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Extrinsic Luminescence Centers in CdI_2 Crystals Doped with PbI_2 (10^{-4} to 1 mol %)

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Abstract—We have studied the luminescence properties of PbI_2 doped (10^{-4} to 1 mol %) CdI_2 crystals in the temperature range 4.2–90 K and those of 2*H*- and 4*H*-PbI_2 crystals at 90 K. The results demonstrate that the Pb atoms produce impurity centers in the form of isolated Pb^{2+} ions and 4*H*-PbI_2 nanocrystals located in the plane of the layers or along linear structural defects of CdI_2. The formation of PbI_2 nanocrystals was confirmed by atomic force microscopy. We discuss excitonic and electron–hole mechanisms of energy transfer to luminescence centers.

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INTRODUCTION

The intermediate position of layered crystals between ionic and molecular crystals and the possibility to tune their physical properties by inserting various compounds into their interlayer spaces have been attracting researchers' attention for several decades now.

Bulk CdI_2 and PbI_2 layered crystals are structurally isomorphic, but the thermodynamically stable form of CdI_2 is its 4*H*-polytype, which has lattice parameters $a = 4.2$ Å and $c = 13.67$ Å, whereas the stable polytype of PbI_2 is 2*H*, with $a = 4.56$ Å and $c = 6.98$ Å. The two crystal lattices are formed by three-layer slabs. In each slab, an atomic metal layer is sandwiched between two identical iodine atomic layers. CdI_2 is an indirect-gap semiconductor. At 2 K, its fundamental absorption edge lies around 356 nm, and there are direct band–band transitions under 320 nm. The absorption edge of PbI_2, a direct-gap material, lies around 490 nm.

Trace levels of lead impurities are present in even the most thoroughly purified CdI_2 single crystals and give rise to an absorption (excitation) band at 384 nm. This band was modeled in terms of a high-energy Frenkel cation exciton, and PbI_2 impurities were shown to be capable of incorporating into the CdI_2 crystal lattice in the form of nanocrystalline inclusions [1]. The presence of nanophase PbI_2 in the CdI_2 crystal lattice was confirmed in studies of trapping centers in such crystals. Combining optical and thermal carrier retrapping techniques, Gal'chinskii et al. [2] identified a heterojunction at interfaces between PbI_2 nanoinclusions and cadmium iodide [2].

The purpose of this work was to find out the origin of emission centers in PbI_2-containing CdI_2 crystals using luminescence spectroscopy and atomic force microscopy.

EXPERIMENTAL

We studied PbI_2-containing (10^{-4} to 1 mol % in the growth charge) CdI_2 crystals grown by the Bridgman–Stockbarger method and PbI_2 crystals (2*H*- and 4*H*-polytypes). The starting materials were purified by a variety of physicochemical techniques, including 30 molten zone passes.

Luminescence was excited by a DKsEl-1000 xenon lamp and nitrogen laser (λ_{ex}= 337.1 nm). Excitation light from the fundamental absorption region and impurity bands was selected using an SF-16 monochromator. Luminescence spectra were analyzed using a grating monochromator (600 lines/mm).

The surface topography of CdI_2 layered crystals containing up to 5 mol % PbI_2 was examined on a Solver P47-PRO atomic force microscope in intermittent contact mode. The probe tip radius was ~10 nm. The measurements were made in air on freshly cleaved CdI_2 (0001) basal planes.

RESULTS AND DISCUSSION

Figure 1 shows the 60- and 77-K photoluminescence (PL) spectra (λ_{ex} = 384 nm) of a CdI_2 crystal containing ~ 10^{-4} mol % PbI_2. The 60-K PL spectrum consists of two bands, centered at 520 and 655 nm (spectrum *1*). At 77 K, the bands are located at 526 and 650 nm (spectrum *2*).

The composite PL band at 520 nm can be decomposed into elementary components centered at 508, 516, and 523 nm. The feature centered at 516 nm is assignable to a high-energy, exciton of small radius in a PbI_2 nanocrystal, self-trapped at bending vibrations of the CdI_2 crystal lattice [1]. Clearly, the 508-nm feature has a similar origin, which will be discussed below

(Fig. 2). The shift of the 520-nm PL band to longer wavelengths as the temperature is raised from 60 to 77 K (spectra *1*, *2*) is probably related to the influence of the longest wavelength component, located at 523 nm.

The PL spectra *3*, *4*, and *5* were obtained at λ_{ex} = 313 nm and temperatures of 30, 60, and 77 K, respectively. Spectrum *3* contains narrow peaks centered at 366, 388, and 397 nm. The shortest wavelength peak, located at 366 nm, is due to the radiative recombination of self-trapped excitons in the CdI_2 crystal [3, 4]. The peaks at 388 and 397 nm, due to the presence of PbI_2, point to the possibility of high-energy exciton formation in PbI_2 nanocrystals when the crystal is excited in the fundamental absorption region of CdI_2. For this reason, spectra *3*–*5* are similar to spectra *1* and *2* in some respects: spectrum *3* is dominated by the 526-nm band (like spectrum *2*), and the shoulder at 640 nm in spectrum *5* corresponds to the longer wavelength band in spectra *1* and *2*.

On the other hand, a number of significant distinctions are worth noting. Under excitonic excitation (spectra *1*, *2*), there are no PL features in the range 540–630 nm. The spectra obtained at λ_{ex} = 313 nm contain, in addition to the strong band at 550 nm, shoulders at 570 and 620 nm (spectra *3*, *4*) and a band at 720 nm (spectrum *3*). These features are obviously due to nonexcitonic mechanisms of excitation energy transfer to luminescence centers.

According to X-ray diffraction data, only one-third of the lead iodide incorporated into the CdI_2 lattice is in molecular form. Some of the dopant can be present in the form of isolated Pb^{2+} centers [5]. Such centers in an octahedral environment of iodide ions (NaI–Pb) have excitation bands at 305 and 315 nm, assigned by Guseva and Lyskovich [6] to the *B*-band of the Pb^{2+} center. The corresponding PL band is located at 600 nm. On the other hand, the isolated Pb centers forming in intercalated PbI_2 crystals as a result of the *A*-excitation of Pb^{2+} centers (λ = 340 nm) are thought to be responsible for the 550-nm PL band [7]. The distinction between the PL peak position of isolated Pb centers in the crystals studied here and that in alkali halide crystals is attributable to the lower site symmetry of a luminescence center having a cation vacancy in its nearest neighbor environment in NaI–Pb.

We believe that the 550-nm PL band of PbI_2-containing CdI_2 crystals under excitation at 313 nm is due to an intracenter transition in an isolated Pb^{2+} luminescence center. This conclusion is consistent with the findings [8] that absorption (excitation) spectra of PbI_2-containing CdI_2 crystals grown from solution show no band at 384 nm (that is, there are no PbI_2 nanocrystals) and that the 550-nm PL band can be excited in the range 320–350 nm. At the same time, Ohata et al. [9] modeled the 550-nm PL in terms of dimer centers.

The other PL bands observed under excitation in the fundamental absorption region are probably due to electron–hole mechanisms of carrier migration to

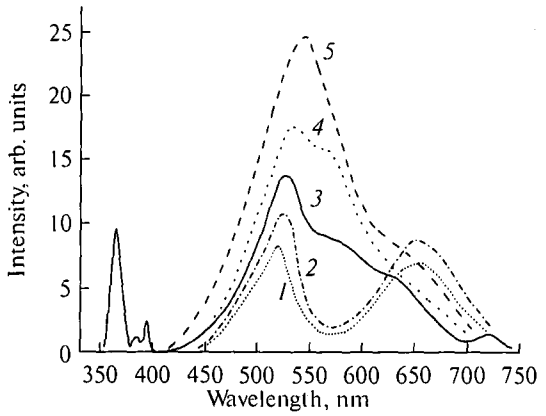

Fig. 1. PL spectra of a CdI_2 crystal containing 10^{-4} mol % PbI_2: λ_{ex} = (*1*, *2*) 384 and (*3*–*5*) 313 nm, T = (*1*, *4*) 60, (*2*, *5*) 77, and (*3*) 30 K.

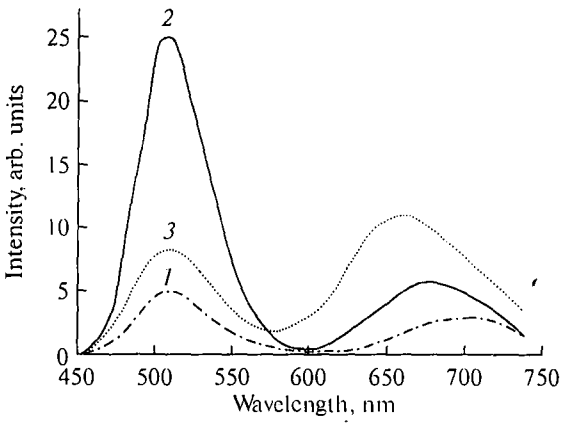

Fig. 2. PL spectra of a CdI_2 crystal containing 0.1 mol % PbI_2: λ_{ex} = 384 nm, T = (*1*) 4.2, (*2*) 50, and (*3*) 77 K.

luminescence centers in a direction normal to the C_6 axis (the in-plane and out-of-plane resistivities differ by three orders of magnitude). In particular, the longest wavelength (720 nm) PL band of PbI_2-doped CdI_2 crystals is similar to the 715-nm band of bulk $2H$-PbI_2 single crystals [10] and is attributable to carrier recombination within an I–Pb–I slab.

Figure 2 shows the 4.2-, 50-, and 77-K PL spectra (λ_{ex} = 384 nm) of a CdI_2 crystal doped with 0.1 mol % PbI_2 (spectra *1*, *2*, and *3*, respectively). The spectra each consist of two bands. The peak position of the 508-nm band is essentially temperature-independent (when its intensity varies within one order of magnitude), whereas the peak position of the longer wavelength band varies with temperature: from 700 nm at 4.2 K (spectrum *1*) to 660 nm at 77 K (spectrum *3*). That these PL bands differ in origin is also evidenced by the temperature dependences of their intensity: the intensity of the 508-nm PL band increases sharply in

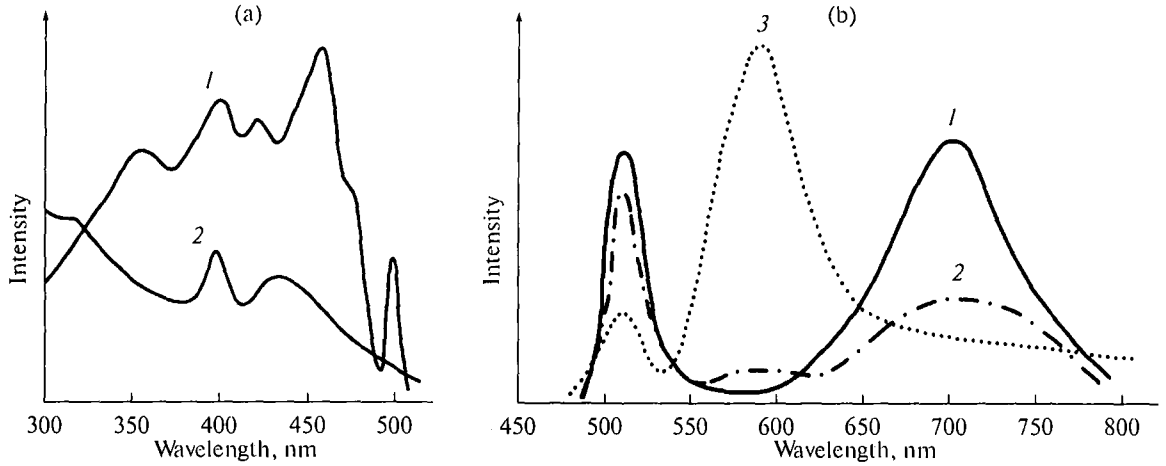

Fig. 3. (a) Excitation spectra of (*1*) the 690-nm PL band of $2H$-PbI_2 and (*2*) the 590-nm PL band of $4H$-PbI_2. (b) Effect of the $2H \rightarrow 4H$ phase transition on the PL spectrum (λ_{ex} = 337 nm) of a PbI_2 crystal: (*1*) before heat treatment, (*2*, *3*) after heat treatment at T = 430 and 460 K, respectively.

the range 4.2–50 K and drops as the temperature is raised to 77 K, whereas the intensity of the longer wavelength PL band increases monotonically with temperature. The temperature dependence of the 508-nm PL intensity is similar to that for the 516-nm band [1, 11].

A cation exciton self-trapped in PbI_2 at bending (membrane) vibrations of the crystal lattice [1] can account for the stability of the peak position of the 508-nm PL band. Its position is identical to that of the corresponding PL band of PbI_2 nanocrystals [12]. Comparison of spectrum *2* in Fig. 1 and spectrum *3* in Fig. 2 indicates that the peak position of the shorter wavelength PL band changes from 526 to 508 nm. The shift of this PL band with increasing doping level can be interpreted in terms of the size and shape of nanocrystalline PbI_2 inclusions in the CdI_2 crystal lattice.

The PL bands of PbI_2 crystals in the range 508–520 nm are commonly assigned to donor–acceptor pairs [13, 14]. Such interpretation is also applicable to the 508- and 516-nm PL bands of PbI_2-containing CdI_2 crystals because, as shown earlier [15], the photoconductivity of such crystals increases markedly (by up to four orders of magnitude) at temperatures below 70 K.

It is worth pointing out that, whereas the peak positions of the PL bands of bulk and nanometer-size PbI_2 crystals in the range 508–520 nm coincide with those of PbI_2-doped CdI_2 crystals, these systems differ in PL excitation spectra. In the latter crystals, excitation in the high-energy exciton region (384 nm) prevails, whereas in PbI_2 the dominant excitations are those at 458 [13] and 488 nm [14]. We believe that this confirms the possibility of the decay of low- and high-energy excitations, with radiative donor–acceptor pair recombination as the final step.

In discussing the origin of the longer wavelength PL band (Fig. 2), we should take into account the hopping mechanism of small radius exciton transport. In a previous study [1], the decrease in the 516-nm PL intensity at temperatures above 36 K (λ_{ex} = 384 nm) was attributed to the influence of the second slab in $4H$-PbI_2. Indeed, the peak position of the longer wavelength PL band at 77 K—650 nm in spectrum *2* in Fig. 1 and 660 nm in spectrum *3* in Fig. 2—is comparable to that of the 646-nm band, which was assigned by Goto et al. [16] to a self-trapped exciton in four monolayer PbI_2 nanocrystals.

Since PbI_2 nanocrystals were shown to be incorporated into the CdI_2 lattice as the $4H$-polytype [1], the luminescence properties of the PbI_2-containing CdI_2 crystals under consideration should be compared to those of $4H$-PbI_2 crystals. The signature of this polytype, resulting from the phase transition induced by high-temperature heat treatment of $2H$-PbI_2 crystals, is a PL band at 590 nm [5, 17].

Figure 3b shows PL spectra of a PbI_2 crystal before and after heat treatment. At λ_{ex} = 337 nm, the PL spectrum of the $2H$-PbI_2 crystal consists of two bands, centered at 510 and 690 nm (spectrum *1*). Heat treatment of the crystal at 430 K (spectrum *2*) reduces the intensity of these bands and produces a new band near 590 nm. Heat treatment at 460 K for 4 h causes 690-nm band to disappear almost completely, further reduces the intensity of the 510-nm band, and greatly increases the 590-nm PL intensity (spectrum *3*).

Figure 3a shows the excitation spectra of the PbI_2 crystals studied. The excitation spectrum of the 690-nm PL band contains peaks at 496, 455, 420, 396, and 350 nm (spectrum *1*). The 590-nm PL band has two excitation bands, at 430 and 396 nm (spectrum *2*).

In PbI_2-containing CdI_2 crystals, excitation in the fundamental absorption region of CdI_2 (350 nm) and on the long-wavelength side (392 nm) of the excitonic band at 384 nm gives rise to a PL band at 580 nm (Fig. 4). The measured temperature-dependent full width at half maximum of the 580-nm PL band of

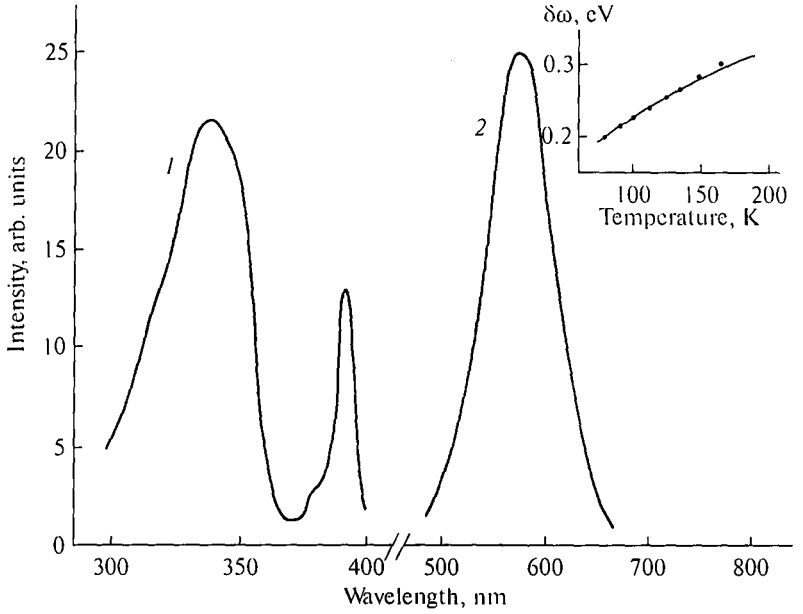

Fig. 4. (*1*) Excitation spectrum of the 580-nm PL band of a PbI_2-containing CdI_2 crystal and (*2*) 77-K PL spectrum of the crystal at λ_{ex} = 392 nm. Inset: temperature-dependent full width at half maximum of the 580-nm PL band.

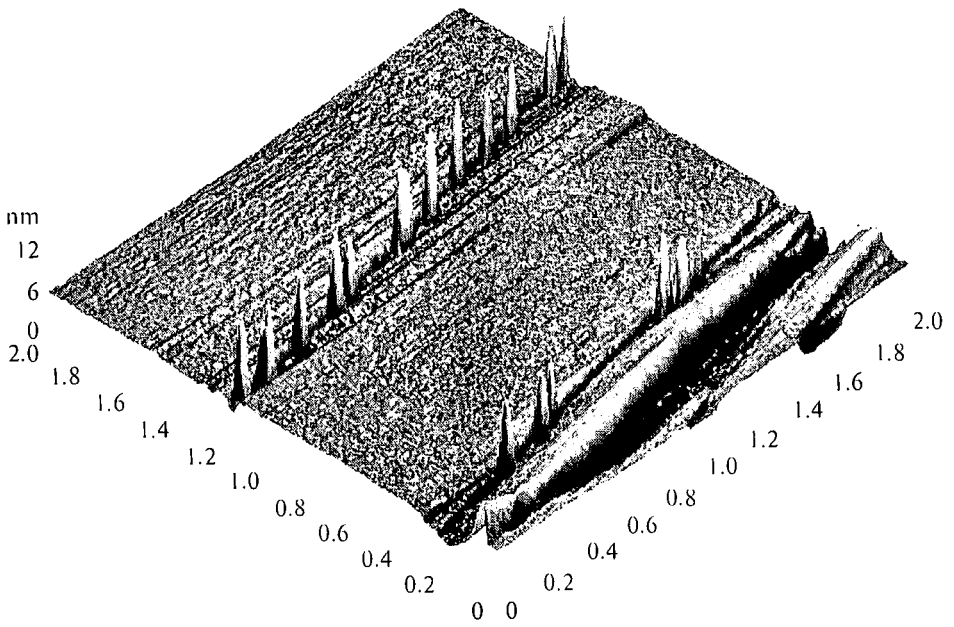

Fig. 5. Atomic force microscopy image of a freshly cleaved surface of a CdI_2 crystal doped with 5 mol % PbI_2.

PbI_2-containing CdI_2 crystals (Fig. 4, inset) was compared to that calculated as [18]

$$\delta\omega(T) = 2\left\{2\ln 2\left[\hbar\Delta\omega\hbar\omega_0\left(\frac{1}{\exp(\hbar\omega_0/kT)-1}+\frac{1}{2}\right)\right]\right\}^{1/2},$$

where $\hbar\Delta\omega$ is the Stokes shift and $\hbar\omega_0$ is the phonon energy.

Comparison of our experimental $\delta\omega(T)$ data and calculation results indicates that the energy of phonons interacting with luminescence centers is 100 cm^{-1}, which corresponds to phonon in the PbI_2 crystal lattice. This finding and the similarity between the spectral characteristics of the 580-nm PL band in PbI_2-containing CdI_2 crystals and those of the 590-nm PL band in 4*H*-PbI_2 crystals suggest that the 580-nm PL band is

related to $4H$-PbI_2 nanocrystals in the CdI_2 lattice. The 580-nm emission in the crystals studied here cannot be excited in the region of the 384-nm exciton band, which is consistent with the conclusion drawn by Baltog et al. [19] that the 590-nm PL band of PbI_2 is mainly due to the radiative recombination of photogenerated carriers, which prevails over the exciton contribution.

Thus, we are led to conclude that the $4H$-PbI_2 inclusions in the crystals under consideration are responsible for two centers which have different excitation bands (384 and 392 nm) and different luminescence bands: one center emits at 525 and 650 nm, and the other, at 580 nm.

Indeed, examination of PbI_2-containing CdI_2 crystals by atomic force microscopy showed that there were two types of nanocrystalline inclusions: "two-dimensional," concentrated in the galleries between the layers of the host crystal lattice [1], and "one-dimensional," located along linear defects in the structure of the host crystal (Fig. 5). We believe that the two-dimensional nanocrystals act as luminescence centers with an excitation band at 384 nm. The 392-nm excitation band, located on its long-wavelength side, may be due to linear structural defects near a luminescence center. Lyskovich et al. [20] assigned a 400-nm room-temperature photosensitivity band to dislocations in CdI_2.

CONCLUSIONS

The present results demonstrate that the electron–hole excitation mechanism results in energy transfer to both an exciton in PbI_2 (followed by emission) and centers with emission bands in the range 510–625 nm and at 720 nm.

The hopping mechanism of Frenkel exciton transport above 36 K leads to exciton transport to the next two-layer slab in nanocrystalline $4H$-PbI_2 inclusions and a PL at 650–660 nm.

The 550-nm PL band in PbI_2-containing CdI_2 crystals at $\lambda_{ex} = 313$ nm is assigned to an intracenter transition in an isolated Pb^{2+} luminescence center.

The $4H$-PbI_2 inclusions in the crystals studied are responsible for two centers which have different excitation bands (384 and 392 nm) and different luminescence bands: one center emits at 525 and 650 nm, and the other, at 580 nm. This is probably due to different positions of the nanocrystals: in the plane of the layers or along linear structural defects in CdI_2.

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