates that a decrease in the pump energy creates conditions for time-delayed second and third pulses in the TEM_{00} mode. An increase in the output energy within a step is caused by increasing inversion to the end of the linear stage of the giant pulse development due to a higher pumping rate (intensity). The output laser energy in the case of Q -switching by the $Co^{2+}:GGG$ passive Q -switch (Fig. 5a) consists of spikes with a duration of 500–700 ns, which are also typical for the transient free-running regime

(Fig. 5b). The difference consists only in the repetition rate, which is determined by the inactive intracavity losses. In addition, the transverse dimensions of the mode decrease due to the inactive losses introduced into the cavity by the plate. The number of generated spikes increases with increasing the pump energy.

4. Conclusions

Thus, we have grown a cobalt-doped GGG crystal and obtained the following results:

(i) Due to the introduction of SiO_2 into the mixture, cobalt in the grown crystal exists in the divalent state and occupies the tetrahedral sublattice of the garnet structure.

(ii) The absorption spectra of the crystal contain a wide band at 1000–1700 nm, which well overlaps with the wavelengths of erbium lasers and crystals emitting near 1600 nm.

(iii) The absorption cross sections of the Co^{2+} ion in the GGG crystal at the wavelength 1535 nm from the ground and metastable levels are found to be 4.8×10^{-20} and $1.4 \times 10^{-20} \text{ cm}^2$, respectively.

(iv) Preliminary experimental results on Q -switching in an erbium laser by a $Co^{2+}:GGG$ passive Q -switch are obtained.

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