

Growth and Properties of Cd-doped PbI₂ Crystals

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PbI₂ single crystals containing cadmium 0.001-10 at. % have been obtained by means of crystallization from vapor phase in an enclosed system with over-stoichiometric iodine vapor pressure. The influence of cadmium concentration in source burden material and the influence of temperature gradient upon the mass-transfer rate in the system and on the crystals' characteristics have been researched. With addition of cadmium within the concentration range from 0.001 to 0.5 at. % into PbI₂-I₂ system at optimal growing conditions for pure PbI₂ crystals, the mass-transfer rate is decreased by not more than 2 %, while Cd concentration in the single crystals grown remains of the same order as their content in the source material. The increase of dopant content from 0.5 to 5.5 at. % in the source material leads to two-fold decrease of mass-transfer rate compared to its initial value, with cadmium content in single crystals 5 times lower than in the source material and with decreased dimensions of single crystals. To obtain Cd-doped crystals up to 10 at. %, temperature gradient in the system has been decreased. Cd doping facilitates the growth of single crystals mainly in the form of plates and tapes. By means of X-ray diffraction spectra, it has been defined that PbI₂ single crystals belong to 4H-polytype. The lattice parameters and the unit cell volume of pure and doped crystals have been determined. The influence of cadmium dopant upon the PbI₂ absorption spectra has been defined. Increasing cadmium content in PbI₂ crystals to 3 at. % results in a shift of intrinsic absorption edge into the short-wave area and increase of the band gap width.

Keywords: Lead iodide, Mass-transfer rate, Doping, Cadmium dopant, Diffraction patterns, Absorption spectra.

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1. INTRODUCTION

Wide-band gap-layered PbI₂ semiconductor attracts attention of researchers due to potentiality of using it in ionizing radiation detectors, electro-optical devices, solar cell technology, solid-state flexible supercapacitors [1-5]. The scientific and practical interest towards Cd-doped PbI₂ crystals is caused by the fact that doping allows purposefully change and improve the crystal's characteristics, since many properties are governed not just by strict correctness of crystal lattice, but exactly by disturbances of this correctness and structure defects. As a result of research of nanostructures of pure PbI₂ and Cd-doped PbI₂, obtained by one-pot synthesis, it was defined that Cd-doping intensifies the photoluminescence, improves the radiation absorption property and increases the electrical conductivity of PbI₂ [6]. Heterogeneous solid solutions of Pb_{1-x}Cd_xI₂, grown by Bridgeman's vertical method, are characterized by intensive photo- and X-ray luminescence at room temperature, in contrast to pure PbI₂, as well as by high radiation resistance [7, 8], while it opens up a possibility of using these materials for the production of high-efficient rapid-action non-cooled scintillation detectors of X-ray and gamma radiation.

In the majority of scientific works published with research results set forth for Cd-doped PbI₂ crystals, obtained mainly from melt, gel, solutions [6-8], the crystals grown from vapor phase have been studied insufficiently. The work presented continues the works [9-11] on studying the process of growth from vapor phase in an enclosed system of pure PbI₂ crystals and ones doped with Fe, Ni, Ag, Cu or Mn, along with studying the properties of the said PbI₂ crystals. Object of

the work – to research the influence of cadmium dopant upon the mass-transfer rate, crystal growth, structure, morphology and absorption spectra of lead iodide.

2. EXPERIMENTAL

Doping of PbI₂ with cadmium has been done during the process of growth from vapor phase in an enclosed system at over-stoichiometric iodine vapor pressure following the same procedure as doping with Mn, described in the work [11]. Lead and cadmium iodides were synthesized from separate components, while the amount of impurities in them did not exceed 10⁻⁵ at. %. Iodide alloy was used as a vaporization source.

Cd concentration in the source material, as well as in grown single crystals, was determined with "Comebacks" X-ray microanalyzer. A carbon film with a thickness of ≈ 10 nm has been deposited upon the single crystals. The analysis was performed in different parts of the sample in 5-10 places with a probe ≈ 1 μm. Several samples have been studied during one cycle. Pure elements were used there as reference standards. The analysis was conducted by L_α-lines at accelerating voltage of 20 kV and beam current of ≈ 10⁻⁸ A.

X-ray diffraction patterns of the crystals were obtained by means of "DRON-3" X-ray diffractometer with iron anode radiation. The analysis of diffraction patterns was done on the basis of "ICSD 1" structural database. Lattice parameters and unit cell volume were determined by means of "DHN_PDS" program package.

The morphology and quality of the crystals grown were studied using both optical microscope and scanning electron microscope.

Crystal absorption spectra in the range from 350 to

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1000 nm have been measured by spectrophotometer "AvaSpec-2048" produced by "AVANTES" company. As a source of optical excitation a halogen lamp has been used.

3. RESULTS AND DISCUSSION

For CdI₂ synthesis, cadmium and iodine (in stoichiometric ratio) were loaded into a quartz ampoule, which was vacuumed, soldered and placed into a two-zone furnace with the source zone temperature of 800-900 K and the crystallization zone temperature of 500-600 K for 3-5 hours. In the low-temperature part of the ampoule, cadmium iodide crystallized as a polycrystalline material and as small single crystals, having area of ≈ 1 mm². To improve the purity of doping material, the CdI₂ synthesized repeatedly recrystallized in vacuum soldered ampoule at lower temperature gradient (8-10 K/cm). As a result of recrystallization, CdI₂ single crystals with an area of up to 6 mm² were obtained, while the temperature range for their settling (550-650 K) was detected, which is close to PbI₂ crystallization temperature.

In order to estimate the influence of mass-transfer rates of cadmium and lead iodides upon the crystal doping level, for CdI₂ there was experimentally detected the mass-transfer rate at optimal technological conditions for pure PbI₂ single crystals growth [10]: source zone temperature of 770 K and crystallization zone temperature of 650 K, at over-stoichiometric iodine vapor pressure of 8.5 kPa. The mass-transfer value for CdI₂ constitutes is $6.4 \cdot 10^{-5}$ mol/(m²s), and it is of the same order that for PbI₂ – $4.5 \cdot 10^{-5}$ mol/(m²s).

To find correlation between the quantity of cadmium added into the system and its concentration in single crystals grown, mass-transfer rate in the system, the studies were conducted at optimal growing conditions for pure PbI₂ crystals with Cd content in the source burden material ranging from 0.001 to 30 at. %.

In the case of changing cadmium concentration from 0.001 to 0.1 at. % in the source material, the mass-transfer rate in the system is the same as for undoped crystals (flow decrease not more than 1 %). Cd concentration in the single crystals grown is of the same order and it changes proportionally to their content in the source alloy. This result coincides with the results obtained for doping PbI₂ with iron, nickel, silver, copper or manganese [10, 11].

Cadmium doping facilitates PbI₂ crystals growth, mainly in the form of plates as long as up to 15 mm, as wide as up to 5 mm and as thick as 0.1 mm, while also in the form of tapes as long as up to 12 mm, as wide as 0.2-2 mm and as thick as up to 0.1 mm. Besides the plate-like and tape-like single crystals, growth of elongated-shape crystals with sharpened ends, crystals having shape of concave tapes, as well as compound formations of tape-like crystals and concretions of plates and tapes is observed.

The increase of Cd content in burden material from 0.1 to 0.5 at. % does not influence PbI₂ flow (Table 1). Dopant content in single crystals is of the same order as in the alloy. Growing crystals are mainly plate-shaped having area of up to 10×3 mm².

Table 1 – Doping of PbI₂ with cadmium (CdI₂)

at. % Cd in the alloy (in the growth charge)	Mass transfer rate $\cdot 10^{-5}$, mol/(m ² s)	Characteristics
0.5	4.4	Single crystals 10×3 mm ² in area; ≈ 0.2 at. % Cd
1	2.93	Single crystals 9×2 mm ² in area; $\approx 0.2-0.5$ at. % Cd
2	2.51	Crystallization zone extended into the low-temperature area; ≈ 0.5 at. % Cd
5.5	2.05	Growth zone is wide. Lower-size crystals 5×1 mm ² ; ≈ 1 at. % Cd. The growth zone for transparent CdI ₂ crystals at $T = 590$ K is formed
10	1.89	Crystals 2×1 mm ² in area; $\approx 2-3$ at. % Cd
30	1.47	In crystallization zone light-yellow crystals; ≈ 10 at. % Cd

Table 2 – Temperature influence upon Cd-doping

at. % Cd in the alloy (in the growth charge)	Mass transfer rate $\cdot 10^{-5}$, mol/(m ² s)	Temperature of cold part of the ampoule, K	at. % Cd in the crystals
5	2.14	590	2
5	2.16	620	3.2

The mass-transfer rate decreases from $4.4 \cdot 10^{-5}$ to $2.05 \cdot 10^{-5}$ mol/(m²s) with dopant content growth in the alloy from 0.5 to 5.5 at. %, while it can be explained by the increase of CdI₂ partial pressure in the system. Due to cadmium concentration of 2 at. % the extension of crystallization zone to the low-temperature area occurs. Starting from cadmium concentration in source material of 5 at. %, the formation of CdI₂ transparent single crystals additional growth zone is observed in the cold part of the ampoule at 590 K. The concentration of cadmium in single crystals, which have grown in the zone of 650 K, is 5 times lower than in the source burden material, while the single crystals' dimensions decrease (Table 1).

To obtain substantially doped with cadmium PbI₂ single crystals, temperature of ampoule's cold part has been raised to 620 K, which resulted in the decrease of temperature gradient. The correction of growth conditions hardly brings change to mass-transfer rate (the flow increases by 5 %), but increases the cadmium content in the single crystals grown (Table 2). In Table 1, the characteristics of the obtained doped single crystals with dopant content in burden material of 10-30 at. % in the adjusted growing conditions are shown. Upon the increase of doping component content from 10 to 30 at. % the mass-transfer rate slowly decreases from $1.89 \cdot 10^{-5}$ to $1.47 \cdot 10^{-5}$ mol/(m²s), while the dopant content in crystals is 2-3 times lower than in burden material. In the crystallization zone, growth of small plate-like crystals (area $\approx 2 \times 1$ mm²) of light-yellow color, as well as polycrystalline material settling, is observed.

It is worth noting that on PbI₂ doped with transition metals (Fe, Ni, Mn) (with doping component concentration in the system exceeding 5 %), additional

crystallization zone in the area with higher temperatures of 670-770 K arises, while the increase of dopant content in single crystals source zone temperature increases (i.e. increased temperature gradient) [11].

Cadmium iodide, as well as lead iodide, belongs to wide-band gap-layered crystals (width of band gap for PbI₂ is $E_g \approx 2.3$ eV, while for CdI₂ – $E_g \approx 3.8$ eV [12]). The iodide structure is formed by layered packets, each of which contains two monolayers of metalloid atoms, and between each there is a monolayer of metal atoms present. Polytypism phenomenon is inherent to lead and cadmium iodides. Due to this phenomenon, modifications of the said substance differ just by the method of packing for identical layers. More than 250 polytypes of CdI₂ and nearly 50 polytypes of PbI₂ are known. The most widespread polytype for CdI₂ is 4H, whereas for PbI₂ crystals: 2H-polytype for growth of crystals from solutions, gels, melt and 4H and 12R-polytypes for growing from vapor phase [12, 13]. Crystals of 4H-polytype have a hexagonal crystal lattice, which is depicted by the space group of symmetry P63mc.

To determine the polytype, as well as the lattice parameters for the crystals grown, X-ray structure analysis of the crystals has been done. In Fig. 1, the X-ray diffraction spectra for the pure and Cd-doped PbI₂ crystals are presented. From the diffraction patterns obtained it can be determined that PbI₂ single crystals grown from the vapor phase in an enclosed system at over-stoichiometric iodine vapor pressure belong to 4H-polytype. This result coincides with the results of work [12]. According to [12], the Bi-, Cd- and Sn-doped lead iodide crystals have 4H and 4H + 12R structure. Thus, doping of PbI₂ with cadmium facilitates the crystals growth for 4H-polytype.

To determine grown crystals' lattice parameters, the diffraction patterns of powder samples were used. In Table 3, determined parameters of the lattice and unit cell volume for pure and Cd-doped crystals are presented. Increasing cadmium concentration till 3 at. % results in non-linear decrease of unit cell volume and parameter c of the lattice.

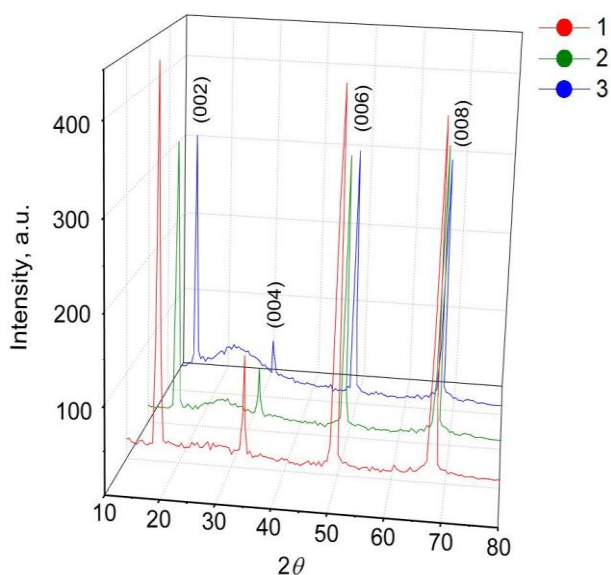
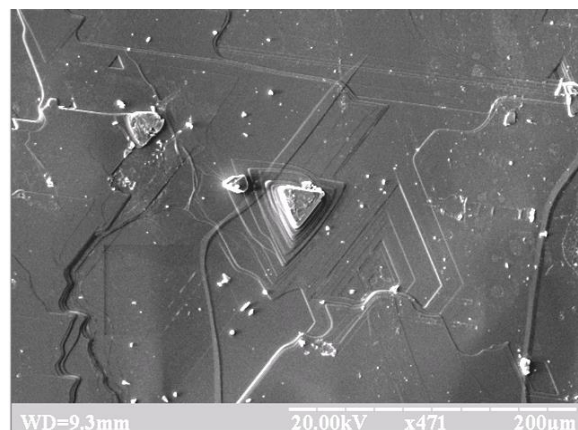


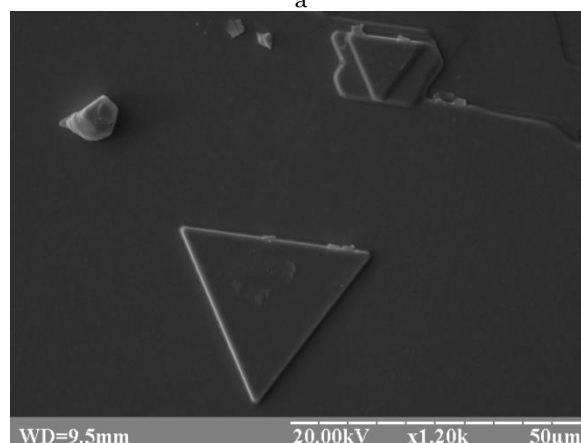
Fig. 1 – X-ray diffraction patterns of 1 – pure, 2 – 1.5 at. %, 3 – 3 at. % Cd-doped PbI₂ crystals

Table 3 – Lattice parameters and unit cell volume for PbI₂ crystals

at. % Cd in the crystals	Lattice parameter a , Å	Lattice parameter c , Å	Unit cell volume, Å ³
0	4.529	14.00	248.6
1.5	4.529	14.02	248.9
3	4.530	13.96	247.9



a



b

Fig. 2 – Morphological features of PbI₂ crystals doped with 3 at. % Cd (see text for explanation). The micrographs were obtained on a scanning electron microscope

The morphology of crystal faces' surface is a sensitive indicator of crystallization conditions for the completing stages of crystal formation, as well as for the degree and character of crystal defectiveness. In Fig. 2, PbI₂ (Cd-doped with 3 at. %) crystal face (0001) areas are shown, obtained by means of scanning electron microscope. Based on Fig. 2, one can see that the crystal's surface is sculptured with growth figures. In particular, these are observed: growth layers, sub-individuals, vicinals, microtwins and other growth accessories. In Fig. 2a, the growth of tangential rectilinear and curvilinear layers on the crystal face is observed, caused by the fact that in large crystal sizes a new layer appears sooner than the previous one is completed. The curvilinear growth layers are formed from rectilinear layers as a result of alignment in certain conditions of speed growth with tangential accretion in different azimuths.

In Fig. 2b, one of the most widespread defects of crystals grown from vapor phase – defects of packing in the form of a triangle – which are inherent to compounds, for which polytypism is typical, are shown. The mechanism of packing defects occurrence is explained by the fact that with the formation of a new atomic layer, small areas appear crystallographically inconsistent with the surrounding material.

The spectral dependences of optical absorption of pure and Cd-doped PbI_2 crystals at room temperature are shown in Fig. 3. Upon growth of cadmium concentration in the crystals studied, the shift of the intrinsic absorption edge into the short-wave area occurs.

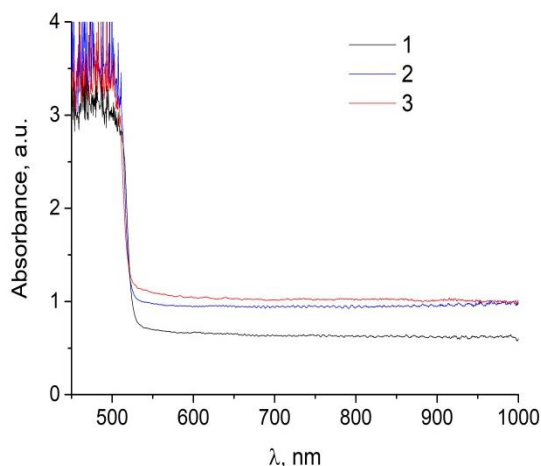


Fig. 3 – Absorption spectra of 1 – pure, 2 – 1.5 at. %, 3 – 3 at. % Cd-doped PbI_2 single crystals

By the crystal absorption spectra, the values of the band gap have been obtained by means of Tauc relation:

$$(\alpha h\nu) = A(h\nu - E_g)^{\frac{n}{2}},$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, A is the coefficient, which depends on the type of interband transition, E_g is the band gap, n is the index, which may take on different values depending on the type of optical transitions. As far as lead iodide is a direct band gap semiconductor, the index $n = 1$, i.e. corresponds to the direct allowed transitions.

In Fig. 4, the dependences of absorption in coordinates $(\alpha h\nu)^2$ on the photon energy $h\nu$ are shown. The crystals' band gap width was determined by means of extrapolation of the linear part of spectrum by straight line till crossing with energies axis. For pure PbI_2 crystals, the band gap width of 2.374 eV was found; this value agrees with the results of the works [14, 15]. In work [14], for lead iodide crystals grown by the chemical

vapor transport method, the band gap width of 2.346 eV at $T = 300$ K has been determined by using the absorption spectra. The band gap width of freestanding single crystal PbI_2 films is 2.38 eV, which has been defined in work [15] by the transmittance spectra.

The band gap width undergoes linear growth from 2.374 to 2.396 eV with cadmium content increase till 3 at. % (Fig. 4).

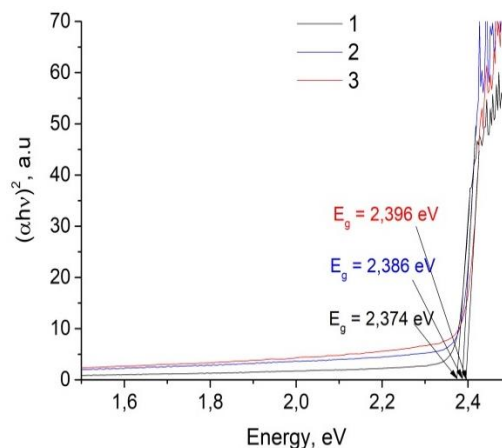


Fig. 4 – $(\alpha h\nu)^2$ versus photon energy: 1 – pure PbI_2 crystals; 2 – 1.5 at. % and 3 – 3 at. % Cd-doped PbI_2 crystals

4. CONCLUSIONS

The present results demonstrate that, when PbI_2 is doped with cadmium during vapor phase growth, dopant concentration in the source material from 0.001 to 0.5 at. % has little effect on the mass-transfer rate in the system, and Cd concentration in the single crystals is of the same order as in the source material. Single crystals grow mainly in the form of plates and tapes. Increase of cadmium content from 0.5 to 5.5 at. % in the source material leads to a two-fold decrease of mass-transfer rate, with Cd content in single crystals 5 times lower than in the source material and with decreased dimensions of plate-like single crystals. For the growth of Cd-doped crystals up to 10 at. %, it is necessary to lower the temperature gradient in the system due to increase of temperature at the cold end of the ampoule.

It was defined by X-ray diffraction spectra that Cd-doping facilitates PbI_2 crystals of 4H-polytype growth. With the increase of Cd concentration to 3 at. %, the unit cell volume and parameter c of the lattice subject to a non-linear decrease.

Upon growth of cadmium concentration to 3 at. % in PbI_2 crystals the shift of intrinsic absorption edge into the short-wave area occurs and it leads to a linear growth of the band gap width from 2.374 to 2.396 eV.

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Вирощування і властивості кристалів PbI_2 , легованих Cd

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Кристалізацією з парової фази у закритій системі при тиску парів надстехіометричного йоду одержані монокристали PbI_2 з вмістом кадмію 0,001-10 ат. %. Досліджено вплив концентрації кадмію у вихідній шихті і температурного градієнту на швидкість масоперенесення в системі та характеристики кристалів. Введення у систему PbI_2 -I₂ кадмію в діапазоні концентрацій від 0,001 до 0,5 ат. % при оптимальних умовах вирощування чистих кристалів PbI_2 зменшує швидкість масоперенесення не більше ніж на 2 %, концентрація Cd у вирощених монокристалах одного порядку з їх вмістом у вихідній шихті. Збільшення вмісту домішки у шихті від 0,5 до 5,5 ат. % зменшує швидкість масоперенесення вдвічі, вміст кадмію у монокристалах у 5 разів нижчий ніж у шихті, розміри монокристалів зменшуються. Зниження температурного градієнту в системі дозволило отримати кристали PbI_2 з вмістом кадмію до 10 ат. %. Легування Cd сприяє росту монокристалів переважно у формі пластин і стрічок. За спектрами дифракції X-променів встановлено, що одержані монокристали PbI_2 належать до 4H-политипу, визначені параметри ґратки і об'єм елементарної комірки чистих і легованих кристалів. Встановлено вплив домішки Cd на спектри поглинання PbI_2 . Зростання вмісту кадмію у кристалах до 3 ат. % супроводжується короткохвильовим зсувом краю власного поглинання і збільшенням ширини забороненої зони.

Ключові слова: Дийодид свинцю, Швидкість масоперенесення, Легування, Домішка кадмію, Дифрактограми, Спектри поглинання.