

Luminescence of PbI_2 nanoinclusions in CdI_2 crystal lattice

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Received March 05, 2016

Luminescence spectra of CdI_2 crystals with PbI_2 inclusions ($10^{-5}\%$) under synchrotron excitation at 8 K are examined in the present work. The spectra of the crystals grown from the melt exhibit luminescence peaks at 2.13 and 2.43 eV which are associated with one-dimensional impurity nanoinclusions near dislocations. In the luminescence spectra of CdI_2 crystals synthesized by the method of diffusion from the gas phase the effect of two-dimensional PbI_2 nanoinclusions with 2.0 and 2.48 eV bands prevails. A new model of the luminescence center is proposed.

Keywords: layered crystals, nanoinclusions, luminescence, synchrotron excitation.

Исследованы спектры люминесценции кристаллов CdI_2 с примесью PbI_2 ($10^{-5}\%$) при синхротронном возбуждении ($T = 8$ К). В спектрах кристаллов, выращенных из расплава, доминируют полосы люминесценции 2.13 и 2.43 эВ, обусловленные одномерными нановключениями примеси, расположенными вблизи дислокаций. В спектрах люминесценции кристаллов CdI_2 , полученных методом диффузии из газовой фазы, преобладает влияние двумерных нановключений PbI_2 с максимумами полос при 2.0 и 2.48 эВ. Предложена новая модель центра люминесценции.

Люмінесценція нановключень PbI_2 в кристалічній ґратці CdI_2 . *І.М.Болеста, В.В.Вістовський, Н.В.Глоковська, І.М.Ровецький.*

Досліджені спектри люмінесценції кристалів CdI_2 з домішкою PbI_2 ($10^{-5}\%$) при синхротронному збудженні ($T = 8$ К). У спектрах кристалів, вирощених з розплаву, домінують смуги люмінесценції 2.13 та 2.43 еВ, зумовлені одновимірними нановключеннями домішки, розташованими біля дислокацій. У спектрах люмінесценції кристалів CdI_2 , отриманих методом дифузії з газОВОЇ фази, переважає вплив двовимірних нановключень PbI_2 з максимумами смуг при 2.0 та 2.48 еВ. Запропоновано нову модель центра люмінесценції.

1. Introduction

Isostructural layered crystals of cadmium and lead iodides are compounds of the intermediate type by the chemical bonding which is ionic-covalent within $|\text{-Cd(Pb)}|$ layer and van-der-Waals between the layers. Structural features of these crystals specify the physical properties, and promote their application as fast scintillators in the nanosec-

ond range and the medium for optical data recording.

With use of atomic force microscopy we have shown that PbI_2 impurity is embedded in CdI_2 crystal lattice in the form of nanocrystalline inclusions, arranged in the layer plane and also along the linear structural defects of the host crystal lattice [1, 2].

Luminescence characteristics of $\text{CdI}_2\text{-PbI}_2$ crystals obtained by diffusion from the gas

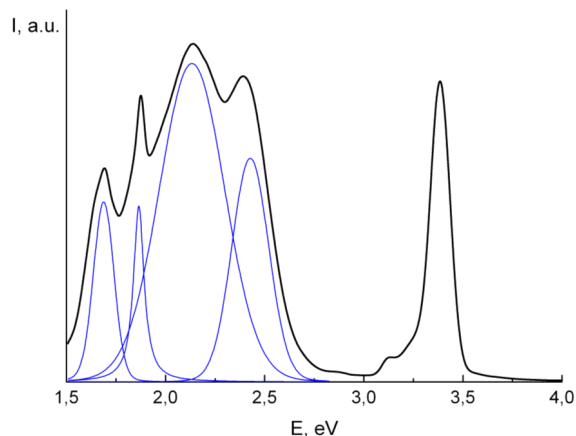


Fig. 1. Luminescence spectrum of CdI₂ crystal grown from the melt under synchrotron excitation ($T = 8$ K).

phase and grown from the melt under synchrotron excitation at 8 K are presented in this work. A new model of the luminescence center is proposed on the base of analysis of luminescence spectra, structural peculiarities of investigated crystals and different possible types of PbI₂ nanocrystalline inclusions in these crystals.

2. Experimental

CdI₂-PbI₂ crystals with $\sim 10^{-4}$ - 10^{-5} mol.% content of lead impurity were synthesized from one batch of raw material previously purified by zone melting. The samples $\sim 10 \times 5 \times 0.2$ mm were obtained by cleaving the crystals grown from the melt by the Bridgman method along the basal planes. The samples obtained by diffusion from the gas phase were grown in the form of "separate" plates with ~ 0.1 mm thickness and were not subjected to additional treatment.

3. Results and discussion

Figure 1 shows luminescence spectrum of cadmium iodide crystals grown from the melt under synchrotron excitation ($E = 13.77$ eV, $T = 8$ K). Decomposition of the luminescence spectrum defines the following peaks: 1.68, 1.87, 2.13, 2.43 and 3.38 (eV). The luminescence spectrum of the crystals synthesized by the method of diffusion from the gas phase (Fig. 2) exhibits the peaks at 1.71, 1.87, 2.0, 2.48 and 3.38 (eV). Comparison of these spectra shows that peak positions coincide for 1.87 and 3.38 eV narrow bands; the broad ones in the range 2.0–2.48 eV and 1.68–1.71 eV differ essentially. Appearance of the broad emission bands can be explained by presence of lead

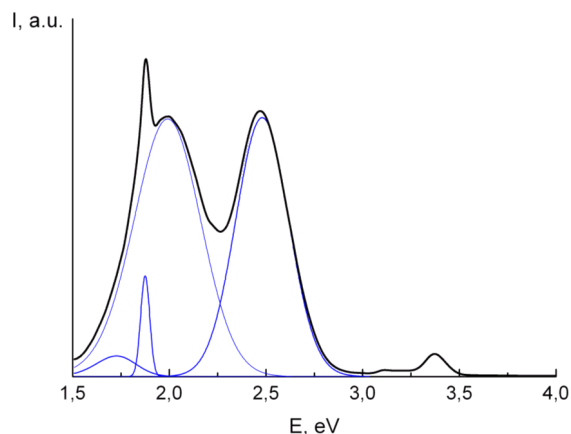


Fig. 2. Luminescence spectrum of CdI₂ crystal obtained by the method of diffusion from the gas phase under synchrotron excitation ($T = 8$ K).

iodide impurity in the raw material used for the crystal growth.

We have shown in [3] that heterojunction may take place at the border of two isostructural layered crystals CdI₂ and PbI₂. Under high-energy excitation of such samples electronic processes originate in the crystal with smaller energy gap width (namely, PbI₂). It must be mentioned that in 4H-CdI₂ crystals grown from the melt lead iodide nanoinclusions gain the structure of the host crystal (4H-PbI₂).

Coincidence of the luminescence peak positions for considered crystals and the lead iodide crystals is general characteristic of the obtained spectra. So, for CdI₂-PbI₂ crystals the peak at 2.13 eV, one of the dominant in Fig. 1, is excited in the region of CdI₂ fundamental absorption and at 3.16 eV band which originates due to presence of PbI₂ phase inclusions arranged near the dislocations [4]. I. Baltog et al. [5] found that similar photoluminescence peak for PbI₂ crystals (2.07 eV at 77 K) is also associated with 4H-PbI₂ inclusions near the dislocations. It was stated that such luminescence centers are mainly excited by the electron-hole mechanism for both PbI₂ and CdI₂-PbI₂ crystals. The nanocrystalline inclusions in the form of cylinders, located along the defined direction, were detected by us with the use of atomic-force microscopy [2] and are now treated as one-dimensional according to the classification of [6].

At the same time, it's known that the peaks of emission bands for PbI₂ and CdI₂ with PbI₂ nanocrystalline inclusions agree with those of photoconductivity bands [7, 8].

To construct the model of radiative transitions let's consider the relationship between nanocrystal sizes and their energy-gap width. Comparison of the absorption bands of 4H-PbI₂ high-energy exciton in the single crystal (3.330–3.425 eV) [9] and its nanocrystalline inclusion in cadmium iodide lattice (3.21–3.24 eV) [1] shows their "red" shift. On the other hand, absorption band position of the low-energy exciton for PbI₂ nanocrystals (in the range 2.5–2.8 eV) demonstrates the "blue" shift about the same value in comparison with macrocrystals [10]. Here we study luminescence properties of cadmium iodide crystals with lead iodide nanoinclusions and, therefore, crystal field influence and quantum-size effect are to be taken into account. That's why we assume the energy gap width to be equal 2.53 eV for PbI₂ nanocrystals the same as for single crystals [11].

So, the emission band of 2.13 eV may be associated with the recombination of the electron trapped at the center with 0.40 eV depth and a free hole. In the work [3] the electronic trapping center was identified, possessing optical depth of 0.43 eV at 77 K.

To understand the nature of structural defects, near which the electron is localized, let's consider the results of EPR studies for UV-irradiated PbI₂ crystals [12]. J.Arends and J.F.Verwey found that previously irradiated crystals of lead halide compounds at 80 K enclose singly charged positive lead ions (as an initial stage in photochemical decomposition) and lead metal particles. Ions are arranged in pairs or clusters of not more than 3 particles and coagulate with the lead atoms formation. The EPR signal intensity of the lead ions sharply falls below 120 K. Thus, it can be supposed that all singly charged lead ions transform into the neutral atoms at this temperature.

As the trapping center with the optical depth of 0.43 eV in CdI₂-PbI₂ crystals corresponds to the thermoluminescence peak of 112 K, we can assume that lead atom acts as the structural defect for it. Consideration of the luminescence characteristics allows us to ascribe the origin of electron localization centers to lead atoms in PbI₂ 4H-polytype, what makes our previous model more exact [3].

A.E.Dugan and H.K.Henisch [7] have shown that the luminescence band in the range of 2.10–2.16 eV at 78 K has the triplet structure with 0.03 eV distance between the components. Along with this, it was found that three different decay times

(from 22 to 1230 nsec) exist for 2.07–2.09 eV luminescence band of 4H-PbI₂ crystals that can be the evidence of the presence of three emitting centers [5].

In view of the existence of charge exchange (at 80 K) in CdI₂-PbI₂ crystals between the trapping centers with the optical depth of 0.43 and 0.57 eV [3] and similarity of the triplet structure of PbI₂ luminescence bands in the range 2.10–2.16 and 1.94–1.99 eV [7], the trapping center with the optical depth of 0.57 eV can correspond to the identical Pb⁰ doubly charged electron trapping centers in 2H-PbI₂ structure or PbI₂ nanocrystals of another type. As the luminescence band of 2.0 eV of CdI₂-PbI₂ crystals has the excitation spectrum different from 2.13 eV band [2], the correspondent luminescence center in the samples obtained from the gas phase may belong to PbI₂ two-dimensional nanocrystals located in the layer plane of the CdI₂ basic crystal lattice [1].

Nanosecond interval of the luminescence decay time is important when developing the model of the emission center. Evidently, absence of the luminescence excitation migration stage can be conclusive factor in the essential reducing of de-excitation time. In [13] the time necessary to thermalize the electron or hole prior to form the exciton in PbI₂ is defined as 10⁻¹¹–10⁻¹³ sec. Thus, taking into account the time characteristics, the luminescence band of 2.13 eV at 8 K can be stipulated by luminescence of the excitons localized near the lead atoms in the 4H-polytype PbI₂ nanoinclusions which are located near the dislocations in the cadmium iodide crystal lattice.

What concerns luminescence bands of 2.43 and 2.48 eV, we suppose their relationship with the exciton localization near Pb⁺ singly charged ions in one- and two-dimensional PbI₂ nanocrystalline inclusions in the CdI₂ crystal lattice. Existence of three values for 2.371 eV X-ray luminescence band decay time of PbI₂ polycrystals in the nanosecond range (at 14 K) and the authors' conclusion on the capability of exciton-binding center to act as radiative one [14] are the evidences in favour of this model of emission center.

It seems useful to compare our experimental data with theoretical calculations of the electronic states in the Pb₆I₁₂ cluster with 4H-packing, where two electrons were added to the orbitals to achieve the stable state of the system [15]. M.M.Marino et al. ascertained bandlike character of six energy

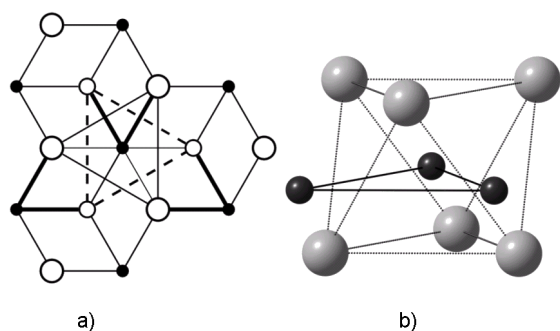


Fig. 3. Scheme of lead iodide structure formation with non-linear PbI_2 molecules: (a) — projection on the (0001) basal plane. Dark circles are the lead ions, big and small circles are the iodine ions up and down the plane of the figure, respectively; (b) — repetition octahedron of PbI_2 structure with Pb_3I_6 stoichiometric composition.

states location in this ionic complex in the range of 2.14–2.49 eV and their relations with metal-metal transitions.

It's clear that in our experiment the luminescence spectra of the crystals grown from the gas phase should be chosen for comparison in order to disregard the effect of dislocations. Adding of two electrons to the neutral system makes it possible to suggest that calculations embrace both states: the singly charged ion and the neutral lead atom. Correlation of the experimental results with the conclusions of the authors [15] lies in the fact that two luminescence bands which origin we attribute to two-dimensional PbI_2 nanocrystals, have peaks at 2.0 and 2.48 eV each of them possessing the triplet structure as it was shown earlier. The lowest computed energy state of the system (0.03 eV) coincides with the distance between the triplet compounds of the PbI_2 emission bands [7].

If the luminescence arises due to the recombination of the electron localized near singly charged ion (or the neutral lead atom) with the free hole in the valence band (its top consists of cation states up to 41 % in PbI_2 [16]), than the theoretical calculations reveal realization of metal-metal transitions in luminescence. Thus, one can see that the main qualitative and quantitative characteristics of our model are in good coincidence with the theoretical data of [15].

As the luminescence properties are tightly bound with the structure of the crystals, the fragment of PbI_2 crystal structure projection on (0001) basic plane is selected in Fig. 3a that shows the non-linear PbI_2 molecules arrangement in this struc-

tural type. PbI_2 specific structure as the transient between ionic and molecular crystals is seen, probably, in the close packing of iodine ions in upper and lower layer of the elementary "sandwich". At the same time molecular bonding between each lead ion and two iodine ions from different "halide" layers is saved. Three PbI_2 configurations are not connected by symmetry element in this geometry that can be explained by specific molecular crystal packing — "hill" to "cavity" (Fig. 3b). Really, PbI_2 ionicity is rather low — 0.35 (0.52 in CdI_2) [17].

Proposed structural model allows us to assume that three luminescence centers with similar spectral and kinetic characteristics are comprised of three lead ions each of which is bound with two iodine ions by covalent bonding. In the aggregate they form the repetition octahedron of lead iodide crystals.

It must be mentioned that similar photoluminescence bands of CdI_2 crystals with PbI_2 impurity traces were observed by H.Nakagawa and H.Matsumoto [18]. As a result of increasing emission intensity ($E = 3.68$ eV) at the liquid nitrogen temperature the new luminescence bands appeared — at 2.0 and 2.37 eV instead of 2.15 and 2.44 eV. The authors have supposed that this phenomenon can be associated with the non-linear processes involving the relaxed exciton states in CdI_2 or formation of the relaxed biexcitons. Our model focuses attention on the uncontrolled PbI_2 impurity. Although its content is of 10^{-5} order, PbI_2 is the first to crystallize during the crystal growth by the Bridgman method and it is incorporated in CdI_2 matrix in the nanocrystalline form.

Thorough study of the broad emission bands 2.07 and 2.44 eV of the PbI_2 nanocrystals built in SiO_2 film was carried out in [19]. E.Lifshitz et al. proposed the model of donor-acceptor pairs where the donor location is attributed to anisotropic iodine vacancy and the acceptor location — to isotropic defect of lead vacancy. So, it is obvious that work on the modeling of the luminescence centers responsible for broad luminescence bands is to be continued.

The low-energy luminescence bands of 1.7 and 1.85 eV are present in the luminescence spectra of considered crystals and they are also observed in lead iodide [2, 7]. Their origin would be studied in the next work.

4. Conclusions

Thus, on the basis of comparison of luminescence spectra of CdI₂-10⁻⁵ PbI₂ crystals grown from the melt and obtained by diffusion method from the gas phase with optical, luminescence and kinetic characteristics of PbI₂ crystals the new model of the luminescence center is proposed in this work. In our model energy transitions are associated with emission of localized cation excitons in one- and two-dimensional PbI₂ nanocrystalline inclusions in CdI₂ lattice.

Acknowledgments. The authors would like to thank Dr.A.Kotlov for the support in the SUPERLUMI experiments.

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