

Atomistic Simulation of High-Temperature Ceramics

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Chemistry & Biochemistry

Aerospace Materials for Extreme Environments Program Review

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Atomistic Simulation of High-Temperature Ceramics

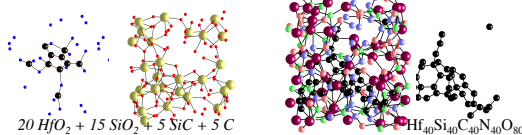
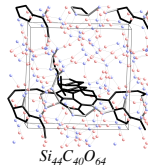
Peter Kroll, UT Arlington; Chemistry & Biochemistry: FA9550-09-1-0477

Status Quo: hierarchical, multi-component materials often comprise amorphous phases that contribute to a multitude of properties, but which individual properties are poorly understood

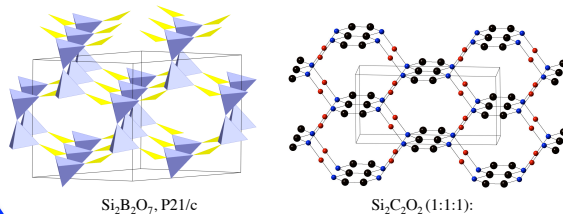
Project Goal: Discover new materials, structures, and their properties; simulate properties at conditions where experiment is too difficult or not feasible. Contribute to a virtual predictive tool that simulates materials properties with high fidelity.

Structure Simulation

- persistence of nano-scale carbon precipitation
- segregation and ordering in ternary and quinary systems

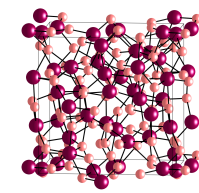
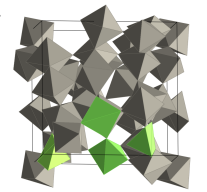
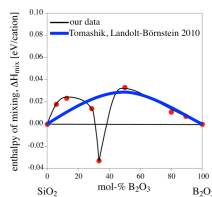


- hypothetical crystalline approximants
- idealized structure motifs

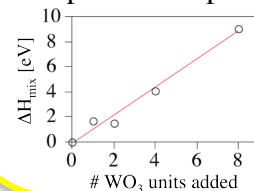


Thermochemistry

- enthalpy of formation of the amorphous state for various compounds
- discovery of a stable region in the B_2O_3 - SiO_2 phase diagram



- enthalpy of mixing for melts and amorphous compounds

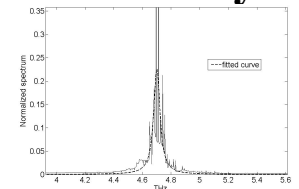


WO_3 in B_2O_3
 $\Delta H_{\text{mix}} \approx 1.1 \text{ eV/WO}_3$

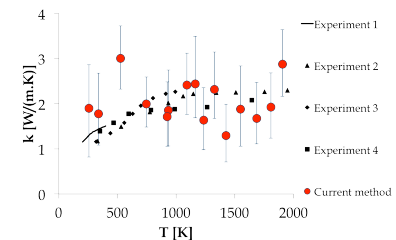
Thermal Conductivity

- kinetic theory
- ab-initio MD

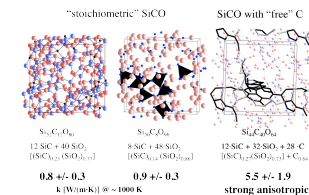
$$k = \sum_s \int \frac{v_{qs}^2}{q} C_{qs} \tau_{qs} dq$$



Thermal conductivity, a- SiO_2



- anisotropy in segregated SiCO



Outline

- Modeling amorphous structures by DFT methods
 - melt-quench approach and ab-initio MD
 - segregation at small length scales, am-HfSiCO
- B_2O_3 - WO_3 - SiO_2 phase diagram; Thermochemistry
 - solubility of WO_3 in a- B_2O_3 : structural implications
 - amorphous B_2O_3 - SiO_2 : stability of B_2O_3 - SiO_2
- Thermal transport in amorphous systems via ab-initio MD
 - kinetic approach
 - amorphous SiO_2 and anisotropy in SiCO

Modeling amorphous structures

- amorphous state depends on history
- transient in temporal and spatial coordinates

Assumption: structure often “more or less” close to crystal

- SiO_2 but SiCO , HfSiCNO

How to model?

Melt-quench

- ab initio
- Empirical potentials / force fields

“question” of
size & quality

Networks

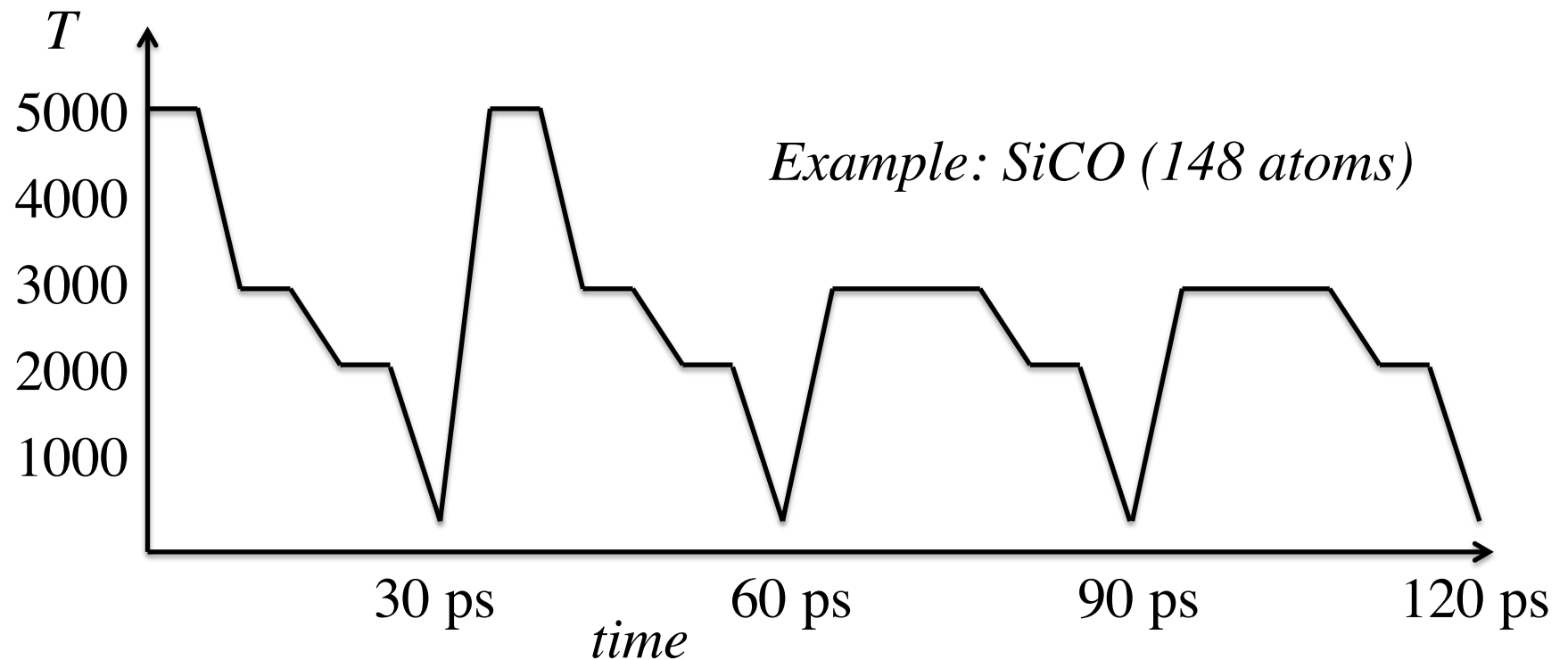
- intuitive assumptions
- testing hypotheses

& desired property

Melt-Quench models

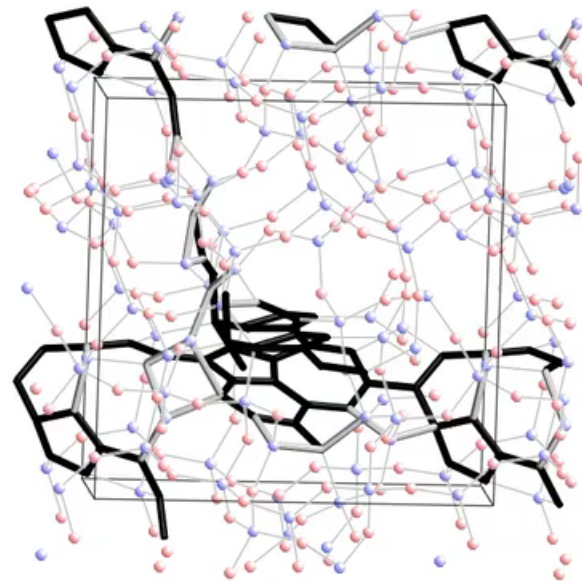
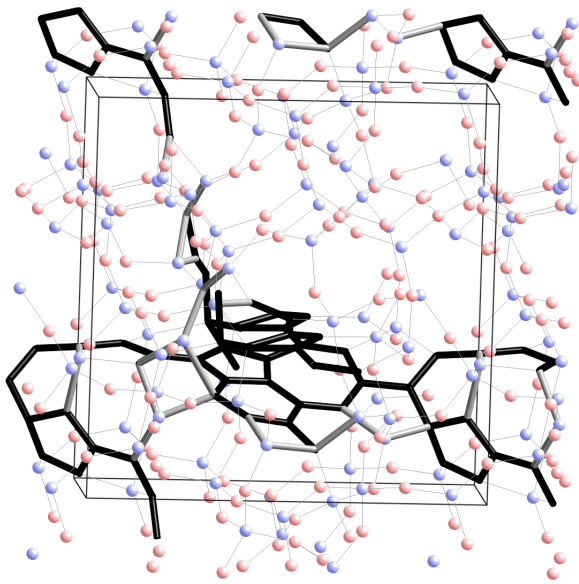
Melt-quench approach

- DFT, *ab initio* molecular dynamics (VASP-code)
- augmented with repeated annealing
to achieve low-energy structures



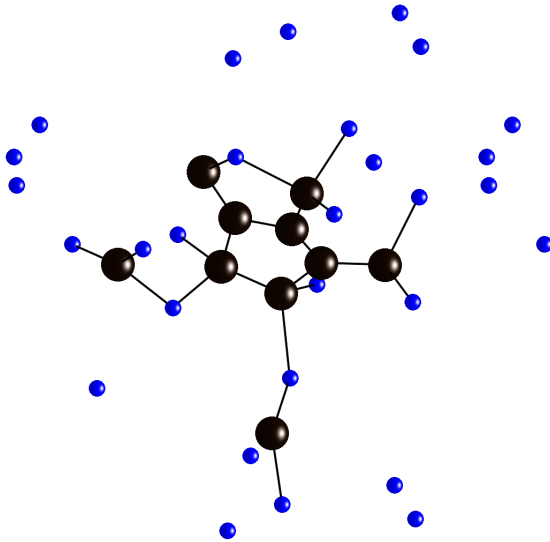
Si-C-O by melt-quench

Example: $\text{Si}_{44}\text{C}_{40}\text{O}_{64} : 32 \text{ SiO}_2 + 12 \text{ SiC} + 28 \text{ C}$

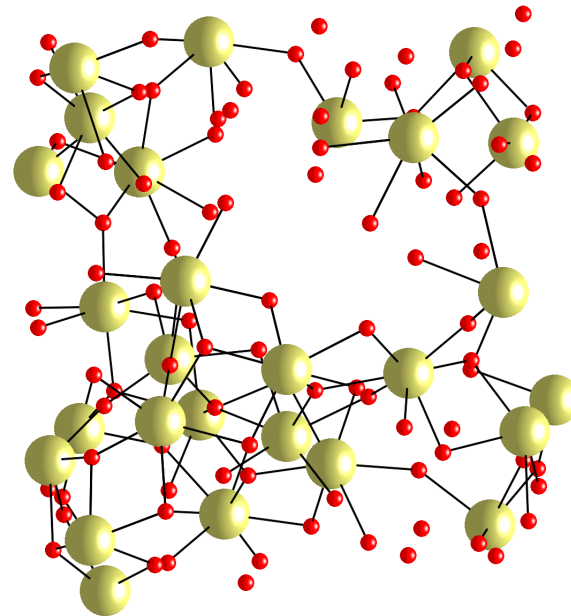


Hf-Si-C-O: segregation

*Example: Hf-Si-C-O : 20 HfO₂ + 15 SiO₂ + 5 SiC + 5 C
or 15 HfSiO₄ + 5 HfO₂ + 5 SiC + 5 C*

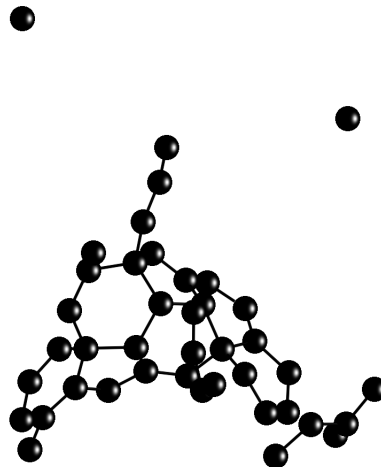
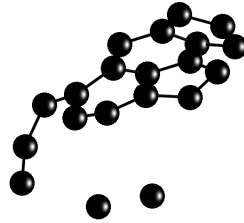
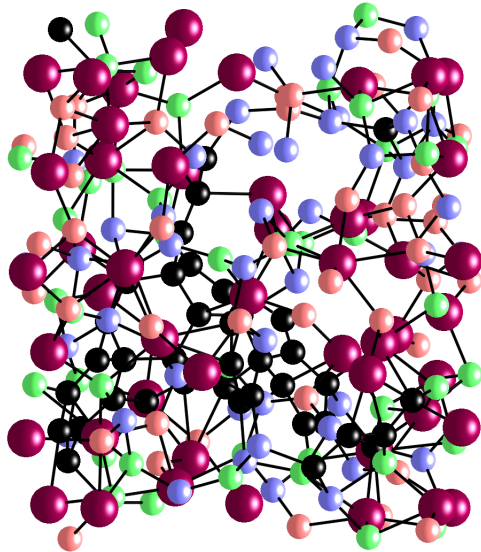
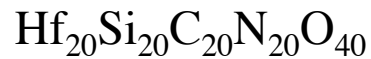
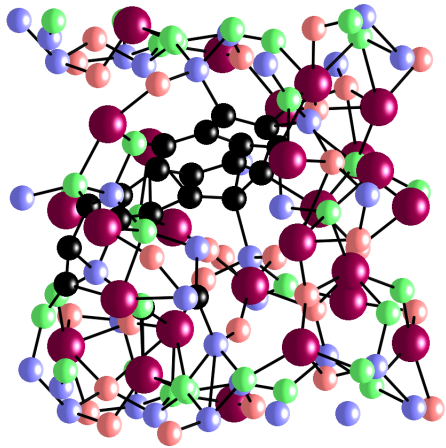


Si-C substructure
(frontview)



Hf-O substructure
(sideview)

Hf-Si-C-N-O, segregation



No empirical potential available!

50 mol% HfO_2 + 50 mol% SiCN
melt-quench method

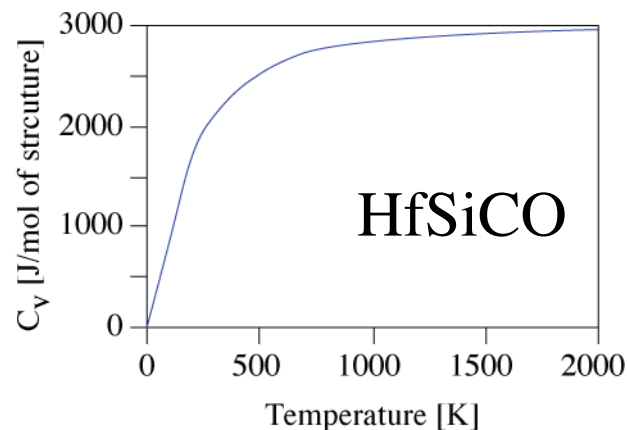
ab-initio molecular dynamics

- carbon segregates into *layer or chunk*
- great “diversity” of bonds

Thermal properties: Heat Capacity

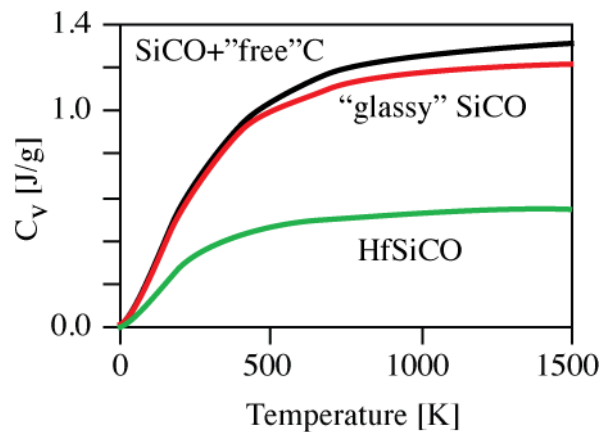
- DFPT calculations (if possible) – up to $V \approx 1800 \text{ \AA}^3$
 - else DFT with finite difference approach
- \Rightarrow phonon DOS

+ quasi-harmonic approximation (QHA)
 $\Rightarrow C_v$ for all amorphous models



Heat Capacities

- refer to 1 g of compound



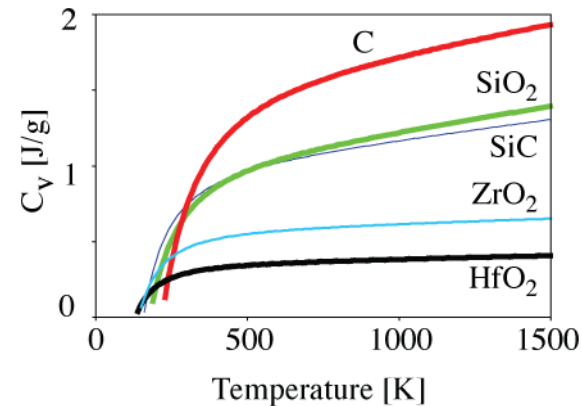
- SiO_2 , SiC, and “glassy” SiCO virtually identical
- addition of C increases $C_{v,g}$
- heavy element decreases $C_{v,g}$ (ultimately: Dulong-Petit)

A rationale

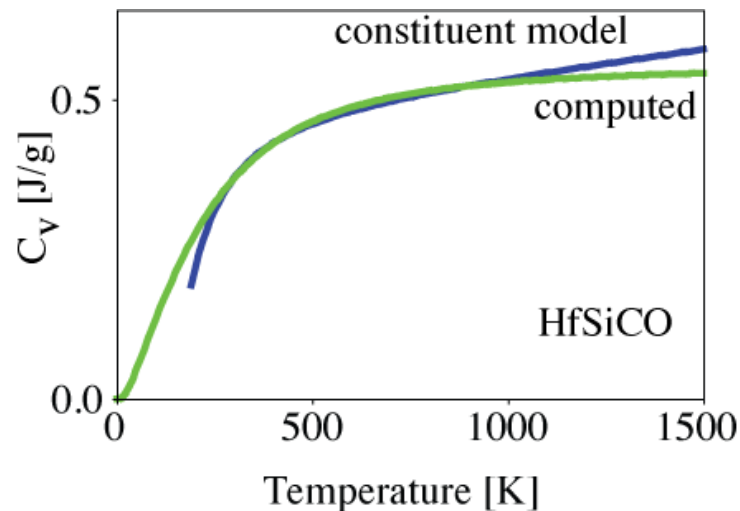
Maier-Kelley expression:

$$C_v = a + b \cdot T + c/T^2$$

- use fit to experimental data (literature values)



Comparison for HfSiCO



- computed & constituent model compare very well for $300 \text{ K} < T < 1000 \text{ K}$

⇒ Overall: no “surprises”

Some problems with “melt-quench”

While often the first “quick & dirty” approach ...

- *great “diversity” of bonds*

⇒ means high proportion of defects

- a-Si, a-Si₃N₄, a-SiC:

emp.pot.: 1-10% Si^[3], but Exp (EPR): < 0.1 % Si^[3]

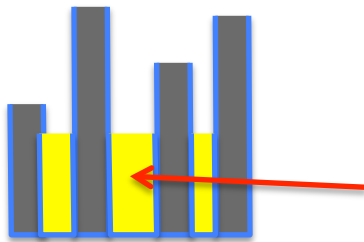
What to do, if “**Chemistry**” is important?

- modeling catalysis
- Li storage & electron transport
- optical properties

B_2O_3 - WO_3 - SiO_2 phase diagram

$\text{B}_2\text{O}_3\text{-WO}_3$

- glassy phases and improvement of oxidation resistance



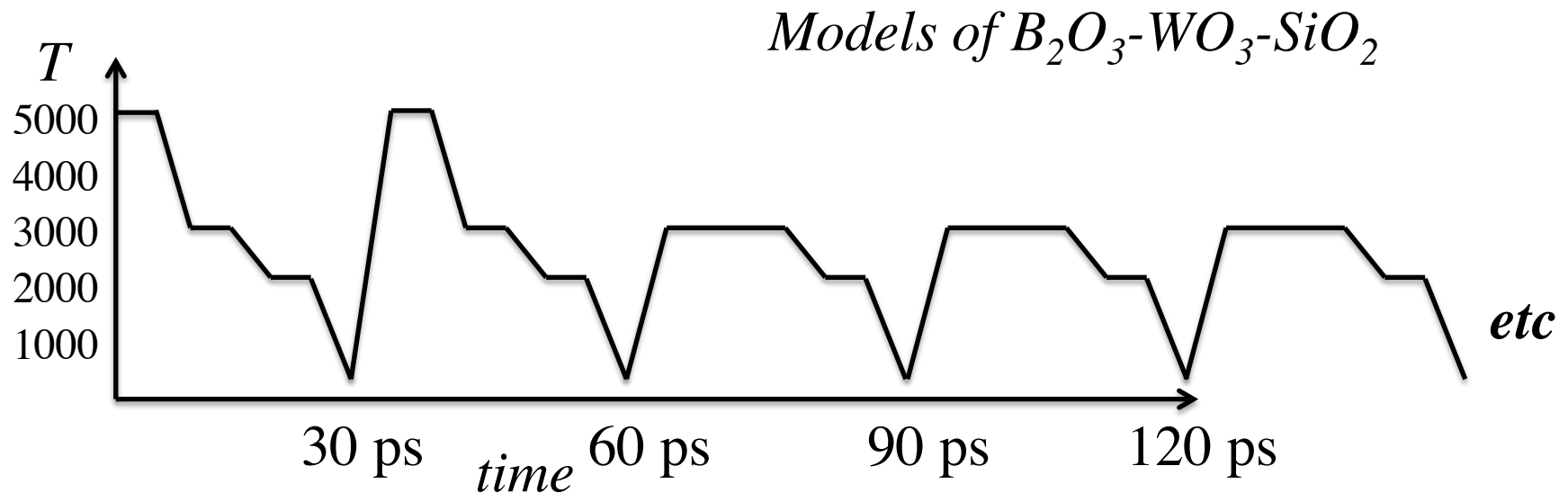
Fahrenholtz & Hilmas, 2010

- Oxidation of ZrB_2/WC -composites
- precipitates of ZrO_2 in glassy “WBO”

\Rightarrow Exp: solubility of WO_3 in $\text{B}_2\text{O}_3 \sim 5 \text{ mol-}\%$

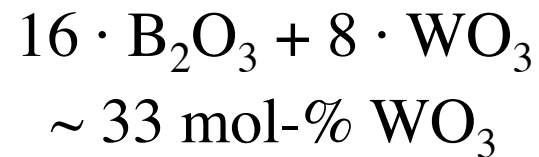
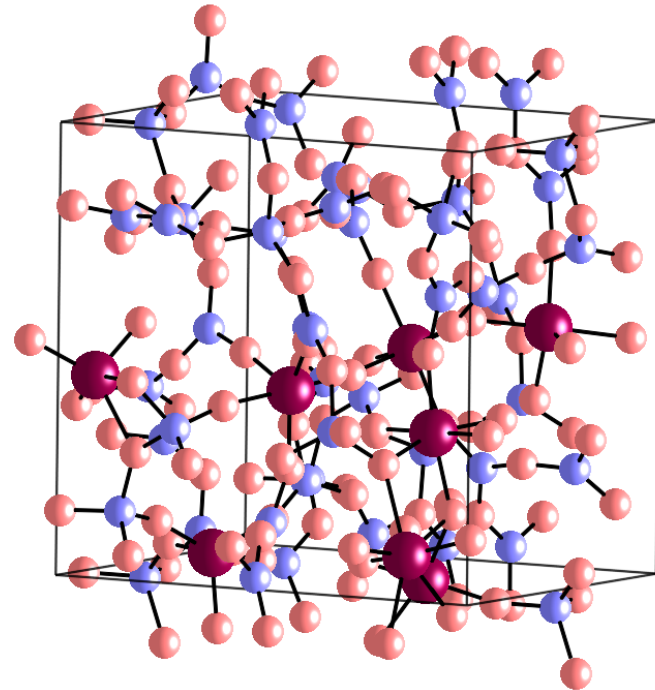
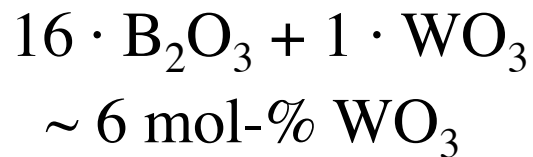
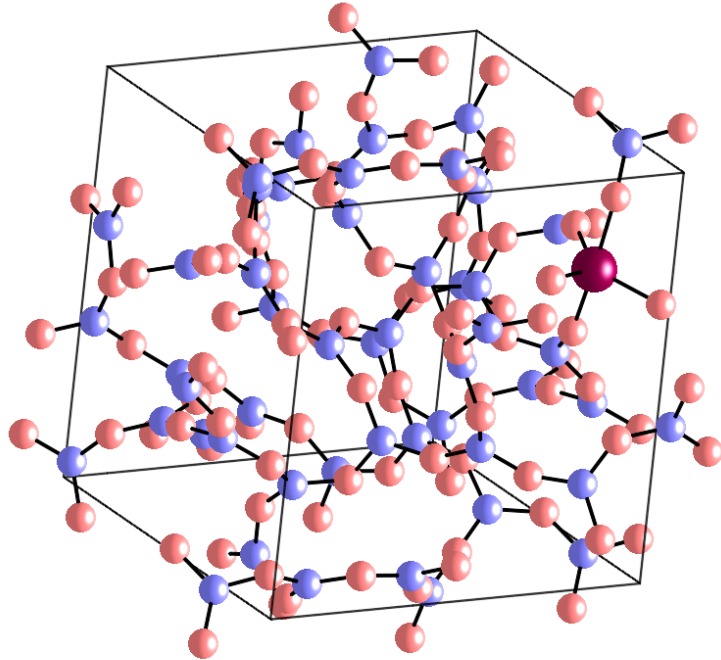
Structure Generation

- melt-quench approach
- DFT, *ab initio* molecular dynamics (VASP-code)
- augmented with repeated annealing
to achieve low-energy structures



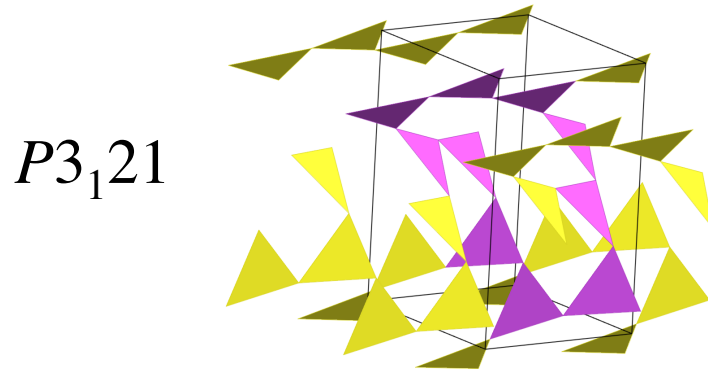
$\text{B}_2\text{O}_3\text{-WO}_3$: structures

- melt-quench approach $16 \cdot \text{B}_2\text{O}_3 + n \cdot \text{WO}_3$
 $n = 0, 1, 2, 4, 8$

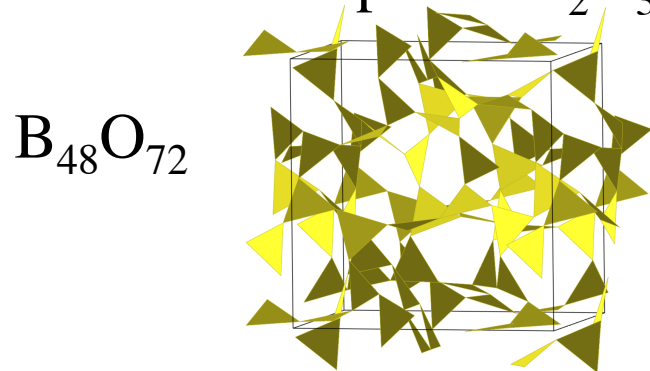


$\text{B}_2\text{O}_3\text{-WO}_3$: ΔH_f of pure glass

$$E(\alpha\text{-B}_2\text{O}_3) = -40.52 \text{ eV/f.u.}$$



amorphous B_2O_3

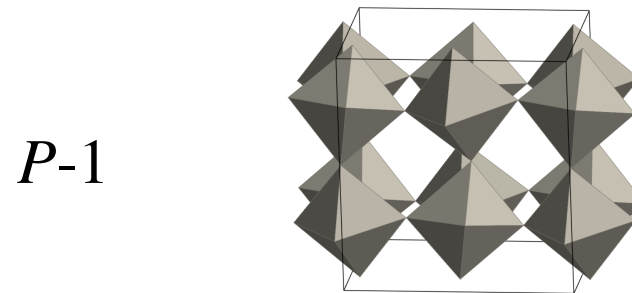


$$E(\text{a-B}_2\text{O}_3) = -40.425 \text{ eV/f.u.}$$

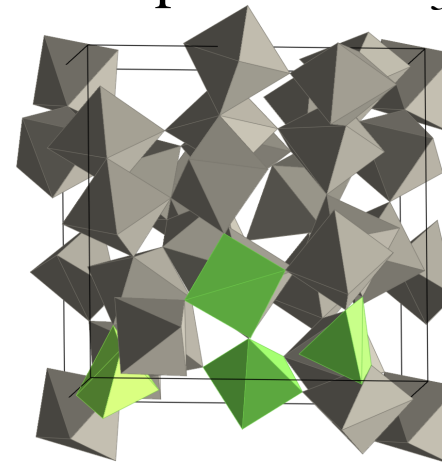
$$\Rightarrow \Delta E_f \approx 0.1 \text{ eV/B}_2\text{O}_3$$

$$\text{NIST: } \Delta E_f \approx 0.18 \text{ eV/f.u.}$$

$$E(\text{t-WO}_3) = -36.35 \text{ eV/f.u.}$$



amorphous WO_3



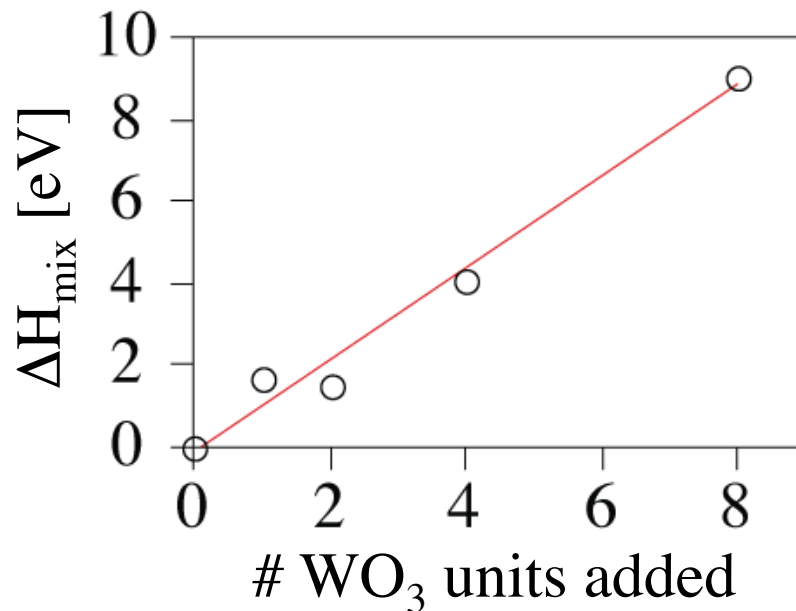
$$E(\text{a-WO}_3) = -35.91 \text{ eV/f.u.}$$

$$\Rightarrow \Delta E_f \approx < 0.44 \text{ eV/WO}_3$$

$\text{B}_2\text{O}_3\text{-WO}_3$: ΔH_{insert} to add WO_3 to B_2O_3

- mixed models: $16 \cdot \text{B}_2\text{O}_3 + n \cdot \text{WO}_3$, $n = 0, 1, 2, 4, 8$

$$\Delta H_{\text{insert}} = E(\text{Model}) - [E(\text{a-B}_2\text{O}_3) + n \cdot E(\text{t-WO}_3)]$$



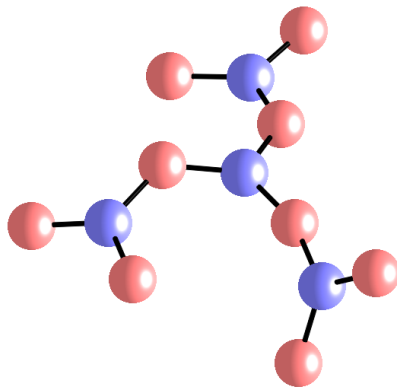
$$\Rightarrow \Delta H_{\text{mix}} \approx 1.1 \text{ eV/WO}_3$$

Significantly higher
than ΔH_{f} of WO_3 !!

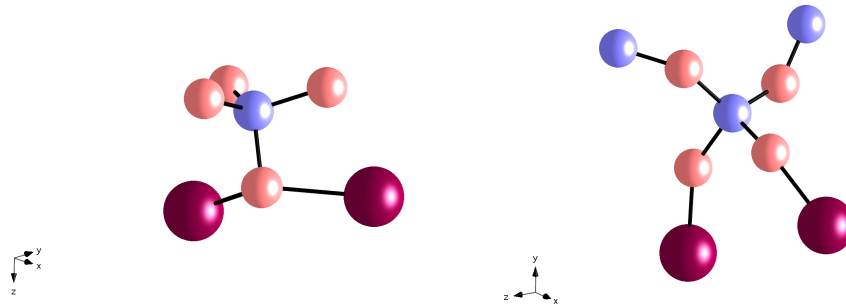
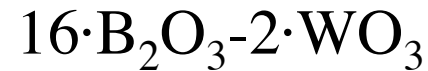
Why?

“*hand-waving*”: entropy (vibr & mix) at 2000 K may
“compensate” for ~ 6 mol-% WO_3

$\text{B}_2\text{O}_3\text{-WO}_3$: structural trends at B



- all B as BO_3



- increasing amount BO_4

⇒ “*chemical pressure*”

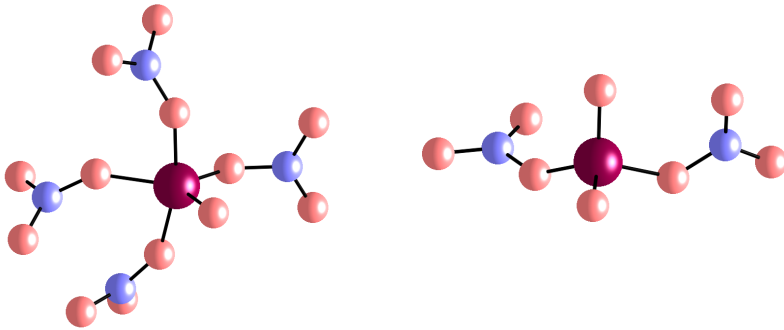
“Analogous” to CaO-SiO_2 ?

⇒ ? B-NMR **experiments** of glass

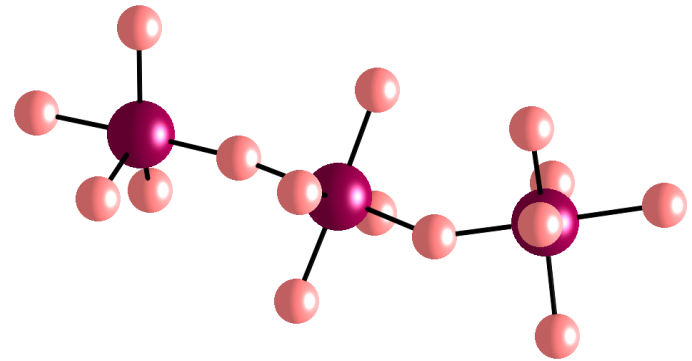
higher diffusivity of O^{2-} in compressed B_2O_3
Diefenbacher&McMillan, **JPC A 2001**

B₂O₃-WO₃: structural trends at W

low WO₃-content

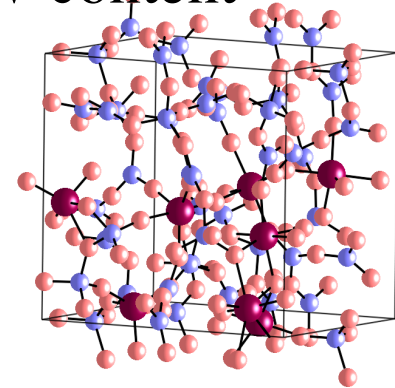


high WO₃-content



- isolated WO₅ and WO₄
- WO₆ and WO₅
- higher coordination of W with increasing W content
- clustering of WO_x-units

⇒ ? IS-EELS experiments ?

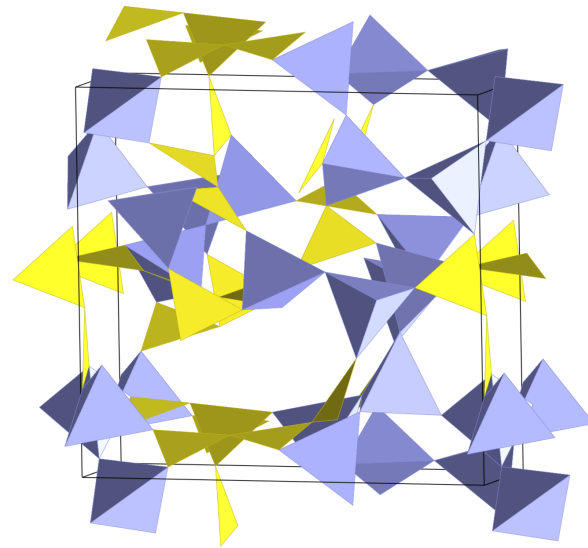
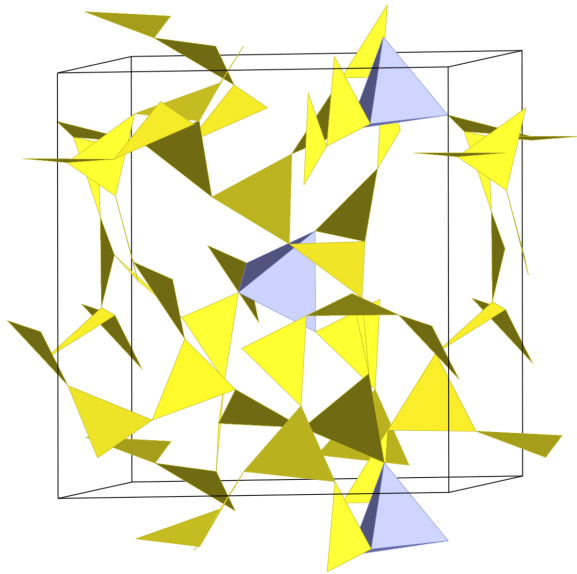


B_2O_3 - SiO_2 : phase diagram

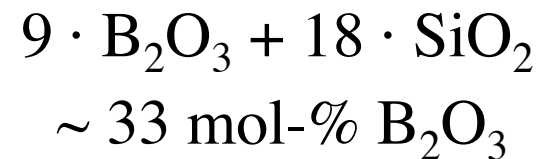
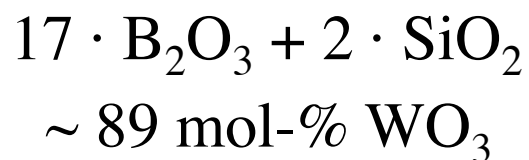
- > 100 years of literature
- many contradicting claims and observations
- no crystalline ternary phase detected
- overview by Tomashik, Landolt-Börnstein 2010

B₂O₃-SiO₂: structures

- melt-quench approach
- ~ 100 models, various compositions



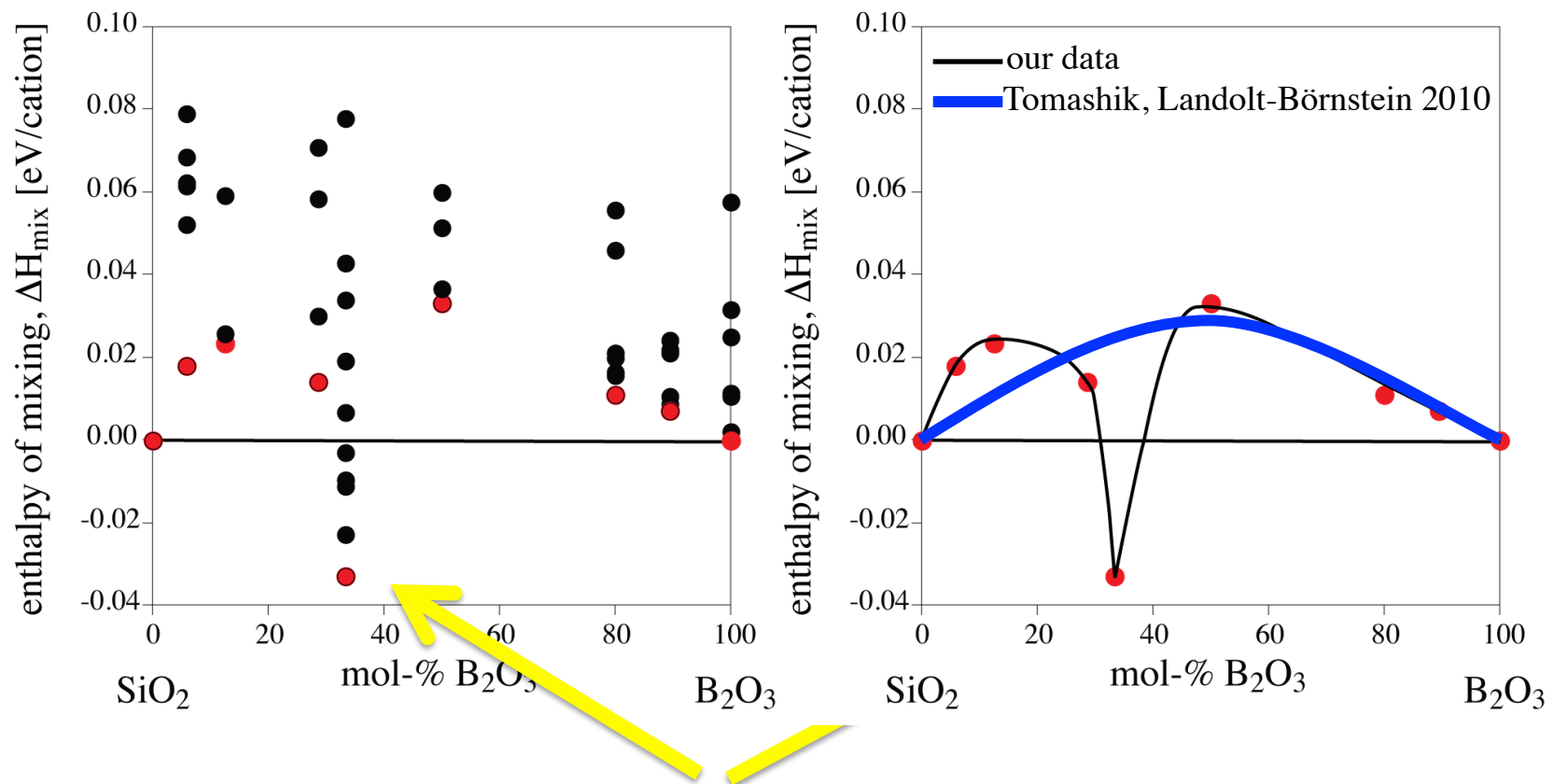
- all models exhibit **SiO₄** and **BO₃**-units only



B₂O₃-SiO₂: enthalpy of mixing, ΔH_{mix}

- mixing amorphous boria and silica

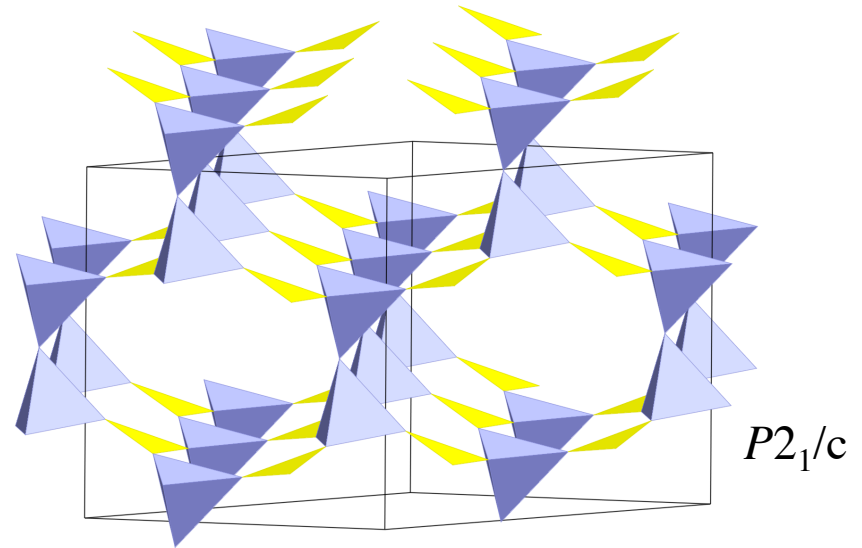
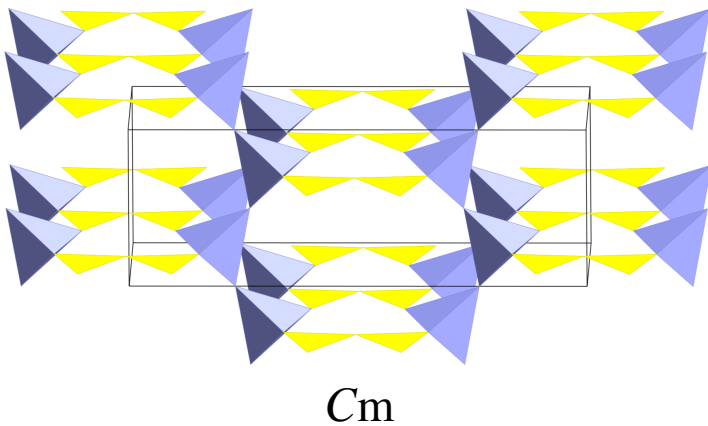
$$\Delta H_{\text{mix}} = E(\text{Model}) - [E(\text{a-B}_2\text{O}_3) + E(\text{a-SiO}_2)]$$



$\Rightarrow 33 \text{ mol-\% B}_2\text{O}_3 == 2 \cdot \text{SiO}_2 + \text{B}_2\text{O}_3 == \text{Si}_2\text{B}_2\text{O}_7$ highly favored

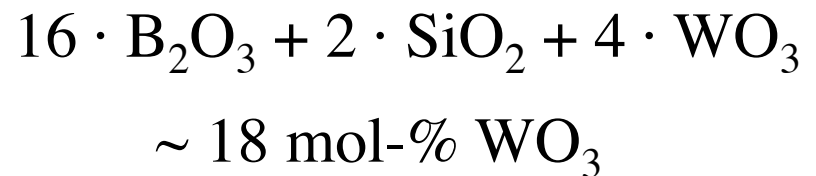
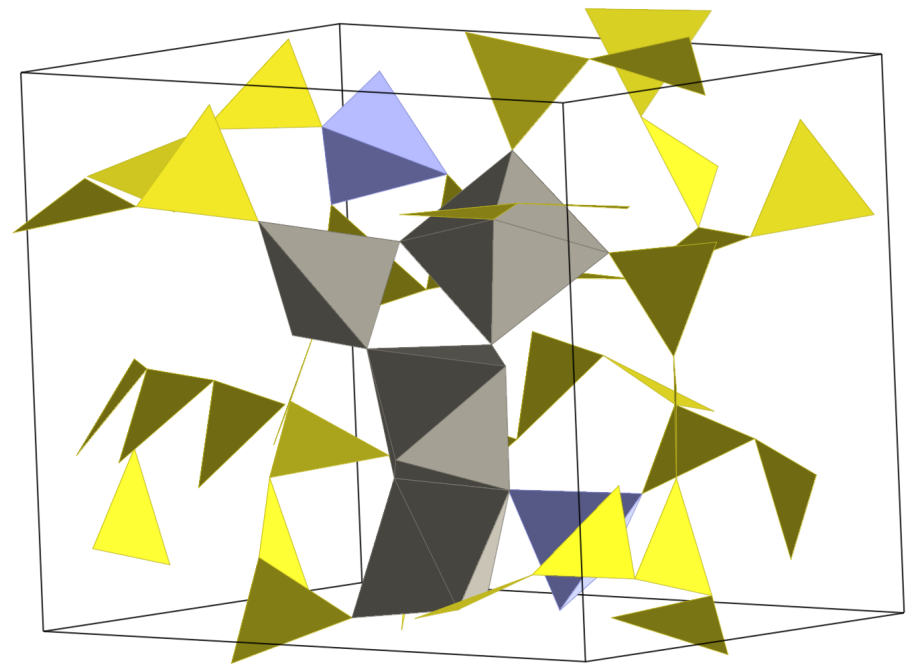
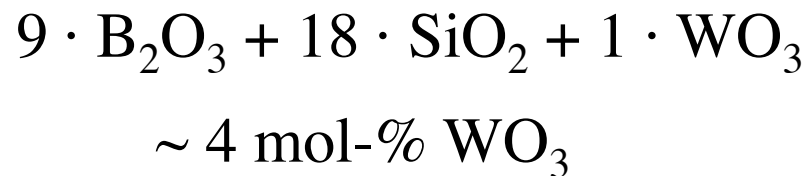
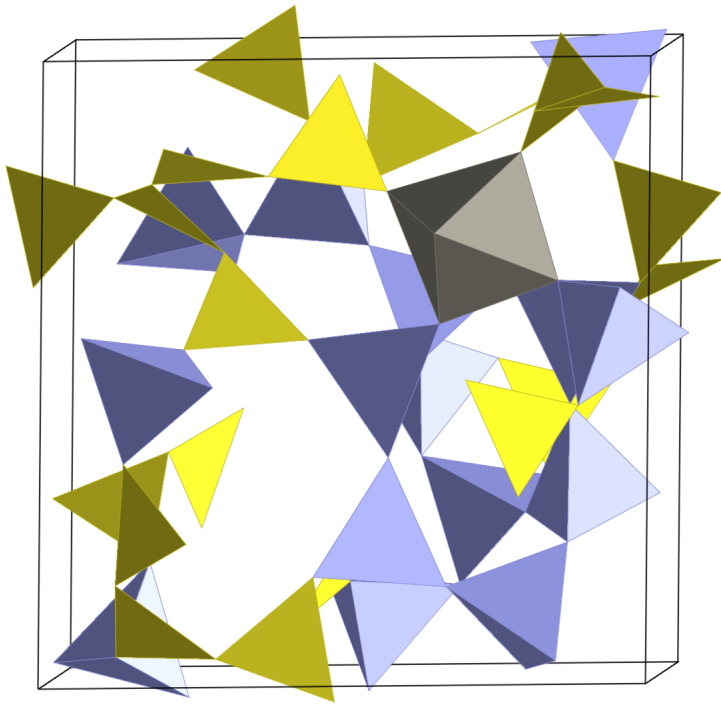
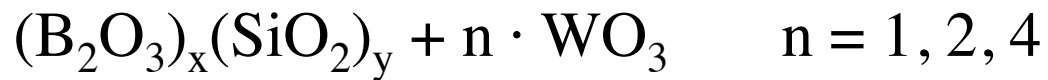
$\text{B}_2\text{O}_3\text{-SiO}_2$: quest for crystalline $\text{Si}_2\text{B}_2\text{O}_7$

- structure search using AIRSS
- > 1000 candidates studied (also at high pressure)

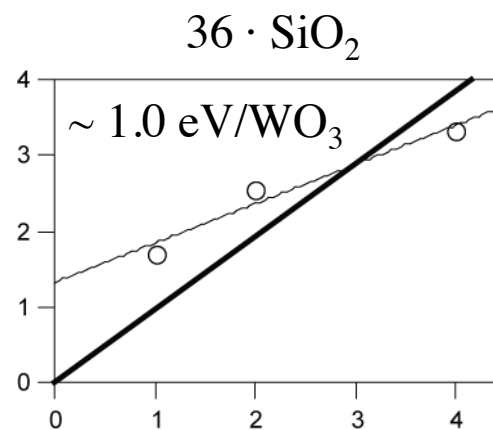
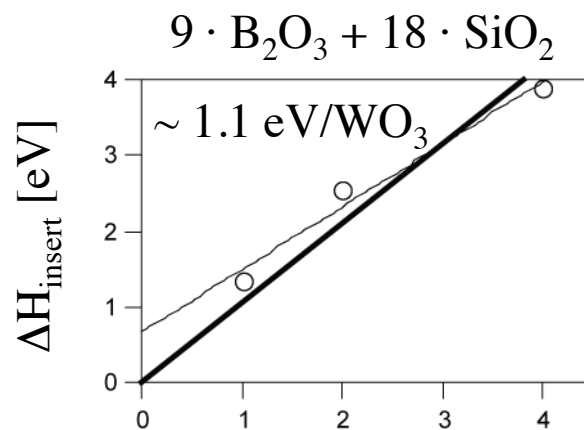
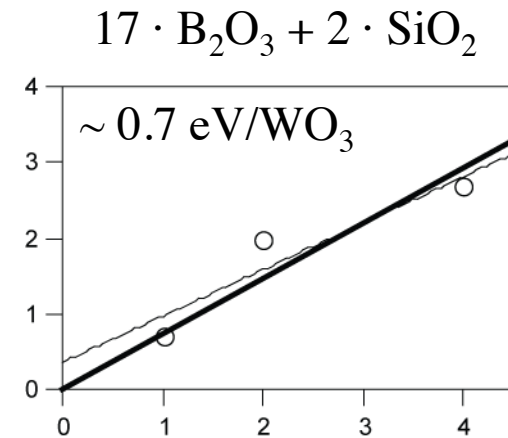
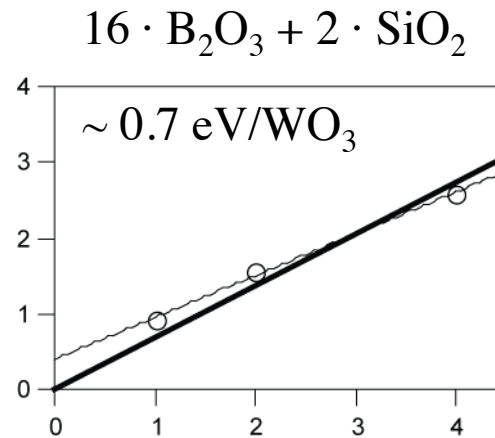
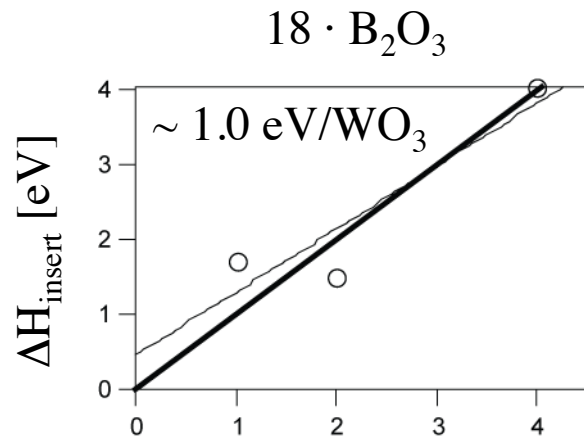


$$\Delta H = 0.01 \text{ eV} \approx 0.003 \text{ eV/cation} \approx 0 !$$

B_2O_3 - WO_3 - SiO_2 : structures

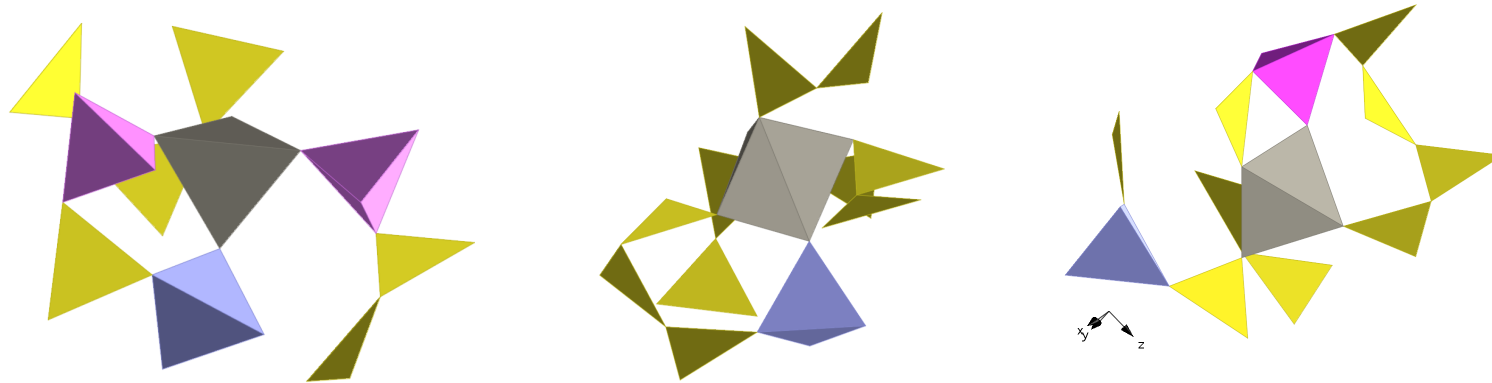


$\text{B}_2\text{O}_3\text{-WO}_3\text{-SiO}_2$: ΔH_{insert} of WO_3

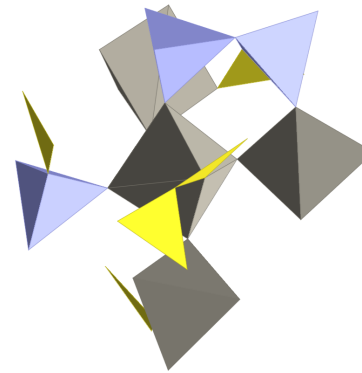
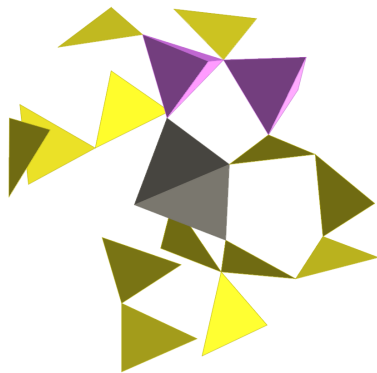


\Rightarrow some SiO_2 improves solubility of WO_3

B₂O₃-WO₃-SiO₂: structural trends



- **W** still surrounded by **BO₄**, but **SiO₄** substitutes



$\text{B}_2\text{O}_3\text{-WO}_3\text{-SiO}_2$: conclusion

- solubility of WO_3 in B_2O_3 estimated to ~ 6 mol-% at 2000 K
high positive ΔH_{mix} and shift towards $\text{sp}^3\text{-B}$
- some SiO_2 in B_2O_3 enhances solubility of WO_3
Si substitutes for $\text{sp}^3\text{-B}$
- highly favorable composition $\text{Si}_2\text{B}_2\text{O}_7$
 $\Delta H_{\text{mix}} < 0$ for glass phases
possible crystal structure has $\Delta H_{\text{f}} \approx 0$

Thermal conductivity

via ab-initio molecular dynamics

Thermal conductivity: kinetic theory

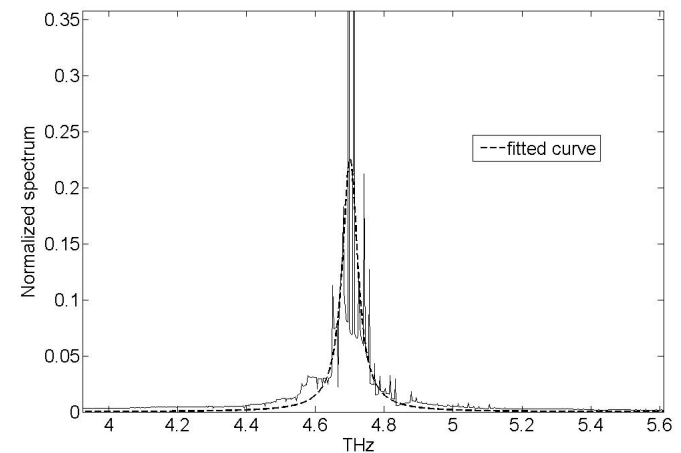
$$k = \sum_s \int_{\mathbf{q}} v_{\mathbf{q},s}^2 C_{\mathbf{q},s} \tau_{\mathbf{q},s} d\mathbf{q}$$

$\tau_{\mathbf{q},s}$: Phonon life time

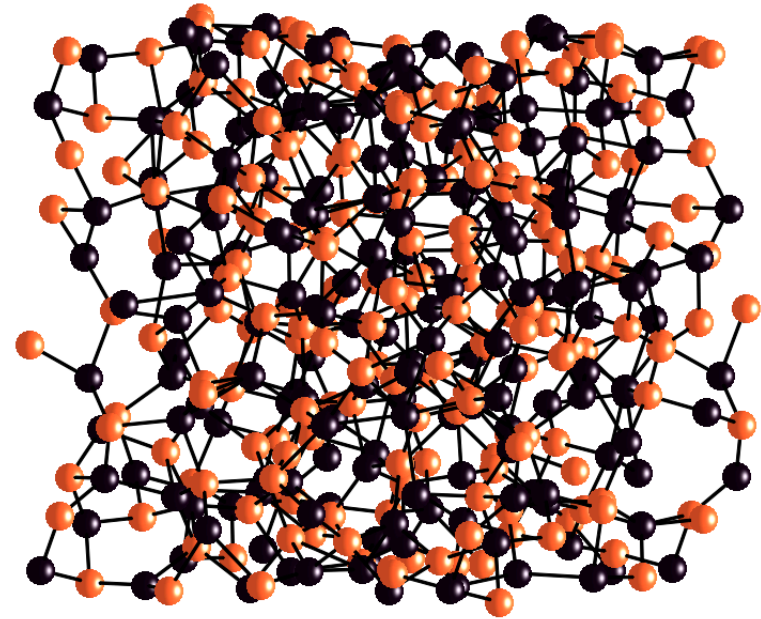
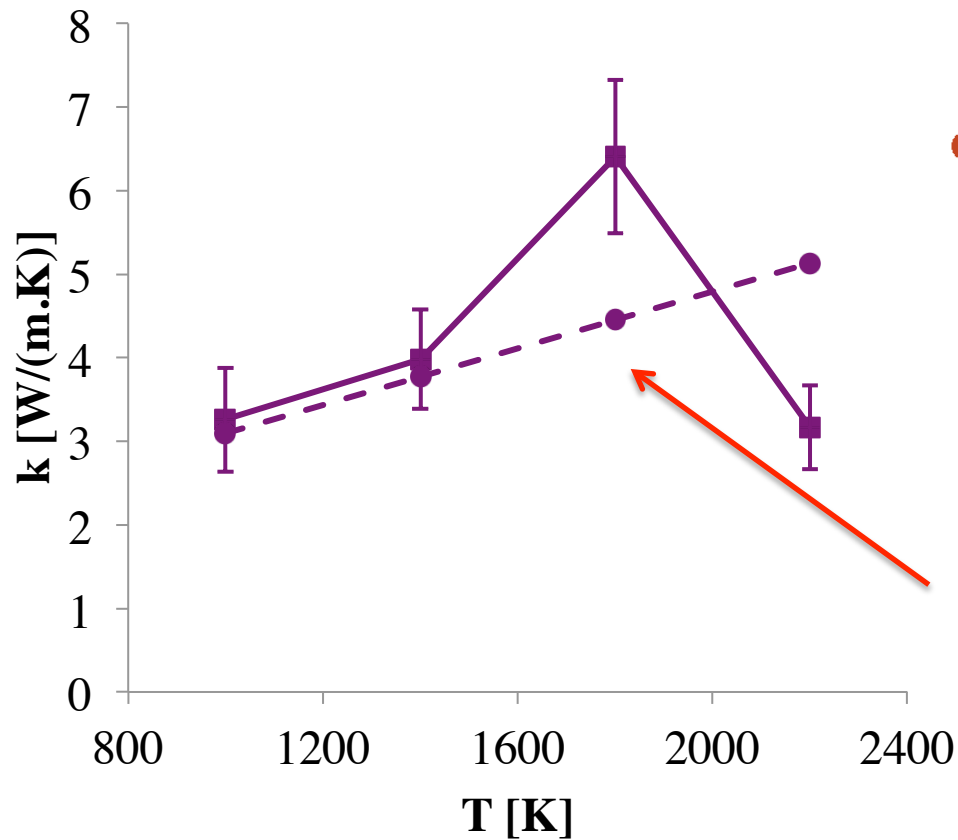
$C_k(\mathbf{q},\vartheta)$: Spectral density of the autocorrelation of velocity modes in reciprocal space

Computational Procedure:

- 100.000 step (50 ps) ab-initio MD-simulation
- analysis, auto-correlation & peak fitting

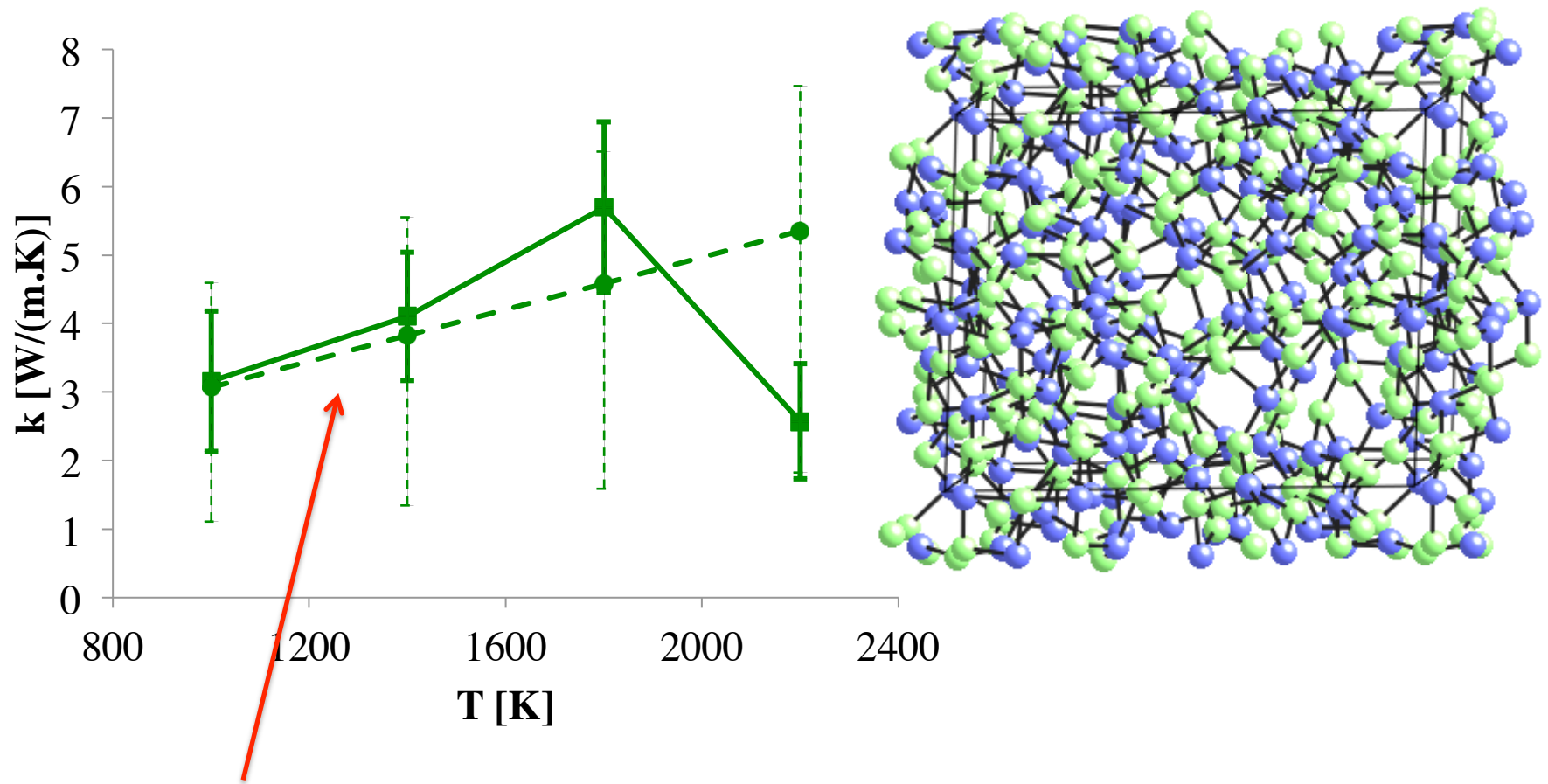


Thermal conductivity, a-SiC



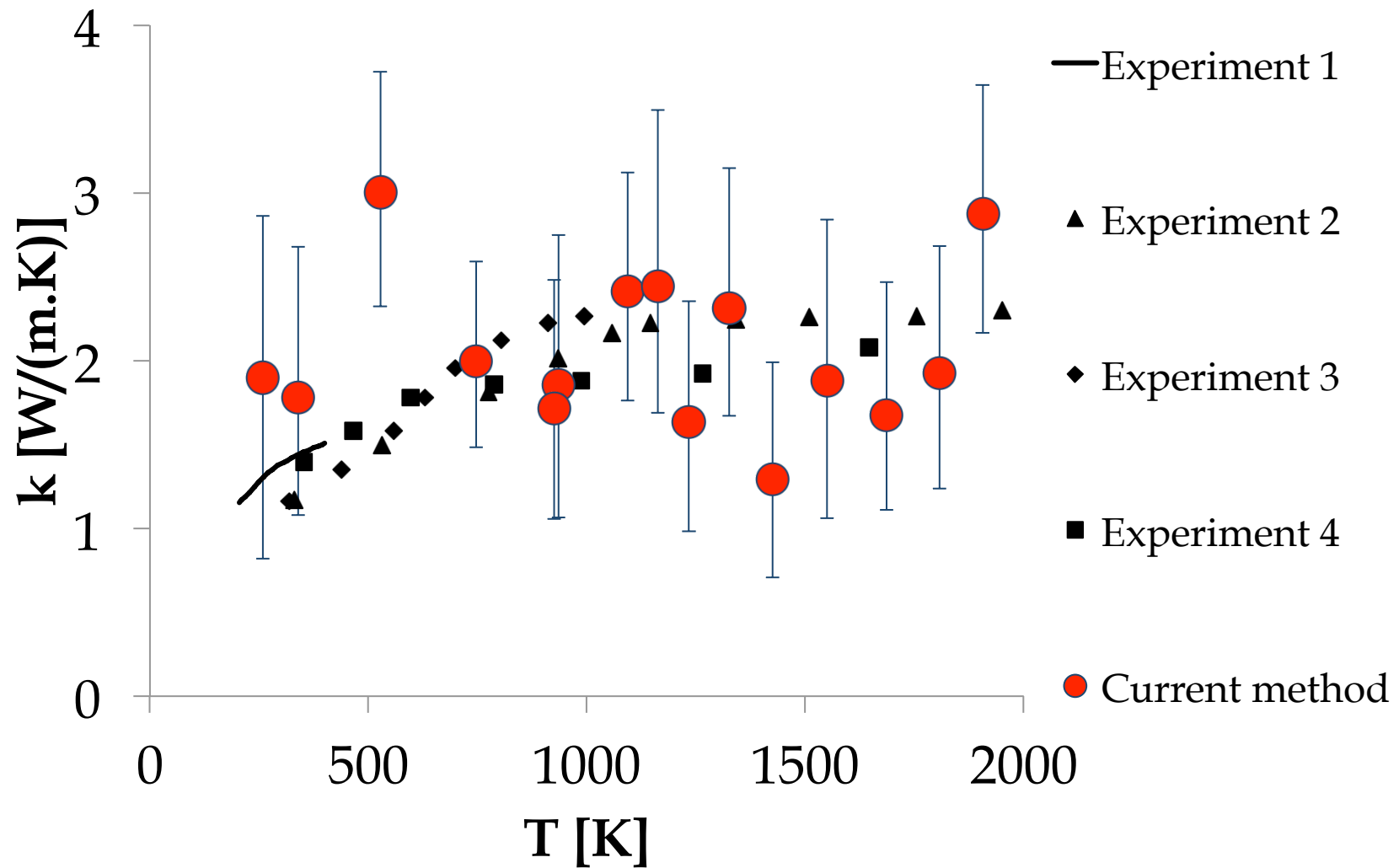
extrapolated from exp. data
at lower temperature
(Brennan 1982)

Thermal conductivity, α - Si_3N_4

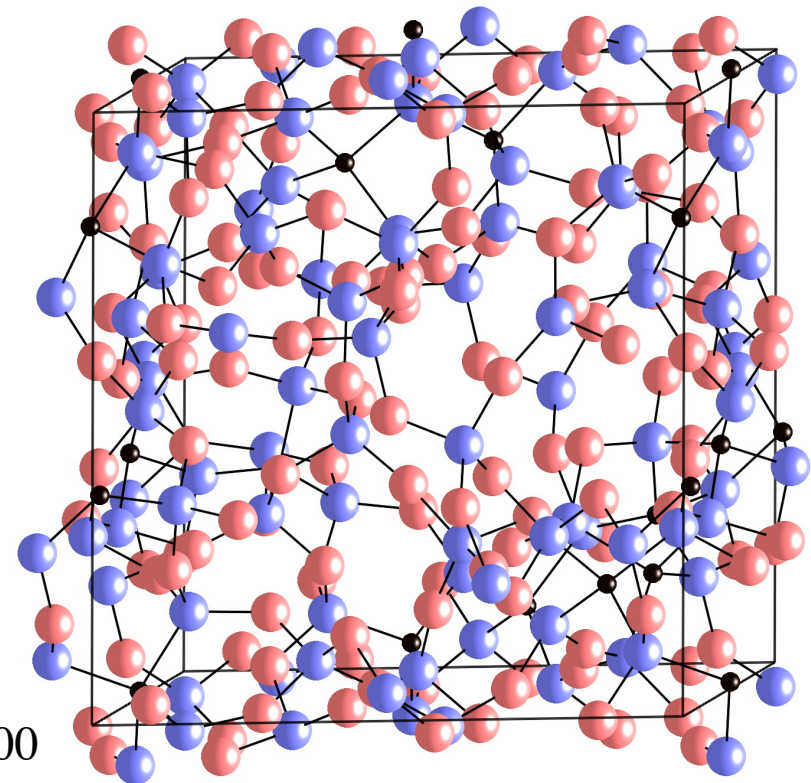
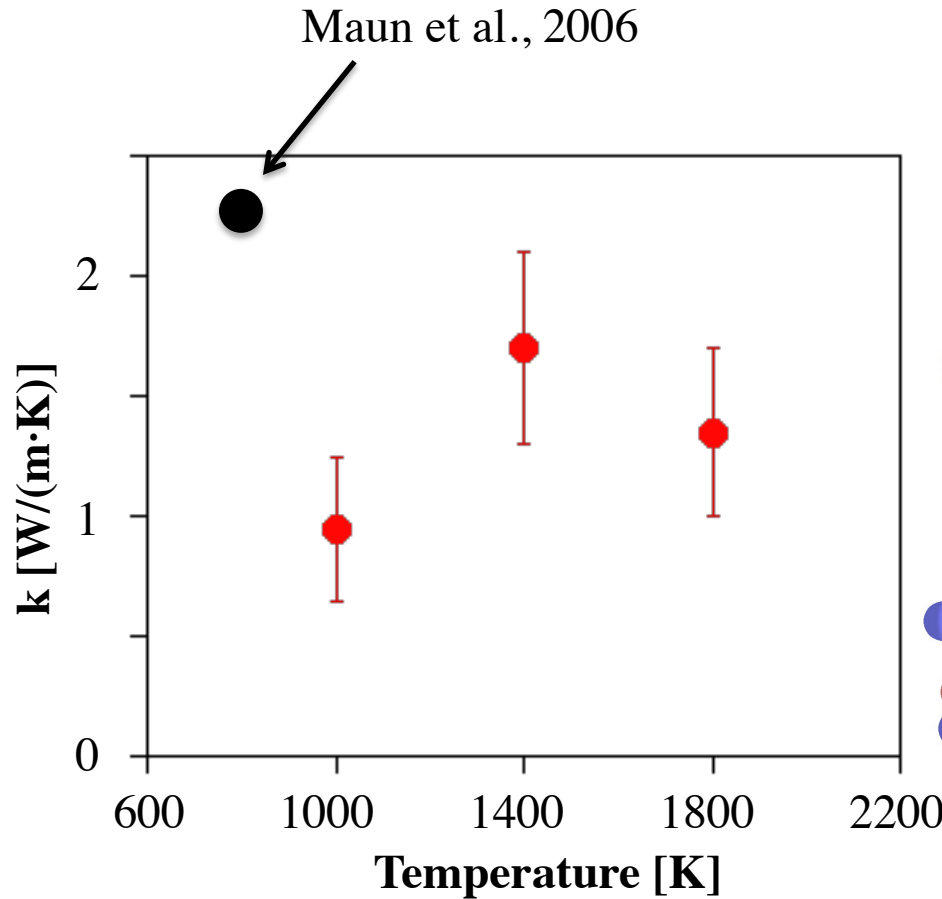


Exp data extrapolated; Zink, Hellman, 2004

Thermal conductivity, a-SiO₂



Thermal conductivity, a-SiCO

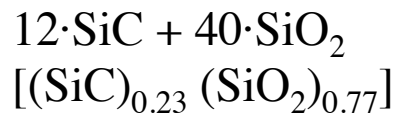
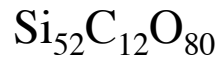
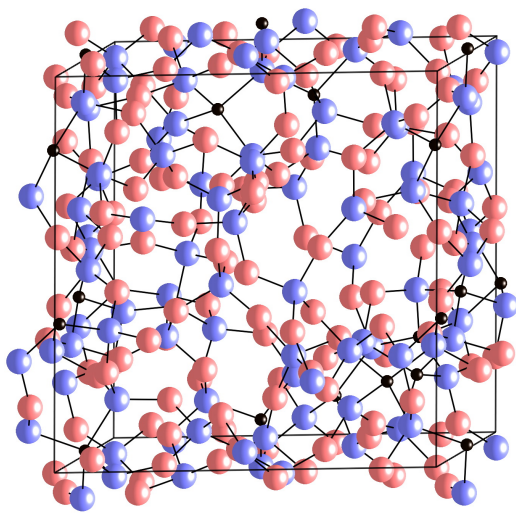


$\text{Si}_{52}\text{C}_{12}\text{O}_{80}$ – “glass”

- no “rule of mixture”

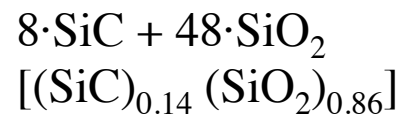
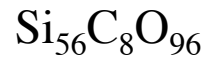
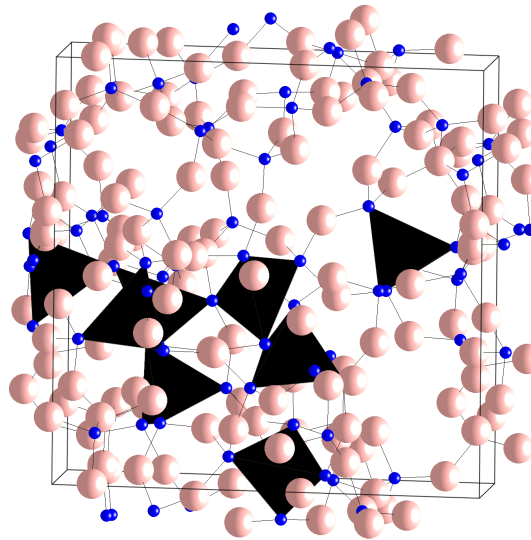
Comparison of a-SiCO model structures

“stoichiometric” SiCO



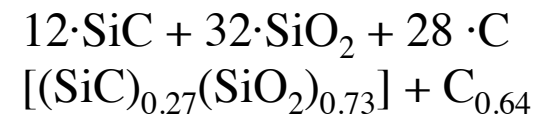
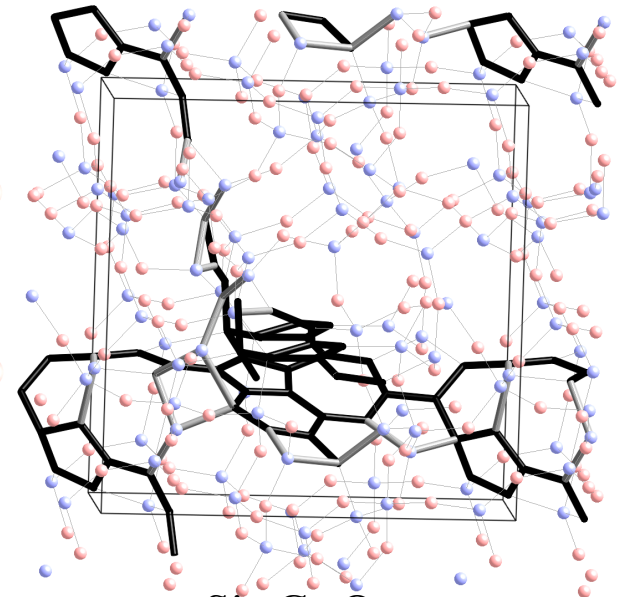
0.8 +/- 0.3

k [W/(m·K)] @ ~ 1000 K



0.9 +/- 0.3

SiCO with “free” C



5.5 +/- 1.9

strong anisotropic

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