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LUMINESCENT PROPERTIES OF $CdBr_2$

M. Rudka[1], S. Charambura[1], V. Antonyuk[2], I. Matviishyn[2], B. Kostyuk[2]
[1]*State University "Lvivska Politechnika",*
12 Bandera Str., Lviv, UA–79013, Ukraine
[2]*Ivan Franko National University of Lviv, Chair of General Physics,*
50 Drahomanov Str., Lviv, UA–79005, Ukraine
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Photo– and X–rays luminescent properties of the layered $CdBr_2$ crystals in the temperature region of 80...500 K have been investigated. It has been found out that the most effective luminescence is excited at the temperatures 100...140 K with the ultraviolet light from the exciton absorption region of crystals (259 nm). The annihilation of excitons autolocalized on the deep acceptors causes the luminescence in the region 380 nm which is quenched completely at the temperatures above 120 K. Strong exciton–phonon and electron–phonon interactions cause the excitons destruction and recombination of nonequilibrium electron–holes pairs through the donor–acceptor (DA) complexes of intrinsic and impurity defects. Nonequilibrium charge carriers generated by the gap light recombine more effectivelly in the surface crystal region causing the yellow–green luminescence with the maximum near 540...570 nm and also diffuse into the sample bulk and are captured on the traps causing the effective red thermoluminescence at $T > 200$ K. The red photoluminescence with the maximum near 650 nm has been caused by irradiative recombination of electrons and holes generated by light long–wave absorption edge at 270...280 nm through DA defect complexes in the $CdBr_2$ crystals bulk. Moreover, in the surface area the nonequilibrium carriers have been captured and thermoluminescenting with green light with the maximum 510 nm at $T < 200$ K. At the room temperature the relaxation time of electron–holes pairs created by radiation on the associated DA light centres has been decreased due to a strong influence of phonon processes which causes the fluorescence of the $CdBr_2$ crystals with the maximum near 510 nm.
Key words: layered crystals, luminescence, donor–acceptor complexes.

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INTRODUCTION

The $CdBr_2$ crystals belong to the group of $A_2B_2{}^7$ layered materials taking up an intermediate position between A_1B_7 dielectrics and A_2B_6 semiconductors. Their struture type C19 is based on a dense cubic packing of the layers in which every fourth layer occupies the identical position forming Br–Cd–Br "sandwiches–packets". There is strong ion–covalent interaction within the packet and weak Van der Vaals forces between the packets.

The $CdBr_2$ crystals were grown in soldered quartz ampules by Bridgeman–Stockbarger method and had a 6R–polytype modification. For experiments the samples of the size of $10 \times 8 \times 2$ mm^3 were formed. Samples irradiation by the X–rays, ultraviolet and visible light has been carried out directed in parallell to the main crystallographic axis C_6 of the $CdBr_2$ crystals. The measurement of luminescent properties of cadmium bromide has been carried out simultaneously with the electric measurements within the temperature region of 80...500 K. The contacts were put on the samples by two orientations:

– on the opposite basic surfaces of the samples under investigation, which ensures direction of external electrical field tension vector (orientation I) parallel to the main crystallographic axis C_6;

– on the illuminated basic surface of the sample, when the external electrical field is directed perpendicularly to the axis C_6 (orientation II).

I. OBTAINED RESULTS

Cadmium bromide crystals are sensitive to the electromagnetic irradiation effect with the wave length less than 400 nm. At the room temperature the excitation with the light from the edge of the fundamental absorption region (280 nm) causses the slight fluorescence ($t_1 > 50$ ns) within a wide spectral range with the maximum near 520 nm (Fig. 1, curve 1). With the temperature decreasing of the $CdBr_2$ crystals the increasing of phosphorescence intensity ($t_2 > 5$ ms) at the temperatures below 180 K has been observed (Fig. 2, curve 1). Moreover, the most effective excitation of luminescence of pure nonactivated cadmium bromide crystals has been carried out in the temperature region of 100...140 K by ultraviolet light from the region of 259 nm (Fig. 1, curve 3), with the corresponding minimum on the photoconductivity spectrum (Fig. 1, curve 4). Ultraviolet light quantums with the indicated wave length at the temperatures near the liquid nitrogen temperature (NT) cause the intensive phosphorescence of the $CdBr_2$ crystals in the wide spectral range with the maximum near 550 nm, which has the properties of donor–acceptor recombination of nonequilibrium charge carriers. On the integral luminescence excitation spectra (LES) of the $CdBr_2$ crystals besides the most intensive band with maximum near 259 nm corresponds to the transition from surface to bulk samples excitation the maxima in the fundamental absorption region of cadmium bromide are present (Fig. 1, curve 3). The excitation of luminescence by ultraviolet light from these maxima and by X–rays is accompanied at NT by a phosphorescent light of less intensity being slightly different from the spectrum described above. It was noted that with the increasing of quantums energy of exciting irradiation the luminescence maximum of the $CdBr_2$ crystals moves towards longer waves (lesser energy) from 550 nm ($l_{ex} = 259$ nm) to 570 nm (excitation by X–rays) (Fig. 1).

In the temperature region below 120 K under the gap excitation of the $CdBr_2$ crystals besides the intensive yellow–green luminescence the less intensive light in the violet spectrum region with the maximum near 380 nm (Fig. 1) is observed. Experimental investigations show that the intensity of this light is dependent on the irradiated surface state and structure perfection of cadmium bromide crystals.

On the long–wave edge of fundamental absorption of the $CdBr_2$ crystals in the luminescence excitation spectra the shelf in the region of the wave lengths 270...290 nm (Fig. 1) has been observed, and its intensity depends on the samples temperature and defects. The quantums of exciting light from this spectral range cause a wide asymmetrical luminescence band of cadmium bromide with the most intensive maximum in the red spectrum region at 650 nm and maximum at 510 nm (Fig. 1).

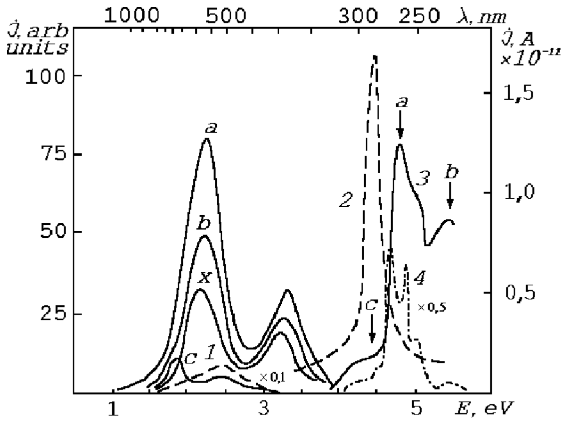

Fig. 1. The photoluminescent (1,a,b,c), X–rays luminescent (x), photoconductivity (2,4) spectra and LES (3) of $CdBr_2$ crystals at the temperature 290 K (1,2) and 80 K (3,4,a,b,c,x).

With the crystals temperature increasing from NT to the room temperature (Fig. 2, curve 1) the quenching of the samples phosphorescence above 140 K and decreasing of photoconductivity in thus a temperature region have been observed. Above 180 K cadmium bromide phosphorescence is slight and on the temperature dependence of photoconductivity the considerable local increasing of photocurrent intensity in the temperature region of 308 K and 232 K has been observed. When contacts are put on the illuminated surface of $CdBr_2$ crystals (orientation II) the narrow intensive maximum near 208 K prevails on the temperature dependence of photoconductivity (Fig. 2, curve 3). At the measurement of the temperature dependence of photoconductivity in the samples bulk (orietation I) the maximum near 208 K is slight, but the most intensive maximum near 232 K becomes absolutely prevailed (Fig. 2, curve 4). Such a behaviour of photocurrent is caused by its boosting due to nonequilibrium carriers which have been released from the deep traps where they have got during the process of gap irradiation of crystals at low temperature.

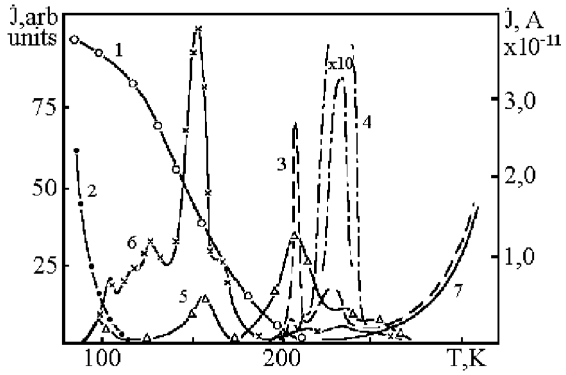

Fig. 2. Temperature dependences of the luminescent bands intensity (1,2) with the maximum of light near 555 nm (1) and 380 nm (2), photoconductivity (3,4) under excitation of $CdBr_2$ crystals with light 235 nm in the contacts orientation I (4) and II (3) and TSL (5,6) of irradiated crystals at the temperature 80 K by light 262 nm (5) and 275 nm (6), background conductivity of $CdBr_2$ (7).

The thermostimulated luminescence (TSL) and thermostimulated conductivity methods (TSC) have been used to probe the local levels in the band gap of the layered cadmium bromides. That is why the $CdBr_2$ crystal was irradiated at NT during 20 minutes by the X–rays or optical light. In this case a part of the generated nonequilibrium electrons and holes recombine radiatively and the other part is captured on the traps with different depth. After the irradiation was turned off the crystal was held in darkness during 5 minutes, the electrical field was applied to the sample and the linear heating of crystal was turned on and the thermoluminescences and temperature dependence of the sample conductivity have been registered (Fig. 2, curve 3–6).

Under the excitation of cadmium bromide with the light from the fundamental absorption region the intensive yellow–green luminescence of the surface crystals region and the capture of charge carriers diffused into the bulk on the deep traps, causing red thermoluminescence at the $T > 200$ K have been observed (Fig. 2, curve 5). Under $CdBr_2$ irradiation with the light from the region of 270...290 nm the bulk centres illuminate by the red light and diffusion of a part of the generated carriers on the surfase traps which cause the exceeding green thermoluminescence near $T < 180$ K takes place (Fig. 2, curve 6).

II. DISCUSSION

The described experimental results and the analysis of the literature data [1–3] show that the luminescence of the cadmium bromide crystals in general is caused by radiative recombination of created by high–power irradiation (ultraviolet, X–rays) nonequilibrium charge carriers through the complex centres of intrinsic and impurities defects — the associated donor–acceptor pairs. Since the other cadmium halides (CdJ_2 and $CdCl_2$ [1]) have a similar luminescence it means that such light centres contain cation defects such as cadmium vacansies (V_{cd}) as an acceptor centre or interstitial cadmium (C_{di}) as a donor centre or both of them as an associated donor–acceptor complex. Such a complex centre can be formed during the growing of $CdBr_2$ crystals or during the shift at high temperatures of point cadmium into the neighbouring octahedrical emptiness or interlayers space with the creation of a $(C_{di} - V_{cd})$ complex.

At the temperatures near the liquid nitrogen boiling temperature the most intensive luminescence (phosphorescence) of the $CdBr_2$ crystals has been excited by ultraviolet light from the exciton absorption region (259 nm) (Fig. 1). The autolocalization of such excitons on structural defects and their further annihilation are accompanied by violet light of cadmium bromide with maximum near 380 nm which is quenched completely at the temperature above 120 K. It can be caused by strong exciton–phonon interactions which cause the excitons destruction and electrons and holes localization on the donor and acceptor centres of intrinsic or impurities nature. As a result the life time of nonequilibrium charge carriers increases. The layered structure of cadmium bromide which causes anisotropy of its electrical properties, different electrons and holes mobility, strong electron–phonon interaction ensure the relatively rapid localization of the one of electron–holes pairs components near the place of their appearance because of crystals excitation and drift another component into the depth of the sample where it is localized on the traps. As a result the cadmium bromide crystals surface light in the yellow–green spectrum region and accumulation of carriers in the samples bulk have been observed.

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ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ $CdBr_2$

М. Рудка[1], С. Харамбура[1], В. Антонюк[2], І. Матвіїшин[2], Б. Костюк[2]

[1] *Державний університет "Львівська Політехніка", вул. С. Бандери, 12, Львів, 79013, Україна*

[2] *Львівський національний університет імені Івана Франка, кафедра загальної фізики вул. Драгоманова, 50, Львів, 79005, Україна*

E–mail: shuwar@wups.franko.lviv.ua

Досліджено фото– та рентґенолюмінесцентні властивості шаруватих кристалів $CdBr_2$ в температурному діяпазоні 80...500 К. Установлено, що найефективніше люмінесценція збуджується при температурах 100...140 К ультрафіолетовим світлом з ділянки екситонного поглинання кристалів (259 нм). Анігіляція автолокалізованих на глибоких акцепторах екситонів зумовлює люмінесценцію в ділянці 380 нм, яка повністю гаситься при температурах вище від 120 К. Сильна екситон–фононна та електрон–фононна взаємодія зумовлює розпад екситонів та рекомбінацію нерівноважних електронно–діркових пар через донорно–акцепторні (ДА) комплекси власних та домішкових дефектів. Ґенеровані зонним світлом нерівноважні носії заряду найефективніше рекомбінують у приповерхневій ділянці кристала, зумовлюючи жовто–зелену люмінесценцію з максимумом при 540 – 570 нм, а також дифундують в об'єм зразка та захоплюються на рівні прилипання, викликаючи ефективну червону термолюмінесценцію при $T > 200$ К. Червона фотолюмінесценція з максимумом при 650 нм зумовлена випромінювальною рекомбінацією ґенерованих світлом з довгохвильового краю поглинання при 270...280 нм електронів та дірок через ДА–комплекси дефектів в об'ємі кристалів $CdBr_2$. При цьому в приповерхневій ділянці "залипають" нерівноважні носії, які ефективно термолюмінесціюють зеленим свіченням із максимумом 510 нм при $T < 200$ К. При кімнатних температурах за рахунок сильного впливу фононних процесів зменшується час релаксації створених опроміненням генетичних електронно–діркових пар на асоційованих ДА–центрах свічення, що зумовлює флюоресценцію кристалів $CdBr_2$ з максимумом у ділянці 510 нм.