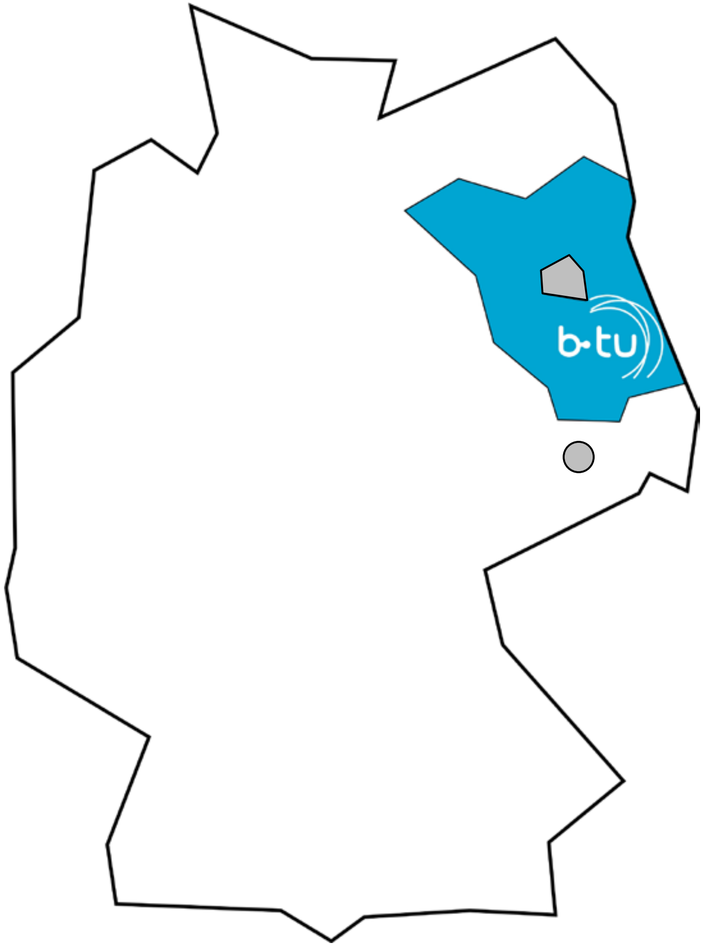
Rational Approaches to Synthesis and Crystal Growth of Rare Earth Metal Tellurides

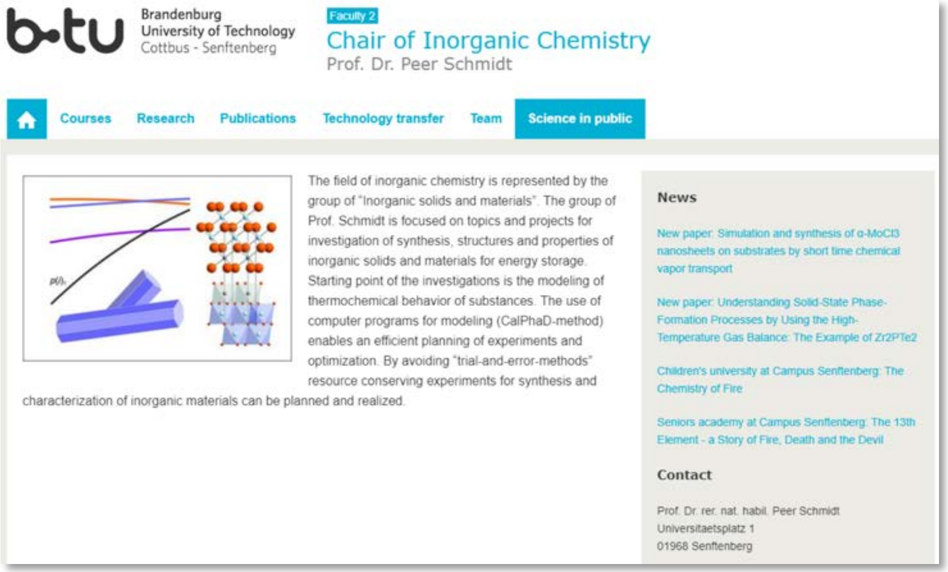
Tom Donath, Peer Schmidt
BTU Cottbus-Senftenberg

Herzogenrath 28.06.2019

INORGANIC SOLIDS AND MATERIALS

Brandenburgische
Technische Universität
Cottbus - Senftenberg





Brandenburg
University of Technology
Cottbus - Senftenberg

Faculty 2

Chair of Inorganic Chemistry

Prof. Dr. Peer Schmidt

The field of inorganic chemistry is represented by the group of "Inorganic solids and materials". The group of Prof. Schmidt is focused on topics and projects for investigation of synthesis, structures and properties of inorganic solids and materials for energy storage. Starting point of the investigations is the modeling of thermochemical behavior of substances. The use of computer programs for modeling (CalPhaD-method) enables an efficient planning of experiments and optimization. By avoiding "trial-and-error-methods" resource conserving experiments for synthesis and characterization of inorganic materials can be planned and realized.

News

New paper: Simulation and synthesis of α-MoCl3 nanosheets on substrates by short time chemical vapor transport

New paper: Understanding Solid-State Phase-Formation Processes by Using the High-Temperature Gas Balance: The Example of Zr2PTe2

Children's university at Campus Senftenberg: The Chemistry of Fire

Seniors academy at Campus Senftenberg: The 13th Element - a Story of Fire, Death and the Devil

Contact

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01968 Senftenberg

CRYSTAL GROWTH

HIGH TEMPERATURE SYNTHESIS

LOW TEMPERATURE SYNTHESIS

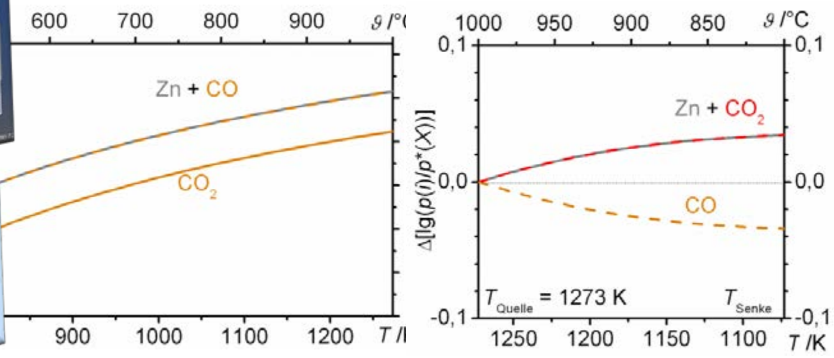
MATERIALS FOR ENERGY STORAGE

SCIENTIFIC INSTRUMENT ENGINEERING

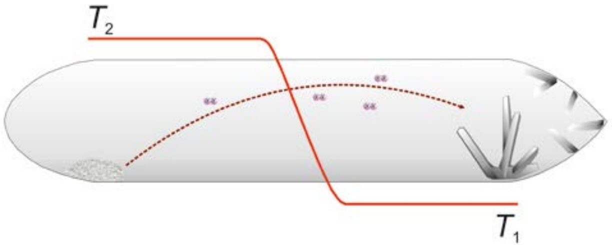
https://www.b-tu.de/en/inorganic-chemistry

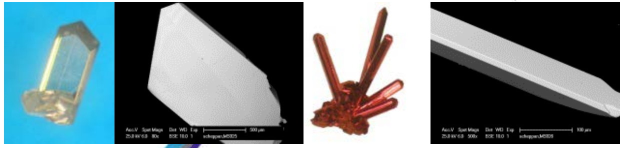
RESEARCH STRATEGY

Thermodynamic modeling of phase diagrams and vapor equilibria



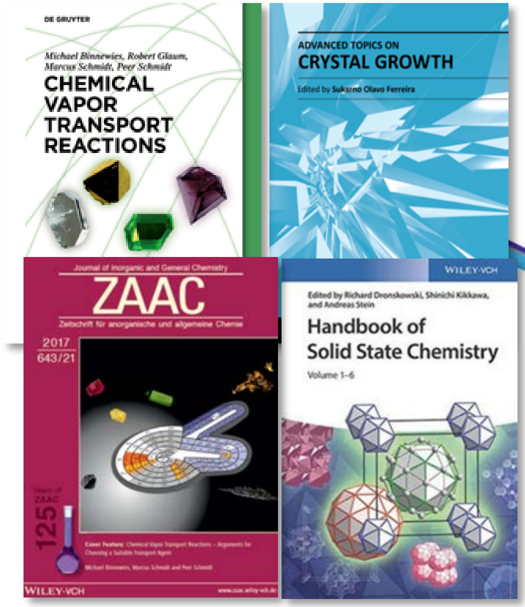
Synthesis and Crystal Growth





Optimization avoiding trial-and-error

Methods, Materials



DE GRUYTER

Michael Binnewies, Robert Glaum, Marcus Schmidt, Peer Schmidt

CHEMICAL VAPOR TRANSPORT REACTIONS

ADVANCED TOPICS ON CRYSTAL GROWTH

Edited by Sukarno Olavo Ferreira

Journal of Inorganic and General Chemistry

ZAAC

Zeitschrift für anorganische und allgemeine Chemie

2017
643/21

125

WILEY-VCH

www.zaac.wiley-vch.de

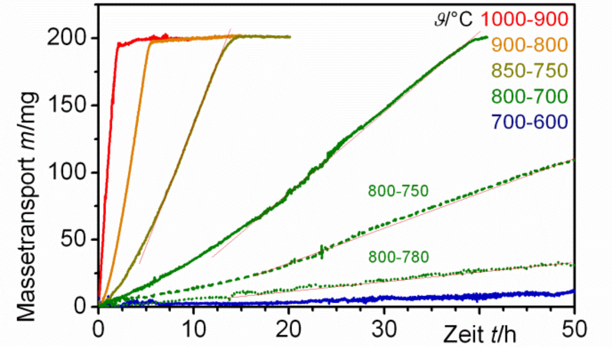
WILEY-VCH

Edited by Richard Dronskowski, Shinichi Kikkawa, and Andreas Stein

Handbook of Solid State Chemistry

Volume 1–6

Identification of reaction products reaction mechanism



Nanoso **2019**, *19*, 100324.
Nanoscale, **2018**,*10*, 19014-19022.
Chem. Mater., **2017**, *29*, 1321–1337.
Z. Anorg. Allg. Chem., **2017**, *643*, 1295–1311.
HSSC, Wiley-VCH, **2017**, ISBN: 978-3-527-32587-0.
Crystal Growth, InTech, **2013**, ISBN 980-9533077913.
CVT, De Gruyter, **2012**, ISBN 978-3110254648.
CTR, De Gruyter Berlin, **2011**, ISBN 978-3112147382.

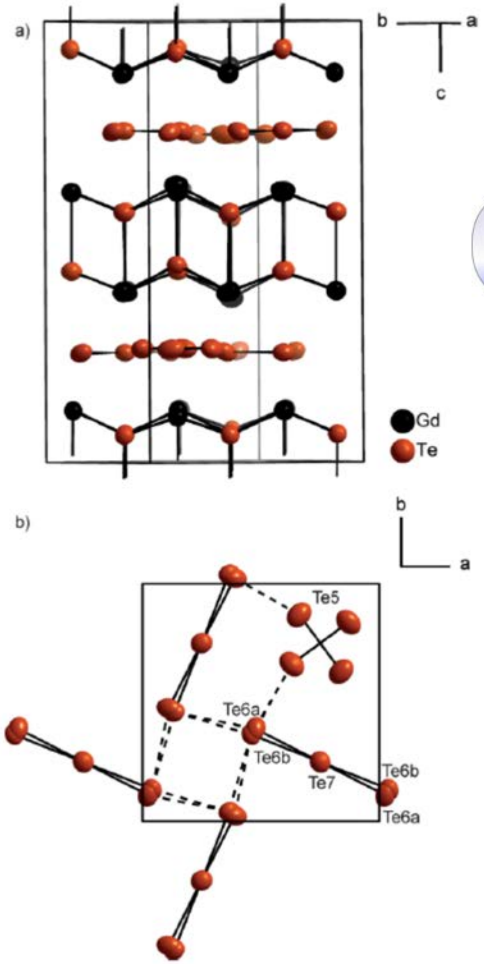
RATIONAL APPROACHES

TO SYNTHESIS OF RARE EARTH METAL TELLURIDES

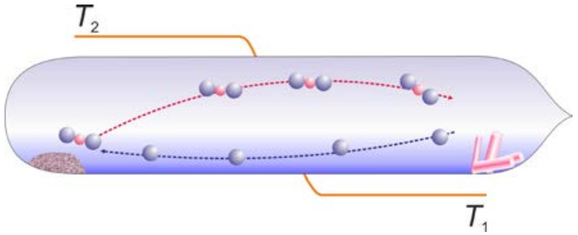
RARE EARTH METAL TELLURIDES

Z. Anorg. Allg. Chem. **2018**, *644*, 1886–1896.

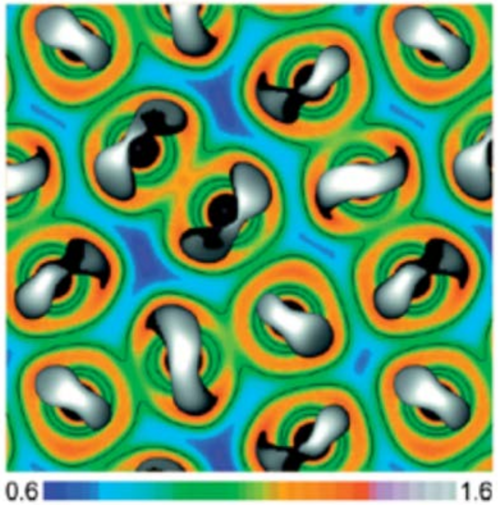
intrinsic doping of tellurides *Ln*Te_{2-x}



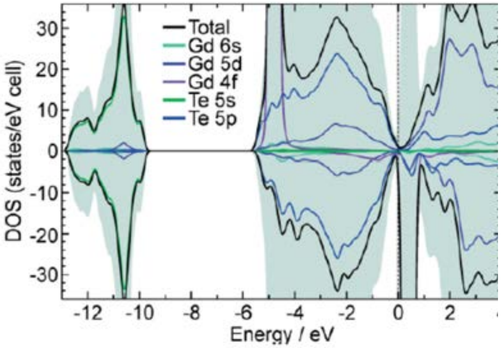
crystal growth

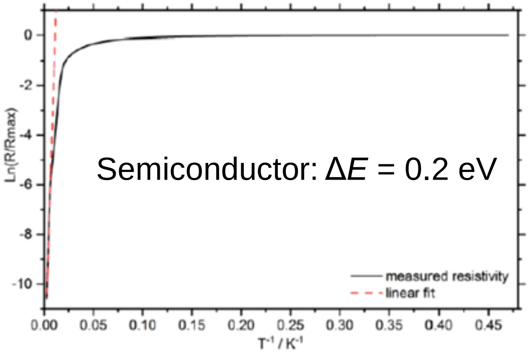


chemical bonding



design of physical properties





Semiconductor: ΔE = 0.2 eV

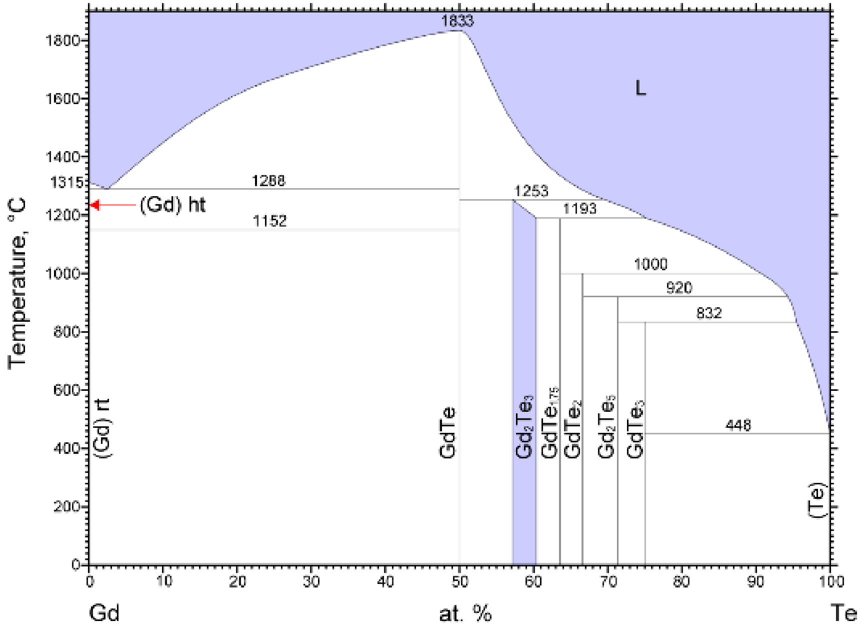
GADOLINIUM TELLURIDES

Phase diagram containing binaries:

GdTe	1825 ºC ± 15 K
Gd_3Te_4… Gd_2Te_3	1255 ºC…1215 ºC
Gd_4Te_7	1190 ºC
$GdTe_2$	1000 ºC
Gd_2Te_5	920 ºC
$GdTe_3$	832 ºC

V.Sh. Zargaryan, N.Kh. Abrikosov, *Izv. Akad. Nauk SSSR, Neorgan. Mater.* 3, **1967**, 769-776.

Massalski, T.B. (editor-in chief): *"Binary Alloy Phase Diagrams"* Sec. Edt., Vol. 2, **1990**.



* all liquidus lines are dashed…

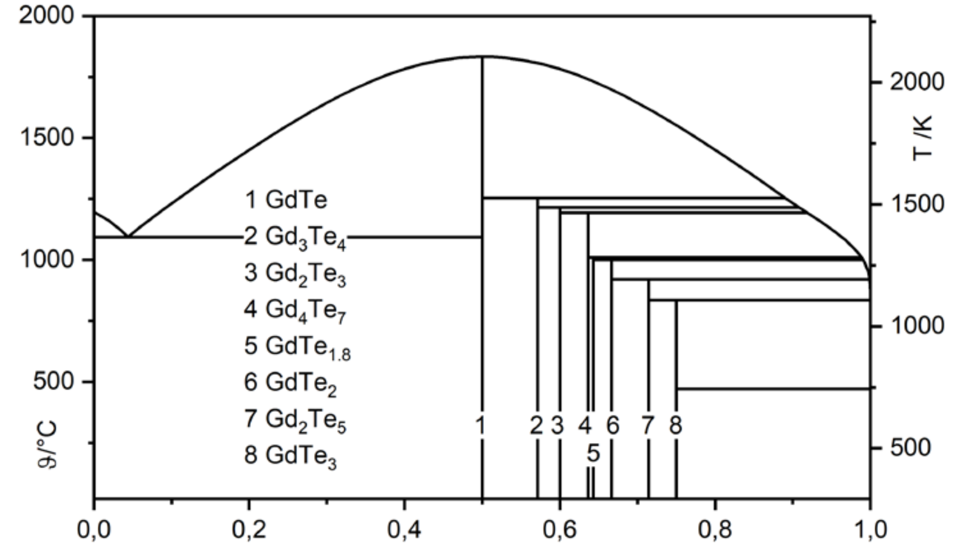
Additional knowledge on existence of $GdTe_{2-x}$ ($GdTe_{1.8}$)

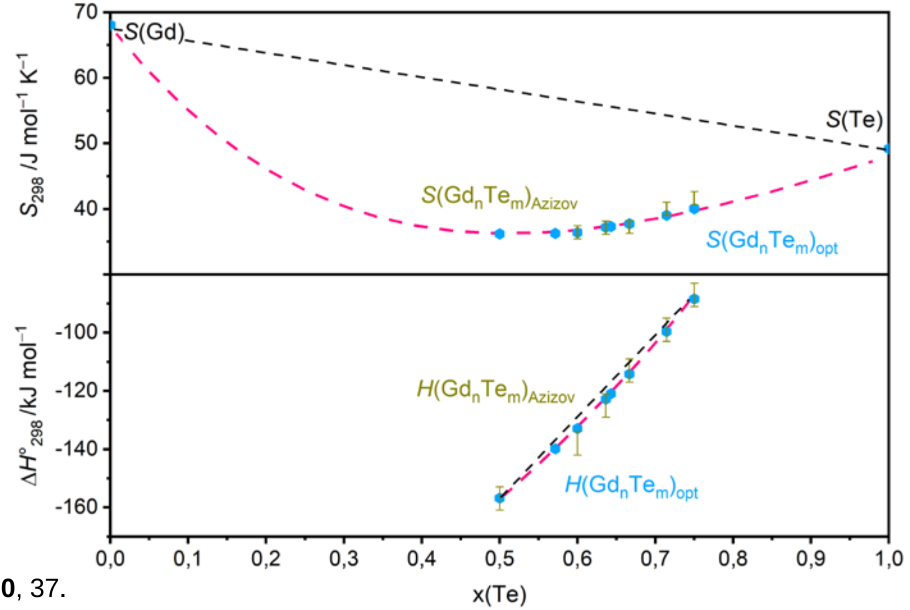
Y. Wu, T. Doert, P. Böttcher, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2216–2216.

Thermodynamic standard data by EMF measurements

T.Kh. Azizov, A.B. Agaev, A.S. Abbassov, A.G. Gusenkov, *Dokl. Akad. Nauk Az. SSR* 36 **1980**, 37.

CALCULATION OF PHASE DIAGRAM

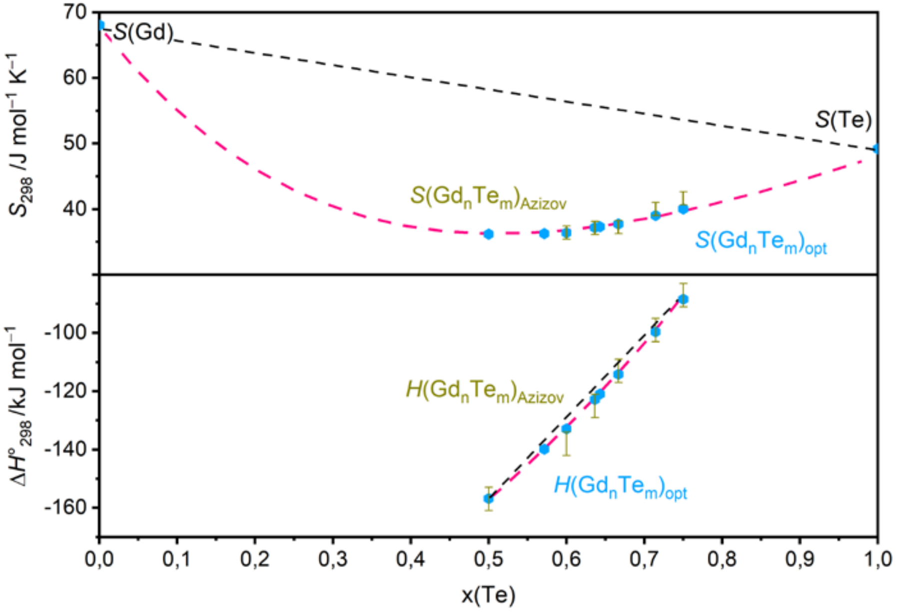


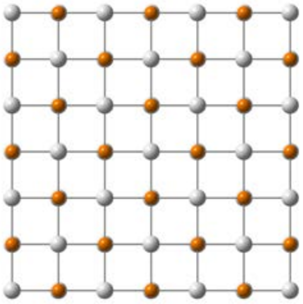


Dokl. Akad. Nauk Az. SSR 36 **1980**, 37.
Z. Anorg. Allg. Chem. **2018**, *644,* 1886–1896.

EVALUATION OF STANDARD DATA

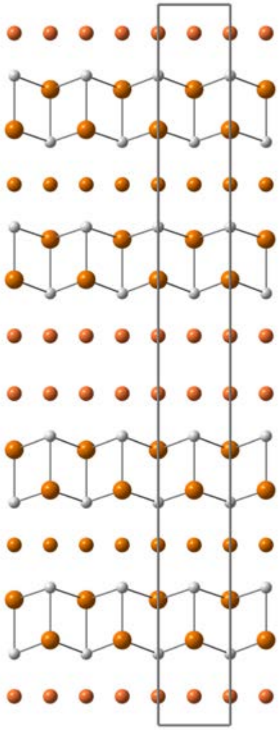
application of Neumann-Kopp`s-rule for estimation of $\Delta S^{o} = 0$ fails



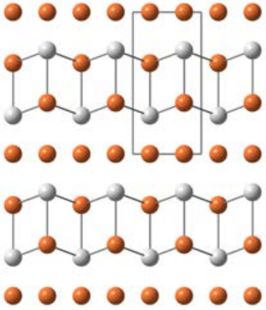


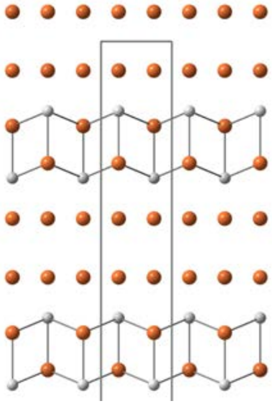
GdTe
3D network (NaCl-type)

Gd_2Te_5

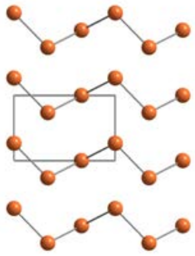


$GdTe_2$



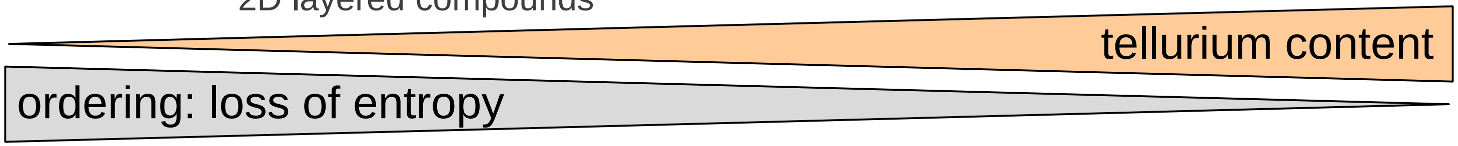


$GdTe_3$



Te
1D chains

2D layered compounds



tellurium content

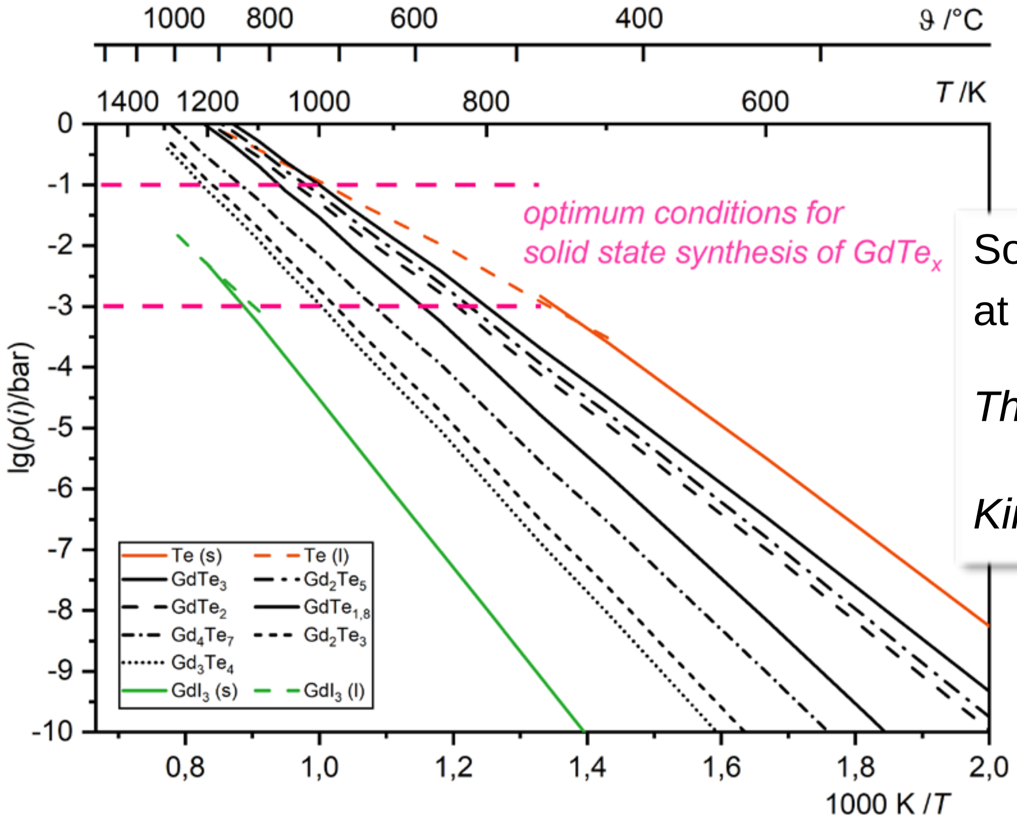
ordering: loss of entropy

CALCULATION OF PHASE BAROGRAM

$$\mathrm{GdTe}_x(s) = \mathrm{GdTe}_y(s) + \frac{(x-y)}{2}\,\mathrm{Te}_2(g) \qquad K_p = p(\mathrm{Te}_2)$$

$$\Delta G^0 = -\mathrm{R}\cdot T\ln K_p = -\mathrm{R}\cdot T\ln(p/p^0)$$

$$\lg(p/p^0) = -\frac{\Delta G^0}{2.303\,\mathrm{R}\cdot T} = -\frac{\Delta H^0}{2.303\,\mathrm{R}}\cdot\frac{1}{T} + \frac{\Delta S^0}{2.303\,\mathrm{R}}$$



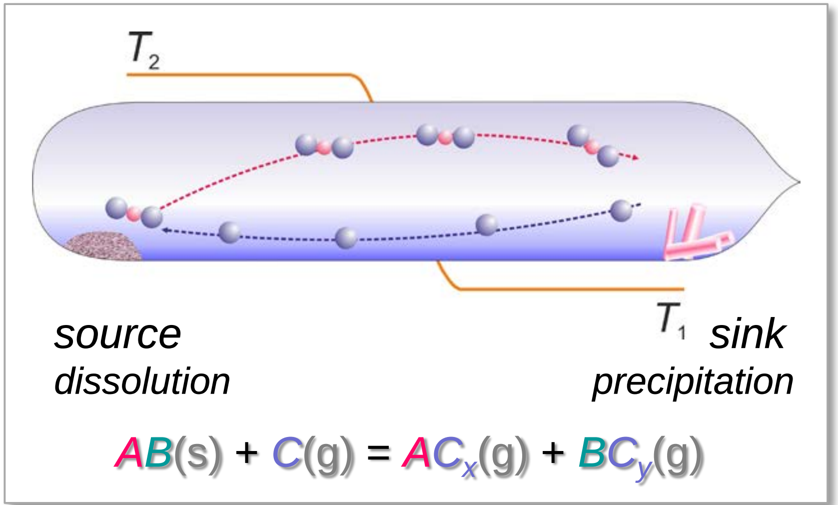
Solid state synthesis at $p = f(T) \approx 10^{-3} \ldots 10^{-1}$ bar

Thermodynamics 👍

Kinetics 👍

CRYSTAL GROWTH
BY VAPOR TRANSPORT

CHEMICAL VAPOR TRANSPORT (CVT)



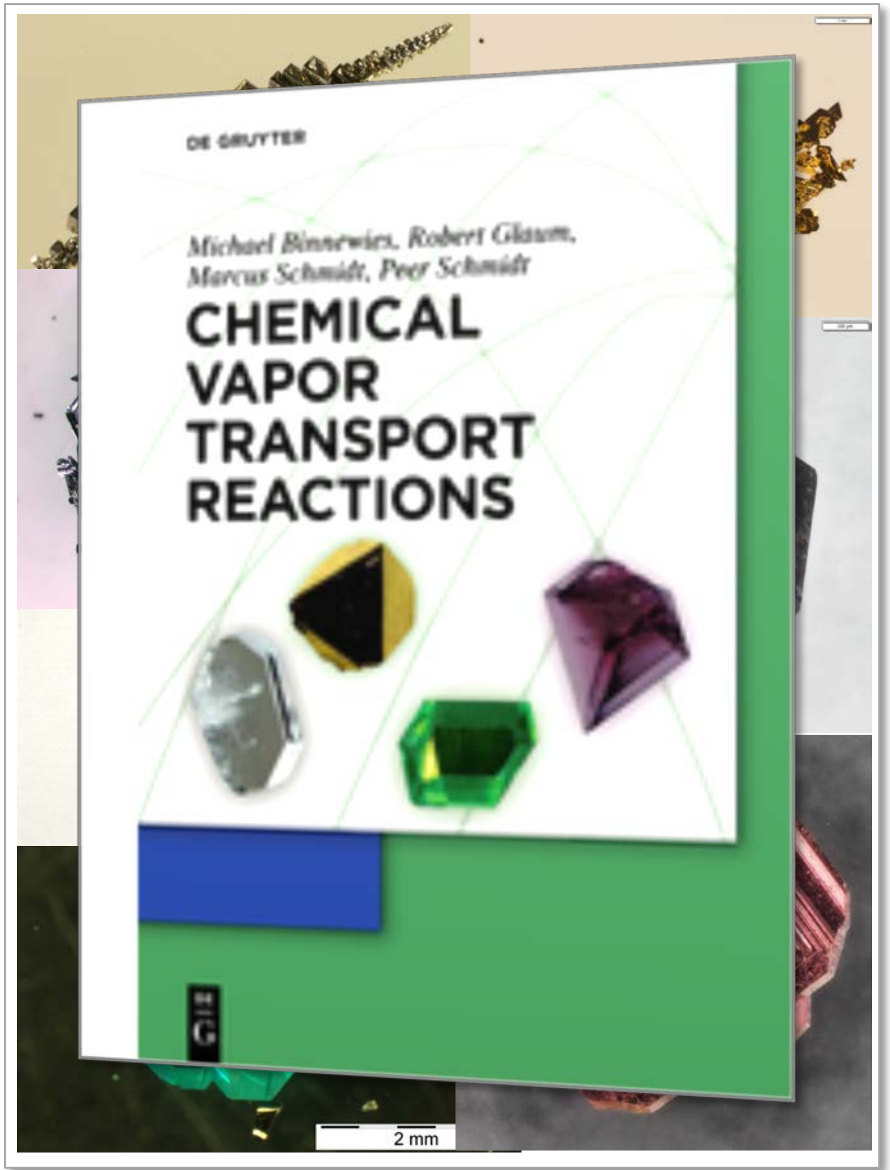
$$AB(s) + C(g) = AC_x(g) + BC_y(g)$$

Metals

Intermetallic phases

Halides, Chalcogenides, Pnictides

Oxides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Michael Binnewies, Robert Glaum,
Marcus Schmidt, Peer Schmidt

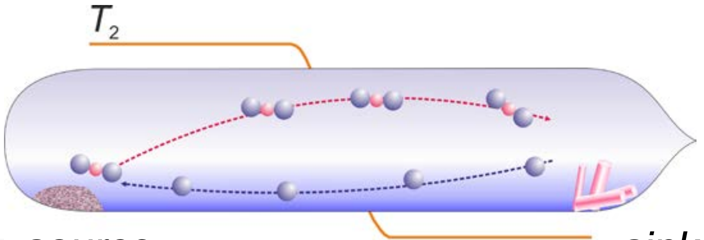
CHEMICAL
VAPOR
TRANSPORT
REACTIONS

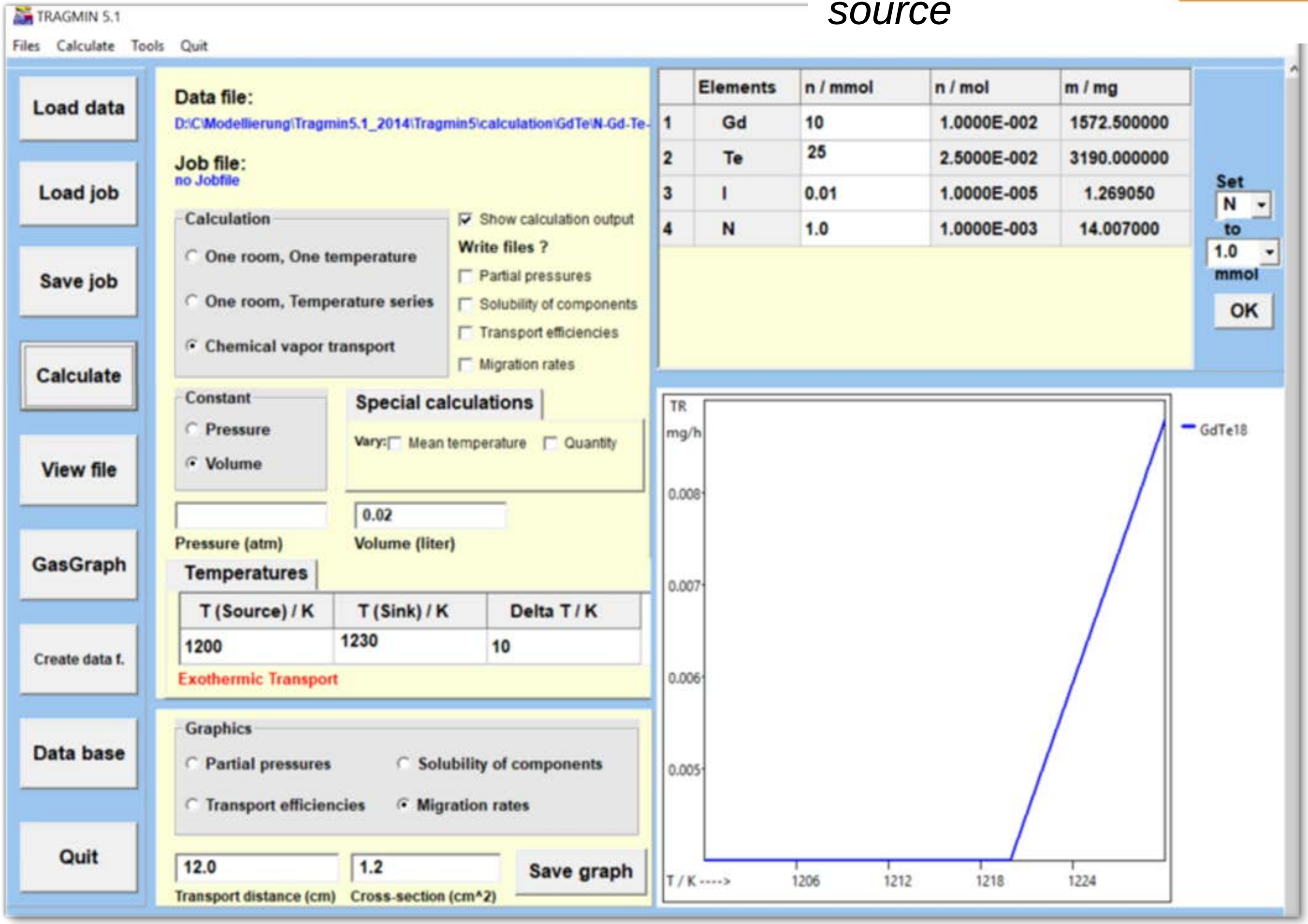
MODELLING OF CVT PROCESSES

- ## *TRAGMIN*

Program package TRAGMIN, v. 5.1, IFW Dresden, TU Dresden, HTW Dresden, **2014**.

based on: G. Eriksson, *Acta Chem. Scand.* **1971**, *25*, 2651.





Data file:
D:\C\Modellierung\Tragmin5.1_2014\Tragmin5\calculation\GdTe\N-Gd-Te-

Job file:
no Jobfile

Calculation
- ○ One room, One temperature
- ○ One room, Temperature series
- ● Chemical vapor transport

☑ Show calculation output

Write files ?
- ☐ Partial pressures
- ☐ Solubility of components
- ☐ Transport efficiencies
- ☐ Migration rates

Constant
- ○ Pressure
- ● Volume

Vary: ☐ Mean temperature ☐ Quantity

Pressure (atm):

Volume (liter): 0.02

	Elements	n / mmol	n / mol	m / mg
1	Gd	10	1.0000E-002	1572.500000
2	Te	25	2.5000E-002	3190.000000
3	I	0.01	1.0000E-005	1.269050
4	N	1.0	1.0000E-003	14.007000

Set N to 1.0 mmol

Temperatures

T (Source) / K	T (Sink) / K	Delta T / K
1200	1230	10

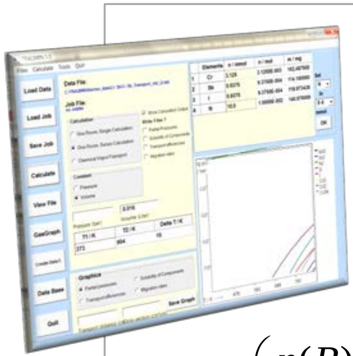
Exothermic Transport

Graphics
- ○ Partial pressures
- ○ Solubility of components
- ○ Transport efficiencies
- ● Migration rates

Transport distance (cm): 12.0

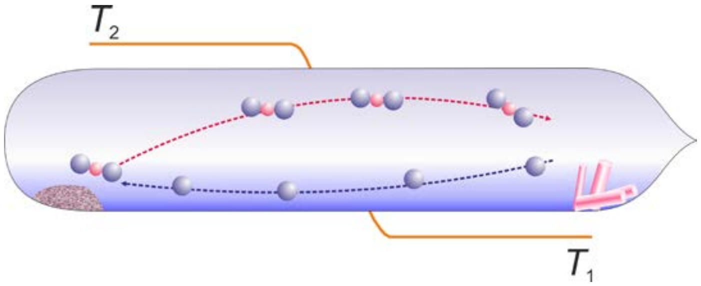
Cross-section (cm^2): 1.2

MODELLING OF CVT PROCESSES



TRAGMIN

(extended transport model)



$$\left(\frac{n(B)}{n(A)}\right)_{T_\text{sink}} = \left(\frac{flux(B)}{flux(A)}\right)_{T_\text{source}\to T_\text{sink}} = \frac{J(B)}{J(A)} = x_\text{sink}$$

the molar flow of A and B

$$\left(\frac{p^*(B) - \mathrm{x}_\text{sink}\cdot p^*(A)}{p^*(X)}\right)_\text{source} = \left(\frac{p^*(B) - \mathrm{x}_\text{sink}\cdot p^*(A)}{p^*(X)}\right)_\text{sink} = \varepsilon$$

$$\frac{\left[\left(\frac{p^*(B)}{p^*(X)}\right)_\text{source} - \left(\frac{p^*(B)}{p^*(X)}\right)_\text{sink}\right]}{\left[\left(\frac{p^*(A)}{p^*(X)}\right)_\text{source} - \left(\frac{p^*(A)}{p^*(X)}\right)_\text{sink}\right]} = \frac{\Delta\lambda(B)}{\Delta\lambda(A)} = \mathrm{x}_\text{sink}$$

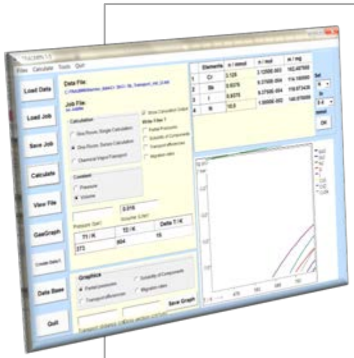
stationarity condition

of precipitation

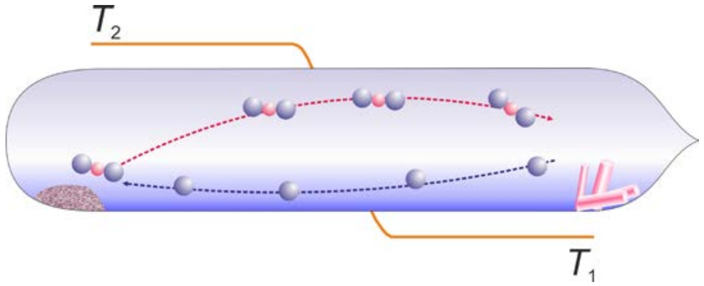
$$w(i) = \Delta\left(\frac{p(i)}{p^*(X)}\right)_{\text{source}\,\to\,\text{sink}} = \left(\frac{p(i)}{p^*(X)}\right)_\text{source} - \left(\frac{p(i)}{p^*(X)}\right)_\text{sink}$$

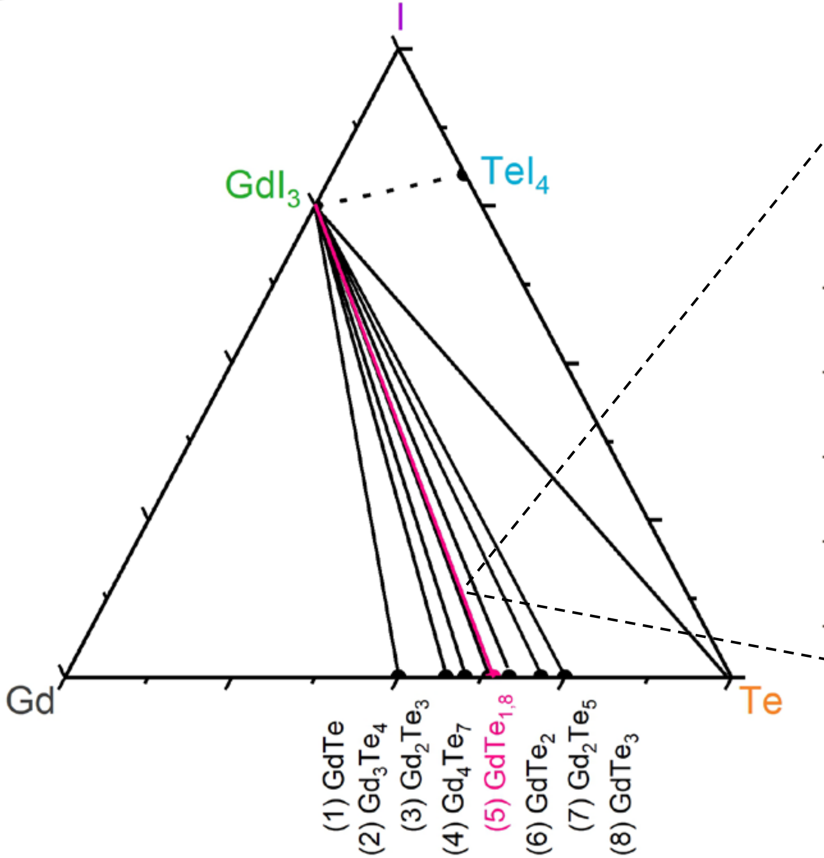
transport efficiency

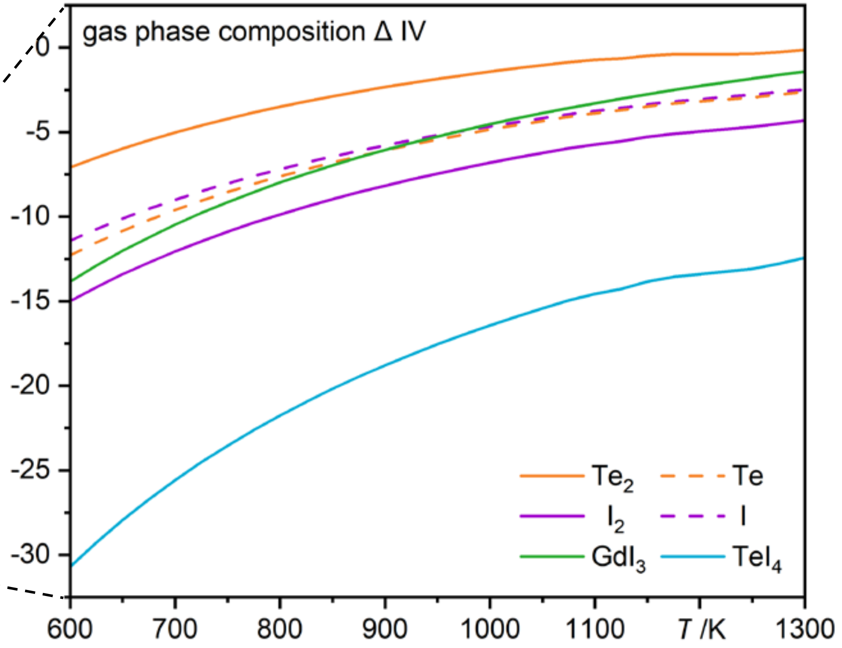
MODELLING OF CVT PROCESSES



to the system Gd/Te:
addition of iodine
as a transport agent:

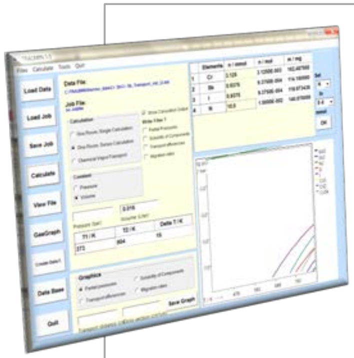




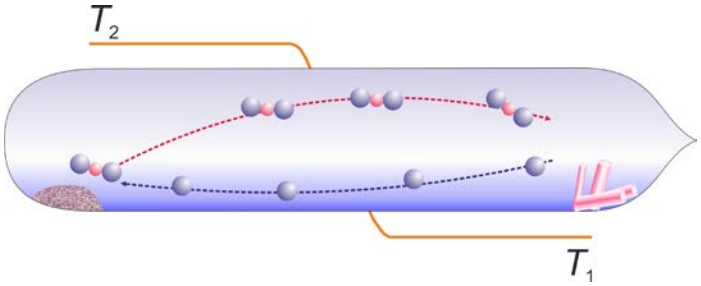


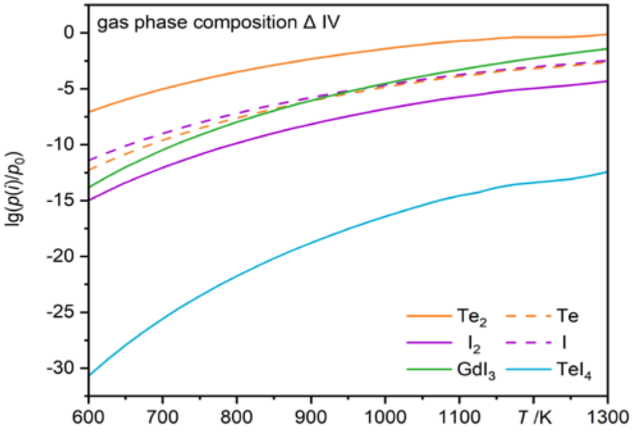
source`s solid: $GdTe_2$, $GdTe_{1.8}$, GdI_3

MODELLING OF CVT PROCESSES

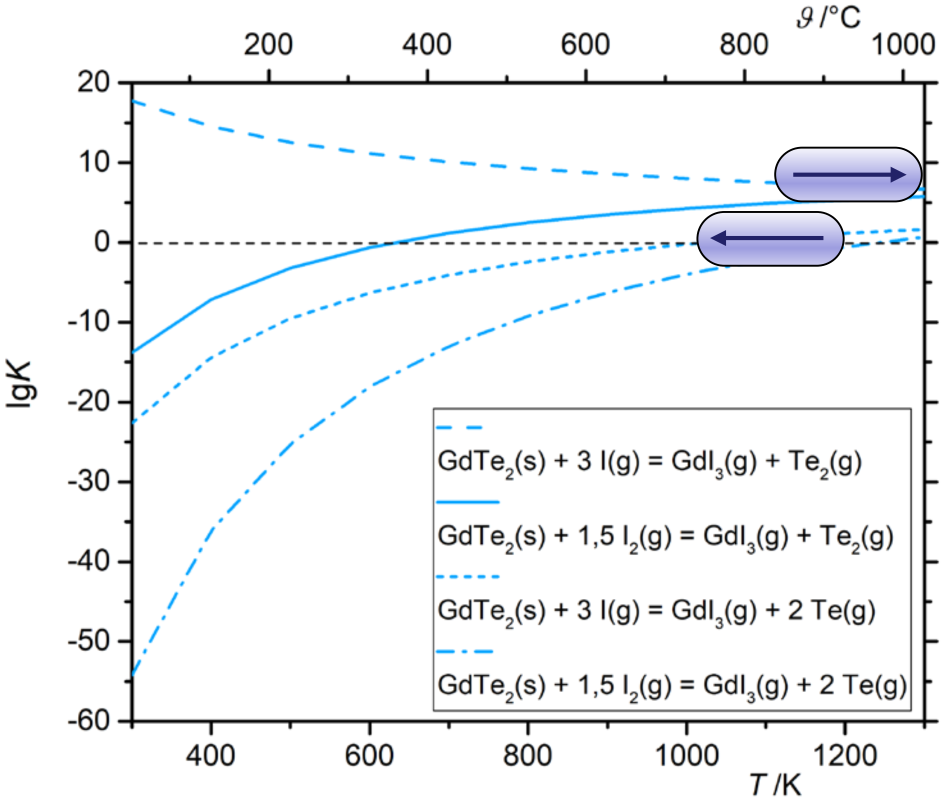


Addition of iodine
as a transport agent:

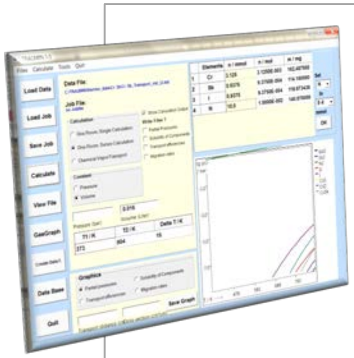


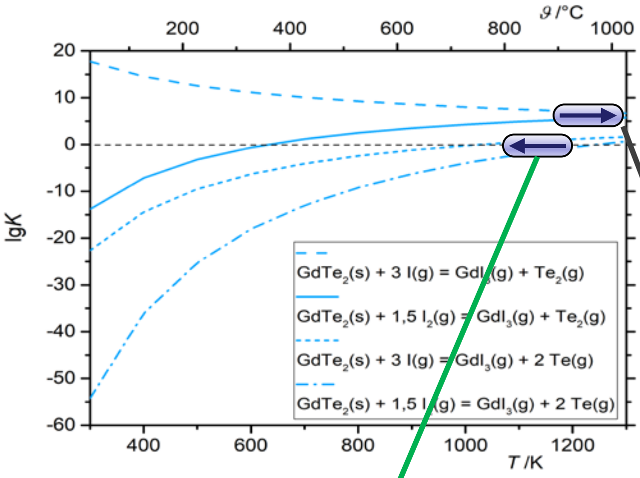


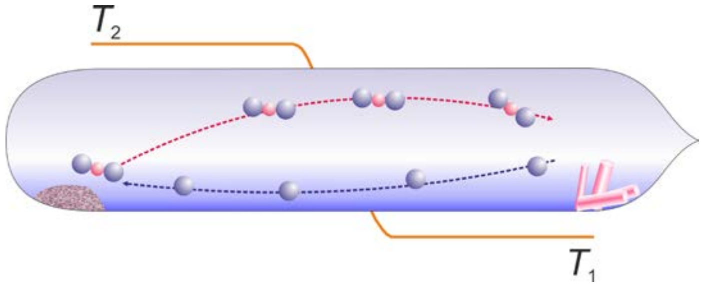
relevant species: Te_2, GdI_3, I_2, I, Te

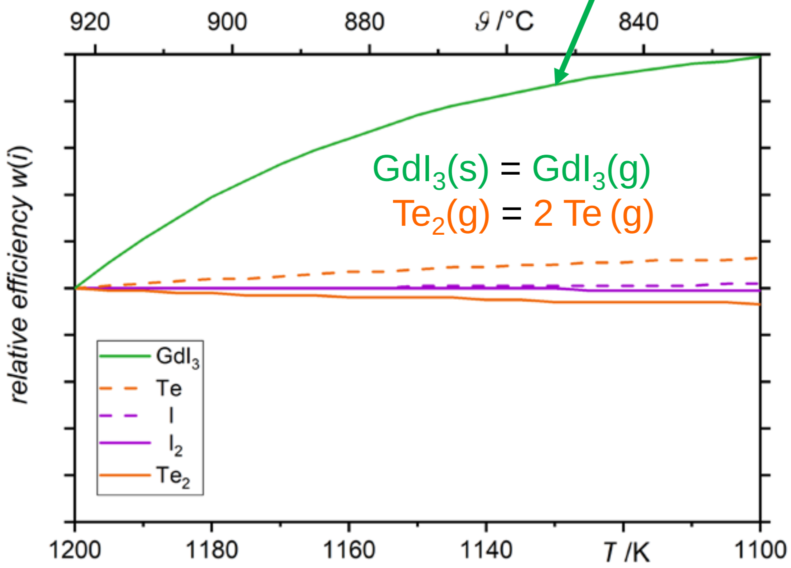


MODELLING OF CVT PROCESSES



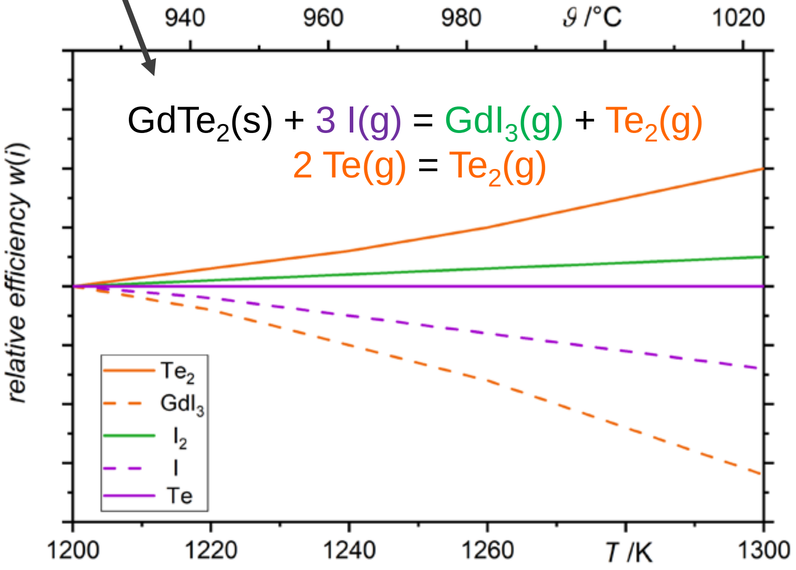






$$GdI_3(s) = GdI_3(g)$$

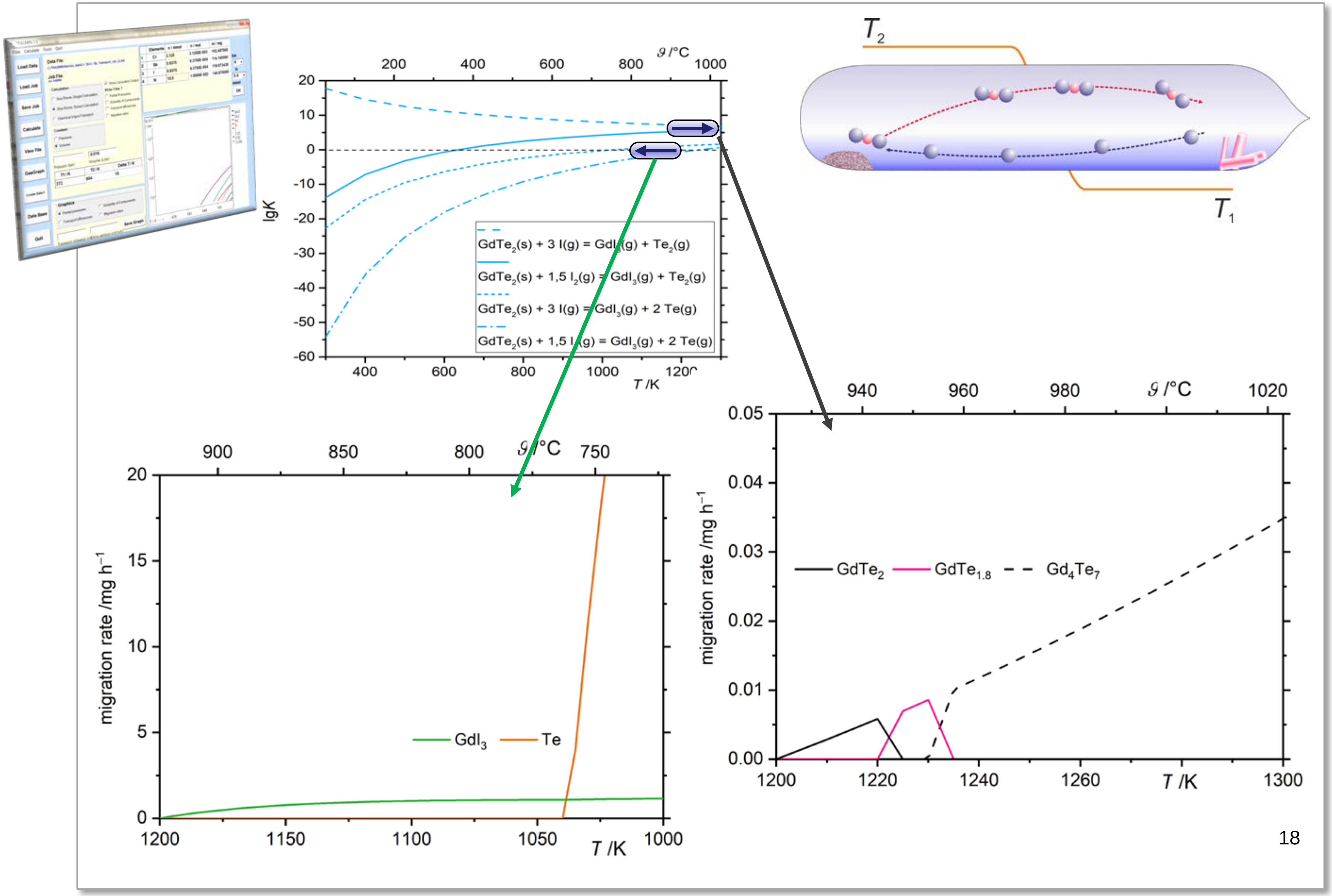
$$Te_2(g) = 2\ Te(g)$$



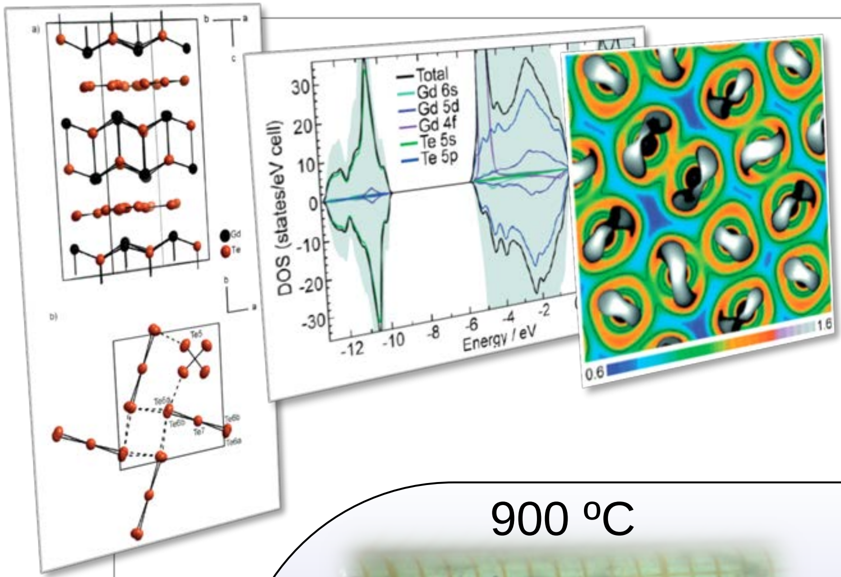
$$GdTe_2(s) + 3\ I(g) = GdI_3(g) + Te_2(g)$$

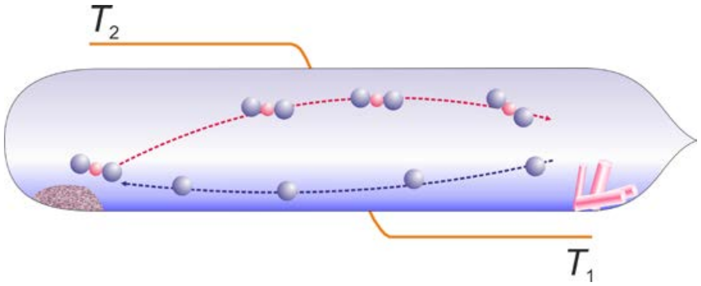
$$2\ Te(g) = Te_2(g)$$

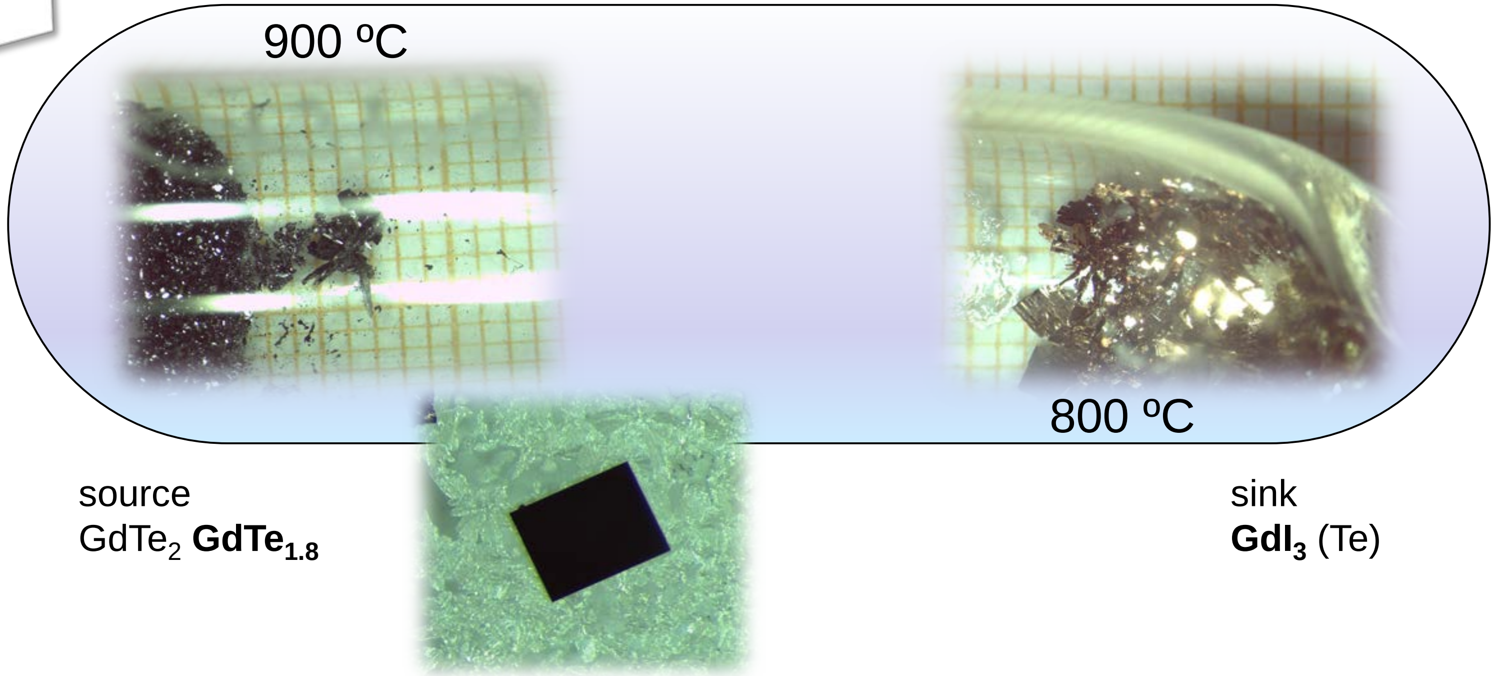
MODELLING OF CVT PROCESSES



EXPERIMENTAL CVT PROCESS







source
GdTe$_2$ **GdTe$_{1.8}$**

sink
GdI$_3$ (Te)

Anastasia Efimova
Tom Donath
Marie-Christin Giese
Martin Grönke
Robert Heinemann
Monika Knorr
Felix Lange
Andre Meißner
Ines Donath
Bruno Reis
Martin Wels

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