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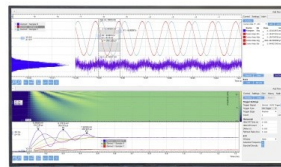
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Origin of color centers in the flux-grown europium gallium garnet

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Europium gallium garnet (EuGG) single crystals were grown from fluxes with various contents. Optical absorption spectra of EuGG grown from a flux containing calcium show an additional band in the ultraviolet and blue regions of the spectra as compared to the case of a calcium-free flux. Mössbauer spectra of the samples grown from the fluxes with different additives show no signs of other valence states of the europium ions except for 3+. However, they indicate changes in the crystal field due to the entrance of additive ions. The nature of the additional absorption must be the same as that for calcium-doped gadolinium gallium garnet, i.e., anion vacancies. Mössbauer isotope shifts and quadrupole splitting for EuGG are determined. © 2008 American Institute of Physics. [DOI: 10.1063/1.2902365]

I. INTRODUCTION

Growth conditions strongly affect the properties of rare earth garnets because of various growth defects. The addition of small amounts of calcium is known to stabilize the large-diameter Czochralski-grown boules of gadolinium gallium garnet (GGG).¹ However, a certain amount of calcium easily enters the lattice of GGG. The presence of calcium in the lattice may lead to the formation of defects *altering* the optical properties of the crystal. In the case of garnets containing rare earth ions with changeable valence, the heterovalent substitution of rare earth ions by calcium and other impurity ions, generally speaking, may lead to a change in the valence of neighboring rare earth ions. However, since gadolinium usually has a 3+ valence state, it is worthless to expect variation in its valence state due to the incorporation of calcium ions into the garnet structure. In fact, it was shown that doping with calcium in this case leads to the formation of defects with a well-known nature, namely, oxygen-deficient centers of several types. Another obtainable valence state of gadolinium, Gd²⁺,² must be put out of consideration for GGG:Ca. As it was shown in comprehensive experimental and theoretical studies,^{3,4} spectroscopic parameters of the GGG-doped crystals are determined by oxygen vacancy states effectively interacting with extrinsic defect states.

In the present communication, the influence of flux content on the absorption spectra of flux-grown europium gallium garnet (EuGG) is investigated. Europium, in contrast to gadolinium, has at least two stable valence states, Eu²⁺ and Eu³⁺. In glasses of a certain content, wherein the environment of europium ions can be easily varied, the relative contents of these ions can be controlled by changing the conditions of the glass preparation and also by postpreparation treatment.⁵ In crystals, the valence state of ions with changeable valence is mainly determined by the nearest environment determined by the crystal structure. For instance, the

strontium tetraborate crystal structure stabilizes europium in the Eu²⁺ valence state with a rather high degree of purity (see, e.g., Ref. 6, and references therein). Garnets are known to stabilize the trivalent state of europium with the same high degree of purity. On the other hand, another ion with a changeable valence state, namely, manganese, introduced into the garnet structure can be easily converted between the Mn³⁺ and Mn⁴⁺ states by the addition of charge-compensating divalent ions into the melt. The aim of this study is to search for possible additional valence states of europium in a flux-grown EuGG with the help of optical and Mössbauer spectroscopies. We must note that europium-containing garnet was studied with the help of Mössbauer spectroscopy in Ref. 7. However, what was used was europium-iron gallium garnet, which possesses strong ferromagnetism, and the focus of this study was the influence of magnetization upon nuclear transitions. Mössbauer spectra of pure EuGG have not been reported to date.

II. CRYSTAL GROWTH AND PROPERTIES

Single crystals of EuGG were grown from fluxes based on oxides of boron and barium. The following four types of crystals have been grown:

- (A) Colorless EuGG from a flux containing no heterovalent components for growth
- (B) Colored EuGG from a flux containing 1% calcium ions with respect to europium ions
- (C) Colored EuGG from a flux containing 2% calcium ions
- (D) Colored EuGG from a flux containing 1% zirconium ions

Introduction of calcium ions, with their slightly larger effective ionic radius, instead of europium ions can lead either to the formation of trapped-hole defects (O⁻ ions), or O²⁻ vacancies, or, at last, to the formation of the charge-compensated pair of Ca²⁺-Eu⁴⁺. Note that the latter possibility is rather hypothetical since a 4+ valence state for eu-

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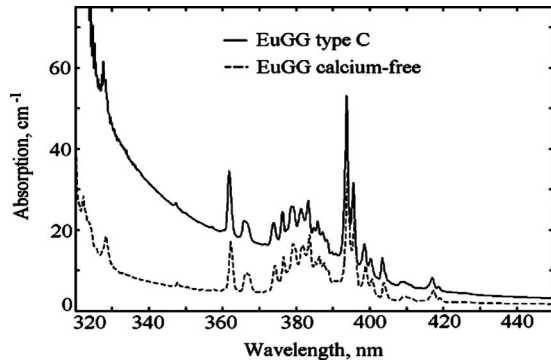


FIG. 1. Absorption spectra of EuGG grown from calcium-containing flux (solid line) and from calcium-free flux (dashed line).

ropium was never observed, to our knowledge. Introduction of zirconium can lead to the formation of either a pair of Zr^{4+} - Eu^{2+} or some kind of cation vacancy.

Among the grown crystals, only the EuGG crystals grown from the flux containing no calcium and zirconium (type A) have shown no noticeable color. The other crystals have shown evident coloration, orange in the case of calcium-containing fluxes and pinkish in the case of zirconium-containing flux. The latter were too small to be suitable for optical absorption measurements. The type A crystals had smaller size and poorer optical homogeneity than the type C samples. This shows that in the case of growth from the flux, the stabilizing effect of calcium added to the flux is preserved.

III. RESULTS AND DISCUSSION

The absorption spectra of types A and C crystals are presented in Fig. 1. The spectra were recorded by a Kontron Instruments Uvikon 943 spectrometer at a resolution of 0.3 nm. Both spectra show all the lines typical of f - f transitions of trivalent europium. No evident differences between the shapes and positions of these lines connected with possible structural changes associated with the introduction of calcium could be detected. However, the colored garnet of type C shows an additional wide band in the near UV region that partially protrudes into the visible region and is the cause of coloration. This band is positioned at approximately the same spectral region as the 340 nm band of calcium-containing GGG,¹ although the latter does not protrude into the visible region and does not lead to coloration. In EuGG, an additional absorption band peaks at an approximate value of $30\,000\text{ cm}^{-1}$ and spans down to $22\,000\text{ cm}^{-1}$. The large width of this band indicates strong electron-phonon interaction in the process of color center excitation. The absorption coefficient of our band at 340 nm is approximately 24 cm^{-1} , while in GGG:Ca, it is on the order of 7 cm^{-1} at 0.0025% calcium content in the melt. For our calcium content, one must expect a much larger absorption coefficient associated with color centers. However, this discrepancy can be referred to the lower ratio of segregation coefficients for the calcium/europium pair than for calcium/gadolinium or to the saturation in the amount of calcium that entered the crystal at high

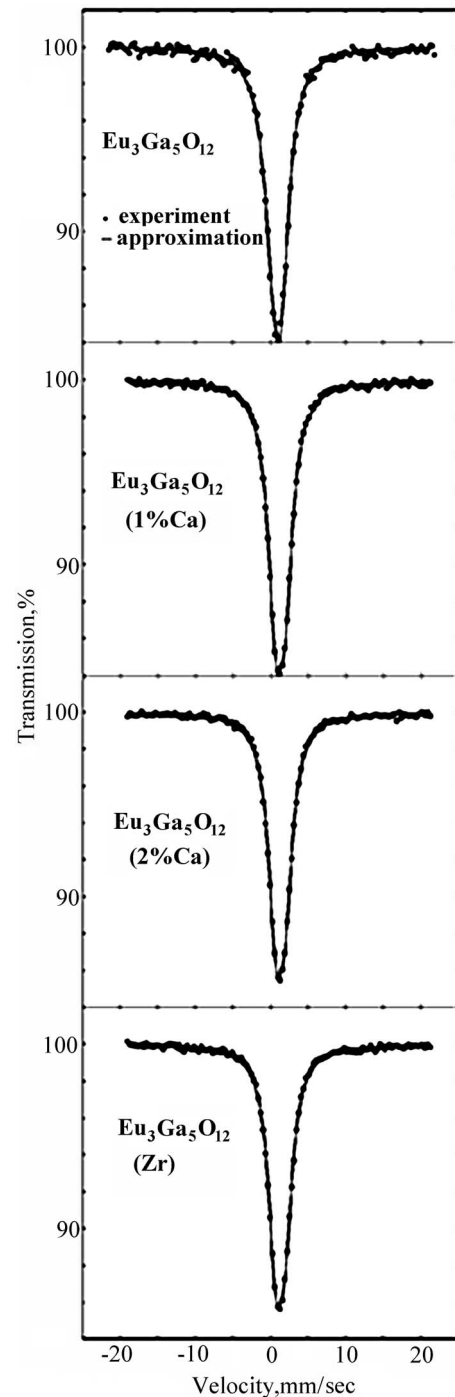


FIG. 2. Mössbauer spectra of the A, B, C, and D samples at the 21.5 keV transition of the ^{151}Eu isotope.

concentrations. It is reasonable to associate the additional absorption band in our type C crystals with the same kind of color centers, which are supposed to be trapped-hole ones. However, the possibility of the existence of an unusual valence state of europium hinders this suggestion to be straightforwardly made. Therefore, we used Mössbauer spectroscopy to check for the presence of additional valence states in our crystals.

Mössbauer measurements were performed for the 21.5 keV transition of the ^{151}Eu isotope. Note that the crystals possess a natural abundance of europium isotopes. The

TABLE I. Isomeric shift and quadrupole splitting for different samples of EuGG.

Eu ₃ Ga ₅ O ₁₂ type	Isomer shifts (relative to EuF ₃) (mm/s)	Quadrupole splitting (mm/s)
A	0.933 ± 0.007	-1.50 ± 0.06
B (with 1% CaO)	0.953 ± 0.008	-1.53 ± 0.04
C (with 2% CaO)	0.933 ± 0.011	-1.42 ± 0.05
D (with 1% ZrO ₂)	0.911 ± 0.011	-1.4 ± 0.1

samples used were powders obtained by milling single sub-millimeter size crystals of types A, B, C, and D. The obtained spectra are presented in Fig. 2 together with their multi-Lorentzian approximation. The latter was obtained by accounting for the quadrupole splitting of the ground state of the Eu¹⁵¹ isotope ($I=5/2$) into three doubly degenerate sub-levels, while the excited state was assumed to be split into four sublevels, the number of allowed transitions contributing to line shape being equal to eight. The best fit was obtained for the zero asymmetry coefficient and $Q_e/Q_g=1.3$. The Mössbauer parameters extracted via this analysis are listed in Table I.

The approximated line shapes of the central part of the Mössbauer spectra are depicted in Fig. 3. As it is well seen from this figure, although the maxima of all four peaks nearly coincide, the Mössbauer peak of the type A garnet is nearly symmetric, while the three others are asymmetric, with their wings shifted to the positive velocity detunings. Hence, the type A garnet represents the Mössbauer spectrum of unperturbed EuGG, and the rest are the spectra of crystals perturbed by heterovalent doping. Therefore, Fig. 3 confirms that additional dopants, in fact, enter the crystal structure. At the same time, we can deduce that both calcium and zirconium produce a somehow similar effect upon the crystal field affecting the nucleus under study.

Examination of the wings of the spectra depicted in Fig. 2 shows no decisive proof for the presence of additional valence states. An Eu²⁺ peak must be observable at negative velocity detunings on the order 10–15 mm/s, while a hypothetical Eu⁴⁺ peak must be positioned at positive detunings. Therefore, we can deduce with an accuracy of 0.3% (to the

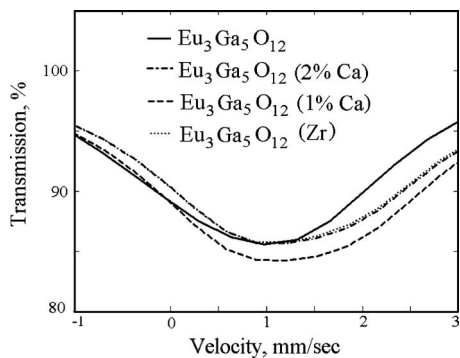


FIG. 3. Shapes of Mössbauer spectra in the vicinity of the maxima.

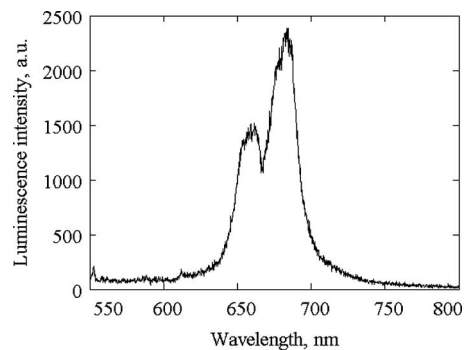


FIG. 4. The luminescence spectrum of calcium-doped EuGG single crystal under 514.5 nm excitation.

Eu³⁺ ionic state) that our samples contain no additional valence states.

In view of this result, the most probable origin of the additional absorption band observed in the UV region in EuGG grown from calcium-containing flux is the color centers analogous to those well known in GGG.

Finally, we measured the luminescence spectrum of calcium-containing EuGG under excitation by the 514.5 nm line of an argon ion laser (Fig. 4). Of course, very strong concentration quenching of europium luminescence is expected at large europium ion content. Moreover, the excitation line lies at the far wing of additional UV/blue absorption in calcium-doped EuGG. In fact, only two of the weak lines correspond to known transitions of trivalent europium, namely, the lines at 552 nm ($^5D_1-^7F_2$) and at 610 nm ($^5D_1-^7F_2$). The spectrum is dominated by two broad bands that are not characteristic of trivalent europium. However, they can be attributed to the luminescence of the color centers discussed above.

IV. CONCLUSION

Optical spectra of EuGG grown from calcium-containing flux show additional absorption in the UV and blue regions of the spectra. Mössbauer spectra of samples grown from fluxes with different additives show no signs of valence states other than 3+ of the europium ions. However, they indicate changes in the crystal field due to the entrance of additive ions. Therefore, the nature of additional absorption must be the same as for GGG:Ca, i.e., anion vacancies. Luminescence of these color centers can be observed via excitation by 514.5 nm laser radiation. Mössbauer isotope shifts and quadrupole splitting for EuGG are determined. The addition of calcium to a flux improves the size and quality of flux-grown EuGG crystals similarly to those of Czochralski-grown GGG crystals.

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