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COLOR CENTERS IN Mn- DOPED $Bi_4Ge_3O_{12}$ SINGLE CRYSTALS

Doping $Bi_4Ge_3O_{12}$ single crystals with Mn leads to the coloration of the crystals, photo- and electrochromic effects. The influence of the UV-light and the electric field using EPR and optical spectroscopy technique is studied. EPR experiments show that Mn^{2+} ions substitute for Bi^{3+} in the crystal lattice and take part in photochromic processes. Gaussian decomposition of the additional optical density spectra caused by doping and UV-irradiation allowed us to distinguish the specific bands of the induced optical absorption. The assumptions about the nature of local centers responsible for the photochromic behaviour of $Bi_4Ge_3O_{12}$ single crystals doped with Mn are made. The optical density spectra changes of the crystals under the electric field are measured at different temperatures. The existence of temperature, field and time dependences of electrochromic coloration of the crystals is established. The electrochromic effect is reversible as well as the photochromic one. The colored crystals are bleached by heating to 500-800 K.

Keywords: $Bi_4Ge_3O_{12}$, photochromic effect, electrochromic coloration, optical absorption.

Легування монокристалів $Bi_4Ge_3O_{12}$ марганцем приводить до їх забарвлення, фото- та електрохромного ефектів. Вплив УФ-світла та електричного поля вивчався з використанням методів ЕПР та оптичної спектроскопії. Експерименти з ЕПР показують, що іони Mn^{2+} заміщують Bi^{3+} в кристалічній ґратці і беруть участь у фотохромних процесах. Розклад на гаусові складові спектрів додаткової оптичної густини викликаної легуванням та УФ-опроміненням дозволив виділити характерні смуги індукованого оптичного поглинання. Зроблені припущення відносно природи локальних центрів, що відповідають за фотохромну поведінку монокристалів $Bi_4Ge_3O_{12}$, легованих Mn. Зміни спектрів оптичної густини кристалів під дією електричного поля були виміряні за різних температур. Було встановлено існування температурної, польової та часової залежностей електрохромного забарвлення кристалів. Електрохромний ефект є зворотнім так само як і фотохромний. Забарвлені кристали знебарвлюють нагріванням до 500-800 K.

Ключові слова: $Bi_4Ge_3O_{12}$, фотохромний ефект, електрохромне забарвлення, оптичне поглинання.

Легирование монокристаллов $Bi_4Ge_3O_{12}$ марганцем приводит к окрашиванию кристаллов, фото- и электрохромному ефектам. Влияние УФ-света и электрического поля изучалось с использованием методов ЭПР и оптической спектроскопии. ЭПР-эксперименты показывают, что ионы Mn^{2+} замещают Bi^{3+} в кристаллической решетке и принимают участие в фотохромных процессах. Разложение на гауссовы составляющие спектров дополнительной оптической плотности, вызванной легированием и УФ-облучением, позволяет выделить характерные полосы индуцированного оптического поглощения. Сделаны предположения относительно природы локальних центров, обусловливающих фотохромное поведение монокристаллов $Bi_4Ge_3O_{12}$, легированных Mn. Изменения спектров оптической плотности кристаллов под действием электрического поля были измерены при разных температурах. Установлено существование температурной, полевой и временной зависимостей электрохромного окрашивания кристаллов. Электрохромный эффект является реверсивным так же, как и фотохромный. Окрашенные кристаллы обесцвечиваются нагревом до 500-800 K.

Ключевые слова: $Bi_4Ge_3O_{12}$, фотохромный эффект, электрохромное окрашивание, оптическое поглощение.

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1. Introduction

Bismuth orthogermanate single crystals ($Bi_4Ge_3O_{12}$, BGO) are widely used in high energy physics and astrophysics as a scintillation material for ionizing radiation detection systems [1-3]. It has short radiation length, relatively high light output and short decay time. The maximum of the emission spectrum of these crystals in the 470-500 nm range matches well with the spectral sensitivity region of the standard photosensors. Crystals are colourless, transparent and nonhygroscopic. But BGO crystals are suffered to radiation damage effect that restricts their usage in some applications. The phenomenon of radiation damage is actively studied and discussed in the literature. It was shown that after UV, X-ray and γ-irradiation the degradation of the principal scintillation characteristics is mainly caused by the loss of the transparency to own emission, i.e., coloring of the crystals [4]. Obviously, the effect is connected with the presence of intrinsic defects and/or impurities in the crystal lattice. It was confirmed by the experiments on the crystals grown from the melt of non-stoichiometric composition and raw materials of different purity [5]. In early works [6] it was established that presence of iron group impurities even in trace concentrations leads to increase of the optical absorption in the visual region.

At the same time BGO has attracted some interests as material for holographic data storage. The existence of defects in the crystal structure leads to generation of charge transport processes responsible for the photochromic ant photorefractive effects which are able to provide more effective and stable holographic recording. Although the holographic gratings were successfully recorded in BGO crystals doped with different transition metals [7-8], the nature of photochromic processes practically in all cases is not completely clear.

According to author’s knowledge, there are no papers devoted to the question of BGO coloration induced by the electric field. But the electrochromic effect in BGO single crystals doped with transition group ions is observed and probably, may be connected with the same defects of the crystal lattice which are responsible for the photochromism.

The present paper is devoted to study of the optical density spectra changes induced by ultraviolet light irradiation and electric field in BGO single crystals doped with Mn.

2. Samples and experimental details

The bismuth germanate single crystals were grown from the melt by the Czochralski technique using high-purity raw materials and standard technology parameters. The obtained BGO crystals were colourless but after UV-irradiation the optical transmittance decreased. This decrease was about 10 % at 480 nm and kept during a few hours at room temperature.

The application of 2-fold regrowth improves the crystal quality. The photochromic change of the optical transmittance of these crystals did not exceed 2-3%.

The BGO crystals doped with Mn were pulled analogously. They had greenish color. When the concentration of Mn was less than 0.01 wt% in the crystals (according the emission spectral analysis) they were transparent and free from inclusions. The concentration of Pt did not exceed 0.001 wt%. The photoinduced change of the optical transmittance reached to 50%. The effect has a large thermal stability. The samples were bleached by heating above 500 K.

The optical density spectra were measured on double polished plates using a "Specord -UV-VIS" spectrophotometer at 77 and 295 K. The thickness of the samples was about 2.5–3 mm. EPR spectra were taken at X-band in (77-295 K) temperature range. The photochromic coloration was obtained using a 250-W high-pressure Hg lamp with $CuSO_4$ filter. (100 J/cm^2 of the incident light energy was required for the coloration at room temperature).

The influence of the electric field on the optical absorption of BGO single crystals doped with Mn was studied on the plane polished samples with two symmetric Ag electrodes in the longitudinal geometry of the experiment and parallelepiped-shaped samples with dimensions 4 x 4 x 6 mm^3 in the transverse geometry. The samples were polarized at fixed temperature, then electrodes were removed and optical transmittance of the samples was measured. The experimental cycle was finished by annealing of the samples at 800 K. The effect is reversible. The measurements show the temperature, field and time dependences of electrochromic coloring.

3. Results and discussion

According to the crystallographic data BGO has an eulytine structure (space group $\overline{4}3m$) with a cubic cell parameter a=1.0513 nm. The structure consists of tetrahedrons $(GeO_4)^{-4}$ connected together by Bi^{3+} ions. Each bismuth ion is surrounded by distorted oxygen octahedron. Three nearest oxygen ions are at distance ~ 0.219 nm, three others – at distance ~0.262 nm [9].

Four body diagonals of the cubic cell are C_3 axes for the Bi^{3+} sites and for each body diagonal there are two different Bi^{3+} sites which may be obtained by a rotation through angle ω about C_3 axis. The data about angle ω are varied from 62.16° for undoped BGO to 69.81° for BGO doped with Gd^{3+} [10].

In order to clarify the positions of transition metal impurities in BGO and their charge state the electron paramagnetic resonance (EPR) technique is traditionally used. The own investigation of author and another works devoted to EPR study of single crystals BGO doped with Mn have shown that manganese is incorporated into crystal lattice as Mn^{2+} in Bi^{3+} sites [6, 9-10].

At room temperature only twelve resonance lines are observed in the spectrum. Decrease of the temperature leads to complicating of the spectrum and in (77-150) K temperature range one can distinguish 4 spectra corresponding to Mn^{2+} for which both fine and hyperfine structure are observed. Analysis of the angular varieties shows that spectra have trigonal symmetry (C-axes are [111] directions) and can be described by a spin Hamiltonian:

$$\mathcal{H} = \beta(g\vec{H}\vec{S}) + B_2^0\hat{O}_2^0 + B_4^0\hat{O}_4^0 + B_4^3\hat{O}_4^3 + A(\vec{S}\vec{I}),$$

where β is Bohr magneton, g is spectroscopic splitting factor, the B_2^0 and B_4^0 – terms corresponding to axial fields of second and forth degree, B_4^3 – the cubic field splitting constant, A is the magnetic hyperfine splitting parameter, S=5/2 and I=5/2 . The estimation of the spin Hamiltonian parameters at 77 K gives following values for all spectra:

g =1.995 ±0,001; A=-91.0·10^{-4}cm^{-1}; B_2^0 =42.3·10^{-4}cm^{-1}; B_4^0 = -0.1·10^{-4}cm^{-1}

Significant anisotropy of g or A has not been observed. The sign of A is known to be negative from literature data about other compounds containing Mn^{2+}. The sign of constant B_2^0 is determined to be opposite to the sign of A because for BGO–Mn splitting of the highfield group of the hyperfine structure lines essentially exceeds that at law values of the magnetic field. Parameter B_4^3 has not been determined experimentally. According to the structural data there are two kinds of Bi^{3+} sites for each body diagonal [6, 9-10]. These centres are slightly differed by the directions of the cubic field axes. In our experiments this non-equivalence was exhibited in strong broadening of the resonance lines at the magnetic field rotation. Doubling of the lines has not been found.

At the illumination with ultraviolet light of the sample mounted in the EPR-cavity the intensity of the EPR spectra caused by Mn^{2+} decreased by about 90%. Thus, Mn^{2+} ions occupying Bi^{3+}sites in BGO take part in photochromic processes turning into another valence state.

The optical density spectra of nominally pure BGO single crystals, BGO doped with Mn before and after the UV-irradiation measured at room temperature are shown in fig.1. Doping with Mn leads to the appearance of the specific absorption bands and the considerable additional optical absorption induced by UV-light.

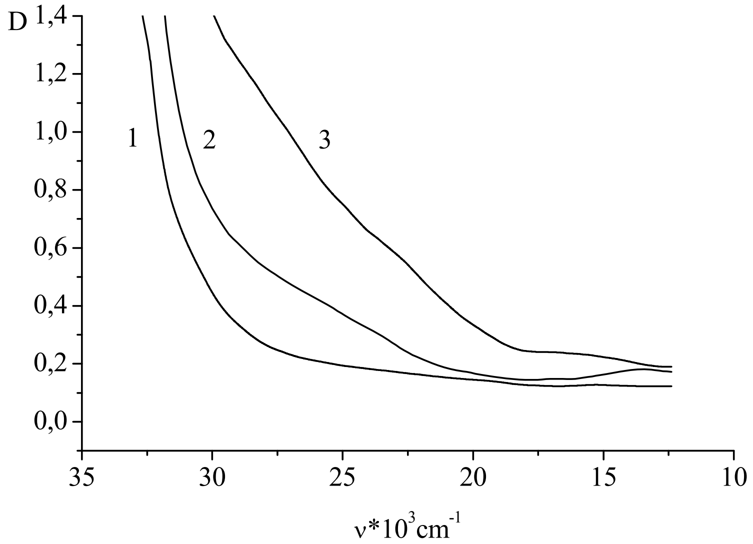

Fig. 1. The optical density spectra of BGO crystals: 1 – undoped BGO; 2 - Mn doped BGO; 3 - Mn doped BGO after UV exposure. The thickness of the samples was about 2.5 mm.

Fig.2 shows Gaussian decomposition of the additional optical density caused by doping and irradiation. It is found that in spectrum of BGO with Mn there are three wide absorption bands with the peaks near 30000 (A), 25000 (B) and 13300 (E) cm^{-1}. The photochromic effect leads to appearance of the intensive bands of absorption with the peaks near 30000 (A), 22000 (C) and 16200 (D) cm^{-1}. At the decrease of the temperature till 77 K the resolution of the bands is slightly increased and their positions are practically not changed.

Photochromic properties of BGO can be caused by both host material defects and impurities. Slight photochromic effect in undoped BGO, the increase of photoinduced change of the optical density and thermal stability in BGO doped with Mn confirms this. The possibility of the existence of manganese in different valence state can lead to the charge compensation and the formation of complex defects.

The charge compensation of Mn^{2+} can be realized with the existence of the oxygen vacancies or defects with the excessive charge. The presence of the oxygen vacancies in the first coordination sphere of Mn^{2+} surrounding should cause the fall of Mn^{2+} point symmetry. However, the comparison of crystallographic and EPR-data testifies about the absence of oxygen vacancies among the nearest neighbours of Mn^{2+} ion. Alternative or additional way of the charge compensation of the deficient positive charge of Mn^{2+} may be the formation of proper defects including Bi^{5+}. It is possible also that some quantity Mn^{3+} and Mn^{4+} is present in the crystal lattice of BGO–Mn.

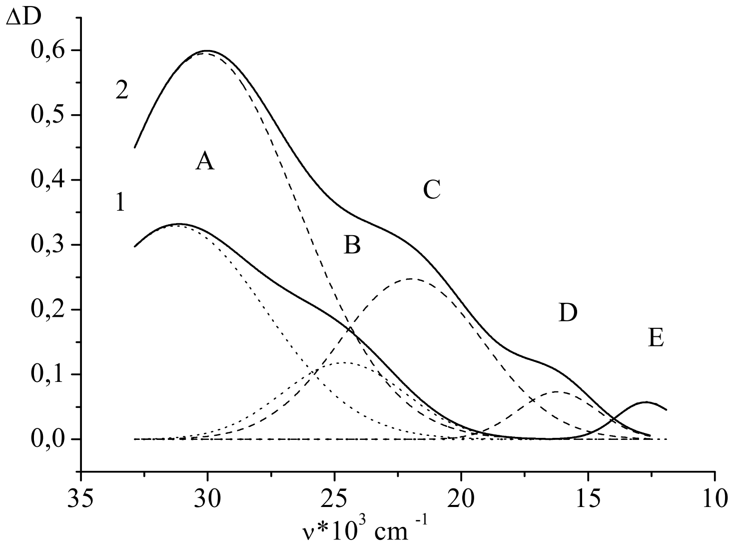

Fig. 2. Fitting of the additional optical density of BGO crystals induced with Mn doping (1) and UV exposure (2). The dashed curves are appropriate Gaussians.

For Mn^{2+} ions having electronic configuration $3d^5$ the main state of free ion is sextuplet ^6S. For crystal fields of octahedral symmetry the main term is $^6A_1$. Optical absorption lines arising from Mn^{2+} are very weak (being both spin and parity forbidden). Apparently, they are not observed because of a low concentration of Mn^{2+} although the presence of Mn^{2+} in BGO is also confirmed by observation of the characteristic luminescence.

Mn^{3+} ions possess electronic configuration $3d^4$ and preferentially occupy the octahedral sites. In the crystal field of the octahedral symmetry at Dq<2200 cm^{-1} the main term is ^5E and there is only one excited quintet $^5T_2$. According to [11] the absorption spectrum contains one broad band (18500-21000cm^{-1}) corresponding to transition $^5E \rightarrow {}^5T_2$. At another values of crystal field force parameter the main term is $^3T_1$ and a number of narrow and broad bands can arise in the spectrum. The configuration $3d^4$ is not stable and easily turns into $3d^5$ or $3d^3$. The intensive absorption in ultraviolet area of spectrum for many compounds containing Mn^{3+} is explained with charge transfer between Mn^{3+} and ligands. The study of a number of the crystals doped with Mn^{3+} has shown the absence of luminescence in the visible area of spectrum.

Mn^{4+} ions have electronic configuration $3d^3$ as well as Cr^{3+} ions and scheme of level splitting for them is well known. In many original works and reviews it was shown that for the optical spectra of Cr^{3+} ions in the complex oxide crystals the existence of the broad bands in the visible and near ultraviolet areas and narrow lines in the longwave area of the spectrum is typical. But the absorption spectrum of Al_2O_3 – Mn^{4+} (grown with adding of bivalent metal as compensator) contains only one broad band with maximum near 21300 cm^{-1} (transition from the main term $^4A_2$ to $^4T_2$ level). The intensive absorption near 30000cm^{-1} is connected with the charge transfer between impurity ion and surrounding oxygen ions [11]. Characteristic for 3d^3-ions fine structure is usually observed in luminescence spectra (R-lines).Our investigation did not show specific luminescence of Mn^{4+} after UV-excitation.

Let us try to identify the absorption bands in the optical spectra of BGO-Mn. We know from EPR that the charge compensation of Mn^{2+} can not be carried out with oxygen vacancies in the nearest neighbourhood of Mn^{2+}. The oxygen vacancies may occupy more distant oxygen sites causing a correspondingly small perturbation of local crystal field. From our experiments it also follows that the absorption bands A, B and E can not be caused by color centers connected with oxygen vacancies because the intensity of these bands increases after high temperature annealing of the samples in oxygen. It seems reasonable to assume that these bands arise due to defects oxidized relatively the initial state. B and E bands may be caused by presence of Mn^{4+}. Under UV-irradiation of the crystals Mn^{2+} ions act as donors of the electrons and Mn^{4+} – as traps. Arising of C- band in the spectrum of irradiated crystals may be connected with the appearance of Mn^{3+} in the crystal lattice. In this case the luminescence of Mn^{4+} at UV-excitation of the crystals can not be observed, however its absence does not except the possibility of the existence of Mn^{4+} in the unirradiated crystals. It is possible also that B and E bands are connected with intrinsic defects including Bi^{5+} ions. The intensive band at 30000 cm^{-1} (A-band) can be traditionally explained by transfer of the charge between the manganese ion and the ligand ions.

Fig. 3 - 6 show the electric field effect on the optical density spectra of BGO–Mn

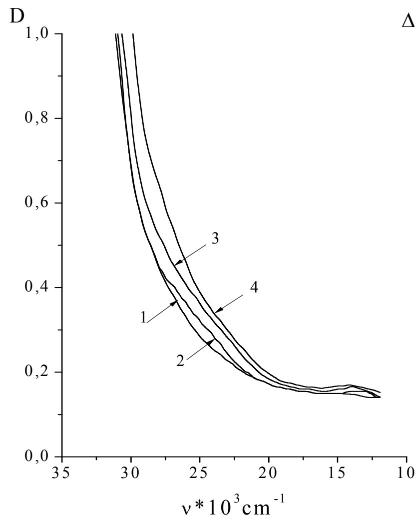

Fig. 3. The optical density spectra of BGO–Mn crystals colored by the electric field at 600 K: 1 – 0 kV/cm; 2 –2 kV/cm; 3 – 2.5 kV/cm; 4 – 3 kV/cm. The thickness of the sample was 3 mm. The longitudinal geometry of the experiment.

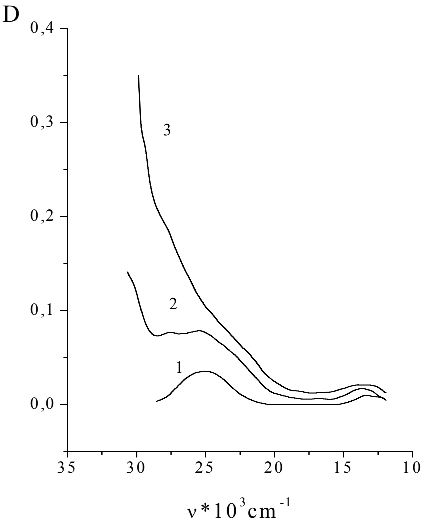

Fig. 4. The additional optical density spectra induced by the electric field at 600 K in BGO–Mn crystals: 1 –2 kV/cm; 2 – 2.5 kV/cm; 3 – 3 kV/cm. The thickness of the sample was 3 mm.

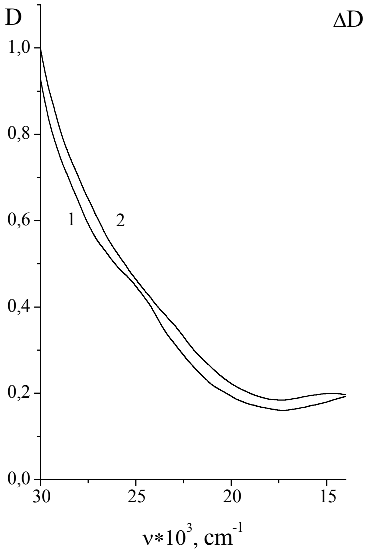

Fig. 5. The optical density spectra of BGO–Mn crystals colored by the electric field at 600 K: 1 – 2 kV/cm; 2 –0 kV/cm; The thickness of the sample was 4 mm. The transverse geometry of the experiment.

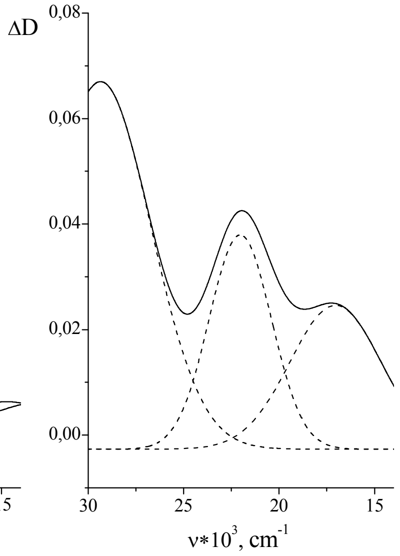

Fig. 6. The difference between optical density spectra induced by the electric field 2 kV/cm at 600 K in BGO–Mn crystals. The dashed lines show Gaussian components of spectrum.

5. Conclusions

BGO doped with Mn has greenish color. Fitting of experimentally obtained optical absorption curves to Gaussian shape lines shows three bands in the spectrum with tops near 30000, 25000 and 13300 cm^{-1}. EPR-spectra of BGO-Mn contain the great number of the overlapping lines. There are eight magnetically nonequivalent sites of Mn^{2+}. An analysis of these complicated spectra reveals that Mn^{2+} ions substitutes for Bi^{3+} in crystal lattice of BGO and has octahedral local environment with trigonal distortion.

After irradiation with UV-light of the BGO-Mn crystals the photochromic effect is observed. The photoinduced broad bands of the optical absorption with maxima near 30000, 22000 and 16200 cm^{-1} appeared in the spectrum. At the same time EPR-spectra corresponding to Mn^{2+} disappeared. Thus, axial Mn^{2+} centers are electron donors and change their valence state at UV-irradiation.

In this paper it is supposed that optical absorption arising from Mn^{2+} is too weak and three broad bands in the initial spectrum are caused by presence of Mn^{4+} ions (or Bi^{5+}). Under UV-irradiation BGO-Mn crystals are colored due to a charge transfer process and formation of Mn^{3+}centers. The effect is reversible. Heating at the temperatures above 500 K returns the colored crystals to the initial state.

The electrochromic effect in BGO doped with Mn is observed. Applying the electric field changes the charge state of the defects due to injection processes.

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