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Cadmium clusters in CdI₂ layered crystals: the influence on the optical properties

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Abstract

The influence of overstoichiometric Cd_i atoms on the optical properties of cadmium iodide layered crystals has been investigated. The results of optical absorption, luminescence, and luminescence excitation studies of CdI₂ crystals with controlled deviation from stoichiometric composition allow observing correlations between the Cd_i concentration and features in absorption and emission spectra up to concentrations of 10¹⁸ cm⁻³. At higher concentrations the overstoichiometric cadmium atoms form clusters, which were observed using scanning electron microscopy. The extinction spectra of (CdI_i)_n clusters are calculated in the frame of Mie theory and are found to correlate with the optical studies.

1. Introduction

Cadmium iodide single crystals, CdI₂, belong to the class of compounds having layered structure [1]. These crystals can be considered as two-dimensional systems and their investigations are important for the physics of low-dimensional structures. Besides that, CdI₂ also has relevance from the industrial point of view as a prospective scintillator with sub-nanosecond luminescence decay time for use in electromagnetic calorimeters [2]. CdI₂ crystals have been also proposed as a recording media for ultraviolet (UV) light etc [1]. In the last few years, several interesting works have been devoted to the studies of various nanostructures which are formed in doped CdI₂ crystals under irradiation [3, 4], in ultrathin layers of cadmium iodide [5–9], or in heterostructures in the case of the evaporation of metal film on the CdI₂ surface [10, 11]. It was shown that these systems exhibit unique properties which do not occur in the pure crystals. In particular, variations of the lattice *c*-parameter and the band gap *E_g* are observed in the thin films [5, 6], and the formation of nano-inclusions under electron-beam irradiation was reported [12], leading to the significant enhancement of the second harmonic generation output [4, 13, 14].

The crystalline structure of CdI_2 is formed by hexagonal close-packed arrangement of iodine atoms. The basic 4H-polytype consist of four iodine layers; therefore, the lattice of this crystal contains four octahedral and eight tetrahedral voids. Half of the octahedral voids existing in such a structure are occupied by Cd atoms. Since the number of octahedral positions in the hexagonal close-packed arrangement is two times larger than the number of cations, cadmium atoms are sandwiched between two similar sheets of I^- atoms. As a result, a basic Cd–I–Cd type layer with strong ionic–covalent bonding between atoms is formed. It is necessary to point out that neighboring Cd–I–Cd basic layers are held together by weak van der Waals forces.

The important consequence that follows from the weak interaction between adjacent layers is the existence of van der Waals gaps in layered structures. The gap consists of the channel net being formed by unfilled octahedral and tetrahedral voids. The localization of metallic atoms and organic molecules in the van der Waals gaps (i.e. the intercalation of crystals) causes significant changes in the structure and physical properties.

An important characteristic property of layered CdI_2 crystals is the presence of non-stoichiometric cadmium atoms, hereafter denoted as Cd_i , regardless of the crystal growth technique used. From the analysis of CdI_2 structure peculiarities it follows that these Cd_i atoms mainly localize within van der Waals gaps, occupying octahedral positions therein. This can be treated as a ‘self-intercalation’ process. In intercalated systems like this, fundamentally new phenomena occur which are not inherent to the host matrix and the intercalated substance individually.

The band gap of ~ 3.8 eV makes optical spectroscopy one of the most suitable tools for investigating of CdI_2 which, as mentioned above, shows promise for some industrial applications. Currently, pure cadmium iodide has been studied extensively; however, much less is known about the optical behavior of non-stoichiometric CdI_2 crystals. Due to the ‘self-intercalation’, their optical properties may be modified. Besides, the possible aggregation of cadmium atoms in clusters is a very interesting subject to study since a crystal containing such clusters can be considered as a nanostructured material. Therefore, the goal of the present study was to investigate the influence of non-stoichiometric cadmium atoms on the optical properties of cadmium iodide layered crystals.

2. Investigated crystals

To study the effect of overstoichiometric Cd_i atoms on the optical properties we have obtained a series of CdI_2 crystals with controlled deviation from the stoichiometric composition (to higher metal concentrations) as well as stoichiometric (reference) crystals, grown from raw material previously purified by means of the zone melting technique. All crystals were grown by the Bridgman method under strictly identical conditions. Overstoichiometric cadmium was introduced in the melt with 10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} mol% Cd_i concentrations. These values correspond to overstoichiometric cadmium atom concentrations $N_{\text{Cd}_i} = 10^{16}$, 10^{17} , 10^{18} and 10^{19} cm^{-3} , respectively. The concentration of CdI_2 matrix atoms, $N_{\text{Cd}} = \frac{\rho N_A}{M}$ ($\rho = 5.6 \text{ g cm}^{-3}$, the CdI_2 density; N_A is the Avogadro constant), is about 10^{22} cm^{-3} . Assuming the even occurrence of Cd_i atoms in the lattice, the distance between overstoichiometric atoms, $r = N_{\text{Cd}_i}^{-1/3}$, has been estimated. For crystals with the N_{Cd_i} values indicated above, these distances equal 46, 21, 10 and 5 nm, respectively.

3. Optical absorption, luminescence and luminescence excitation studies

Figure 1 illustrates the difference absorption spectra of $\text{CdI}_2\text{--Cd}_i$ crystals (with respect to the spectra of nominally pure crystals) at $T = 290 \text{ K}$. It is evident that the overstoichiometric

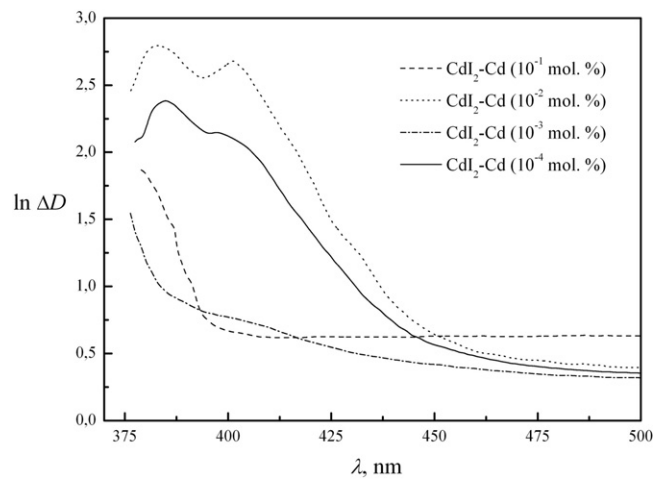


Figure 1. The difference absorption spectra of non-stoichiometric CdI_2 crystals at $T = 290$ K.

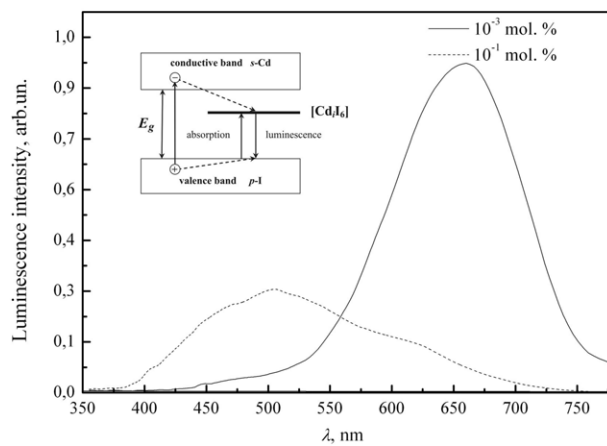


Figure 2. Cathodoluminescence of CdI_2 crystals with different Cd_i concentrations at 290 K. The inset shows the scheme of electronic transitions which cause the additional absorption and emission bands connected with non-stoichiometric cadmium.

cadmium gives rise to additional bands, peaked at 385–387 nm and 397–400 nm. The absorption coefficient in these regions increases with the Cd_i concentration only up to 10^{-2} mol%. At higher concentrations ($c_{\text{Cd}_i} \geq 10^{-1}$ mol%) the bands mentioned above disappear. Simultaneously, the transmittance of crystals in the transparent region decreases, and a shift of the intrinsic absorption edge to the long-wavelength region is observed. Such a shift may be concerned with the existence of an additional higher-energy band, which overlaps with the intrinsic absorption edge.

The cathodoluminescence spectra of $\text{CdI}_2\text{-Cd}_i$ crystals, measured under 10 keV electron irradiation, are shown in figure 2. At room temperature, CdI_2 emission spectra are characterized by the broad band centered around 500 nm. The introduction of overstoichiometric cadmium atoms leads to the appearance of an additional band long-wavelength luminescence band with

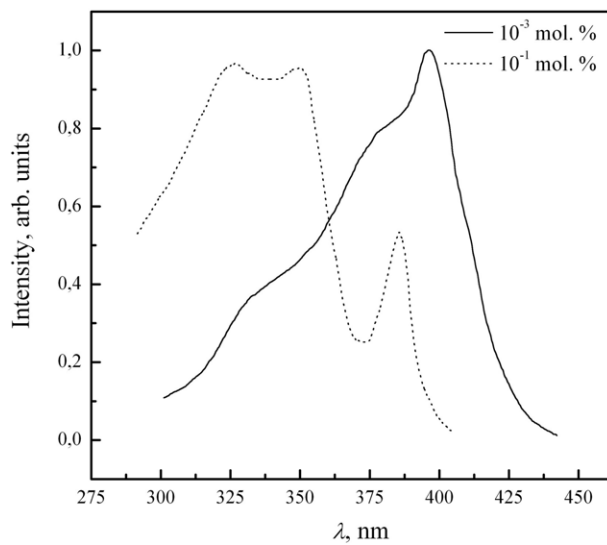


Figure 3. Luminescence excitation spectra for the red emission of $\text{CdI}_2\text{-Cd}$ (10^{-3} mol%) and $\text{CdI}_2\text{-Cd}$ (10^{-1} mol%).

the maximum at 660–670 nm (curve 1). The intensity of this emission band increases with Cd_i concentration, up to 10^{-2} mol%. When the concentration of overstoichiometric cadmium exceeds 10^{-1} mol% this band disappears and the luminescence of $\text{CdI}_2\text{-0.1 mol% Cd}$ crystals is characterized by the broad band centered at nearly 500 nm, as in stoichiometric crystals.

In figure 3 the excitation spectra of the long-wavelength luminescence of $\text{CdI}_2\text{-Cd}_i$ crystals with 10^{-3} and 10^{-1} mol% concentration are presented. Experimental data show that for the lower concentration of non-stoichiometric cadmium, the excitation band peaked at 395 nm is dominating, whose spectral position is in good agreement with the absorption data. Minor peaks at 370–390 nm and 330–350 nm appear at the high-energy shoulder of the 395 nm band (solid line).

At the cadmium concentration of 10^{-1} mol%, the character of the spectrum is completely different (dashed line in figure 3). The band peaked at 395 nm disappears; at the same time, a band at nearly 384 nm, characteristic for pure CdI_2 [2], is observed. Furthermore, in the spectral region, corresponding to the interband absorption, peaks at 325 nm and 350 nm are revealed.

In excitation spectra of the green emission (figure 4) the non-elementary band with a peak at 350 nm is observed. This band is a specific feature of CdI_2 crystals with both concentrations. In crystals with 10^{-1} mol% concentration of non-stoichiometric Cd the long-wavelength slope shifts to lower energies. As with the absorption spectra, this shift may be confirmation of the appearance of the new band (around 360 nm).

Thus, the analysis of absorption, luminescence and excitation spectra shows that the overstoichiometric cadmium leads to the appearance of additional absorption (luminescence excitation) bands at 385–387 nm and 395–400 nm and luminescence bands at 660–670 nm. The above-mentioned bands exist only for $c_{\text{Cd}_i} \leq 10^{-2}$ mol%. At higher concentrations these bands disappear and, at the same time, a high-energy absorption band arises, causing the shift of CdI_2 low-energy absorption edge.

To explain the experimental observations the following model can be proposed. We assume that non-stoichiometric Cd_i atoms, upon growth and further treatment, most probably localize

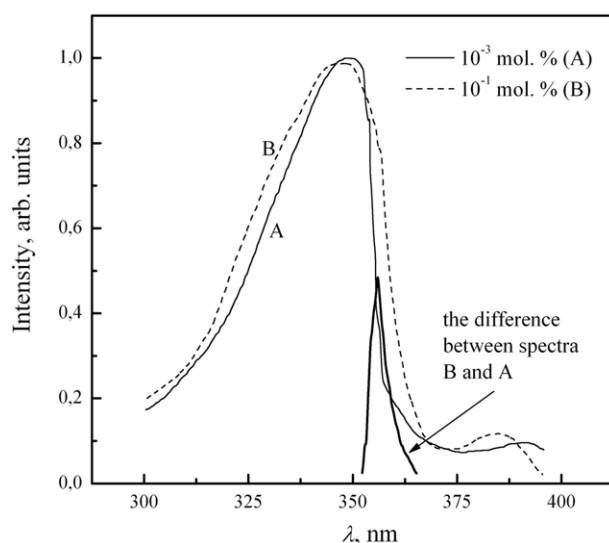


Figure 4. Luminescence excitation spectra for the green emission of $\text{CdI}_2\text{-Cd}$ (10^{-3} mol%) and $\text{CdI}_2\text{-Cd}$ (10^{-1} mol%).

in the octahedral holes of the van der Waals gaps. Consequently, a chemical bond between these and the lattice iodine atoms from the adjacent sandwiches is formed. This results in the formation of the $[\text{Cd}_i\text{I}_6]$ centers, which are connected with the interaction of cadmium s states and iodine p states. Since the conduction band of CdI_2 is formed by the atomic orbitals of cadmium [15], the existence of these centers leads to the appearance of a local level under the bottom of the conduction band. In this scheme the electronic transitions between the valence band, which are formed by p states of iodine and the local level are responsible for the additional luminescence and absorption bands (see the inset in figure 2).

The proposed model predicts the changes of some physical parameters of crystals, which were observed experimentally. For example, the c lattice parameter decreases due to the attraction between adjacent sandwiches [16], the nuclear quadrupole resonance frequency of I^{127} nuclei varies due to the electric field gradient changes caused by addition chemical bonds between Cd_i and I atoms [17], and changes of the nonlinear susceptibility are also observed [14, 18].

4. Scanning electron microscopy studies

The increase of Cd_i atom concentration leads to a decrease of the $\text{Cd}_i\text{-Cd}_i$ distance. This results in a change of the character of the overstoichiometric cadmium atoms from $s\text{-Cd}_i\text{-p-I}$ to $s\text{-Cd}_i\text{-s-Cd}_i$ interaction. When the $s\text{-Cd}_i\text{-s-Cd}_i$ interaction prevails, the $[\text{Cd}_i\text{I}_6]$ complexes disappear and, consequently, the initial properties of the CdI_2 matrix are restored. At the same time, the $s\text{-Cd}_i\text{-s-Cd}_i$ interaction directly addresses the formation of the cadmium clusters, referred to below as $(\text{Cd}_i)_n$ (where n denotes the number of atoms in the cluster). To check if this assumption is correct we carried out scanning electron microscopy (SEM) studies of these crystals.

The SEM studies of the freshly cleaved (0001) surface of non-stoichiometric CdI_2 crystals were performed using a JSM-T 220A instrument. The samples were examined in reflected and inelastically scattered electron beams with an energy of 20 keV.

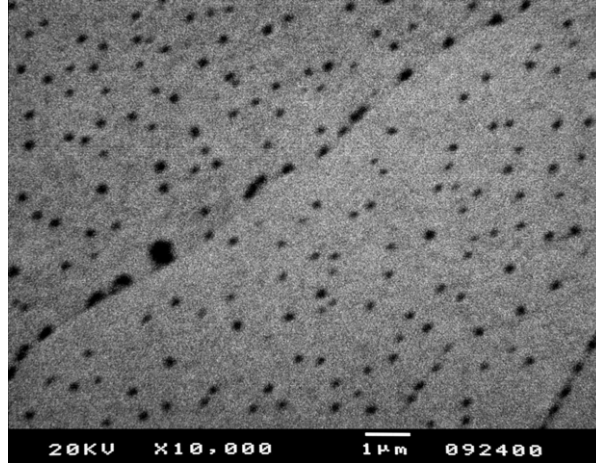


Figure 5. SEM image of a freshly cut CdI₂-Cd_i surface.

It was established that, in CdI₂ crystals with 10⁻¹ mol% concentration of Cd_i atoms, cadmium clusters are observed (figure 5). It was shown that the cluster distribution on the surface is very heterogeneous: in some regions, the cluster density is incidental. We have also found the correlation between the deviation from the stoichiometry and the cluster concentration.

Some quantities which characterize clusters in the CdI₂ matrix have been determined. The most crucial characteristic is the cluster size distribution, which is in our case Gaussian, and gives an average cluster size of approximately 0.1 µm.

Since the radius of the cluster is connected with the number of atoms as follows,

$$R = r_s N^{1/3},$$

where $r_s = 2.59 a_B$ and a_B is the Bohr radius, we obtain the number of atoms in the cluster

$$N = \left(\frac{R}{r_s}\right)^3 \approx 3.3 \times 10^8 \text{ (atoms)}.$$

The value obtained allows us to classify the (CdI_i)_n clusters as large ones.

5. Optical spectra modeling

It is well known [19–24] that metallic clusters influence the optical properties of the host medium. In particular, the absorption spectra of clusters exhibit an intensive absorption band in the UV or visible range which is not observed in bulk samples without clusters. Such absorption is due to the collective movement of electrons interacting with the electromagnetic wave inside the metallic cluster (so-called surface plasmon resonance) [21]. Metallic clusters also have an effect on the luminescence spectra of the materials [25].

To study such influence in the case of the cadmium clusters detected in CdI₂ we performed extinction spectra modeling.

The extinction spectra of (CdI_i)_n clusters were calculated by using the Mie theory [20]. In the framework of this approach the extinction cross section, $\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{sca}}$, is given by

$$\sigma_{\text{ext}} = \frac{2\pi}{k^2} \sum_{L=1}^{\infty} (2L+1) \text{Re}(a_L + b_L),$$

where $k = \frac{2\pi}{\lambda}$ and L is the order of the multipole extinction.

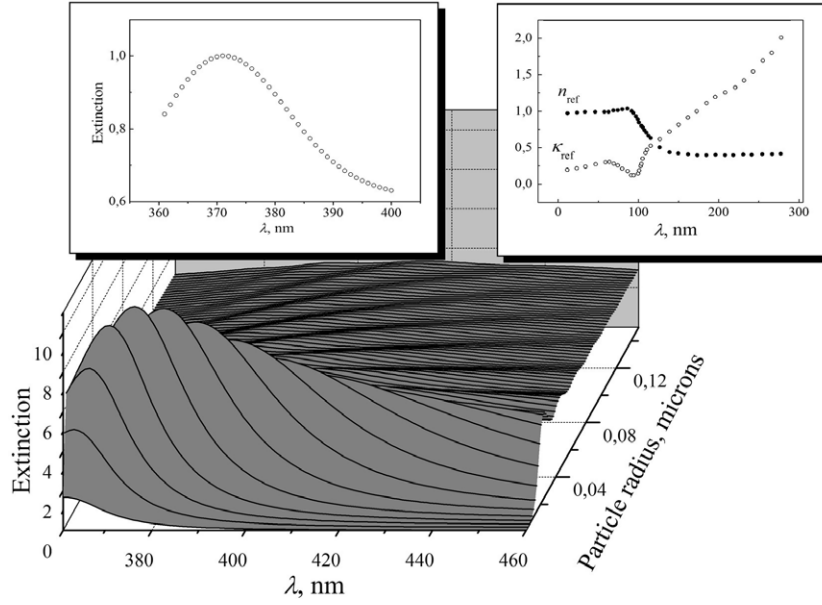


Figure 6. Panoramic extinction spectra of cadmium iodide crystals with cadmium clusters calculated in the frame of Mie theory. The inset on the right shows the refractive index dispersion (according to [26]). The inset on the left illustrates the calculated extinction spectrum, which represents the averaged contribution of the clusters observed in the crystals with 10^{-1} mol% Cd_i concentration.

The a_L and b_L coefficients can be expressed through the cylindrical functions

$$a_L = \frac{m\psi_L(m_x)\psi'_L(x) - \psi'_L(m_x)\psi_L(x)}{m\psi_L(m_x)\eta'_L(x) - \eta'_L(m_x)\eta_L(x)},$$

$$b_L = \frac{\psi_L(m_x)\psi'_L(x) - m\psi_L(m_x)\psi'_L(m_x)}{\psi_L(m_x)\eta'_L(x) - m\eta_L(x)\psi'_L(m_x)},$$

where $m_x = \frac{\epsilon_{Cd}}{\epsilon_{CdI_2}}$, $x = |k|R$ (R denotes the cadmium cluster radius).

Thus, the energy of the Mie resonances depends on the complex dielectric functions of the matrix (ϵ_{CdI_2}) and the metal (ϵ_{Cd}) and as well on the size and the shape of clusters.

Whereas the radii of $(CdI_i)_n$ are large, the extinction coefficient is determined only by the dipole moment ($L = 1$).

The dimensional dependence of the metal optical constant was not used in calculations, since the free path of the electron in cadmium is much smaller than the cluster radius.

The optical constants n_{ref} , κ_{ref} (the real and imaginary parts of the refractive index, respectively) of cadmium were taken from [26, 27]. It should be clarified that since only the values in the 50–280 nm range are reported (see top right inset in figure 6) an extrapolation to the visible range is necessary. Considering that $n_{ref}(\lambda)$ is almost constant within the 100–300 nm region we use the approximate value of $n_{ref} = 0.41$ in the whole range of modeling. Different $\kappa_{ref}(\lambda)$ approximations have been checked and the best agreement between experiment and calculations was reached assuming an exponential law for κ_{ref} dispersion.

Panoramic extinction spectra are shown in figure 6. As one can see, cadmium clusters give rise to the additional absorption in the range 360–450 nm. Calculations show that the spectral

dependence, half-width and intensity of these bands are sensitive to cluster radii as well as to the energy of photons interacting with the particles.

From the calculations it follows that, generally, the contribution of the clusters in CdI₂ is manifested as the extinction band close to the absorption edge. This is in agreement with our optical absorption data (where the band overlapping the absorption edge is predicted) and luminescence excitation studies (after the subtraction of spectra in figure 4, the narrow band peaked near 358 nm appears). The exact position of the extinction band depends strongly on the size of the cluster, but the integral contribution of clusters which were experimentally observed (see the top left inset on figure 6) results in the band peaked at about 370 nm. Moreover, the measured spectra may differ slightly from the theoretically calculated ones, whereas the clusters are distributed non-uniformly in the samples, and some absorption caused by impurities might be present.

6. Conclusions

CdI₂ layered crystals with controlled deviation from stoichiometric composition were grown and characterized by means of optical spectroscopy techniques, SEM and theoretical modeling. The results obtained indicated the appearance of new bands in the optical absorption, luminescence and luminescence excitation spectra. A model explaining the spectroscopic results Obtained is proposed, which assumes the formation of cadmium clusters in layered cadmium iodide crystals with deviation from stoichiometric composition. The model is consistent with SEM observations. The results of the experiments performed are also in agreement with theoretical calculation of the extinction of CdI₂-Cd_i crystals.

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