

Comparison of Electrophysical Characteristics of Undoped $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ and $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ ($x, y \leq 0.1$) Crystals

P. Fochuk¹, E. Nykonyuk², Z. Zakharuk¹, S. Dremlyuzhenko¹, S. Solodin¹, O. Kopach¹, A. Opanasyuk³

¹ Chernivtsi National University, 2, Kotsyubynskii St., 258012 Chernivtsi, Ukraine

² National University of Water Management and Nature Resources, 11, Soborna St., 33000 Rivne, Ukraine

³ Sumy State University, 2, Rymskogo-Korsakova St., 40007 Sumy, Ukraine

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The temperature dependence ($T = 80 \div 360$ K) analysis of the electrophysical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ and $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ ($x, y \leq 0.1$) crystals grown by the vertical Bridgman method is carried out. It is established that in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals, the conductivity is controlled by both the acceptors A_1 ($\varepsilon_A^0 = 0.03 \div 0.05$ eV) and the acceptors A_2 ($\varepsilon_A^0 \approx 0.12$ eV), whose ionization energy does not depend on the composition, and in $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ and $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystals – only by the acceptors A_2 ; in this case, the dependence $\varepsilon_{A_2}(y)$ is described by the equation $\varepsilon_{A_2} = 0.12(1 + 5.5y)$ eV.

Keywords: $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$, $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ solid solutions, Single crystal, Bridgman method, Electrophysical properties.

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1. INTRODUCTION

The prospects for practical applications of semiconductor materials are primarily caused by the electrical properties of the crystals. $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ solid solutions are widely used in various optoelectronic devices, such as optical filters, photorefractive elements, X-ray and gamma-ray detectors [1-4], etc. The advantage of solid solutions is the possibility of wide variation of the band gap, lattice parameters and some other characteristics of the materials when the component ratio is changed [5]. In the process of growing such crystals, we have established that the quality of the obtained crystallites of the material depends on the uniform distribution of components in a solid solution and the duration of the synthesis and ingot growth [6, 7]. The main factor affecting the interaction between the charge and the container material is the presence of residual oxides, which are introduced along with the initial material, and also the degree of their purity. It should be noted that the segregation coefficients of manganese ($k = 1$) and zinc ($k = 1.35$) in CdTe differ significantly among themselves. Therefore, $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals have a uniform distribution of Mn throughout the ingot and are more homogeneous than the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals [2]. Study of a new $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ solid solution should extend the possibilities of technological influence on the electrophysical parameters of the crystals of this group. Note that the vast majority of works existing in our time is devoted to the study of crystals with low carrier concentration (with high resistance), as a rule, especially doped with shallow donors. Much less attention is paid to undoped crystals with high carrier concentration grown by the traditional Bridgman method. It is reasonable to compare the electrophysical characteristics of these crystals. We have previously investigated the optical and some electrophysical characteristics of $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ films and single crystals [8-10].

2. OBJECTS AND METHODS OF STUDY

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZT), $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ (CMT), $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ (CZMT) crystals were obtained from the charge prepared of stoichiometric weights of the initial components of purity class not less than 5N. After prolonged synthesis (72 hours), single crystals were grown by the Bridgman method (the temperature gradient at the crystallization front is $10 \div 15$ K/cm, the growth rate is 2 mm/h).

Samples for electrophysical studies were prepared of the grown crystals in the form of rectangular parallelepipeds of size $(12 \times 2 \times 1.5)$ mm³. The current contacts and two pairs of symmetric Hall contacts to the experimental samples were made by deposition of a gold layer from a drop of AuHNO₃ after spark treatment of the contact pads. The direct-current measurements were carried out in a magnetic field with an induction of 0.5 T. The signals were detected by a digital voltmeter with an input resistance of 10⁷ Ohm and sensitivity of 0.01 mV, and at low temperatures – by an electrometer with an input resistance of 10¹² Ohm and sensitivity of 0.1 mV.

The temperature dependences (TD) of the Hall coefficient R_H and the Hall carrier mobility μ were studied in the temperature range of $T = 80 \div 360$ K. The value of μ was determined by the formula $\mu = \sigma R_H$, where σ is the specific electrical conductivity of the crystal.

3. EXPERIMENTAL RESULTS

The studied samples had p type conductivity with a resistivity at 300 K in the range of $\rho = (3 \div 20)$ Ohm·cm and a hole mobility in the range of $\mu = (50 \div 70)$ cm²/V·s. In Fig. 1 we present the TD of the Hall coefficient R_H of the samples of different composition.

The presence in the curves of both the carrier freeze out range (low temperatures) and the region of full ionization (ρ_{sat}) of acceptors (high temperatures) allowed, in the framework of the compensated acceptor model,

to determine their ionization energy ε_{A^0} , the degree of compensation $[A^-]/[A]$, and the concentration of the corresponding acceptors $[A]$ by the point $p_{sat} = [A] - [A^-]$. In this case, it was considered that the carrier effective mass in samples of all compositions is $m_p = 0.63m_0$, the statistical factor for shallow acceptors A_1 (samples 1, 2) is $\beta = 4$ and for deeper acceptors A_2 (samples 3-8) – $\beta = 2$. The results of the analysis are summarized in Table 1 and in Fig. 2.

Additional information on the parameters of the defect-impurity system is obtained from the analysis of the hole mobility TD (see Fig. 3).

In particular, the concentration of ionized scattering centers N_i was estimated. For this end, according to the

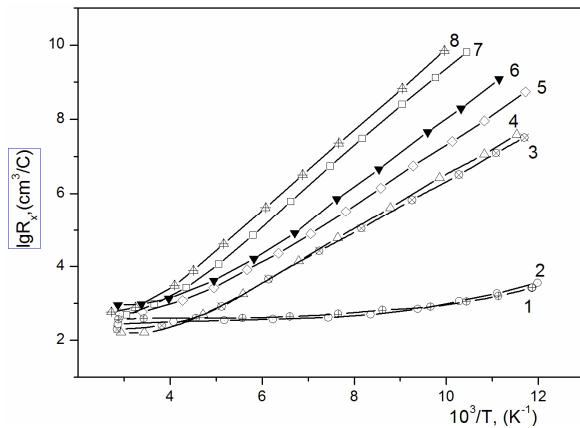


Fig. 1 – Temperature dependence of the Hall coefficient in samples of $Cd_{1-x}Zn_xTe$ (1, 3 – $x = 0.04$; 2, 4 – $x = 0.10$); $Cd_{1-y}Mn_yTe$ (5, 6, 7 – $y = 0.04$; 0.06; 0.100, respectively); $Cd_{1-x-y}Zn_xMn_yTe$ (8 – $x = 0.05$, $y = 0.10$) crystals

Table 1 – Concentration of centers in solid solution crystals

Crystals	Acceptor type	$[A_2], 10^{16}, cm^{-3}$	$[A_1], 10^{16}, cm^{-3}$	$N_i, 10^{16}, cm^{-3}$
$Cd_{1-x}Zn_xTe$	A_1, A_2	0.5÷2	3÷10	6÷22
$Cd_{1-y}Mn_yTe$	A_2	0.5÷6	4÷20	8÷50
$Cd_{1-x-y}Zn_xMn_yTe$	A_2	1.7; 2.3	9; 16	20; 35

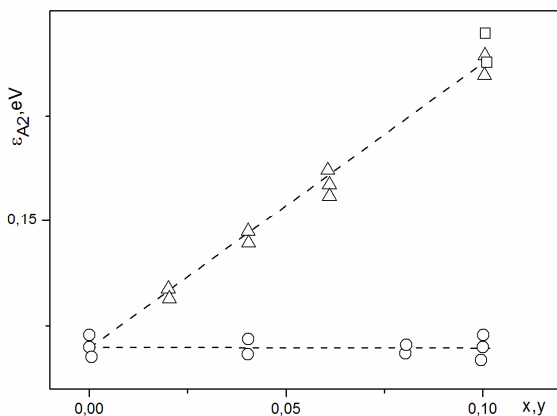


Fig. 2 – Dependence of the of acceptor ionization energy (ε_{A^0}) on the composition (x, y) of $Cd_{1-x}Zn_xTe$ (O), $Cd_{1-y}Mn_yTe$ (Δ) and $Cd_{1-x-y}Zn_xMn_yTe$ (\square) crystals

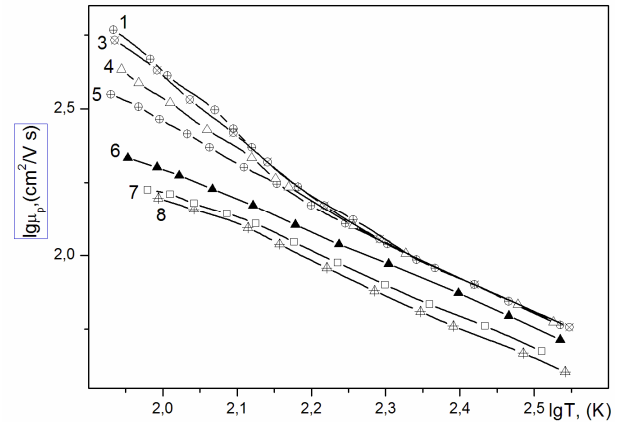


Fig. 3 – Temperature dependence of the hole mobility in samples of $Cd_{1-x}Zn_xTe$, $Cd_{1-y}Mn_yTe$ and $Cd_{1-x-y}Zn_xMn_yTe$ crystals (numbering of curves corresponds to Fig. 1)

Matthiessen rule, the mobility μ_0 and μ_i caused by ionized impurity scattering were separated, and the value of N_i was calculated by the Brooks-Herring formula:

$$1/\mu = 1/\mu_0 + 1/\mu_i; \mu_0 = 57[\exp(252/T) - 1], (cm^2/V\cdot s);$$

$$\mu_i = 0.83 \cdot 10^{18} T^{3/2} N_i^{-1} (\ln b + 3.4) / (\ln b + 3.8)^2, (cm^2/V\cdot s),$$

where $b = 10^{13} T^2 (p')^{-1}$ and $p' \approx p_{sat}$.

4. DISCUSSION OF THE RESULTS

In undoped cadmium telluride crystals grown by the vertical Bridgman method (without additional pressure), p type conductivity is always realized and is controlled by acceptors of two types: A_1 with ionization energy of (0.03-0.05) eV and A_2 with ionization energy of ~ 0.12 eV. In the case of solid solution crystals, the situation does not change drastically. At that, if in $Cd_{1-x}Zn_xTe$ crystals, the R_H TD is determined by both the acceptors A_1 (1, 2 in Fig. 1) and the acceptors A_2 (3, 4), then in the case of $Cd_{1-y}Mn_yTe$ crystals, no sample was detected, where the acceptors A_1 would control the R_H TD. But in this case, the concentration of such acceptors is not less than that in $Cd_{1-x}Zn_xTe$ crystals (Table 1) (it is calculated through N_i : $[A_1] = 0.5 N_i - [A_2]$).

A wide concentration range of acceptor centers in $Cd_{1-x}Zn_xTe$ and $Cd_{1-y}Mn_yTe$ crystals (Table 1) is due to the generalization over a large array of samples (more than 10 of each composition). At the same time, only two samples made of one $Cd_{1-x-y}Zn_xMn_yTe$ crystal have been studied. We note that the lower limit of concentrations refers to samples from the initial (in the crystal growth direction) sections of ingots. This indicates that the vast majority of uncontrolled impurities have a segregation coefficient less than one.

Since the acceptors A_1 in $Cd_{1-y}Mn_yTe$ crystals are completely compensated, it is possible to state that the concentration of compensating donors in $Cd_{1-y}Mn_yTe$ crystals is higher than that in $Cd_{1-x}Zn_xTe$ crystals. Probably, the reason is trivial: manganese used by us is contaminated with an impurity, which has a donor effect. Noteworthy is the fact that CdTe-Mn crystals at an Mn impurity concentration less than $10^{19} cm^{-3}$ have n type conductivity that is not observed in $Cd_{1-x}Zn_xTe$ crystals grown under similar conditions.

The fundamental difference between $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals, on the one hand, and $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals (as well as $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$), on the other hand, is in the nature of the dependence of the ionization energy of acceptors A_2 on the crystal composition (Fig. 2).

In $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals, there are no significant changes in the values of ε_{A_2} with increasing x . At the same time, in $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals, a similar dependence $\varepsilon_{A_2}(y)$ is described by the equation $\varepsilon_{A_2} = 0.12(1 + 5.5y)$, eV. This equation contains the values of ε_{A_2} for $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystal samples. It should be noted that almost the same dependence $\varepsilon_{A_2}(y)$ is obtained in the study of the luminescence spectra of $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals.

It is assumed that the acceptors A_2 are the complexes ($\text{D}_{\text{Cd}}\text{V}_{\text{Cd}}$), i.e. both components of cationic origin. Therefore, the energy position of the complex is bound to the conduction band bottom. Here, in solid solution crystals, the rate of removal of the acceptor level A_2 from the valence band top should be commensurate with the rate of change of the band gap. Averaging the data of [5, 11], we can write $(\Delta E_g/E_g)/\Delta x = (\Delta \varepsilon_{A_2}/\varepsilon_{A_2})/\Delta x \approx 1$ eV/mole. Then at $\Delta x = 0.1$ we obtain $\Delta \varepsilon_{A_2} \approx 0.01$ eV which lies within the experiment error. This means that there are no problems with $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals in this aspect. As to the "problem" $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals, taking into account the conservation of the magnetic moment by a Mn^{2+} ion in the crystal matrix [12], one can propose, as a working one,

version about the "localized" and "delocalized" incorporation of Mn atoms into the lattice for different concentrations. On the basis of such an idea, one can try to explain the change in the material conductivity type at 10^{19} cm^{-3} Mn and an abnormally high rate of change of ε_{A_2} . But this is the subject of a separate study.

5. CONCLUSIONS

In $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals, the conductivity is controlled by both the acceptors A_1 ($\varepsilon_{A_1}^0 = 0.03 \div 0.05$ eV) and the acceptors A_2 ($\varepsilon_{A_2}^0 \approx 0.12$ eV), while in $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ and $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystals – only by the acceptors A_2 . The energy level position of the acceptor A_2 in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals is rigidly connected to the valence band top. At the same time, in $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals, the dependence $\varepsilon_{A_2}(y)$ is described by the equation $\varepsilon_{A_2} = 0.12(1 + 5.5y)$, eV. This equation contains the value of ε_{A_2} obtained for $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystal samples. In $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals, the concentration of acceptors A_2 is in the range of $(5 \cdot 10^{15} \div 2 \cdot 10^{16}) \text{ cm}^{-3}$, and in $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals – in the range of $(5 \cdot 10^{15} \div 6 \cdot 10^{16}) \text{ cm}^{-3}$. The value of N_I is greatest in $\text{Cd}_{1-y}\text{Mn}_y\text{Te}$ crystals ($N_I^{\text{max}} = 5 \cdot 10^{17} \text{ cm}^{-3}$).

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REFERENCES

1. A.V. Bushuyev, *Atomnaya energiya* 92(5), 371 (2002).
2. L. Davydov, P. Fochuk, A. Zakharchenko, et al. *IEEE T. Nucl. Sci.* 62 No 4, 1779 (2015).
3. Y. Cui, A. Bolotnikov, A. Hossain, *Proc. SPIE* 7079, 70790N (2008).
4. K. Shcherbin, V. Volkov, V. Rudenko, S. Odoulov, A. Borshch, Z. Zakharuk, I. Rarenko, *phys. status solidi (a)* 183 No 2, 337 (2001).
5. A. Mycielski, A. Burger, M. Sowinska, M. Groza, A. Szadkowski, P. Wojnar, B. Witkowska, W. Kaliszek, P. Siffert, *phys. status solidi (c)* 2 No 5, 1578 (2005).
6. Z.I. Zakharuk, V.V. Horbunov, S.H. Dremlyuzhenko, *Naukovyy visnyk Chernivets'koho universytetu* 66, 88 (1999).
7. Z.Y. Zakharuk, E.V. Rybak, S.H. Dremlyuzhenko, *Novi tekhnolohiyi* 2 No 12, 22 (2006).
8. V.V. Kosyak, A.S. Opanasyuk, P.V. Koval, P.M. Fochuk, V.V. Starikov, *J. Nano-Electron. Phys.* 3 No 2, 48 (2011).
9. P.V. Koval, V.V. Kosyak, A.S. Opanasyuk, P.M. Fochuk, A.E. Bolotnikov, R.B. James, *Proc. SPIE* 8507, 85071K (2012).
10. E.S. Nykonyuk, Z.I. Zakharuk, A.I. Rarenko, A.S. Opanasyuk, V.V. Grynenko, P.M. Fochuk, *J. Nano Electron. Phys.* 7 No 4, 04054 (2015).
11. P.V. Zhukovskii, Ya. Partyka, P. Vengerek, Yu.V. Sidorenko, Yu.A. Shostak, A. Rodzik, *Semiconductors* 35 No 8, 900 (2001).
12. V.F. Agekyan, N.G. Filosofov, *Razbavlenyye magnitnyye poluprovodniki: Magnitnyye i opticheskiye svoystva: Uchebnoye posobiye* (SPb.: 2014).