

Time dependence of the luminescence intensity in $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ crystals under N_2 -laser excitation at room temperature*

I.M. BOLESTA, B.M. KALIVOSHKKA, I.D. KARBOVNYK, V.M. LESIVTSIV, I.S. NOVOSAD,
S.S. NOVOSAD[†], I.M. ROVETSKYY, S.R. VELGOSH

Ivan Franko National University of Lviv, 1 Universytetska str., 79000 Lviv, Ukraine

Results of optical-luminescence studies of polydoped photochromic $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ crystals are presented. It is shown that the luminescence decrease vs. time under N_2 -laser excitation in the range of A-band of Pb^{2+} absorption is due to photochemical reactions. The empirical model describing the decrease of the luminescence related to silver impurities due to photochemical processes is suggested. Model parameters (trapping cross-section – σ – and the amount of centres destroyed by irradiation – β) were determined using the comparative analysis of experimental and calculated luminescence decay curves.

Keywords: cadmium bromide; luminescence; absorption; photochemical reactions

© Wrocław University of Technology.

1. Introduction

Among the variety of light induced effects, photoinduced dichroism and related phenomena [1, 2] are of significant interest. Investigation of these effects is important in view of numerous practical applications [3]. In particular, advances in photochromic material physics and chemistry allowed development of now widely used transition protection lenses by Roger Araujo from Corning Glass Works Inc. (see, for instance [4] and references therein).

In the search of new photochromic materials, several crystalline substances [5] were considered, including CdCl_2 and CdBr_2 crystals [6]. Herein, we discuss the influence of photochromic effect on radiative processes in $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ crystals. Specific attention is paid to the mathematical model of luminescence time degradation during photochemical transformations.

Cadmium bromide crystals belong to the family of layered compounds, which are characterized

by ionic-covalent bonding inside a single structural layer and by weak van der Waals bonding between layers [7, 8]. Such structural arrangement, on the one hand, determines strongly anisotropic mechanical, electrical and optical properties and, on the other hand, provides favorable conditions for the creation of impurity centres localized at different crystallographic lattice sites. CdBr_2 crystals doped with copper and silver impurities exhibit photochromic properties [9–17]. Therefore, it is interesting to study optical and luminescent properties of photochromic crystals derived from cadmium bromide and investigate electronic processes that are responsible for the photochromic behavior.

The influence of silver impurity on the optical-luminescent characteristics of CdBr_2 crystals has been studied in [15, 16]. In the photoluminescence spectra of low-doped transparent $\text{CdBr}_2 : \text{AgCl}$ (measured at 85 K under N_2 -laser excitation), an intensive band around 630 to 640 nm and less pronounced band at 490 to 505 nm have been reported. Irradiation (coloring) of the sample with the N_2 -laser at room temperature causes a decrease of the 630 to 640 nm band intensity at 85 K and amplifies the emission at 490 to 500 nm. Decomposition of these spectra makes possible to establish

*This paper was presented at 19th International Seminar on Physics and Chemistry of Solids and Advanced Materials (IS-PCS19) June 12 – 15, 2013, Częstochowa, Poland.

[†]E-mail: novosadss@rambler.ru

the positions of spectral components, ascribed to host matrix, at 490, 560, 635 and 730 nm, and a weak activator band at 428 nm. In heavily doped crystal an additional emission band peaked at 465 nm is also observed. The origin of these bands and photochemical processes during the irradiation of the crystal have been discussed in details by Novosad et al. [16].

During the irradiation of $\text{CdBr}_2 : \text{AgCl}$ with 270 to 320 nm light at room temperature, photoinduced absorption appears with the maximum at 515 to 520 nm. The disadvantage of the photosensitive crystal is the fact that the additional absorption induced by UV-light is characterized by a small change of optical density ($\Delta D = 0.15$ to 0.20). Moreover, the material shows weak luminescence at room temperature when excited by N_2 -laser and this luminescence is further diminished during photochemical reactions. Restoring of the luminescence properties of silver-doped cadmium bromide crystals after thermal or optical bleaching is explained by Novosad et al. [16] by the decay of colloidal $n\text{Ag}^0$ centres, which can be regarded as release of carriers from trapping centres related to silver impurity.

Additional doping of $\text{CdBr}_2 : \text{AgCl}$ with PbBr_2 impurity leads to the amplification of the luminescence peaked at 460 to 465 nm and to the increase in efficiency of photochemical transformations [18]. At room temperature, during N_2 -laser excitation, CdBr_2 crystal doped with silver and lead exhibit remarkable degradation of luminescence.

Present work continues the investigation of the photochromic effect in $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$. The utmost attention is paid to the mathematical model of electronic processes that describe time dependence of luminescence intensity during photochemical transformations induced by N_2 -laser irradiation.

2. Experimental and results

$\text{CdBr}_2 : 0.3 \text{ mol } \% \text{ AgCl}, 1.0 \text{ mol } \% \text{ PbBr}_2$ were grown by means of Bridgman-Stockbarger technique from purified salt [7]. Samples with linear dimensions of approximately $15 \times 15 \times 1 \text{ mm}$ were

cut from a single crystal and then sliced along the cleavage planes. Absorption spectra were measured exploiting Specord M-40 spectral photometer. Coloring of crystals was performed at room temperature ($T = 295 \text{ K}$) by exposing them to the UV-light of DKsEL-1000 xenon lamp through UFS-2 filter or by irradiation with N_2 -laser ($\lambda = 337.1 \text{ nm}$). Luminescence spectra were collected using a SF-4A monochromator equipped with FEU-51 photomultiplier tube (PMT). The time dynamics of the light stimulated luminescence intensity decrease was measured using N_2 laser pulsed excitation. Short ($\sim 10^{-8} \text{ s}$) periodic pulses ($T = 0.01 \text{ s}$) with a nearly constant average energy per second were focused onto the crystal under study. Resulting luminescence was detected by the PMT over a relatively long time (compared to the pulses repetition rate). The detected intensity represents the integrated contribution of many emission centres and decreases exponentially versus time.

The absorption spectrum of a transparent $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ crystal is shown in Fig. 1 (curve 1). This spectrum, apart from activator A-band observed within the range of 305 to 340 nm, exhibits also a step-like feature in the region of 360 to 380 nm. Optical coloring of the material gives rise to the additional background absorption in the 350 to 800 nm range. On this basis there appears a wide and intensive band peaked around 530 to 540 nm (Fig. 1, curve 2). At the coloring saturation stage (after 2 minute irradiation) the change of the optical density ΔD in this material reaches the value of approximately 2.2.

In case of N_2 -laser excitation in the range of A-band of Pb^{2+} -centres absorption, at the beginning of excitation $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ have almost 50 times larger luminescence intensity than that of the $\text{CdBr}_2 : \text{AgCl}$ (luminescence is peaked around 460 to 465 nm). Additional generation of non-equilibrium charge carriers appears during the photothermal ionization of Pb^{2+} ions [19]. When coloring of the samples is performed, the intensity of this emission (measured with respect to the maximum of the band) decreases by almost 20 times compared to the initial value (Fig. 2) after ~ 200 seconds due to photochromic reactions.

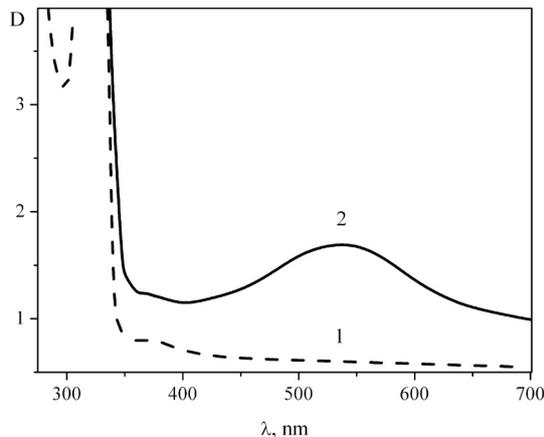


Fig. 1. Absorption spectra of transparent (curve 1) and optically colored (curve 2) CdBr_2 : 0.3 mol % AgCl, 1.0 mol % PbBr_2 crystal at 295 K.

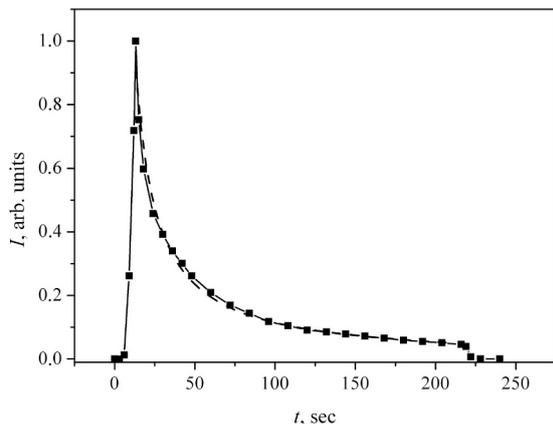


Fig. 2. Time dependence of 460 nm emission decrease in CdBr_2 : 0.3 mol % AgCl, 1.0 mol % PbBr_2 crystal during the irradiation with N_2 -laser at 295 K. Dashed line represents the approximation result.

At the same time, the spectral characteristics of the emission are almost unchanged. A photoluminescence spectrum of CdBr_2 : AgCl, PbBr_2 crystal, irradiated with N_2 -laser at 295 K, is shown in Fig. 3. This spectrum is characterized by the asymmetric band peaked at nearly 462 nm and several features in the long-wavelength tail of this band. Emission with the maximum at 460 to 470 nm is pronounced in heavily doped CdBr_2 : AgCl crystals.

Optical bleaching of CdBr_2 : AgCl, PbBr_2 crystal by irradiation through the OS-5 optical filter

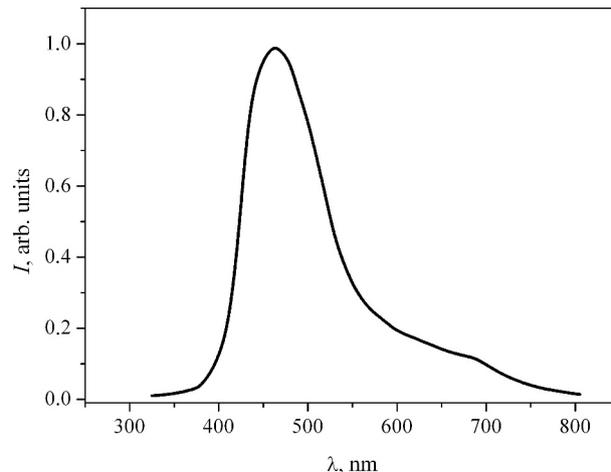


Fig. 3. Photoluminescence spectrum of CdBr_2 : 0.3 mol % AgCl, 1.0 mol % PbBr_2 , irradiated by N_2 -laser at 295 K.

(transparency region of 480 to 2800 nm) at 295 K leads to the recovery of its absorption spectra and luminescent properties. Previously colored samples can also be bleached thermally by heating up to 590 to 600 K. Coloring-bleaching processes are repeatedly reversible. Photochromic transformation in the crystals under study has not caused the creation of new radiative centres, however, they created luminescence damping zones, since deep charge trapping centres were formed.

3. Discussion

The results of CdBr_2 : AgCl, PbBr_2 optical studies confirm that photoinduced absorption in this material (as well as in CdBr_2 : AgCl [15, 16]) is caused by the photodissociation of the matrix [11] and by photochromic transformations of silver centres [15, 16]. Considering the results of [20–23] one can assume that in case of the activation of melt-grown CdBr_2 with AgCl, $(\text{Ag}_{\text{Cd}}^+)^-$ impurity, single-charge acceptor centres are formed as the dopant: Ag^+ ion substitutes Cd^{2+} ion in the regular lattice sites. In the optical absorption spectra of CdBr_2 : AgCl at 295 K, activator bands related to $4d^{10} \rightarrow 4d^9 5s$ (or $4d^{10} \rightarrow 4d^9 5p$) transitions in Ag^+ ions have not been detected neither in the present study nor in [15, 16]. This is explained by the fact that at room temperature excited states are

located in the conduction band of the matrix. In the $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ absorption spectra the activator band in the range of 305 to 340 nm is clearly observed, which can be ascribed to $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transitions in Pb^{2+} ions. Taking into account the results reported in [15, 16], the band at 530 to 540 nm, which is observed in the absorption spectra after the irradiation of polydoped crystal, may be connected with colloidal $n\text{Ag}^0$ particles. Background absorption is mainly determined by light scattering on the crystal inhomogeneities, which – in turn – are formed as a result of photodissociation of the matrix.

In [16] it was assumed, that in low-doped photochromic $\text{CdBr}_2 : 0.02 \text{ mol } \% \text{ AgCl} \{(\text{Ag}_{\text{Cd}}^+)^- - \text{V}_{\text{Br}}^+\}$ light-sensitive centres, which are responsible for 635 nm luminescence band, are dominating. Photostimulated dissociation of these donor-acceptor pairs in the studied photochromic $\text{CdBr}_2 : \text{Ag}^+$ as well as in $\text{CdI}_2 : \text{Ag}^+$ [22] probably follows the mechanism of $(\text{Ag}_{\text{Cd}}^+)^-$ impurity centres excitation. This mechanism involves the transition of Ag^+ ion through an excited state into the interstitial position and the formation of the colloidal $n\text{Ag}^0$ particles in the near-surface area of the sample (after capturing of electrons, delocalized from Br^- ions). At the same time, localization of the donor associates takes place near dislocations and other macroscopic defects of the crystal, which serve as coagulation centres. In turn, photoholes (Br^0) under the influence of Dember field migrate into the volume of the crystal and then localize at $\text{V}_{\text{Cd}}^{2-}$ associated with V_{Br}^+ .

In $\text{CdBr}_2 : \text{Ag}^+, \text{Pb}^{2+}$ with significant amount of silver impurity the effective negative charge of $(\text{Ag}_{\text{Cd}}^+)^-$ may also be compensated by interstitial Cd_i^+ and Ag_i^+ ions. In this case, in addition to $\{(\text{Ag}_{\text{Cd}}^+)^- - \text{V}_{\text{Br}}^+\}$, photosensitive associated donor-acceptor pairs of $\{(\text{Ag}_{\text{Cd}}^+)^- - \text{Cd}_i^+\}$ and $\{(\text{Ag}_{\text{Cd}}^+)^- - \text{Ag}_i^+\}$ types are formed. After photostimulated destruction of such associates, photoholes are localized at halogen ions near $(\text{Ag}_{\text{Cd}}^+)^-$ centres, while photoelectrons are captured by Cd_i^+ and Ag_i^+ centres with further creation of $n\text{Cd}^0$ and $n\text{Ag}^0$ colloidal particles. Photochemical reactions that are connected to photostimulated

destruction of similar light-sensitive centres $\{(\text{Cu}_{\text{Cd}}^+)^- - \text{Cu}_i^+\}$, $\{(\text{Ag}_{\text{Cd}}^+)^- - \text{Cd}_i^+\}$ and $\{(\text{Au}_{\text{Cd}}^+)^- - \text{Cd}_i^+\}$ in $\text{CdBr}_2 : \text{Cu}^+$, $\text{CdI}_2 : \text{Cu}^+$, $\text{CdI}_2 : \text{Ag}^+$ and $\text{CdI}_2 : \text{Au}^+$ crystals were discussed in our previous reports [11, 12, 23].

Additional doping of $\text{CdBr}_2 : \text{AgCl}$ with PbBr_2 impurity leads to the appearance of additional activator absorption A-band ascribed to $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transitions in Pb^{2+} ions and increases the efficiency of luminescent and physico-chemical processes. $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ photochromic material at room temperature exhibits remarkable photostimulated degradation of luminescence.

The results of luminescence studies of $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$ are in agreement with previous investigations of light emission processes in $\text{CdBr}_2 : \text{AgCl}$ [15–17]. Complex emission spectrum of polydoped crystal at room temperature in case of excitation by laser in the range of Pb^{2+} -centres absorption is probably caused by centres, which are characteristic of $\text{CdBr}_2 : \text{AgCl}$ [16]. The analysis of the results has indicated that in order to describe the kinetics of luminescence intensity decrease in $\text{CdBr}_2 : \text{AgCl}, \text{PbBr}_2$, the empirical model proposed in [24] for time-dependent luminescence from $\text{CdI}_2 : \text{Cd}$ and $\text{CdI}_2 : \text{Ag}$ crystals can be employed.

Degradation of emission intensity during photochemical transformations at fixed excitation conditions in a cadmium bromide based material are related to the decrease in the concentration of radiative centres. Considering the techniques described in [25, 26], let us assume that at $t = 0$ there were n_0 radiative centres, and during the coloring process n centres disappeared. Thus, for the time moment t , the number of radiative centres n_L is given by:

$$n_L = n_0 - n \quad (1)$$

The number of centres that have disappeared in the time interval dt at the distance x with respect to the crystal surface is:

$$dn(x, t) = -\sigma I(x)(n_0 - n)dt \quad (2)$$

where σ ($\text{cm}^2/\text{photon}$) is the parameter that characterizes trapping process cross-section of the time dependence of emission intensity.

The intensity of light in the crystal volume decays according to:

$$I(x) = I_0 \exp(-\alpha x) \quad (3)$$

where α – stands for absorption coefficient, I_0 is the intensity of excitation light of the crystal surface (photon/(cm²·s)).

From equation 2, taking into account (3) and (1), we have:

$$n(x,t) = n_0 (1 - \exp[-\sigma I_0 t \exp(-\alpha x)]) \quad (4)$$

The analysis of (4) shows that when $t \rightarrow \infty$, $n(x,t \rightarrow \infty) \rightarrow n_0$ and $n_L = 0$, i.e. radiative centres totally disappear. This conclusion does not agree with the experimental data (Fig. 2), which points to the fact that only a part of centres disappears. Considering this, the equation for $n(x,t)$ can be re-written as follows:

$$n(x,t) = \beta n_0 (1 - \exp[-\sigma I_0 t \exp(-\alpha x)]) \quad (5)$$

where β is the parameter that corresponds to the number of disappeared centres.

From equation 5 one can obtain the time dependence of luminescence intensity $I(t)$ for the crystals under study:

$$I(t) = A \int_0^d I(x) n_L(x,t) dx = A \int_0^d I(x) [n_0 - n(x,t)] dx \quad (6)$$

where A is the constant that considers the emission quantum yield and the irradiated area.

Considering (3) and (5), from equation 6 one gets:

$$I(t) = \frac{AI_0 n_0}{\alpha} \left\{ (1 - \beta) [1 - \exp(-\alpha d)] + \frac{\beta}{\sigma I_0 t} [\exp(-\sigma I_0 t \exp(-\alpha d)) - \exp(-\sigma I_0 t)] \right\} \quad (7)$$

When absorption is strong ($\alpha d \gg 1$), equation 7 can be re-written:

$$I(t) = \frac{AI_0 n_0}{\alpha} \left[1 - \beta + \frac{\beta}{\sigma I_0 t} [1 - \exp(-\sigma I_0 t)] \right] \quad (8)$$

The derived expression for the time dependence of luminescence intensity includes β and σ parameters, which can be compared to experimental data. In particular, when $t = 0$ and $t \rightarrow \infty$ from (8) it follows that

$$\frac{I(t \rightarrow \infty)}{I(0)} \rightarrow 1 - \beta \quad (9)$$

and the value of σ is calculated by an approximation of the experimental curve (Fig. 2) with the equation 8.

Obtained in such a manner σ and β values for CdBr₂ : AgCl,PbBr₂ crystal are 1.446 and 0.94, respectively.

Localization of electrons and holes at the respective trapping levels connected to the silver impurity can be interpreted as “disappearing” of radiative centres, which makes the radiative transition impossible. The presence of remaining emission (~5 % of the initial intensity) can be explained by reaching the fill limit of the respective trapping levels that determines the disappearance of only some part of all luminescent centres.

4. Conclusions

It is established that luminescent and photochemical transformations in CdBr₂ : AgCl,PbBr₂ material run more effectively as compared to CdBr₂ : AgCl crystals. Photoinduced absorption bands can be bleached thermally and optically with the light from the absorption range of colloidal silver centres. During bleaching optical and luminescence properties of the compound are restored. CdBr₂ : AgCl,PbBr₂ photochromic crystal at room temperature, when excited by N₂-laser in the region of Pb²⁺ ions absorption, is characterized by remarkable photostimulated degradation of the luminescence (related to presence of silver impurity). The empirical model describing the time dependence of the luminescence intensity during photochemical reactions is proposed.

Photochromic CdBr₂ : AgCl,PbBr₂ crystals with an optimal concentration of impurities can be used as efficient UV-detectors whose principle is based on luminescence degradation. Also these

crystals can find application as materials for the reversible optical information recording and luminescent reading at room temperature.

References

- [1] DÜRR H., BOUAS-LAURENT H., *Photochromism: Molecules and Systems*, Elsevier, 2003.
- [2] DELAIRE J.A., NAKATANI K., *Chem. Rev.*, 100 (5) (2000), 1817.
- [3] MEGLA G.K., *Appl. Optics*, 5 (6) (1966), 945.
- [4] ARAUJO R.J., *Appl. Optics*, 7 (5) (1968), 781.
- [5] SCOTT J.L., TANAKA K., *Cryst. Growth Des.*, 5 (3) (2005), 1209.
- [6] BENSOUICI A., PLAZA J.L., DIEGUEZ E. *et al.*, *J. Lum.*, 130 (4) (2010), 688.
- [7] LYSKOVICH A.B. (Ed.), *Wide-gap Layered Crystals and Their Physics Properties*, Vyscha Shkola, Lvov, 1982 (in rus.).
- [8] BRODIN M.S., BLONSKY I.V., *Excitonic Processes in Layered Crystals*, Kiev, Naukova Dumka, 1986 (in rus.).
- [9] LYSKOVICH O.B., NOVOSAD S.S., KRAVCHUK O.Y., *Ukr. J. Phys.*, 40 (9) (1995), 1001 (in ukr.).
- [10] NOVOSAD S.S., GAL'CHYNSKYI O.V., KOVALYUK R.O., *Nucl. Instrum. Meth.*, 116, 1916 (1996), 265.
- [11] NOVOSAD S.S., NOVOSAD I.S., *PCSS*, 8 (4) (2007), 759 (in ukr.).
- [12] NOVOSAD S.S., NOVOSAD I.S., *Funct. Mater.*, 11, 2 (2004), 258.
- [13] NOVOSAD S.S., NOVOSAD I.S., BORODCHUK A.V., *Inorg. Mater.*, 41, (2) (2005), 235.
- [14] NOVOSAD S.S., KOSTYUK B.M., *Ukr. J. Phys.*, 42 (5) (1997), 568 (in ukr.).
- [15] LYSKOVICH A.B., MARTYNIV S.D., NOVOSAD S.S., KOSTYUK B.M., *Inorg. Mater.*, 34 (8) (1998), 974 (in rus.).
- [16] NOVOSAD S.S., NOVOSAD I.S., KALIVOSHKA B.M., *Phys. Solid. State*, 53, 8 (2011), 1548 (in rus.).
- [17] NOVOSAD S.S., KOSTYUK B.M., *Ukr. J. Phys.*, 43, 7 (1998), 871 (in ukr.).
- [18] NOVOSAD S.S., KOSTYUK B.M., *Funct. Mater.*, 5, 2 (1998), 171.
- [19] NOVOSAD S.S., *Ukr. J. Phys.*, 43, 3 (1998), 338 (in ukr.).
- [20] GEORGOBIANI A.N., SHEIKMAN M.K. (Eds.), *Physics of $A^{II}B^{VI}$ Compounds*, Nauka, Moscow, 1986 (in rus.).
- [21] GURVICH A.M., *Introduction in Physical Chemistry of Crystal Luminophors*, Vysshaya Shkola, Moscow, 1982 (in rus.).
- [22] NOVOSAD S.S., KALIVOSHKA B.M., *Phys. Solid. State*, 51, 6 (2009), 1072 (in rus.).
- [23] NOVOSAD S.S., KALIVOSHKA B.M., *PCSS*, 8, 4 (2007), 753 (in ukr.).
- [24] BOLESTA I.M., VELGOSH S.R., KARBOVNYK I.D. *et al.*, *Phys. Solid. State*, 54, 10 (2012), 1935 (in rus.).
- [25] KOLOMIETS B.T., MAMONTOVA T.N., CHERNYSHOV A.V., *Sov. Phys. Semicond.*, 17, 9 (1983), 708 (in rus.).
- [26] MAMONTOVA T.N., CHERNYSHOV A.V., *Sov. Phys. Semicond.*, 18, 3 (1984), 332 (in rus.).

Received 2014-03-28

Accepted 2014-07-24