

## HIGH TEMPERATURE CONDUCTIVITY AND PHASE TRANSITIONS OF SOLID SOLUTIONS $\text{CdSe}_x\text{Te}_{1-x}$

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**Abstract.** The solid solutions of  $\text{CdSe-CdTe}$ , obtained by sintering of  $\text{CdSe}$  and  $\text{CdTe}$  powders, were investigated by the method of high temperature conductivity. The data on the temperatures of the structural phase transition between a hexagonal and a cubic modification in solid solutions of various compositions were obtained experimentally. It was found that the doubly charged anion vacancies are the dominant native defects both in crystals with a hexagonal and a cubic lattice.

**Key words:**  $\text{CdSe}$ ,  $\text{CdTe}$ , solid solutions, phase transition, conductivity.

### 1. INTRODUCTION

$\text{A}^2\text{B}^6$  compounds are an important class of optoelectronic materials. Among them, ternary systems, which change physical parameters as a function of composition, occupy a special place. The solid solutions, based on  $\text{A}^2\text{B}^6$  compounds, are potential materials for producing electrochemical solar cells, radiation detectors, and electro-optic devices [1]. One of the most interesting materials among the solid solutions of  $\text{A}^2\text{B}^6$  compounds is  $\text{CdSe}_x\text{Te}_{1-x}$ . At a certain concentration of components, the symmetry of  $\text{CdSe}_x\text{Te}_{1-x}$  crystal lattice changes [2]. A crystal can be either in a cubic or in a hexagonal modification. This indicates that the structural phase transition should be at a certain composition and temperature. Studies of  $\text{CdSe}_x\text{Te}_{1-x}$  by the X-ray diffraction method at room temperature indicate that such phase transition exists [2]. In this study, an attempt is made to measure the temperature of the phase transition as a function of composition at high temperature by the conductivity method.

## 2. EXPERIMENTAL

$\text{CdSe}_x\text{Te}_{1-x}$  solid solutions with  $x = 0.30$ ;  $0.40$ ;  $0.45$  and  $0.50$  were prepared by sintering of CdSe and CdTe powders at  $900^\circ\text{C}$  for 48 h. The X-ray diffraction studies of powders indicate that the solid solutions with cubic crystal structure formed. For conductivity measurements, samples of solid solutions were made by pressing powders into tablets.

Using a two-zone quartz ampoule (Fig. 1), the high temperature equilibrium conductivity  $\sigma$  was measured as a function of sample temperature  $T$  and cadmium vapour pressure  $p_{\text{Cd}}$ . The vapour pressure of cadmium was maintained by controlling the temperature of a reservoir, which contained pure cadmium and by using vapour pressure data [3]. The ampoule had four sealed tungsten electrodes, and the four-probe method was used. In all cases, the ampoule was placed into a quartz furnace tube, which was evacuated to  $10^{-2}$  Pa to prevent oxidation of the electrodes.

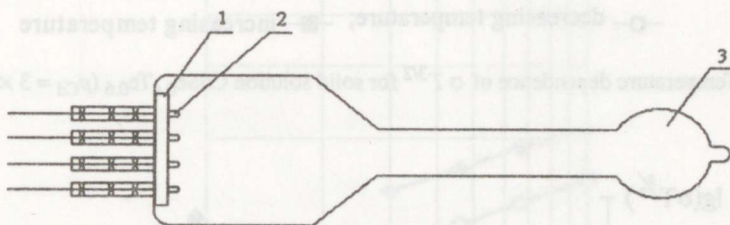


Fig. 1. Two-zone quartz ampoule: 1 – sample, 2 – electrode, 3 – reservoir.

## 3. RESULTS AND DISCUSSION

Figures 2 and 3 show the dependence of  $\sigma T^{3/2}$  on reciprocal temperature at two constant values of  $p_{\text{Cd}}$  for  $\text{CdSe}_{0.4}\text{Te}_{0.6}$ . The  $T^{-3/2}$  dependence of mobility is taken into account by the factor  $T^{3/2}$  so that  $\sigma T^{3/2}$  is proportional to the electron concentration and

$$\sigma T^{3/2} \sim \exp\left(-\frac{\Delta E}{kT}\right), \quad (1)$$

where  $\Delta E$  is the activation energy of conductivity.

At an increased temperature of the sample, the dependence was linear with  $\Delta E = 0.42$  eV. In the temperature range of  $897$  to  $901^\circ\text{C}$ , a step-like change of conductivity was observed. Above this temperature, the conductivity increased with an activation energy  $\Delta E = 0.61$  eV (Fig. 3). As the temperature decreased, in the range of  $877$  to  $881^\circ\text{C}$ , conductivity jumped. Subsequently, a linear dependence reoccurred with  $\Delta E = 0.42$  eV.

For all the other objects studied, except for  $\text{CdSe}_{0.5}\text{Te}_{0.5}$ , jumps of equilibrium conductivity at the temperatures increasing and decreasing were observed. Before and after a sharp jump, almost linear dependences occurred.

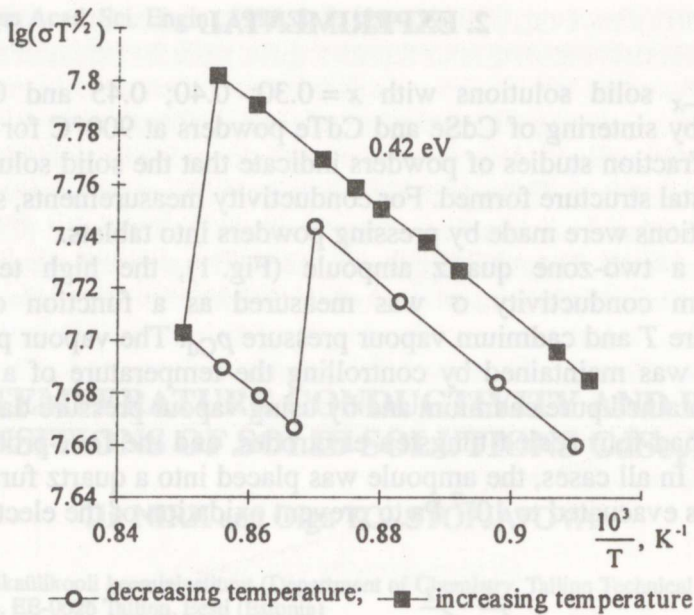


Fig. 2. Temperature dependence of  $\sigma T^{3/2}$  for solid solution  $CdSe_{0.4}Te_{0.6}$  ( $p_{Cd} = 3 \times 10^3$  Pa).

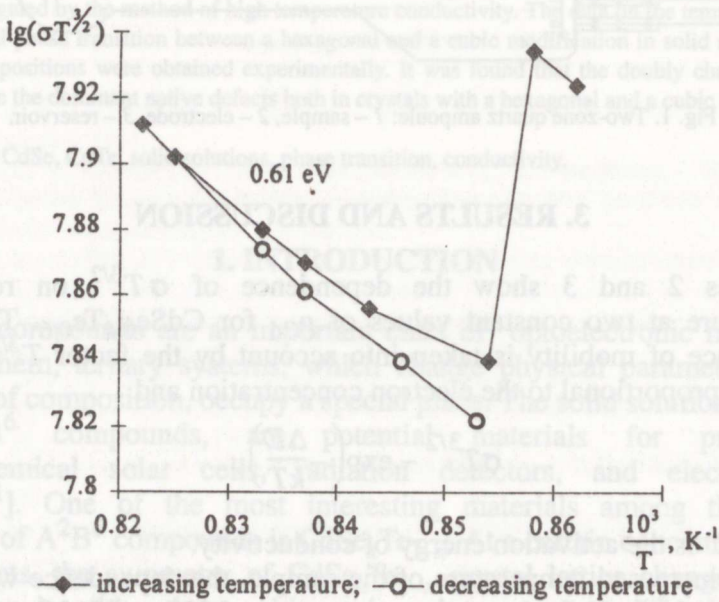


Fig. 3. Temperature dependence of  $\sigma T^{3/2}$  for solid solution  $CdSe_{0.4}Te_{0.6}$  ( $p_{Cd} = 10^5$  Pa).

Figure 4 shows the relation between the vapour pressure of cadmium  $p_{Cd}$  and the conductivity for  $CdSe_{0.4}Te_{0.6}$  with a cubic and a hexagonal lattice. The dependences may be expressed by  $\sigma \sim p_{Cd}^\gamma$ , where  $\gamma = 1/3$ .

The sharp jumps of conductivity, found in solid solutions  $\text{CdSe}_x\text{Te}_{1-x}$  with  $x = 0.3; 0.4$  and  $0.45$ , can be explained only if the structural phase transition between a cubic and a hexagonal modification occurs. From [2] we can assume that at lower temperatures, the cubic modification and at higher temperatures, the hexagonal modification is stable. In all dependences, the loop of hysteresis was observed, which was between the borders of phase transitions. This may be assumed to be a zone of biphasic samples. The zone is limited by the temperatures of phase transitions, and it decreases with the reduction of  $x$ .

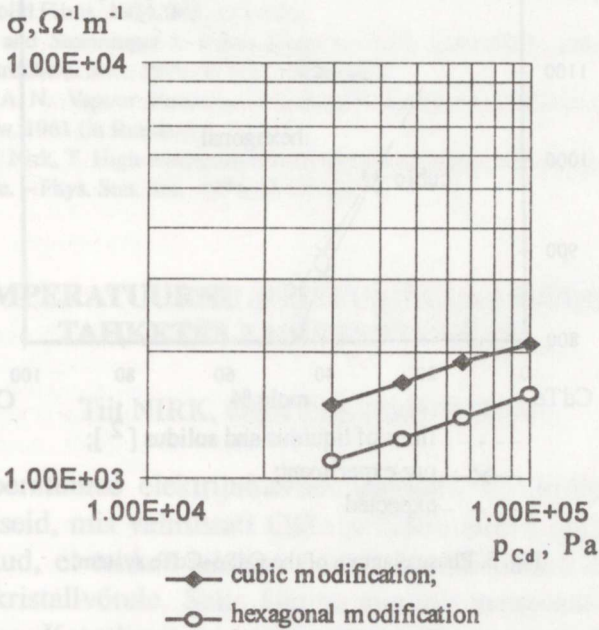
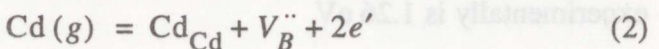


Fig. 4. Cd vapour pressure dependence of conductivity for  $\text{CdSe}_{0.4}\text{Te}_{0.6}$  at  $888^\circ\text{C}$ .

Figure 5 illustrates the improved phase diagram of the system  $\text{CdSe}-\text{CdTe}$ , where at  $870^\circ\text{C}$  the biphasic area takes 4.8 mole %, at  $900^\circ\text{C}$  – 3.4 mole % and at  $950^\circ\text{C}$  – 2 mole %. We may assume that below the biphasic area only cubic crystal lattice and under biphasic area only hexagonal lattice occur. The authors of [2] assume that the width of the biphasic area is approximately 3 mole % of the whole temperature range.

For one sample, the area of phase transition was investigated at two different cadmium vapour pressures (Figs. 2 and 3). These figures demonstrate that the temperature of phase transition does not depend on the vapour pressure of cadmium.

The dependence of sample conductivity on  $p_{\text{Cd}}$  gave for all the samples studied  $\gamma = 1/3$ . In this case, the formation of the dominant native defects may be described by the equation



with mass action relation

$$K_{Cd}'' = [V_B^{''}] \times n^2 / p_{Cd}, \quad (3)$$

where  $V_B^{''}$  is a doubly charged anion vacancy.

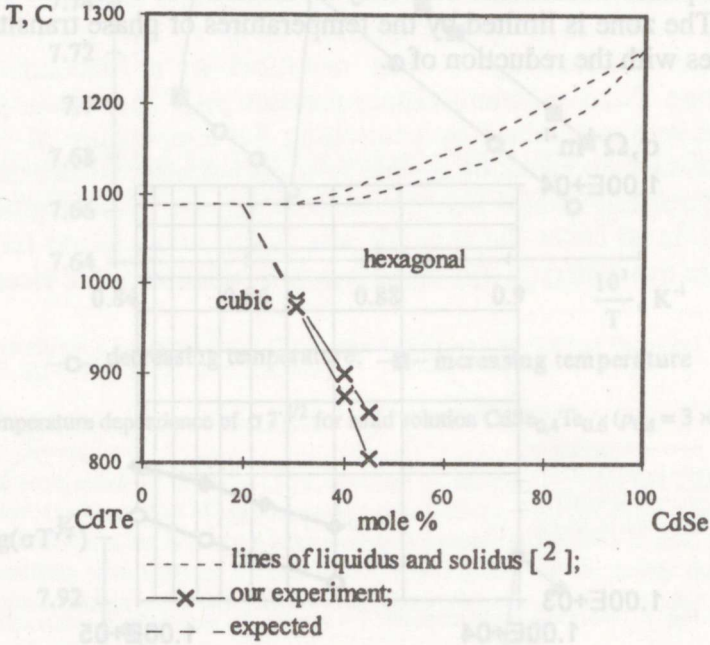


Fig. 5. Phase diagram of the CdSe-CdTe system.

The approximated electroneutrality condition

$$n = 2 [V_B^{''}] \quad (4)$$

leads to

$$n = (2K_{Cd}'' )^{1/3} \times p_{Cd}^{1/3} = (2K_{Cd}^{0''} )^{1/3} \times p_{Cd}^{1/3} \exp\left(-\frac{\Delta H_{Cd}}{3kT}\right). \quad (5)$$

From Eqs. (1) and (5) it follows that the enthalpy of formation of doubly charged anion vacancies  $\Delta H_{Cd} = 3\Delta E$ . So for a solid solution with a hexagonal lattice  $\Delta H_{Cd} = 3 \times 0.61 = 1.83$  eV. This value of  $\Delta H_{Cd}$  is very close to the value 1.86 eV, observed in CdSe with a hexagonal lattice [4]. For a solid solution with the cubic lattice,  $\Delta H_{Cd}$  found experimentally is 1.26 eV.

## CONCLUSIONS

The results show that, as a function of solid solution composition, phase transition temperatures can be determined very precisely by the high temperature conductivity measurements of the solid solution  $\text{CdSe}_x\text{Te}_{1-x}$ .

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## KÕRGTEMPERATURENE JUHTIVUS JA FAASIÜLEMINEKUD TAHKETES LAHUSTES $\text{CdSe}_x\text{Te}_{1-x}$

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Kõrgtemperatuurse elektri juhtivuse meetodil on uuritud CdSe–CdTe tahkeid lahuseid, mis valmistati CdSe ja CdTe pulbri segu kuumutamise teel. On leitud, et tahkes lahuses esineb faasiüleminek heksagonaalselt kuubilisele kristallvõrele. Selle käigus muutub hüppeliselt tahke lahuse elektri juhtivus. Katseliselt on määratud faasiüleminekute temperatuuride sõltuvus tahke lahuse koostisest. Arvestades elektri juhtivuse sõltuvust Cd aururõhust on selgitatud, et nii heksagonaalse kui ka kuubilise kristallvõrega tahke lahuse korral on domineerivateks omadefektideks kahekordselt laetud aniooni vakantsid.