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Band Structure and Optical Properties of the Layered Hg_3TeCl_4 Crystal

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First experimental investigations on absorption and photoluminescence of the novel Hg_3TeCl_4 monocrystals grown by the Bridgman method are reported. A comparison of the measurement results with theoretical band structure calculations of the Hg_3TeCl_4 crystal confirmed that Hg_3TeCl_4 is a wide-band-gap photoconductor ($E_g = 3.64$ eV at 24 K) with the effective masses of charge carriers characteristic for semiconductors. Energetic position of the main photoluminescence peak and its temperature dependence indicates the presence of an additional energy level in the energy gap which takes part in the radiative recombination process and whose origin was discussed.

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1. Introduction

The Hg_3TeCl_4 crystal belongs to a group of the mercury chalcohalogenides exhibiting good acousto-optical properties. Properties of this crystal have been not investigated experimentally so far, except its crystalline structure [1]. From the *ab initio* band structure calculations within a framework of density functional theory (DFT) follows that Hg_3TeCl_4 is a wide band-gap layered photoelectric with a smallest band gap located in the Γ point of the Brillouin zone [2]. Hence, a characteristic dependence of the absorption coefficient α on $h\nu$ as well as the inter-band photoluminescence should be expected for this crystal. We present in this paper first experimental investigations on the basic absorption edge and photoluminescence of Hg_3TeCl_4 in a wide temperature range 24–300 K.

2. Experimental

To perform experimental investigations monocrystals of Hg_3TeCl_4 were grown for the first time by the Bridgman method. The maximum temperature of the molten material was 640–650 K, velocity of the solid–liquid interface was 0.18–0.25 mm/h, and temperature gradient 2–3 K/mm. As a result, layered transparent blocks of the size $5(6) \times 7(8) \times 10(15)$ mm^3 were grown. Samples prepared for transmission measurements (0.1–0.17 mm of width) were mounted on the pinhole ($\phi = 2$ mm) at the "cold finger" of close cycle cryostat APD Cryogenic DE-202 (20–300 K). The transmission spectra measurements were performed using dual grating spectrometer DIGIKROM DK242 of CVI production. The halogen lamp and the photomultiplier Hamamatsu R636 in photon counting mode were used as a light source and as a light detector, respectively. The transmission spectra were registered in unpolarized light mode. The photoluminescence spectra were measured using the Spex 500M (HORIBA Jobin-Yvon) monochromator with CCD detector Hamamatsu C7045. He–Cd Omnichrome 56 laser ($\lambda = 325$ nm, $P = 10$ mW) was used for photoluminescence excitation.

3. Results and discussion

According to X-ray investigations [1], the Hg_3TeCl_4 crystal belongs to the orthorhombic system and its symmetry is described by the $Pbca$ (D_{2h}^{15}) space symmetry group. Mechanical properties of the crystal as well as the X-ray investigations point to its layered properties, there are 64 atoms in the unit cell which are arranged into two double, translationally non-equivalent layers perpendicular to the y axis. It was shown that the anisotropy of the overlap of electron wave functions is different in various energy ranges and leads to the Davydov splittings in the band structure, in particular in the Γ point of the conduction band [2, 3]. Hence, the anisotropy of the electron and hole effective masses does not correspond to the mechanical anisotropy of the crystal and it is not typical for layered crystals ($m_x^{\mathrm{e}} = 0.55m_0$, $m_y^{\mathrm{e}} = 0.44m_0$, $m_z^{\mathrm{e}} = 0.38m_0$, $m_x^{\mathrm{h}} = 7.86m_0$, $m_y^{\mathrm{h}} = 2.01m_0$, $m_z^{\mathrm{h}} = 0.92m_0$) [2].

Figure 1 presents absorption coefficient α vs. photon energy $h\nu$ at various temperatures. An analysis of the

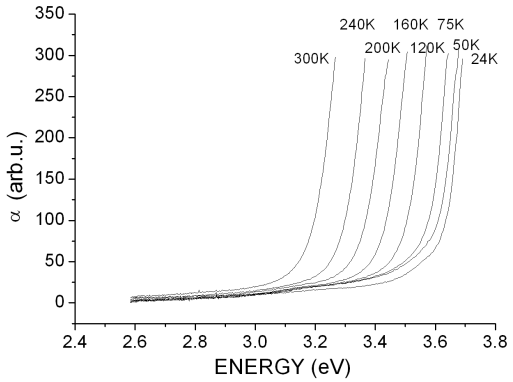

Fig. 1. Absorption coefficient vs. energy for Hg_3TeCl_4 crystal at various temperatures.

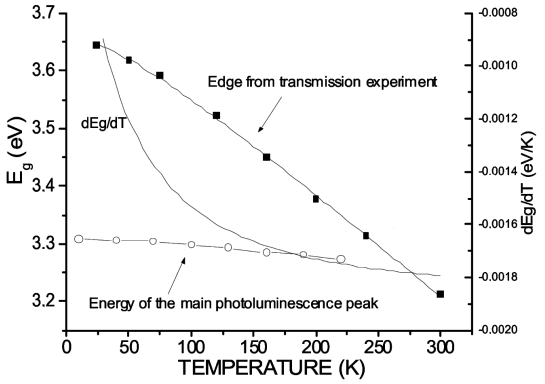

Fig. 2. Energy gap vs. temperature.

$\alpha^2(h\nu)$ dependence points to the presence of the direct optical transitions in the crystal which is in agreement with the theoretical band structure calculations. Based upon this dependence, values of the energy gap at various temperatures were calculated and presented in Fig. 2. The resulting function in Fig. 2 is described by the Varshni law: $E_g(T) = E_g(0) - \alpha T^2/(T + \Theta_D)$, where $E_g(0) = 3.66$ eV, $\alpha = 0.002$ eV/K, $\Theta_D = 74$ K. A small value of Θ_D indicates the presence of a weak total binding between layers of the crystal and its strong mechanical anisotropy. The dependence dE_g/dT has a negative slope and value in the whole investigated temperature range (Fig. 2) does not change the sign, as it takes place in the case of typical layered crystals (e.g. BiI_3 [4]). The values of dE_g/dT are considerably larger than those of typical bulk semiconductors and of some layered ones [4]. Therefore, the behavior of the energy gap of Hg_3TeCl_4 shows some features typical for layered semiconductors and some of traditional ones. It is connected with fact that the topology of the conduction band bottom is a result of a large Davydov splitting in this energy range, caused by an enhanced interaction between the electron states of atoms constituting the double layers in the unit cell. In other words, the spatial electron density distribution is observed in the so-called van der Waals gap. Additionally, for the same energy range, an enhanced interaction between $6s$ Hg and $5p$ Te electron states belonging to atoms of neighboring single layers creating the double layer in the unit cell takes place.

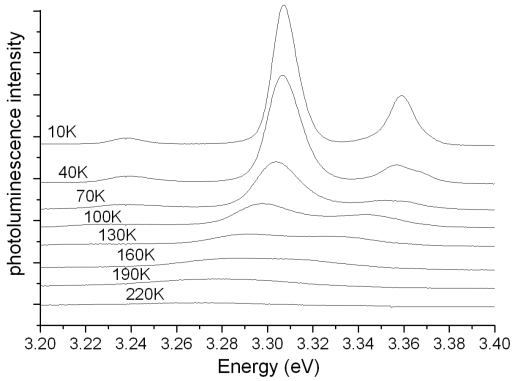

Fig. 3. Photoluminescence intensity spectra.

Figure 3 presents the photoluminescence intensity vs. energy in a wide temperature range. Two peaks at 10 K corresponding to the energies 3.30 and 3.36 eV can be recognized there. The temperature dependence of the peak of higher intensity is also depicted in Fig. 2. The energetic position of points of this curve does not correspond to the value of energy gap of the Hg_3TeCl_4 crystal obtained from the basic absorption edge measurements. Moreover, this curve is not parallel to that one, describing the temperature position of the energy gap. This fact testifies to the presence of an additional local level in the energy gap of Hg_3TeCl_4, from which a non inter-band photoluminescence occurs, and whose position strongly depends on temperature. It should be noted that the investigated photoluminescence did not take place from the whole surface of the sample. In order to obtain the inter-band photoluminescence in Hg_3TeCl_4 one should improve the technology of the monocrystal growth.

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