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Optimal Donor Doping of Cd(Zn)Te Detector-Grade Crystals

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Chernivtsi National University (1875)

OPTIMAL DONOR DOPING of Cd(Zn)Te DETECTOR-GRADE CRYSTALS

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Outline:

- **introduction**
- **electrical properties at RT (after annealing)**
- **high-temperature electrical properties under P_{Cd}**
- **high-temperature electrical properties under P_{Te2}**
- **point defect structure modeling**
- **2-step annealing results**
- **1-step annealing results**
- **conclusions**

It is possible to get high-resistive CdTe/CZT/CMT crystals using 0.1-100 ppm of donor dopant in the melt

Goal

To determine the optimal dopant donor concentration in the samples for the simple obtaining of stable high-resistive n-type material under Te-rich conditions

Why it is important to study properties just at high temperature *in situ*?

- the point defect (PD) structure is formed at high temperature and determines the RT properties;

- only at these conditions it is possible "to feel" the influence of native PDs and determine the nature and type of foreign PDs and successfully to study them;

- the possibility to observe directly all changes in the crystals, by changing the temperature, component pressure, heating/cooling rate.

That all favors the obtaining the material with specified and reproducible properties

Annealing conditions

(main experiment)

Indium content in the samples – **~10^{16}-10^{19}** at/cm^3

Annealing temperature - 1170 K under P_{Cd}

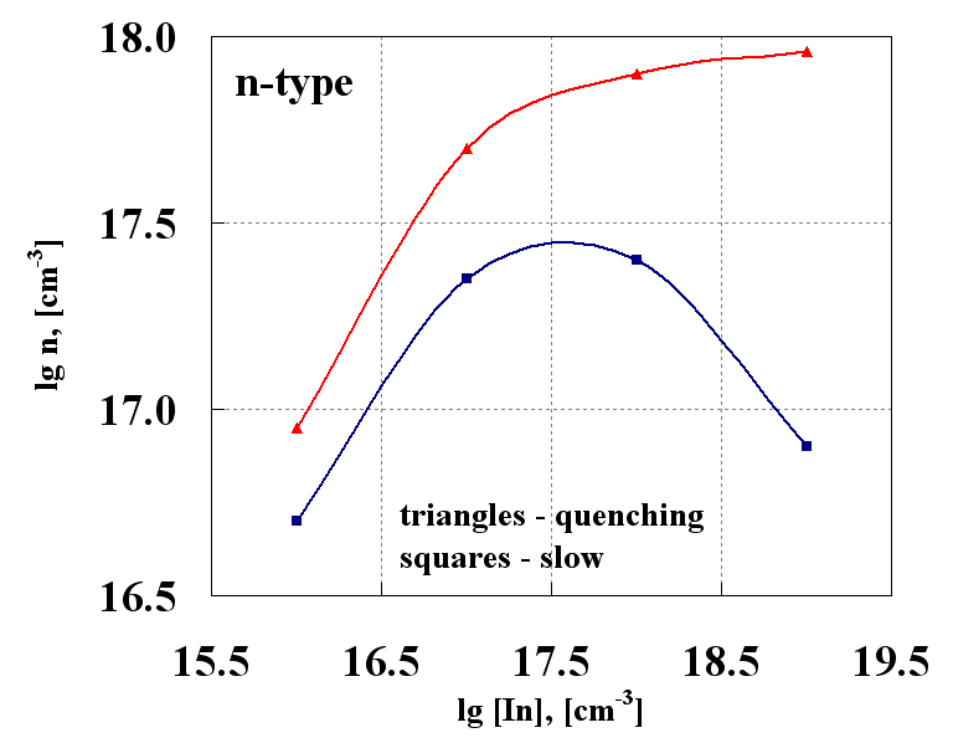
Annealing temperature - 1070 K under P_{Te2}

Annealing time - ~40 hours

Cooling procedure – quenching (50 % of samples),

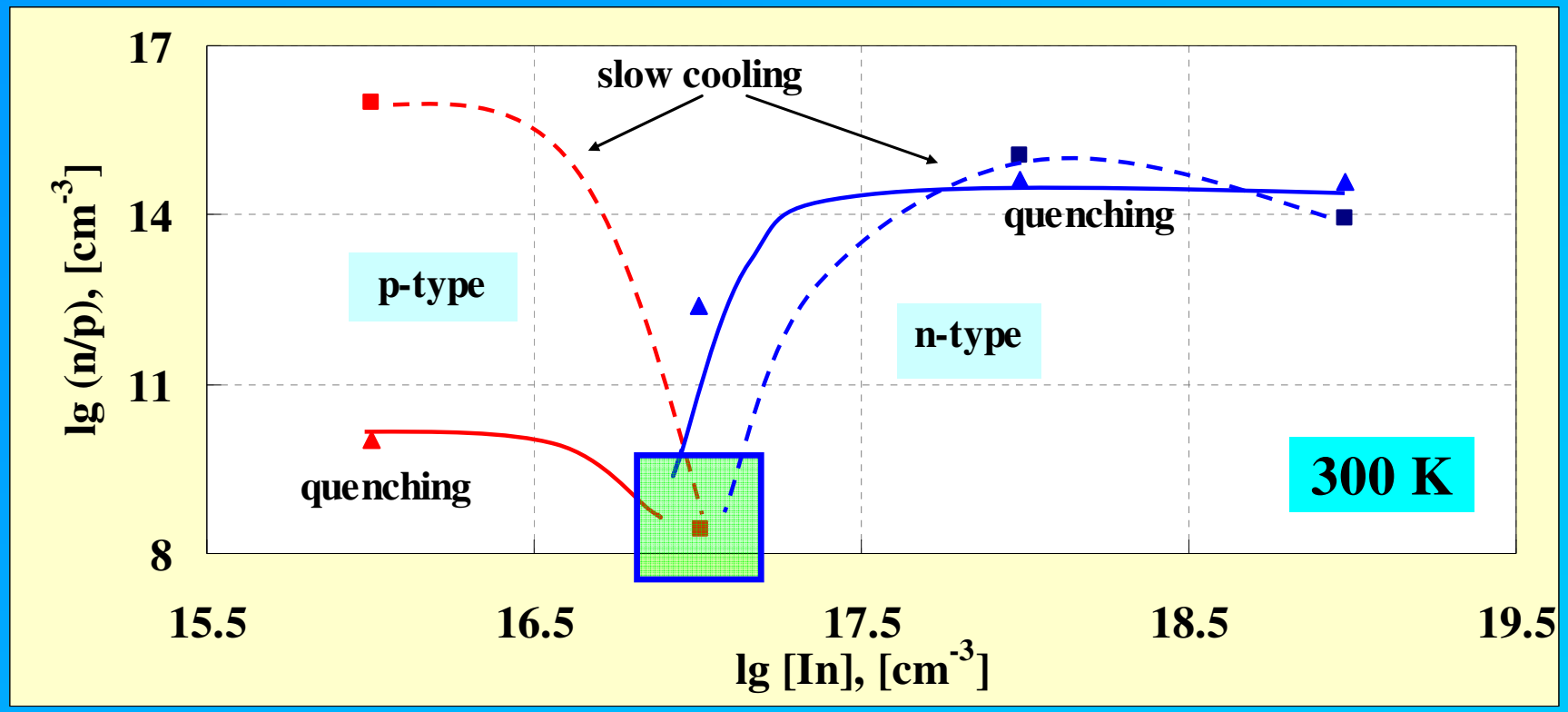
another ones were slowly cooled

Dependence of charge carrier density on In content at 300 K



Quenched (q) and slowly cooled (s) CdTe:In samples after annealing under $P_{Cd,max}$ (left) are low-resistive

Dependence of charge carrier density on In content in CdTe samples after annealing under $P_{Te2,max}$.



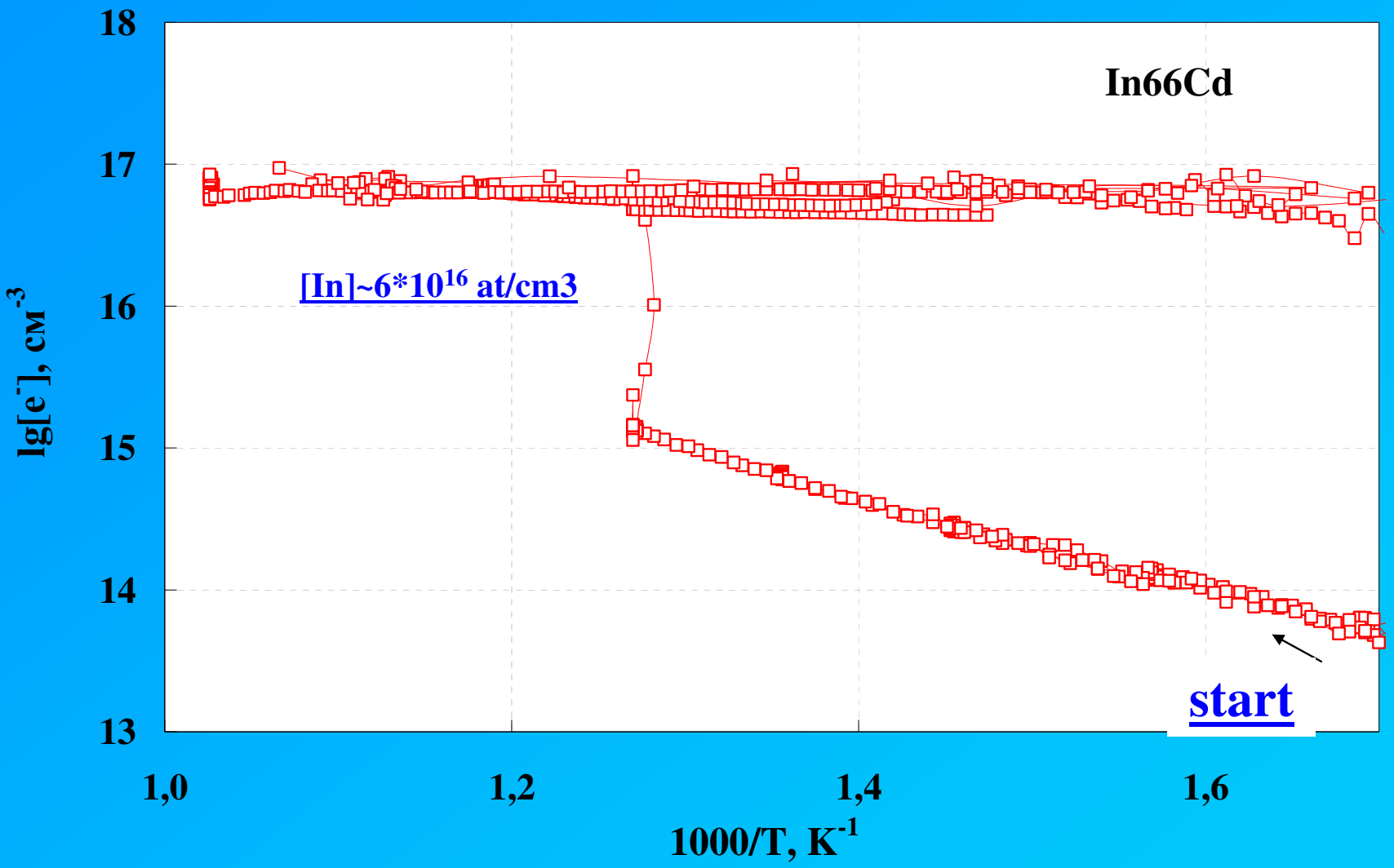
Annealing of CdTe:In samples with $[In] \approx 10^{17}$ at/cm^3 under Te overpressure allows to produce high-resistive material !

Electrical properties of CdTe:In samples at 300 K, annealed under $P_{Te2,max}$ (800°C, 40 h.)

№	Samples	[In], cm^{-3}	Cooling procedure	Conductivity type	σ, $(Ohm*cm)^{-1}$	R_x, cm^{-3}	μ, $cm^2/(Vs)$	k, %
1	Te1s	$\sim 10^{16}$	slow	p	$9.6*10^{-2}$	$7.7*10^{2}$	75	58
2	Te1q	$\sim 10^{16}$	quenching	***p***	$6.5*10^{-8}$	***$7.3*10^{8}$***	48	71
3	Te2s	$\sim 10^{17}$	slow	***n***	$9.0*10^{-9}$	***$1.8*10^{10}$***	160	-
4	Te2q	$\sim 10^{17}$	quenching	p	$1.6*10^{-5}$	$2.5*10^{6}$	40	83
5	Te3s	$\sim 10^{18}$	slow	n	-	$1.8*10^{4}$	-	-
6	Te3q	$\sim 10^{18}$	quenching	n	$1.4*10^{-3}$	$1.8*10^{4}$	24	-
7	Te4s	$\sim 10^{19}$	slow	n	$4.3*10^{-4}$	$4.9*10^{4}$	21	-
8	Te4q	$\sim 10^{19}$	quenching	n	$7.2*10^{-4}$	$2.5*10^{4}$	18	-

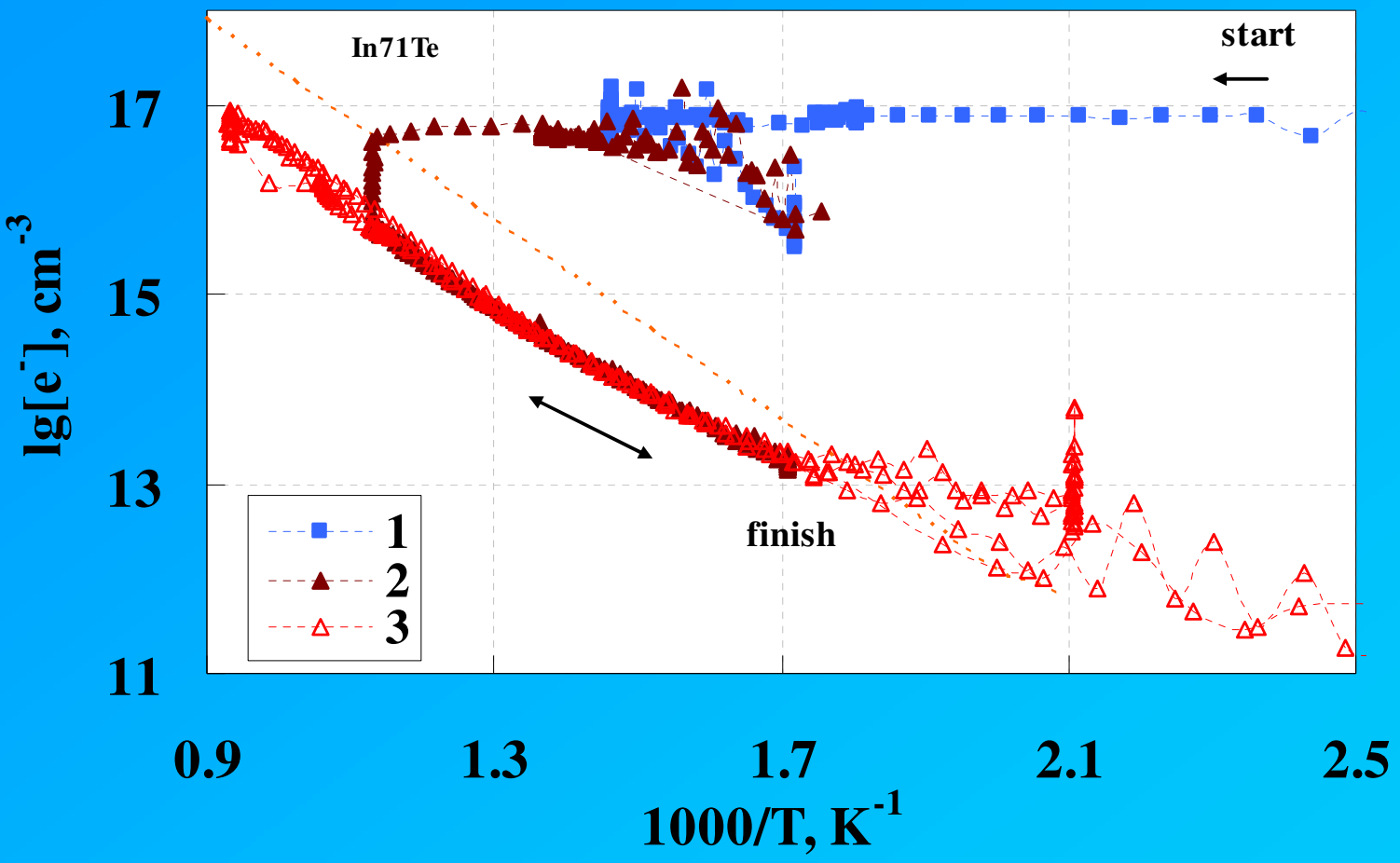
k - acceptor compensation degree; R_x - Hall constant;

Temperature dependence of electron density in CdTe:In under Cd saturation



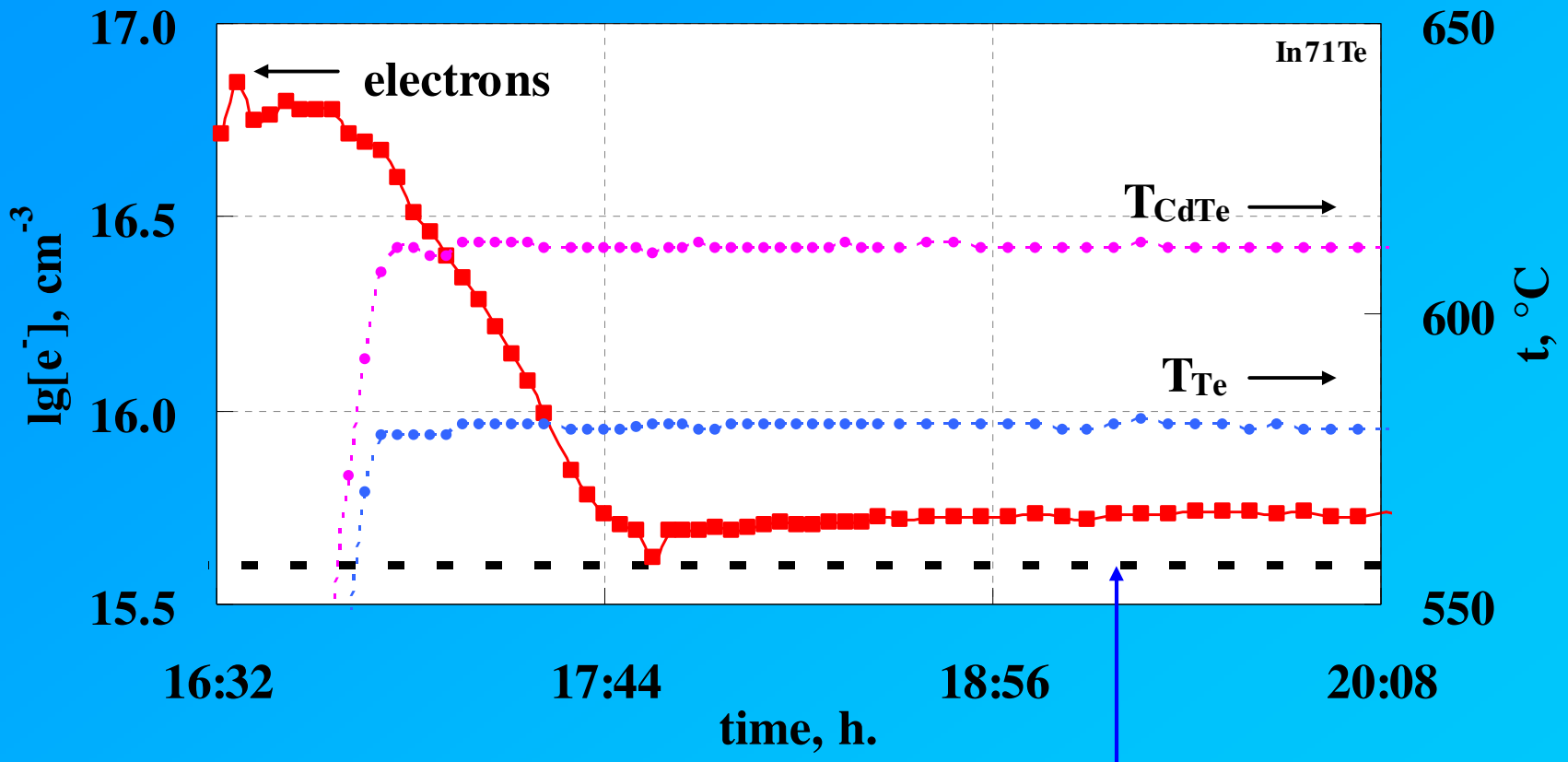
$$(In^{+}_{Cd}\,V^{2-}_{Cd})^{-} + Cd(g) \leftrightarrow In^{+}_{Cd} + Cd_{Cd} + 2e^{-}$$

Temperature dependence of electron density in CdTe:In under Te saturation ([In] ~10^{17} at/cm^3)



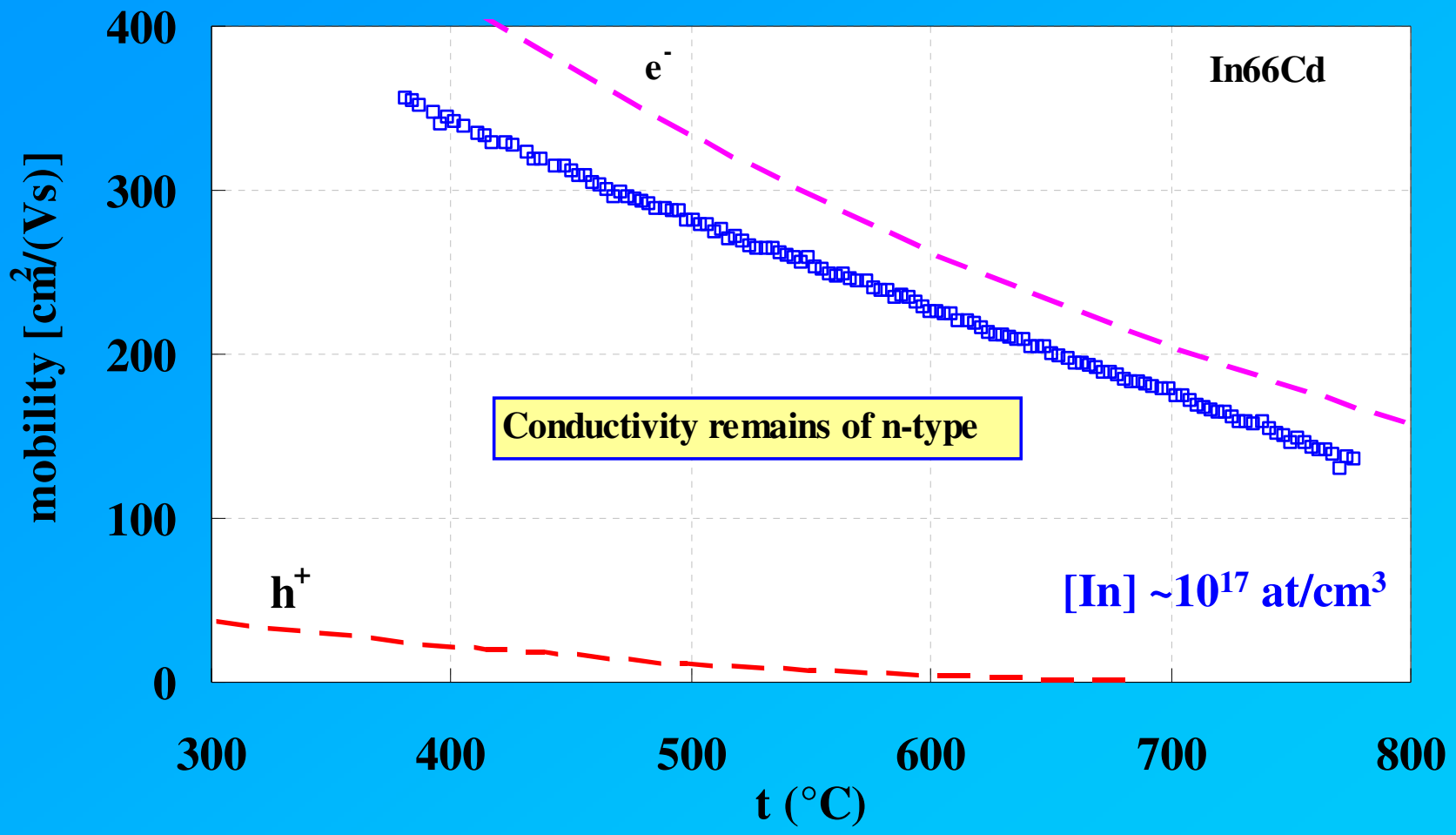
After annealing at ~870 K under Te overpressure the sample became <u>high-resistive</u> and <u>stable</u> to any changes (T or P_{Te2})

Reducing of electron density at holding under Te overpressure at ~610°C ([In] ~10^{17} at/cm^3)



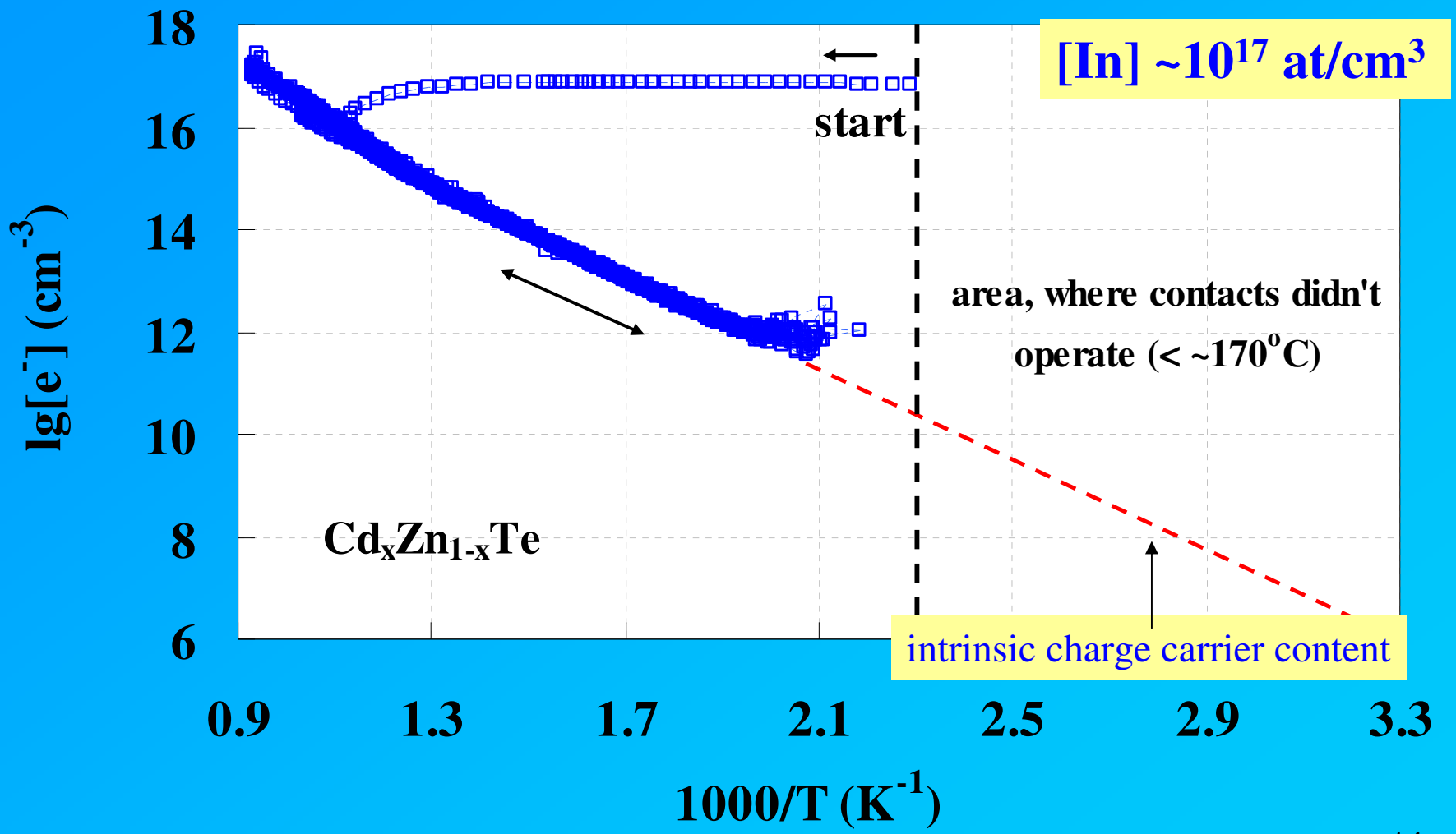
Electron density is close to intrinsic charge carrier content

Temperature dependence of electron mobility in CdTe:In under Cd saturation



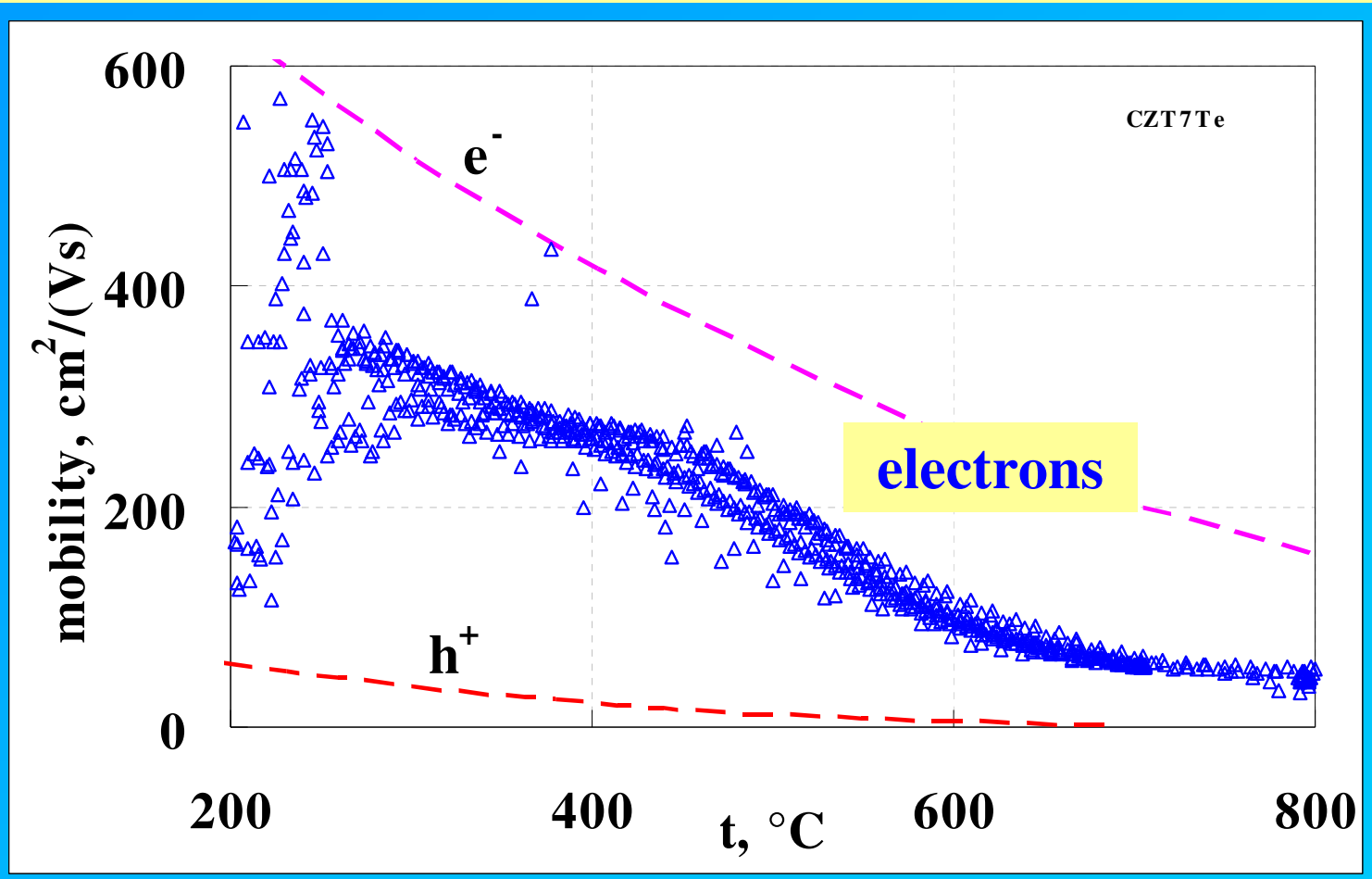
Dashed lines: e^- - electron mobility; h^+ – hole mobility in CdTe.

High-temperature Hall effect measurements in CZT:In sample under Te overpressure



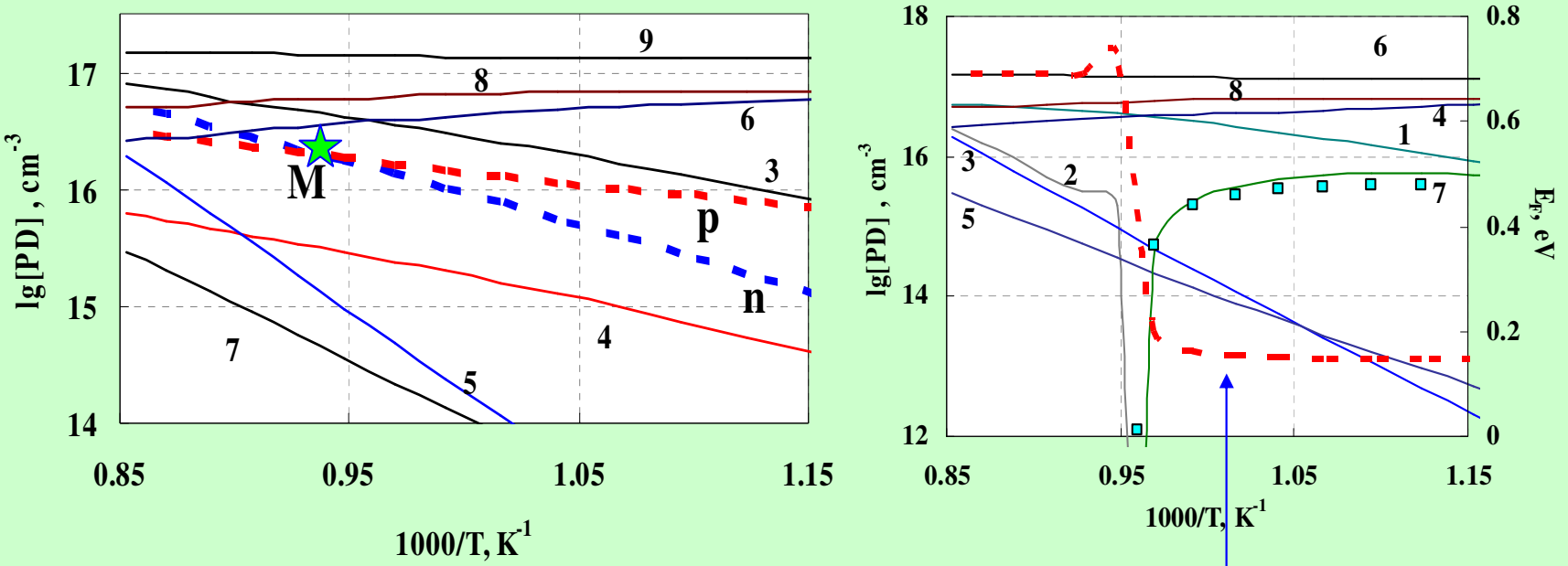
Electron mobility temperature dependence in CZT:In under Te saturation

(Dashed lines: e^- - electron mobility; h^+ – hole mobility in undoped CdTe)



[In] ~10^{17} at/cm^3

Modelling of point defect content vs temperature in CdTe crystals with [In]=2×10^{17} at/cm^3 at $P_{Te2,max}$



1 - n; 2 – p; 3 - V_{Cd}^{-} ; 4 - V_{Cd}^{2-} ; 5 - Cd_{i}^{2+} ; 6 – Te_{i}^{-} ; 7 - V_{Te}^{2+} ; 8 - A_{In}^{-} ; 9 - In_{Cd}^{+}

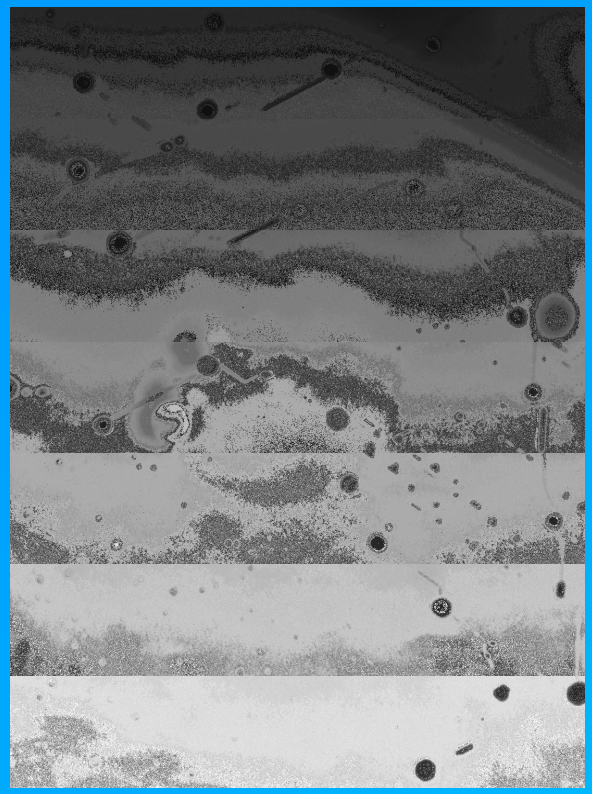
Fermi level

Experiment: n~10^8 cm^{-3}

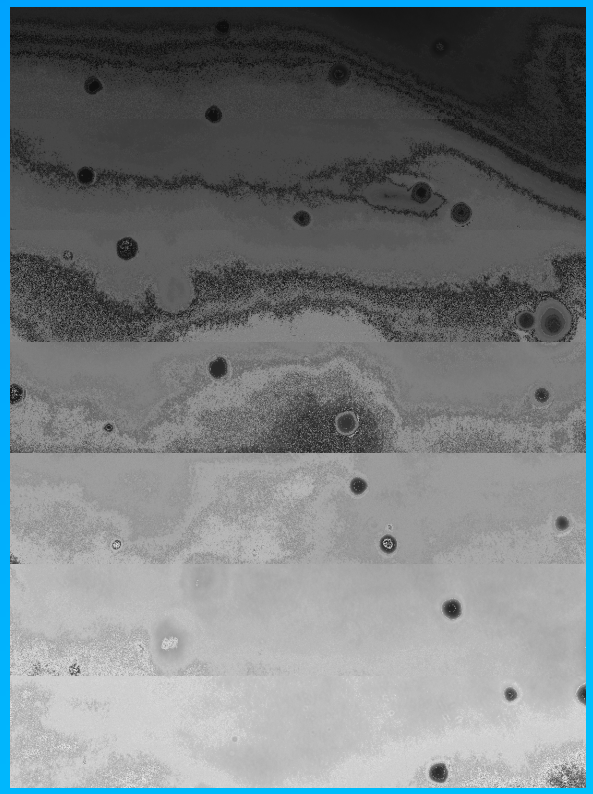
Left – high temperature PD equilibrium modelling at $P_{Te2,max}$.

Right: squares – hole density after simulated quenching to 0 K and subsequent reheating to 300 K.

Inclusions elimination after annealing under Cd overpressure



before annealing

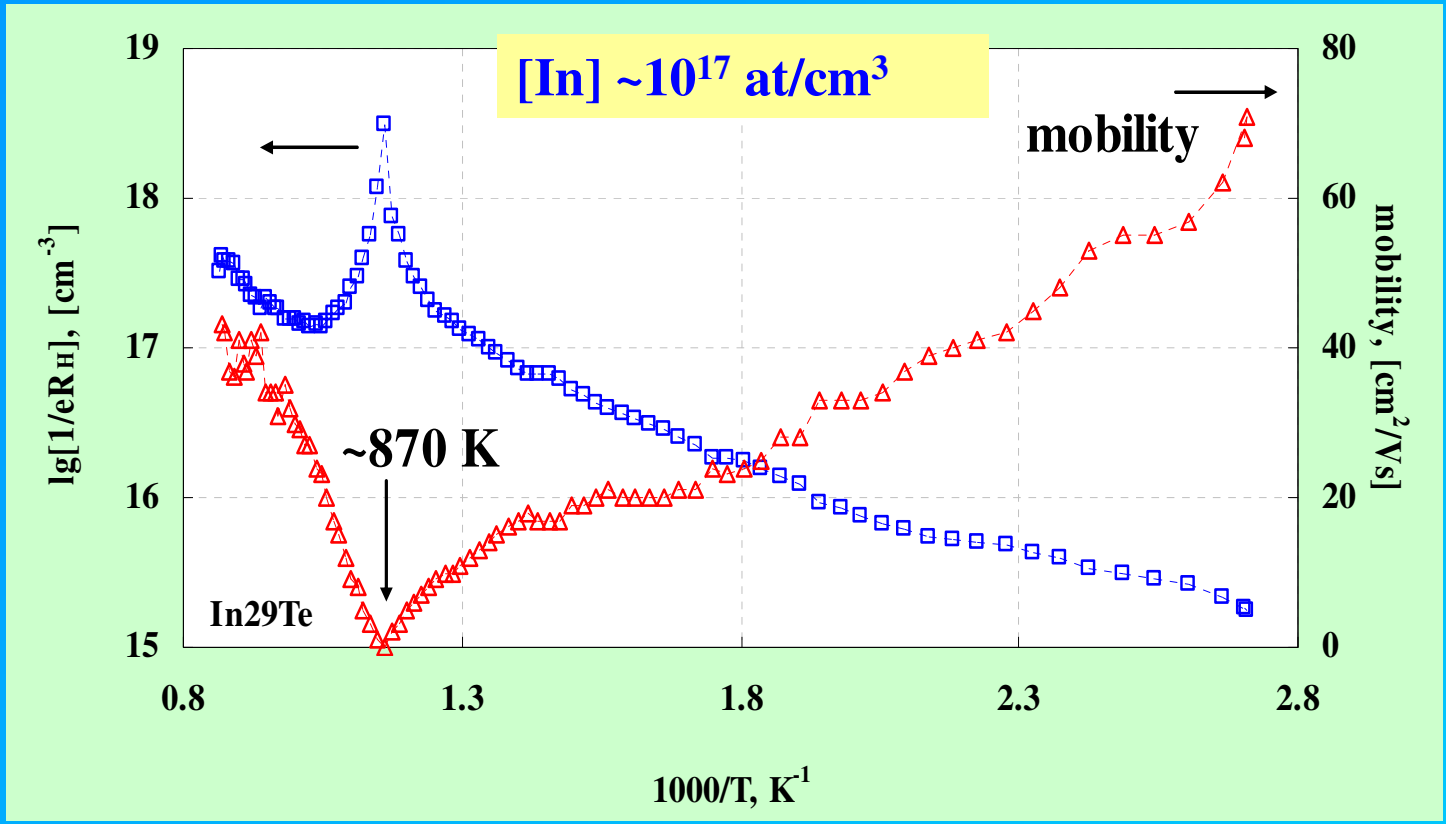


after 1st annealing

after 2nd annealing

T=1100 K; 15 min. each

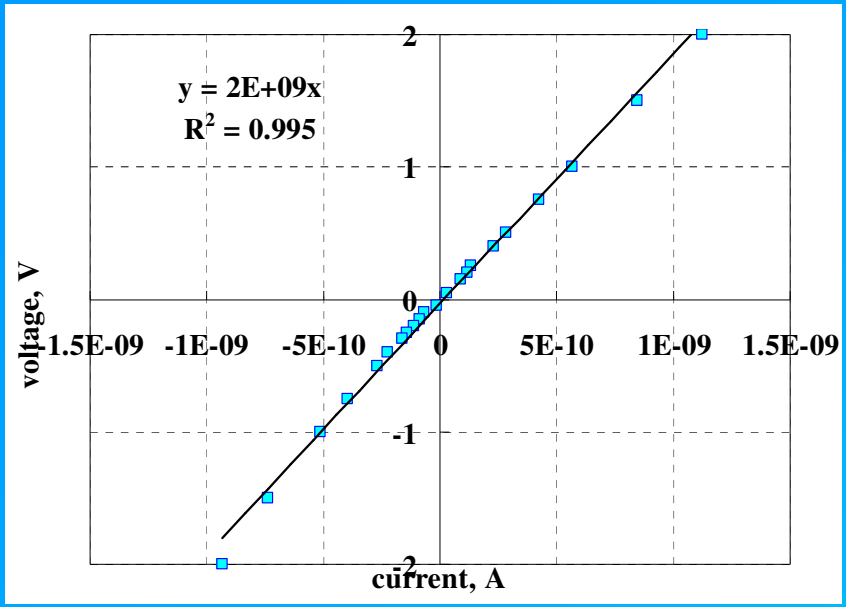
Conductivity type inversion in CdTe:In under Te saturation

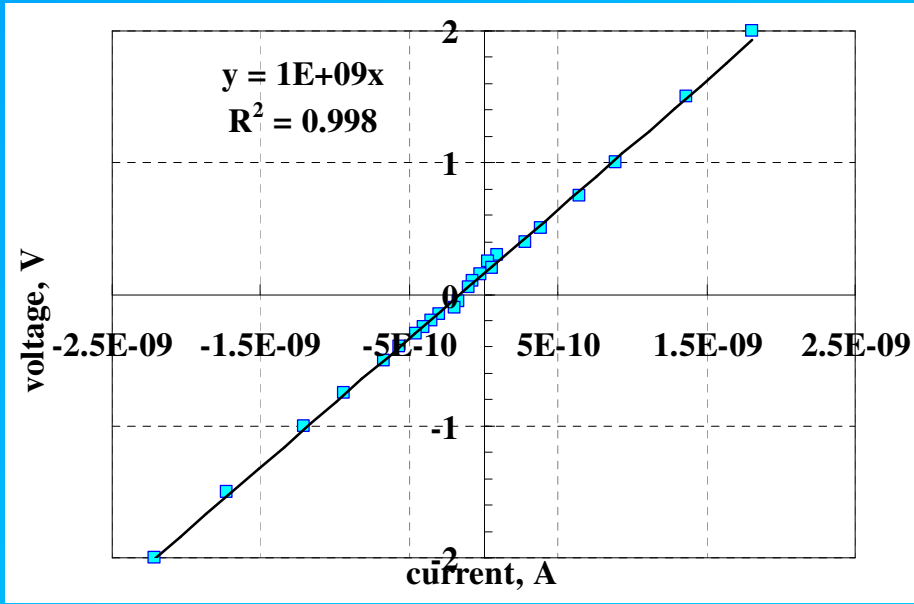


Annealing and quenching at ~870 K under Te overpressure is prospective for producing high resistive material

Renewal of CdTe:In sample resistance after annealing under $P_{Cd,max}$

as-grown (left) and after 2nd (under P_{Te2}) annealing (right)





R ~ $2*10^9$ Ohm **R ~ $1*10^9$ Ohm**

[In] ~10^{17} at/cm^3

Annealing conditions under Te overpressure:

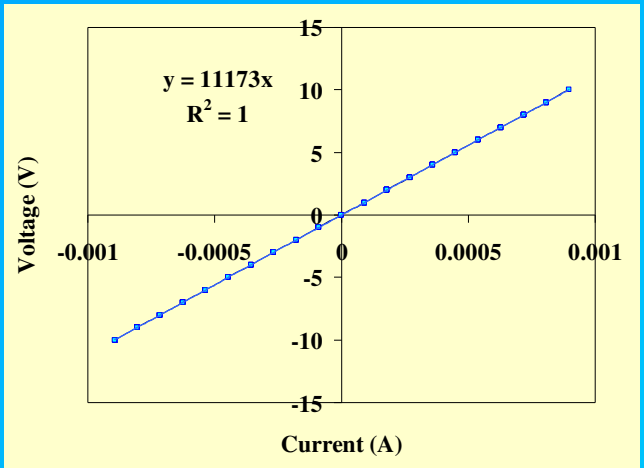
$T_{CdTe:In}$= 600°C P_{Te}=0.0003 atm. τ=21 h.

quenching

2-step annealing to maintain CZT samples resistance (initial resistance ~10^{10} Ohm*cm)

[In] ~10^{17} at/cm^3

After 1-step annealing under Cd overpressure the initial resistance dropped to ~10^4-10^5 Ohm

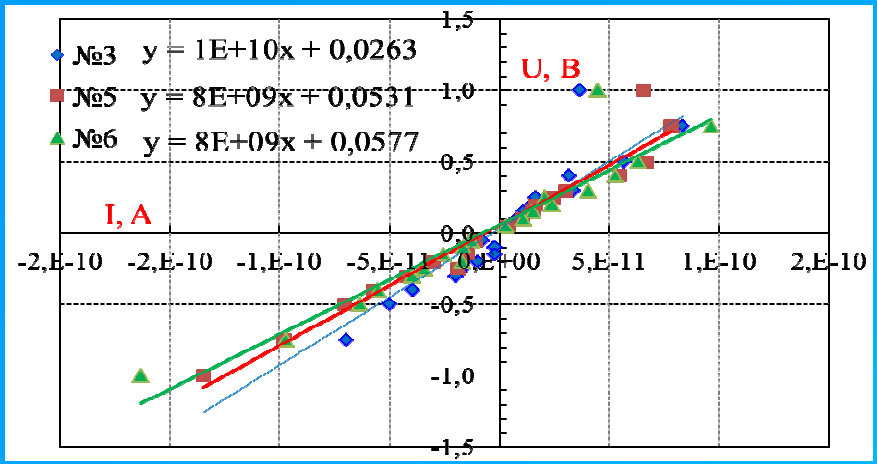


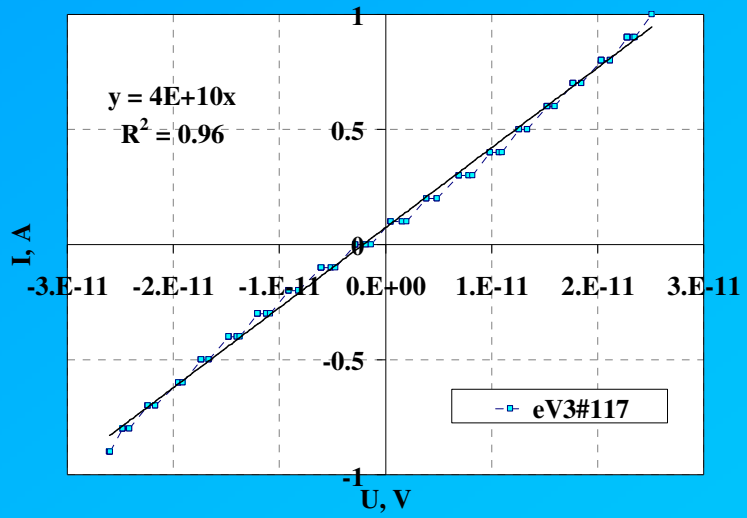
Results of the 2nd annealing under Te overpressure

#	T_{sample}, ° C	T_{Te}, ° C	Time, hs.	Cooling rate	R, Ohm·cm	Sample origin
1	800	700	12	quick	$1.4 \cdot 10^4$	Ukraine
2	700	660	12	slow	$2 \cdot 10^4$	Ukraine
3	800	700	4	slow	$1 \cdot 10^{10}$	Ukraine
4	700	660	4	quick	$6 \cdot 10^6$	Ukraine

2nd annealing of CZT samples under Te overpressure

(initial resistance ~10^{10} Ohm*cm)





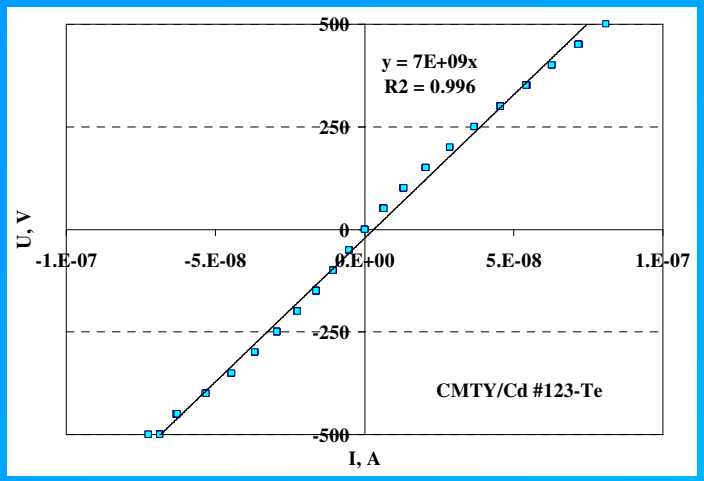
Results of the 2nd annealing under Te overpressure

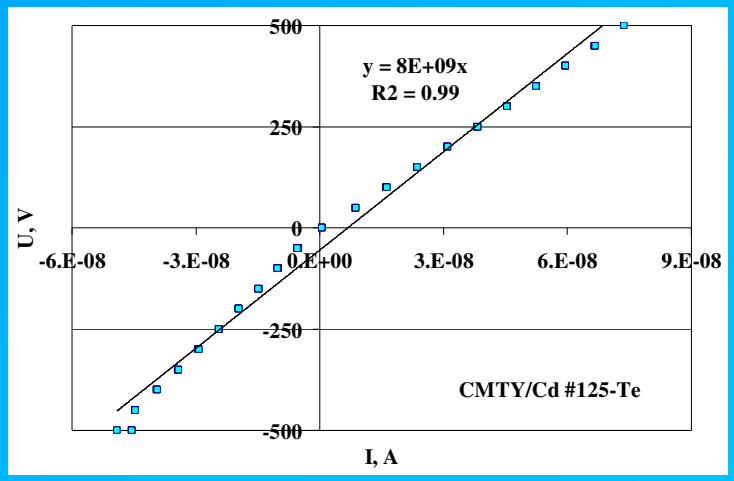
#	T_{sample}, ° C	T_{Te}, ° C	Time, hs.	Cooling rate	R, Ohm	Sample origin
117	729	657	10	QS	~$2\cdot10^{9}$	eV
158	800	708	*	*	~$7\cdot10^{7}$	eV
3	800	700	4	slow	~10^{10}	eV
5	800	700	4	slow	~$8*10^{9}$	eV
6	800	700	4	slow	~$8*10^{9}$	eV

2-step annealing of Cd(Mn)Te samples resistance

(initial resistance ~10^{10} Ohm*cm)

[In] ~10^{17} at/cm^3





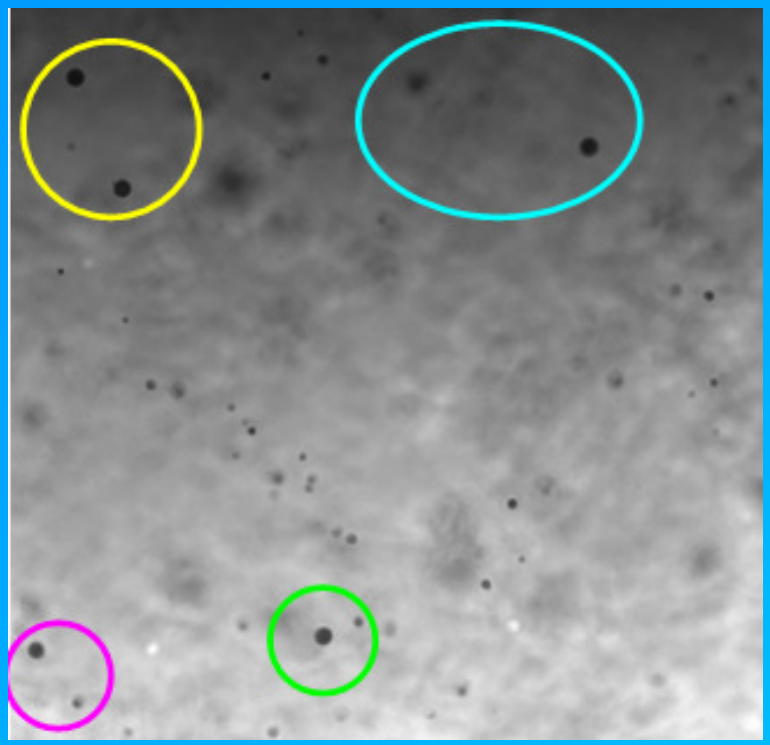
2-step annealing of as-grown CMT samples

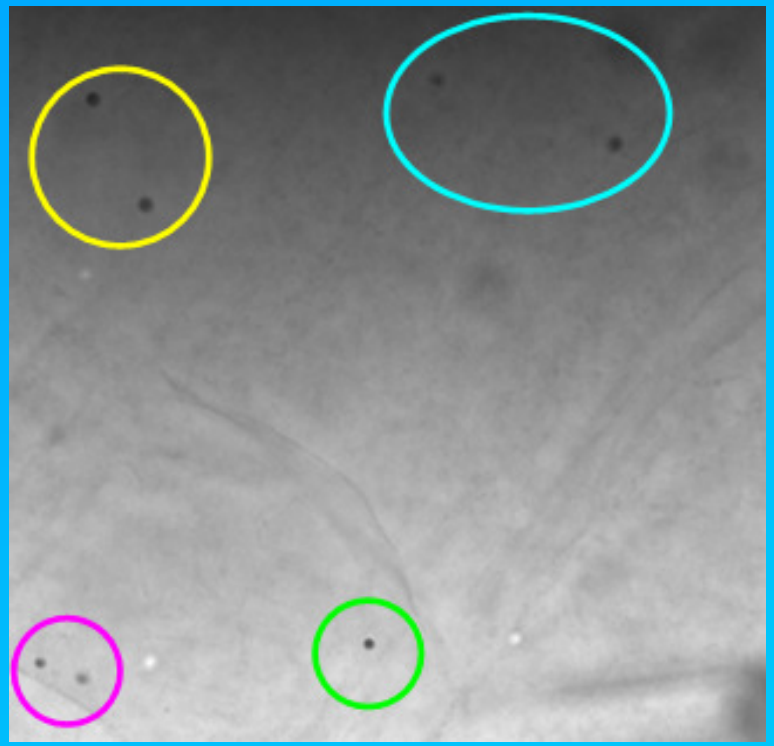
(1 - under Cd overpressure; 2 - under Te overpressure)

Sample №	$T_{samp.}$, ^oC	$T_{comp.}$,. ^oC	Duration, hrs	Cooling type	R, Ohm	Sample origin
123	800	700	4	2 K	10^{10}	#1
125	800	700	4	2 K	$5*10^9$	#1
126	806	695	4	quenching	$2*10^9$	#1
127	805	697	2	2 K	$3*10^9$	#1

Annealing under Te overpressure

(T~1100 K; 20 min.)



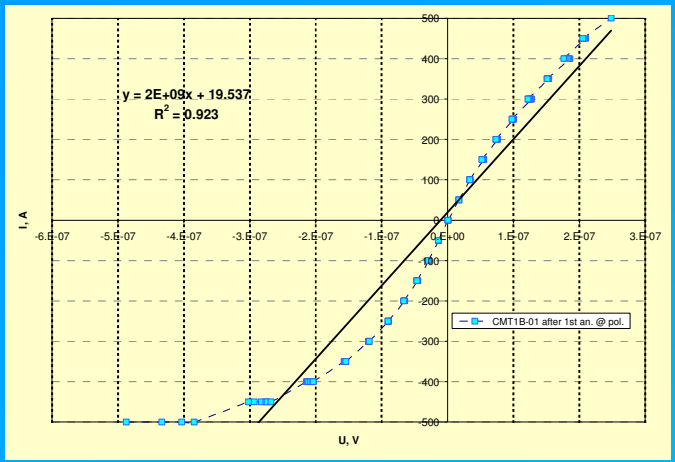


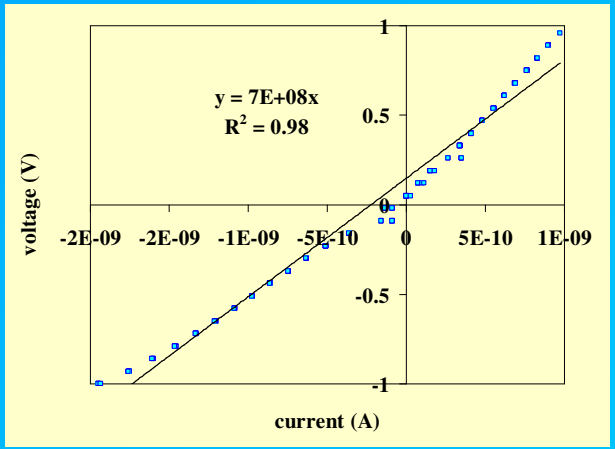
before (left) and after (right) annealing

1 step annealing to maintain samples resistance

(initial resistivity ~10^{10} Ohm*cm)

[In] ~10^{17} at/cm^3



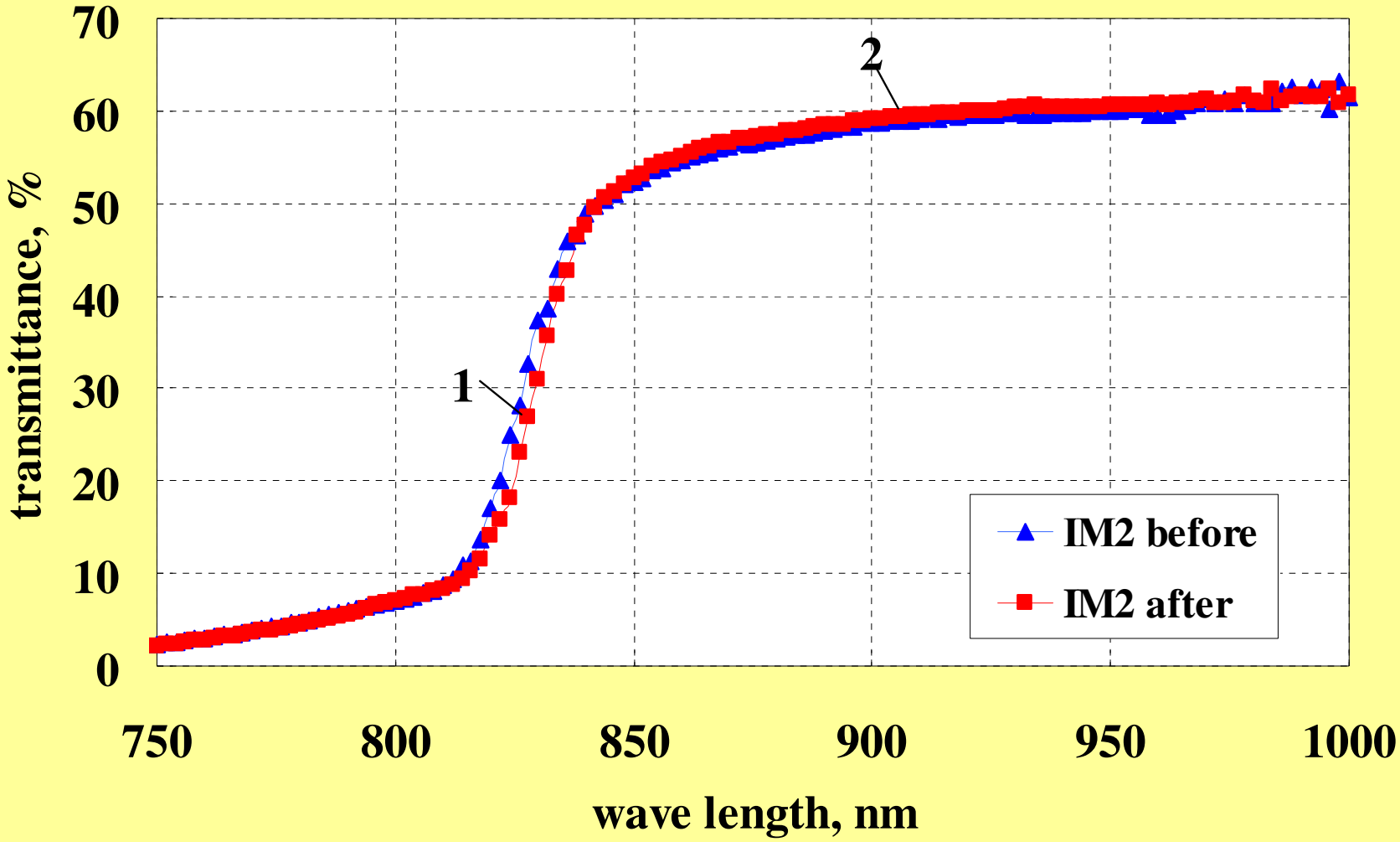


1-step annealing of as-grown CMT samples under Te overpressure

Sample №	$T_{samp.}$, ^oC	$T_{comp.}$, ^oC	Duration, hrs	Cooling type	R, Ohm	Sample's origin
86	727	670	10	quenching	$2*10^8$	#1
87	727	715	10	quenching	10^{10}	#1
113	734	662	10	quenching	$2*10^{10}$	#1
157	800	700	5	1.5 K/min	$2*10^9$	#1
184	733	667	10	2 K/min	$8*10^8$	#2

CdTe:In transmittance before and after annealing

1 – before; 2 – after annealing



Experimental annealing (CdTe:Cl)

(Karlov University, Prague, Czech Republic)

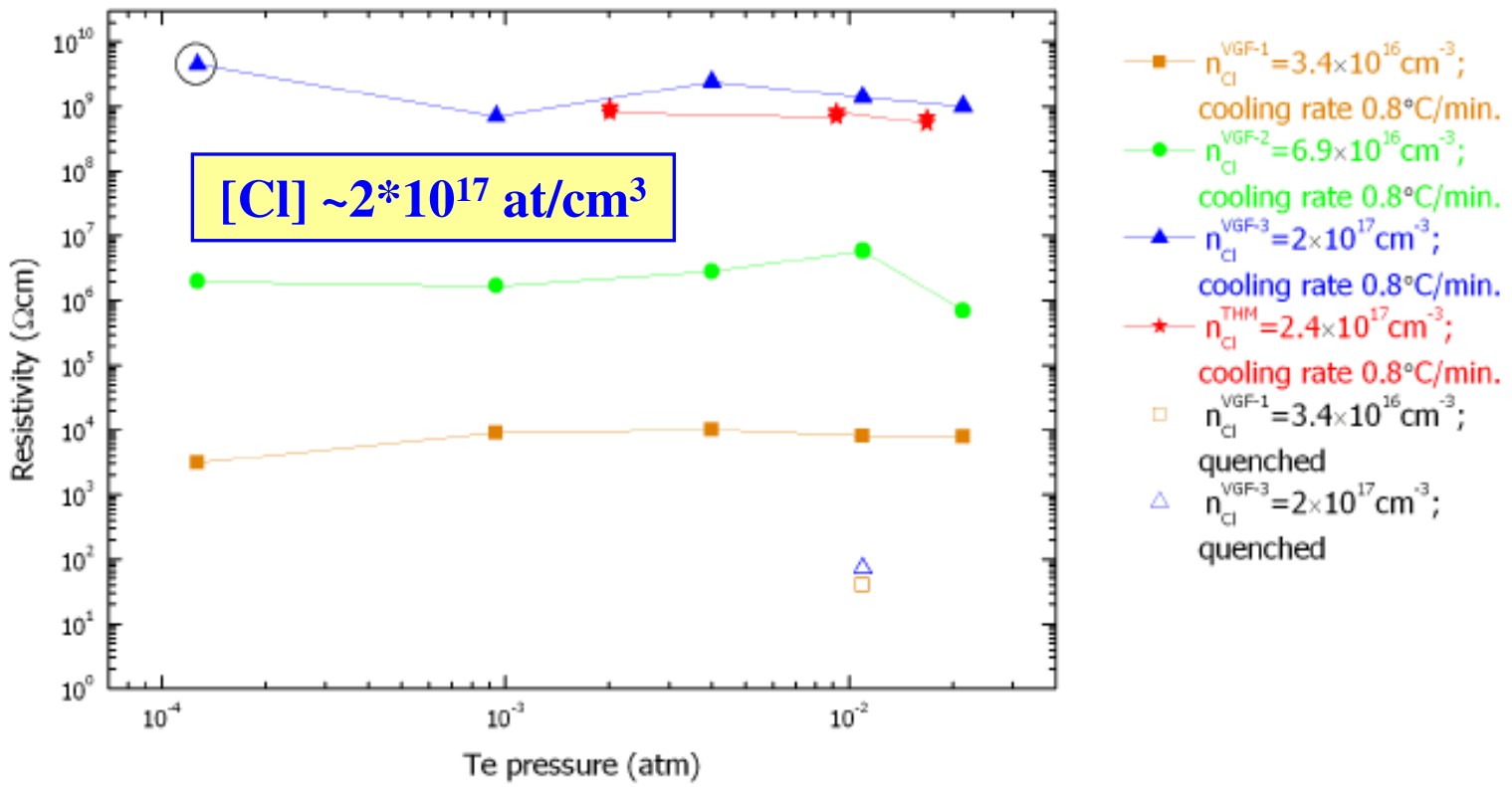
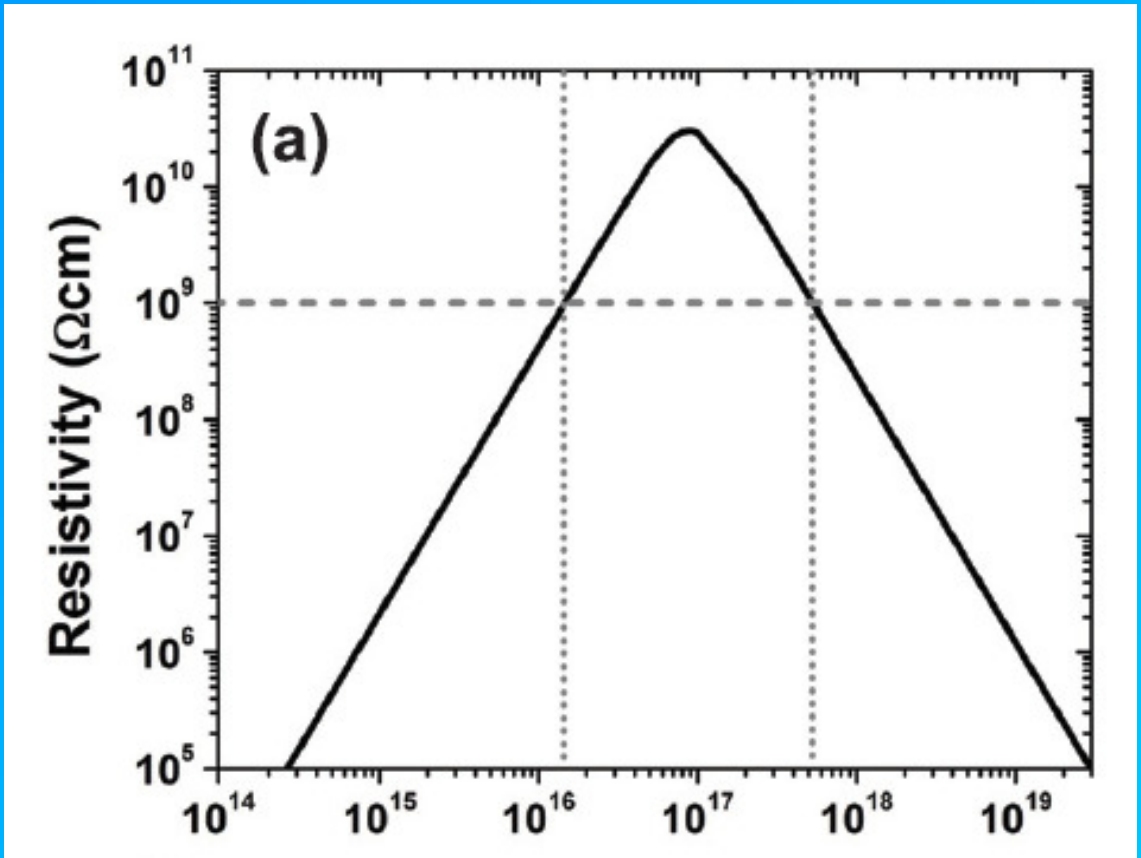


Fig.3.21: The resistivity dependence on Te overpressure after the second annealing step in Te vapor. Every point represents the resistivity of one sample after two-step annealing. Most of the samples were annealed at 700°C for 24 hours. Samples annealed at the lowest Te pressure 1.26×10^{-4}atm were annealed at 600°C for 50 hours. Filled symbols are samples cooled slowly after the second Te-rich annealing. Empty symbols represent samples quenched in the air after the second Te-rich annealing step. Lines are guides for eyes only.

Theoretical calculations for CdTe:In crystals under Te-rich conditions



Biswas K, Du M-H. What causes high resistivity in CdTe // New J. Physics. -V.14. -2012, pp.20.

CONCLUSIONS

- to produce high-resistive material under Te-rich conditions the optimal concentration of Indium in Cd(Zn,Mn)Te have to be ~10^{17} at/cm^3;

- it allows easy to obtain <u>stable material with high electron mobility</u> in as-grown ingot and after 2-step annealing treatment (Cd, then Te overpressure);

- 1-step annealing under Te overpressure at ~1000 K is promising as a stage of post-growth cooling; it favors for inclusion elimination and keeps high resistivity.

Thanks for your attention!