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# OPTICAL CONSTANTS OF YTTRIUM–IRON GARNET SINGLE-CRYSTAL FILM STRUCTURES

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*Light-attenuation spectra of yttrium–iron garnet single-crystal film structures grown on a gallium–gadolinium garnet substrate by liquid-phase epitaxy from the undercooled solution in the melt have been studied and compared with those of bulk yttrium–iron garnet samples. The calculated optical constants are discussed taking into account the influence of crystal field on the splitting of the energy states of iron ions in the film samples.*

Key words: *light-attenuation spectrum, single-crystal film structure, yttrium–iron garnet, gallium–gadolinium garnet, optical constants, energy state of ion.*

**Introduction.** A developing area of modern materials science is the fabrication and improved synthesis of film structures based on already known compounds. Yttrium–iron garnet ($Y_3Fe_5O_{12}$) and compounds related to it are traditional materials that are critical for solving many practical problems. This class of materials, which was discovered about a half century ago, is attractive because it contains magnetic dielectrics and combines properties that are broadly applicable in information technology systems [1–10]. The thee cationic positions of different sizes in the garnet structure that are created in the cubic closest packing of the comparatively large oxygen anions make it possible to substitute into the composition many chemical elements. The properties of the material can be modified for any type of application, in particular, for magneto-optical systems, owing to the rather complicated chemical structure and the large number of atoms in the unit cell, which includes eight formula units. Thus, substitution of a certain fraction of the Y ions by Bi ions intensifies the Faraday rotation effect. It is important that the nature of the optical properties of the material are determined to a large extent by the presence of iron ions in the structure that can be found in a nonstandard charge state if heterovalent impurities are present [5–12]. Dopant atoms usually enter the material composition during synthesis with an increase of the growth rate that destroys the quasi-equilibrium. On the other hand, even rational replacement of ions in order to improve certain properties increases invariably the level of defects in the material and can affect certain other properties. Materials with significant optical activity and low absorption of radiation in the photosensitive structure are required for information processing systems based on the Faraday effect. Therefore, the effect of crystal lattice defects on the optical constants of yttrium–iron garnet remains critical, especially in light of improvements in the synthesis of thin-film structures.

The transparency of yttrium–iron garnet in the $\lambda = 1–9$ μm range was reported as far back as 1958 [1]. Further research found that this material transmits exceptionally well radiation in the 1.1–5.0 μm range whereas at shorter wavelengths electronic transitions between iron-ion states have an effect [1–4] and absorption increases. The transmission limit should be shifted into the visible region in order to increase the effectiveness of this material in optical devices. This is possible with circuit designs based on doped film structures because of attenuation of the total absorption at short optical lengths [5–7] and decreased absorption due to a change of chemical composition of the material. Information on the frequency dependence of the absorption coefficient and index of refraction of large $Y_3Fe_5O_{12}$ single crystals is at present somewhat contradictory and does not agree with data from thin-film layers of this material.

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The physical properties of film structures may differ from large samples as the result of the surface effect of the substrate itself (like a two-dimensional defect) on the material structure.

Herein light-attenuation spectra of yttrium–iron garnet single-crystal films in the 0.6–2.0 μm range are measured and analyzed. The effect of the structure thickness on the intensity of transmitted radiation is taken into account. Spectral dependences of the absorption coefficient and the real and imaginary components of the index of refraction are calculated from the experimental results. The capabilities to control the optical constants of the materials in order to achieve high optical gain, primarily by decreasing the loss of beam energy in the short-wavelength range, are discussed.

**Experimental.** Samples of single-crystal films of $Y_3Fe_5O_{12}$ were selected for the investigation. Optical properties of a series of large single-crystals of ytrrium–iron garnet (1–3 mm thick) that were synthesized by dynamic directed crystallization on a seed from a solution in the melt were studied and analyzed for comparison. Single-crystal film structures were grown by liquid-phase epitaxy on gallium–gadolinium garnet ($Gd_3Ga_5O_{12}$) substrates [12]. Three series of samples (total number 20) grown on the same substrate of thickness 140 μm were selected for the study. The scatter of overall thickness including the substrate fell in the range 160–180 μm in the series of samples. The overall dimensions were measured with an ordinary micrometer with an acceptable tolerance (5 μm). A change in the film thickness by 20–40 μm affected the light-attenuation spectra and was used to calculate the optical characteristics.

Phase analysis was performed on a DRON-3 automated x-ray apparatus (Cu $K_\alpha$-radiation, $\lambda_{\alpha 1} = 1.540562$ Å, $\lambda_{\alpha 2} = 1.544398$ Å, exposure time 2–3 sec, scan step equal to the doubled angle $2\theta = 0.04^\circ$) in order to monitor the film crystal structure. The angular positions of diffraction maxima were determined from the centers of gravity of their peaks.

Light-attenuation spectra of the samples were recorded on a Cary-500 Scan spectrophotometer as the spectral dependence of the optical density $D$ (logarithm of the ratio of intensities of incident $I_0$ and transmitted radiation $I$). Optical constants were calculated assuming that Burger's law, which describes quantitatively the decrease of intensity of a planar monochromatic light wave upon propagation in an absorbing medium, was obeyed. Such an approach correlated with the absorption coefficient of the film calculated using successive recording of optical density in the light-attenuation spectrum recorded directly from the substrate and with the film structure deposited on it. If the intensity of the radiation transmitted through the substrate is divided by the intensity of radiation transmitted through the substrate with the deposited film and the natural logarithm of the resulting fraction is taken, then the absorption coefficient of the film material can be easily calculated for certain conditions, including a known film thickness. In particular, this method was used to study absorption lines in the spectrum of homoepitaxial films of Ga–Gd garnet doped with rare-earth ions [13, 14]. The calculation method using the calculated intensity ratio in light-attenuation spectra was based on the fact that the contribution of additional interfaces to the optical signal could be neglected for low doping levels in the substitution positions.

**Results and Discussion.** Figure 1 shows the x-ray diffraction pattern of a thin-film layer of $Y_3Fe_5O_{12}$ that is consistent with a single-crystalline material. The lattice constant calculated as the arithmetic mean of the values determined from the positions of the high-angle reflections (660) and (880) was $1.2373 \pm 0.0005$ nm, which agreed with the literature [15]. As a result, the distance between structural atoms of $Y_3Fe_5O_{12}$ was slightly less than that between atoms of the $Gd_3Ga_5O_{12}$ substrate (1.2383 nm).

Figure 2 shows light-attenuation spectra of certain samples. It can be seen that the optical density of large and film samples of $Y_3Fe_5O_{12}$ is small in the 1.1–2.0 μm range (curves 1–3) and close to $D$ of the $Gd_3Ga_5O_{12}$ substrate (curve 4). The results show that the presence of additional interfaces in the film structure had an insignificant effect on the intensity of transmitted light in this spectral range. This was explained by the similarity of the lattice constants of the substrate and film, which (even taking into account the insignificant effect of absorption on components of the index of refraction) produced a small difference in the real components of the indices of refraction of these materials. It is important to note that the large $Y_3Fe_5O_{12}$ sample transmitted radiation in the range $\lambda < 1.6$ μm worse than thin-film layers of this material. Clearly the larger optical density of the large sample in this range was due to the same concentration of structure defects that attenuated more strongly light passing through the sample because of the longer optical path length in the large sample. The attenuation spectrum of the samples in an even shorter wavelength range ($\lambda < 1.1$ μm) was due to transitions between electronic states of iron ions, as noted above.

In general, the intensity of reflected and transmitted radiation is determined by complex indices of refraction taking into account the relative weight of its real and imaginary components. The expression for the index of refrac-

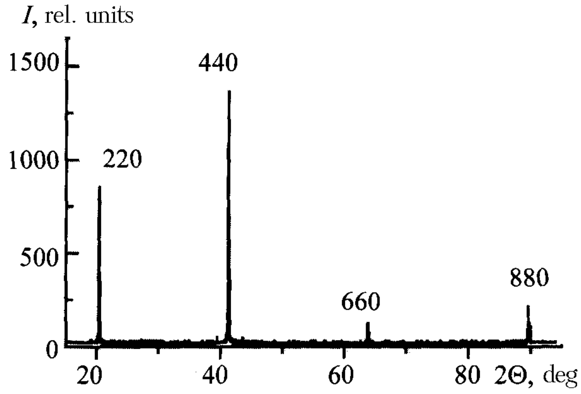

Fig. 1. X-ray diffraction pattern of yttrium–iron garnet thin film on $Gd_3Ga_5O_{12}$ substrate.

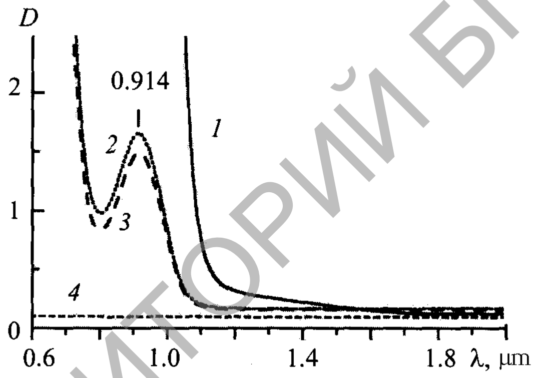

Fig. 2. Light-attenuation spectra of single-crystal yttrium–iron garnet (1–3) and $Gd_3Ga_5O_{12}$ substrate (4): bulk sample 2.6 mm thick (1) and $Y_3Fe_5O_{12}$ films on $Gd_3Ga_5O_{12}$ substrate with total thickness 180 and 160 μm (2, 3).

tion and the corresponding form of the reflection and transmission coefficients are defined only by the dielectric properties for a material that has no residual paramagnetism [16, 17]. The dielectric permeability of a material is known to characterize its ability to react to the electric component of the wave field. The response delay of a medium to an external perturbation disappears at infinitely large frequencies. The medium becomes transparent regardless of whether or not it conducts an electric current. For example, the dielectric permeability for conducting metallic materials at frequencies much greater than the frequency of plasma vibrations approaches unity whereas it is negative for frequencies less than the plasma frequency in the visible spectral range because the material absorbs strongly in this range. Therefore, the index of refraction in the visible range is an imaginary quantity that corresponds to high reflectance. On the other hand, a hypothetical ideal dielectric with a real index of refraction $\approx 10$ even without absorption does not transmit 70% of the radiation because of its reflectance at the interface with air.

Therefore, the real component of the index of refraction for Ga–Gd garnet substrate, which is optically transparent starting in the UV range, is close to 2 and affects to a certain extent the transmission of radiation through the substrate–air or substrate–$Y_3Fe_5O_{12}$ interfaces [18]. Because in this instance the film and substrate materials are different, the method of taking the logarithm of the intensity ratio of radiation transmitted directly through the substrate and through the film structure was corrected for the different properties of the materials. Therefore, the scatters of the index of refraction and the absorption coefficient were calculated using expressions for the intensity of transmitted radiation with two (substrate) and four interfaces (film structure), respectively [19]:

$$I = I_0 (1 - R)^2 e^{-\alpha d} ,$$
$$I = I_0 (1 - R)^2 (1 - R')^2 e^{-\alpha' d'} e^{-\alpha d} , \tag{1}$$

where $R$ and $R'$ are the reflectance coefficients at the air–substrate (garnet) and garnet–substrate interfaces; $\alpha$, $\alpha'$ and $d$, $d'$, coefficients of absorption and thickness of $Gd_3Ga_5O_{12}$ substrate and $Y_3Fe_5O_{12}$ film. The expanded forms of the equations used to calculate the spectral dependences of the optical constants were

$$D = \frac{l}{\ln 10}\left[-2 \ln \frac{4n}{n^2 + 2n + 1 + k^2} + \frac{4\pi}{\lambda} kd\right],$$
$$D = \frac{l}{\ln 10}\left[-2 \ln \frac{4n}{n^2 + 2n + 1 + k^2} - 2 \ln \frac{4\,(nn' + kk')}{(n + n')^2 + (k + k')^2} + \frac{4\pi}{\lambda} kd + \frac{4\pi}{\lambda} k'd'\right], \tag{2}$$

where $n$, $n'$ and $k$, $k'$ are real and imaginary components of the refractive indices of substrate and yttrium–iron garnet.

We calculated the absorption coefficients and the real and imaginary components of the refractive index of $Y_3Fe_5O_{12}$ garnet single-crystal film structures by determining the spectral dependences of the substrate optical constants using the optical density of film structures of different thickness (Fig. 3).

It seemed advantageous to compare the optical properties of yttrium–iron garnet with those of $Gd_3Ga_5O_{12}$, which is a material with the same structural class and transparency in the 1.3–2.0 μm range, during the analysis of the effect of the yttrium–iron garnet structure on its properties. The absorption coefficient and refractive index components for Ga–Gd garnet (substrate), which does not absorb over the whole studied wavelength range (Fig. 2, curve 4), could be readily determined from the optical density $D = 0.09$ and its thickness. The compatibility condition of Eq. (2) was fulfilled for the substrate with $n \approx 1.85$ and $k \approx 10^{-6}$. The calculated $k$ was equivalent to an absorption coefficient $\alpha \approx 0.2$ cm$^{-1}$ and agreed with the literature [18]. The imaginary component of the refractive index $n \approx 1.85$ was slightly less than the literature value (1.94) [18]. The scatter of optical constants of the substrate was inconsequential. The values $n$ and $\alpha$ slowly increased in the short wavelength range.

According to the calculations, the imaginary component of the refractive index of yttrium–iron garnet exhibited behavior typical of normal scatter that was transformed at $\nu > 10{,}000$ cm$^{-1}$ into an anomalous type. This confirmed the mechanism of action as resonance absorption of radiation energy. It is noteworthy that the values $n$ in the spectral range where electric dipole transitions were activated had a weak effect on the intensity of transmitted light, attenuation of which was determined primarily by the imaginary component $k$. By analogy with acoustic waves, for which conservative and dissipative components of the energy transfer mechanism from the field to the medium and back are related to elastic and plastic deformations of the medium elements, the real part of the refractive index, which describes reversible energy transfer processes, was responsible for elastic interactions during propagation of electromagnetic waves. Irreversible effects resulting in wave destruction were related to structural defects and resonance absorption accompanied by transitions between levels with a finite lifetime. The finite rate of energy exchange processes between the field and medium in the transparent range decreased the rate of wave propagation compared with a vacuum.

As mentioned above, a short-wavelength boundary ($\lambda \approx 1.1$ μm) of the transparency range in yttrium–iron garnet was formed due to the presence of iron ions in the chemical structure. These occupied distorted octahedral and tetrahedral positions within polyhedra formed by O ions. The 3$d$-shell in iron-group elements, which is responsible for the paramagnetism of the ions, is rather accessible. The internal field with a weak influence of translation symmetry on the placement of the energy levels is sufficient to classify it as intermediate. The level splitting is greater than the distance between different multiplets under its influence. In this approximation, the coupling between the orbital and spin-moment vectors is negligibly small and the spin–orbit coupling energies can be ignored. Sublevels $2L + 1$ ($L$ is the orbital moment of the number of motion) are degenerate in the solitary $Fe^{3+}$ ion and are split in the internal field. In essence this means that the symmetry of the Hamiltonian for the isolated $Fe^{3+}$ ion, which is responsible for the continuous group of three-dimensional rotations and reflections, decreases under the influence of perturbations by sur-

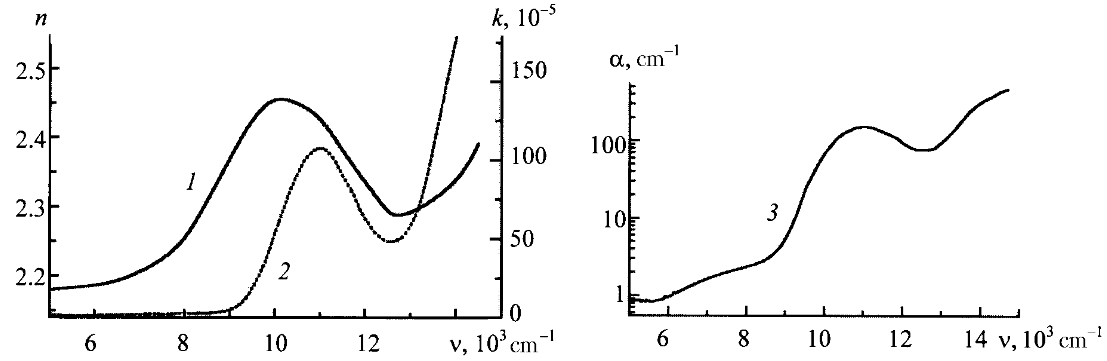

Fig. 3. Spectral functions of real (1) and imaginary (2) components of the complex index of refraction and absorption coefficient (3) of yttrium–iron garnet thin film.

rounding ions. The number of split sublevels is determined using the so-called deconvolution of irreducible group representations of rotations and reflections into irreducible representations of a finite group describing the field symmetry at this point. The $Fe^{3+}$ ion is known to contain five *d*-electrons. Its energy states according to Hund's rule are placed in the sequence $^6S$, $^4G$, $^4D$, $^4S$, $^2J$, $^2G$, $^2P$, etc. The degeneracy of these levels is partially lifted in the crystal. They are split according to the deconvolution of irreducible representations of an infinite group of spherical symmetry [20, 21]. Atomic terms of the *S*- and *P*-types are known not to split in a field with octahedral symmetry so that the ground state level of the iron ion remains degenerate. It is noteworthy that octahedral and tetrahedral fields have different effects on iron ions and lift the degeneracy of perturbed levels to different extents. Because the crystal field and symmetry of octahedral positions are greater than those of tetrahedral positions, the manifestation of electronic energy states of $Fe^{3+}$ starts from positions surrounded by six anions. In particular, the first excited state $^4G$ is split (following the terminology of Baukart and Wigner) into $\Gamma'_{15}$-, $\Gamma'_{25}$-, $\Gamma_{12}$-, and $\Gamma_1$-levels. Lowering the symmetry of the $^4D$ state generates two $\Gamma'_{25}$'- and $\Gamma_{12}$-levels. As mentioned above, the $^4S$ state is not split and is designated $\Gamma_1$, etc. The short-wavelength boundary of the maximum transparency range is formed by electric dipole transitions of iron ions between groups $\Gamma_1$- and first excited $\Gamma'_{15}$-states. According to the literature [4–6], the maximum of the corresponding absorption band is located at 917.4 nm. According to this work, $\lambda_{max}$ is 914.0 nm (Fig. 2). The observed spectral shift of the band is naturally related to the action of the crystal environment on the Fe ions.

Distortions of the oxygen octahedra and tetrahedra should shift the positions of the energy levels and increase the force of transition optical oscillators in the film structure because it exists in a more non-equilibrium state than the large sample. It was impossible to determine the scale of the change of absorption coefficient of the film sample and compare it with that of the large sample because the latter was too thick. Nevertheless, the film structure undoubtedly showed additional absorption. In addition to the additional stresses in the film structure and the distortion of the shapes of the oxygen octahedral, the frequency of the transition from the ground state to the first excited one could both increase and decrease. The experimental results indicated that the splitting of the $^4G$-state decreased in the film structure. This was naturally linked to the influence of the surface and the interface. The slight mismatch of the crystal-lattice constants of the substrate and $Y_3Fe_5O_{12}$ film probably resulted in a unique gradient of film lattice constant from the interface to the free surface of the film. The distortion was propagated into a significant part of the film unit cells. The mismatch of lattice constants of the order of 0.1% compressed the oxygen octahedra and distanced anions lying at the base of the four-faceted prism from the iron cation. This increased the absorption coefficient and slightly decreased the splitting of the levels for iron ions in oxygen octahedra of the large samples. The observed increased frequency of the $\Gamma_1$–$\Gamma'_{15}$-transition means in essence that the effectiveness of the crystal field had decreased.

**Conclusion.** Scatter of the index of refraction of yttrium–iron garnet film structures in the range of frequencies corresponding to transitions into the excited state of $Fe^{3+}$ ions was studied by recording light-attenuation spectra. It was shown that splitting of the first excited energy level of iron ions in the film structure decreased because of less distortion of the oxygen octahedra that may have been due to replacement of a small fraction of the iron ions by boron and/or the formation of oxygen vacancies during the synthesis.

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