PHOTOCHROMISM INFLUENCE ON THE LUMINESCENCE SPECTRUM OF $Bi_4Ge_3O_{12}$ SINGLE CRYSTALS DOPED WITH Mn

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$Bi_4Ge_3O_{12}$ crystals doped with Mn exhibit a considerable thermally stable photochromic effect. An additional absorption of light appears in the visible region of the optical absorption spectrum of the crystals irradiated with UV light. In the photoluminescence spectrum, both the intrinsic emission of a pure $Bi_4Ge_3O_{12}$ crystal and the emission in the region of 580 nm caused by the presence of Mn^{2+} ions are observed. After UV exposure, the luminescence intensity of Mn-doped $Bi_4Ge_3O_{12}$ crystals decreases. The emission associated with by Mn^{2+} ions disappears. The luminescence intensity of pure $Bi_4Ge_3O_{12}$ decreases due to strong photoinduced absorption of light in this spectral region.

Keywords: $Bi_4Ge_3O_{12}$, photoluminescence, photochromic effect..

Received 25.10.2021; Received in revised form 03.12.2021; Accepted 10.12.2021

1. Introduction

The main direction of the application of bismuth orthogermanate crystals ($Bi_4Ge_3O_{12}$, BGO) is scintillation detectors of ionizing radiation. They are used in radiometry, high energy physics, space research [1-2]. There are a large number of publications devoted to both the issues of growing and the study of scintillation characteristics, and issues of practical applications. However, the nature of the luminescence in BGO is still discussed. And the reason for this, first of all, is the dependence of luminescence on the quality of the crystals grown.

The study of the optical absorption and luminescence of BGO crystals after irradiation with fast electrons, neutrons, protons, and gamma radiation shows that the appearance of stable radiation defects depends not only on the type of radiation and its power, but also on the existence of pre-radiation defects and impurities [3]. Investigation of the effect of UV irradiation on the optical characteristics of BGO is much more accessible experimentally. It is known that BGO crystals with iron group impurities show a significant thermally stable photochromic effect [4, 5]. It is this property that increases the efficiency of using BGO crystals as photorefractive media in holographic applications. However, the effect of photochromic switching on the luminescence of doped crystals has been insufficiently explored. In this work, we studied the influence of photochromic coloration of BGO crystals doped with Mn on their photoluminescence.

2. Samples and experimental details

Nominally pure and doped with Mn bismuth germanate single crystals were grown from the melt by the Czochralski technique using 2-fold regrowth and standard technology parameters [6]. Pure crystals were colorless, doped with Mn had a greenish color. The amount of impurities in the crystals was determined by method of emission spectral analysis. For concentrations of Mn less than 0.01 wt% the crystals were transparent and free from inclusions. For (0,004–0,006) wt% concentrations the impurity was uniformly distributed in the longitudinal and transversal directions.

The measurements of the optical spectra were carried out on the polished $10\times10\times2$ mm^3 samples cut perpendicular to the [100] crystallographic direction. Three types of the samples were prepared: 1) as grown pure BGO crystal; 2) BGO crystal doped with Mn and 3) BGO-Mn crystal irradiated with UV-light. The last sample changed its color to brown due to photochromic effect. This 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 maximum coloration at room temperature). The effect has a large thermal stability. The samples can be bleached by heating up to 500 K.

The photoluminescence spectra of the BGO crystals were obtained at 295 K. A pulsed laser (10 ns) with a wavelength of radiation 337.1 nm was used for excitation of luminescence. The optical density spectra were measured using a "Specord-UV-VIS" spectrophotometer at 295 K.

3. Results and discussion

The photoluminescence of BGO crystals is well studied. A good review of the scientific literature on the nature of luminescence and radiation defects in BGO is given in the monograph [7]. Photoluminescence spectrum of BGO is a broad asymmetric band, the shape of which depends on the quality of the crystal, the method of luminescence excitation, and the temperature. The structure of the spectrum is better manifested with selective excitation by laser light and usually has from three to eight subbands. As a rule, the main luminescence band has a maximum at 480 – 500 nm. Green luminescence is characteristic of various crystals doped with Bi^{3+} and is caused by the lowest allowed electronic dipole transition $^3P_1 \rightarrow {}^1S_0$. The origin of this band in bismuth germanate is associated with the presence of self-trapped Frenkel excitons, which are the excited state of molecular ions $(BiO_6)^{9-}$ [7, 8]. The presence of other components in the spectrum is attributed to the existence of structural defects in the crystal lattice, including those associated with oxygen vacancies, and with recombination processes [9, 10].

Fig. 1 shows the photoluminescence spectrum of a nominally pure BGO crystal grown by us. Decomposition into Gaussians shows the presence of three components with maxima at 415, 480 and 650 nm, which correlates well with the results of other authors. It should be noted that the 337.1 nm wavelength used for the excitation of the emission is not optimal for BGO, since at room temperature the maximum in the excitation spectrum falls on 265 – 290 nm and already at 300 nm the luminescence intensity sharply decreases [7].

Fig. 2 shows the photoluminescence spectrum of BGO with Mn crystal and its decomposition into Gaussian components. In addition to the bands already existing in the spectrum of a nominally pure BGO crystal, an intense luminescence band appears with a maximum near 580 nm. The results of the study of BGO – Mn crystals by the EPR method show that manganese ions enter into the crystal lattice in the form of Mn^{2+} and have trigonal local symmetry. The axes of the third order for them are the spatial diagonals of the cubic crystal lattice of the BGO. It coincides with the X-ray diffraction data for bismuth ions. Thus, Mn^{2+} ions replace Bi^{3+} ions in the crystal lattice [4, 11-12].

The study of the photoluminescence of BGO – Mn crystals was carried out in [13] and of thin films in [14]. The emission with the peak at 580 nm in [13] was attributed to the $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition of Mn^{2+} in an approximation of the cubic crystal field with one [001] axis lying along the [111] crystallographic axes. It was also shown that, at low temperatures, excitation with light with a wavelength of up to 275 nm does not lead to Mn^{2+} emission. Only emission of pure BGO was observed. In the excitation region of 275 – 300 nm, an overlap of the intrinsic radiation of BGO and the Mn^{2+} impurity was observed. It was suggested that there is energy transfer from the Bi^{3+} ion to the Mn^{2+} ions. Upon excitation with light with a wavelength of 300 – 540 nm, only Mn^{2+} luminescence was observed. The radiation intensity decreases with increasing measurement temperature and above 250 K, the authors of [13] did not observe Mn^{2+} luminescence.

In our experiments, luminescence was excited by a nitrogen laser with a wavelength of 337.1 nm, and even at room temperature, both the intrinsic BGO emission and the Mn^{2+} emission can be observed.

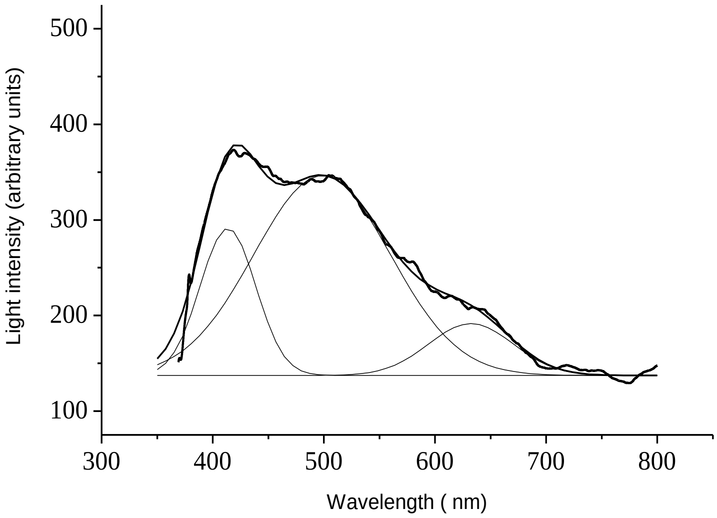

Fig. 1. The photoluminescence spectrum of BGO and its decomposition into Gaussian components.

An increase in the power and duration of UV irradiation of BGO – Mn crystals causes a photochromic effect. In our experiment, a 250 W mercury lamp was used to irradiate the crystals. The most intense line in the UV spectrum of its radiation is the line with a wavelength of 365 nm. After irradiation, the color of the crystals changes from light green to dark brown. Fig. 3 shows the changes in the optical density spectra due to doping with manganese and UV irradiation. As shown in [4] by means of Gaussian decomposition of the additional optical density caused by doping, in spectrum of BGO with Mn there are three wide absorption bands with the peaks near 330, 400, and 750 nm. The photochromic effect leads to appearance of the intensive bands of absorption with the peaks near 330, 450, and 620 nm.

Color centers responsible for the appearance of these absorption bands in the optical density spectra can be caused by both host material defects and impurities. There are many papers dealing with the “radiation damage” problem in undoped BGO [15-17]. Doping crystals with ions of the iron group causes the increase of photoinduced absorption. Such impurity as manganese can exist in different valence states. It can lead to the need of the charge compensation and the formation of complex defects.

The deficiency of positive charge of Mn^{2+} ions can be compensated for by the presence of the oxygen vacancies or defects with the excessive positive charge. The comparison of crystallographic and EPR-data shows the absence of oxygen vacancies in the first coordination sphere of Mn^{2+} surrounding [4, 11-12].

An alternative or additional way of Mn^{2+} charge compensation may be the formation of intrinsic defects including Bi^{5+}. The presence of a certain amount of Mn^{3+} and Mn^{4+} in the crystal lattice of BGO – Mn is also possible.

In [4] it is assumed that the optical absorption lines associated with Mn^{2+} ions are very weak (as the corresponding transitions are forbidden) and are not observed. After UV irradiation, the EPR spectrum caused by Mn^{2+} disappears. Therefore, under the influence of UV light, the Mn^{2+} centers become electron donors and change their valence state.

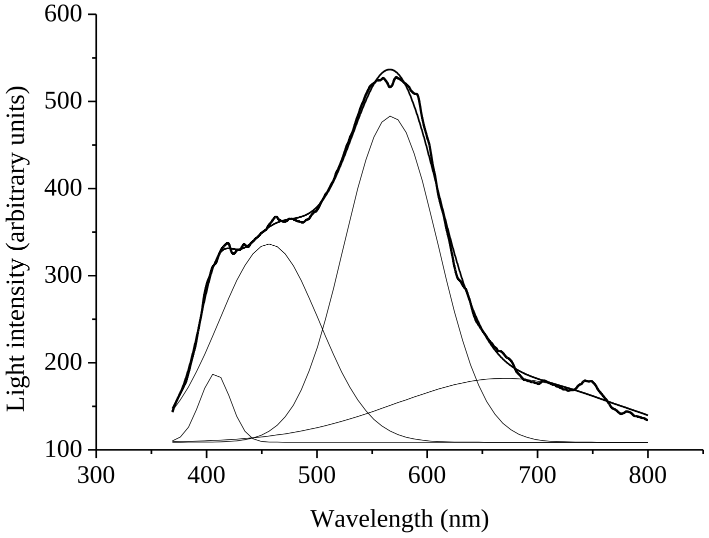

Fig. 2. The photoluminescence spectrum of BGO – Mn and its decomposition into Gaussian components.

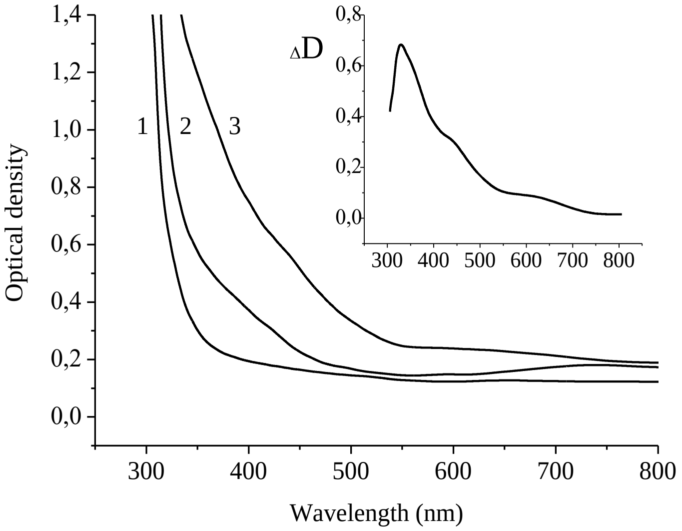

Fig. 3. The optical density spectra of BGO crystals: 1 – undoped BGO; 2 – Mn doped BGO; 3 – Mn doped BGO after UV exposure. The inset shows the additional optical density ΔD caused by irradiation of BGO – Mn. The thickness of the samples was about 2.5 mm.

Investigation of a number of inorganic crystals doped with Mn^{3+} showed the absence of luminescence in the visible spectral range [18]. Mn^{4+} ions have a $3d^3$ electronic configuration, like Cr^{3+} ions, and the scheme of energy level splitting for them is well known. The luminescence spectra usually exhibit a fine structure characteristic of $3d^3$ ions (R lines). However, our studies did not show any specific luminescence of Mn^{4+} after UV excitation.

In Fig. 4 the photoluminescence spectra of all three samples of BGO crystals are shown for comparison. The spectrum 3 of the BGO – Mn sample exposed to UV light from a mercury lamp is the most interesting for us. It can be seen that the luminescence of Mn^{2+} ions with a maximum near 580 nm is largely suppressed. Obviously, this result coincides with the EPR data and shows a change in the valence state of manganese after UV irradiation. The absence in the spectrum of the main radiation of the BGO crystal, which has a maximum near 480 nm is the second important fact. Perhaps this result can be explained by the strong absorption of light in this region, caused by photochromic processes.

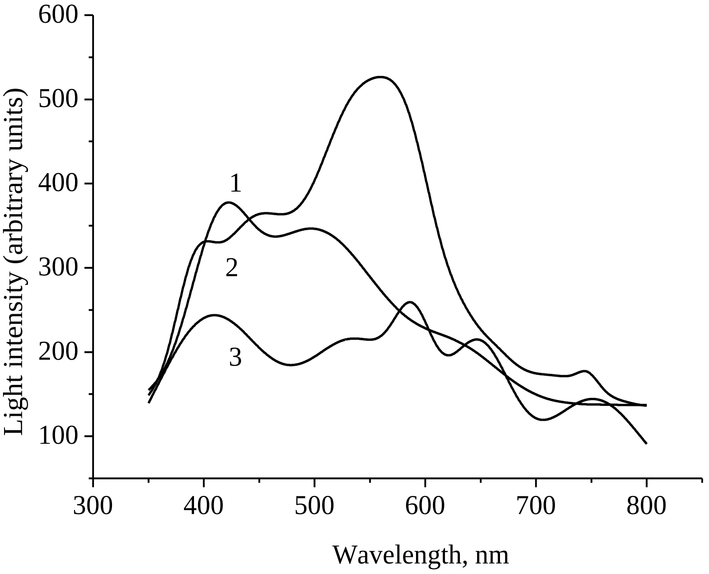

Fig. 4. The photoluminescence spectra of BGO crystals: 1 – undoped BGO; 2 – Mn doped BGO; 3 – Mn doped BGO after UV exposure.

4. Conclusions

The photoluminescence of BGO crystals is strongly dependent on intrinsic defects, impurities, and external influences. The emission spectrum of a pure crystal consists of three characteristic bands and correlates with the literature data. The main luminescence band with a maximum at about 480 nm is typical for various crystals doped with Bi^{3+} and attributed to the presence of self-trapped Frenkel excitons, which are an excited state of molecular ions $(BiO_6)^{9-}$. Other components can be caused by distortion of the environment of Bi^{3+} ions by structural defects, including those associated with oxygen vacancies or with recombination processes.

The luminescence band with a maximum near 580 nm which associated with the presence of Mn^{2+} ions, dominates in the luminescence spectrum of BGO crystals doped with manganese. No luminescence characteristic of Mn^{4+} was observed. The luminescence spectrum changes after UV irradiation causing the photochromic effect. The emission band associated with the presence of Mn^{2+} is suppressed, that agrees with the EPR data. At the same time the intensity of own luminescence of BGO crystal in the region of 480 nm decreases, that may be attributed to strong optical absorption induced by UV light.

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