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Optical and magneto-optical properties of $Fe_xGa_{1-x}BO_3$ crystals

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The single crystals of $Fe_xGa_{1-x}BO_3$ with $0 < x < 1$ have been synthesized by solution-melt method. Optical absorption spectra demonstrate substantial changes in the region of the strong absorption band edge depending on Fe concentration. This is explained, preferably, by Fe–Fe charge transfer transition processes. Magnetic circular dichroism spectrum in the region of ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ d–d transitions and its temperature dependence were measured in the crystal containing 67 % of Fe for the first time.

Монокристаллы $Fe_xGa_{1-x}BO_3$ с $0 < x < 1$ синтезированы раствор-расплавным методом. Оптические спектры поглощения продемонстрировали существенные изменения в области края полосы сильного поглощения в зависимости от концентрации железа. Это объясняется, преимущественно, переходами с переносом заряда Fe–Fe. Спектр магнитного кругового дихроизма в области d–d переходов ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ и его температурная зависимость впервые измерены в кристалле, содержащем 67 % Fe.

1. Introduction

Weak ferromagnet $FeBO_3$ synthesized for the first time in [1] is the unique crystal: it is one of few materials combining room temperature magnetism and a high transparency up to near ultraviolet. $FeBO_3$ has the rhombohedral calcite structure with the space group D_{3d}^6 and, hence, it is optically uniaxial. From the magnetic point of view, $FeBO_3$ is two-sublattice easy-plane antiferromagnet with a weak in-plane moment and Neel temperature $T_N = 348$ K. The review of its magnetic, optical, and magneto-optical properties can be found in [2]. Several authors studied an effect of diamagnetic dilution of the crystal on its magnetic properties (e.g. [3–6]). In particular, $Fe_xGa_{1-x}BO_3$ single crystals with x varied from 0 to 0.45 were synthesized in [3], and their magnetic properties were studied using magnetometric techniques and Mossbauer measurements. It was shown that at these levels of diamagnetic dilution the crystal and magnetic structures did not change and Neel temperature decreased with increasing gallium ion concentration. For $x = 0.45$ T_N was about 200 K. Substitution of paramagnetic ions by diamagnetic ones in magnetic materials, generally, and in $FeBO_3$, specifically, effects substantially on their optical properties which can be useful ащк studying in solving of some problems common for all antiferromagnets containing $3d^5$ ions. Appearance of clusters of magnetic ions at high levels of diamagnetic substitution and properties of the clusters in dependence on concentration of such ions, on the one hand, and appearance of a long-range magnetic order and evolution of magnetic and optical properties of a crystal with the increase of the magnetic ions concentration, on the other hand, are among these problems. Diluted $FeBO_3$ crystal is the

proper substance for investigations of such kind. It possesses the majority of antiferromagnetic properties and presence of the weak ferromagnetic moment leads to the existence of the linear on magnetization magneto-optical effects (Faraday rotation and magnetic circular dichroism (MCD)), that essentially expands possibilities of experimental researches. It is important for the present investigation that undiluted crystal of $FeBO_3$ has been comprehensively investigated.

In the present work we study optical absorption and magnetic circular dichroism for crystals $Fe_xGa_{1-x}BO_3$ with variation of x from 0 to 1.

2. Experimental

The experimental samples are isostructural series of rhombohedral crystals $Fe_xGa_{1-x}BO_3$ of optical quality with a wide range of substitution $0 < x < 1$. The crystals were grown by solution-melt method using the system of Fe_2O_3–Ga_2O_3–B_2O_3–PbO–PbF_2. The main problem was to determine the ratio of incoming components and temperature conditions of crystallization for each composition. The concentration of iron and gallium in the synthesized samples was determined by methods of X-ray fluorescence analysis (XRFA) and energy-dispersive spectroscopy (EDS). It is important to note that the concentration of these elements in the crystals differs significantly from the concentration in the starting charge.

The synthesized crystals range in size from 1.5 to 6 mm in diameter and from 50 to 100 μm in thickness. Samples of $GaBO_3$ are colorless transparent hexagonal plates. With the increasing concentration of iron atoms the crystals' color gradually changes to green one (Fig. 1).

Optical absorption and MCD spectra were investigated in the spectral range of 350–1000 nm and at temperatures 85–293 K.

2. Results and discussion

There are three possibilities for the strong absorption associated with Fe^{3+} ions. There are: allowed $d \rightarrow p$ transitions inside Fe^{3+} ion with the energy ~10^5 cm^{-1} (λ ~ 100 nm); allowed charge transfer transitions $2p \rightarrow 3d$ between molecular $2p$-orbitals of ligands and $3d$-orbitals of Fe^{3+} ion inside FeO_6 cluster (energies ~36000 cm^{-1} (λ ~ 275 nm)); charge transfer transitions between Fe^{3+} ions (Mott-Hubbard transitions):

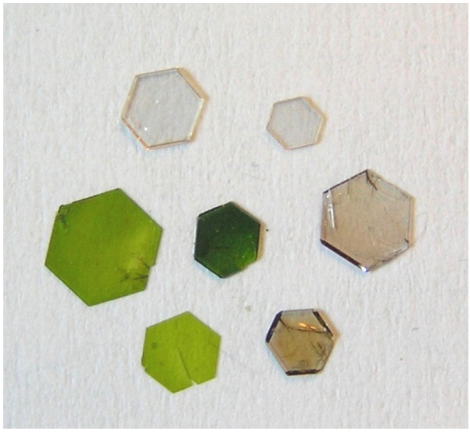

Fig. 1. $Fe_xGa_{1-x}BO_3$ monocrystals charge for single crystals.

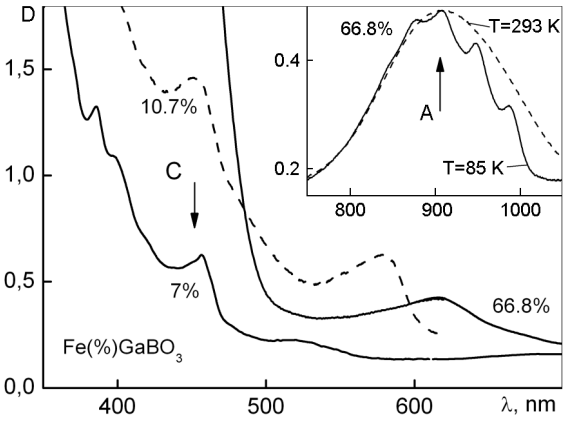

Fig. 2. Absorption spectra of $Fe_xGa_{1-x}BO_3$ single crystals at T = 85 K. Inset: absorption spectra of $Fe_xGa_{1-x}BO_3$ (66.8 % Fe) single crystal in the region of ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition at T = 85 K and 293 K.

$$3d^5 + 3d^5 + E_g \rightarrow 3d^4 + 3d^6. \qquad (1)$$

These transitions are forbidden in the first approximation by parity and also by spin selection rules, if total spins of the ions in the ground state have the same directions. However, the transitions are spin allowed if they take place between antiferromagnetically coupled ions with the opposite spin orientations. Parity forbiddenness is removed since the pair of atoms under consideration has no center of inversion, at least, in the excited state. Thus, these transitions can be considered as partially parity allowed ones without participation of odd vibrations. They are weaker than $2p \rightarrow 3d$ transitions between molecular orbitals of the cluster, but much stronger than d–d transitions inside $3d$ ions. Position of the strong absorption band edge of the studied crystals

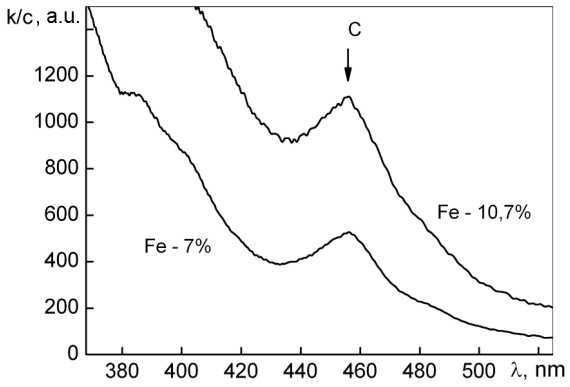

Fig. 3. Absorption spectra of $Fe_xGa_{1-x}BO_3$ single crystal harge for single crystals.at T = 293 K.

(energy ~20000 cm^{-1} (λ ~ 400 nm)) depends on Fe ions concentration (see Figs. 2, 3) and it is far from the mentioned $2p \rightarrow 3d$ transitions, whose position weakly depends on Fe^{3+} concentration. Therefore we can suppose that the observed strong absorption band edge refers to Fe → Fe charge transfer transitions.

Pair states in the left and right sides of equation (1) give rise to Mott-Hubbard bands. Activation energy (or insulating gap or optical gap) is equal to:

$$E_g = U - (B_1 + B_2)/2. \qquad (2)$$

Here $U = E(d^4 + d^6) - E(2d^5)$ is the electron correlation energy modified by crystal field (CF) and covalence. In particular, instead of one transition between high spin states in the free ion approximation (1) we have four transitions in the cubic CF approximation:

$$^6A_1, ^6A_1 \rightarrow {}^5E(d^4), {}^5T_2(d^6); {}^5T_2(d^4), {}^5T_2(d^6);$$
$$^5E(d^4), {}^5E(d^6); {}^5T_2(d^4), {}^5E(d^6). \qquad (3)$$

For samples containing lower Fe concentration, absorption maxima near 380 and 450 nm are observed. Maximum near 450 nm (C-band) corresponds to that observed at 443 nm in $FeBO_3$ single crystal and can be ascribed to the $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ transition in Fe^{3+} ion (see Figs. 2, 3). Position of this maximum does not depend on Fe concentration. Intensity of C-band reduce with Fe concentration growth (Fig. 3) that testifies to the pair exchange assisted absorption. In the higher concentrated samples absorption bands associated with $^6A_{1g} \rightarrow {}^4T_{2g}$ (B-band) and $\rightarrow {}^4T_{1g}$ (A-band) transitions are observed. Their positions are also close to those in $FeBO_3$ [7]. But decrease of Fe concentration results in shift of these bands to lower wave lengths (Fig. 2). The fine structure on the long wave length edge of $^6A_{1g} \rightarrow {}^4T_{1g}$ transition in the sample with 67 % Fe (Fig. 2, Inset) is similar to that observed in $FeBO_3$ [7]. It is due to exciton-magnon lines and testifies to appearance of the magnetic ordering.

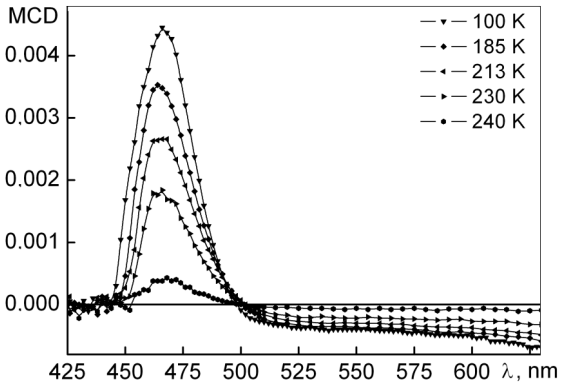

Fig. 4. MCD spectra of $Fe_xGa_{1-x}BO_3$ (66.8 % Fe) single crystal at different temperatures.

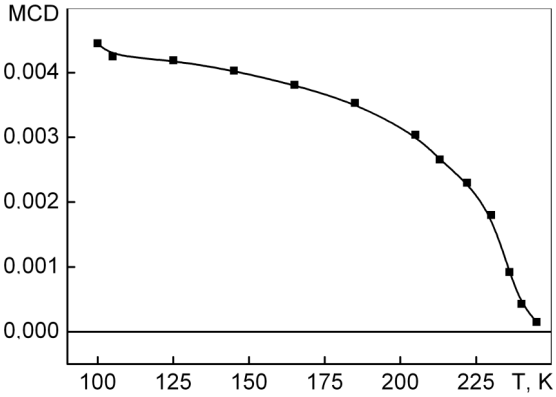

Fig. 5. Temperature dependence of MCD intensity of $Fe_xGa_{1-x}BO_3$ (66.8 % Fe) single crystal on λ = 466 nm.

MCD spectra of $Fe_xGa_{1-x}BO_3$ (66.8 % Fe) single crystal at different temperatures are presented in Fig. 4. The maximum near 460 nm corresponds to C-transition. Temperature dependence of the MCD intensity of $Fe_xGa_{1-x}BO_3$ with 66.8 %Fe (Fig. 5) permits to find Neel temperature T_N ~ 245 K. It correlates with T_N ~ 200 K obtained in [3] from magnetic measurements for the crystal containing lower Fe^{3+} concentration (55 %).

4. Conclusion

Thus, measurements of $Fe_xGa_{1-x}BO_3$ single crystals optical absorption spectra have shown the complicated changes in the region of strong absorption band edge. The main features of the spectra in this region are ascribed to the processes of charge transfer between Fe^{3+} ions in sublattices with the opposite spin directions. Weak absorption bands associated with d–d transitions are mainly due to pair exchange assisted absorption. Absorption and MCD spectra of the crystal containing ~ 67 %Fe are very similar to that of the nominally stoichiometric $FeBO_3$, and temperature dependence of the MCD testifies to the magnetic ordering in this crystal at T_N ~ 245 K.

Acknowledgements.

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References

1. R.Wolfe, A.J.Kurtzig, R.C.LeCraw, *J.Appl. Phys.*, **41**, 1218 (1970).
2. R.Diehl, W.Jantz, B.I.Nolang, Wettling, in: Current Topics in Material Science, ed. by E.Kaldis, Elsevier Sci. Publ. New-York (1984), v.11, Chapt.3, p.241.
3. A.S.Kamzin, L.P.Ol'khovik, E.V.Snetkova, *Physics of the Solid State*, **45**, 2128 (2003).
4. S.R.Boidedaev, B.Yu.Sokolov, *Phys. Solid State,* **45**, 2128 (2003)
5. B.Yu.Sokolov, *Zh. Eks. Teor. Fiz.*, **99**, 417 (2004).
6. B.Yu.Sokolov, *Phys. Solid State*, **47**, 1892 (2005).
7. V.N.Zabluda, A.V.Malakhovskii, I.S.Edelman, *Phys. Stat. Sol.(b)*, **125**, 751 (1984).

Оптичні і магнітооптичні властивості кристалів $Fe_xGa_{1-x}BO_3$

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Монокристали $Fe_xGa_{1-x}BO3$ з $0 < x < 1$ синтезовано розчин-розплавним методом. Оптичні спектри поглинання продемонстрували істотні зміни в області краю смуги сильного поглинання, залежно від концентрації заліза. Це пояснюється, переважно, перехідними процесами перенесення заряду Fe–Fe. Спектр магнітного кругового дихроїзму в області d–d переходів ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ і його температурна залежність уперше виміряно у кристалі, що містить 67 % Fe.