Spectroscopy of Radiation-Induced and Structural Defects in Garnet Crystals with V and Cr Impurity Ions

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Abstract—The optical absorption spectra of crystals with garnet structure (A$_3$B$_2$C$_3$O$_{12}$), containing V or Cr impurity ions, before and after oxidation annealing, γ irradiation, and coactivation with Ca and Mg ions have been experimentally and theoretically investigated. It is shown that V$^{3+}$ and Cr$^{4+}$ ions are incorporated into both octahedral and tetrahedral sites of the garnet lattice. The absorption spectra and energy level diagrams of impurity ions are identified.

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INTRODUCTION

Crystals of complex oxides (in particular, those with garnet structure, A$_3$B$_2$C$_3$O$_{12}$) belong to the most intensively studied objects [1–4].

It is well known [5, 6] that oxides may have a high concentration of anion vacancies. A deviation from stoichiometry, i.e., a change in the concentration ratios of cations and oxygen (A/O, A/B, B/C), during growth or thermal annealing leads to a higher concentration of structural defects and formation of additional optical absorption bands [7, 8]. After thermal treatment (annealing) or exposure to different types and doses of radiation, most oxide compounds with iron-group impurity ions exhibit a change in the electronic state of regular and impurity ions and a corresponding change in the spectral properties of the samples [6, 7].

Variations in the conditions of growth and subsequent thermal annealing (technical or high-temperature) has been used for a long time as a processing procedure for changing the spectral properties of crystals. The effect of thermal treatment is especially pronounced in study of the influence of radiation on the properties of oxide single crystals and in introduction of additional impurities [9, 10]. Many studies (see, for example, [6]) have been devoted to the radiation spectral properties of oxide single crystals of different crystallographic structure. The properties of crystals with garnet structure have also been widely studied (see, for example, [1, 2]).

It is known that the introduction of iron-group (Me) or rare earth (RE) impurity ions leads to a change in the spectral properties of crystals, which is related to both the appearance of absorption and luminescence bands of impurity ions in the entire transparency range and generation of structural and impurity defects and color centers [8, 9].

The exposure of crystals to different types and doses of radiation leads in most cases to the appearance of an additional optical absorption band (so-called induced absorption [7]). Generally, induced absorption bands are related to the charge exchange in structural defects and the change in the electronic state (valence) of impurity ions.

Thus, the significant influence of the crystal growth conditions on the spectral properties allows one to obtain and study samples with different concentrations of structural and impurity defects, i.e., samples with different electronic structure and spectral properties [11]. The fabrication of samples with new spectral characteristics expands their range of application, which was shown by the example of V$^{3+}$ and Cr$^{3+}$ ions in some oxide single crystals [11–14].

In this paper, we report the results of further study of the radiation spectral properties of crystals with garnet structure, including yttrium aluminum garnet Y$_3$Al$_5$O$_{12}$ (YAG), gadolinium scandium gallium garnet Gd$_3$Sc$_2$Ga$_5$O$_{12}$ (GSGG), gallium aluminum scandium garnet Ga$_5$Sc$_2$Al$_3$O$_{12}$ (GSAG), and yttrium scandium gallium garnet Y$_5$Sc$_2$Ga$_5$O$_{12}$ (YSGG), with V and Cr impurity ions. Application of the samples obtained from charges of different quality and by different methods makes it possible to establish to some extent the effect of the production conditions of garnet crystals on their spectral properties.
EXPERIMENTAL

We studied samples with garnet structure prepared by methods of directional crystallization (horizontal and vertical gradient freeze (HGF and VGF, respectively)) and by the Czochralski method. Crystalization conditions, container material (iridium, molybdenum), growth atmosphere, and thermal treatment conditions (vacuum, H₂SO, CO₂, Ar at T = 600–1800 K) were varied.

Charges of different quality were used. Charge 1 contained primarily iron-group impurity ions and Cr and Fe ions with concentrations of about 10⁻¹⁹ cm⁻³. Charge 2 was chemically purified from iron-group ions (their concentration decreased by an order of magnitude). Charge 3 was purified by recrystallization. Nominal undoped crystals nevertheless contained some impurity ions, including iron-group ions; these crystals can be referred to as nominally pure samples. The samples with iron-group ions were activated in the stage of charge preparation. In some cases, garnet charge was prepared using the coactivation with magnesium or calcium oxides.

YAG, GSAG, YSGG, and GSGG crystals were grown by the Czochralski method in iridium crucibles in an argon atmosphere. During growth of gallium-containing garnets in an argon atmosphere, oxygen was added to decrease evaporation from the Ga melt.

Aluminum-containing crystals (YAG, GSAG) were also grown by the VGF method in molybdenum tubes in an Ar–H₂ atmosphere. Thus, the crystals were synthesized under both oxidative and reducing conditions.

Chromium or vanadium oxides with concentrations C.imp = (1–2) × 10²⁰ and magnesium (calcium) oxides with concentrations C.imp = 5 × 10¹⁹–1 × 10²⁰ cm⁻³ were added to the initial garnet charge. Plane-parallel (1–5)-mm-thick polished plates were prepared from the grown crystals. YAG:V crystals were grown by the VGF method.

The spectral properties of the samples were studied using the standard absorption and luminescence spectroscopy methods in the entire transparency range of the crystals. The electron spin resonance (ESR) spectra were investigated at λ = 3 cm and T = 77 and 300 K [15]. To determine the sample stoichiometry and the stability of the electronic state of regular and impurity ions, we applied the method of valence shifts of X-ray lines using a Camebax X-ray microanalyzer [7, 8].

The samples were irradiated by 1.25-MeV γ rays at T = 90 and 300 K with doses up to 10⁴ Gy, and by electrons with energies E = 2 and 10 MeV at T = 300 K with doses to 10¹⁵ cm⁻². Some of the samples studied were irradiated by a PRK-4 mercury lamp with subsequent annealing in air at T < 1500 K.

SPECTRAL PROPERTIES OF DOPED GARNET CRYSTALS

The spectral properties of the initial nominally pure and doped garnet crystals are well-known [1, 2]. The fundamental absorption edge of undoped YAG crystals corresponds to λ = 152 nm [16].

The optical absorption spectrum of YAG crystals with Cr³⁺ impurity ions contains two wide strong bands near 430 (Y band) and 590 nm (U band), corresponding to the \( ^4A_2(t^2_2) \rightarrow ^4T_2 (^4T_1) \) transitions in the approximation of crystal field with cubic symmetry. Allowance for the trigonal distortion leads to splitting of some energy levels [2]. The third (electronic vibrational) transition with a wavelength of about 220 nm is weakly pronounced due to the strong UV absorption of YAG crystals, which is caused by the presence of residual impurities. This absorption spectrum is characteristic of other crystals with garnet structure containing Cr impurity ions and grown under standard conditions. Note that the garnet lattice contains two different cationic sites, \( B \) and \( C \), with octahedral and tetrahedral environments, respectively. Cr³⁺ ions, as well as other ions with the 3d⁵ configuration, form centers with predominantly octahedral environment and a coordination number of 6. V³⁺ ions (with the ground electronic configuration 3d⁶) form initially centers of both octahedral and tetrahedral symmetry with a coordination number of 4.

The optical absorption spectrum of YAG:V³⁺ (Fig. 1) contains five absorption bands, corresponding to the \( ^3T_1(t^2_2) \rightarrow ^3T_2( t^2_2), ^3T_1(t^2_2), ^3A_2(e^2) \) transitions with the maximum absorption for octahedral vanadium positions at \( \lambda = 425 \) and 625 nm. The ground state for tetrahedral sites is \( ^3A_2(e^2) \). The absorption spectra at a coordination number of 4 are determined by the transitions to the \( ^3T \) triplets and \( ^1A_1(e^2) \) singlet in the absorption peaks at \( \lambda = 820 \) and 1280 nm. The absorption