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Studies of CdI$_2$–Bi$_3$ microstructures with optical methods, atomic force microscopy and positron annihilation spectroscopy

Ivan Karbovnyk[1]*, Ivan Bolesta[1], Ivan Rovetskii[1], Sergiy Velgosh[1], Halyna Klym[2]

[1]Ivan Franko National University of Lviv, Ukraine

[2]Lviv Polytechnic National University, Ukraine

Results of the comprehensive morphological study of CdI$_2$–BiI$_3$ layered crystals are presented. Direct AFM observations of micro- and nanostructures formed in the volume of the crystals confirm the predictions made on the basis of positron annihilation spectroscopy studies. The model explaining the possible pores formation mechanism is proposed and validated by the results of luminescence measurements at 8 K.

Keywords: *layered crystals; microstructures; atomic force microscopy; positron annihilation*

1. Introduction

Cadmium iodide crystals are representatives of MX$_2$ halogenides family with pronounced layered structure. This structure is characterized by close hexagonal packing of iodine atoms. Half of the octahedral voids that are available in the structure are filled with cadmium atoms [1]. Strong ionic-covalent bonds between Cd and I lead to the formation of triple sandwich-like I–Cd–I layers. Due to peculiarities of the structural arrangement of CdI$_2$ there are specific ways of the incorporation of impurities or overstoichiometric Cd atoms into the crystal lattice. Therefore, a number of reports were devoted to the studies of doped CdI$_2$ crystals and crystals with excess of cadmium (see [2–4]). In particular, as demonstrated earlier [5], interesting changes in optical absorption are observed when CdI$_2$ is doped with BiI$_3$ (which is another layered compound). Present work is devoted to the investigation of structural and morphological modifications that occur after adding BiI$_3$ into CdI$_2$ crystals; correspondence between these modifica-

tion and light emission/absorption processes is also discussed.

To provide further insight into the complex microstructure of layered compound under study, new characterization techniques can be used in complement to traditional ones. One of such novel tools is the positron annihilation lifetime spectroscopy (PALS), a method that can be applied for studying defect structure of surface layers [6]. Analysis of the positron lifetimes (the main goal of PALS method) helps a lot in understanding the electronic processes in the material under study. Combining well-established optical spectroscopy approaches with relatively novel techniques, such as AFM phase analysis and PALS, we expect to shed light on the formation of microstructures within surface layers of cadmium iodide crystals doped with BiI$_3$.

2. Experimental

Van der Waals surface morphology of CdI$_2$–BiI$_3$ crystals was examined exploiting Solver P47-PRO atomic force microscope (AFM) [7], successfully used earlier for the study of nanoclusters in other layered compounds [8, 9]. With the

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*E-mail: ivan‗karbovnyck@yahoo.com

AFM instrument it was possible to achieve 10 nm in-plane and 0.1 nm height (z-direction) resolution.

PALS experiments were carried out with OR-TEC spectrometer [10]. ^{22}Na isotope was used as a positron source. Measurements were performed at room temperature (293 K) and ambient humidity (35 %). A series of a few independent experiments were connected with samples of the same prehistory to exclude data scatter because of differences between actual status of samples and uncontrolled instabilities in the experimental setting of PALS spectrometer [11]. The obtained results agreed well with each other within experimental uncertainties, being no more than ±0.005 ns in lifetimes and ±0.01 in component intensities. Obtained positron lifetime spectra were fitted in the frame of two-component positron trapping model. PALS spectra of the investigated layered compound were processed with a standard LT 9.0 computer program [12]. The average positron lifetime τ_{av} was determined as a centre of mass of a whole lifetime spectrum according to the well-known expression:

$$\tau_{av} = \sum_i I_i \tau_i \qquad (1)$$

where τ_i and I_i denote lifetime and intensity of the corresponding fitting components, respectively.

All experimental PALS spectra were fitted by two components with τ_1 and τ_2 lifetimes and I_1 and I_2 intensities, respectively. Then, the positron lifetime in "defect-free" bulk τ_b, and positron trapping rate in "defects" κ_d, were calculated using a formalism of two-state positron trapping model ($I_1 + I_2 = 1$) [6, 10]:

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}} \qquad (2)$$

$$\kappa_d = \frac{I_2}{I_1} \left(\frac{1}{\tau_b} - \frac{1}{\tau_2} \right) \qquad (3)$$

In addition, $(\tau_2 - \tau_b)$ difference was accepted as a size measure for extended free-volume entities, where positrons are trapped and τ_2/τ_b ratio determined by the nature of these defects was estimated [6].

Photoluminescent properties of BiI_3 doped CdI_2 crystals were measured with SUPERLUMI HASYLAB facility (Hamburg) using experimental equipment described by Zimmerer [13]. Luminescence was excited by synchrotron radiation extracted from DORIS III accelerator ring. Synchrotron radiation intensity was at the level of 10^{12} photons per second. Emission from the sample was focused onto the entrance slit of the BM50 monochromator, set to work in 200 to 1000 nm spectral range. SI-440-UV photomultiplier in photon counting mode was used as a detector.

3. Results and discussion

Fig. 1 shows AFM scans performed on van der Waals surface of CdI_2–BiI_3 crystal grown by vapor deposition technique and freshly cleaved surface of CdI_2–BiI_3 crystal grown from melt using Bridgman method. The surface of the crystal grown by vapor deposition is covered with hexagonal pores, the shape of which has been determined by hexagonal close packing of the layered structure. Depending on size, the pores can be labeled as "micro" (marked with A letter in Fig. 1) and "nano" (marked with B letter in Fig. 1). Rough estimation provides that an average "nano" pore depth is less that 1 nm, while its average diameter is about 300 nm. As far as "micro" pores are considered, these values are ∼10 nm and ∼2 μm, respectively.
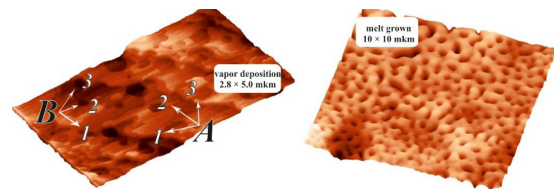

Fig. 1. AFM images showing van der Waals surfaces of CdI_2–BiI_3 crystals grown by vapor deposition (left) and crystal grown from melt (right).

Porous structure was observed also while examining the fresh cut of the crystal grown from melt (the right side of Fig. 1). Assuming the preferable shape of pores as oval, pores sizes range from as small as 25 nm up to as large as 600 nm. The average depth of the pores is around 40 nm.

Summarizing results obtained using AFM technique one can conclude that micro- and nanosized pores are formed in CdI$_2$–BiI$_3$ layered compound independently of the crystal growth technique.

In order to clarify the pore formation mechanism, the PALS method described in the previous section was used. Assuming two-state positron trapping model [6], the two components in the fit of the experimental PALS spectra (τ_1, I_1) and (τ_2, I_2) can be associated with the properties of the dominating phase of the material and positron lifetime in the free-volume entities, respectively. In this case, the positron trapping modes (bulk lifetime τ_b and positron trapping rate in defects κ_d) can be determined according to the expressions 2 and 3. The open volume entities free of the electron density are treated as "defects", while hypothetical structure without these entities is treated as "defect-free" bulk (represented by τ_b value). Within accepted two-state positron trapping model, we will focus our further analysis on the second (τ_2, I_2) component, where τ_2 lifetime is directly related to the size of free-volume entity (trapping center) and the intensity I_2 is proportional to the number of such "defects" [10].

Results of the comparative (pure CdI$_2$ vs. CdI-BiI$_3$) PALS analysis are summarized in Table 1. One can notice that BiI$_3$ additives to pure CdI$_2$ cause an increase in τ_2 values indicating an increase in the average free-volume size. At the same time, the I_2 value decreases in these crystals confirming the decrease in the number of this kind of free-volume entities. Thus, we can conclude that doping of CdI$_2$ with BiI$_3$ leads to the increase of the dimensions of free-volume entities with simultaneous decrease of their total amount. At the same time such positron trapping parameters as $\tau_{av.}$ and τ_b are almost unchanged, while positron trapping rate in defects, κ_d in CdI$_2$–BiI$_3$ decreases to 0.30 ns as compared to CdI$_2$ (Table 1). It means that existing free volume voids in pure CdI$_2$ should be converted into a smaller number of larger voids after doping with BiI$_3$. In other words, we can argue that doping CdI$_2$ crystals with BiI$_3$ causes agglomeration of smaller free-volume entities and formation of complex clusters composed of smaller vacancies. Such

process should give rise to the increase of τ_2 and the decrease of I_2. However, in both cases the same type of positron trapping centre is formed (τ_2/τ_b values are nearly 0.2 ns). The characteristic size of positron traps estimated due to ($\tau_2 - \tau_b$) difference is comparable to the size of atomic vacancy [6, 14].

Considering experimental AFM observation of pores in CdI$_2$–BiI$_3$ crystals and conclusions drawn from PALS measurements, the following model explaining pore formation mechanism at the atomic scale can be proposed. When CdI$_2$ is doped with BiI$_3$, Bi^{3+} ions substitute Cd^{2+} ions at regular lattice sites. Since the charge balance has to be maintained, cadmium vacancies (hereafter denoted as V_{Cd}) appear. As BiI$_3$ concentration increases, more compensating combinations are possible, e.g. when four Bi^{3+} ions substitute for six Cd^{2+} ions, a pair of V_{Cd} vacancies is produced. Generalizing, $2n$ Bi^{3+} ions substitute for $2m$ Cd^{2+} ions creating ($m - n$) vacancies. If m is large enough, a number of created vacancies can coagulate and a pore is formed.

One should expect that the above described ion substitution would affect the light emission from CdI$_2$–BiI$_3$ crystals. In order to verify whether the proposed mechanism is somehow manifested in optical properties, we have measured the photoluminescence spectrum of CdI$_2$–BiI$_3$. The spectrum was recorded at low temperature ($T = 8$ K) in order to minimize temperature broadening of emission bands and thus achieve better resolution. The result is depicted in Fig. 2.

Three main peaks can be resolved from the spectrum in Fig. 2. The band at ~2.05 eV is commonly attributed to intrinsic luminescence of CdI$_2$ [15, 16]. A signature of BiI$_3$ phase is a band peaked at 1.26 eV. At the same time we can observe a sharp maximum centered at 1.74 eV, which is very likely produced by centres composed of two bismuth ions and a vacancy. Possible structural arrangement corresponding to the abovementioned centre is illustrated in Fig. 3.

The model shown in Fig. 3 corresponds to the simplest charge compensation scheme, according to which three Cd^{2+} ions are replaced with two Bi^{3+} ions and a single cation vacancy is created.

Table 1. Results of PALS analysis for CdI_2 and CdI_2 doped with BiI_3.

Sample	Fitting parameters				Positron trapping modes				
	τ_1	I_1	τ_2	I_2	$\tau_{av.}$	τ_b	κ_d	$\tau_2 - \tau_b$	τ_2/τ_b
	ns	a.u.	ns	a.u.	ns	ns	ns^{-1}	ns	
CdI_2	0.248 ± 0.004	0.75 ± 0.01	0.451 ± 0.004	0.25 ± 0.01	0.30	0.28	0.45	0.15	1.0
CdI_2-BiI_3	0.267 ± 0.005	0.82 ± 0.01	0.481 ± 0.004	0.18 ± 0.01	0.31	0.29	0.30	0.19	1.6
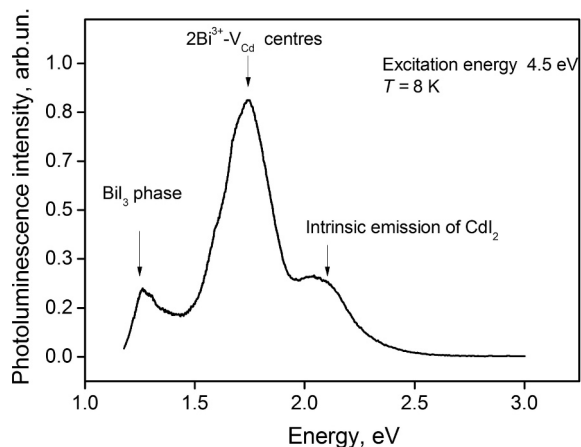
Fig. 2. Low-temperature photoluminescence spectra of CdI_2-BiI_3 crystal.
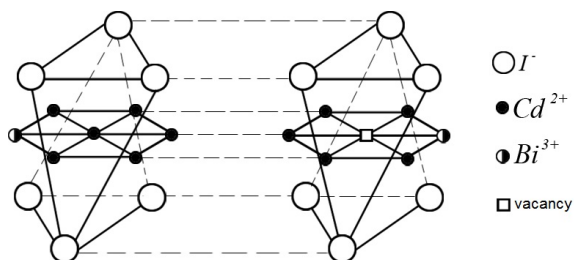
Fig. 3. Model of the luminescence centre formed by ion substitution in CdI_2-BiI_3 crystal.

In this case, a cluster composed of two BiI_3 molecules and a cadmium vacancy is formed. This model is in a good agreement with our earlier studies, in which it was established that bimolecular clusters might be the source of additional absorption band in CdI_2-BiI_3 crystals [5].

4.   Conclusions

Morphology of van der Waals surface of layered CdI_2 crystals doped with BiI_3 has been examined using atomic force microscopy. For crystals grown by vapor deposition as well as for those grown from melt, the formation of pores at the submicron scale is observed. Positron annihilation lifetime spectroscopy analysis combined with luminescence measurements speak in favor of the assumption that cadmium vacancies created due to bismuth/cadmium ion substitution are responsible for the pore formation process.

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