

<https://doi.org/10.15407/ujpe63.9.816>

I.M. BOLESTA,<sup>1</sup> I.N. ROVETSKII,<sup>1</sup> S.R. VELGOSH,<sup>1</sup> S.V. RYKHLYUK,<sup>1</sup>  
I.D. KARBOVNYK,<sup>1</sup> N.V. GLOSKOVSKAYA<sup>2</sup>

<sup>1</sup> Ivan Franko National University of Lviv, Faculty of Electronics and Computer Technologies,  
Chair of Radiophysics and Computer Technologies  
(107, Gen. Tarnavs'kyi Str., Lviv 79017, Ukraine)

<sup>2</sup> Bogolyubov Institute for Theoretical Physics, National Academy of Sciences of Ukraine  
(14b, Metrolohichna Str., Kyiv 03143, Ukraine)

## MORPHOLOGY AND OPTICAL PROPERTIES OF NANOSTRUCTURES FORMED IN NON-STOICHIOMETRIC CdI<sub>2</sub> CRYSTALS

---

*The morphology of nanostructures formed in non-stoichiometric CdI<sub>2</sub> crystals has been studied, by using the atomic force microscopy methods. Morphological changes are observed, when the concentration of cadmium atoms approaches a non-stoichiometric threshold value of 0.1 mol%. The features in the phase composition of nanostructures are analyzed with the help of Raman and infrared absorption spectroscopies. The influence of the researched nanostructures on the optical characteristics of non-stoichiometric CdI<sub>2</sub> crystals is analyzed.*

*Keywords:* atomic force microscopy, nanostructures, surface morphology, Raman spectra, absorption spectra.

### 1. Introduction

The formation and properties of nano-sized structures in layered crystals are intensively studied nowadays. Cadmium iodide (CdI<sub>2</sub>) is a typical representative of the latter. In most of relevant works [1–5], the surface morphology of CdI<sub>2</sub> grown from an aqueous solution was a matter of interest. Using the atomic force microscopy (AFM) methods, linear steps, dips, and islands on the CdI<sub>2</sub> surface were revealed, between which the surface is atomically smooth.

In works [6, 7], we studied cadmium iodide crystals grown from a melt. With the help of AFM methods, we found that if CdI<sub>2</sub> crystals are held in the air environment under thermodynamically equilibrium conditions, nanostructures (nanopores, nanoclusters, and nanowires) are formed on their surface. Those

nanostructures include cadmium oxide and cadmium hydroxide. A mechanism of nanostructure formation was determined, which consisted of a few stages.

At the same time, there are practically no works dealing with the surface topology and the formation of nanostructures in non-stoichiometric cadmium iodide crystals grown from a melt. Such studies are important because cadmium atoms are a building material for the nanostructure formation [6, 7]. Therefore, the aim of this work was to study the morphology and phase composition of nanostructures emerging on the surface and in the bulk of non-stoichiometric CdI<sub>2</sub> crystals, as well as the influence of those nanostructures on the material optical properties.

### 2. Experimental Specimens and Methods

For experimental researches, crystals with a controlled deviation from the stoichiometric composition were grown by introducing metallic cadmium to concentrations of 10<sup>-3</sup>, 10<sup>-2</sup>, 10<sup>-1</sup>, and 6 × 10<sup>-1</sup> mol%

---

© I.M. BOLESTA, I.N. ROVETSKII, S.R. VELGOSH,  
S.V. RYKHLYUK, I.D. KARBOVNYK,  
N.V. GLOSKOVSKAYA, 2018

and iodine to a concentration of  $10^{-1}$  mol% into a melt. The indicated mole fractions correspond to the concentrations of over-stoichiometric cadmium atoms  $N_i = 10^{17}$ ,  $10^{18}$ ,  $10^{19}$ , and  $6 \times 10^{19}$   $\text{cm}^{-3}$ , respectively. The atomic concentration in the  $\text{CdI}_2$  matrix was evaluated as the ratio  $N = \frac{\rho N_A}{M}$ , where  $\rho = 5.6$   $\text{g}/\text{cm}^3$  is the  $\text{CdI}_2$  density,  $N_A$  the Avogadro number, and  $M$  the  $\text{CdI}_2$  molar mass, and was found to equal about  $10^{22}$   $\text{cm}^{-3}$ .

The morphology of as-cleaved surfaces and surfaces of non-stoichiometric  $\text{CdI}_2$  crystals held in the air environment was examined. Fresh chips of the crystals were obtained by removing the upper layers of the specimen making use of a scotch tape.

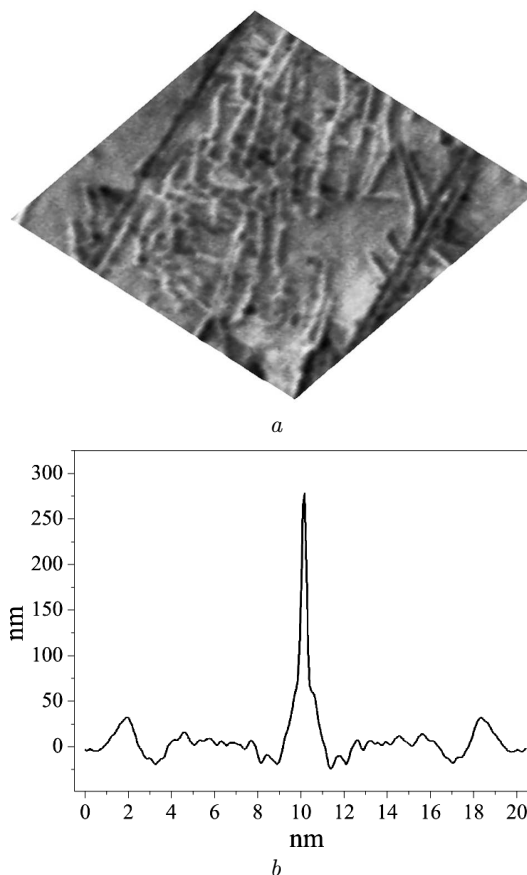
The morphology of the crystal surface was studied, by using the methods of semicontact atomic force microscopy on a Solver P47-PRO microscope. The probe tip radius did not exceed 10 nm. The device resolution with respect to the surface profile height was about 1 Å.

The statistical parameters of nanostructures and surfaces were calculated by processing the digital microscopic images using the MATLAB software.

The Raman scattering spectra of  $\text{CdI}_2$  crystals were measured on a DFS-52M diffraction photospectrometer. While studying the absorption spectra, the KSVU-2 installation mounted on the basis of an MDR-23 monochromator was applied. The specimen dimensions did not exceed  $5 \times 5$   $\text{mm}^2$ , and their thickness was within an interval of 0.5–1 mm. To prevent a mechanical damage and deformation, the specimens were fixed on special substrates with the help of a double-sided adhesive tape.

### 3. Surface Morphology of As-Cleaved Non-Stoichiometric $\text{CdI}_2$ Crystals

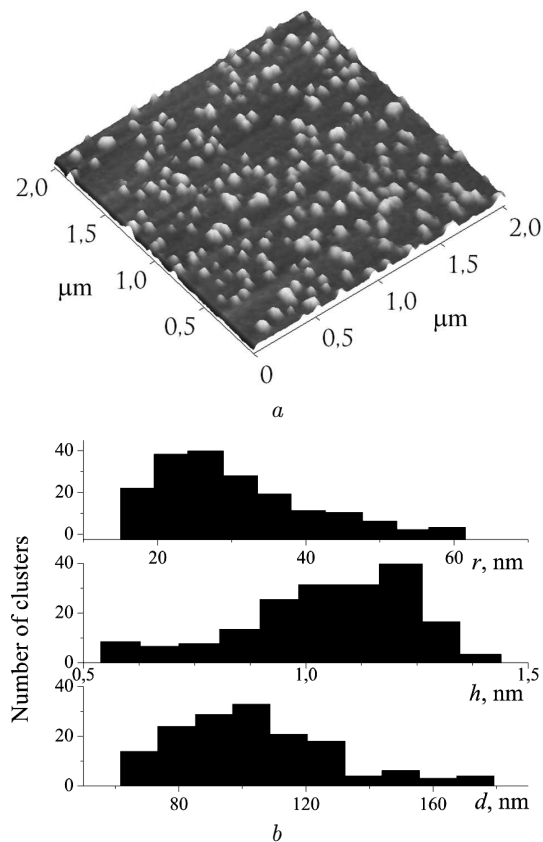
If the concentration  $c$  of over-stoichiometric cadmium atoms did not exceed 0.1 mol%, the surface morphologies of both as-cleaved  $\text{CdI}_2\text{-Cd}_i$  crystals and nominally pure ones were atomically smooth (Fig. 1, *a*), with a roughness of about 0.5 nm. The surface roughness (if the surface irregularities have the Gaussian distribution) can be estimated by approximating the surface autocorrelation function by the Gaussian dependence  $C(r) = \delta^2 e^{-r^2/\sigma^2}$ , where  $\delta$  and  $\sigma$  are the surface roughness and correlation length, respectively.



**Fig. 1.** AFM image of the surface morphology of as-cleaved  $\text{CdI}_2\text{-Cd}_i$  (0.01 mol%) crystals. The area size is  $10 \times 10$   $\mu\text{m}^2$ . The height interval equals 5 nm (*a*). The surface autocorrelation function (*b*)

Unlike  $\text{CdI}_2\text{-Cd}_i$  (0.01 mol%) crystals, the surface of as-cleaved crystals with the  $\text{Cd}_i$  concentration  $c > 0.1$  mol% revealed nanostructures of two types: island-like nanoclusters (Fig. 2, *a*) and nanostripes (Fig. 3). The radius and height of most nanoclusters were about 30 and 1 nm, respectively (Fig. 2, *b*). The distances between the clusters were stochastically distributed, and the mean distance value was about 100 nm (Fig. 2, *b*).

The numerical values of the parameters of nanostructures formed in the  $\text{CdI}_2\text{-Cd}_i$  (0.6 mol%) crystals are quoted in Table. The height of nanostripes lies within an interval of 0.6–0.7 nm. The width of nanostripes A, B, and C is about 80 nm, and their length does not exceed 2  $\mu\text{m}$  (Figs. 3, *a* and *b*). As a result of the nanostripe aggregation (D in Fig. 3, *b*),

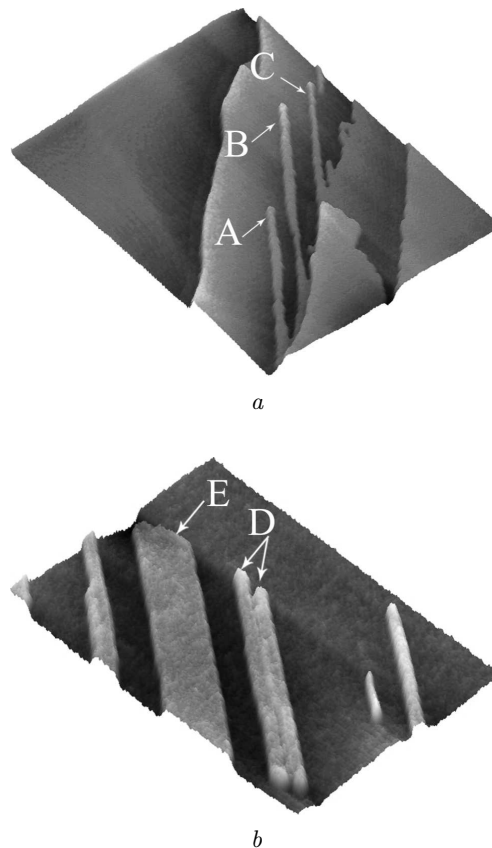


**Fig. 2.** AFM image of island-like nanostructures formed in the bulk of  $\text{CdI}_2\text{-Cd}_i$  (0.6 mol%) crystals. The area size is  $2 \times 2 \mu\text{m}^2$ . The height interval equals 3 nm (a). The distribution of nanostructures over their radius  $r$ , height  $h$ , and the distance between them  $d$  (b)

**Parameters of nanostructures in  $\text{CdI}_2\text{-Cd}_i$  (0.6 mol%) crystals**

Number of clusters	$r_{\text{min}}$ , nm	$r_{\text{max}}$ , nm	$r_{\text{aver}}$ , nm
156	22	66	34
Average distance to the nearest cluster	$h_{\text{min}}$ , nm	$h_{\text{max}}$ , nm	$h_{\text{aver}}$ , nm
103	0.5	1.4	1.1

larger aggregates are formed (E in Fig. 3, b), whose length and height remain in the same dimension interval, whereas the width corresponds to the number of nanostripes in the aggregate. For example, the width of nanostripe E in Fig. 3, b is about 320 nm (4 iden-



**Fig. 3.** Nanowires formed on the as-cleaved surface of  $\text{CdI}_2\text{-Cd}_i$  (0.6 mol%) crystals. The area size is  $3 \times 2.2$  (a) and  $2 \times 1.3 \mu\text{m}^2$  (b). The height interval equals 5 (a) and 1.5 nm (b)

tical nanostripes each 80 nm in diameter), and its length amounts to about 1.5  $\mu\text{m}$ .

From the experimental AFM data, it follows that the nanostructures observed in crystals with an over-stoichiometric concentration of cadmium atoms that is higher than the threshold value are formed in the crystal bulk during the crystal growth and/or during the further specimen storage. The AFM researches showed that the surface morphology of crystals with the iodine excess practically does not differ from that of stoichiometric crystals.

**4. Surface Morphology of Non-Stoichiometric  $\text{CdI}_2$  Crystals Held in the Air Environment**

In Fig. 4, an AFM image of the surface morphology of (a)  $\text{CdI}_2\text{-Cd}_i$  (0.1 mol%) and (b)  $\text{CdI}_2\text{-I}_2$  crystals held in the air environment for 168 h (7 days)

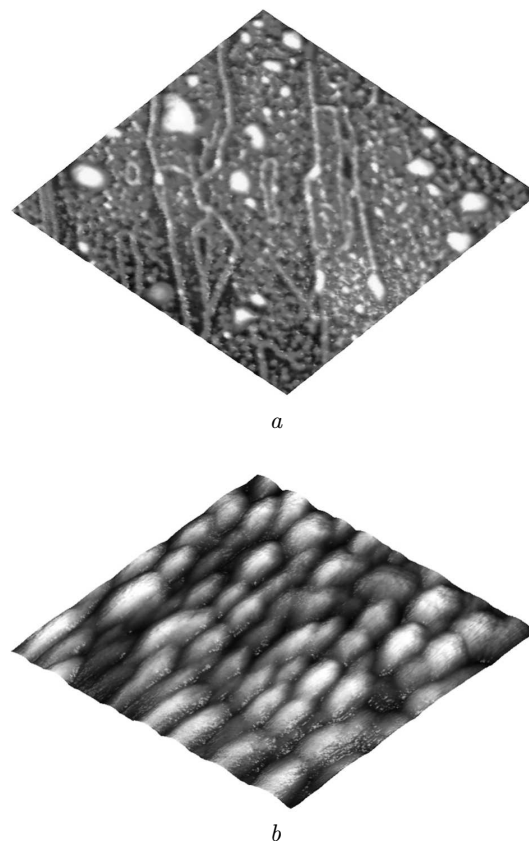
is exhibited. A characteristic feature of the surface morphology of  $\text{CdI}_2\text{-Cd}_i$  (0.1 mol%) crystals held in the air environment is the formation of nanowires and nanoclusters on it (Fig. 4, *a*). Those entities are formed as a result of the aggregation of nanoclusters with smaller sizes. The lateral sizes of nanowire-forming nanoclusters are about 100 nm, and the corresponding heights are within an interval of 1.5–3 nm.

Unlike the previous case, the surface morphology of the  $\text{CdI}_2\text{-I}_2$  crystals held in the air environment is characterized by the presence of island-like nanoclusters (Fig. 4, *b*). Their lateral sizes and heights lie within intervals of 100–200 and 3–8 nm, respectively. This difference can result from different concentrations of  $\text{CdI}^{2+}$  cations and  $\text{I}^-$  anions, which form nanostructures in those crystals.

### 5. Phase Composition of Nanostructures Formed in Non-Stoichiometric $\text{CdI}_2$ Crystals

Figure 5 illustrates the Raman scattering spectra of non-stoichiometric cadmium iodide crystals held in the air environment. One can see the presence of a few bands in the low- ( $\nu < 1000 \text{ cm}^{-1}$ ) and high-frequency ( $\nu > 3000 \text{ cm}^{-1}$ ) spectral intervals. Since the  $\text{CdI}_2$  lattice eigenmodes are observed at frequencies  $\nu < 120 \text{ cm}^{-1}$  [8], the additional vibrational bands can be associated, taking the AFM data into account, with the nanostructures that are formed in non-stoichiometric crystals held in air.

The band with a maximum at  $290 \text{ cm}^{-1}$  was registered in the spectra of non-stoichiometric crystals (Fig. 5, *a*). Its intensity was significantly (by approximately a factor of three) higher for the  $\text{CdI}_2\text{-Cd}_i$  (0.01 mol%) crystals than for the  $\text{CdI}_2\text{-I}_2$  (0.1 mol%) ones. In addition, the  $\text{CdI}_2\text{-Cd}_i$  crystals also exhibit weakly pronounced bands at about 470 and  $650 \text{ cm}^{-1}$ . The comparison of the obtained experimental results with the data on the Raman spectra of cadmium oxide allows the observed bands to be associated with the inclusion of CdO groups [9, 10]. This model describes well the difference between the intensities of those bands in the  $\text{CdI}_2\text{-Cd}_i$  and  $\text{CdI}_2\text{-I}_2$  crystals as a result of the higher concentration of metallic cadmium for the formation of its oxide in the former case.

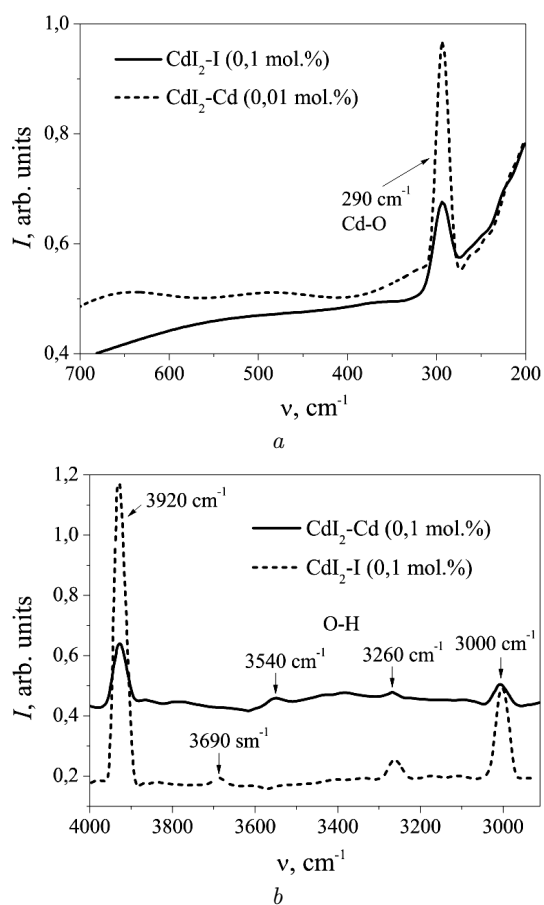


**Fig. 4.** Surface morphology of  $\text{CdI}_2\text{-Cd}_i$  (0.1 mol%) (*a*) and  $\text{CdI}_2\text{-I}_2$  (0.1 mol%) (*b*) crystals held in air for 7 days. The area size is  $3 \times 3$  (*a*) and  $1 \times 1 \mu\text{m}^2$  (*b*). The height interval equals 18 (*a*) and 10 nm (*b*)

The high-frequency sections in the Raman spectra of both non-stoichiometric crystals contain intensive bands with maxima at  $3000$  and  $3920 \text{ cm}^{-1}$ , as well as a band with a maximum at  $3260 \text{ cm}^{-1}$  (Fig. 5, *b*), whose intensity does not exceed 5%. At the same time, a band with a maximum at  $3540 \text{ cm}^{-1}$  was observed in the spectrum of  $\text{CdI}_2$  crystals doped with excess cadmium, and a band with a maximum at  $3690 \text{ cm}^{-1}$  in the spectrum of the same crystals doped with excess iodine.

The bands at  $3260$  and  $3549 \text{ cm}^{-1}$  are related to the vibrations of O–H groups in  $\gamma\text{-Cd(OH)}_2$  [11], and the mode at  $3690 \text{ cm}^{-1}$  is induced by the vibrations of free hydroxide O–H groups [12].

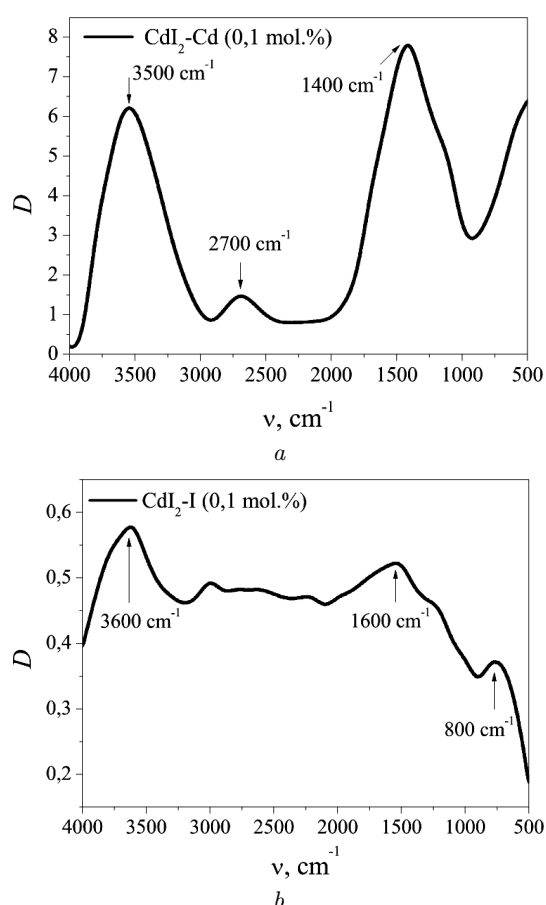
The intensities of the  $3000\text{-cm}^{-1}$  and  $3920\text{-cm}^{-1}$  bands in the Raman spectra of stoichiometric cadmium iodide crystals were 14% and 50%, respectively. The intensities of those bands decreased to 5%



**Fig. 5.** Raman spectra of the  $\text{CdI}_2\text{-Cd}_i$  (0.1 mol%) and  $\text{CdI}_2\text{-I}_2$  (0.1 mol%) crystals held in air:  $\nu < 1000 \text{ cm}^{-1}$  (a) and  $\nu > 3000 \text{ cm}^{-1}$  (b)

and 15%, respectively, when introducing excess cadmium into the  $\text{CdI}_2$  crystal, and increased to 22% and 70%, respectively, when introducing excess iodine. Such results allow us to suggest that the bands concerned can be associated with nanostructures that include iodine compounds. Since the iodine molecule possesses a nonpolar covalent bond, the energy of its interaction with water is insignificant. As a result, the bond O–H–I in the  $\text{Cd}(\text{OH})\text{I}$  compound is weak. Accordingly, the number of free hydroxidal groups increases, and the frequencies of their vibrations are shifted toward higher frequencies (at about  $3900 \text{ cm}^{-1}$ ). Thus, the band with a maximum at  $3000 \text{ cm}^{-1}$  is associated with the vibrations of O–H groups in  $\text{Cd}(\text{OH})\text{I}$ .

Hence, it follows from the Raman spectroscopy data that the nanostructures formed on the surface



**Fig. 6.** IR absorption spectra of  $\text{CdI}_2\text{-Cd}_i$  (0.1 mol%) (a) and  $\text{CdI}_2\text{-I}_2$  (0.1 mol%) (b) crystals held in air

of non-stoichiometric crystals include cadmium oxide and cadmium hydroxide, as well as the  $\text{Cd}(\text{OH})\text{I}$  compound. This conclusion is confirmed by the infrared (IR) absorption spectra of non-stoichiometric  $\text{CdI}_2$  crystals (Fig. 6). In particular, additional bands in the IR absorption spectrum of  $\text{CdI}_2\text{-Cd}_i$  (0.01 mol%) crystals were registered at  $3500$  and  $1400 \text{ cm}^{-1}$ , as well as a less intensive band at about  $2700 \text{ cm}^{-1}$  (Fig. 6, a). In  $\text{CdI}_2\text{-I}_2$  (0.01 mol%) crystals, there arise bands at  $3600$ ,  $1600$ , and  $800 \text{ cm}^{-1}$  against the total absorption background (Fig. 6, d).

Nanostructures that include  $\text{Cd}(\text{OH})_2$  are responsible for the additional absorption at  $1600$ ,  $2700$ , and  $3600 \text{ cm}^{-1}$  [11], whereas nanostructures that include  $\text{CdO}$  for the additional absorption at  $3500$ ,  $1400$ , and  $800 \text{ cm}^{-1}$  [13].

Thus, the comparison of the phase compositions of nanostructures of non-stoichiometric and stoichio-

metric cadmium iodide crystals testifies to the formation of cadmium oxide and cadmium hydroxide in them.

## 6. Absorption Spectra of Non-Stoichiometric $\text{CdI}_2$ Crystals

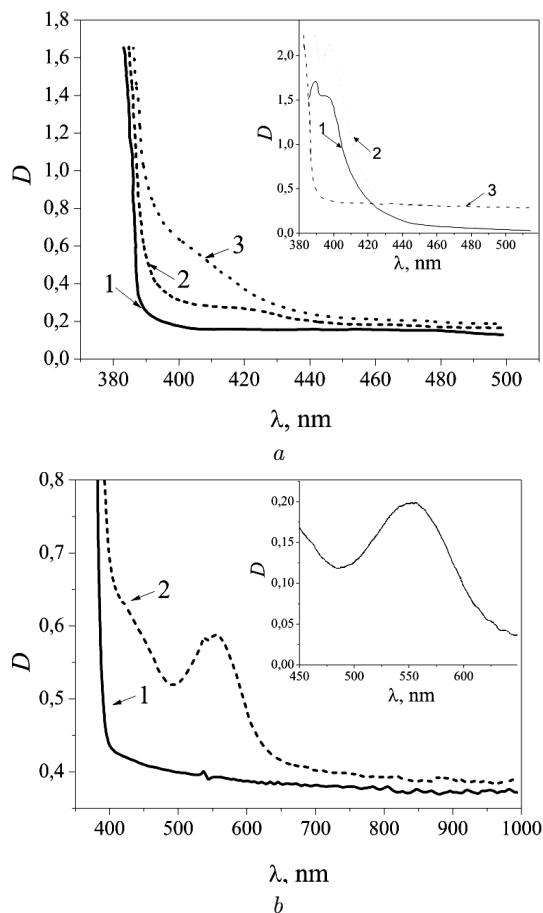
In Fig. 7, the absorption spectra of non-stoichiometric  $\text{CdI}_2$ - $\text{Cd}_i$  and  $\text{CdI}_2$ - $\text{I}_2$  crystals and their difference with the corresponding spectra of stoichiometric crystals are depicted. The introduction of over-stoichiometric cadmium into the melt brings about a shift of the self-absorption edge toward the long-wave region and the additional absorption in the crystal transparency interval (390–450 nm). In the difference spectra, bands with maxima at 388 and 397 nm can be distinguished (see the inset in Fig. 7, a), whose intensities increase with the  $\text{Cd}_i$  concentration. However, the introduction of metallic cadmium to a concentration higher than 0.1 mol% leads to the disappearance of absorption bands and a significant growth of the nonselective light scattering in the crystal transparency interval (curve 3 in the insert in Fig. 7, a) [14].

The introduction of over-stoichiometric iodine results in a long-wave displacement of the  $\text{CdI}_2$  absorption edge and the emergence of additional bands at about 440 and 555 nm (Fig. 7, b).

## 7. Discussion of Experimental Results

In view of the data of our AFM studies, the concentration dependence of the additional absorption bands of  $\text{CdI}_2$ - $\text{Cd}_i$  crystals can be explained in the framework of the following model. At concentrations  $c < 0.1$  mol%, over-stoichiometric  $\text{Cd}_i$  atoms are localized in the octahedral cavities of van der Waals gaps and, together with six iodine atoms, form local complexes  $\text{I}^1\text{-Cd-[I}^1\text{-Cd}_i\text{-I}^2\text{]-Cd-I}^2$ . The distance between the latter is considerable, if the  $\text{Cd}_i$  concentration is low. The appearance of chemical bonds between the  $\text{Cd}_i$  atoms and halogens from two neighboring layers  $\text{I-Cd-[I-Me-I]-Cd-I}$  is also confirmed by changes in the nonlinear-optical properties and the NQR frequencies of  $^{127}\text{I}$  [15–17].

In this case, the interaction between the  $s$ -states of  $\text{Cd}_i$  and the  $p$ -states of iodine [the  $s(\text{Cd}_i)$ - $p(\text{I})$  interaction] may be assumed to dominate. As the concentration of over-stoichiometric atoms decreases, the



**Fig. 7.** Absorption spectra of  $\text{CdI}_2$ - $\text{Cd}_i$  (a) and  $\text{CdI}_2$ - $\text{I}_2$  (b) crystals. Curves 1 demonstrate the absorption spectra of corresponding stoichiometric crystals. In panel a, the  $\text{Cd}_i$  concentration equals  $10^{-3}$  (curve 2) and  $10^{-2}$  (curve 3). The difference spectra of the  $\text{CdI}_2$ - $\text{Cd}_i$  crystals (a) with concentrations of  $10^{-3}$  (1),  $10^{-2}$  (2), and  $10^{-1}$  (3) and the  $\text{CdI}_2$ - $\text{I}_2$  crystal (b) with respect to the corresponding stoichiometric crystal are shown in the insets

distance  $r$  between them decreases. At  $r \leq r_{\text{cr}}$ , the interaction character changes: the  $s(\text{Cd}_i)$ - $p(\text{I})$  interaction disappears and, simultaneously, there arises the  $s(\text{Cd}_i)$ - $s(\text{Cd}_i)$  interaction as a result of the extension of the cadmium  $s$ -states. The parameter  $r_{\text{cr}}$  evaluated from the experimental data amounts to about 3 nm. As the concentration of over-stoichiometric cadmium increases, those formations coagulate into larger aggregates, which are the main source of light scattering.

According to the spectral composition, the light absorption by  $\text{CdI}_2$ - $\text{I}_2$  crystals in a vicinity of 440 nm

is identical to that of  $\text{CdI}_2\text{-Cd}_i$  crystals. An intensive band with a maximum at 555 nm in the  $\text{CdI}_2\text{-I}_2$  spectrum, which is responsible for the red color of those crystals, can be associated with the light absorption by centers including over-stoichiometric iodine atoms. Those centers can be formed as follows. The presence of excess iodine gives rise to the formation of vacancies in the cationic subsystem  $V_{\text{Cd}}^{2-}$ . As a result, the iodine  $p$ -orbitals form a  $\sigma_p$ -bond with one another, i.e. there appears an  $\text{I}_2^-$  quasimolecule. This process is highly probable, if  $V_{\text{Cd}}^{2-}$  vacancies are localized on the edge of the  $\text{I-Cd-I}$  structural layer, where they are pushed out by elastic forces emerging owing to a lattice deformation. At the edge of the structural layer, the coordination number of a Cd atom equals 4 (rather than 6 as in the  $[\text{CdI}_6]^{4-}$  complex), which additionally favors the formation of a  $\text{I}_2^-$  molecular center.

## 8. Conclusions

A threshold concentration of over-stoichiometric cadmium atoms (0.1 mol%) is revealed in  $\text{CdI}_2\text{-Cd}_i$  crystals, at which the morphological parameters of nanostructures formed in the crystal bulk change. If the Cd concentration exceeds the threshold value, the surface of as-cleaved  $\text{CdI}_2\text{-Cd}_i$  crystals contains nanoclusters with lateral sizes of about 70 nm and nanostripes about 80 nm in width and up to 2  $\mu\text{m}$  in length. The height of those nanostructures does not exceed 1 nm.

It is found that when  $\text{CdI}_2\text{-Cd}_i$  (0.1 mol%) crystals are held in air, a considerable number of nanowires are formed on their surface, in contrast to nominally pure crystals. The surface morphologies of both  $\text{CdI}_2\text{-I}_2$  (0.1 mol%) crystals held in the air environment and the nominally pure  $\text{CdI}_2$  crystals are characterized by the presence of only island-like clusters.

Using the Raman scattering and IR absorption spectroscopy methods, it is found that the composition of nanoclusters formed on the surface of non-stoichiometric  $\text{CdI}_2$  crystals includes cadmium hydroxide  $\text{Cd}(\text{OH})_2$  and cadmium oxide  $\text{CdO}$ .

The absorption spectra of  $\text{CdI}_2\text{-Cd}_i$  crystals contain two bands with the maxima at 388 and 397 nm, which are formed by  $[\text{CdI}_6]^{4-}$  centers. If the concentration of over-stoichiometric cadmium exceeds the threshold value, those bands disappear.

1. R. Singh, S.B. Samanta, A.V. Narlikar, G.C. Trigunayat. Some novel results of scanning tunneling microscopy (STM) study of cadmium iodide crystals. *J. Cryst. Growth*. **204**, 233 (1999).
2. R. Singh, S.B. Samanta, A.V. Narlikar, G.C. Trigunayat. A combined optical, SEM and STM study of growth spirals on the polytypic cadmium iodide crystal. *Bull. Mater. Sci.* **23**, 131 (2000).
3. B. Kumar, N. Sinha. Micromorphology of pure and  $\text{PbI}_2$ -doped  $\text{CdI}_2$  dendritic single crystals. *Cryst. Res. Technol.* **40**, 887 (2005).
4. R. Singh, S.B. Samanta, A.V. Narlikar, G.C. Trigunayat. Influence of weak atomic bonding on the height of growth spiral steps on cadmium iodide crystals. *Surf. Sci.* **422**, 188 (1999).
5. N.Y. Cui, M.D. Brown, A. McKinley. An exploratory study of the topography of a  $\text{CdI}_2$  single crystal using AFM. *Appl. Surf. Sci.* **152**, 266 (1999).
6. I.M. Bolesta, I.M. Rovetskii, I.D. Karbovnyk, S.V. Rykhlyuk, M.V. Partyka, N.V. Gloskovskaya. Formation and optical properties of nanostructures in  $\text{CdI}_2$ . *Zh. Prikl. Spektrosk.* **82**, 89 (2015) (in Russian).
7. I.M. Bolesta, I.M. Rovetskyi, Z.M. Yaremko, I.D. Karbovnyk, S.R. Velgosh, M.V. Partyka, N.V. Gloskovska, V.M. Lesivtsiv. On the mechanism of nanostructure growth on the  $\text{CdI}_2$  surface. *Ukr. Fiz. Zh.* **60**, 1144 (2015) (in Ukrainian).
8. A. Cingolani, M. Ferrara, M. Lugara, F. Levy. The Raman spectra of  $\text{CdI}_2$ . *Solid State Commun.* **50**, 911 (1984).
9. Z.V. Popovic, G. Stanistic, D. Stojanovic, R. Kostic. Infrared and Raman spectra of  $\text{CdO}$ . *Phys. Status Solidi B* **165**, K109 (1991).
10. A. Ashrafi, K. Ostrikov. Raman-active wurtzite  $\text{CdO}$  nanophase and phonon signatures in  $\text{CdO}/\text{ZnO}$  heterostructures fabricated by nonequilibrium laser plasma ablation and stress control. *Appl. Phys. Lett.* **98**, 133119 (2011).
11. M. Schmidt, H.D. Lutz.  $\gamma\text{-Cd}(\text{OH})_2$ , a common hydroxide or an aquoxy-hydroxide? *Mater. Res. Bull.* **26**, 605 (1991).
12. C.M. Johnson, E. Tyrode, S. Baldely, M.W. Rutland, C. Leygraf. A vibrational sum frequency spectroscopy study of the liquid-gas interface of acetic acid-water mixtures: 1. Surface speciation. *J. Phys. Chem. B* **109**, 321 (2005).
13. Z. Guo, M. Li, J. Liu. Highly porous  $\text{CdO}$  nanowires: preparation based on hydroxy- and carbonate-containing cadmium compound precursor nanowires, gas sensing and optical properties. *Nanotechnology* **19**, 245611 (2008).
14. I. Bolesta, I. Rovetskyi, I. Karbovnyk, M. Partyka, S. Rykhlyuk, N. Gloskovskaya. Nanostructures formed in  $\text{CdI}_2$  crystals intercalated by overstoichiometric cadmium.

In *Book of Abstracts of the 19th International Seminar on Physics and Chemistry of Solids and Advanced Materials (Czestochowa, Poland, June 12–15, 2013)*, p. 66.

15. I. Bolesta, I. Kityk, V. Kovalisko, O. Syrбу. The luminescence of metal-cadmium iodide heterostructures. *Phys. Status Solidi A* **147**, K53 (1995).
16. I.M. Bolesta, I.V. Kityk, V.I. Kovalisko, R.M. Turchak. Electronic structure and optical spectra of overstoichiometric cadmium atoms in CdI<sub>2</sub> crystals, *Radiat. Eff. Def. Solids* **137**, 95 (1995).
17. I.M. Bolesta, I.V. Kityk, J. Filipecki, H. Zount. Low-temperature anomalies in the CdI<sub>2</sub>-Cd crystalline system. *Phys. Status Solidi B* **189**, 357 (1995).

Received 03.07.17.

Translated from Ukrainian by O.I. Voitenko

*I.M. Болеста, I.M. Ровецький, С.Р. Вельгош,  
С.В. Рихлюк, I.Д. Карбовник, Н.В. Глосковська*

МОРФОЛОГІЯ  
ТА ОПТИЧНІ ВЛАСТИВОСТІ  
НАНОСТРУКТУР, ЯКІ ФОРМУЮТЬСЯ  
У НЕСТЕХІОМЕТРИЧНИХ КРИСТАЛАХ CdI<sub>2</sub>

Резюме

Методами атомно-силової мікроскопії досліджено морфологію нанорозмірних структур, які формуються у нестехіометричних кристалах CdI<sub>2</sub>. Встановлено існування граничної концентрації надстехіометричних атомів кадмію (0,1 мол.%), при якій спостерігається зміна морфології. Особливості фазового складу сформованих наноструктур вивчалися методами комбінаційного розсіяння світла та інфрачервоного поглинання. Проаналізовано вплив цих наноструктур на оптичні характеристики нестехіометричних кристалів CdI<sub>2</sub>.