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Radiative recombination in BiI₃(Mn) and BiI₃(Cr) layered single crystals

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Abstract. The photoluminescence spectra of BiI₃(Mn) and BiI₃(Cr) single crystals were studied. The new bands at $\lambda = 1.1$ and $\lambda = 1.83$ μm were registered at the temperature 4.2 K. It was shown that the first and second bands arise due to Mn²⁺ and Cr³⁺ ions, accordingly. The experimental results were explained using the configuration model. The energies between minima of configuration curves of excited and basic states for both centres were estimated.

Keywords: photoluminescence, transition metals, layered semiconductors, configuration model.

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1. Introduction

Ferro-group transition ions in solid state matrixes manifest intracentre optical transitions in unfilled 3d-shells thoroughly considered in review [1]. Besides scientific interest, radiative transitions have practical interest because ZnS:Mn substances are particularly one of the most effective orange luminescence luminophors. Moreover, semiconductors with magnetic impurities can reveal spin effects, and therefore they are perspective materials for application in spintronic devices [2]. In contrast to diluted magnetic semiconductors based on traditional A^{II}B^{VI} and A^{III}B^V compounds, the layered semiconductors are poorly investigated.

The influence of Mn and Cr impurities on three-dimensional and quasi-surface exciton states of BiI₃ layered single crystals were studied in [3]. It was found that the reason for broadening their bands may be ionization of three-dimensional and quasi-surface exciton states by the electric field of Mn²⁺ and Cr³⁺ ions. On the other hand, at the temperature $T = 4.2$ K in infrared (IR) photoluminescence (PL) spectra of such objects, two broad bands at the energies 1.13 (BiI₃(Mn)) and 0.68 eV (BiI₃(Cr)) caused by the defects of the crystal lattice were early registered [4].

The aim of this work is to study the PL spectra of BiI₃(Mn) and BiI₃(Cr) single crystals at different temperatures as well as obtain information about centres and mechanisms of radiative recombination.

2. Results and discussion

We used the same *n*-type samples with mirror surface as those in [3]. The samples were grown by the Bridgman

method. The concentration of paramagnetic impurities was 10^{18} cm⁻³. Photoluminescence spectra were excited in the region of the intrinsic absorption edge by tungsten lamp light with the power 50 W through the double filter (Cu₂SO₄ saturated water solution and SZS-14 optical filter with the thickness of 20 and 7 mm, respectively). When necessary, the He-Ne laser was used because of its photon quantum energy $h\nu = 1.98$ eV is less than the energy of the exciton state with basic quantum number $n = 1$ ($E_{n=1}^{\text{ex}} \approx 2.10$ eV ($T = 4.2$ K) [5]) in BiI₃. The maximum intensity of a focused beam of light did not exceed 10^{19} quanta/cm², which corresponds to the exciton concentration $n_{\text{ex}} = 10^{16}$ cm⁻³ (it was determined using the formula $n_{\text{ex}} = N_{\text{ph}}\alpha\tau_{\text{ex}}$, where N_{ph} is the density of photon number, α is the absorption coefficient at the maximum of the exciton band and τ_{ex} is the lifetime of free excitons) and indicates neglecting of the exciton-exciton interaction. PL spectral composition was analyzed from the side of exciting light using the experimental setup based on DMR-4 monochromator with glass prisms. The KS-13 filter was placed in front of the monochromator slit. The FEU-62 photomultiplier or the PbS photoresistor were used as signal detectors. The spectral curves were built up taking into account the setup spectral sensitivity.

The typical PL spectral of pure (specially non-doped) and doped with Mn and Cr impurities BiI₃ single crystals at $T = 4.2$ K are shown in Fig. 1. One can see that in the spectrum of the pure sample (curve 1) there is one well-known single band at the wavelength $\lambda = 1.34$ μm with the large halfwidth ($W = 148$ meV) due to the vacancies of Bi atoms [6], whereas in the spectra of BiI₃(Mn) (curve 2) and BiI₃(Cr) (curve 3) the new two

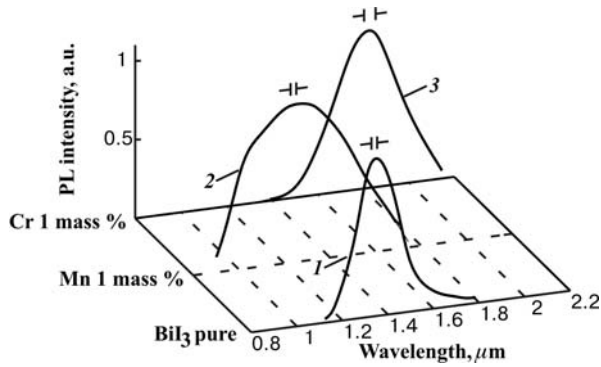


Fig. 1. Infrared photoluminescence spectra of BiI₃ single crystals at $T = 4.2$ K and the photon excitation in the region of the intrinsic absorption edge: curve 1 is for the pure sample, curves 2 and 3 describe doped samples containing Mn²⁺ and Cr³⁺ ions with the concentration $\sim 10^{18}$ cm⁻³.

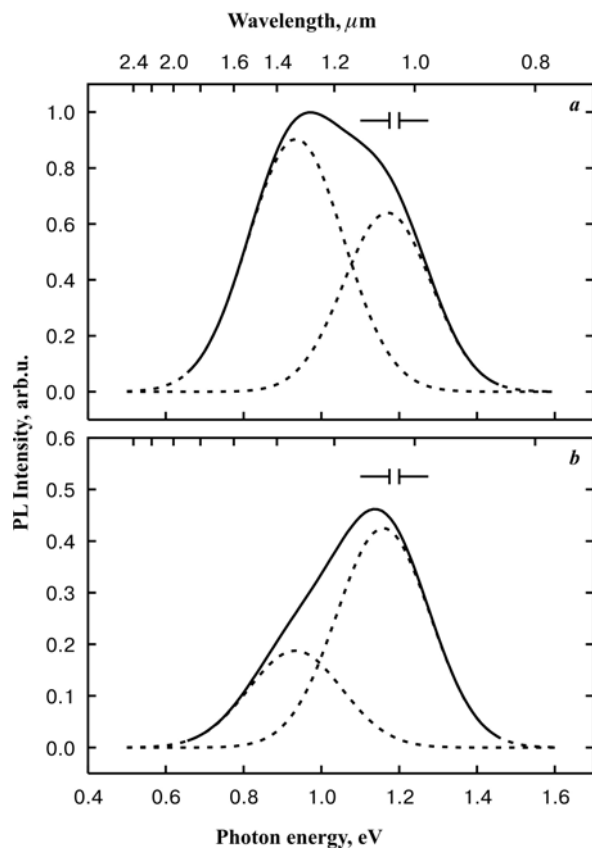


Fig. 2. Infrared photoluminescence spectra of BiI₃(Mn) single crystals at the temperatures 4.2 (a) and 77 K (b) and the photon excitation in the region of the intrinsic absorption edge. Solid lines are the experimental ones and dotted lines are the Gauss curves.

broad bands appear, one of which being structural with the maximum at $\lambda = 1.24$ μm in the spectral region 0.8...1.7 μm and another nonstructural with the maximum at $\lambda = 1.83$ μm within the range of 1.4 to 2.2 μm , accordingly. The following facts should be also pointed out: a) the band at $\lambda = 1.24$ μm consists of two

bands at $\lambda = 1.1$ and $\lambda = 1.34$ μm , b) the band at $\lambda = 1.34$ μm is more intense than that at $\lambda = 1.1$ μm , and c) the contours of the bands at $\lambda = 1.1$, 1.34, and 1.83 μm are very well approximated by Gaussian curves. Moreover, using He-Ne laser we have possibility to observe all the named bands at the photon excitation energy $h\nu < E_{n=1}^{\text{ex}}$.

Temperature investigation data are presented in Figs 2 and 3. When the temperature increases from 4.2 up to 77 K, we found out the following changes: first, the intensity of infrared PL decreases essentially, and second, the intensity of the band at $\lambda = 1.34$ μm decays faster than that of the band at $\lambda = 1.1$ μm .

At $T = 300$ K, the infrared PL of BiI₃(Mn) and BiI₃(Cr) single crystals was not found.

The absence of visible PL and manifestation of the infrared one at low temperatures is the characteristic peculiarity of the obtained data. This points out the appearance of new defect centres in BiI₃(Mn) and BiI₃(Cr) samples, which catch the excitation energy of the crystal lattice and essentially changes radiative recombination channels. As was shown in [4,7], the impurity atoms Mn and Cr are introduced into BiI₃ crystal lattice as Mn²⁺ (the probable compensators may be Cu⁺ ions) and Cr³⁺ ions, accordingly, and substitute in their sites Bi³⁺ ions do have local symmetry of C_{3v} type. So, the vacancy concentration of Bi atoms may be reduced. As a result, the band at $\lambda = 1.34$ μm in PL spectrum of BiI₃(Cr) is absent, and its intensity in PL spectrum of BiI₃(Mn) decreases.

The appearance of the bands at $\lambda = 1.1$ and $\lambda = 1.83$ μm is caused by the defects of crystal lattice created by Mn²⁺ and Cr³⁺ ions, respectively. As far as the local symmetry of recombination centres is C_{3v}, and the bands manifest themselves as Gauss curves, they may be attributed to intracentre transitions in Mn²⁺ and Cr³⁺ ions and described within the configuration model. In this model, these Mn²⁺ and Cr³⁺ centres may be considered as interacting with crystal lattice garmonic oscillators, which corresponds to the presence of equidistant levels in basic and excited states. All the possible transitions from different vibrational levels of basic state to the vibrational levels of excited states form the excitation bands. The transitions from the vibrational levels of the lowest excited state to the vibrational levels of basic state form the PL band. The PL and absorption maxima of the bands are given by the formulae:

$$\begin{aligned} h\nu_{\text{em}} &= E_0 - S_e h\nu_g, \\ h\nu_{\text{ab}} &= E_0 + S_a h\nu_e. \end{aligned} \quad (1)$$

Here $h\nu_e$ ($h\nu_g$) is the phonon energy for the excited (basic) state and S_a (S_e) is the average number of phonons emitted after absorption (emission) of photon. If one suppose*) that $h\nu_e = h\nu_g$ and $S_e = S_a$, it is easy to

*) This supposition may take place because in BiI₃ the energies of phonons interacting with excitons and electrons differ not considerably and equal 9.4 [4] and 8.28 [8,9] meV, respectively.

estimate the difference of energy E_0 between minima of configuration curves of excited and basic states. It equals 1.56 and 1.33 eV for $\text{BiI}_3(\text{Mn})$ and $\text{BiI}_3(\text{Cr})$, accordingly.

The unit energy distribution $I(h\nu)$ is described by the equation:

$$I(h\nu) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(h\nu - h\nu_0)^2}{2\sigma^2}\right], \quad (2)$$

where σ is the average quadratic deviation of unit distribution and $h\nu_0$ is the energy position of the Gauss curve maximum. The association of σ with W is given by the relation:

$$\sigma = \frac{W}{\sqrt{8 \ln 2}} \quad (3)$$

Since at $T=4.2$ K, W is 0.265 and 0.137 eV for the bands at $\lambda=1.1$ and $\lambda=1.83$ μm , respectively, σ is 0.113 eV for the first curve and 0.058 eV for the second one.

The large halfwidths of the bands and high Stokes losses indicate the strong interaction of electron state of impurity centres with vibrations of the crystal lattice. The decrease of PL intensity of the bands at $\lambda=1.1$ and $\lambda=1.83$ μm with an increase of the temperature can be caused by the electron delocalization.

In conclusion, it is necessary to notice the following. The PL band due to Mn^{2+} ions manifests itself in $\text{BiI}_3(\text{Mn})$ spectrum at the less energy than PL bands due to Mn^{2+} ions in spectra of $\text{ZnS}(\text{Mn})$ [10], $\text{CdCl}_2(\text{Mn})$, $\text{CdBr}_2(\text{Mn})$ and $\text{CdI}_2(\text{Mn})$ [11]. This difference in the energy position of the Mn^{2+} band in PL spectra of the listed crystals may be connected with the fact that the centre of emission recombination in $\text{BiI}_3(\text{Mn})$ is probably more complex than Mn^{2+} ion. It is possible that such centre may be Mn^{2+} + compensator (for example, Cu^+ ion). As concerning radiative recombination centres in $\text{BiI}_3(\text{Cr})$, they are simple centres of substitution. In contrast to $\text{GaAs}(\text{Cr})$, in semi-insulating crystals where Cr may have the different charge states (Cr^+ , Cr^{2+} , Cr^{3+} and Cr^{4+}) [12], we found only Cr^{3+} state in $\text{BiI}_3(\text{Cr})$.

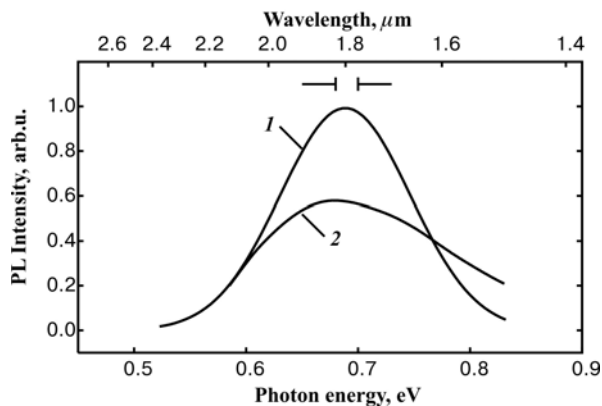


Fig. 3. Infrared photoluminescence spectra of $\text{BiI}_3(\text{Cr})$ single crystals at the temperatures 4.2 (1) and 77 K (2) and the photon excitation in the region of the intrinsic absorption edge.

3. Summary

The PL spectra of $\text{BiI}_3(\text{Mn})$ and $\text{BiI}_3(\text{Cr})$ single crystals were studied as the function of the temperature within the range 4.2 to 300 K at intrinsic and impurity excitation. The new bands at $\lambda=1.1$ μm and $\lambda=1.83$ μm were registered. It was found that the band at $\lambda=1.1$ μm caused by Mn^{2+} ions and the band at $\lambda=1.83$ μm by Cr^{3+} ones. It was shown that the obtained experimental results can be explained using the configuration model. The energies between the minima of the lowest excited states and the basic ones in the configuration curves for both centres equal approximately to 1.56 and 1.33 eV for $\text{BiI}_3(\text{Mn})$ and $\text{BiI}_3(\text{Cr})$, accordingly. It was shown that in studied samples the strong interaction of the electron states of impurity centres with vibrations of the crystal lattice takes place. The temperature quenching of both bands may be caused by electron delocalization.

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