

Influence of stoichiometric cadmium excess on photoelectret properties of $\text{CdI}_2\text{-PbI}_2$ crystal system

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Simultaneous study of thermostimulated depolarization and spectral sensitivity of photoelectret state of the binary $\text{CdI}_2\text{-PbI}_2$ crystal system allowed to separate characteristics of the trapping centers associated with one- and two-dimensional nanocrystalline inclusions of PbI_2 in CdI_2 matrix. Presence of non-stoichiometric cadmium in the studied layered system and its mobility lead to complete disappearance of two maxima — of thermostimulated depolarization and spectral sensitivity of the photoelectret state belonging to one-dimensional PbI_2 nanocrystals. Mechanisms of non-stoichiometric cadmium influence on one- and two-dimensional PbI_2 nanocrystalline inclusions in CdI_2 crystal lattice are proposed.

Keywords: layered crystals, nanocrystal, photoelectret state, thermostimulated depolarization, contact phenomena.

Одновременное исследование термостимулированной деполяризации и спектральной чувствительности фотоэлектретного состояния бинарной кристаллической системы $\text{CdI}_2\text{-PbI}_2$ позволило разделить характеристики центров захвата, обусловленных одно- и двумерными нанокристаллическими включениями PbI_2 в матрицу CdI_2 . Присутствие нестехиометрического кадмия в исследуемой слоистой системе и его подвижность приводят к полному исчезновению как максимума термостимулированной деполяризации, так и максимума спектральной чувствительности фотоэлектретного состояния, принадлежащих одномерным нанокристаллам PbI_2 . Предложены механизмы влияния нестехиометрического кадмия на одно- и двумерные нанокристаллические включения PbI_2 в кристаллической решетке CdI_2 .

Вплив стехіометричного надлишку кадмію на фотоелектретні властивості кристалічної системи $\text{CdI}_2\text{-PbI}_2$. *О.В.Гальчинський, В.В.Вістовський, Н.В.Глоковська, Л.І.Ярицька, Т.М.Демків.*

Одночасне дослідження термостимульованої деполяризації та спектральної чутливості фотоелектретного стану бинарної кристалічної системи $\text{CdI}_2\text{-PbI}_2$ дозволило розділити характеристики центрів захоплення, зумовлених одно- та двовимірними нанокристалічними включеннями PbI_2 в матрицю CdI_2 . Присутність нестехіометричного кадмію у шаруватій системі, що досліджувалася і його рухливість приводять до повного зникнення як максимуму термостимульованої деполяризації, так і максимуму спектральної чутливості фотоелектретного стану, що належать одновимірним нанокристалом PbI_2 . Запропоновано механізми впливу нестехіометричного кадмію на одно- та двовимірні нанокристалічні включення PbI_2 у кристалічній ґратці CdI_2 .

1. Introduction

CdI_2 and PbI_2 layered crystals occupy an intermediate position between classical dielectrics of A_1B_7 type and A_2B_6 semiconductors by their physical properties. They can substantially change their properties due to polytypism and ability to intercalate, what is of considerable practical interest.

Coexistence of strong ion-covalent bonding within the I-Cd(Pb)-I layer and weak interlayer interactions creates the basis for synthesis of semiconductor compounds with various physical properties — from ionizing radiation detectors [1, 2] to devices for holographic recording of information [3, 4].

Our previous studies of luminescence and photoelectric properties of $\text{CdI}_2\text{-PbI}_2$ system and crystal surface by atomic force microscopy have established that PbI_2 is embedded in CdI_2 crystal lattice in the form of nanocrystalline inclusions [5, 6], the shape of which is well described by a microcylinder model [7]. In this model, one- and two-dimensional nanocrystals are distinguished by the ratio of cylinder radius and its height: long rods of small radius and tablets of small thickness, respectively.

In this paper, investigation of spectral sensitivity of photoelectret state (SS PES) and thermally stimulated depolarization curves (TSD) of $\text{CdI}_2\text{-PbI}_2$ crystal system was carried out, and influence of excess cadmium on these characteristics was studied.

2. Experimental

In our work, crystals grown by Bridgman-Stockbarger method from the salt of cadmium iodide, purified by a complex of physical and chemical methods including 40-fold zone fusion were investigated. Spectral analysis of purified raw material didn't reveal lead impurity in it, but optical and luminescence characteristics of grown crystals make it possible to estimate its concentration as $\leq 0.001\%$. In addition, crystals doped with lead iodide and cadmium (up to 0.01 mol.%) were also studied.

To produce PES, samples were exposed to light from the region of long-wave edge of CdI_2 self-absorption (355 nm) at low temperatures in the electric field in order to provide spatial generation of electron-hole pairs. After photopolarization procedure, the sample was short-circuited and stored in PES. Curves TSD of photopolarized samples were obtained by recording currents of the electret state discharge upon heating of the crystal at constant velocity.

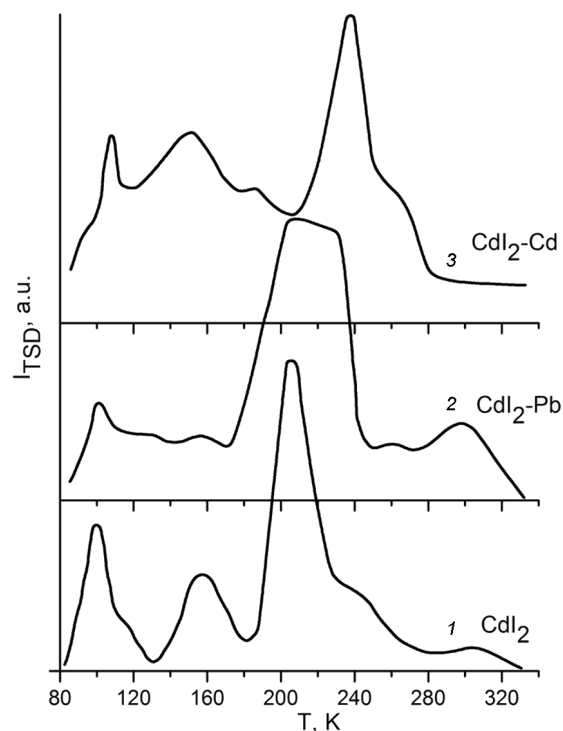


Fig. 1. Curves of thermostimulated depolarization of undoped (1) and doped by lead (2) and cadmium (3) CdI_2 crystals.

Spectral sensitivity of photoelectret state was determined in the process of photodepolarization by scanning low-intensity irradiation with a constant number of light quanta from the region of sample photosensitivity, starting from long-wave edge. At the same time, current of photodepolarization was registered, which is proportional to spectral sensitivity on the assumption of slight release of initial photoelectret charge.

3. Results and discussion

Fig. 1 shows TSD curves of undoped (curve 1) and doped with lead and cadmium (curves 2 and 3, respectively) CdI_2 crystals. Qualitative similarity of curves 1 and 2, obviously, is due to the fact that undoped CdI_2 crystals contain traces of lead impurity. Doping with lead allows us to recognize the effect of activating impurity. In particular, comparison shows that maxima at 100, 160, 200 and 300 K are present in both cases. Difference between TSD curves of $\text{CdI}_2\text{-PbI}_2$ crystals reveals itself in the growth of intensity and widening of maxima in the range of 180–240 K, as well as at 300 K.

Since crystals with non-stoichiometric cadmium were grown from the same CdI_2 salt as undoped crystals, they contained traces of the PbI_2 impurity. Dominant TSD

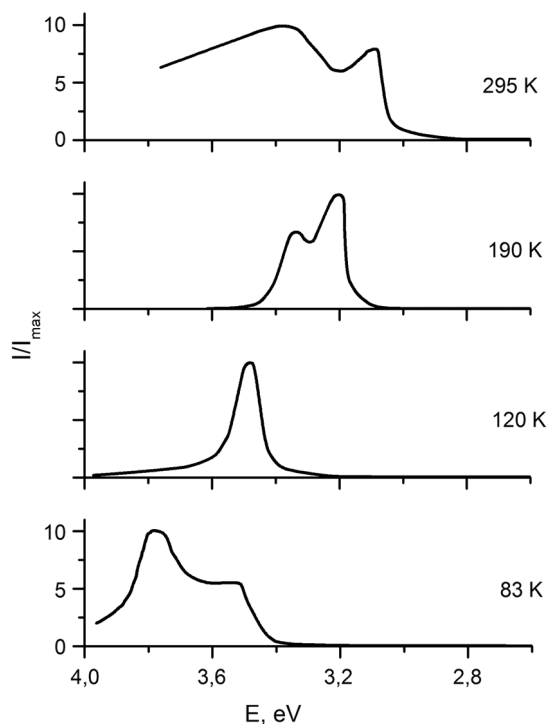


Fig. 2. Spectral sensitivity of photoelectret state of CdI_2 crystals with traces of lead impurities at different temperatures.

maxima of such crystals (curve 3) are located at 110, 150 and 235 K, stair-like regions are present at 180 and 260–270 K. Comparison of curves 1 and 3 demonstrates that the effect of cadmium excess on characteristics of trapping centers in CdI_2 crystals associated with PbI_2 impurity is that TSD maxima at 100, 200 K and also above 280 K disappear and the intensity of higher-temperature maxima at 110, 240 and 260 K increases.

Spectral sensitivity of CdI_2 crystal with traces of lead at 83 K is given by maximum at 3.8 eV (direct band-to-band transitions) and step at 3.5 eV (indirect transitions in CdI_2) (Fig. 2). The first maximum disappears already at 120 K, and the step converts to a clear maximum, which position, with increasing temperature, shifts to 3.4 eV and disappears after 220 K. Impurity maximum at 3.23 eV associated with nanocrystalline inclusions of PbI_2 arises at 140 K and is present in the spectra up to 280 K. Within the range of 280–295 K, the broad maximum at 3.4 eV located at CdI_2 self-absorption edge becomes predominant in the SS PES. At 295 K, 3.1 eV maximum of SS PES originates, which intensity increases at 305 K, and the nature is associated with the influence of dislocations [5].

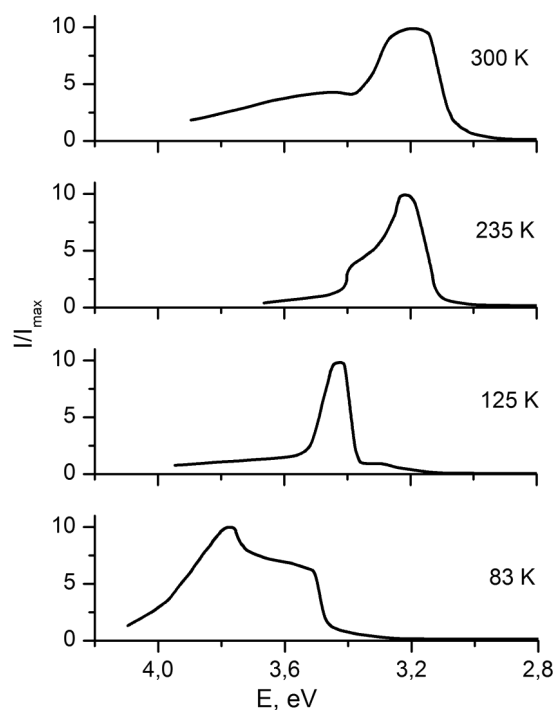


Fig. 3. Spectral sensitivity of photoelectret state of CdI_2 crystals with excess cadmium at different temperatures.

SS PES curves of CdI_2 crystals with cadmium excess (Fig. 3) at 83 K possess maxima within the band-to-band transitions (3.5–3.8 eV). When temperature rises from 125 to 235 K, maximum 3.23 eV becomes larger similar to the case of undoped crystals. Wide photosensitivity maximum at 3.2 eV and 3.5 eV step within band-to-band transitions are observed in CdI_2 -Cd crystals at room temperature. Spectral sensitivity of lead-doped CdI_2 crystals at 83 K (Fig. 4) consists of two maxima 3.8 and 3.5–3.3 eV. At 153–203 K temperatures, narrow maxima of SS PES are located at 3.35 and 3.15 eV. At higher temperatures, low-energy peak dominates, its position at 315 K is shifted to 2.9 eV, inflexions are observed at 3.2 and 3.1 eV.

CdI_2 - PbI_2 crystal system consists of isomorphous compounds belonging to the structural type of cadmium iodide in which layers of metal ions are located between two layers of iodine ions. One-dimensional impurity PbI_2 crystals are localized near linear defects of cadmium iodide structures (dislocations); two-dimensional nanocrystalline inclusions 4H-PbI_2 are located on (0001) crystallographic planes of cadmium iodide, their optical characteristics are similar to corresponding PbI_2 single crystals [8].

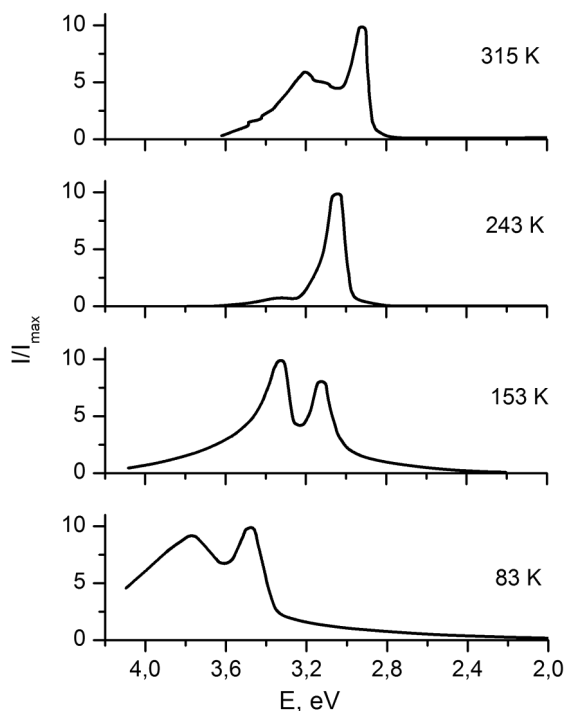


Fig. 4. Spectral sensitivity of photoelectret state of lead-doped CdI_2 crystals at different temperatures.

Experimental results presented above allow us to analyze the properties of two-dimensional PbI_2 nanocrystals in cadmium iodine matrix by comparing characteristics of lead-doped crystals and specially not doped crystals containing "traces" of lead impurities (Fig. 2, 4). The most significant feature of two-dimensional PbI_2 nanocrystals in CdI_2 crystal lattice is the dependence of SS PES on impurity concentration. In the presence of lead impurity "traces" in SS PES, high-energy activator exciton 3.2 eV band dominates. Its spectral position doesn't depend on temperature. In lead-doped crystal there is minimum of SS PES in this spectral region. Clear intensive maximum is predominant, its position shifts from 3.1 (at 150 K) to 2.9 eV (at 315 K), what may be related to interband transitions in PbI_2 inclusions.

Comparing TSD and SS PES curves, it can be noted that certain temperature intervals of the former correspond to characteristic maxima of the latter. In the first approximation, four temperature intervals are observed: low-temperature (100–120 K), around 160 K, in the range of 190–240 K and in the vicinity of room temperature (see Table). Positional association shows that in investigated $\text{CdI}_2\text{-PbI}_2$ system there are at least four main types of trapping centers responsible for photoelectret state genera-

Table. Fitting of spectral sensitivity of $\text{CdI}_2\text{-PbI}_2$ crystal photoelectret state to certain temperature intervals of thermally stimulated depolarization maxima

TSD, K	100–120	160	190–240	295–305
SS PES, eV	3.8	3.6–3.35	3.2	3.1

tion. According to SS PES characteristics, two low-temperature centers are associated with CdI_2 lattice, the third and fourth appear due to PbI_2 nanocrystalline inclusions and dislocations, respectively. It should be noted that in CdI_2 crystals with traces of PbI_2 impurity 3.2 eV maximum is prevailing in the third temperature range. It is owing to PbI_2 high-energy exciton, which spectral position practically doesn't depend on temperature. In lead-doped CdI_2 crystal minimum is observed under such conditions and beginning from 153 K there appears maximum 3.15 eV, which shifts to 2.9 eV at 315 K. Such spectral characteristics may belong to optical transitions to lower conduction band of two-dimensional PbI_2 nanocrystals.

Thus, our studies allowed to separate characteristics of one- and two-dimensional PbI_2 nanocrystals. One-dimensional crystals are associated with dislocations that determine high-temperature TSD maximum at 295–305 K. In the 190–240 K range, high-energy exciton (at the lowest impurity concentration) or optical interband transitions of two-dimensional PbI_2 nanocrystals (with increasing concentration of the latter) are observed.

Comparison of properties of undoped cadmium iodide crystals and cadmium-rich crystals from the same raw material shows significant effect of the latter on one-dimensional PbI_2 nanocrystals in cadmium iodide matrix. It follows from our results that presence of non-stoichiometric cadmium impurity leads to complete disappearance of TSD maximum (Fig. 1) and SS PES maximum (Fig. 3) belonging to one-dimensional nanocrystals.

Non-stoichiometric cadmium also affects the characteristics of two-dimensional PbI_2 crystals: TSD maximum at 202 K disappears and higher-temperature maximum at 240 K come into existence, as well as redistribution of intensity of low-temperature maxima in the range of 90–110 K is observed. Authors of [9] suggest a model of hole center associated with cationic lead vacancy for trapping center at 202 K. In the presence of non-stoichiometric cadmium, the latter can fill it, destroying the existing hole trapping center. In the same work, TSD

maximum 110 K was ascribed to $Pb^{++}e$ center. It is easy to see that the presence of non-stoichiometric cadmium impurity near this center will promote electron trapping by the latter.

Shift of TSD maxima in CdI_2 crystals with non-stoichiometric cadmium, typical for the case of two-dimensional PbI_2 nanocrystalline inclusions, may be due to formation of deeper trapping centers in the metal layer of investigated crystals, which include both lead impurities and non-stoichiometric cadmium.

It should be noted that below room temperature CdI_2 -Cd crystals exhibit significantly larger dark depolarization than in CdI_2 crystals. Its kinetics doesn't change with excitation of this crystal in wide spectral range (2–4 eV) typical for polarization processes of non-electronic nature. This implies that cadmium ions in CdI_2 lattice are mobile.

Consequently, taking into account that CdI_2 layered crystals and PbI_2 inclusions are isostructural, cadmium and lead ions within metal layer will be located at a distance of the order of unit cell parameters in metal layer of corresponding crystals when the joint system is formed. Basing on the range of metal activity, electron, appearing at the boundary between them, will be localized on cadmium ions with such a contact. This effect allows us to explain disappearance of TSD maxima of one- and two-dimensional PbI_2 nanocrystals in the presence of non-stoichiometric cadmium in CdI_2 - PbI_2 .

4. Conclusions

Simultaneous study of TSD and SS PES in CdI_2 - PbI_2 crystal system allowed us to

separate characteristics of trapping centers associated with one- and two-dimensional PbI_2 nanocrystals in CdI_2 matrix. Four main types of trapping centers are proposed, which are responsible for PES formation in the studied system: two of them are related to CdI_2 lattice, the third and fourth are due to PbI_2 nanocrystals and dislocations, respectively.

It was established that the presence of non-stoichiometric cadmium impurity results in complete disappearance of both TSD and SS PES maxima that belong to one-dimensional PbI_2 nanocrystals. Possible models of excess cadmium influence on characteristics of two-dimensional PbI_2 crystals are considered.

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