Luminescence of Single Crystals Cadmium Bromide Doped with Impurities of Argentum

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Temperature behaviors of X-ray luminescence (XL or RL), photoluminescence (PL), and thermoluminescence (TL) were studied in CdBr₂: Ag+ single crystals from room temperature to liquid nitrogen temperature. The luminescence is practically absent in the interband (including X-rays) excitation crystals CdBr₂: Ag+, but manifested in the excitation light from the region 3.68 eV. In this region of the spectrum selective absorption band of silver impurity centers is observed. It was found that the crystals CdBr₂: Ag+ are sensitive to the action of X-rays and ultraviolet light through the flow of photochemical reactions (FHR) in these crystals.

Keywords: Layered crystals, Luminescence, Cadmium bromide, Photochromic impurities.

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1. INTRODUCTION

Optical properties of CdBr₂ crystals have been studied in previous works as well as applied research. Cadmium bromide is a layered crystal having fundamental energy gap of 5.4 eV [1] and therefore have widely been used as optical material. Representing the wide group of divalent metal halides, CdBr₂ has been thoroughly studied by optical spectroscopy techniques [2], [3]. Particular attention has been paid to explain the photochromism effect in pure and doped CdBr₂ [4]. Much interest has recently been given to the search of new materials, which can be used for efficient laminators.

Computed radiography (CR) using photostimulable phosphor storage media allows the combination of highly advanced photographic technology with digital computer techniques. This digital X-ray imaging technique is one of the primary candidates to replace the long-established screen-film radiography. Photostimulated luminescence (PSL) is a process where exposure to high-energy (X-ray or UV) photons results in the accumulation of stored charges such as [Cu + Cd - Cu + i] centers. These stored charges can then be photostimulated to the conduction band using, for example, low-energy visible or near-infrared photons where they may recombine with holes to produce visible photostimulated luminescence. X-ray storage crystals such as CdBr₂: Cu+ have been widely discussed [3].

Unlike CdBr₂: Cu+ crystals, silver doped cadmium bromide has not been studied that much so far. Although Ag+ ions (electronic configuration $4d^{10}$) are homologically identical to Cu+, some differences in the absorption properties and in the nature of photochromism for this material may be expected which were not investigated in details [5].

The present authors have reported briefly on new results of the storage luminescence of $CdBr_2$: Ag+ crystals. In this paper, we present detailed observations and a discussion on the temperature behaviors of the X-ray luminescence (XL), photoluminescence (PL), and thermoluminescence (TL) of $CdBr_2$: Ag+ single crystals from room temperature (RT) to liquid nitrogen temperature (LNT).

2. EXPERIMENTAL TECHNIQUES

Investigated samples were the undoped as well as the Ag-doped CdBr2 crystals. These nanocrystals were grown using the standard Bridgman–Stockbarger technique in sealed quartz ampoules (CdBr2: Ag - 0,7 % by mass). Their crystalline structures were monitored using an x-ray diffractometer. The samples for measurements were then cut along the cleavage planes. Linear dimensions of the prepared rectangular specimens were nearly 5×5 mm. Several samples of different thickness were cut in order to select the best absorption layer thickness, thus ensuring the good quality of the absorption measurements. The investigations were performed at liquid nitrogen temperature because at this temperature the effect should be the enhanced.

The X-ray irradiations were performed between 80 and 300 K with a W tube (40 kV, 15 mA). For the UV illuminations, a 150 W Xe high-pressure lamp and a 0.25 m grating monochromator were used. The heating rate above RT was 5 °C/s. The emission and excitation spectra were taken with the luminescence spectrometer.

3. RESULTS AND DESCUSSION

The XL (Rentgen Luminescence) in the short-wavelength region at temperature range 48...170 K is shown by curves in Figure 1 and Figure 2. The emission consisted of a main narrow band at 365 nm as well as of some broad bands at about 500, 510, and 525 nm.

The 500, 510 and 525 nm bands increase in intensity during cooling from 170 K to 100 K; however, these three emission peaks are almost invisible at room temperature. Similarly, the 365 nm emission is not seen at room temperature, but it appears at about 190 K and increases in intensity during further cooling and becomes dominant at liquid nitrogen temperature. These three emissions disappear at room temperature, indicating that they are not emissions from Ag+ ions; they might be from some species created by X-ray irradiation that is only stable at low temperatures. Under X-ray irradiation, defects are created in the crystals. These defects may yield luminescence.

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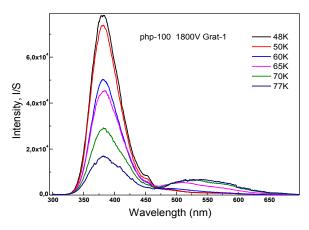


Fig. 1 – The rentgen luminescence (RL or X-Ray) spectrum of $CdBr_2$: Ag+ in the short-wavelength region. The main band was a narrow band at $365~\rm nm$

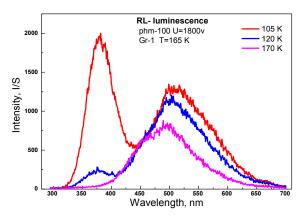


Fig. 2 – The rentgen luminescence spectrum of $CdBr_2$: Ag+ in the short-wavelength region. The main band was a narrow band at 365 nm as well as of some broad bands at about 500, 510, and 525 nm

3.1 Photoluminescence of CdBr₂: Ag+ Single Crystals

Activation CdBr₂ with using by impurities allows considerably to increase the intensity, and to change the spectrum of their fluorescent glow. The presence of impurities causes the increasing concentration both their own complexes, and the generate own-impurity or pure- impurity defects. It is shown in the absorption spectra, especially in photoluminescence excitation spectra of crystals [1], [2]. Impurities of silver in cadmium bromide crystals are photochromic (Figure 3). On the one hand, they are increasing the intensity of luminescence of cadmium bromide, and on the other hand they are sensitive to the action of X-rays and ultraviolet light through the flow of photochemical reactions (FHR) in these crystals.

Figure 3 shows that activation crystals CdBr₂: Ag+ of silver is accompanied by the appearance luminescence with a maximum at 2.7 eV region, which is internally-central character: the maximum position and its indicated luminescence intensity do not change in the investigated temperature range 90 ... 300 K. This luminescence is practically absent in the interband (including X-rays) excitation crystals CdBr₂: Ag+, but manifested in the excitation light from the region 3.68 eV. In this region of the spectrum selective absorption band of silver impurity centers is observed.

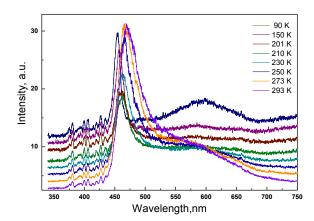
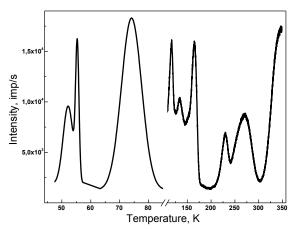


Fig. 3 – The photoluminescence spectrum of crystals $CdBr_2:Ag+$

3.2 Thermoluminescence in CdBr2: Ag+

The direct-gap layered crystals CdBr₂ have a strong ion-covalent bond within the structural layer Br-Cd-Br and weak van der Waals interaction between the layers. Significant defects layered crystals, including CdBr2, are accompanied by the presence of charge transfer tail on the long wavelength fundamental absorption edge and the advent of selective weakly intensive peaks on the SEL bulk samples at 4.54 eV. At excitation of crystals by the luminescence light 4.54 eV is observed a wide range of superior maximum in the region 1.8 eV. Excitation CdBr₂: Ag+ at nitrogen temperature between band ultraviolet (UV) light or (X) rays of the curve thermoluminescence present slight maxima in the temperatures 50-60 K, 70-80 K and 90-170 K (Figure 4). Besides these there are intense peaks of thermoluminescence (TSL) in the range 200-300 K.



Excitation crystals of "impurity" band 4.54~eV in the curve is dominated by low-temperature TSL peaks with maximum green fluorescence at 2.48~eV and mild highs in the 236~K and 254~K with a predominant orange glow with a maximum at 1.8~eV.

4. CONCLUSIONS

In summary, the X-ray luminescence (XL or RL), photoluminescence (PL), and thermoluminescence (TL)

were studied in CdBr₂:Ag+ single crystals from room temperature (RT) to liquid nitrogen temperature (LNT).

The rentgen luminescence spectrum in the short-wavelength region at temperature range 48...170 K is consisted of a main narrow band at 365 nm as well as of some broad bands at about 500, 510, and 525 nm. Luminescence is practically absent in the interband (in-

cluding X-rays) excitation crystals CdBr₂-Ag+, but manifested in the excitation light from the region 3.68 eV. The crystals CdBr₂-Ag+ are sensitive to the action of X-rays and ultraviolet light through the flow of photochemical reactions (FHR) in these crystals. As a result, FHR cause the increasing of optical density in the samples and decreasing of the luminescence intensity.

Люмінесценція монокристалів бромистого кадмію із додаванням домішки срібла

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Робота описує дослідження температурної поведінки рентгенолюмінесценції (РЛ), фотолюмінесценції (ФЛ) і термолюмінесценції (ТЛ) монокристалів $CdBr_2$: Ag+ від кімнатної температури до температури рідкого азоту. Люмінесценція практично відсутня при міжзонному (у тому числі рентгенівському) збудженні кристалів $CdBr_2$: Ag+, але проявляється при збудженні світлом в області 3,68 еВ. У цій області спектру спостерігається селективне поглинання срібла домішковими центрами. Було виявлено, що кристали $CdBr_2$: Ag+ є чутливими до дії рентгенівських променів і ультрафіолетового світла через протікання в них фотохімічних реакцій (ФХР).

Ключові слова: Шаруваті кристали, Люмінесценція, Бромід кадмію, Фотохромні домішки.

Люминесценция монокристаллов бромистого кадмия с добавлением примеси серебра

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Работа описывает исследования температурного поведения рентгенолюминесценции (РЛ), фотолюминесценции (ФЛ) и термолюминесценции (ТЛ) монокристаллов $CdBr_2$: Ag+ от комнатной температуры до температуры жидкого азота. Люминесценция практически отсутствует при межзонных (в том числе рентгеновском) возбуждениях кристаллов $CdBr_2$: Ag+, но проявляется при возбуждении светом в области 3,68 B. В этой области спектра наблюдается селективное поглощение серебра примесными центрами. Было обнаружено, что кристаллы $CdBr_2$: Ag+ чувствительны к действию рентгеновских лучей и ультрафиолетового света из-за протекания в них фотохимических реакций (ФХР).

Ключевые слова: Слоистые кристаллы, Люминесценция, Бромид кадмия, Фотохромные добавки.

REFERENCES

- 1. A.B. Lyskovich, Wide-layered crystals and their physical properties (Lviv: High School: 1982) 148 p. [In Russian].
- M. Rudka, S. Charambura, V. Antonyuk, I. Matviishyn, B. Kostyuk, J. Phys. Stud. 4 No3 (2000).
- 3. N. Stetsyk, M. Rudka, V. Antonyuk, *The XIXth International Seminar on Physics and Chemistry of Solids ISPCS-13* (Częstochowa: Poland: 2013).
- N. Stetsyk, V. Antonyuk, M. Rudka, Electronics and Nanotechnology. Proceedings of the XXXII International Scientific Conference ELNANO-2013, 134 (Kiev: 2013).
- S.S. Novosad, I.S. Novosad, A.V. Borodchuk, *Inorg. Mater.* 41, 187 (2005).