ISSN 2224-087X. Електроніка та інформаційні технології. 2018. Випуск 9. С. 164–171
Electronics and information technologies. 2018. Issue 9. P. 164–171

UDC 535.376

X-RAY LUMINESCENCE OF Tl_4CdI_6 CRYSTALS

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We report on the study of low-temperature spectra (80-130 K) of X-ray luminescence of Tl_4CdI_6 crystals. Temperature behavior of the studied X-ray luminescence spectra and identification of their maxima are presented. The recombination mechanisms associated with natural anisotropy of the compounds under study are discussed and the possibility of their practical application is analyzed

Key words: luminescence, structural parameters, excitation, spectrum, admixture.

Introduction. At now reports of an episodic character are being published in the periodical literature which deal with the possibility of obtaining one class of crystals of the A_4BX_6 group (in particular, such as Tl_4CdI_6) [1–4]) and studying their optical, mechanical and spectral characteristics [5-9]. It has been expected that along with the conservation of relatively high component of ionic bond the structural anisotropy should be large. Obviously, obtaining new single crystals put forward priority task of investigation of their basic physical and chemical characteristics: X-ray structural parameters, temperature dependence of the linear expansion coefficient in the region of phase transitions, determination of the band gap, establishemend of the basic optical characteristics, investigation of luminescence spectra and their interpretation.

The prospects of the compounds under study are caused by their practical application as working elements of temperature sensors and detectors of ionizing radiation [10]. That is, these are the materials with controlled physical parameters which are promising ones for optoelectronics and nonlinear optics.

We have previously reported on synthesis of the Tl_4CdI_6 compounds and their structural, band - energy and optical properties. In this paper, we present the results of studies of low-temperature X-ray luminescence spectra (XL) of Tl_4CdI_6 crystals and their temperature behaviour.

Specimens and method of experiment

A. Synthesis and Crystal Growth

In order to synthesize thallium cadmium iodide, we used commercially produced salts of the relevant metal halides. The initial components were taken according to equi-molar ratios.

Preliminary purification of the salts was performed using reiterated recrystallisation from the melt in quartz ampoules, and a vacuum sublimation. Tl_4CdI_6 single crystal was grown with a standard Bridgman–Stockburger technique [3], [4], [11].

B. Crystal structure of Tl_4CdI_6

In order to be sure of the purity and homogeneity of the grown bulk samples, the large single crystals were powdered.

X-ray powder diffraction (XRPD) data for X-ray phase analysis and crystal structure refinement were collected in the transmission mode on a STOE STADI P diffractometer [12] at the room temperature $T = 295$ K with the following setup: Cu Kα1-radiation (X-ray tube voltage $U = 40$ kV, current $I = 35$ mA), curved Ge (111) monochromator on primary beam, $2\theta/\omega$-scan, 2θ angular range for data collection 10.000^o – 100.225^o with the increment of 0.015^o, linear position sensitive detector with the 2θ step of recording 0.480^o and time per step 100 – 270 s. A calibration procedure was performed employing NIST SRM 640b (Si) [13] and NIST SRM 676 (Al_2O_3) [14] standards. Analytical indexing of the powder patterns and determination of the space group were performed using N-TREOR09 [15]. The crystal structure was refined by the Rietveld method [16] with the program FullProf.2k (version 5.40) [17], [18], applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters. Absorption correction was accounted by measuring the absorption factor for a sample transmission foil [12] and by Rietveld refinement, according to the type "Transmission geometry (STOE)" [18], [19]. The crystallographic data were standardized with the program STRUCTURE TIDY [19] and the program VESTA [20] was used for structural visualization [21].

Morphology of the samples was examined using REMMA- 102- 02 Scanning Electron Microscope-Analyzer (JCS SELMI, Ukraine) [22].

C. Optical Experiments

For the X-ray luminescence studies the sample was put in the special helium cryostat, containing quartz windows for light detection and a beryllium window. The direction of the X-ray beam as well as that of the light beam was normal to the ***ab***- plane of the crystal.

The X-ray tube URS-60 with a Mo-anticathode operating at 1580 V and 10 mA was used as an excitation source (~750 mR/min). The contribution of the low-energy continuum was reduced by means of a 0.5 mm aluminum filter. A photomultiplier FEU-79 operating in the singlephoton counting regime was used as a photodetector.

A temperature controller "UTREX K43" provided necessary precision of the temperature measurements and stabilization ($\Delta T = \pm 0.1$ K) [23], [24].

Luminescence spectra were measured in the range of 415 – 825 nm with a resolution of 2.5 nm. The temperature was measured in a helium cryostat using a silicon thermodiode as the temperature sensor. The detailed XL setup description can be found in Ref. [25].

Experimental results and discussion. We obtained Tl_4CdI_6 single crystals of fairly good optical quality, with the diameter of ~12 mm and the typical length of ~15 mm (see Fig. 1, 2). The crystalline structure identified by us is tetragonal, being described by the spatial symmetry class P4/*mnc*. The calculated cell parameters are present in table 1.

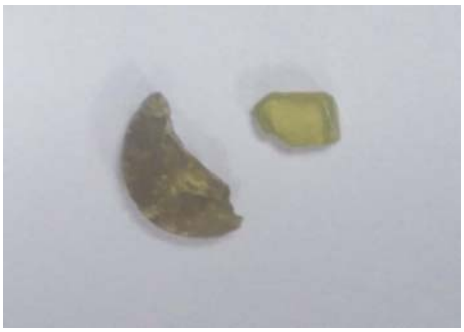

Fig. 1. Appearance of Tl_4CdI_6 single crystal grown with a Bridgman–Stockburger technique.

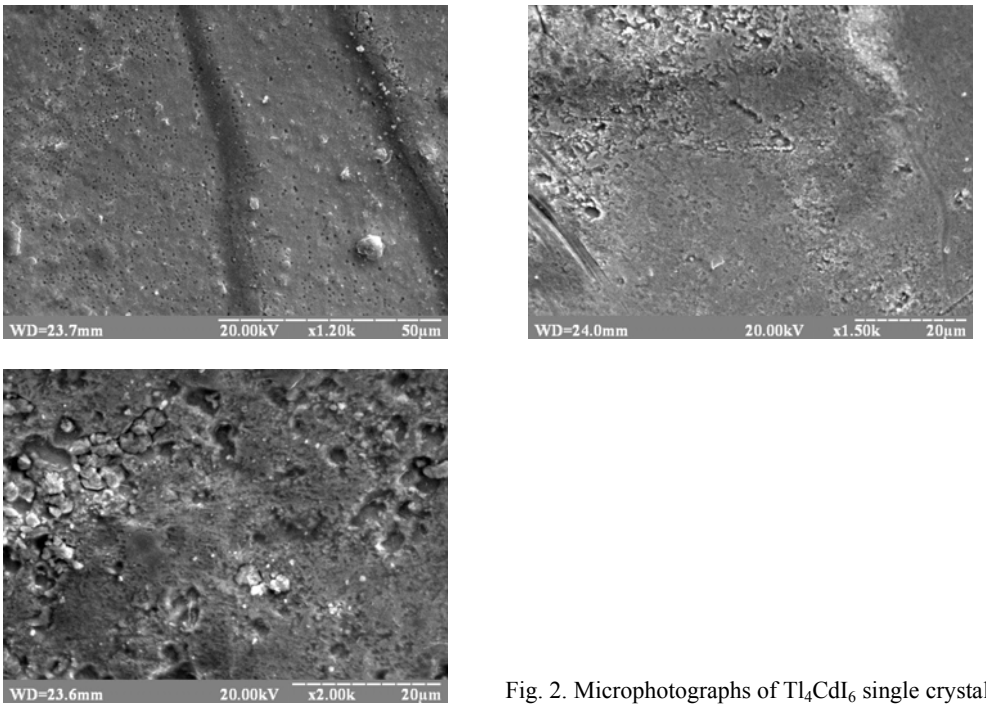

Fig. 2. Microphotographs of Tl_4CdI_6 single crystal.

Table 1.
Crystal data and structure refinement for Tl_4CdI_6. [26].

Lattice parameters	**Tl_4CdI_6**
a*=*b, Å	9.231
c, Å	9.592
V, Å	817.35
α=β=γ, o	90
ρ, g/cm	6.87
Z	2

The structure is illustrated in figure 3.

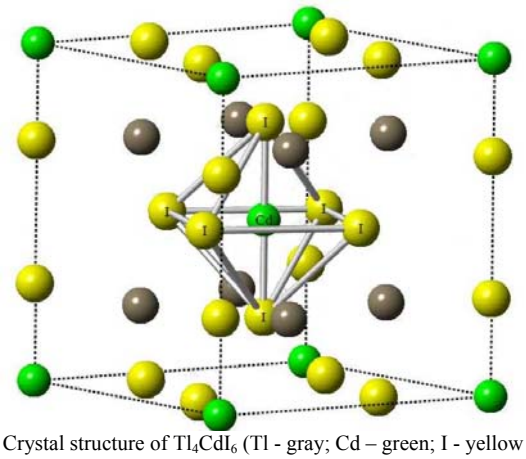

Fig. 3. Crystal structure of Tl_4CdI_6 (Tl - gray; Cd – green; I - yellow balls).

Optical luminescent properties of crystals are of interest in the scientific aspect, providing important information about the features of phonon and exciton spectra as well as the impurities and defects of the crystal structure. By means of XL spectra, due to deeper penetration of excited electrons in a material, you can explore its volume.

Low-temperature XL spectra of Tl_4CdI_6 crystals are present in Fig.4. We have carried out decomposition of these spectra on the bands with the Gauss profiles. As a result, we get the bands at approximately 1.97, 2.36 and 2.85 eV for Tl_4CdI_6.

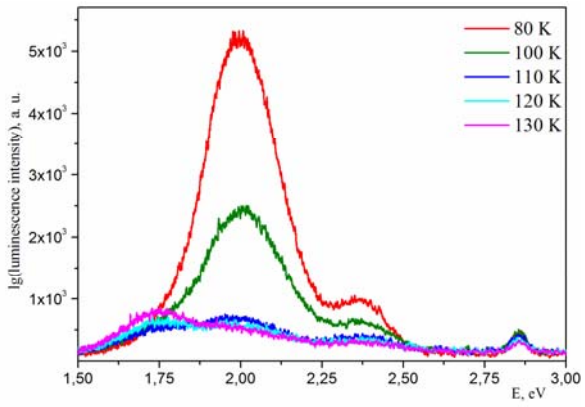

Fig. 4. X-ray luminescence spectrum of the Tl_4CdI_6 crystal in the process of irradiation.

Generally, positions of the spectral bands of XL are independent of temperature (the luminescence intensity and position of the 1.97 eV band are changed but this shift by ~ 0.2 eV toward the lower energies may be associated with the redistribution of radiation). Figure 5 shows the temperature dependence of the integral intensity of XL bands for the Tl_4CdI_6 crystal.

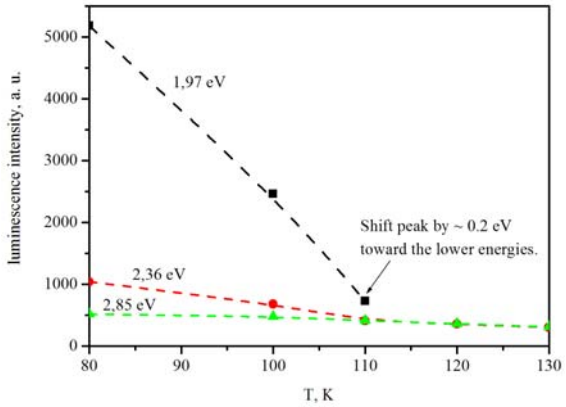

Fig. 5. Temperature dependence of the integral intensity of XL bands for the Tl_4CdI_6 crystal.

Generally speaking, accurate conclusions about the nature of the luminescence bands in the sample under study are difficult to draw at least for the reason that in the literature there are no sufficient data on the spectra of exciton and phonon excitations. In our opinion, the XL bands can be caused by both recombination of exitons and mainly intercenter transitions in uncontrolled impurities. The only information about the nature of the origin of luminescence bands in the Tl_4CdI_6 crystal is given in [5], [9].

In paper [9], the authors have found the strong band at 2.4 eV and two weak bands at 2.8 and 3.0 eV. The first of them is associated with the phase impurity TlI, for which the absorption peak at room temperature was found at 2.28 eV, and the third band is interpreted as a consequence of the low temperature displacement of the absorption edge found at 2.83 eV.

To test the hypothesis [5], our data for the Tl_4CdI_6 crystal are quite useful because the TlI phase impurity, if present, would have to reproduce the band at 2.4 eV. An analysis of our data for the peaks of the XL indicates the presence of a luminescence band in the vicinity of ~ 2.4 eV. In this regard, we assume that the impurity of the TlI structural phase in our crystal may be present. However, it would be more natural to admit the presence of ionic impurities.

Conclusion. Taking into account the information on the luminescence spectra presented in [5], [9] and the results of our studies, we can assume the presence of some common mechanisms of the formation of these spectra. Therefore, we assume that the wide low energy band may have an impurity character and be attributed to the recombination of a "band-impurity center" type. As follows from the spectral position, the next (central) band of the XL probably can be caused by the recombination with the formation of a bound exciton or an exciton-impurity complex localized on thalium impurities or vacancies. The hypothesis about the excess of thallium atoms is generally correct what is connected with the peculiarities of the crystalline structure and the technological conditions of obtaining our crystals. Finally, the high-energy band can correspond to the recombination of a free or autolocalized exciton.

It should be noted that the noticeable XL response is positive in terms of possible applications of the studied crystals as scintillation materials, but relatively high luminescence intensity means unproductive energy losses of high-energy excitation in the case when the crystal serves as a material for semiconductor detector of X- or gamma rays [5].

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Стаття: надійшла до редакції 16.04.2018,
доопрацьована 11.05.2018,
прийнята до друку 11.05.2018.

РЕНТГЕНОЛЮМІНЕСЦЕНЦІЯ КРИСТАЛА Tl_4CdI_6

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Перспективність досліджуваних сполук зумовлена їхнім практичним застосуванням як робочих елементів давачів температури та детекторів іонізаційного випромінювання. Тобто ці матеріали з керованими фізичними параметрами є перспективними для оптоелектроніки та нелінійної оптики. Серед відомих матеріалів (CdTe, CdTe–CdZn, TlBr, MI_2 (M = Pb, Hg)) для детектування іонізаційного випромінювання вирізняється трикомпонентна сполука Tl_4CdI_6, адже саме в ній реалізуються всі необхідні вимоги для детекторів радіаційного випромінювання. Кристал Tl_4CdI_6 має велике значення ширини забороненої зони (E_g = = 2,83 еВ). Наявність Tl компоненти підвищує коефіцієнт поглинання матеріалу для рентгенівських та γ-променів через високу густину (ρ = 6,87 г/см^3 та Z (Tl = 81, Cd = 48, I = 53).

Оптичні люмінесцентні властивості кристалів цікаві в науковому плані, оскільки надають важливу інформацію про особливості фононного та екситонного спектрів, а також домішки і дефекти кристалічної структури. За допомогою спектрів рентгенолюмінесценції завдяки глибшому проникненню електронів збудження в речовину можна дослідити його об'єм. Спектри рентгенолюмінесценції виявляють якісно подібну структуру для обох досліджених кристалів, принаймні для спектрального розподілу інтенсивності світіння. Для них ми виконали розклад на складові смуги з гаусовим профілем.

Описано дослідження низькотемпературних спектрів (80–130 K) рентгенолюмінесценції та морфологічних особливостей кристалів Tl_4CdI_6. Наведено аналіз особливостей поверхні кристала з використанням сканувального електронного мікроскопа. Схарактеризовано структурні параметри та змодельовано структуру кристала Tl_4CdI_6. Проаналізовано температурну поведінку спектрів рентгенолюмінесценції та ідентифікацію положення максимумів. Обговорено рекомбінаційні механізми, пов'язані з природною анізотропією досліджуваних сполук. Названо галузь можливого практичного застосування досліджуваних сполук.

Ключові слова: люмінесценція, збудження, спектр, домішка, структура.