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HIGH-TEMPERATURE ANNEALING OF Mn-DOPED $Bi_4Ge_3O_{12}$ SINGLE CRYSTALS

The influence of high-temperature annealing of $Bi_4Ge_3O_{12}$ single crystals doped with Mn on the optical density spectra was studied. Experiments show that annealing in oxygen leads to increased intensity of lines of the optical absorption caused by centers oxidized relatively their initial states. It is supposed that Mn^{4+} (or Bi^{5+}) ions, situated in oxygen octahedrons distorted along body diagonals of the cubic crystal lattice of $Bi_4Ge_3O_{12}$, are these centers. Crystal sample reduction in hydrogen discolors the crystals and significantly increases the additional optical absorption arising under ultraviolet irradiation. Manganese is assumed to be reduced to Mn^{2+} during annealing in hydrogen and turns into Mn^{3+} under UV exposure. Thus, photochromic processes in $Bi_4Ge_3O_{12}$–Mn single crystals can be controlled by means of thermal annealing procedure.

Keywords: bismuth orthogermanate $Bi_4Ge_3O_{12}$, doping with Mn, photochromic effect, high-temperature annealing, optical absorption.

Досліджено вплив високотемпературного відпалу на спектри оптичної густини кристалів $Bi_4Ge_3O_{12}$, легованих марганцем. Експерименти показують, що відпал у кисні приводить до посилення інтенсивності ліній оптичного поглинання, викликаних центрами, окисленими відносно вихідного стану. Передбачається, що цими центрами є іони Mn^{4+} (або Bi^{5+}), що знаходяться в кисневих октаедрах, спотворених уздовж просторових діагоналей кубічної кристалічної решітки $Bi_4Ge_3O_{12}$. Відновлення кристалічних зразків у водні приводить до знебарвлення кристалів та істотного збільшення додаткового оптичного поглинання, що виникає під дією ультрафіолетового опромінювання. Припускається, що марганець відновлюється у водні до Mn^{2+} та переходить у Mn^{3+} під впливом УФ опромінення. Таким чином, фотохромними процесами в монокристалах $Bi_4Ge_3O_{12}$–Mn можна управляти за допомогою процедури термічного відпалу.

Ключові слова: ортогерманат вісмуту $Bi_4Ge_3O_{12}$, легування марганцем, фотохромний ефект, високотемпературний відпал, оптичне поглинання.

Исследовано влияние высокотемпературного отжига на спектры оптической плотности кристаллов $Bi_4Ge_3O_{12}$, легированных марганцем. Эксперименты показывают, что отжиг в кислороде приводит к усилению интенсивности линий оптического поглощения, вызванных центрами, окисленными относительно исходного состояния. Предполагается, что этими центрами являются ионы Mn^{4+} (либо Bi^{5+}), находящиеся в кислородных октаэдрах, искаженных вдоль пространственных диагоналей кубической кристаллической решетки $Bi_4Ge_3O_{12}$. Восстановление кристаллических образцов в водороде приводит к обесцвечиванию кристаллов и существенному увеличению дополнительного оптического поглощения при ультрафиолетовом облучении. Подразумевается, что марганец восстанавливается в водороде до Mn^{2+} и переходит в Mn^{3+} под воздействием УФ облучения. Таким образом, фотохромными процессами в монокристаллах $Bi_4Ge_3O_{12}$–Mn можно управлять посредством процедуры термического отжига.

Ключевые слова: ортогерманат висмута $Bi_4Ge_3O_{12}$, легирование марганцем, фотохромный эффект, высокотемпературный отжиг, оптическое поглощение.

1. Introduction

In recent years well known scintillation single crystals of bismuth orthogermanate ($Bi_4Ge_3O_{12}$, BGO) are used as photorefractive material for high-density holographic data storage and optical information processing [1−2]. The presence of iron group impurities leads to the appearance of the considerable photochromic effect and enhances the absorption of light in a certain range of the spectrum. As a result, the efficiency and stability of holographic recording are improved. Color centers in $Bi_4Ge_3O_{12}$ single crystals doped with Mn were studied by optical and radiospectroscopic methods [3−6]. The investigations show the existence of heterovalence substitution of bismuth ions for manganese ions in crystal lattice and the change of valence state of impurities under the influence of irradiation or electric field. EPR spectra are attributed to Mn^{2+} ions in the Bi^{3+} sites. The issues about the charge compensation of this defect, the influence of oxygen vacancies on photochromic coloring of the crystals and existence of Mn^{3+}, Mn^{4+} ions in crystal structure remain unclear. The elucidation of them is necessary for the increase of the ability to control the optical properties of BGO-Mn crystals. In the present article the author considers the effect of high-temperature annealing of BGO-Mn single crystals in oxidizing and reducing atmospheres on the spectra of optical density and photoinduced absorption.

2. Samples and experimental details

The BGO crystals doped with Mn were pulled from the melt by the Czochralski technique in air using standard technology parameters for pure BGO including 2-fold regrowth [6]. For concentrations of Mn less than 0.01 wt% in the crystals (according to the emission spectral analysis) they were transparent and free from inclusions.

Annealing of the crystal samples was carried out in a stream of oxygen or hydrogen produced by the electrolysis of water. The crystals were annealed in a quartz furnace at 1225−1275 K (the melting temperature of BGO single crystals is ~1317 ±4K) during 48 hours and then were cooled with a rate ~10 K/h.

The optical density spectra were measured on double polished plates using a "Specord -UV-VIS" spectrophotometer 295 K. The thickness of the samples was about 2 mm. The crystals were irradiated by ultraviolet light using a 250 W high-pressure mercury lamp with $CuSO_4$ filter.

3. Results and discussion

The optical density spectra of BGO single crystals are presented in Fig. 1. Nominally pure, undoped crystals are colorless (curve 1). As it was previously reported [6], 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%. Doping with Mn leads to the appearance of green color (curve 3). According to [6] three bands of the light absorption with tops near 30000 (A), 25000 (B) and 13300 (E) cm^{-1} can be distinguished in the optical density spectra of BGO-Mn single crystals. High-temperature annealing of the samples in reducing atmosphere bleaches the crystals (curve 2). Fig.2a shows the change of the optical density of the BGO-Mn crystals due to annealing in hydrogen as difference of the curves 3 and 2 presented in Fig. 1. Gaussian decomposition of this spectrum indicates intensity decreasing of the A, B and E bands of the optical absorption.

Thermal annealing in oxygen, on the contrary, enhances green color of the samples. It corresponds to the curve 4 in Fig. 1. The influence of oxidizing is shown in Fig. 2b.

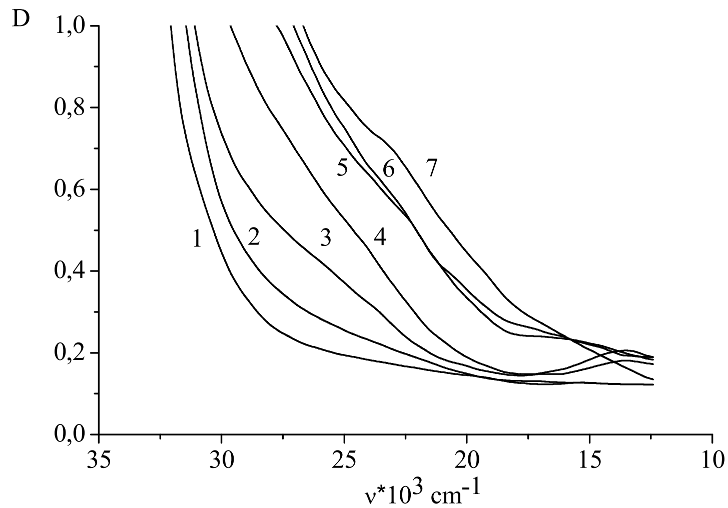

Fig. 1. The optical density spectra of BGO crystals: 1 – undoped BGO; 2 – BGO–Mn after annealing in hydrogen; 3 – BGO–Mn; 4 – BGO–Mn after annealing in oxygen; 5 – oxidized BGO–Mn after UV exposure; 6 – BGO–Mn after UV exposure; 7 – reduced BGO–Mn after UV exposure; the thickness of the samples was about 2 mm.

Difference of the curves 4 and 3 from Fig. 1 is presented as the spectrum of additional optical density caused by annealing. The intensity of A, B and E bands increases.

BGO crystals have a forbidden gap >4.5 eV [7] that corresponds to approximately 36350 cm^{-1}. The aim of this experiment was the investigation of the impurity absorption in BGO-Mn crystals so the thickness of 2 mm was chosen for the samples. Therefore the range near the fundamental absorption edge is not studied in this work and the absorption bands observed above 30000 cm^{-1} can not be accurately assigned.

The irradiation of the crystals by ultraviolet light leads to their darkening in all three cases (curves 5–7 in Fig. 1). The additional photoinduced absorption of light is appeared in the optical spectrum of BGO-Mn. Decomposition into Gaussians of the spectrum in the work [6] shows that photochromic effect leads to appearance of the intensive bands of absorption with the peaks near 30000 (A), 22000 (C) and 16200 (D) cm^{-1}. The change of optical density spectra of all three crystals is presented in Fig. 3. As can be seen, the smallest photocromic change is observed for oxidizing crystals and the biggest change – for reduced ones.

It is well known that BGO has an eulytine crystal structure where each Ge^{4+} ion is surrounded by four oxygen ones arranged in a tetrahedron which is slightly distorted along the [100] distortion. Each Bi^{3+} ion is coordinated by six oxygen ions arranged in a octahedron with strong trigonal distortion along body diagonal of cubic unit cell. EPR study of Mn-doped BGO single crystals have shown that Mn^{2+} ions substitute for the Bi^{3+} ions [3, 6]. Usually, the charge compensation of such defects in oxide crystals was connected with the presence of oxygen vacancies. Especially, if there is a photochromic effect. However, according to EPR data the local symmetry of Mn^{2+} paramagnetic center agrees with crystallographic symmetry of Bi^{3+} ions. Therefore, oxygen vacancies in the nearest coordination sphere are absent. Local charge compensation of Mn^{2+} ion can be realized by an ion positioned along the [111] direction that would still maintain the same symmetry. It may be native defects connected with further oxidizing of Bi^{3+}or Mn^{4+}ions in Bi^{3+} sites. Oxygen vacancies in the crystal lattice are present but their spatial distribution is chaotic.

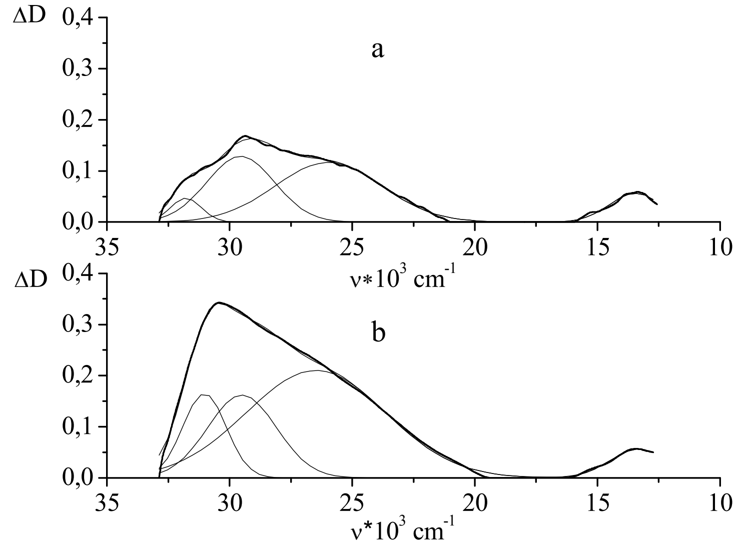

Fig. 2. The changes of the optical density of BGO-Mn crystals after annealing in hydrogen (a), in oxygen (b), and decomposition of them. The thin curves are appropriate Gaussians.

It was shown earlier by the author that irradiation of BGO-Mn crystals with ultraviolet light leads to disappearance of EPR signal of Mn^{2+} ions. Thus Mn^{2+} centers take part in photochromic process changing their charge state. In the paper [6] it is supposed that optical absorption arising from Mn^{2+} is too weak and three broad bands in the initial spectrum are caused by the 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.

If this assumption is true, annealing of the BGO-Mn crystals in oxygen will be lead to reactions of manganese and bismuth oxidizing and, correspondingly, to increase the intensity of A, B and E bands. This phenomenon observed in experiment confirms also that A, B and E bands of optical absorption could not be connected with oxygen vacancies. Fig.3 proves that Mn^{2+} ions are electron donors in photochromic processes in BGO-Mn. We can see that reduced crystals demonstrate the greatest photoinduced absorption of light.

Photoinduced absorption of the light in oxidized samples is considerably less than in the initial BGO-Mn crystals. The greatest intensity of the photochromic absorption bands is observed in reduced single crystals.

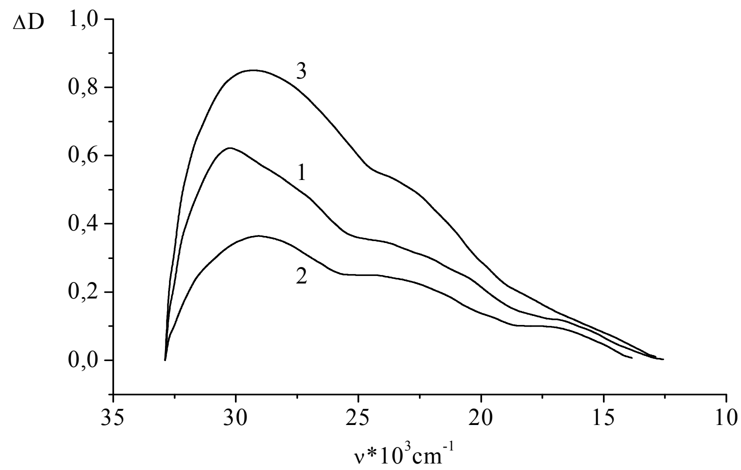

Fig. 3. The additional optical density spectra of BGO–Mn crystals after UV exposure: 1 – oxidized BGO-Mn; 2 – initial BGO-Mn; 3 – reduced BGO-Mn. The thickness of the samples was about 2 mm.

4. Conclusions

High-temperature annealing of BGO-Mn crystals in oxygen atmosphere leads to increase of the intensities of three specific bands of the light absorption with tops near 30000 (A), 25000 (B) and 13300 (E) cm^{-1} caused by presence of the centers oxidized relatively of the initial state such as Mn^{4+} (or Bi^{5+}) ions in Bi^{3+} sites. Annealing of the samples in hydrogen reduces manganese to Mn^{2+} and bleaches the crystals. The intensities of A, B and E bands are sharply falls.

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