

## TECHNOLOGY OF CdTe MONOGRAIN POWDERS

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**Abstract.** Monograin CdTe powders were grown by recrystallisation in isothermal ampoules in the presence of CdCl<sub>2</sub> or CdCl<sub>2</sub>-NaCl liquid phases. We found that NaCl in CdCl<sub>2</sub> flux inhibits crystal growth and dopes CdTe with Na, which acts as an effective acceptor impurity in CdTe. Te in the flux enabled us to convert the *n*-type conductivity to *p*-type. The cooling rate was found to be the most important technological factor to control electrical parameters of powders. The highest values of *p*-conductivity ( $\sim 10 \Omega \text{ cm}$ ) in undoped CdTe were achieved in the CdCl<sub>2</sub>-Te flux by combined cooling: quenching from 650°C to the room temperature and additional annealing at 400°C followed by slow cooling. Nearly the same results were obtained in samples lightly doped with Na ( $[\text{Na}]_{\text{dos}} = 5 \times 10^{17} \text{ cm}^{-3}$ ) and Te in the flux and quenched from 750°C or slowly cooled from 510°C. The prerequisites for the high conductive *n*-CdTe monograin powders are the lowest possible recrystallisation temperature and the use of unmodified CdCl<sub>2</sub>.

**Key words:** semiconductor, cadmium compounds, tellurium compounds, crystal growth, flux, doping, chlorine, sodium, gallium, electrical conductivity type, conductivity conversion.

### 1. INTRODUCTION

In [1] we showed that monograin powders of CdS, CdSe, CdTe, their solid solutions, and CuInSe<sub>2</sub> can be produced by the isothermal recrystallisation of initial polycrystalline powders in different molten fluxes. These monograin powders, consisting of single-crystalline grains with narrow granulometric composition, are useful in designing monograin membranes and layers for photovoltaic and photoelectrochemical cells [2]. Monograin powder technology is distinguished by a

liquid ambient (so-called flux) used to accelerate crystal growth. The composition of the flux and recrystallisation temperature determine the equilibrium conditions in a closed isothermal system as well as the properties of the crystals produced. The aim of this research was to study:

- 1) the influence of flux nature on the homogeneity, perfection and morphology of grains and to develop CdTe monograin powders;
- 2) the influence of preparative conditions (temperature and duration of recrystallisation, cooling rate, and the flux nature) on the electrical characteristics of the produced monograin materials;
- 3) the influence of impurities such as Na and Ga and that of Cd or Te, added into the flux, on the electrical properties of CdTe crystals.

## 2. EXPERIMENTAL DETAILS

In our recrystallisation studies, different CdTe polycrystalline powders were used as initial materials. We used the powders synthesised from the constituent elements in the vapour phase, containing residual impurities up to  $10^{-5}\%$  (A) and those synthesised from the elements in molten sodium chloride, containing sodium and chlorine at undetermined level (B). Initial CdTe powders were treated thermally during 2 h at  $590^{\circ}\text{C}$  in a quartz tube in the dynamic vacuum (so-called partial vacuum sublimation) to remove separate phases of constituent elements and to obtain a homogeneous starting material [3]. Vacuum-annealed powders were ground in an agate ball mill and fractions smaller than  $100\ \mu\text{m}$  were used in recrystallisation studies. Cadmium chloride was used as the main component of the flux. In some experiments, NaCl and Te were added to  $\text{CdCl}_2$  to modify the flux nature. The amount of the flux was calculated on the basis of the phase diagram of CdTe– $\text{CdCl}_2$  [4]. The condition of monograin growth mechanism, dominating only if the volumes of liquid and solid phases at the recrystallisation temperature are nearly equal, was considered [5]. The concentrations of dopants were given for the initial CdTe amount. The dopant concentration in the final product is always less than the added initial concentration due to the distribution of a dopant between different phases in a closed system. The mixtures of CdTe and  $\text{CdCl}_2$  with the corresponding dopants (NaCl for Na doping,  $\text{GaCl}_3$  for Ga doping, elemental Cd or Te) were dried and sealed into evacuated quartz ampoules and placed into a preheated tube furnace. After firing, the ampoules were cooled down slowly in the furnace or quenched in deionised water. The  $\text{CdCl}_2$  flux was dissolved in deionised water. Electrical resistivity of the materials was measured by pressing powder crystals between two In contacts. The type of conductivity was determined by the thermo-probe method. V–A characteristics of the newly produced powder crystals were linear, however, highly conductive materials lost their linearity after exposure to open atmosphere. A short-time etch of these powders in 1:4 diluted  $\text{HNO}_3$  restored the linear behaviour of the V–A characteristics.

### 3. RESULTS AND DISCUSSION

#### 3.1. Comparison of different initial powders

Recrystallised in  $\text{CdCl}_2$  materials based on the initial CdTe polycrystalline powders produced by vapour-phase synthesis from the elements had nearly equal electrical parameters.

Electrical parameters of recrystallised materials prepared from different initial CdTe powders (A) and (B) were substantially different. Resistivity of *n*-type CdTe (B) recrystallised in  $\text{CdCl}_2$  flux at 750 °C and quenched in water (grain resistivity  $R=2\times 10^7 \Omega$ ) was about four orders of magnitude higher than that of CdTe (A) (grain resistivity  $R=(1-2\times 10^3 \Omega)$ ). The higher Na content in initial cadmium telluride (B) in comparison with residual concentration of Na in (A) materials might be the reason of the observed difference. During the isothermal growth of CdTe crystals in the liquid phase of  $\text{CdCl}_2$ , all recrystallised materials are uniformly saturated with chlorine, which is a well-known donor impurity in II-VI compounds. As a result, the effect of co-solubility of different impurities could occur. The differences found in electrical parameters of materials from different initial powders aroused our interest to study the influence of intentional Na doping on the CdTe characteristics.

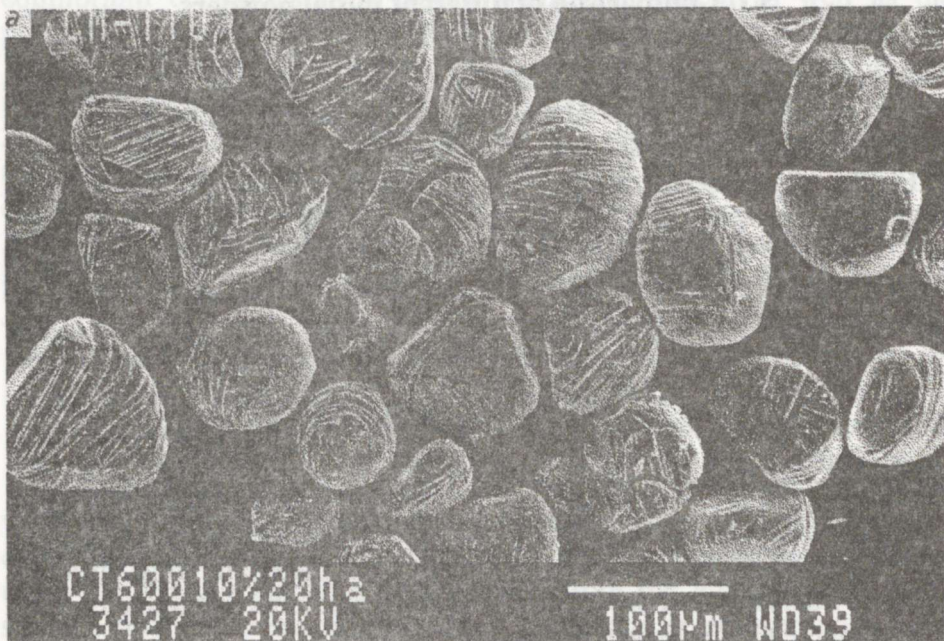
#### 3.2. Influence of Na doping

CdTe doping by adding NaCl into the  $\text{CdCl}_2$  flux led to the following effects.

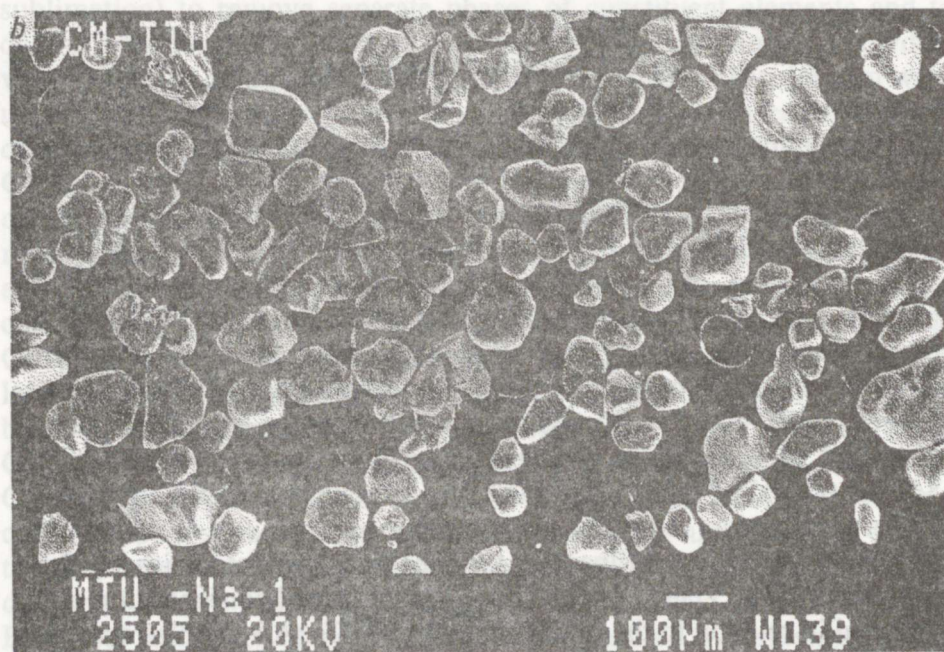
First, NaCl content in  $\text{CdCl}_2$  results in lower growth rate of crystals as compared to  $\text{CdCl}_2$  and  $\text{CdCl}_2$ -Te fluxes, but smoother surfaces and higher perfection of crystals was achieved (Figs. 1a and 1b). The maximum rate of crystal growth was observed in the  $\text{CdCl}_2$ -Te flux. The median grain size, determined graphically from the data of sieving analysis concerning log-normal probability graph paper [6], 340  $\mu\text{m}$  was achieved at 650°C in 3 h. In the same conditions, the recrystallisation in  $\text{CdCl}_2$ -NaCl resulted in an average grain size of 78  $\mu\text{m}$ . The form factor 0.84 was typical of the  $\text{CdCl}_2$ -NaCl flux as compared to the form factor 0.75 for the powders recrystallised in other fluxes.

Second, Na doping influenced the electrical characteristics of CdTe monograins (Figs. 2 and 3). The  $[\text{Na}]_{\text{dos}}$  is the added concentration of Na calculated in relation to the initial amount of CdTe. All samples quenched from 750°C had *n*-type electrical conductivity, except for the one annealed in the Te-containing flux (Fig. 2).

liquid ambient (SEM) AND DISCUSSION) crystal growth. The composition of the flux and recrystallisation temperature determine the morphology of the crystals. The flux composition as well as the



(b). Initial CdTe powders were treated thermally during 2 h at 590 °C in a quartz tube in the dynamic vacuum (so-called partial vacuum



determined by the thermo-probe method. The newly produced powder crystals were linear, however, highly conductive materials lost their linearity after exposure to open atmosphere. A short-

Fig. 1. SEM photos of CdTe monograin powders grown at 650°C in 3 h in the presence of fluxes: CdCl<sub>2</sub> + Te (a) and CdCl<sub>2</sub> + NaCl + Te (b), [Na]<sub>dos</sub> = 10<sup>21</sup> cm<sup>-3</sup>.

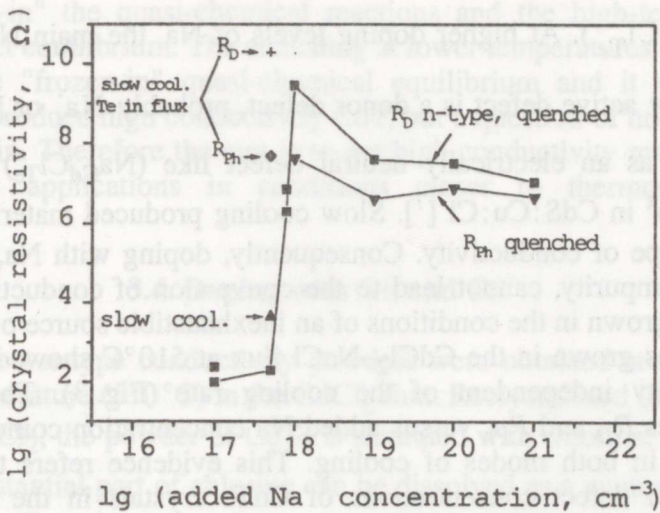


Fig. 2. Crystal resistivity versus added Na concentration. Growth temperature 750°C.

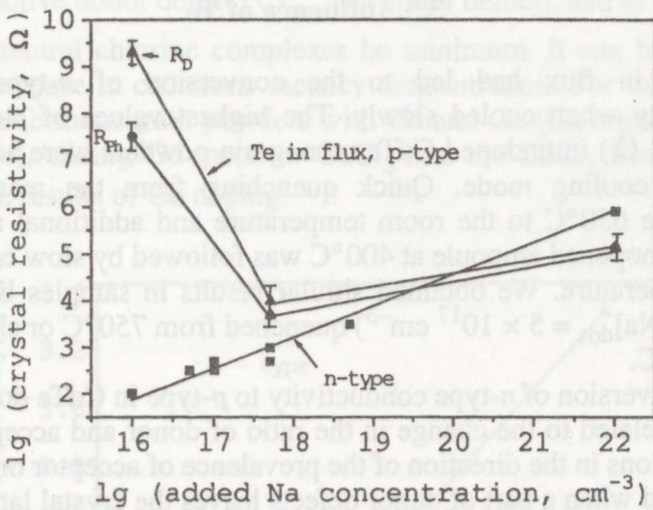


Fig. 3. Crystal resistivity versus added Na concentration. Growth temperature 510°C.

At low added Na concentrations, the resistivity of quenched CdTe samples grown in CdCl<sub>2</sub> flux was low. Resistivity increased steeply with the simultaneous appearance of photosensitivity in a very narrow region of added Na concentrations (near 10<sup>18</sup> cm<sup>-3</sup>), and then it decreased slowly with increasing Na concentrations (Fig. 2). At the same time, photosensitivity decreased also with an increase in Na concentration and became negligible in the material synthesised in molten sodium chloride (B). The shape of the crystal resistivity curve versus Na concentration was similar to the titration curve, showing the effective influence of Na acceptor at the point of sharp rise of resistivity, where negatively charged acceptor defects (Na'<sub>Cd</sub>) completely compensated the donor defects of

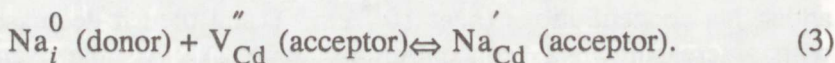
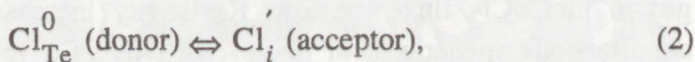
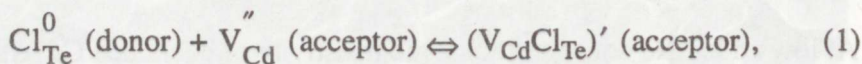
chlorine ( $\text{Cl}_{\text{Te}}^{\cdot}$ ). At higher doping levels of Na, the main Na-containing electrically active defect is a donor defect, probably  $\text{Na}_i^{\cdot}$  or Na is mainly dissolved as an electrically neutral defect like  $(\text{Na}_{\text{Cd}}\text{Cl}_{\text{Te}})^x$ , similar to  $(\text{Cu}_{\text{Cd}}\text{Cl}_{\text{S}})^x$  in CdS:Cu:Cl [7]. Slow cooling produced materials with the same *n*-type of conductivity. Consequently, doping with Na, as the only acceptor impurity, cannot lead to the conversion of conductivity type in CdTe:Cl grown in the conditions of an inexhaustible source of chlorine.

Samples grown in the  $\text{CdCl}_2$ -NaCl flux at 510°C showed also *n*-type conductivity independent of the cooling rate (Fig. 3). The curves of resistivities  $R_D$  and  $P_{\text{Ph}}$  versus added Na concentration coincide and rise smoothly in both modes of cooling. This evidence refers to negligible changes in defect concentrations of CdTe crystals in the presence of  $\text{CdCl}_2$ -NaCl flux during the cooling process from 510°C.

### 3.3. Influence of Te

Excess in flux had led to the conversion of *n*-type to *p*-type conductivity when cooled slowly. The highest values of *p*-conductivity ( $R = 2 \times 10^3 \Omega$ ) in undoped CdTe monograin powders were achieved by a combined cooling mode. Quick quenching from the recrystallisation temperature 650°C to the room temperature and additional annealing of the same unopened ampoule at 400°C was followed by slow cooling to the room temperature. We obtained similar results in samples lightly doped with Na ( $[\text{Na}]_{\text{dos}} = 5 \times 10^{17} \text{ cm}^{-3}$ ) quenched from 750°C or slowly cooled from 510°C.

The conversion of *n*-type conductivity to *p*-type in CdTe doped with Na and Cl is related to the change in the ratio of donor and acceptor defects' concentrations in the direction of the prevalence of acceptor ones. This can be achieved when a part of donor defects leaves the crystal lattice of CdTe due to the decrease in solubility at lower temperatures or when the impurity defects transfer from donor state to acceptor state as follows:



All these three quasi-chemical reactions are influenced by Te in phases being in equilibrium with solid CdTe in the closed system. Excess tellurium can shift the equilibrium of these reactions to the right side by enhancing the concentration of cadmium vacancies and promoting the transition of chlorine from lattice site into interstitial site. The quenching

will "freeze-in" the quasi-chemical reactions and the high-temperature atomic defect equilibrium. The annealing at lower temperatures will partly melt up the "frozen-in" quasi-chemical equilibrium and it will make possible to produce high conductivity CdTe, but a question of how stable it is will remain. Therefore the aim is to get high conductivity materials for photovoltaic applications in conditions closer to thermodynamical equilibrium.

### 3.4. Doping with Ga and Cd

The highest *n*-type conductivity powders were obtained at the lowest growth temperature (510°C) in the CdCl<sub>2</sub> flux. Recrystallised in the liquid phase of CdCl<sub>2</sub>, the powder of CdTe is saturated with chlorine. As shown in [8], a substantial part of chlorine can be dissolved as a neutral complex [V<sub>Cd</sub> (Cl<sub>Te</sub>)<sub>2</sub>]<sup>x</sup>. To achieve high *n*-type conductivity in CdTe, it is necessary to find conditions where chlorine is dissolved mainly as an electrically active donor defect (Cl<sub>Te</sub><sup>-</sup> is a donor defect), and to ensure that the part of neutral chlorine complexes be minimum. It can be achieved through a decrease in cadmium vacancy concentration. For this purpose, we doped CdTe monograin powders with Cd and Ga (Ga replaces the Cd sites in CdTe), adding Cd metal or GaCl<sub>3</sub> into the CdCl<sub>2</sub> flux. Figure 4 illustrates the results of Ga doping.

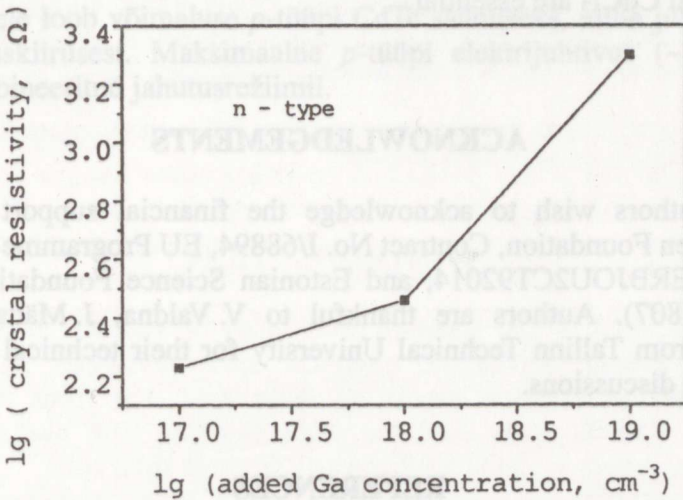


Fig. 4. Crystal resistivity versus added Ga concentration. Growth temperature 510°C, growth time 5 h, slow cooling.

All samples grown in the CdCl<sub>2</sub> fluxes containing Cd showed the same resistivity as the material grown in an unmodified CdCl<sub>2</sub> flux. So the cooling annulled the influence of excess Cd at the annealing temperature if

it existed. Doping with Ga, another foreign donor impurity, in addition to chlorine, led to higher resistivities probably due to lower electron mobility. The results could be summarised as follows: *n*-type conductivity can obviously be improved by decreasing the temperature of recrystallisation. As a result, the concentration of dissolved chlorine decreases, and electron mobility improves.

#### 4. CONCLUSIONS

Our study showed that highly conductive *p*- and *n*-type CdTe perfect monograin powders can be grown. We found that in the CdCl<sub>2</sub>-NaCl flux, sodium chloride inhibits crystal growth and provides for doping CdTe with Na. From the dependence of crystal resistivity on added Na concentration, we can conclude that Na acts as an effective acceptor impurity in CdTe. The region of the most effective added Na concentrations was found. Among technological factors used for creating high *p*-type conductivity, the cooling rate and the presence of Te in the flux were found most significant. In CdTe monograin powders undoped with Na, the highest values of *p*-conductivity (grain resistivity  $R = 2 \times 10^3 \Omega$ ) were achieved by growing in the CdCl<sub>2</sub>-Te flux and in the combined cooling conditions: the quenching from the recrystallisation temperature 650°C to the room temperature and additional annealing at 400°C followed by slow cooling to the room temperature. To produce highly conductive *n*-CdTe monograin powders, the lowest possible recrystallisation temperature and the use of unmodified CdCl<sub>2</sub> are essential.

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#### REFERENCES

1. Mellikov, E., Hiie, J., Altosaar, M., and Meissner, D. Monograin powders for solar energetics. 12th European Photovoltaic Solar Energy Conference, 11–15 April 1994. Amsterdam, 1994, 1619–1622.
2. Velde, T. S. te and Helden, G. W. M. T. van. Monograin layers. – Philips Techn. Rev., 1968, 29, 8/9, 238–242.
3. Mellikov, E. and Krunk, M. The standardization of composition of A<sub>2</sub>B<sub>6</sub> materials. – J. Surface and Coatings Techn., 1993, 62, 688–690.



4. Andronik, I. K., Kuleva, P. Z., and Suchkevich, K. D. Study of possibilities to grow crystals of CdTe by recrystallization in the CdCl<sub>2</sub> flux. – Neorg. mater., 1976, 12, 4, 759–760 (in Russian).
5. Mellikov, E. and Hiie, J. Recrystallization of cadmium sulphide powders activated in molten fluxes. – J. Neorg. Khim., 1981, 26, 9, 2304–2309 (in Russian).
6. Ozawa, L. Preparation of Y<sub>2</sub>O<sub>2</sub>S: Eu phosphor particles of different sizes by a flux method. – J. Electrochem. Soc., 1977, 124, 3, 413–417.
7. Kukk, P. L. and Altosaar, M. E. Defect structure of Cl and Cu doped CdS heat treated in Cd and S<sub>2</sub>. – Vapor. J. Sol. State Chem., 1983, 48, 1–10.
8. Agrinskaja, N. V. and Matvejev, O. A. About reciprocal influence of impurities and crystal lattice defects in CdTe. – Fiz. Techn. Poluprov., 1976, 10, 162–165 (in Russian).

## CdTe MONOTERALISTE PULBRITE TEHNOLOOGIA

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On uuritud miniatuursete CdTe monokristallide kasvu ja elektrijuhtivuse kujunemist CdTe pulbri isothermilisel rekristalliseerimisel CdCl<sub>2</sub> ja CdCl<sub>2</sub>-NaCl sulades faasides eesmärgiga saada kõrge *n*- ja *p*-tüüpi juhtivusega kristalle. On leitud, et NaCl-lisand sulas CdCl<sub>2</sub>-s vähendab kasvukiirust ja võimaldab legerida CdTe kristalle Na-ga. 510–750°C juures kasvatatud kristallid jäävad *n*-tüübilisteks sõltumata jahutuskiirusest ja Na kontsentratsioonist, kuigi Na-lisand käitub CdTe-s tugeva aktseptorina. Kasvutemperatuuri alanedes suureneb kristallide juhtivus (12 Ω cm-lt (750°C) 0,5 Ω cm-ni (510°C)). Elementaarse Te lisamine ülalnimetatud sulandajatele loob võimaluse *p*-tüüpi CdTe saamiseks, mille juhtivus sõltub jahutuskiirusest. Maksimaalne *p*-tüüpi elektrijuhtivus (~10 Ω cm) saadi kombineeritud jahutusrežiimil.