PHOTOLUMINESCENCE PROPERTIES OF LAYERED Pb$_{1-x}$Cd$_x$I$_2$ SOLID SOLUTIONS

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We have studied the photoluminescence spectra, including the time-resolved ones, and the photodiffusion spectra of PbI$_2$ crystals and Pb$_{1-x}$Cd$_x$I$_2$ solid solutions. It is established that these crystals have monopolar (hole) photoconductivity. The possibility of the formation of PbI$_2$ clusters with various sizes in solid solutions is shown. It is found that the value of splitting between Γ_3^-- and Γ_1^--exciton states in such clusters is 30 and 36 meV for $x = 0.50$ and $x = 0.70$, respectively. We have revealed that, for $x = 0.50$, the self-trapping excitons in PbI$_2$ clusters happens.

The crystals with layered structure, particularly PbI$_2$ and HgI$_2$, are promising materials for the development of radiation emission detectors on their basis [1–3]. The physical properties of PbI$_2$ crystals are less studied than those of HgI$_2$ crystals [2]. At the same time, PbI$_2$ is a more promising material for the development of radiation detectors due to its higher chemical stability [4, 5]. Such materials are suitable for the development of radiation detectors based on the direct transformation of a radiation signal in an electric signal and for the design of radiation scintillators. The use of Pb$_{1-x}$Cd$_x$I$_2$ solid solutions allows one to extend the spectral region and to improve the the characteristics of scintillators.

It is well known that the study of the optical and photoelectric properties of semiconductor crystals is important for the acquisition of information about their defect structure and peculiarities of the formation of solid solutions on their basis [6–8]. As distinct from semiconductor solid solutions on the basis of crystals of group A$^{\text{II}}$B$^{\text{VI}}$ [9–11], there occurs the nonisoelectronic replacement of components of the composition for Pb$_{1-x}$Cd$_x$J$_2$ [12]. For binary crystals PbJ$_2$, the upper valence band and the lower conduction band are mainly determined by Pb^{2+} ions. At the same time, the top of the valence band for CdJ$_2$ is determined by iodine, and the conduction band bottom is determined by Cd^{2+} ions. In this connection, the exciton states of PbJ$_2$ in Pb$_{1-x}$Cd$_x$J$_2$ are not directly transformed into the exciton states of CdJ$_2$.

In the present work, we study the photoluminescence (PL) spectra, including the time-resolved ones, and the spectra of a photodiffusion current (PDC) of semiconductor Pb$_{1-x}$Cd$_x$I$_2$ solid solutions. This allowed us to reveal the structure defects present in such crystals, to establish their nature and energy spectrum, and to clarify the role of PbJ$_2$ clusters in the formation of such semiconductor solid solutions.

1. Experimental Results and Their Discussion

In Fig. 1, we present the PL spectrum of PbI$_2$ (*a*) and Pb$_{0.98}$Cd$_{0.02}$I$_2$ (*b*) crystals at $T = 4.5$ K. It is seen that the intense line in the short-wave region of the spectrum for PbI$_2$ crystal is located at an energy of 2.492 eV. According to [13], this line corresponds to the recombination of excitons localized on neutral donors, i.e., it is the (D^0X)-line for PbI$_2$ crystals of the 4H-modification. In the long-wave region of the spectrum, we observe two intense bands with energies of 2.435 and 2.385 eV. On the long-wave edge of the first of these bands, we see a structure with the participation of LO-phonons with an energy of 7.0–8.0 meV. The presence of such a structure is a characteristic feature of optical transitions caused by the recombination of donor-acceptor pairs. The PL spectrum of Pb$_{1-x}$Cd$_x$I$_2$ crystals for $x = 0.02$ is shown in Fig. 1,*b*, where the D^0X-line with an energy of 2.509 eV is revealed as well. In this case, we observe its short-wave shift by 17 meV, which is related to the formation of the Pb$_{1-x}$Cd$_x$I$_2$ substitutional solid solution.

The corroboration of the fact that the emission in the interval 2.43–2.44 eV is caused by the recombination of donor-acceptor pairs is given by the results of measurements of the spectra of photoconduction (PC) and PDC for PbI$_2$ crystals (see Fig. 2). The PC spectrum (*a*)
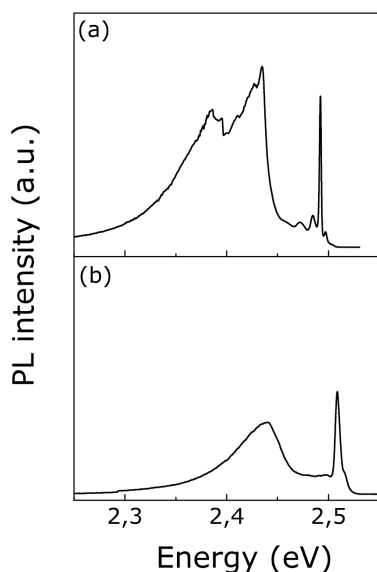
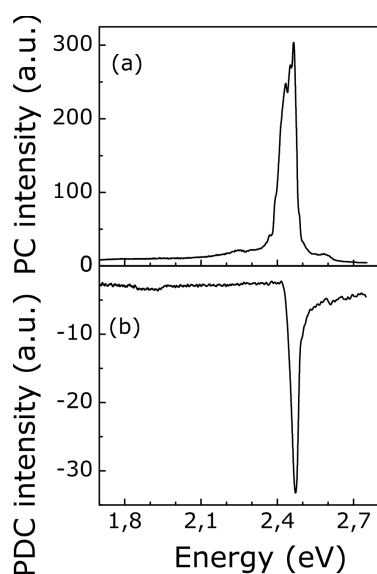Fig. 1. PL spectra for PbI$_2$ (*a*) and Pb$_{1-x}$Cd$_x$I$_2$ (*b*) crystals for $x = 0.02$ at $T = 4.5$ K

Fig. 2. PC (*a*) and PDC (*b*) spectra for PbI$_2$ crystal at $T = 77$ K

Fig. 3. PL spectra for Pb$_{1-x}$Cd$_x$I$_2$ solid solutions ($x = 0.10$–0.70) at $T = 4.5$ K

contains the intense line at an energy of 2.465 eV. The analogous band with negative polarity with an energy of 2.470 eV is revealed also in the PDC spectrum (*b*). This testifies that such a band is caused by the photoionization transitions from the valence band on a relatively deep donor level with an energy of $E_c - 0.070$ eV. The absence of any PDC bands inn the interval 2.38–2.43 eV testifies to the absence of photoionization transitions [8–9]. In turn, this confirms that the PL in the given spec-
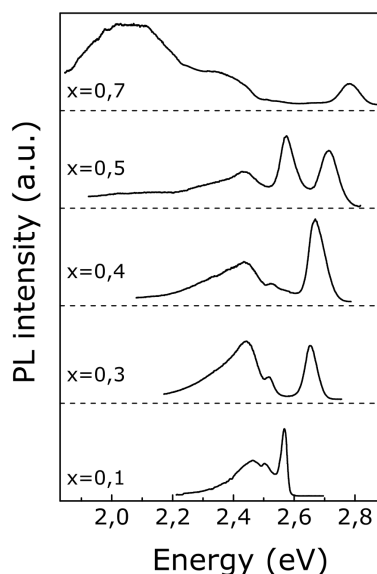
tral region for PbI$_2$ and Pb$_{1-x}$Cd$_x$I$_2$ crystals ($x = 0.02$) is due to the recombination of donor-acceptor pairs.

The PL spectra of Pb$_{1-x}$Cd$_x$I$_2$ crystals for various values of components of the composition at $T = 4.5$ K are presented in Fig. 3, where the short-wave band is caused by the emission of localized excitons. The appearance of such states is a characteristic feature of the formation of semiconductor solid solutions. For such crystals analogously to the solid solutions on the basis of semiconductors of group A^{II}B^{VI} [9–11, 14, 15], there occurs the inhomogeneous introduction of components of the composition in a crystal, which leads to the appearance of fluctuations of the potential of the crystal field. This causes the localization of exciton states. As is seen, the band with an energy of 2.43 eV is observed in PL spectra at $x \leq 0.50$. This indicates the formation of clusters or island-like aggregates of PbI$_2$ in Pb$_{1-x}$Cd$_x$I$_2$ solid solutions. Their sizes are greater than the Bohr radius of an exciton (R_B), i.e., > 19 Å. The possibility of the appearance of such clusters in Pb$_{1-x}$Cd$_x$I$_2$ was earlier discussed in works [16–19], where it was shown, in particular, that, in these solid solutions at $x \geq 0.50$, the most short-wave PL band can be assigned to the optical transitions from excited states of Pb^{2+} ions, i.e., from $^3P_1$- and $^3P_0$-states. The latter is the lower one. It follows from Fig. 3 that the energy splitting between these states for $x = 0.40$ is 10 meV and increases, as the size of clusters decreases. Thus, the exciton states in PbI$_2$ clusters at $x \geq 0.40$ are changed to molecular-like excited states. An increase in the concentration of Cd^{2+} ions leads to a
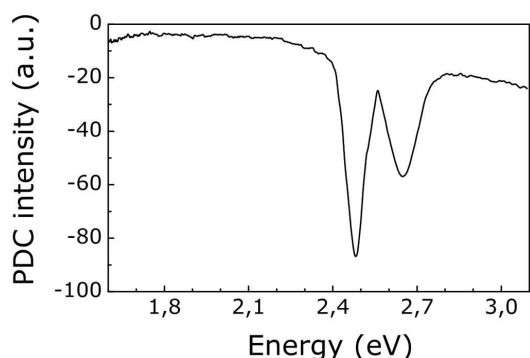
Fig. 4. PDC spectrum for $Pb_{1-x}Cd_xI_2$ crystals at $T = 77$ K

Fig. 5. PL spectra for $Pb_{1-x}Cd_xI_2$ solid solutions ($x = 0.30$–0.70) at $T = 300$ K

Fig. 6. PL spectra of PbJ_2 crystals at $T = 4.2$ K for various delays of the registration (curves *1* and *2* for 0.7 ns and 10 ns, respectively) and at the stationary excitation (curve *3*)

decrease in sizes of these clusters and, respectively, to a high-energy shift of the short-wave PL band [17]. Thus, the short-wave PL bands for $Pb_{1-x}Cd_xI_2$ solid solutions with $x = 0.50$ and 0.70 correspond to the emission from the excited states related to the presence of PbI_2 clusters. The short-wave shift of the PL band for $x = 0.70$ relative to its energy position for $x = 0.50$ (2.72 eV and 2.78 eV, respectively) is obviously caused by a decrease in the size of such clusters. Since $Pb_{1-x}Cd_xI_2$ solid solutions can contain clusters with various sizes, we observe the inhomogeneous widening of the corresponding PL bands. It is worth noting the appearance of a new PL band with an energy of 2.57 eV for $x = 0.50$. We may assume that the presence of the PL bands with energies of 2.57 eV and 2.72 eV can be caused by the emission of localized excitons and excitons in clusters, respectively. The obtained results testify that, in $Pb_{1-x}Cd_xI_2$ solid solutions, both large ($> R_B$) and small ($< R_B$) PbI_2 clusters are formed.

In Fig. 4, we show the PDC spectrum for $Pb_{1-x}Cd_xI_2$ with $x = 0.50$ at $T = 77$ K, where two bands with energies of 2.48 and 2.64 eV are distinguished. The first band corresponds to photoionization transitions from the valence band to the donor level $E_c - 0.070$ eV for large PbI_2 clusters. The energy position of another band practically coincides with the short-wave PL band of localized excitons.

In the PL spectrum presented in Fig. 5 for $x = 0.70$, we also see a wide band with an energy of 2.1 eV, whose intensity increses strongly, as the concentration of Pb^{2+} ions decreases. The dependence of this band on the temperature and the excitation energy indicates that it is caused by the self-trapping of excitons in small clusters of PbI_2 formed in $Pb_{1-x}Cd_xI_2$ solid solutions [17]. We note that the PL band with an energy of 2.1 eV is also observed for $x = 0.50$ at $T = 300$ K, where its intensity is significant. The structure observed on the short-wave
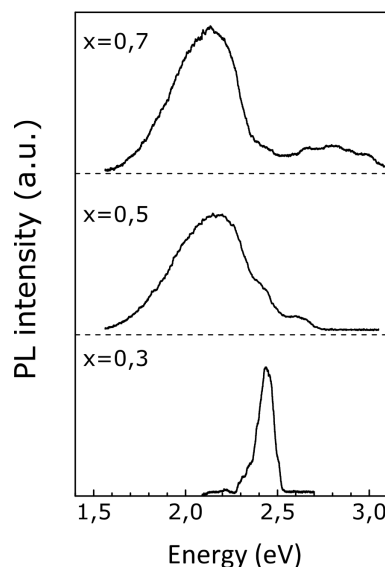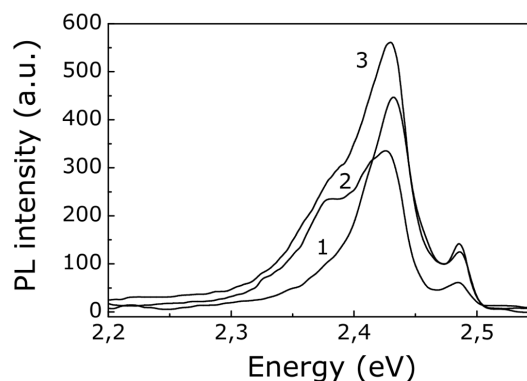
edge of the PL band can be caused by the emission of localized excitons, the phototransitions from excited states of ions Pb^{2+} in small clusters, and the recombination of donor-acceptor pairs in large clusters.

With the purpose to obtain the more complete information about PbI_2 clusters, which are formed in $Pb_{1-x}Cd_xI_2$ solid solutions, we also studied the time-resolved PL spectra, by using a pulse nitrogen laser ($\lambda = 337$ nm) for the excitation of PL.

In Fig. 6, we give the PL spectra of PbI_2 crystals at $T = 4.5$ K for various delays (τ_d) of the registration of the spectra after their excitation. Curves *1, 2* correspond to $\tau_d = 0.7$ ns and 10 ns, and curve 3 corresponds to the stationary excitation. It is seen that the
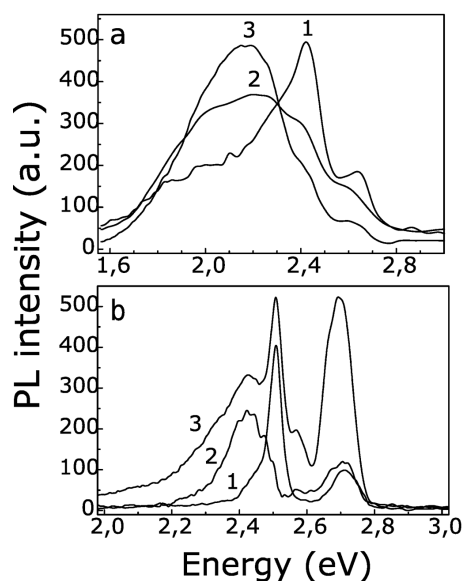
Fig. 7. PL spectra of $Pb_{1-x}Cd_xJ_2$ crystals ($x = 0.5$) a) at $T = 300$ K, b) at $T = 4.5$ K for various delays of the registration (curves 1 and 2 for 0.7 ns and 10 ns, respectively) and at the stationary excitation (curve 3)

short-wave spectral region contains a relatively narrow line with an energy of 2.492 eV, which confirms the 4H-modification of PbI_2 crystals under study. The energy positions of this line are somewhat different for different values of τ_d. For example, these values are 2.494 eV and 2.492 eV, respectively, for $\tau_d = 0.7$ and 10 ns. As was shown earlier [13], this line corresponds to the recombination of excitons bound on neutral donors, i.e., it is the D^oX-line. In addition to this line, the long-wave spectral region near 2.43 eV includes the wide band of PL related to the recombination of donor-acceptor pairs. For $\tau_d = 10$ ns and at the stationary excitation, we observe another wide band with an energy of 2.38 eV on the long-wave edge. This band has an analogous nature with the participation of a deeper acceptor level. The first acceptor level corresponds to the duration of the recombination of charge carriers in the picosecond range, whereas the deeper acceptor level corresponds to the nanosecond one.

In Fig. 7,a, we present the PL spectra of $Pb_{1-x}Cd_xI_2$ crystals ($x = 0.5$) for various delay times of the registration of the spectrum at $T = 300$ K. Curve 1 corresponds to $\tau_d = 0.7$ ns. We see that the short-wave spectral region contains the line at an energy of 2.646 eV. As the delay time increases, $\tau_d = 10$ ns (curve 2), the structure of the PL spectrum is significantly changed. For example, the line with an energy of 2.605 eV is observed in the short-wave part of the spectrum. The spectrum

also includes the most intense wide PL band at an energy of 2.14 eV. For the stationary excitation (curve 3), the characteristic peculiarity of the PL spectrum is the presence of the intense wide band with a maximum at 2.14 eV. Thus, the characteristic feature of $Pb_{1-x}Cd_xI_2$ crystals ($x = 0.5$) is the manifestation of the fast component (narrow PL lines in the short-wave spectral region) and the slow one (a wide band in the long-wave spectral region). The PL spectrum for $Pb_{1-x}Cd_xI_2$ crystals ($x = 0.5$) at $T = 4.5$ K is shown in Fig. 7,b. For the shortest delay time ($\tau_d = 0.7$ ns), we see two lines in the PL spectrum with energies of 2.712 eV and 2.513 eV (curve 1). At $\tau_d = 15$ ns, the short-wave line manifests the doublet structure at energies of 2.712 eV and 2.680 eV.

The PL spectrum of $Pb_{1-x}Cd_xI_2$ crystals ($x = 0.7$) at $T=300$ K is shown in Fig. 8,a, whose peculiarity is the presence of a structural wide band in the region (2.5–3.1) eV, which is observed in both nanosecond (curve 2) and subnanosecond (curve 1) ranges, as well as at a stationary excitation (curve 3). At $\tau_d = 10$ ns, the spectrum contains a wide band (curve 2), whose maximum corresponds to an energy of 2.14 eV. At the stationary excitation, the intensity of this band increases significantly (curve 3). The PL spectrum of $Pb_{1-x}Cd_xI_2$ crystals ($x = 0.7$) at $T = 4.5$ K for various delays of the registration time (curves 1 and 2 correspond to $\tau_d = 0.7$ ns and $\tau_d = 15$ ns) and at the stationary excitation (curve 3) is presented in Fig. 8,b. It is seen that, at $\tau_d = 0.7$ ns, the PL spectrum (curve 1) includes two lines at energies of 2.814 eV and 2.447 eV. The former reveals a structure in the form of bends at energies of 2.686 eV and 2.966 eV. As the delay time τ_d increases up to 15 ns, the PL spectrum (curve 2) contains practically a single line at an energy of 2.418 eV. In other words, we have a long-wave shift by 29 meV as compared with the previous spectrum (curve 1). The short-wave region of the spectrum (2.6–3.1) eV is characterized by the low-intensity emission. Essential changes in the PL spectrum occur at the stationary excitation (curve 3), where the wide band with an energy of 2.05 eV becomes determining. In addition, another line at an energy of 2.778 eV is observed, i.e., this line is shifted to the low-energy region relative to the line with an energy of 2.814 eV characteristic of $\tau_d = 0.7$ ns (curve 1).

The presented results of executed studies of $Pb_{1-x}Cd_xI_2$ crystals and their analysis testify that the short-wave part of the PL spectrum contains lines with a rather low duration of the recombination, namely in the nano- and subnanosecond ranges. As a specific feature of $Pb_{1-x}Cd_xI_2$ solid solutions, we mention the possibil-

ity of the formation of small PbI_2 clusters with various sizes, which are dispersed into a matrix [17, 19] at $x \geq 0.5$. The excitation energy of excitons and, respectively, the energy of exciton emission lines increase, as the size of PbI_2 nanoclusters decreases. This allows us to consider that the wide structural PL band (Fig. 8,a) in the region (2.6–3.1) eV at $x = 0.70$ is caused, obviously, by the emission with participation of nanoclusters with various sizes. Such wide PL band is characterized by the inhomogeneous broadening. For these crystals, the decrease of the temperature down to 4.2 K induces the appearance of a fast component with an energy of 2.814 eV in the spectral region under study and a low component with an energy of 2.778 eV (Fig. 8,b, curve 3). The presence of these two components can be related to the optical transitions with participation of exciton states with the Γ_3^-- and Γ_1^--symmetries, which originate of the $^3P_1$ – and $^3P_0$-states of a free Pb^{2+} ion. The low and fast components of PL are related to the $^3P_1$ – and $^3P_0$-states, respectively. We note that the energy distance between these states for individual Pb^{2+} ions is equal to 75 meV. At $x = 0$, i.e., for crystals PbI_2, the splitting between the Γ_3^-- and Γ_1^--states is 2 meV [19], which agrees well with the value of splitting determined by us for D^0X-excitons. For PbI_2 nanoclusters, the splitting between the $^3P_1$- and $^3P_0$-states will be less than that for individual ions. This value will decrease, as the size of clusters increases. The above-presented results for $x = 0.70$ and $x = 0.50$ indicate that the values of splitting are 36 meV and 30 meV, respectively.

The nature of the wide PL band near 2.0 eV can be related to the recombination of donor-acceptor pairs with participation of a deep acceptor level ($E_V + 0.42$ eV) and to the possible self-trapping of excitons [20] caused by the presence of PbI_2 clusters [17, 19]. The last assumption is supported by the fact that this band in the PL spectrum does not practically manifest itself in $Pb_{1-x}Cd_xI_2$ crystals with large contents of Pb (> 0.5). In addition, the appearance of this band is accompanied by the strong decrease of the exciton emission intensity in the short-wave spectral region corresponding to the optical transitions with participation of exciton states of the Γ_3^-- and Γ_1^--symmetries. We note that the possibility of the formation of PbI_2 clusters in $Pb_{1-x}Cd_xI_2$ and PbI_2–BiI_3 solid solutions is indicated by the results obtained by us in the study of their NQR spectra [19, 21]. Thus, the presented results testify that $Pb_{1-x}Cd_xI_2$ solid solutions can be considered as promising fast-operating materials for the development of radiation emission detectors on their basis and, in partic-
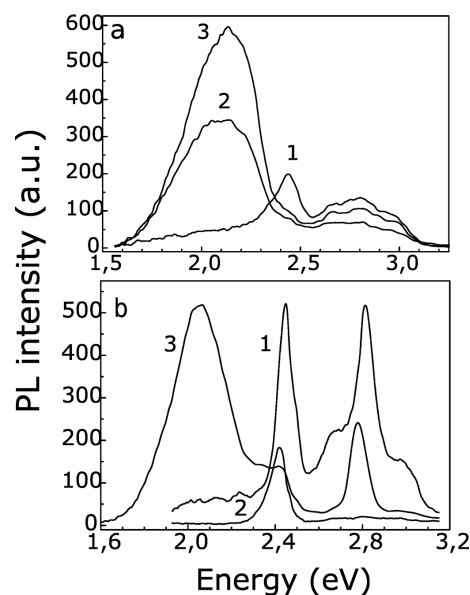

Fig. 8. PL spectra of $Pb_{1-x}Cd_xJ_2$ crystals ($x = 0.7$) a) at $T = 300$ K, b) at $T = 4.5$ K for various delays of the registration (curves 1 and 2 for 0.7 ns and 15 ns, respectively) and at the stationary excitation (curve 3)

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ФОТОЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ ШАРУВАТИХ ТВЕРДИХ РОЗЧИНІВ $Pb_{1-x}Cd_xI_2$

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Р е з ю м е

Проведено дослідження спектрів фотолюмінесценції, в тому числі із розділенням в часі, і фотодифузійного струму кристалів PbI_2 та твердих розчинів $Pb_{1-x}Cd_xI_2$. Встановлено, що дані кристали мають монополярну (діркову) провідність. Показана можливість утворення в твердих розчинах кластерів PbI_2 різних розмірів. Встановлено, що величина розщеплення між Γ_3^-- та Γ_1^--екситонними станами в таких кластерах становить 30 та 36 меВ для $x = 0{,}50$ та $x = 0{,}70$, відповідно. Виявлено, що для $x \geq 0,50$ має місце автолокалізація екситонів в кластерах PbI_2.