Experimental and Theoretical Analysis of PbTe–CdTe Solid Solution Grown by Physical Vapour Transport Method

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Bulk monocrystals of $Pb_{1-x}Cd_xTe$, with the Cd content x up to 0.11, were grown by physical vapour transport method. The structural, electrical and optical properties of these ternary crystals were studied experimentally and theoretically. All investigated samples exhibit rock-salt structure and high crystal quality, which was confirmed by X-ray rocking curve width parameter of about 100 arcsec. The decrease of the lattice parameter with increasing Cd content x was found experimentally, in agreement with *ab initio* calculations. The band structures of $Pb_{1-x}Cd_xTe$ mixed crystals for x values up to 0.2 were calculated using *tight binding* approach. The calculated band gap in the L-point increases with the Cd content in qualitative agreement with photoluminescence measurements in the infrared. For all studied $Pb_{1-x}Cd_xTe$ samples, the Hall effect and electrical conductivity measurements, performed in the temperature range from 4 to 300 K, revealed p-type conductivity.

PACS numbers: 81.10.Bk, 61.50.Ah, 71.20.Nr, 78.60.Lc, 72.20.Fr

1. Introduction

Lead telluride along with cadmium telluride constitutes an attractive system for development of mid-IR optoelectronic devices based on quantum dots. This material system is also ideal for investigations of the quantum dots growth process alternative to the Stranski–Krastanov growth mode. The nucleation of PbTe quantum dots in CdTe matrix is governed by extremely low relative solubility of these materials [1], resulting from the difference in their crystal structure — rock-salt (RS) for PbTe and zinc-blende (ZB) for CdTe. Due to the same reasons, the growth of uniform $Pb_{1-x}Cd_xTe$ bulk crystals with high Cd content, which would be important for certain, e.g., thermoelectric, applications is very difficult. So far, only polycrystalline $Pb_{1-x}Cd_xTe$ bulk samples were obtained by rapid quenching and annealing method [2–4] or by the Bridgman technique [5]. For $Pb_{1-x}Cd_xTe$ quenched alloys, the change of the lattice parameter and energy gap with x as well as the solubility limit have been studied by Rosenberg et al. [2], Nikolic [3] and Leute and Schmidt [4].

In this paper we report the successful growth of $Pb_{1-x}Cd_xTe$ monocrystals by physical vapour transport (PVT) method [6]. In the PVT method polycrystalline source is used for growth of final, monocrystalline material. The crystals grown by PVT are free from mechanical stress and have excellent compositional uniformity. The experimental and theoretical studies of structural, optical and electrical properties of the obtained crystals are presented.

2. Results and discussion

In the PVT method the growth takes place inside the quartz ampoule placed in the electrical oven with carefully controlled temperature profile. During the growth process the material evaporates from the hotter part, and subsequently condenses on the cooler part of the polycrystalline source. The transport of the material is driven by small temperature gradients along the furnace. Therefore, the nucleation takes place at the coolest part of the source material (for further details of the growth procedure see Ref. [6]).

The $Pb_{1-x}Cd_xTe$ samples, with Cd content in the range $1 \div 11$ at.%, were grown at temperatures about 850–870 °C, with the source materials in the form of polycrystalline PbTe and CdTe, which were synthesized with excessive Te and Cd, respectively. As a result of growth processes, the crystals of about 1 ccm volume with (100) natural crystal facets were obtained (see Fig. 1). The cadmium content was determined in samples cleaved from various parts of monocrystals by energy dispersive X-ray fluorescence method. This study reveals a uniform distribution of Cd ions in the whole crystal. The structural properties of the samples were examined by standard X-ray diffraction method, revealing their high

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crystal quality with the X-ray rocking curve width parameter of about 100 arcsec. All obtained $Pb_{1-x}Cd_x Te$ monocrystals have RS structure. The experimentally determined dependence of the lattice parameter a_0 on Cd content x follows the Vegard law (see Fig. 2). The lattice parameter of $Pb_{1-x}Cd_x Te$ monocrystals decreases with x according to the equation

$$a_0\,[\text{Å}] = 6.462 - 0.433\,x \quad \text{for} \quad x \leq 0.11$$

with the slope $\mathrm{d}a_0/\mathrm{d}x = -0.43$ Å, whose absolute value is much bigger than for the slope found in the earlier studies of Rosenberg ($\mathrm{d}a_0/\mathrm{d}x = -0.30$ Å [2]) as well as for that observed in the Bridgman ingots. On the other hand, it is only slightly higher than for the slope determined by Leute and Schmidt in polycrystals subjected to long term annealing ($\mathrm{d}a_0/\mathrm{d}x = -0.40$ Å [4]). This experimental finding indicates that $Pb_{1-x}Cd_x Te$ samples grown by PVT method provide key reference crystals. It is expected that in these crystals the number of Cd ions located in the interstitial positions is strongly reduced as compared to the crystals grown by Bridgman method. These results show also the uniqueness of PVT technique, which allows to obtain $Pb_{1-x}Cd_x Te$ bulk crystals with Cd content exceeding 5 at.% and still of very good quality.
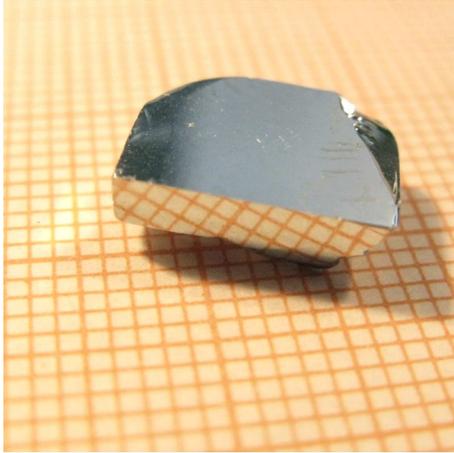

Fig. 1. $Pb_{0.96}Cd_{0.04}Te$ crystal with (100) natural crystal facets grown by physical vapour transport method (squares correspond to 1 mm^2).

The above described experimental studies were supported by a theoretical analysis of the structural stability of $Pb_{1-x}Cd_x Te$ crystals. We found, using *ab initio* methods, that the total energy of the mixed crystal for RS structure is lower than for ZB, for Cd content x up to 0.75. This means that virtual $Pb_{1-x}Cd_x Te$ crystals with such high Cd concentrations would have RS structure. However, for any x value this energy is slightly higher than the total energy of separate phases. The latter energy difference, taken per atomic pair, is, however, lower than $k_B T$ in the growth conditions for x up to 0.2. This result may suggest that the highest Cd content in our
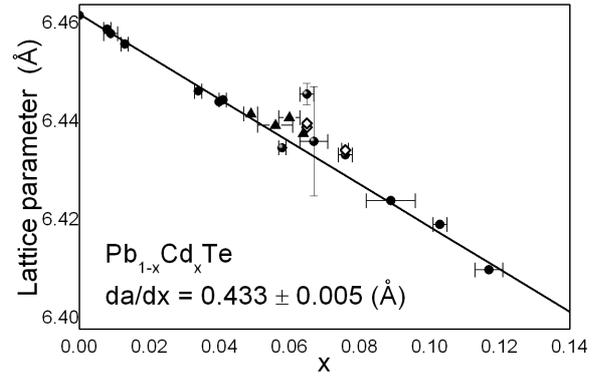

Fig. 2. The dependence of the lattice parameter on the Cd content for monocrystalline $Pb_{1-x}Cd_x Te$ samples.

samples is close to the solubility limit. The calculated lattice parameters, diminish with x like $\mathrm{d}a_0/\mathrm{d}x \approx -0.39$ Å (for $x \leq 0.2$), which remains in good agreement with our experimental data.

For optical characterization of $Pb_{1-x}Cd_x Te$ crystals, the photoluminescence (PL) measurements were carried out in the infrared range ($2 \div 4.5\ \mu$m) for different temperatures in the range $4.2 \div 300$ K. For excitation, the 1064 nm line of Nd:YAG pulsed laser was used. In the PL spectra obtained at 4.2 K, we observe a strong, broad luminescence, which we attribute to the band-to-band transitions. For samples with the composition $x = 0.11$, the low energy edge of the luminescence peak appears at 0.32 eV. This result implies that in our $Pb_{1-x}Cd_x Te$ mixed crystals the band gap increases with x like $\mathrm{d}E_g/\mathrm{d}x \approx 1.2$ eV. Furthermore, we do not observe any significant distinction in energetic location of the photoluminescence peak for different samples cleaved from the same crystals. This indicates again a uniform distribution of Cd ions in the sample.

The band structure of $Pb_{1-x}Cd_x Te$ for different Cd contents up to $x = 0.2$ was calculated within the tight binding approach and virtual crystal approximation. An increase of the L-point band gap with x by about $\mathrm{d}E_g/\mathrm{d}x \approx 1.0$ eV was obtained in agreement with the experimental observations. The details of the calculations mentioned above will be published elsewhere.

Electrical characterization, performed by the Hall effect and conductivity measurements, revealed p-type conductivity in $Pb_{1-x}Cd_x Te$ for all studied samples. The carrier concentration decreases from $p \approx 3.5 \times 10^{18}$ cm^{-3} for samples containing 1% Cd to p below 10^{17} cm^{-3} for 11% sample. At the same time, the carrier concentration shows a weak dependence on temperature (see Fig. 3) — e.g., for sample with 4% Cd it varies from $p \approx 2.4 \times 10^{18}$ cm^{-3} at 300 K to $p \approx 3 \times 10^{18}$ cm^{-3} at 4.2 K. The mobility of the samples increases monotonically with the decrease of the temperature, from $\mu \approx 60$ cm^2 V^{-1} s^{-1} to $\mu \approx 1300$ cm^2 V^{-1} s^{-1}, respectively.
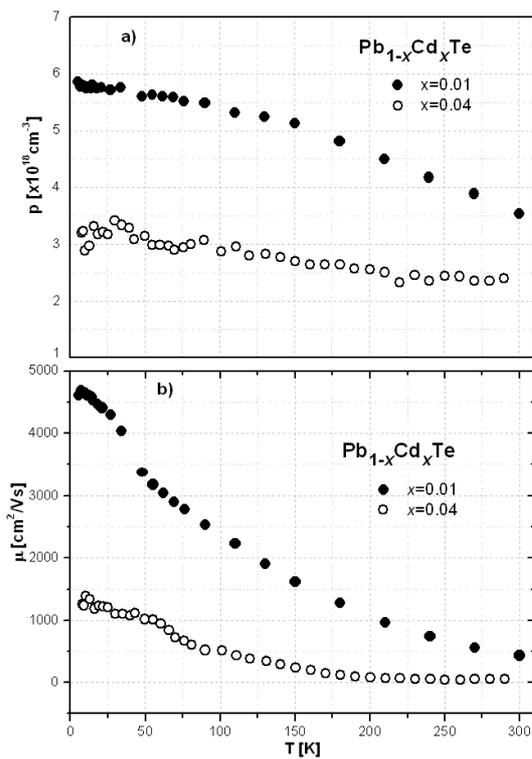
Fig. 3. Hall concentration (a) and mobility (b) as a function of temperature for samples with 1% ($\bullet$) and 4% ($\circ$) of Cd content.

3. Conclusions

We have shown that high quality $Pb_{1-x}Cd_xTe$ monocrystals with Cd content up to $x = 0.11$ can be obtained by physical vapour transport method. X-ray diffraction analysis showed rock-salt crystal structure with parameter a_0 decreasing with increasing Cd content x in accordance with the Vegard law. The stability of the rock-salt structure in $Pb_{1-x}Cd_xTe$ alloys and the decrease of the lattice parameter were confirmed by theoretical *ab initio* calculations. $Pb_{1-x}Cd_xTe$ monocrystals showed strong photoluminescence in the mid-infrared region revealing an increase of the band gap with increasing x. This experimental finding was also explained theoretically by tight binding calculations of the electronic band structure of $Pb_{1-x}Cd_xTe$.

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