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Vapor Phase Growth and Properties of Mixed Layered $Pb_{1-x}Cd_xI_2$ Semiconductors

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$Pb_{1-x}Cd_xI_2$ crystals ($x = 0.1; 0.9$) have been obtained by crystallization from a vapour phase in a closed system at over-stoichiometric iodine vapour pressure. An alloy of CdI_2 and PbI_2 was used as a source of evaporation. As a result of X-ray diffraction studies, it has been found that the obtained crystals belong to 4H-polytype, the space symmetry group is $P6_3mc$. The lattice parameters and the unit cell volume of crystals have been determined: for $Pb_{0.9}Cd_{0.1}I_2$ $a = 4,529 \text{ \AA}$, $c = 13,96 \text{ \AA}$, $V = 247,9 \text{ \AA}^3$; for $Pb_{0.1}Cd_{0.9}I_2$ $a = 4,258 \text{ \AA}$, $c = 13,70 \text{ \AA}$, $V = 215,0 \text{ \AA}^3$. The morphology of $Pb_{1-x}Cd_xI_2$ solid solutions crystals has been studied by scanning electron microscopy. Grown light orange $Pb_{0.9}Cd_{0.1}I_2$ crystals have the shape of plates and ribbons, the surface of which is sculpted by growth figures. The transparent mixed $Pb_{0.1}Cd_{0.9}I_2$ crystals have been grown from the vapour phase only in the form of plates. The spectral dependences of the optical absorption of $Pb_{1-x}Cd_xI_2$ crystals at room temperature have been studied. The optical widths of the band gaps of the grown crystals have been determined from the absorption spectra using the Tauc relation.

Keywords: $Pb_{1-x}Cd_xI_2$ crystals, vapour phase, solid solutions, polytype, X-ray diffraction study, absorption spectra.

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Introduction

The layered wide-band gap semiconductors PbI_2 and CdI_2 form a continuous series of non-isoelectronic solid solutions $Pb_{1-x}Cd_xI_2$ (configuration of Cd^{2+} ions - $4d^{10}$ and Pb^{2+} ions - $5d^{10}6s^2$). Heterogeneous solid solutions of $Pb_{1-x}Cd_xI_2$ are characterized by intensive photo- and X-luminescence at room temperature and high radiation resistance, while it opens up a possibility of using these materials for the production of high efficient rapid-action non-cooled scintillation detectors of X- and γ - radiation [1, 2]. In [3], the possibility of using CdI_2 crystals with an optimal impurity concentration of Pb ~ 1.0 mol.% as a scintillator for the registration of α -particles was shown. Studies of PbI_2 nanostructures with a Cd content of up to 7.5 % have shown that they are a promising material for optoelectronic devices and ionizing radiation detectors. Cadmium doping intensifies the photoluminescence, increases electrical conductivity, and improves the radiation absorption property of lead iodide [4]. In PbI_2

crystals doped up to 2 at.% Cd in the process of the growth from vapour phase, a noticeable enhancement for the effect of magneto-photo-induced generation of the second optical harmonic is observed – in comparison with pure PbI_2 crystals, which opens up a principal possibility to create magneto-controlled laser radiation frequency multipliers on a basis of these materials [5]. Moreover, in solid substitution solutions of $Pb_{1-x}Cd_xI_2$ a unique opportunity to control the fundamental constant of exciton-phonon coupling by means of changing x component composition is realized [6]. Therefore, the study of layered mixed semiconductors $Pb_{1-x}Cd_xI_2$ is of scientific and practical interest.

Most of the published works are devoted to the study of the properties of $Pb_{1-x}Cd_xI_2$ solid solutions grown from melt the Bridgman-Stockbarger technique [1, 3] and grown from solutions [4]. The growth of $Pb_{1-x}Cd_xI_2$ crystals from the vapour phase and their properties have been insufficiently studied. The structure and micromorphology of CdI_2 dendritic single crystals 3 % doped (wt./wt.) with PbI_2 grown from vapour phase were

studied in [7]. The influence of Cd concentration in the $\text{PbI}_2\text{-I}_2$ system and technological regimes on the characteristics of crystals grown from the vapor phase has been studied in [8, 9].

The purpose of this work is to study the peculiarities of obtaining layered $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ semiconductors ($x = 0.1; 0.9$) from the vapour phase in a closed system at the vapour pressure of over-stoichiometric iodine, as well as the structure, morphology, and optical absorption of grown crystals.

I. Experimental

$\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ single crystals were grown from the vapour phase in a closed system at over-stoichiometric iodine vapor pressure according to the method described in detail in [8, 9].

Cadmium iodide (CdI_2) and lead iodide (PbI_2) were previously synthesized from separate components to grow crystals of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ solid solutions. An alloy of lead iodide and cadmium iodide of appropriate percentage and a capillary with iodine were loaded into a quartz ampoule with a diameter of $2.4 \cdot 10^{-2}$ m and a volume of $8 \cdot 10^{-5}$ m³, which was evacuated to 10^{-3} Pa and desoldered. In order to remove moisture and volatile oxides from the ampoule, iodine was in the quartz capillary during pumping, and the ampoule for 10 - 30 minutes warmed up to a temperature of 373 - 473 K. The sealing process was carried out at a temperature of 373 - 423 K, which made it possible to completely remove from the ampoule water vapour, which plays a significant role in the transport of the substance and affects the properties of the obtained single crystals. After opening the capillary with iodine by shaking, the ampoule was placed in a preheated two-zone furnace, which allowed to independently regulate the temperature of the source zone and the crystallization zone with an accuracy of 0.1 - 1 K. The alloy of iodides was located in the source zone, and a portion of iodine in the crystallization zone. Metal temperature equalizers were used to create a linear temperature gradient between the source zone and the crystallization zone. After the growing process, the ampoule was removed from the furnace, cooled to room temperature, opened and the obtained single crystals were selected.

In the course of the research, it was found that to obtain single crystals of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ solid solutions requires correction of growth conditions in comparison with the optimal conditions for growing pure crystals of lead iodide [8]. $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals were obtained in the following technological regime: source zone temperature $T_s = 870$ K, crystallization zone temperature $T_{cr} = 470$ K, the mass of over-stoichiometric iodine introduced into the system 90 mg, duration of the growing process 4.5 hours. To obtain $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ crystals, the zone temperatures were increased: $T_s = 920$ K, $T_{cr} = 510$ K. In [7], CdI_2 crystals doped with PbI_2 up to 3 % (wt./wt.) were grown from the vapour phase in a flow system at a lower temperature gradient: $T_s = 823$ K, $T_{cr} = 573 - 598$ K.

The component composition of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ solid solutions was determined by an X-ray microanalyzer "Camebax" from the French company "CAMECA". The analysis was performed on the L_α -lines at the

accelerating voltage 20 kV and the beam current $\approx 10^{-8}$ A.

X-ray powder diffraction patterns of the crystals were obtained using a STOE Transmission Diffractometer System STADI P. The following parameters and conditions were used in the X-ray diffraction experiments: $\text{Cu-K}\alpha_1$ radiation, a curved (111) Ge Johann-type monochromator working on a primary beam, $2\theta/\omega$ scanning mode, the angular range $5.0 - 96.665^\circ 2\theta$ for data collection (with the $0.015^\circ 2\theta$ step), a linear position-sensitive detector with the recording step $0.480^\circ 2\theta$ and the shooting time 120 s, the voltage $U = 40$ kV, the current $I = 30$ mA, and room temperature ($T = 17^\circ\text{C}$) measurement conditions. Analytical indexing of our samples and determination of their space group were performed using an N-TREOR09 device. The crystal structure was refined with a Rietveld method and a FullProf.2k software package (version 5.60), using a pseudo-Voigt profile function and isotropic approximation for the atomic-shift parameters.

The morphology of the grown crystals was investigated using optical microscope MBS-10 produced by VO "Rubin" and scanning electron microscope REM-106I produced by OJSC "Selmi".

Crystal absorption spectra in the range from 350 to 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.

II. Results and discussion

Lead and cadmium iodides have layer structures. The layer package of PbI_2 and CdI_2 crystals consists of three monolayers of I-Pb-I or I-Cd-I atoms, in which the monolayers of metalloid atoms are translationally nonequivalent. The thickness of the layer package PbI_2 is 0.7 nm [10], CdI_2 is 0.32 nm [11]. Inside the layered package, the atoms are bound together by a strong ionic-covalent bond, and weak van der Waals forces operate between the layers. Lead and cadmium iodides, like many other layered crystals, are characterized by the phenomenon of polytypism, in which various modifications of the substance differ only in the way they pack layered packages. About 250 CdI_2 polytypes and more than 50 PbI_2 polytypes are known. With different methods of growing CdI_2 crystals often get 4H-modification, which is stable at low and high temperatures. The most common polytype at the growing of PbI_2 from solutions, gels, and melt is the 2H-polytype, when grown from the vapor phase, crystals of 4H- and 12R-polytypes are most often obtained [10, 12].

To determine the polytype of grown $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ crystals and the parameters of their crystal lattice, X-ray diffraction analysis of samples was performed. Fig. 1 shows the X-ray diffraction pattern of a powder sample of $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ crystals. Reflexes on the X-ray diffraction patterns of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ crystals at $x = 0.1$ and $x = 0.9$, grown from the vapour phase in a closed system at over-stoichiometric iodine vapour pressure, are described by

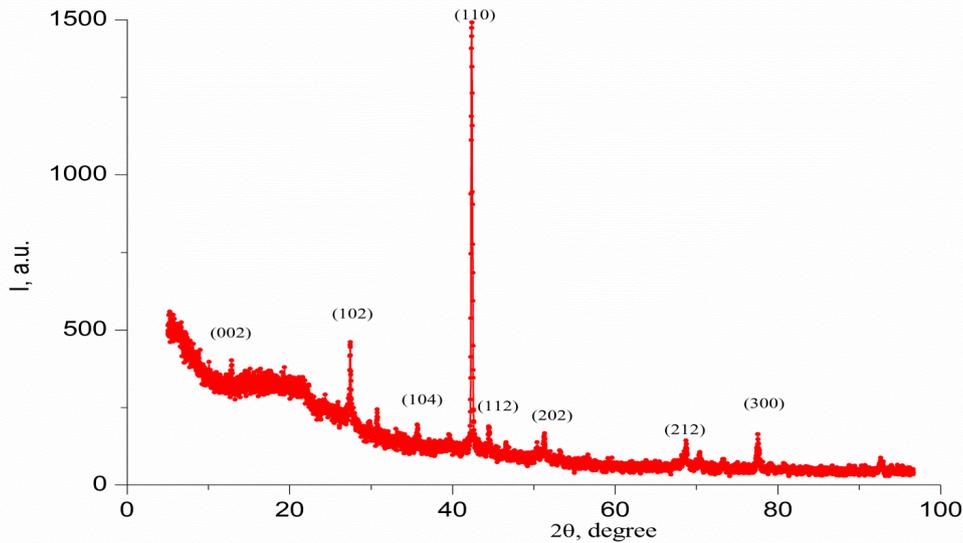


Fig. 1. X-ray diffraction pattern of $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ crystals.

4H-modification, space group of symmetry $P6_3mc$. This result is consistent with studies conducted in [7, 9, 12]. In [7], X-ray diffraction analysis of pure and PbI_2 doped crystals of CdI_2 grown from the vapour phase was performed, and it was found: 100 % of the studied pure CdI_2 crystals of 4H-polytype; 48 % of lead iodide-doped crystals are 4H- polytypes, and 52 % are a mixture of 4H+12R- polytypes. X-ray diffraction studies of pure and Cd doped up to 1.5 at.% and 3 at.% lead iodide crystals obtained by crystallization from the vapour phase in a closed system at vapour pressure of over-stoichiometric iodine revealed that the crystals belong to the 4H-polytype. According to studies conducted in [12], CdI_2 crystals doped with Pb, Bi, Sn, Zn belong to the 4H- or 6H- polytype, and PbI_2 crystals doped with Cd, Bi, Sn have 4H- and 4H+12R- structures.

PbI_2 and CdI_2 crystals are characterized by the same structural type of lattice and similar crystal lattice parameters. According to Crystallography Open Database in the case of 4H- polytype structure, $P6_3mc$ space symmetry group, lattice parameters, and unit cell volume for CdI_2 crystals [13]: $a = 4.24 \text{ \AA}$, $c = 13.67 \text{ \AA}$, $V = 212.829 \text{ \AA}^3$; for PbI_2 [14]: $a = 4.557 \text{ \AA}$, $c = 13.958 \text{ \AA}$, $V = 251.022 \text{ \AA}^3$.

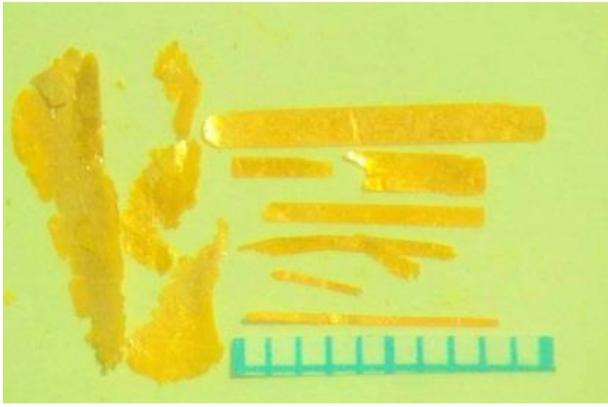
The lattice parameters and the volume of the unit cell for crystals $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$: $a = 4.258 \text{ \AA}$, $c = 13.70 \text{ \AA}$, $V = 215.0 \text{ \AA}^3$; for crystals $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$: $a = 4.529 \text{ \AA}$, $c = 13.96 \text{ \AA}$, $V = 247.9 \text{ \AA}^3$ determined by the results of X-ray diffraction studies. The increase in the lattice parameters a and c and the unit cell volume with increasing lead content in layered mixed semiconductors $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ can be explained by the substitution of Cd atoms by Pb atoms in the structure, i.e. the formation of solid substitution solutions.

Important information about crystal growth can be obtained by studying the morphology of crystals, which includes the final shape, surface condition and degree of imperfection of the crystal. The form of growth and defects of crystals are determined by their individual characteristics (ideal and real structure) and growing conditions. On the other hand, the form of growth affects

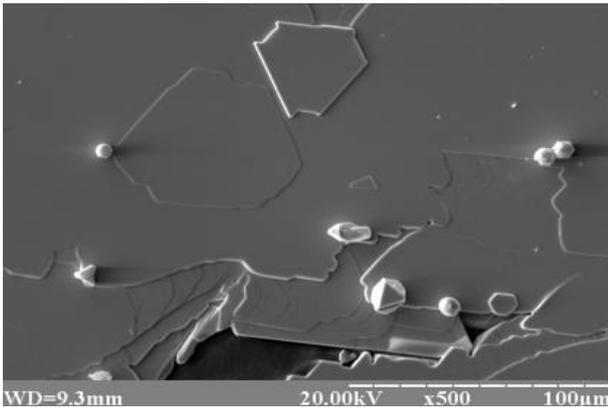
the quality and perfection of crystals [15].

Fig. 2a shows a general appearance of layered mixed $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals. Light orange $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals have the form of ribbons and plates of irregular shape, as well as splices of ribbons and plates. Dimensions of plates: length 5 - 12 mm, width 3 - 7 mm, thickness up to 0.1 mm; ribbons dimensions: length 3 - 10 mm, width 0.4 - 1.5 mm, thickness up to 0.1 mm. Transparent $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ crystals from the vapour phase grow only in the form of irregularly shaped plates 3 - 6 mm long, 2.5 - 3 mm wide, up to 0.1 mm thick. Increasing the concentration of CdI_2 in the vapour phase promotes the growth of crystals of solid solutions in the form of plates, increases the number of grown crystals, and reduces their surface area. It should be noted that pure PbI_2 crystals grow under optimal conditions from the vapour phase in a closed system at a vapor pressure of over-stoichiometric iodine, mainly in the form of ribbons [16]. In [7], the micromorphology of pure and PbI_2 -doped CdI_2 crystals grown from the vapour phase in the form of dendrites was studied and it was found that the dislocation density is higher in doped crystals.

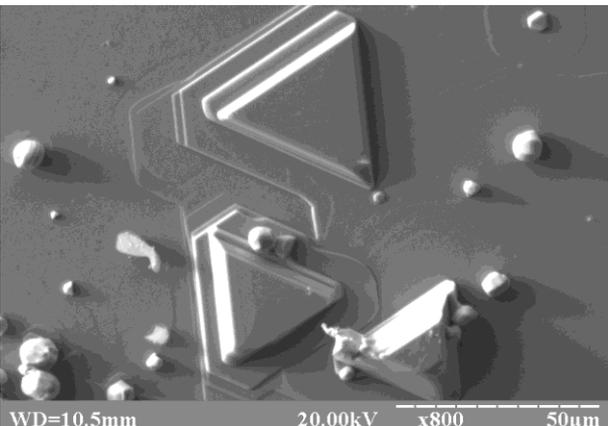
The surface of the grown crystal reflects the last stages of crystal formation. The surface of a real crystal always contains growth layers, stairs, vicinals, hatching, subindividuals, and other growth accessories. Fig. 2b shows the surface of the $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystal. The upper layers of growth have the form of irregular hexagons, which turn into triangles due to growth anisotropy: planes that move at the lowest normal speeds, growing tangentially, displace fast-growing faces. Also in Fig. 2b on the face of the crystal (001), there are thin curved layers of growth, characteristic of faces with weak bonding forces. At the bottom of Fig. 2b kinematic (shock) waves of the density of stairs are observed, which is a collective effect, caused by the influence on the movement of the echelon of stairs of various disturbances (temporary increase in over-saturation, temperature, the disintegration of a large stair, etc.). Echelons of moving stairs are formed because at the big sizes of crystals the new layer of growth is formed earlier the previous layer will come to the end.



a



b



c

Fig. 2. Morphological features of $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals: a – general appearance of crystals grown from the vapor phase (division 1 mm); b – growth layers, kinematic waves of stairs density; c – vicinals.

Fig. 2c shows vicinals (growth hillocks) in the form of triangular truncated pyramids. Layers that reflect the symmetry of the face appear on the surface of the vicinal. The appearance of vicinals can be explained by the diffusion inhomogeneity of the field near the crystal surface.

Fig. 3 shows the absorption spectra of mixed semiconductors $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ crystals at room temperature. Increasing the concentration of Cd causes the shift of the absorption edge in the short-wavelength region.

The optical band gap of solid solutions of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ was determined by the absorption spectra using the Tauc

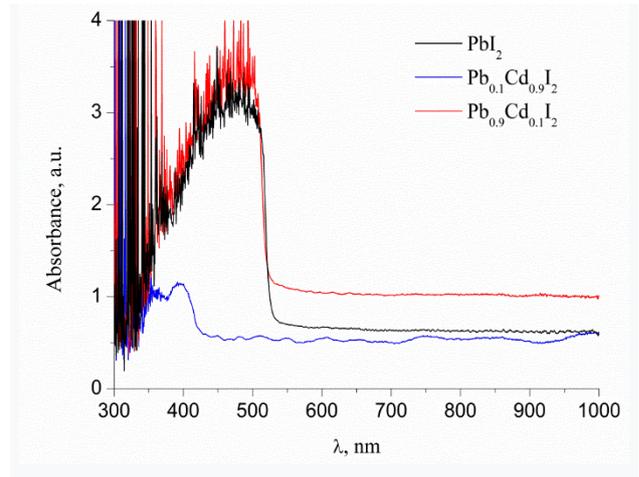


Fig. 3. Absorption spectra of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ crystals.

equation for electronic transitions between the valence band and the conduction band:

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

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 CdI_2 is an indirect band gap semiconductor, the index $n = 4$, i.e. corresponds to the indirect allowed transitions. PbI_2 is a direct band gap semiconductor, that is $n = 1$, it corresponds to direct allowed transitions.

Fig. 4 for $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals and Fig. 5 for $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ solid solutions show the spectral dependence of the absorption in the coordinates $(\alpha h\nu)^2$ on the photon energy ($h\nu$). The band gap width of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ crystals was determined by means of extrapolation of the linear part of the spectrum by straight-line till crossing with the energies axis.

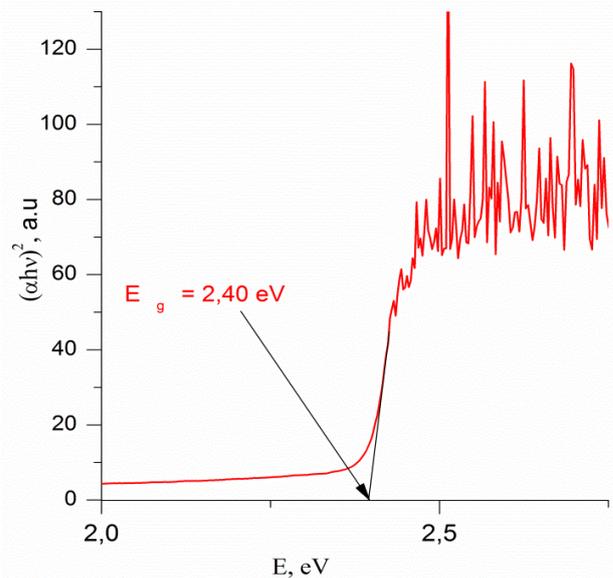


Fig. 4. $(\alpha h\nu)^2$ versus photon energy of $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals.

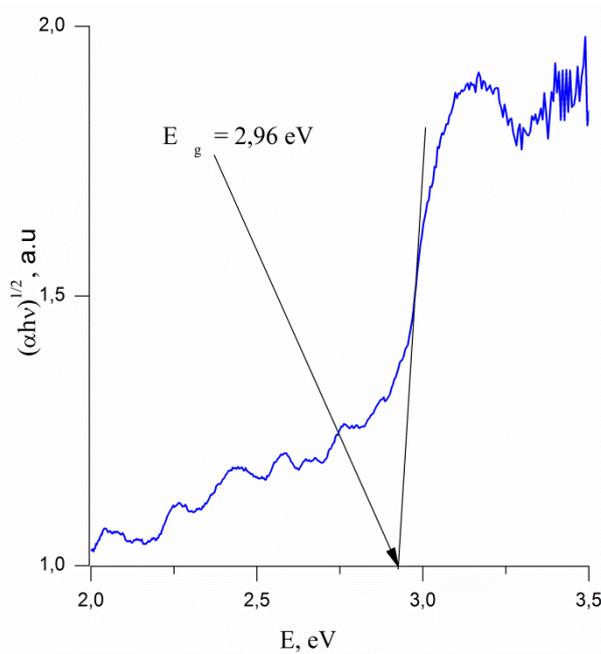


Fig. 5. $(\alpha h\nu)^{1/2}$ versus photon energy of $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ crystals.

For $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals, the value of the band gap optical width $E_g = 2.40$ eV was obtained, and for solid solutions $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ $E_g = 2.96$ eV. The optical width of the band gap increases with increasing cadmium content in the crystals. The band gap width for pure PbI_2 crystals is determined by the absorption spectra at room temperature $E_g = 2.346$ eV [17], and pure CdI_2 crystals $E_g = 3.2$ eV [18]. The nonlinearity of the dependence of the band gap width as a function of the composition of the

solid solution can be explained by the nonisoelectronicity of the $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ solid solutions.

Conclusions

To obtain crystals of solid solutions of $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ ($x = 0.1; 0.9$) from the vapour phase in a closed system, it is necessary to correct the technological regimes of growth compared to the optimal conditions for obtaining pure PbI_2 crystals. $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ crystals have been grown at higher temperatures of the source zone and the crystallization zone compared to $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals.

By means of X-ray diffraction spectra, it has been defined that $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ crystals belong to 4H- polytype. The lattice parameters and the volume of the unit cell of the grown crystals have been determined. Layered $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ crystals grow from the vapor phase only in the form of plates, and $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ crystals grow in the form of plates and ribbons.

The optical width of the band gap of the obtained crystals have been determined from the absorption spectra at room temperature: for $\text{Pb}_{0.9}\text{Cd}_{0.1}\text{I}_2$ – $E_g = 2.40$ eV; for $\text{Pb}_{0.1}\text{Cd}_{0.9}\text{I}_2$ – $E_g = 2.96$ eV.

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О.В. Рибак, М.В. Чекайло, Н.Т. Покладок

Вирощування з парової фази і властивості змішаних шаруватих напівпровідників $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$

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Кристали $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ ($x = 0,1; 0,9$) одержані кристалізацією з парової фази в закритій системі при тиску парів надстехіометричного йоду. Сплав CdI_2 і PbI_2 використовували як джерело випаровування. У результаті рентгеноструктурних досліджень встановлено, що одержані кристали належать до 4Н-політипу, просторова група симетрії $R\bar{6}3mc$. Визначені параметри ґратки і об'єм елементарної комірки кристалів: для $\text{Pb}_{0,9}\text{Cd}_{0,1}\text{I}_2$ $a = 4,529 \text{ \AA}$, $c = 13,96 \text{ \AA}$, $V = 247,9 \text{ \AA}^3$; для $\text{Pb}_{0,1}\text{Cd}_{0,9}\text{I}_2$ $a = 4,258 \text{ \AA}$, $c = 13,70 \text{ \AA}$, $V = 215,0 \text{ \AA}^3$. Морфологія кристалів твердих розчинів $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ досліджена методом скануючої електронної мікроскопії. Вирощені світло-оранжеві кристали $\text{Pb}_{0,9}\text{Cd}_{0,1}\text{I}_2$ мають форму пластин і стрічок, поверхня яких скульптурована фігурами росту. Прозорі змішані кристали $\text{Pb}_{0,1}\text{Cd}_{0,9}\text{I}_2$ вирощені з парової фази лише у формі пластин. Досліджені спектральні залежності оптичного поглинання кристалів $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$ при кімнатній температурі. За спектрами поглинання визначені оптичні ширини заборонених зон вирощених кристалів за допомогою співвідношення Тауца.

Ключові слова: кристали $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$, парова фаза, тверді розчини, політип, рентгеноструктурне дослідження, спектри поглинання.