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Deep acceptor trapping centers in CdI_2–PbI_2 crystal system

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The model of acceptor trapping centers which consists of Pb^{3+} ion and two atomic I^0 centers in the temperature range 200–270 K has been suggested. It was constructed on the basis of measurements of thermally stimulated depolarization and spectral sensitivity of photoelectret state in CdI_2 crystals with PbI_2 nanoinclusions.

На основании измерений термостимулированной деполяризации и спектральной чувствительности фотоэлектретного состояния кристаллов CdI_2 с нановключениями PbI_2 предложена модель акцепторных центров захвата в интервале температур 200–270 К в виде йона Pb^{3+} и двух атомарных центров I^0.

Глибокі акцепторні центри захоплення у кристалічній системі CdI_2–PbI_2. *О.В.Гальчинський, Н.В.Глосковська, Л.І.Ярицька.*

На основі вимірювань термостимульованої деполяризації та спектральної чутливості фотоелектретного стану кристалів CdI_2 з нановключеннями PbI_2 запропоновано модель акцепторних центрів захоплення в інтервалі температур 200–270 К у вигляді іона Pb^{3+} та двох атомарних центрів I^0.

1. Introduction

Layered systems are one of the most promising research objects in the physics of semiconductors and dielectrics. Cadmium and lead iodide crystals have been actively studied for over half a century, but the interest in these compounds is still high. Ultra-fast dosimetry of ionizing radiation [1–3], photo- and holographic information recording and read-out [4, 5], nonlinear optic processes [6, 7], photoelectret state existence [8], possibility of photovoltage generation [9] are among the main properties attractive to researchers. During the last two decades much attention is paid to lead iodide nanocrystals embedded in zeolite cells [10], polymers [11], and films [12].

Visualization of PbI_2 nanoscale inclusions in CdI_2 crystal matrix [13] has enabled the comparison of photoelectric properties of CdI_2–PbI_2 system and PbI_2 single crystals [8]. This work presents extension of such investigations to the temperature range 200–270 K.

2. Experimental

Crystals for our study were grown by Bridgman-Stockbarger method with the use of cadmium iodide salt purified by a set of physicochemical techniques, including 40 times zone melting. Spectral analysis of the raw material didn't show any lead impurity, but the optical and luminescence characteristics of the crystals allowed to estimate the Pb content at <0.001 %.

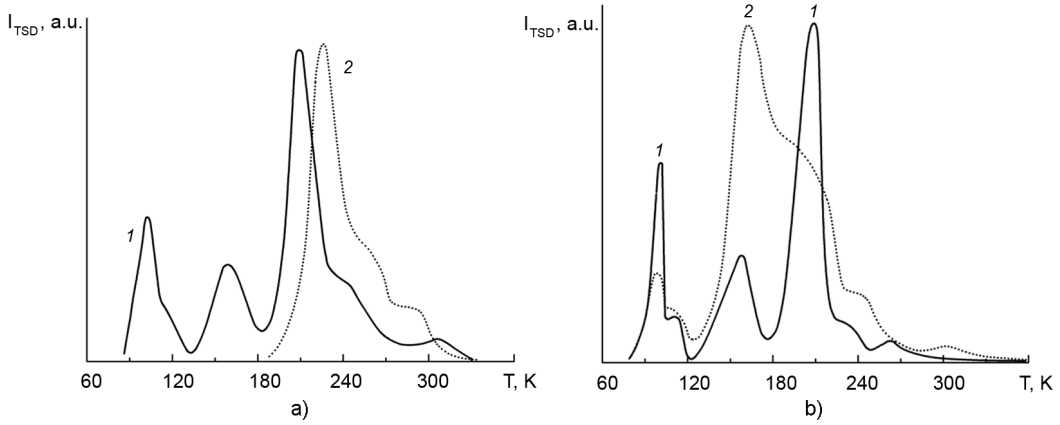


Fig. 1. a) TSD curves of CdI_2–PbI_2 crystals before (*1*) and after (*2*) relocalization of charge carriers to the deeper trapping centers; b) TSD curves of CdI_2–PbI_2 crystals: natural cleaved facet (*1*) and crystal cut-off (*2*).

To produce photoelectret state (PES), CdI_2–PbI_2 samples were exposed to the light from the region of CdI_2 low-energy intrinsic absorption edge (3.48 eV) at low temperature in the electric field. It was done in order to ensure spatial electron-hole pair generation. After photopolarization procedure, the sample was short-circuited and stored in the PES. Thermally stimulated depolarization (TSD) curves of photopolarized CdI_2–PbI_2 samples were obtained by means of registration of the electret state discharge current while the crystal was heated at a constant rate.

The spectral sensitivity of the photoelectret was determined during its depolarization by scanning low-intensity irradiation with a constant number of photons in the photosensitivity region of the sample, starting from the long-wavelength edge. In these experiments, we measured the photodepolarization current, proportional to spectral sensitivity when the release of the initial photoelectret charge was insignificant.

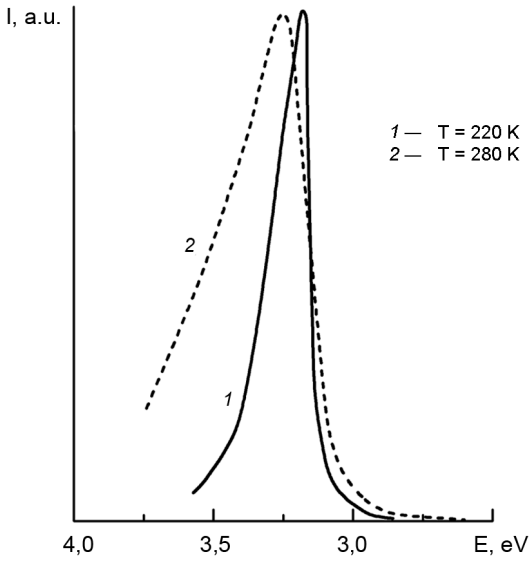


Fig. 2. Spectral sensitivity of the PES curves for CdI_2–PbI_2 crystal.

3. Results and discussion

Figure 1a presents the TSD curves of CdI_2 crystals containing ~ 10^{-4} mol.% PbI_2. There are peaks at 98, 112, 158, 202 and 266 K and inflections at 230 and 305 K (curve *1*). In [8], peaks at 112 and 158 K were identified as electron ones, and a peak at 202 K was attributed to the hole trapping center. In order to relocate hole charge carries, the crystal, previously polarized at 81 K, was heated up to 202 K in the electric field. During the process of heating, thermally released charge carriers are retained in near-electrode regions of the sample by the external electric field, and they cannot drift to the region where the opposite sign charges are localized. Therefore, retrapping of these carriers at the deeper centers prevails over their recombination. After such procedure, the charge density of the PES remains, mainly, the same, but the charge is now localized in the deeper traps (Fig. 1a, curve *2*). The TSD curve consists of an intense peak at 225 K and two inflections at 260 and 290 K, the presence of which in this experiment can be considered as evidence of their hole nature.

The TSD spectra for the samples which are oriented perpendicular and parallel to the crystallographic axis are given by curves *1* and *2*, respectively (Fig. 1b). They have essential differences in the investigated temperature range 200–260 K.

Spectral sensitivity of the PES curves for CdI_2 — 10^{-4} mol.% PbI_2 crystal at 220 K (curve *1*) and 280 K (curve *2*) is shown in Fig. 2. The peak at 3.23 eV related to PbI_2 nanoinclusions [12] dominates at 220 K. Further temperature increase to 290 K leads to the shift of this peak to the high-energy edge, and 3.4 eV band appearance. At the temperature values higher than 290 K, character of the PES spectral sensitivity changes dramatically, a new peak is seen at 3.1 eV [8], therefore, we have limited the temperature range of our studies to 270 K. The region of higher temperatures will to be investigated later.

As shown in our previous works [8, 13], PbI_2 impurity is incorporated into the crystalline lattice of CdI_2 in the form of nanocrystals (for CdI_2–PbI_2 crystals obtained from the melt by Stockbarger method). With this, at the phase boundary of two isomorphic layered crystals CdI_2 and PbI_2, heterojunction arises. Optical and photoelectric features of the system are defined by the narrow gap of PbI_2 nanocrystal.

For the investigated crystals, it was established that under excitation E = 3.23 eV in the low-temperature region, intense photoluminescence emerges. Its quenching and photoconductivity increase at 140–160 K are characterized by the same activation energy E = 0.17 eV [14]. The band at 3.23 eV is interpreted by us [13] as high-energy cationic exciton related to the PbI_2 nanoinclusions in CdI_2 lattice. Therefore, it can be supposed that the temperature interval 200–270 K corresponds to the region of non-radiative decay of the cationic exciton in PbI_2 nanocrystals.

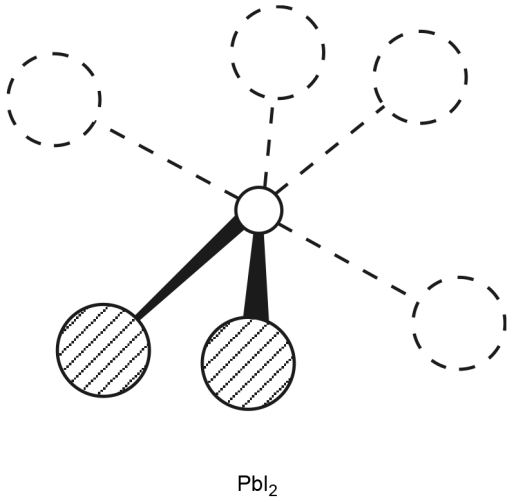
As 3.23 eV peak is the only dominating at 220 K in the curve of spectral sensitivity of the PES (Fig. 2), we suggest the following mechanism of the electron processes: cationic Frenkel exciton decays with formation of Pb^{3+} hole and an electron:

$$ex \rightarrow Pb^{3+} + e\ ,$$

i.e. the TSD peak at 225 K can be attributed to the Pb^{3+} hole trap (the electron would be captured at the deeper trapping centers).

At temperatures above 225 K, the hole Pb^{3+} transforms into the mobile hole which can move to I^- orbital, because the PbI_2 valence band top is composed of iodine *p*-orbitals to the 59 % [15]:

$$Pb^{3+} + I^- \rightarrow Pb^{2+} + I^0.$$



PbI_2

Fig. 3. Relationship between the crystal structure and PbI_2 molecule configuration [19].

So, the hole is localized at the deeper trap. The TSD peak at 260 K can correspond to such I^0 hole center. Indeed, in the EPR studies of the hole trapping centers of lead halides the complex resonance spectrum was observed [16]. It was formed due to the holes captured by the halide ion, X_2^- center, and holes trapped at more complex sites.

It was shown in [5, 17] that the trapping centers of PbI_2 nanocrystals are the hole ones in the temperature range 160–270 K. After prolonged preliminary irradiation, J.P.Zielinger et al. [5] have detected "photomemory" effect, increase in photosensitivity, neutralization of the hole traps, and residual conductivity in these crystals.

Effects of long-time relaxation and residual photoconductivity are associated with acceptor type centers in CdI_2–PbI_2 crystals in the temperature range 150–270 K. They were detected after preliminary irradiation of the samples within the limits of fundamental absorption [18]. Similarity of the effects and the same temperature range of their appearance may indicate that the trapping centers in CdI_2–PbI_2 are related to PbI_2 nanoinclusions. The authors of [18] consider that photoconductivity appears as a result of polarization charges formation due to orientation of the recombination centers. They have found that such center can be located in two equivalent sites of the crystalline lattice which may exchange their charges with the increase of irradiation intensity.

As the angular (non-linear) orientation of I–Pb–I molecular bonds is kept in the

crystalline lattice (Fig. 3) and I–Cd–I molecule is linear [19], it can be concluded that $I_{(1)}^0$ and $I_{(2)}^0$ trapping centers exist, bound with the same lead ion in PbI_2.

Such hole traps in CdI_2–PbI_2 crystals are of different temperature stability: the less deep trapping center is stable up to 220 K, the deeper —to 260 K [20]. Comparison of the TSD curves of the samples with different orientation in the range 180–225 K (Fig. 1b) enables us to assume that the peaks near 195 and 260 K correspond to the less $I_{(1)}^0$ and more deep $I_{(2)}^0$ trapping centers, respectively.

Similar centers were detected after photolysis of PbI_2 crystals. In the thermally stimulated photoconductivity spectra of these samples the peak at 195 K increase considerably and at 260 K — less sharply [21]. These results are consistent with our model: iodine atoms are the products of PbI_2 photolysis.

As one can see in Fig. 2 (curve *2*), the peak at 3.4 eV appears in CdI_2–PbI_2 spectral sensitivity of the PES in the range 230–290 K. It lies within the limits of CdI_2 indirect exciton absorption edge. T.Hayashi et al. [22] supposed that this peak arises due to the lead impurity in CdI_2 crystals. Besides, it was shown in [23] that under excitation at 80 K of CdI_2–PbI_2 crystal, spectral sensitivity of the PES contains 3.4, 3.23, 1.1 and 0.82 eV bands. On the basis of long-wavelength edge position of these bands optical activation energy of $I_{(1,2)}^0$ trapping centers were determined at 0.68 and 0.9 eV.

4. Conclusion

Thus, relying on the measurements of thermally stimulated depolarization and spectral sensitivity of photoelectret state for CdI_2 crystals with PbI_2 nanoinclusions in the temperature range 200–270 K, we have proposed the model of acceptor trapping centers in the form of Pb^{3+} ion and two atomic I^0 centers associated with the certain lead ion by the covalent bonds.

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