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BiI₃ nanoclusters in melt-grown CdI₂ crystals studied by optical absorption spectroscopy

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ABSTRACT

Optical absorption spectroscopy of CdI₂–BiI₃ layered crystals has been performed in the temperature range of 77–300 K. The main absorption, observed in these crystals at 2.59 eV is related to quantum confined exciton absorption of bimolecular BiI₃ cluster. Low energy absorption peaks at 2.38 eV, 2.06 eV and 1.94 eV can be tentatively assigned to larger clusters composed of 4, 6 or more BiI₃ molecules. In ultra-thin samples of CdI₂–BiI₃ several bands at 2.84 eV, 3.03 eV and 3.27 eV were observed which are ascribed to higher excited states of the excitons in bimolecular BiI₃ cluster.

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1. Introduction

Cadmium iodide (CdI₂) is a well known layered-structure compound. Due to weak interaction between layers and stronger bonding within an individual layer this material exhibits strong anisotropy of physical properties. Both pure and doped CdI₂ crystals have demonstrated several potentially attractive applications as scintillator and photochromic materials, candidate materials for memory elements, electroplating and lithography, etc. [1–4]. Previous investigations of CdI₂ crystals have been performed both theoretically [1,5–7] and experimentally [2–4,8–12]. Note that CdI₂ crystals strongly differ from alkali and alkaline earth halides, where F centers and exciton defect formation are well established [13].

Structural anisotropy of CdI₂ crystals gives the motivation to study the specific mechanisms of impurity introduction into the crystal lattice. There are several possibilities of impurity localization: nets of the lattice, interstitial sites within triple I–Cd–I layer and between two layers in van der Waals gaps of the lattice. Due to these different impurity states one observes a variety of

the radiation point defects as well as the formation of several phases [11].

Both CdI₂ and BiI₃ are layered structures in which a layer of metal ions is stacked between two closely packed layers of I[−] (forming so-called I–Me–I «sandwich»). The bonding type inside the layer ions is ionic–covalent and adjacent layers interaction is due to weak van der Waals forces. In CdI₂, Cd²⁺ ions form close-packed hexagonal net; on the contrary Bi³⁺ ions form honeycomb structure. Cd–I–Cd layer thickness is 6.84 Å and the thickness of I–Bi–I layer is 6.89 Å. The distance between neighboring I[−] ions within the same layer (the lattice parameter *a*) is 4.24 Å and 4.33 Å for I–Cd–I and I–Bi–I layers, respectively. Due to such similarity of both structures and due to fairly close layer parameters the formation of solid solutions in the CdI₂–BiI₃ system is very likely, despite of the fact that the valence of cadmium and bismuth ions is different. Since cadmium and bismuth ions are non-isovalent, various ion substitution options are possible. Therefore, the formation of various cluster structures at the micro/nanoscale can be expected. In this respect, in the present report CdI₂ is considered as a natural choice for the creation of novel BiI₃ based nanostructures.

Impurity centers formed by BiI₃ in the CdI₂ lattice were investigated in [3,14–18]. In these studies, however, attention is paid mostly to thin films [14,15], while results for doped crystals are reported for low concentration of impurities [3]. It is demonstrated [14,15] that in case of CdI₂–BiI₃ films (up to 10 mol% of

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BiI_3 bimolecular clusters of BiI_3 are formed and absorb light at nearly 2.50 eV (FWHM of the absorption band is ~ 0.21 eV). Such clusters are formed after the annealing of the films. At higher concentrations (above 20 mol%) there is a chance of planar tetramers (4-molecular clusters) and hexagon (6-molecular clusters) formation, which cause the optical absorption bands at 2.32 eV and 2.19 eV.

Here we report the investigation of the optical absorption of CdI_2 crystals doped by BiI_3 (1 mol%). Absorption spectra of these crystals are discussed with the particular focus on clusters contribution to the optical properties of the investigated medium.

2. Experimental

Bridgman–Stockbarger technique was employed to obtain $\text{CdI}_2\text{–BiI}_3$ crystals. Sealed quartz ampules were used in order to ensure the control of stoichiometry. BiI_3 salt was introduced as an impurity into the melt. The samples with linear dimensions of about 5 mm for optical measurements were then cut along the cleavage plane (001). In order to analyze the absorption features that are very sensitive to the crystal thickness, samples of different thickness were prepared.

Obtained samples were examined visually using a standard optical microscope.

Optical absorption measurements were performed under low vacuum using the experimental set-up tested in [12]. Sample was placed in the cryostat with transparent windows. Non-polarized light from a conventional lamp was focused on the sample (incident beam was perpendicular to the sample surface). Transmitted light was split into spectral components by using the MDR-23 grating monochromator (1200 grooves per millimeter) from LOMO (Russia), capable of working in the energy range of 1.3–3.6 eV. Light was collected from the exit slit of the monochromator by a PMT-based detector.

3. Results and discussion

Optical microscopy data show that the impurity is unevenly distributed over crystal volume: visually there are dark red and more transparent yellow regions. Dark regions correspond to higher concentration of BiI_3 impurity as compared to yellow regions. The optical absorption spectra done at 77 K for both regions of $\text{CdI}_2\text{–BiI}_3$ crystals are presented in Fig. 1.

In the spectra of regions with higher impurity concentration there is a complex band with main maximum around 2.5–2.6 eV. Long-wavelength slope of this band exhibits shoulders at ~ 2.3 and ~ 2.0 eV (Fig. 1, curve 1).

Same features can be observed as well for low-doped (yellow) regions, but overall spectrum structure is different. There are bands at 2.02 eV, 2.53 eV and 3.05 eV with smaller features at nearly 2.93 and 2.86 eV.

Some weak features were detected in the absorption spectrum of $\text{CdI}_2\text{–BiI}_3$ above 2.6 eV, however, due to the thickness of the sample they could not be clearly resolved. In order to have a further look into the structure of the dark-red region spectrum above 2.6 eV, the ultra-thin cuts have been prepared from the thick sample. These cuts were made from the sample part with high impurity contamination. The spectrum of ultra-thin crystal-line $\text{CdI}_2\text{–BiI}_3$ is shown in Fig. 2. It has been verified that the spectrum shape as well as the absorption level do not depend on temperature in the range of 77–300 K.

The Gaussian fit of the optical absorption curve was performed using a PeakFit software and allowed to outline the components of the spectrum. Decomposition results are presented in Table 1.

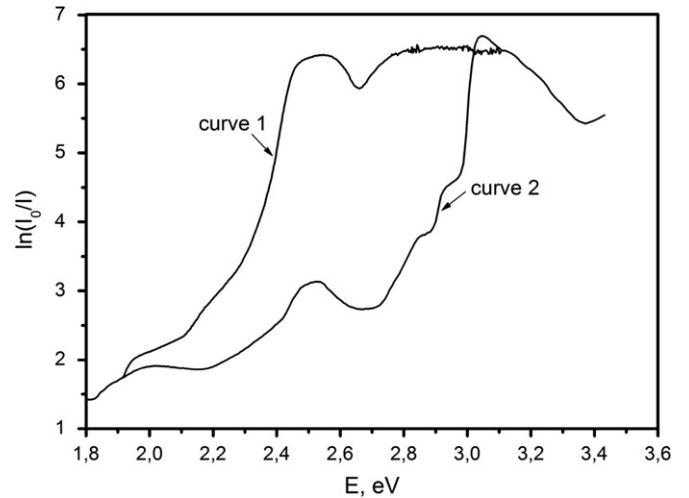


Fig. 1. Absorption spectra of dark red (curve 1) and yellow (curve 2) regions of $\text{CdI}_2\text{–BiI}_3$ crystals at $T=77$ K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

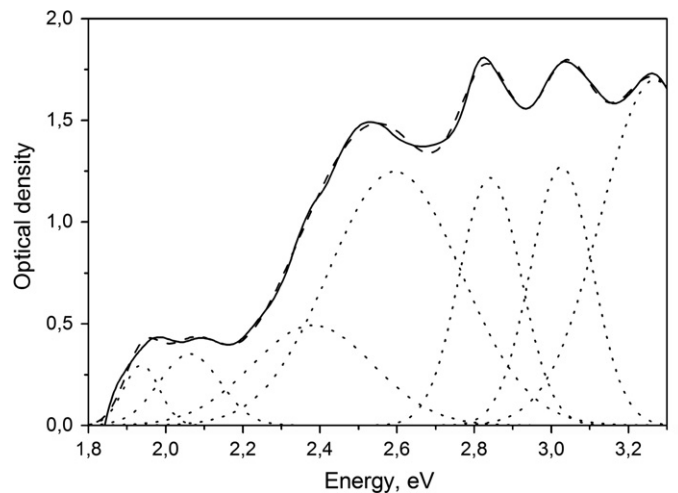


Fig. 2. Absorption spectrum of ultra-thin $\text{CdI}_2\text{–BiI}_3$ samples with high BiI_3 contamination at 77 K. Dotted lines are Gaussian components; dashed line represents the fitting curve.

As it follows from Table 1, the performed fit produced bands which are in good agreement with those observed in the optical absorption spectrum of thicker crystals. However, there are specific bands at 2.84; 3.03 and 3.27 eV which were not resolved for thick sample.

Absorption band at 2.5–2.6 eV (2.59 eV according to fit result) is observed for both low and highly doped crystals and usually is ascribed to the center which appears when three Cd^{2+} ions are replaced with two Bi^{3+} ions. Impurity atoms and cadmium vacancy form bimolecular BiI_3 cluster having an exciton peak at nearly 2.5 eV [14,15]. For the bulk BiI_3 crystal this peak is found at 2.072 eV [18], having FWHM of 65 meV and small exciton effective Bohr radius (6 Å) [19]. In our case this peak shifts towards higher energies for $\Delta E=0.52$ eV which can be connected with quantum confinement of excitons inside bimolecular BiI_3 clusters in CdI_2 host. Estimations for a simple model of an exciton in the rectangular potential well give

$$\Delta E = \frac{h^2}{2\mu R^2}, \quad (1)$$

where μ is the electron reduced mass ($\mu = 1.4 m_0$, m_0 denotes the free electron mass [20]) and R denotes the well depth, determined by the

Table 1
Gaussian fit parameters for the spectrum of CdI₂–BiI₃ thin sample at 77 K (Fig. 2).

Peak position, eV	Width (eV)	Origin
1.94	0.11	6- (or more) molecules BiI ₃ clusters
2.06	0.19	4-molecules BiI ₃ clusters [14,15]
2.38	0.38	4-molecules BiI ₃ clusters [14,15]
2.59	0.44	Bimolecular BiI ₃ clusters
2.84	0.18	
3.03	0.20	
3.27	0.22	

cluster size. From (1) it follows that $R \approx 14 \text{ \AA}$. This value allows rough estimation of the cluster size, assuming the cluster is cylindrical, its diameter is about $3a$ ($a=4.33 \text{ \AA}$ is BiI₃ lattice parameter) and height approximately equals to the thickness of two structural I–Bi–I “sandwiches”.

Absorption bands at $h\nu \geq 2.6 \text{ eV}$ in the proposed model can be tentatively ascribed to higher energy states of an exciton in a potential well.

Bands at 2.38 eV and 2.06 eV (see Table 1) were also observed previously [14,15] and correspond to 4-molecules BiI₃ clusters in CdI₂. On the other hand, their spectral position almost coincides with absorption peaks R, S and T excitons bounded at stacking faults of BiI₃ [21].

Most simple mechanism of the charge compensation can be realized by substituting three Cd²⁺ ions for two BiI₃ ions. In this case, the cluster consisting of two BiI₃ molecules and a cadmium vacancy are formed. In general, the formation of complex clusters in which $m \text{ Bi}^{3+}$ ions substitute $n \text{ Cd}^{2+}$ ions is possible. The numbers m and n must satisfy the condition $3m=2n$, and the number of vacancies is determined as $n-m$. Thus, band at $\sim 1.94 \text{ eV}$ (Fig. 2) can be an evidence of larger clusters (composed of 6 and more BiI₃ molecules) presence. Such larger clusters can be formed by vacancies, impurity atoms and host lattice atoms.

At lower concentration of BiI₃ the probability of such larger clusters formation is small due to high energy barrier for Bi³⁺ ion couples, which contribute to the formation process. If the crystal is grown from melt one should consider also elastic deformation fields. Due to the influence of such fields Bi³⁺ ions may localize at dimensional defects of the lattice (e.g. dislocations). Transfer of Bi³⁺ ions to the dislocation borders and the interaction between Bi³⁺ ions, vacancies and anion sublattice may lead to the appearance of BiI₃ microphase containing large (at the atomic scale) clusters.

4. Conclusions

Complex structure of the optical absorption spectra of CdI₂–BiI₃ crystals has been investigated in details. The main optical absorption peak was identified at 2.59 eV and related to bimolecular BiI₃ centers that are formed by substitution of three Cd²⁺ ions for two Bi³⁺ ions. Considering the spectral shift of this peak in CdI₂–BiI₃ with respect to the bulk BiI₃, the radius of the bimolecular cluster of BiI₃ ($R \approx 14 \text{ \AA}$) has been roughly estimated. Bands peaked at higher energies (found in thin samples) are attributed to higher energy states of an exciton confined within the BiI₃ cluster. The possible origin of long-wavelength absorption peaks could be attributed to larger clusters.

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