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ABSTRACT

Synchrotron radiation is applied to study visible and UV luminescence spectra and their excitation spectra of undoped as well as In and Sb doped cadmium iodide crystals at 10 K. The origin of principal luminescence bands and the role of impurities in the formation of emission centers are discussed. The luminescence properties have been explained based on the electronic structure of CdI_2 crystals.

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INTRODUCTION

Cadmium compounds such as cadmium zinc telluride (CdZnTe) and cadmium telluride (CdTe) showing good detection efficiency and high energy resolution, demonstrate themselves as attractive detection materials in many applications for detecting x-ray and gamma radiation at room temperature, such as medical and industrial images, industrial measurements and non-destructive testing, safety and monitoring, nuclear safeguards and non-proliferation, as well as astrophysics.^{1–4} Cadmium iodide (CdI_2) crystals are long known for their descent scintillating properties which have been extensively studied by spectroscopic techniques.^{5–12} Comparing it with other scintillators and phosphors^{13–21} it shows comparable detector characteristics in some parameters, and therefore it is still of interest, especially when considering its improvement by doping.^{22–24}

Among existing and potential application areas of CdI_2 , one can mention detectors, photolithography, and optical recording. In the solid electrolyte system $\text{CdI}_2\text{-AgI}$ addition of cadmium iodide effectively lowers the superionic transition temperature from 146 °C (in pure silver iodide) to about 110 °C.^{25–29} It has been identified that at helium temperatures there exist yellow (Y), green (G), and UV emission bands.^{30–32} This luminescence is generally

ascribed to excitons composed of p -states of iodine and s -states of cadmium.^{33,34} Donors and acceptors come into play as the temperature increases as confirmed by thermoluminescence studies.³⁵ The layered structure of crystals makes it likely for the impurities to enter different crystallographic positions therefore possibly serving as centers for recombination.^{5–7,36} From this point of view, it is interesting to see how luminescence properties change upon doping under high-density excitation.

The aim of the present work is to shine a light on the electronic processes in nominally pure as well as in doped with In and Sb cadmium iodide crystals exploiting high energy synchrotron radiation as a source of excitation.

EXPERIMENTAL

Cadmium iodide crystals were grown from melt by means of the Bridgman technique.³⁷ The impurities doping was done by adding 0.1 mol % of the In or Sn metals into the initial melt. After the completion of the growth process, samples were cut along cleavage planes taking into account that the adjacent layers of the crystal are held together by relatively weak forces. The final specimens had a thickness of approximately 50 mm.

Luminescence excitation spectra and emission spectra of pure and doped cadmium iodide crystals were studied at the temperature of 10 K using the SUPERLUMI setup of line I of DORIS III storage ring at the DESY synchrotron facility.^{38,39} This experimental set-up was a unique tool for investigations of different types of wide bandgap bulk and nanomaterials.^{40–45}

The mathematical treatment of collected data and the deconvolution of the experimental spectra into individual Gaussian components were performed by means of the OriginLab Origin software package.

RESULTS AND DISCUSSION

The luminescence spectrum of the nominally pure cadmium iodide at 10 K under 13.77 eV excitation is shown in Fig. 1. The shape of the spectrum does not depend on the excitation energy in VUV spectral range. The deconvolution of the luminescence spectrum to the Gauss components allows us to identify three principle emission bands denoted hereafter as Y, G, and UV and emphasized on the graph with respective energies shown above the peaks.

The fitting procedure based on the data shown in Fig. 1 could refine peak positions, which are 2.03 eV for Y-band, 2.44 eV for G-band and 3.37 eV for UV-band. These values are fairly close to those, observed earlier (2.16, 2.50 and 3.35 eV, respectively).^{36–38} It was suggested that the origin of these emission bands to is connected with the radiative recombination of the self-trapped exciton in $[\text{Cd}^{2+}\text{I}_6]^{4-}$ a molecular complex that possesses octahedral symmetry D_{3d} .

For doped crystals, three above mentioned bands can still be resolved at 10 K (see Fig. 2), however the luminescence bands Y and UV are significantly suppressed. Slight variations of the exact peak positions in Figs. 1 and 2 most likely related to the accuracy of the fitting procedure approximations.

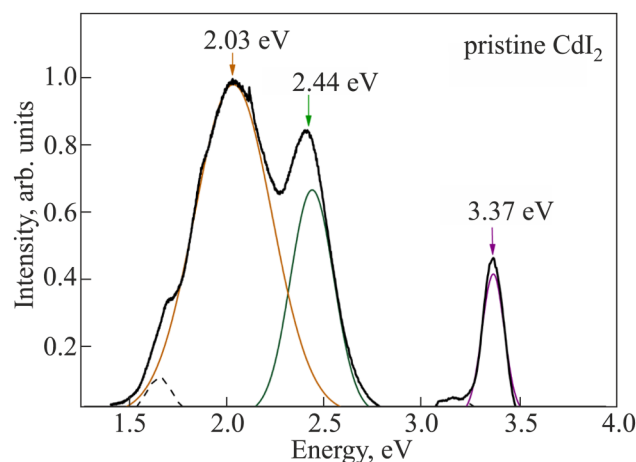


FIG. 1. Photoluminescence spectrum of pristine cadmium iodide under synchrotron radiation excitation (13.77 eV) at 10 K. The spectrum is deconvoluted to the Gauss components, which are shown as solid and dashed lines.

The differences between the luminescence spectra observed in undoped and doped cadmium iodide crystals can be explained assuming the following model. Dopant ions and intrinsic lattice defects, such as vacancies or interstitial atoms, are forming nanosized clusters. Driving forces that facilitate the formation of clusters originate from elastic, Coulomb or chemical interactions between cluster components. Nanosized clusters exhibit discrete energy spectra. Some of energy levels that fall within the bandgap of the crystal can serve as centers for radiative or non-radiative recombination effectively responsible for additional absorption, photoconductivity, and other features.^{46–48} It is assumed that at least three types of nanocluster-like formations can be created and impurity atoms may selectively “amplify” some of them.

Figure 3 shows the photoluminescence excitation spectrum (1, red curve) of CdI_2 for G-band which is the most prominent one in both pure and doped crystals. On the same energy scale, the reflectivity spectrum of cadmium iodide crystal is presented (2, blue curve).

As one can see from Fig. 3, in the range 5.7–6.2 eV there is an anticorrelation in the structures of luminescence excitation and reflectivity spectra. The peak at 5.9 eV in the luminescence

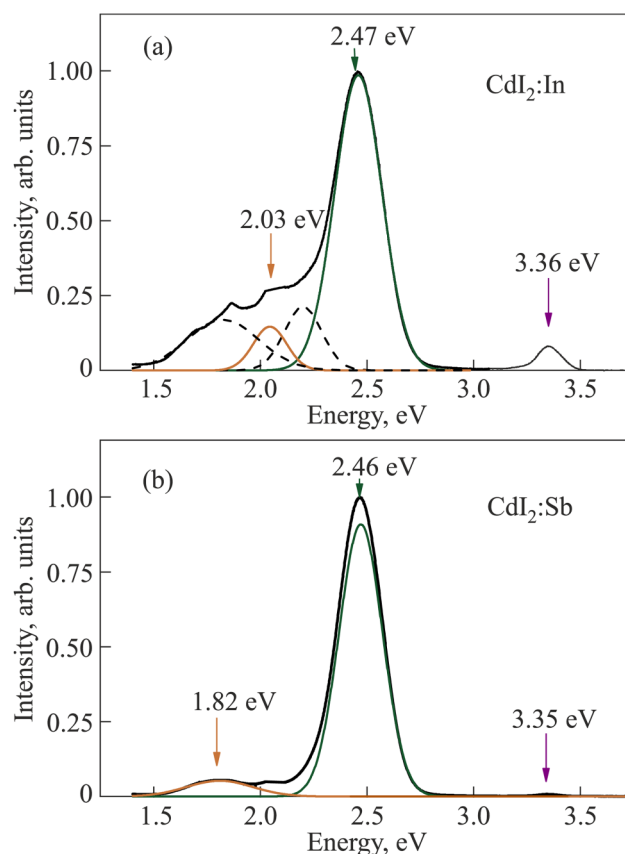


FIG. 2. Photoluminescence spectra of cadmium iodide doped by In (a) or Sb (b) ions at 10 K. The excitation energy is 13.77 eV.

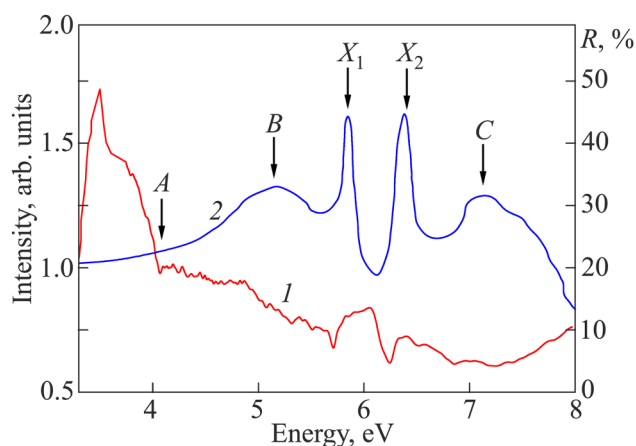


FIG. 3. Photoluminescence excitation (1, red line) and reflectivity (2, blue line) spectra of CdI_2 crystals at 10 K.

excitation spectrum coincides with the minimum in the reflectivity spectrum. At the same time, exciton peaks denoted as X_1 and X_2 in the reflectivity spectrum correspond to the minima in the luminescence excitation spectrum (It should be noted that three additional anomalies A, B, C were also found in the spectra.). This type of anticorrelation is known for the luminescence excitation spectra of self-trapped excitons⁵⁰ and luminescence excitation spectra of core-valence luminescence.⁵¹ Such behavior is explained by luminescence damping on surface defects and losses due to reflection. At the energies of the reflection peak light penetration depth is small and the majority of electronic excitations are formed in the near-surface layer. High concentration of defects in this layer facilitates non-radiative recombination of such excitations, consequently decreasing the emission intensity in the intrinsic absorption range.

Note that CdI_2 crystals are very different from alkali and alkaline earth metal halides, where the F centers, self-trapping of holes (V_k center), and exciton defect formation are well known and thoroughly studied.^{52–54}

CONCLUSIONS

Low-temperature photoluminescence from layered cadmium iodide crystals was studied using synchrotron radiation as an excitation source. Main emission lines characteristic for CdI_2 scintillator crystal were identified and refined with Gaussian decomposition. Spectral features of pristine CdI_2 luminescence were compared to those of cadmium iodide doped by indium and antimony ions. The model suggesting the formation of nanoclusters that alter the distribution of luminescence intensities of principal yellow, green, and ultraviolet bands is discussed.

Luminescence excitation spectrum of cadmium iodide is analyzed with respect to its reflectivity spectrum. Anticorrelated extremal points in these spectra may be due to high probability of non-radiative recombination processes in the near-surface area of the crystals.

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