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Colour centers in doped $Gd_3Ga_5O_{12}$ and $Y_3Al_5O_{12}$ laser crystals

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Abstract

The influence of rare earth and 3d impurities on the process of ionizing recharge of genetic defects under gamma-irradiation in $Gd_3Ga_5O_{12}$ and $Y_3Al_5O_{12}$ laser crystals has been studied by absorption spectroscopy. Impurities with stable trivalent states (Nd^{3+}, Er^{3+}, Sm^{3+}, etc) do not change the character of absorption spectra of the colour centers formed during gamma-irradiation. Impurities (Cr, Fe, Ce) which can easily change valency during irradiation, compete with growth defects in trapping of the charge carriers generated by irradiation.

Keywords: Colour centers; $Gd_3Ga_5O_{12}$; $Y_3Al_5O_{12}$; Radiation defects

1. Introduction

Gadolinium gallium garnet $Gd_3Ga_5O_{12}$ (GGG) and yttrium aluminium garnet $Y_3Al_5O_{12}$ (YAG) single crystals doped with rare earth ions (Nd^{3+}, Er^{3+}, Tm^{3+}, Ho^{3+}, Pr^{3+}, Ce^{3+}) or with 3d-ions (Cr^{4+}, Cr^{3+}, Co^{2+}, V^{3+}) are the most prospective materials for laser engineering [1,2]. Irradiation with UV light and ionizing radiation (IR) often worsens the crystal optical and lasing properties since it creates stable or transient colour centers with additional absorption (AA) bands both in the UV and visible spectrum range [3,4]. The radiation-stimulated changes of the garnet crystals properties are associated with two main processes: ionizing recharging of growth defects and formation of radiation defects through the impact mechanism [3]. The first process prevails in the case of UV, gamma and electron irradiation at absorbed doses up to 10^7 Gy. In this work the results of investigation of the influence of impurities on the process of ionizing recharge of growth defects under the gamma-irradiation are presented.

2. Samples and experimental methods

The examined crystals (GGG; YAG; YAG-Nd (1%); GGG-Nd (1%); $(Y_{0.5}Er_{0.5})_3Al_5O_{12}$ (YAG-Er); YAG-Ce (0.2%); YAG-Cr (0.0017%), Mg (0.01%); YAG-V (0.7%); $Gd_3Sc_2Ga_3O_{12}$ (GSGG); GGG-In (0.1%); GGG-Ca (0.01%); GGG-Mg (0.01%); GSGG-Co (0.01%); GSGG-Fe (0.01%); $Nd_3Ga_5O_{12}$ (NGG); $Sm_3Ga_5O_{12}$ (SGG)) were grown by Czochralski method from iridium crucibles in Ar or Ar+O_2 atmosphere. Samples for the investigations of crystal optical properties were made in the form of plane-parallel polished plates of 0.5–2 mm thickness. The transmission spectra were recorded with a spectrophotometer SPECORD M 40 (Carl Zeiss, Germany). The AA values were determined as:

$$\Delta K = \frac{1}{d} \ln \frac{T_1}{T_2},$$

where d is the sample thickness, T_1 and T_2, the crystal transmission before and after irradiation influence, respectively.

The samples were irradiated with gamma-quanta from a ^{60}Co source with average energy of 1.25 MeV up to 10^7 Gy absorbed doses.

3. Results and discussion

After irradiation by gamma-quanta with doses 10^2–10^7 Gy, the AA wide band in the range of 35 000–11 000 cm^{-1} with maxima at 32 000, 25 000 and 16 000 cm^{-1} arise in YAG crystal spectra. The same shape and position

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of the AA peaks are observed in the spectrum of the YAG crystals doped with Er or Nd. In Fig. 1a the AA spectra of YAG-Nd crystals are shown. The AA value increases as irradiation dose rises and it saturates in the range of gamma-quanta absorbed doses of 10^4–10^6 Gy. A maximal value of the AA does not exceed of 1.5 cm^{-1}. In some irradiated YAG-Nd crystals, a clearing near the edge of fundamental absorption with a maximum near 39 000 cm^{-1} takes place [5].

In irradiated gamma-quanta GGG and GGG-Nd crystals, a wide band in the region of 34 000–12 000 cm^{-1} with maxima at 31 000 and 23 000 cm^{-1} as well as a clearing with a maximum near 39 000 cm^{-1}arise (Fig. 1b). Similar AA spectra are observed in GSGG, NGG, SGG and GGG-In. A maximal value of AA does not exceed 1 cm^{-1} and a saturation of the AA dose dependence takes place at doses higher than 10^4 Gy. The same AA spectra are observed in doped YAG and GGG crystals irradiated by UV light and high energy (3.5 MeV) electrons with doses of 10^2–10^7 Gy.

An analysis of published papers [3–5] on radiation-induced colouration of YAG and GGG crystals, has shown that the form and intensities of AA spectra depend on the

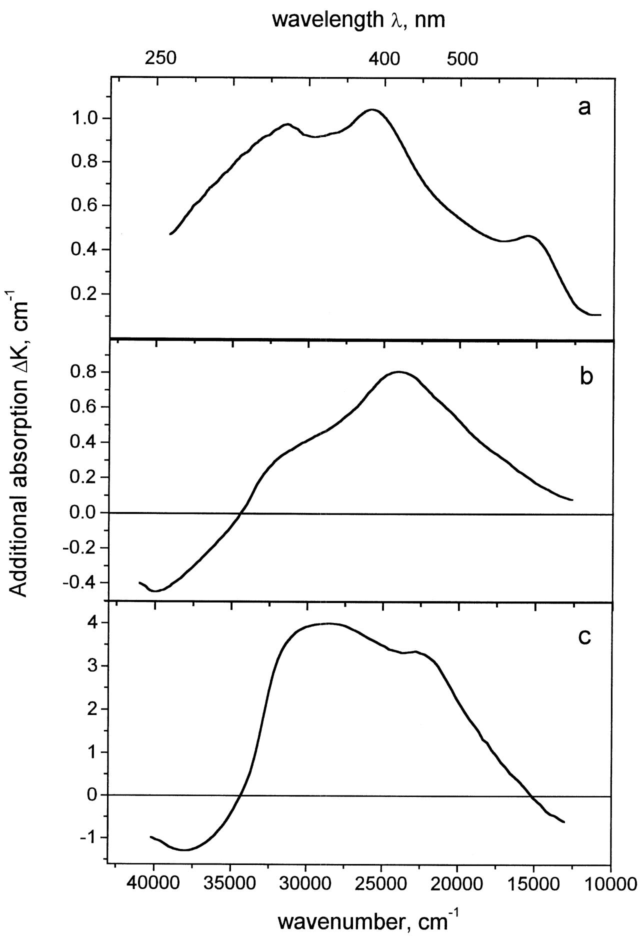

Fig. 1. The AA spectra of gamma-irradiation (10^5 Gy) YAG-Nd (a), GGG-Nd (b) and GSGG-Fe (c) crystals.

growth conditions of the crystals (method and growth atmosphere, purity of raw materials, etc). The AA band near 39 000 cm^{-1} is usually explained as being associated with absorption of non-controlled Fe^{3+} impurities, the band placed near 31 000–32 000 cm^{-1} is mostly attributed to absorption of Fe^{2+} ions or O^- hole centers localized near defects of the cation sublattice. The bands with maxima near 23 000–25 000 cm^{-1} and 15 000–17 000 cm^{-1} in oxide crystals are interpreted as F and F^+-type colour centers consequently [6,7].

Different spectra are observed in YAG doped with Ce that exists in crystal not only in the Ce^{3+} state but also as Ce^{4+} [8]. Moreover, Ce presence in YAG at optimal concentration improves the crystal radiation resistance [9]. The AA-spectrum of YAG-Ce is presented in Fig. 2. In irradiated YAG-Ce^{3+} (0.2%) crystals, the AA in the visible range ($\lambda > 500$ nm) is absent. The short wave AA maxima correspond to the Ce^{3+} ions (4f–5d transition [10]) that are formed as a result of the radiation recharging mechanism $Ce^{4+} \rightarrow Ce^{3+}$.

The AA spectra of YAG-V^{3+}, YAG-Cr^{4+}, GSGG-Co^{2+} and GGG-Mg^{2+} are presented in Fig. 3. Only one intensive band with maxima at 24 000 cm^{-1} is observed in the AA spectrum of GSGG-Co (Fig. 3a), and bands at 32 000 cm^{-1} (intensive) and 25 000 cm^{-1} (weak) for YAG-V (Fig. 3c). In YAG-MgCr, the chromium ions are both in the three- and four-valent state. As the result of radiation treatment, the reaction $Cr^{3+} \rightarrow Cr^{4+}$ takes place, and the Cr^{4+} absorption (transition $^3A_2 \rightarrow {}^3T_2$ [11]) in tetrahedral position (16 500 cm^{-1}) and octahedral position (22 000 cm^{-1}) increases (Fig. 3d).

The AA spectrum of GSGG-Fe (Fig. 1c) has a typical form for garnets, but its intensity increases some times (reaching 4 cm^{-1}) and the short wave AA maximum (31 000 cm^{-1}) dominates. This band coincides with the

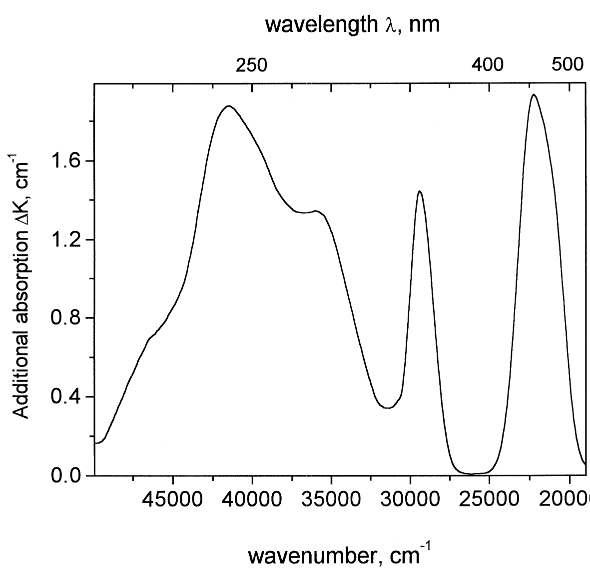

Fig. 2. The AA spectrum of gamma-irradiated (10^6 Gy) YAG-Ce (0.2%).

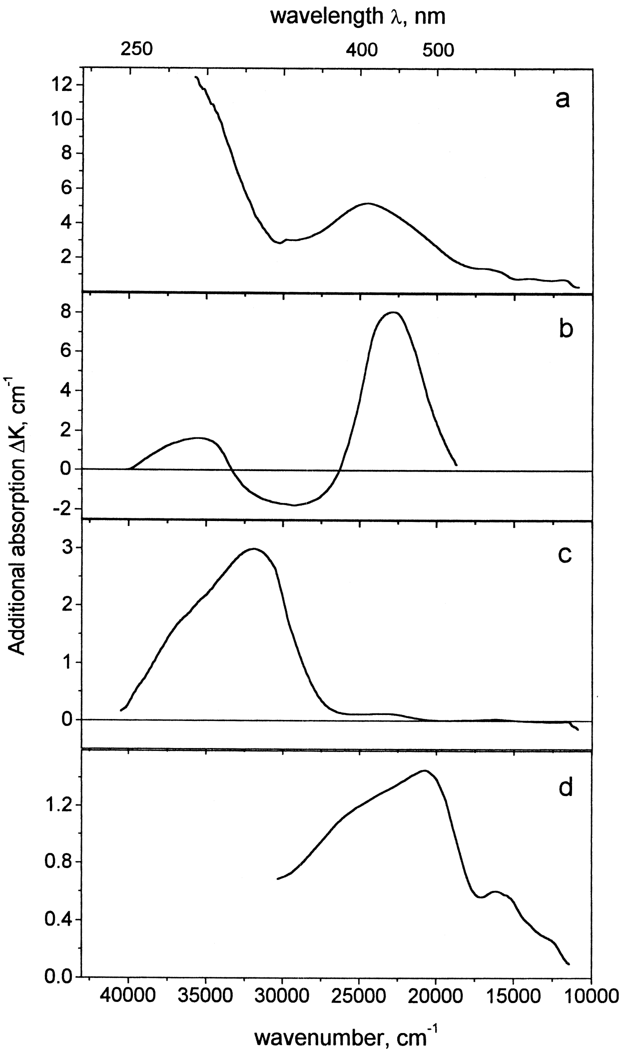

Fig. 3. The AA spectra of gamma-irradiated (10^5 Gy) GSGG-Co (a), GGG-Mg (b), YAG-V (c), YAG-Cr, Mg (d).

Fe^{2+} absorption band [5]. Both colour centers associated with recharging of growth defects and ion impurities that change their charge state ($Fe^{3+} \rightarrow Fe^{2+}$) contribute to the AA. Also, the clearing increases in the region of Fe^{3+} ions absorption (39 000 cm^{-1}).

In as-grown GGG-Ca and GGG-Mg crystals, the absorption band at 29 000 cm^{-1} of complex defects $[F^{+}Mg^{2+}]$ or $[F^{+}Ca^{2+}]$ appears [12]. These complex defects cause a change in the character of the crystal radiation colouration. The AA spectrum of $GGG\text{-}Mg^{2+}$ is presented in Fig. 3b. After UV or gamma irradiation, a clearing in the region near 29 000 cm^{-1} and absorption bands at 23 000 cm^{-1} (intensive) and 38 000 cm^{-1} (weak) takes place.

4. Conclusion

Doping of GGG and YAG with In^{3+}, Sc^{3+}, Nd^{3+}, Er^{3+} or Sm^{3+} ions does not change the character of absorption spectra of the colour centers formed as a result of ionizing recharge of genetic defects. The Fe, Cr and Ce impurity ions being introduced into the crystal can easily change valency during irradiation. They compete with genetic defects in the trapping of charge carriers generated by irradiation causing the AA spectra with other absorption bands.

In garnets doped with Ca^{2+} or Mg^{2+} ions, the state of the crystal defect subsystem changes significantly. In this case, complex defects $[F^{+}Me^{2+}]$ which are nontypical for pure garnet crystals are formed. Their appearance causes a change of additional absorption in the crystals after gamma irradiation.

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