Thermodynamic database development on the $CaO\text{-}SiO_2\text{-}M_2O$ (M= Na, K) systems

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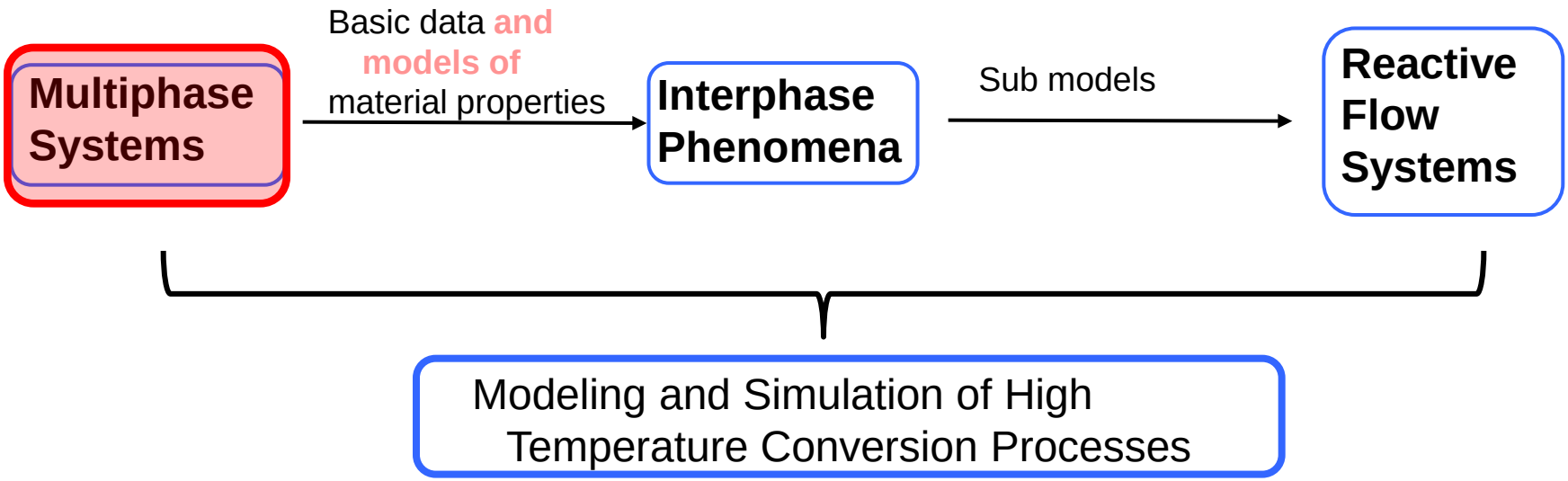
Content

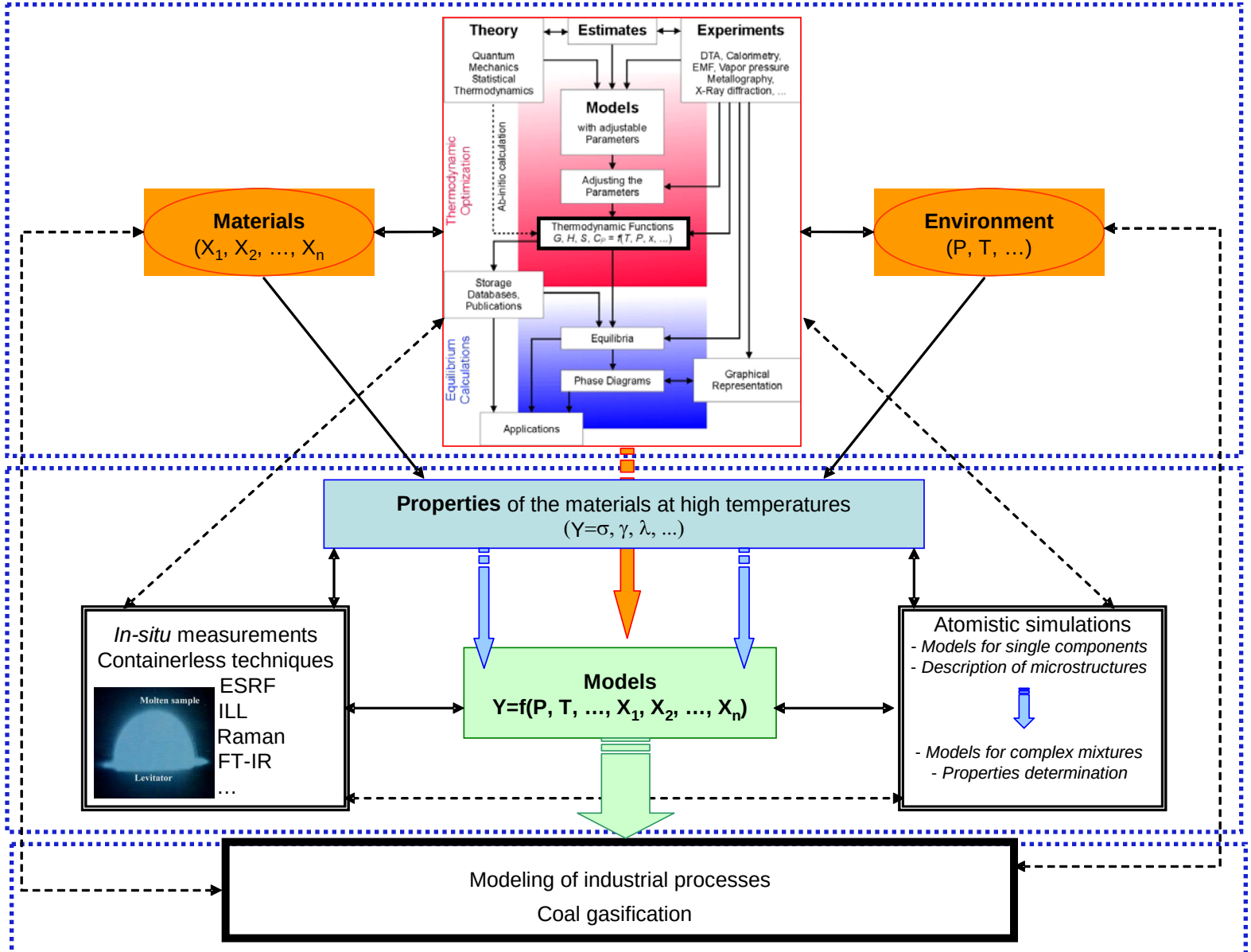
- **Motivation**
- **Calorimetry determination on Cp of intermediate phases in M_2O-CaO-SiO_2 (M= K, Na) ternary systems**
- **Ab initio calculations on the intermediate phases**
- **Phase diagram and thermodynamic database of M_2O-CaO-SiO_2 (M= K, Na) ternary systems**

Research Project VIRTUHCON

- acronym for **Virtu**al **H**igh Temperature **Con**version
- established in 2009 as **Centre of Innovation Competence**
- combined initiative of 8 institutes at **TU Freiberg**
- consists of three research groups (about 20 research associates)



Motivation



THERMOCHEMICAL PROPERTIES

THERMOPHYSICAL PROPERTIES

Calphad modeling

Theory

VASP

Quantum chemistry, ab initio, thermodynamics

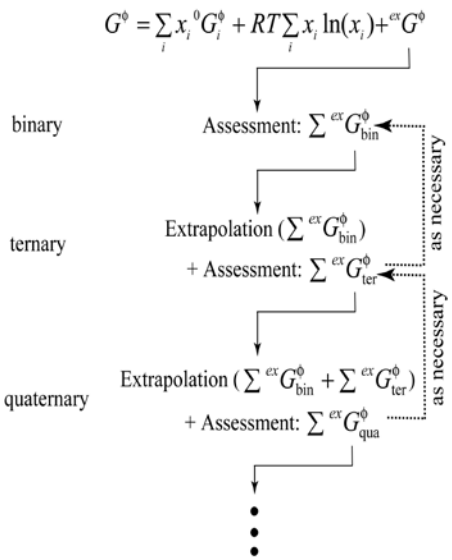
Experiments

DTA, DSC, Calorimetry

Optimization (Thermo-calc)

$$G^{\phi} = \sum_i x_i {}^0G_i^{\phi} + RT\sum_i x_i \ln(x_i) + {}^{ex}G^{\phi}$$

$$^{E}G_m = \sum_{v=o}^{v=s} y_i y_j y_k \sum_{v=0}^{v=n} {}^{v}L_{i:j,k}(y_j - y_k)^v + \sum_{v=o}^{v=n} y_i y_j y_k y_l L_{i,j:k,l}(y_i - y_j)(y_k - y_l)$$



Phase diagram

Application

Part I

Cp of intermediate phases

Calphad modeling

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Quantum chemistry, ab initio, thermodynamics

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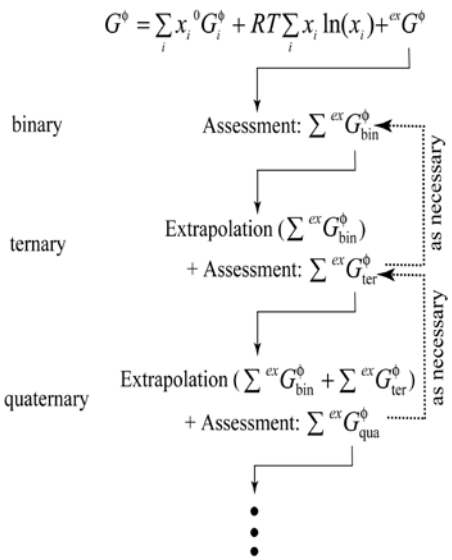


Phase diagram

Application

Cp of intermediate phases

- Setaram AlexSys 1000 Calvet Calorimeter
- Setaram MHTC96 Calorimeter

Drop Calorimetry:
calibration with sapphire pieces (NIST)
operation under Air
three to four drops per T-step

$$\Delta_{rel}H = \int_{T_{reservoir}}^{T_{furnace}} Cp(T)\,dT$$

$$\Delta_{rel}H = f(T)$$

$$\frac{\partial \Delta_{rel}H(T)}{\partial T} = Cp(T)$$

Calorimetry - Drop model

Single phase samples were prepared by Dr. V. Kahlenberg, Univ. Innsbruck

$K_2Ca_2Si_2O_7$
$K_4CaSi_3O_9$
$K_8CaSi_{10}O_{25}$

Preparation via co-precipitation
Supplied as powders
Checked for presence of other phases (XRD)

- Samples are sensitive to environment, especially moisture

use immediately
store in desiccator

- Powders not suitable for drop calorimetry

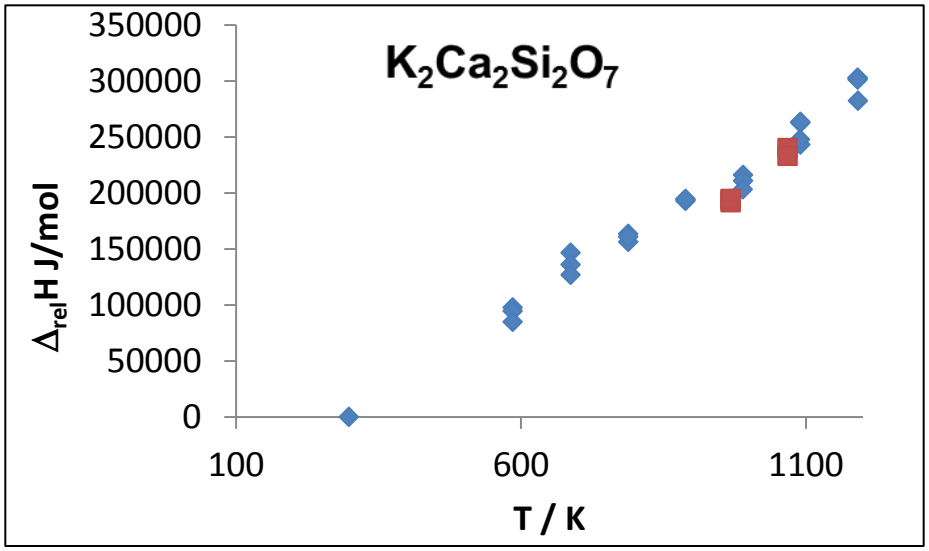
press sample pellets

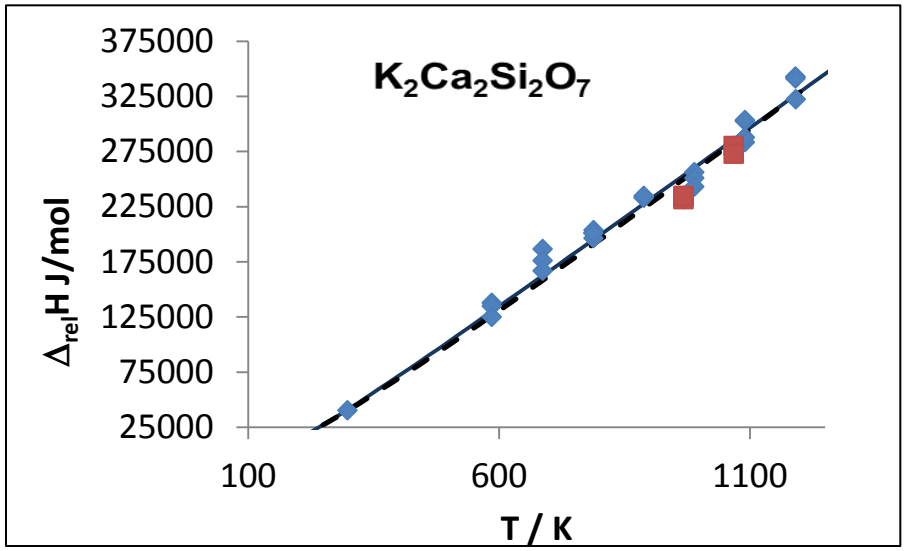
- Pellets are fragile

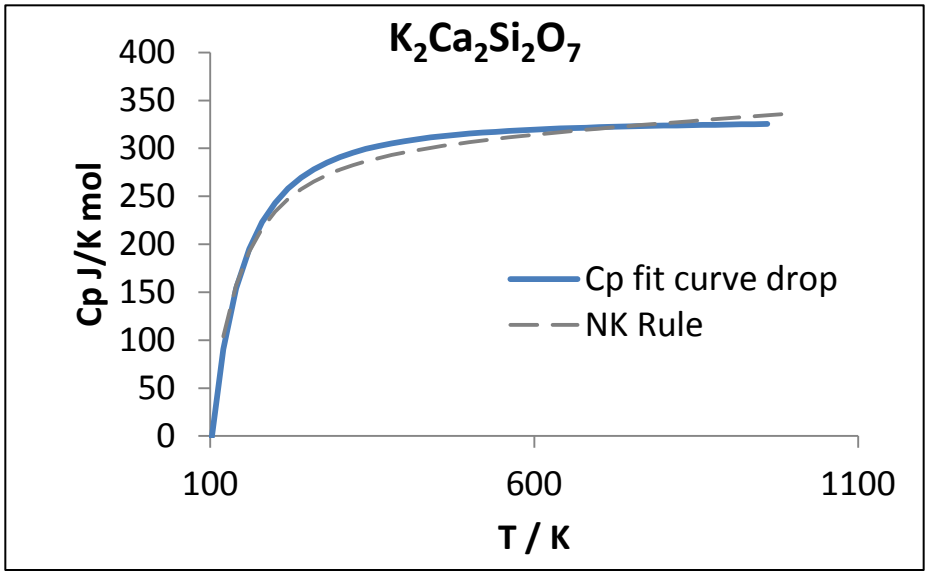
careful handling during weighing and actual drop

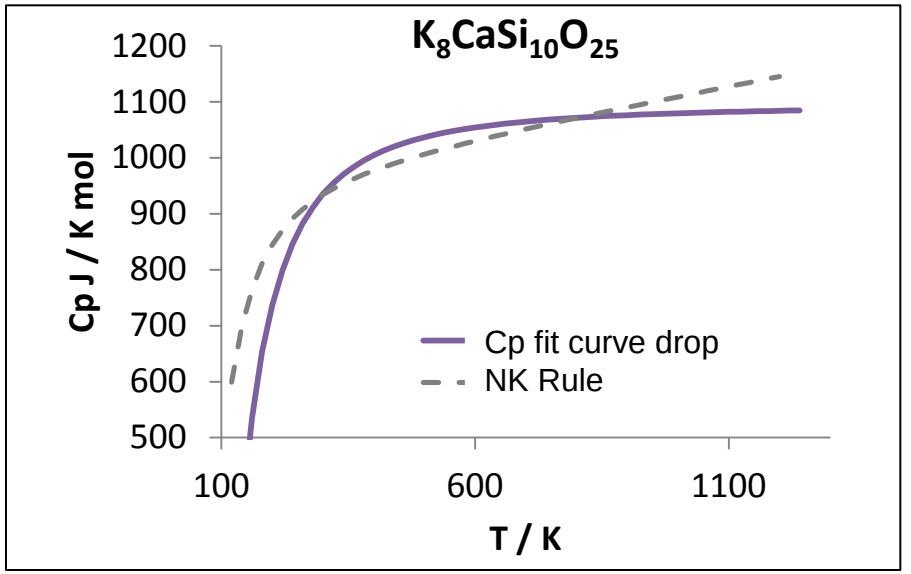
… experiments are time consuming and delicate

Calorimetry - Drop model









Cp functions; Cp in J/K mol

$K_2Ca_2Si_2O_7$:

$$Cp = 329.1 - 3.43 \cdot 10^{6} \cdot T^{-2} - 6.59 \cdot 10^{-15} \cdot T^{-0.5}$$

$K_4CaSi_3O_9$:

$$Cp = 329.1 - 1.73 \cdot 10^{-13} \cdot T^{-2} - 5.6475 \cdot 10^{3} \cdot T^{-0.5}$$

$K_8CaSi_{10}O_{25}$:

$$Cp = 1094 - 1.43 \cdot 10^{7} \cdot T^{-2}$$

- Setaram MHTC96 Calorimeter

HF-DSC measurement:
Standard with sapphire pieces (NIST)
operation under air
300-1200 °C

A set of three measurements is required, each with a different substance in the measurement crucible:

1. empty crucible (the “base line”)
2. standard
3. sample

$$C_{PS} = \frac{m_s \cdot M_{Std}}{M_s \cdot m_{Std}} \cdot \frac{S_S - S_{BL}}{S_{Std} - S_{BL}} \cdot Cp_{Std}$$

Quantities:

m … mass (mg) M … molar mass (g/mol) S … DSC signal (µV)

Indices:

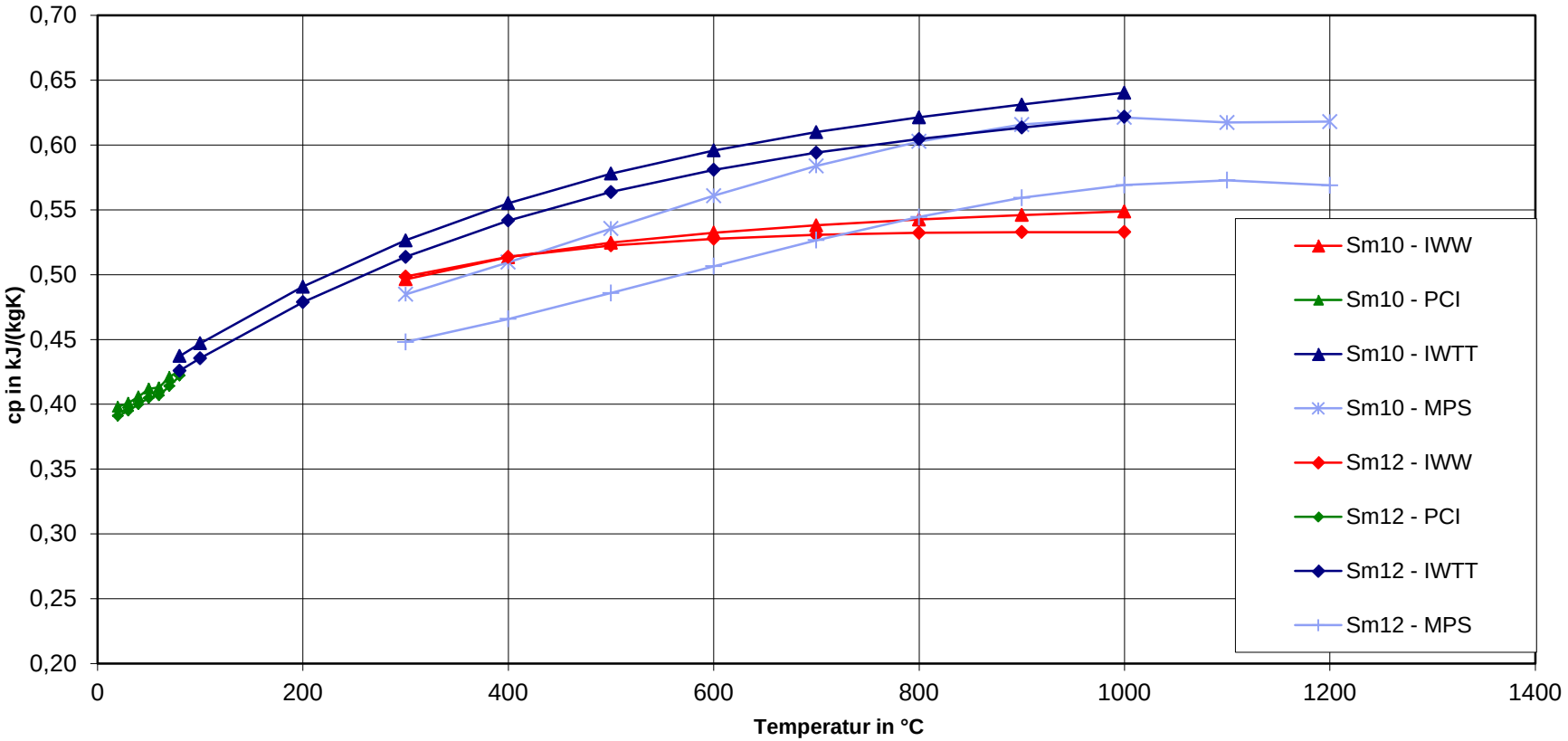
S … sample Std … standard BL … base line

Calorimetry - Stepwise model- Ring Test

- Samples and Participants:
- SM10: ZrO_2-40mol%, $SmO_{1.5}$-40mol% and $YO_{1.5}$-20mol%
- SM12: ZrO_2-45mol%, $SmO_{1.5}$-45mol% and $YO_{1.5}$-10mol%

Group	Equipment	Sample	Atomosphere	Mode
VTC-MPS	SETARAM MHTC 96	Powder	Air	Stepwise: 25K/Step 2K/min Stability for 2 Hours
PCI-Institut für Physikalische Chemie (Dr. Seidel)				
IWTT-Institut für Wärmetechnik und Thermodynamik (Frau Dr. Wulf)	SETARAM MHTC 96	Powder	Air	Continuous Method: 3K/min
IWW-Institut für Werkstoffwissen-schaft (Herr Kriegel)	SETARAM TG-DTA	Powder	Ar	Continuous Method: 20K/min

Calorimetry - Stepwise model – Ring Test



→ Results within scattering of calorimetric measurements (0.15-0.20 KJ Kg^{-1} K^{-1} [1])

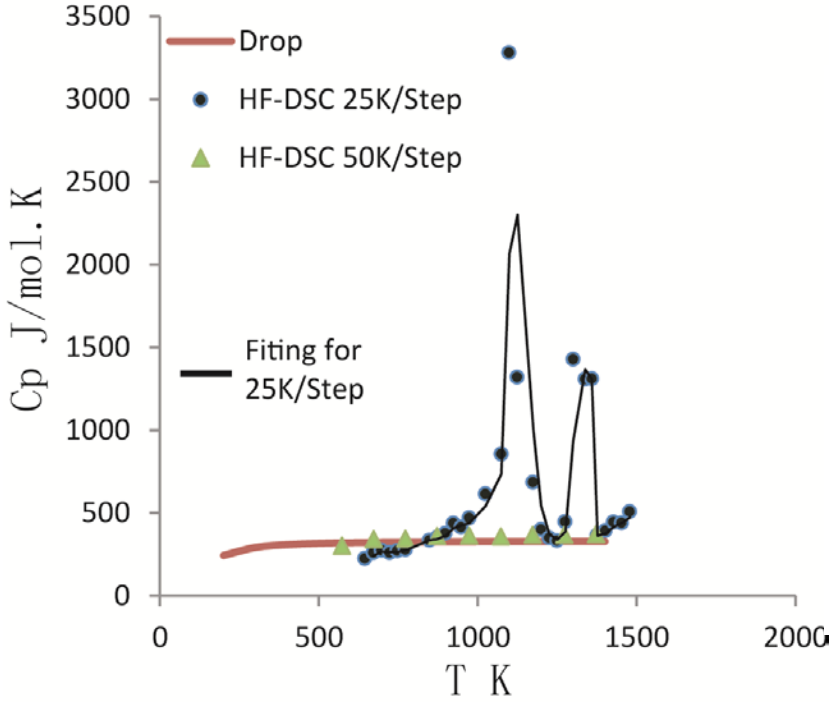
→ Application of DSC mode beside Drop method within MPS (T-resolution, time saving)

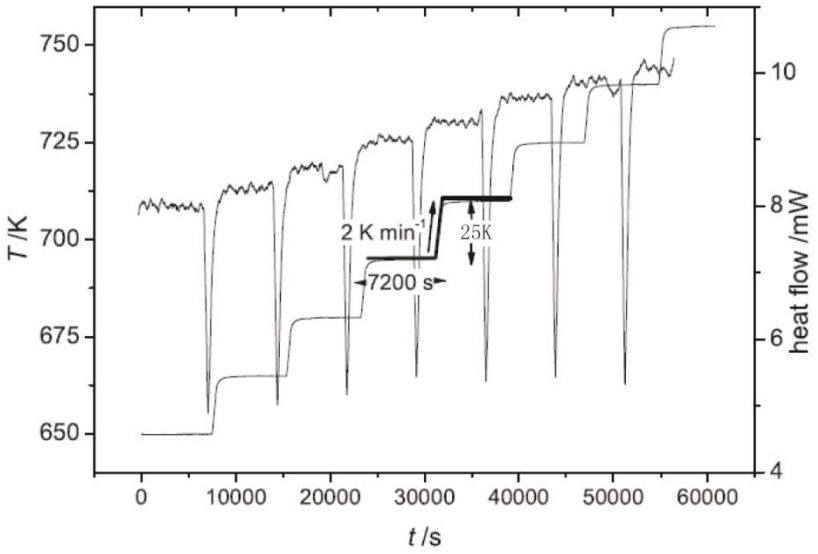
[1] O. Fabrichnaya et al.: Calorimetric investigation of the La2Zr2O7, Nd2Zr2O7, Sm2Zr2O7 and LaYO3 compounds and CALPHAD assessment of the La2O3–Y2O3 system. Thermochimica Acta 526, 2011

Calorimetry - Stepwise model

- **Application of DSC-mode and comparison to Drop mode for $K_2Ca_2Si_2O_7$**

- DSC-mode with 50 K- and 25 K steps, **1-2 weeks**

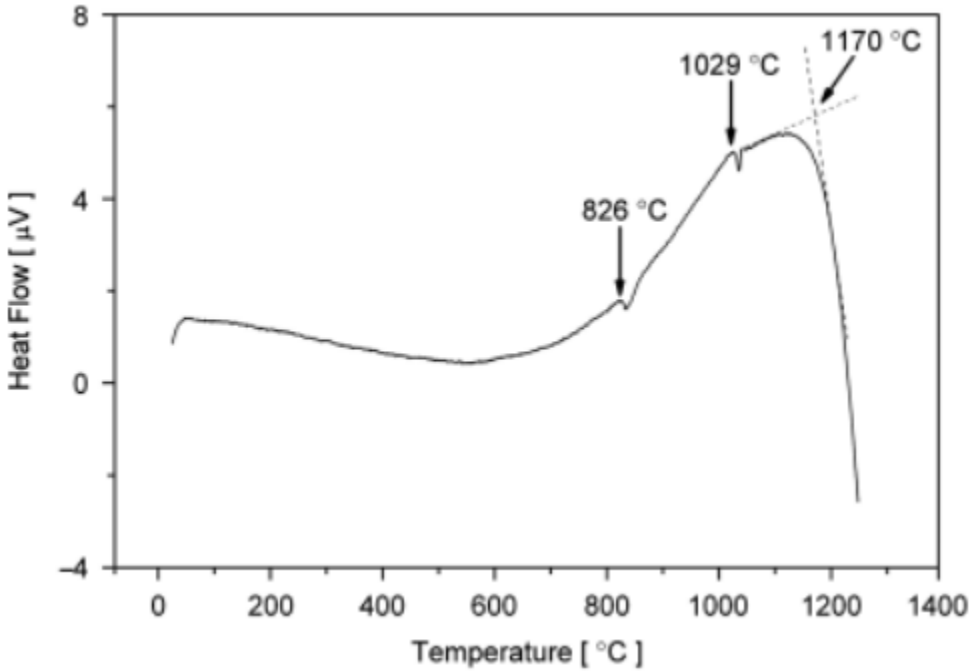




Calorimetry - Stepwise model

- **Application of DSC-mode and comparison to Drop mode for $K_2Ca_2Si_2O_7$**

- Comparison to DTA-data from literature [1]:



→ **Repetition measurement**

→ **XRF analysis?**

[1] E. Arroyabe, R. Tessadri, D. M. Tobbens, V. Kahlenberg, J. American Ceramic Society, 98, 2652-2655

Part II

VASP (Vienna Ab initio Simulation Package)

Calphad modeling

Theory

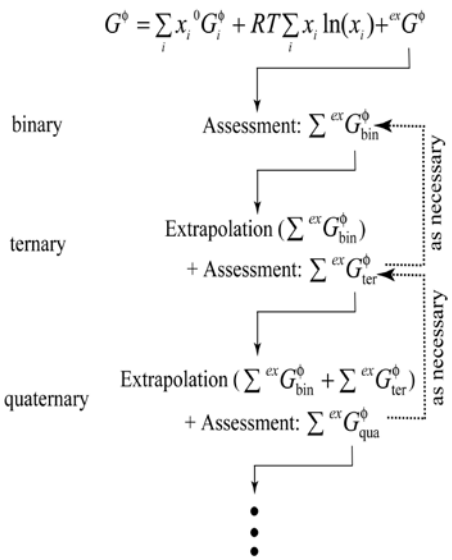
VASP

Quantum chemistry, ab initio, thermodynamics

Experiments

DTA, DSC, Calorimetry

Optimization



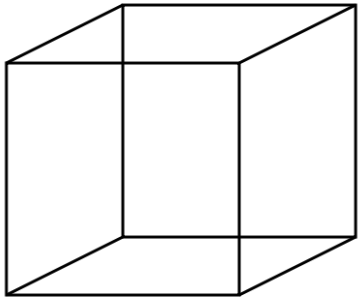
Phase diagram

Application

Input parameters

Structure detail:

- Structure: FCC, BCC, HCP …
- Kinds of atoms
- How many atoms in one cell
- Atoms occupied sites



System studied (input file) :

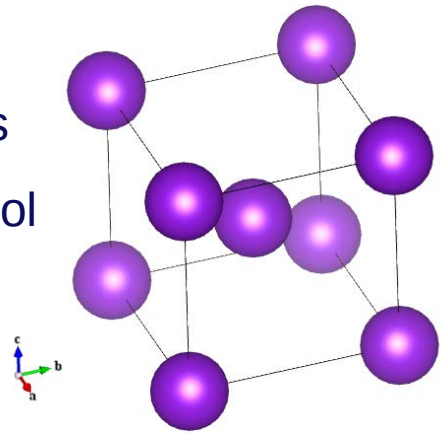
INCAR (how to do)
POSCAR (position + car)
POTCAR (Pseudo-potential)
KPOINTS (how many steps)

Pure elements

Calculated Enthalpy at 0K H_f^0

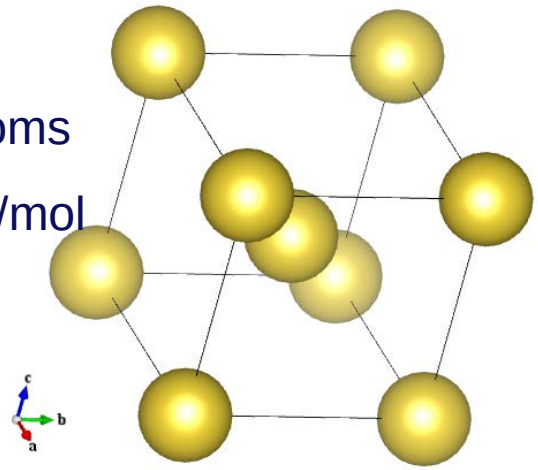
K: 2 atoms

-113.3 kJ/mol



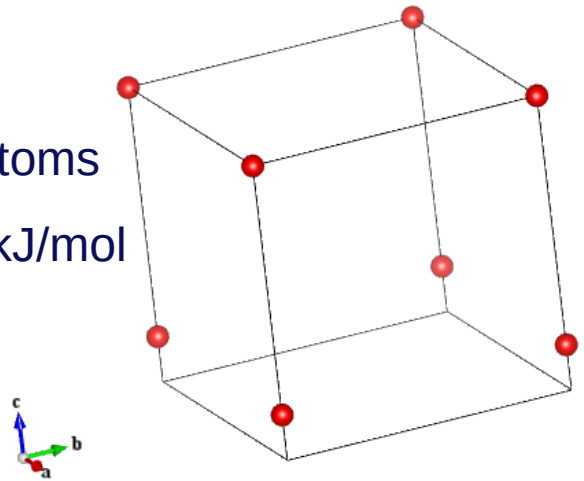
Na: 2 atoms

-138.8 kJ/mol



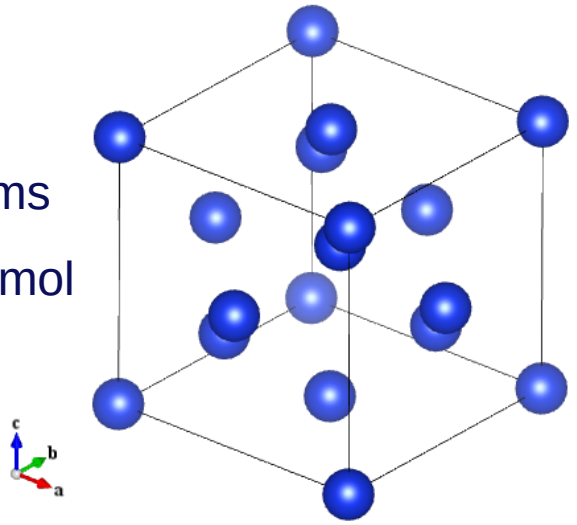
O: 2 atoms

-475.7 kJ/mol



Si: 8 atoms

-573.8 kJ/mol

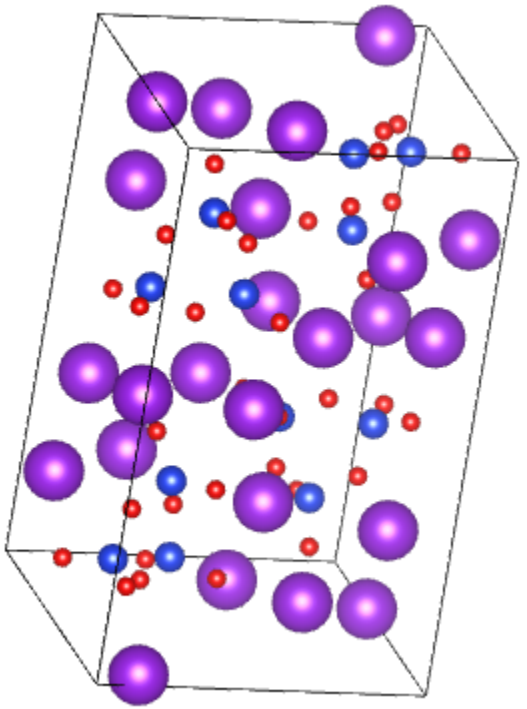


K_2SiO_3: 72 atoms

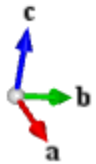
-643.11 kJ/mol

Reference state: K, Si and O

H_f^0 = -1634 kJ/mol



NIST-JANAF data : H_f^{298} = -1548.08 kJ/mol



In CALPHAD approach: the reference state should be: K_2O and SiO_2

The enthalpy is -63.9 kJ/mol

From our own optimization [1] :

H_f^{298} = -61.3 kJ/mol

[1] L. Zhang, C. Schmetterer, P. Masset, Computational Materials Science, In press 2012

Comparing the VASP with CALPHAD results

Compounds	K_2SiO_3	$K_2Si_2O_5$	$K_2Si_4O_9$	Na_2SiO_3	Na_4SiO_4	$Na_2Si_2O_5$	$Na_6Si_8O_{19}$
Atoms	72	108	30	24	18	36	136
Reference state are K2O, Na2O and SiO2							
Enthalpies of formation kJ/mol							
VASP At 0K	-63.9	-55.8	-50.4	-103.7	-106.4	-68.4	-88.1
CALPHAD At 298K	-61.3	-55.0	-49.9	-95.8	-104.5	-67.4	-61.7

The quasi-harmonic Debye model (GIBBS)
Cp

- As the limited computational resources, we just using quasi-harmonic Debye model to calculate the Cp.

E(V) $\Rightarrow$ $B_S \simeq B_{\text{static}}(\mathbf{x}) \simeq B_{\text{static}}\left(\mathbf{x}_{\text{opt}}(V)\right) = V\left(\frac{\mathrm{d}^2 E(\mathbf{x}_{\text{opt}}(V))}{\mathrm{d}V^2}\right) = V\left(\frac{\mathrm{d}^2 E(V)}{\mathrm{d}V^2}\right)$

$$\Theta = \frac{\hbar}{k}[6\pi^2 V^{1/2} n]^{1/3} f(\sigma)\sqrt{\frac{B_S}{M}} \qquad f(\sigma) = \left\{3\left[2\left(\frac{2}{3}\frac{1+\sigma}{1-2\sigma}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2}\right]^{-1}\right\}^{1/3}$$

$$C_{\text{v,vib}} = 3nk\left[4D(\Theta/T) - \frac{3\Theta/T}{\mathrm{e}^{\Theta/T}-1}\right] \qquad D(y) = \frac{3}{y^3}\int_0^y \frac{x^3}{\mathrm{e}^x - 1}\,\mathrm{d}x$$

$$\gamma = -\frac{\mathrm{d}\ln\Theta(V)}{\mathrm{d}\ln V} \Rightarrow \alpha = \frac{\gamma C_{\text{v,vib}}}{B_T V}$$

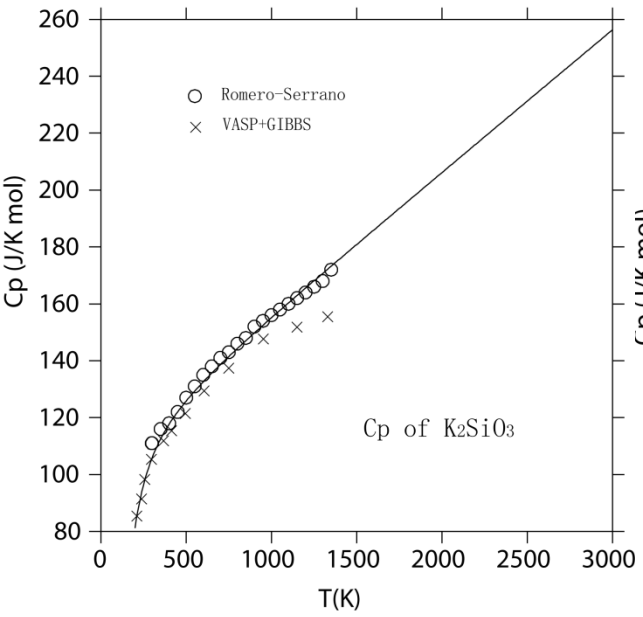
$$C_{\text{p,vib}} = C_{\text{v,vib}}(1 + \alpha\gamma T)$$

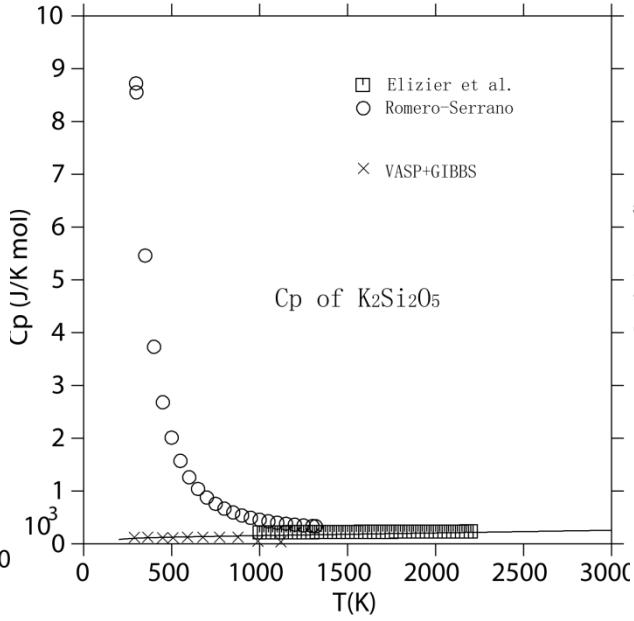
Reference:

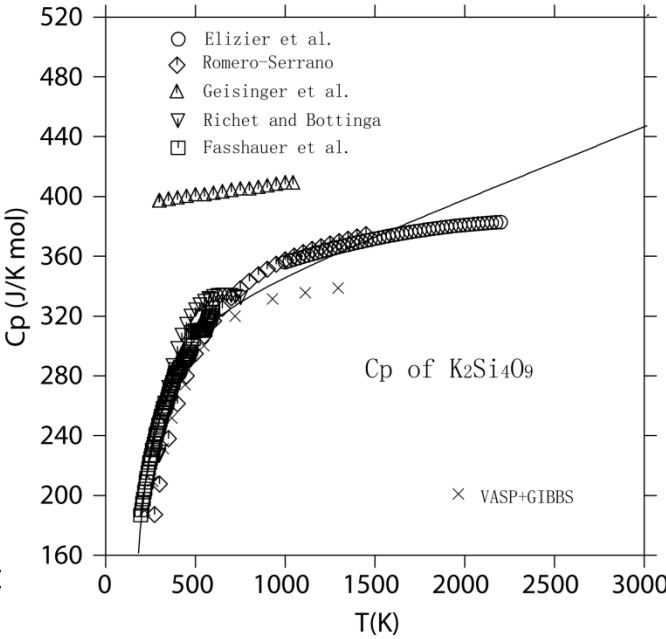
M.A. Blanco et.al., Computer Physics Communications, Vol 158,2004,P57-72

The quasi-harmonic Debye model
Cp results

Here show some results on K_2O-SiO_2 system from VASP+GIBBS comparing to our CALPHAD results and literature data







We can easily find that Cp from VASP+GIBBS is in good agreement with both CALPHAD and literature results, however, when it come to high temperature (＞1000K), the results are more and more negative compare to CALPHAD results, that is because both VASP and GIBBS are more reliable in low temperature range.

That means we still need experimental measurements.

Part III

CALPHAD optimization

Calphad modeling

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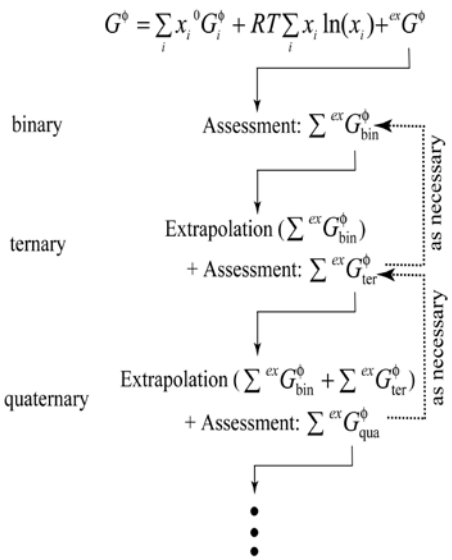
VASP

Quantum chemistry, ab initio, thermodynamics

Experiments

DTA, DSC, Calorimetry

Optimization



Phase diagram

Application

CALPHAD details

Model of Liquid phase:

Two sublattice model for the ionic liquid phase (the Gibbs energy is extrapolated from the three binary systems)

$$(Ca^{+2}, K^{+1}, Na^{+1})_p (O^{-2}, SiO_4^{-4}, SiO_2^{0})_q$$

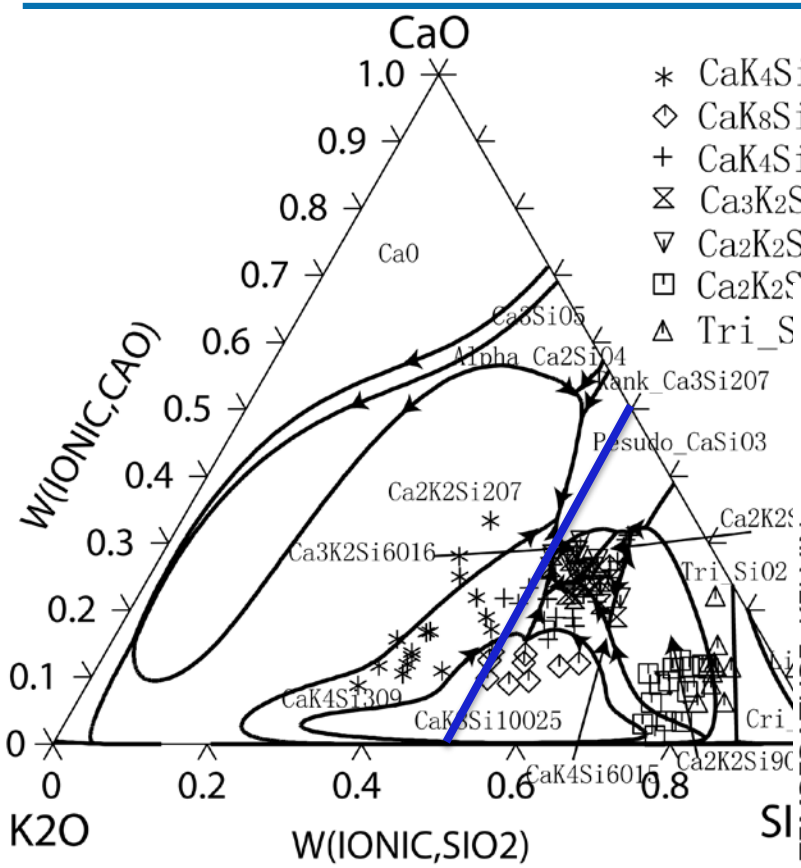
Model of solid phases:

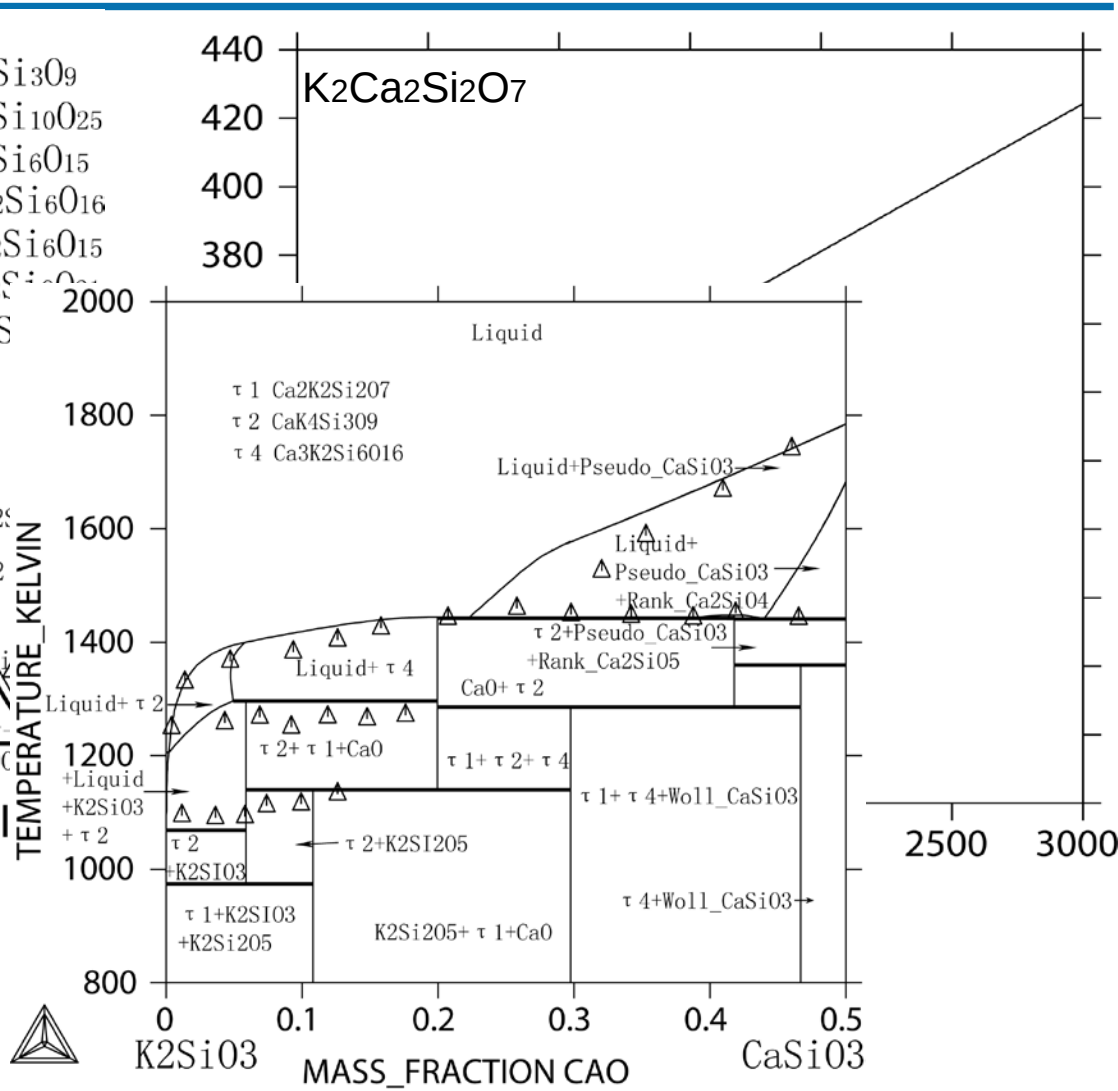
All of the Gibbs energy values (7 ternary compounds) are given relative to enthalpy of selected reference states for the elements at 298.15K. This state is denoted by SER (Stable Element Reference).

$$^{0}G - H^{SER} = A + B/T + CT + DT\ln T + ET^{2}$$

Where the parameters A, B, C, D, E should be optimized in this work

CaO-SiO_2-K_2O ternary system





Calculated thermodynamic of K_2O-CaO-SiO_2 system

Database Development

- **Cooperation with GTT-Technologies:**

GTT oxide Database

-developed since 2009

-Components: SiO_2, CaO, MgO, K_2O, Na_2O, Al_2O3, FeO, Fe_2O_3, CrO, Cr_2O_3, P_2O_5, CaS, FeS, MgS and CaF_2

-consistent treatment of the alkali components, improved modelling of spinel, mullite, mellilite and several other solid solutions

-non-ideal associate model for liquid

VTC-MPS

- M_2O-SiO_2-CaO-Al_2O_3 systems (M= K, Na)
- Thermodynamic Data (H_f, c_p) from calorimetric measurement and ab initio calculations
- G(T)-functions of optimized subsystems by CALPHAD method

FZ IEK-2

Synthesis of ternary compounds for calorimetry

- Integration of VTC-MPS DATA in GTT oxide Database by GTT Technologies
- Application of Database for the estimation of the ash/ slag behaviour within VTC

Database Development

- Datapool MPS

System	Phases	Gibbs energy function (CALPHAD)	Enthalpy of formation (VASP)	Heat capacity (VASP+GIBBS)	Heat capacity (EXP.)
$CaO\text{-}SiO_2$	1	1			1 (Drop mode)
$K_2O\text{-}SiO_2$	3	3	3	3	
$Na_2O\text{-}SiO_2$	8	8	3	3	
$Al_2O_3\text{-}K_2O$	3	(3)	1	[1]	
$Al_2O_3\text{-}Na_2O$	3	(3)	1	[1]	
$CaO\text{-}K_2O\text{-}SiO_2$	7	7	(2)	(2)	3 (Drop mode) 1 (Stepwise mode)
$CaO\text{-}Na_2O\text{-}SiO_2$	6	6	[4]	[4]	2[Drop mode]
$Al_2O_3\text{-}K_2O\text{-}SiO_2$	2	[2]			
$Al_2O_3\text{-}Na_2O\text{-}SiO_2$	2	[2]			

- () = in work
- [] = planed

30

Conclusion and Outlook

In this work, CALPHAD optimization of ternary phase diagrams were reached based on experimental and ab-initio data

…work in progress…

There is still a lot do …

… Heat capacities of ternary system need to be caculated

… experimental Cp need to repeat

Thanks to: Colleagues from VIRTUHCON

Prof. V. Kahlenberg (Univ. Innsbruck)

For financial support:

SPONSORED BY THE

Federal Ministry of Education and Research

Thank you for your attention