SiO_2 activity measurements in the Gd_2O_3-SiO_2 system via Knudsen Effusion Mass Spectrometry (KEMS)

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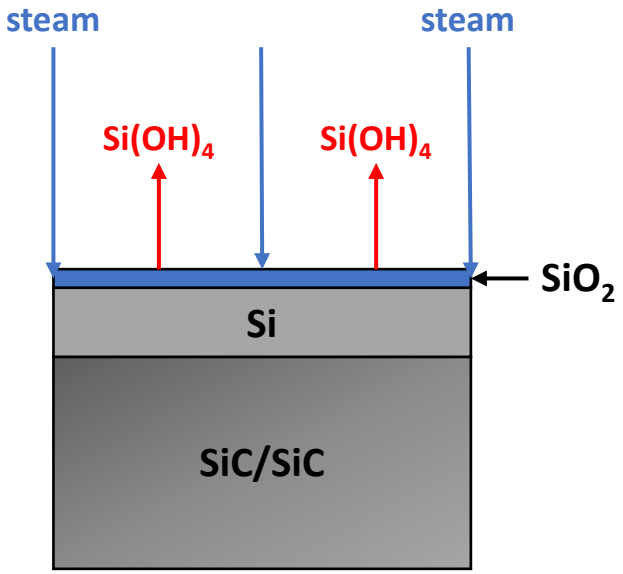
Background

- Rare earth silicates ($RE_2Si_2O_7$, RE_2SiO_5) are currently being utilized as topcoat materials for current-generation environmental barrier coatings (EBCs)
- The *primary* role of the topcoat is to act as a recession barrier



$$SiO_2 + 2H_2O(g) \rightarrow Si(OH)_4(g)$$

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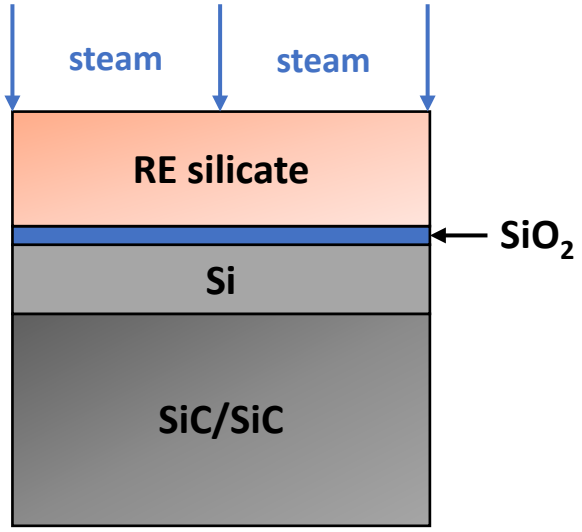

$$SiO_2 + 2H_2O(g) \rightarrow Si(OH)_4(g)$$

$$RE_2Si_2O_7 + 2H_2O(g) \rightarrow RE_2SiO_5 + Si(OH)_4(g)$$

$$RE_2SiO_5 + 2H_2O(g) \rightarrow RE_2O_3 + Si(OH)_4(g)$$

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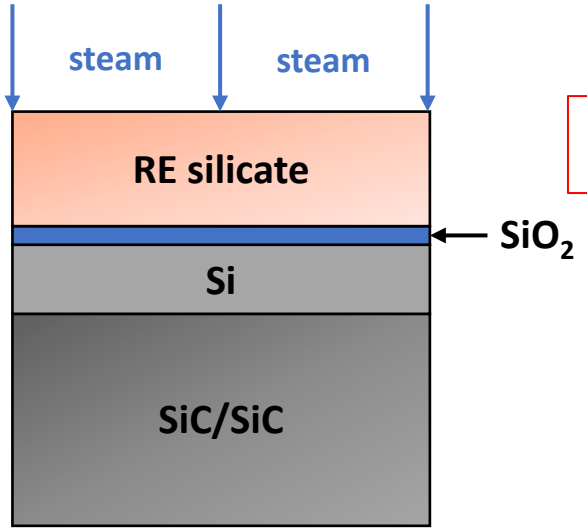
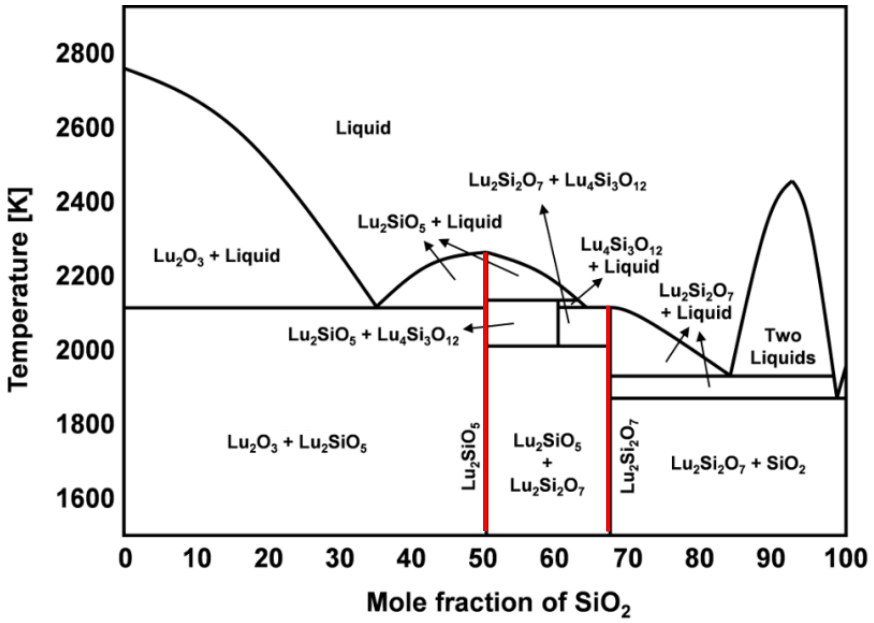


RE silicates are also subject to recession in water vapor.

$$RE_2Si_2O_7 + 2H_2O(g) \rightarrow RE_2SiO_5 + Si(OH)_4(g)$$
$$RE_2SiO_5 + 2H_2O(g) \rightarrow RE_2O_3 + Si(OH)_4(g)$$

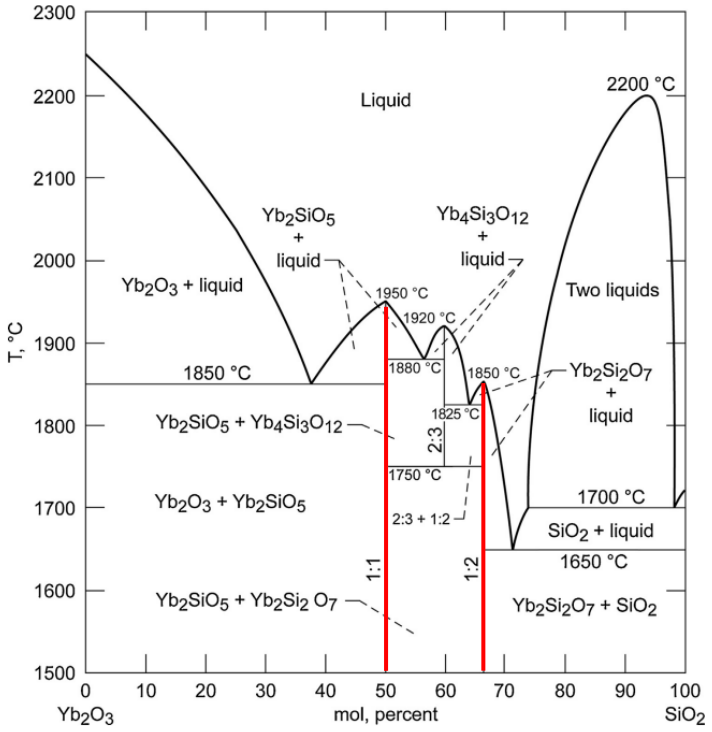
Motivation

RE = Lu



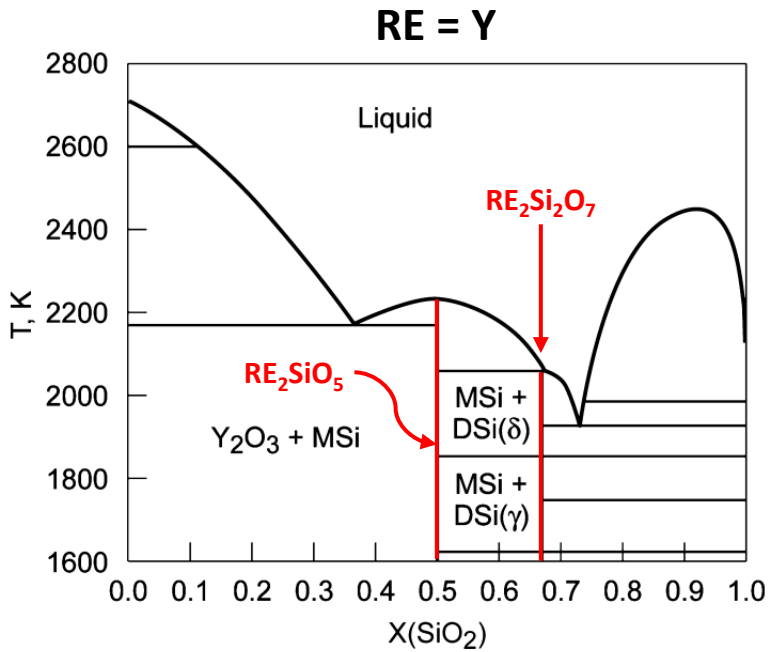
Kowalski et al. *J. Chem. Thermodyn.* (2021).

RE = Yb



Costa and Jacobson. *J. Eur. Ceram. Soc.* (2015).

RE = Y

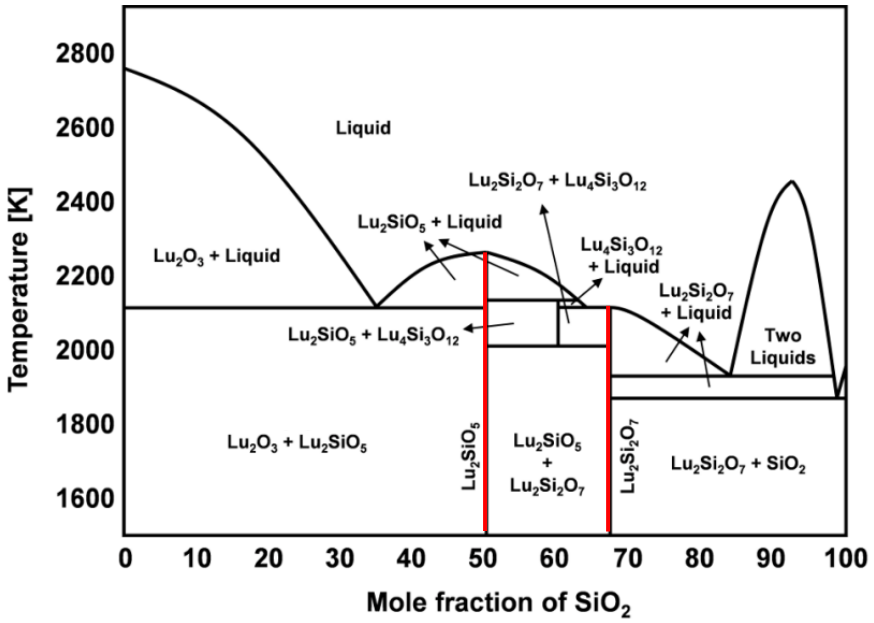


Jacobson. *J. Am. Ceram. Soc.* (2014).

The activity of SiO_2 (a_{SiO_2}) has been measured in some $RE_2Si_2O_7$ and RE_2SiO_5 materials.

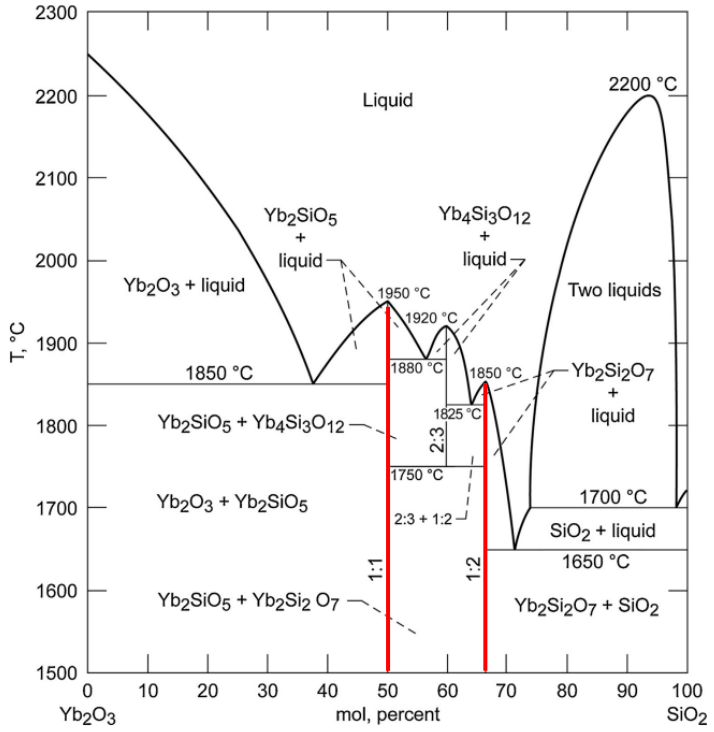
Motivation

RE = Lu



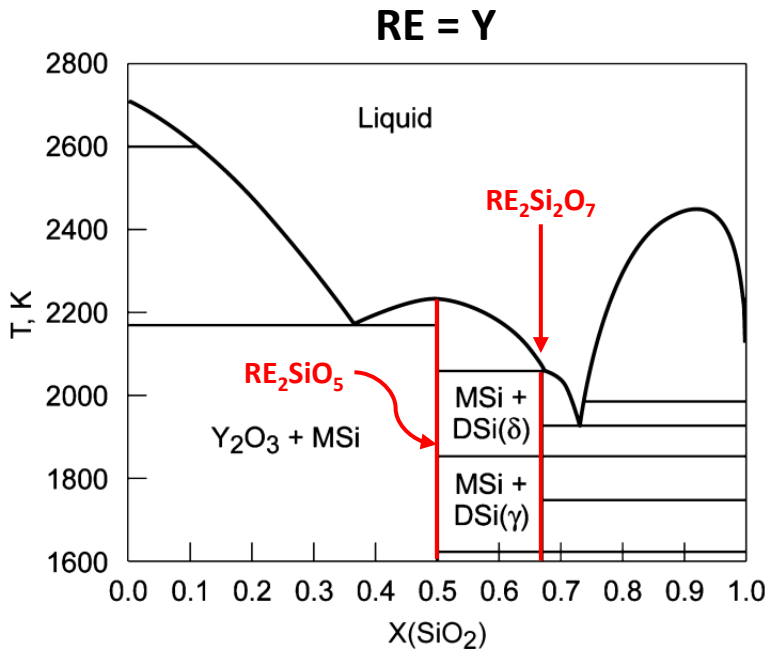
Kowalski et al. *J. Chem. Thermodyn.* (2021).

RE = Yb



Costa and Jacobson. *J. Eur. Ceram. Soc.* (2015).

RE = Y

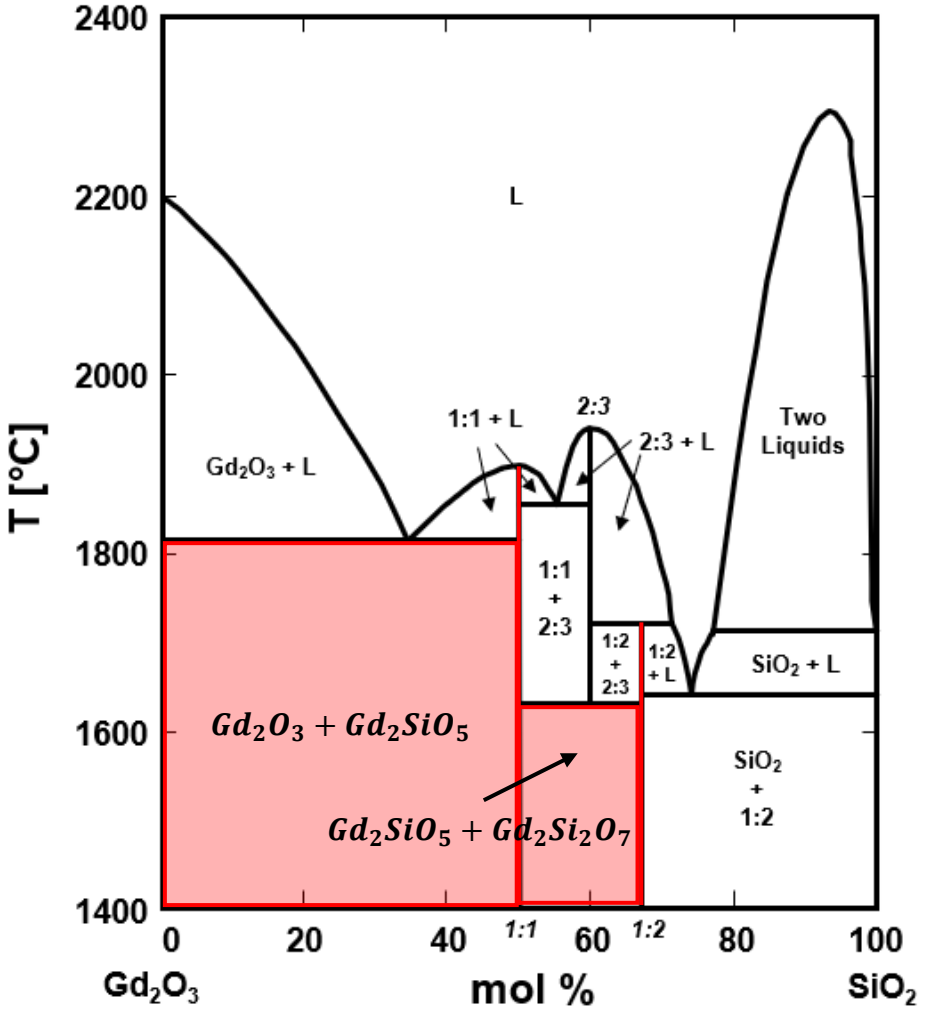


Jacobson. *J. Am. Ceram. Soc.* (2014).

Measuring a_{SiO_2} can help us understand viability of RE silicate topcoat as a recession barrier.

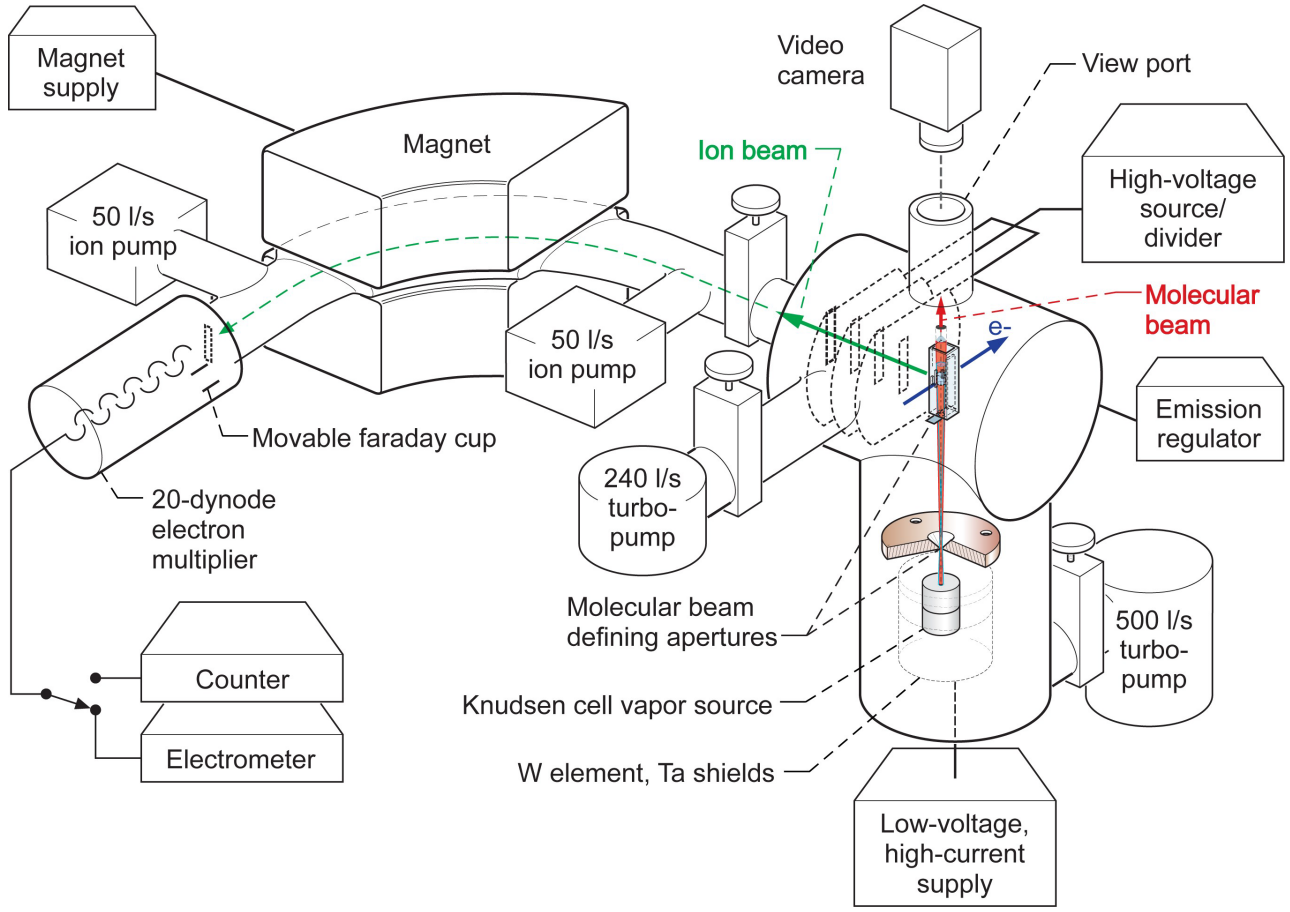
Objective

- Measure a_{SiO_2} within the Gd_2O_3-SiO_2 system via Knudsen Effusion Mass Spectrometry (KEMS)
- Analyze Gd_2O_3-Gd_2SiO_5 and Gd_2SiO_5-$Gd_2Si_2O_7$ phase regions, as expected below ≈1600°C



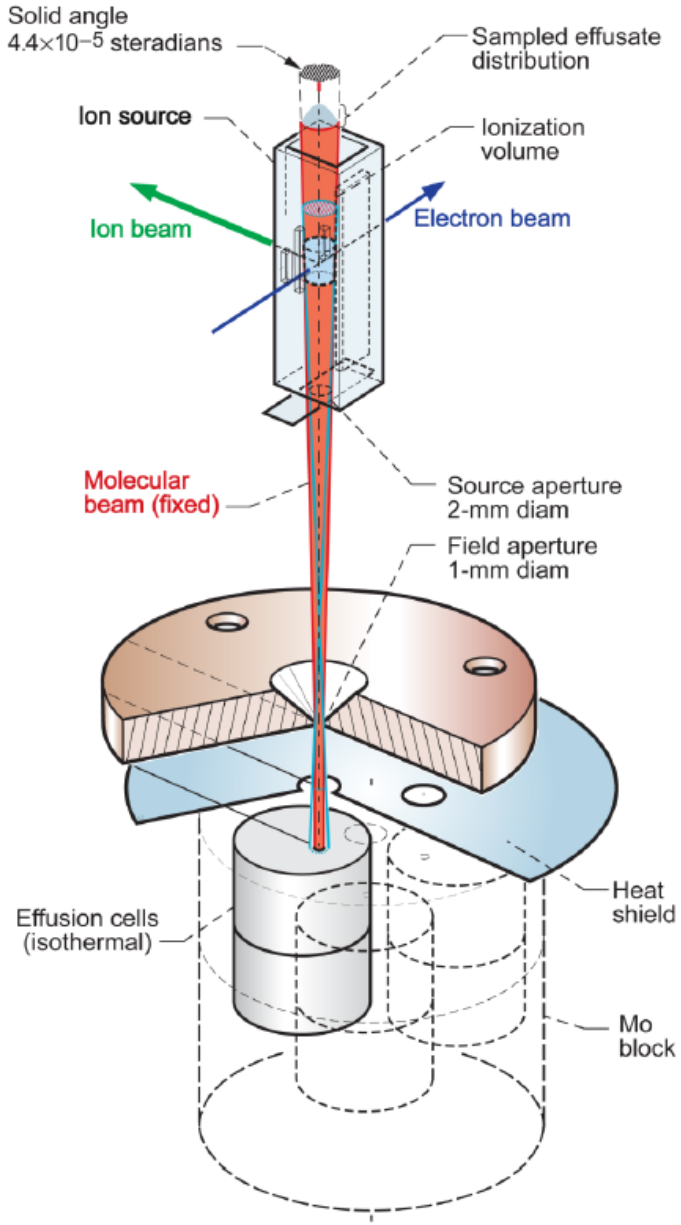
Experimental

- Modified Nuclide type 12-HT-90 KEMS system



Experimental

- Three-cell flange configuration with X/Y translation
  - Au = temperature calibration
  - SiO_2 = composition calibration
  - Gd silicate mixture = sample
- Resistive heating up to ≈1500°C under vacuum
- Mo or Ta added to SiO_2 and/or Gd silicate mixture as reducing agent
  - Cells consist of Mo or Ta → no contamination issues



Calculations

- Mo added to SiO_2 and Gd silicate mixture as reducing agent

$$3SiO_2(sample\ or\ SiO_2\ alone) + Mo \rightarrow 3SiO(g) + MoO_3(g)$$

$$K = \frac{[I_{SiO}]^3[I_{MoO_3}]}{[a_{SiO_2}]^3[a_{Mo}]}$$

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$$K^{*} = \underbrace{\frac{[I^{*}_{SiO}]^3[I^{*}_{MoO_3}]}{[a_{SiO_2}]^3[1]}}_{sample}$$

$$a_{SiO_2} = \left\{\frac{[I^{*}_{SiO}]^3[I^{*}_{MoO_3}]}{[I^{\circ}_{SiO}]^3[I^{\circ}_{MoO_3}]}\right\}^{\frac{1}{3}}$$

Calculations

- Ta added to Gd silicate (Gd_2O_3-Gd_2SiO_5) mixture as reducing agent

$$3SiO_2(sample) + 2Ta \rightarrow 3SiO(g) + TaO(g) + TaO_2(g)$$

$$P_{SiO} = \frac{kI_{SiO}T}{\sigma_{SiO}(E)}$$

$k = calibration\ constant\ determined\ at\ invariant\ point\ of\ Au$

$\sigma_{SiO} = ionization\ cross\ section\ of\ SiO, function\ of\ ionizing\ electron\ energy\ (E)$

Partial pressures of SiO (g) were determined from experimental SiO intensity values.

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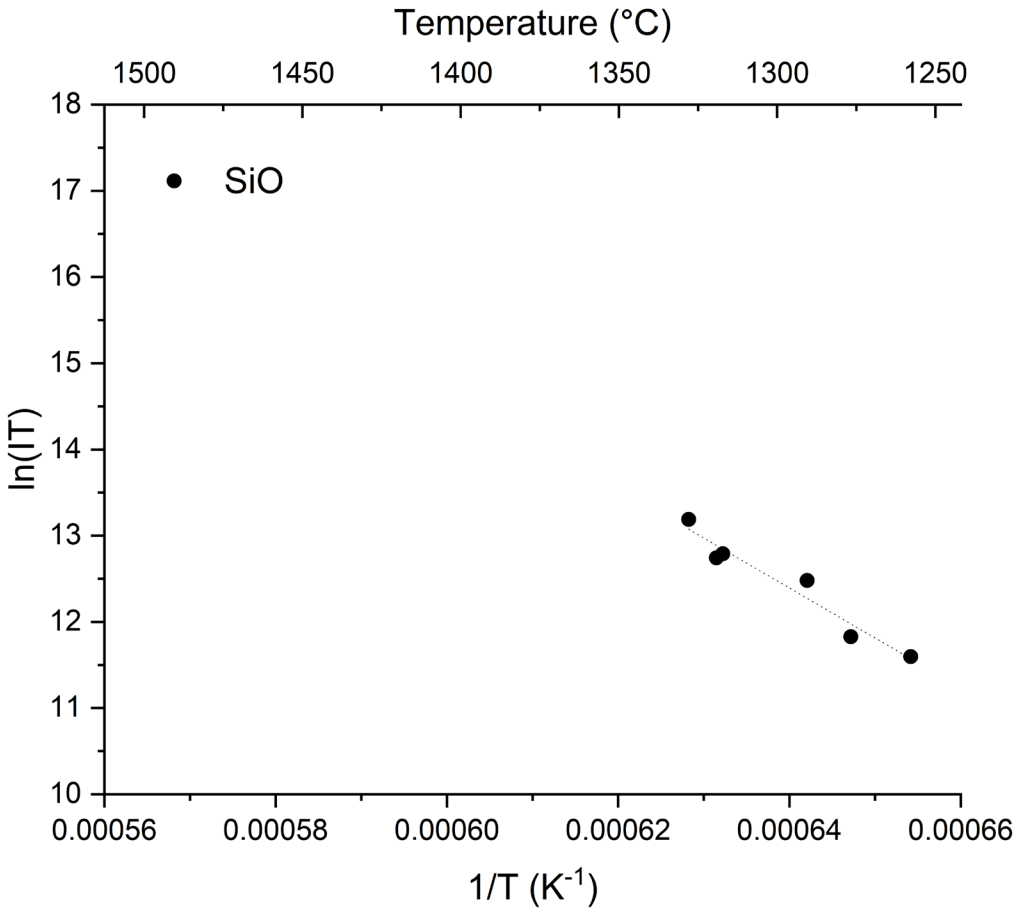
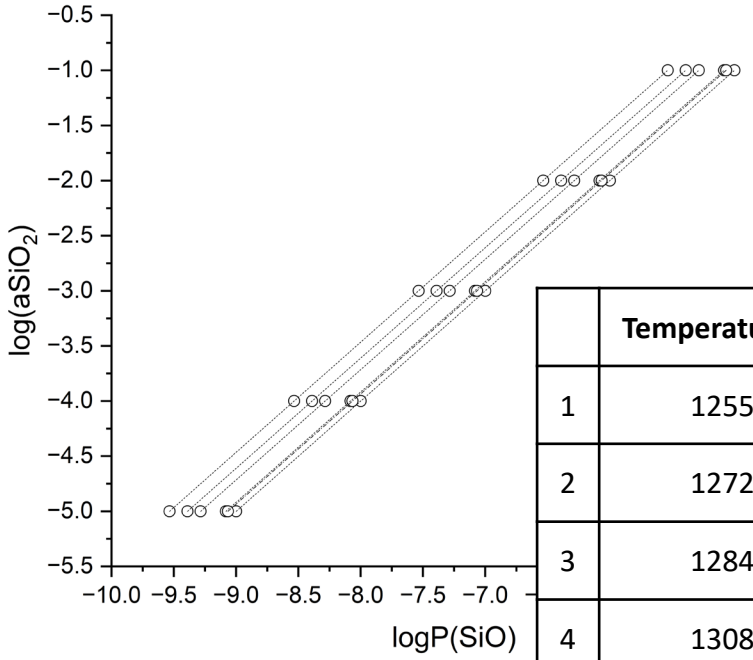
Partial pressures of SiO (g) then converted to a_{SiO_2} values using FactSage energy minimization software.

Results: $Gd_2O_3 + Gd_2SiO_5$ (+Ta)

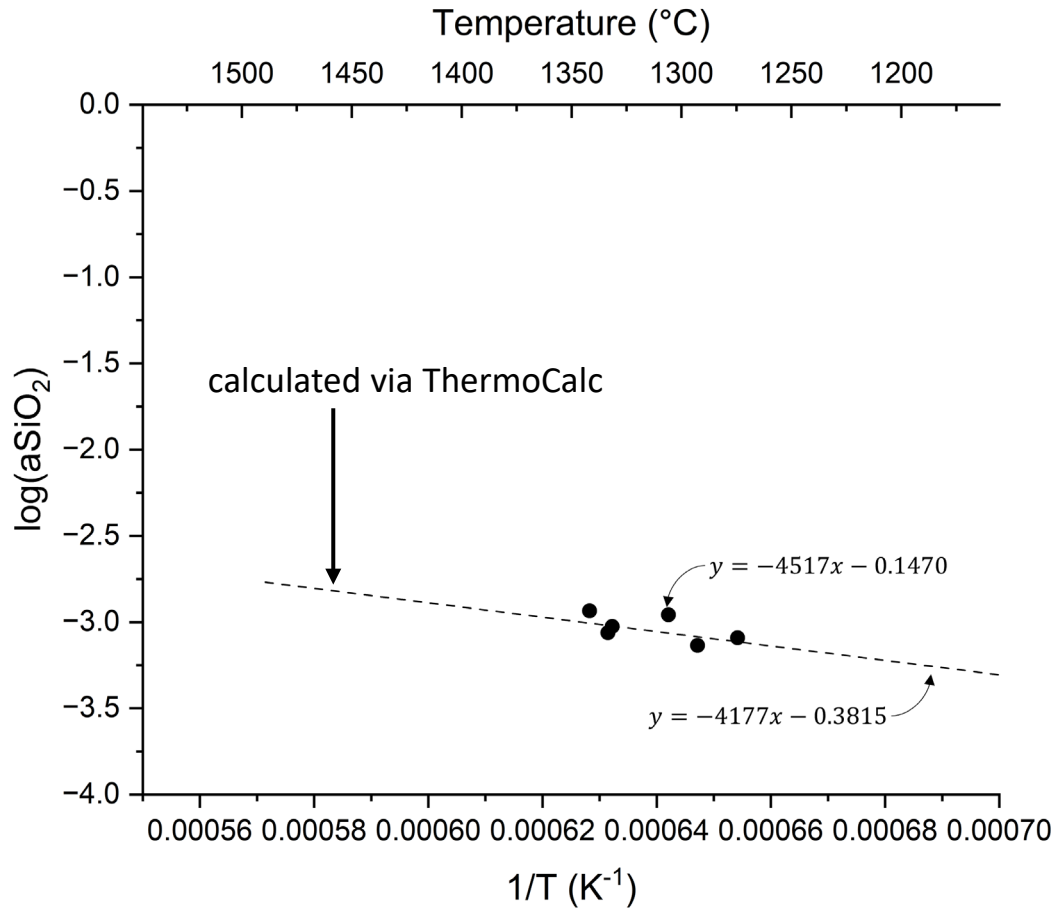




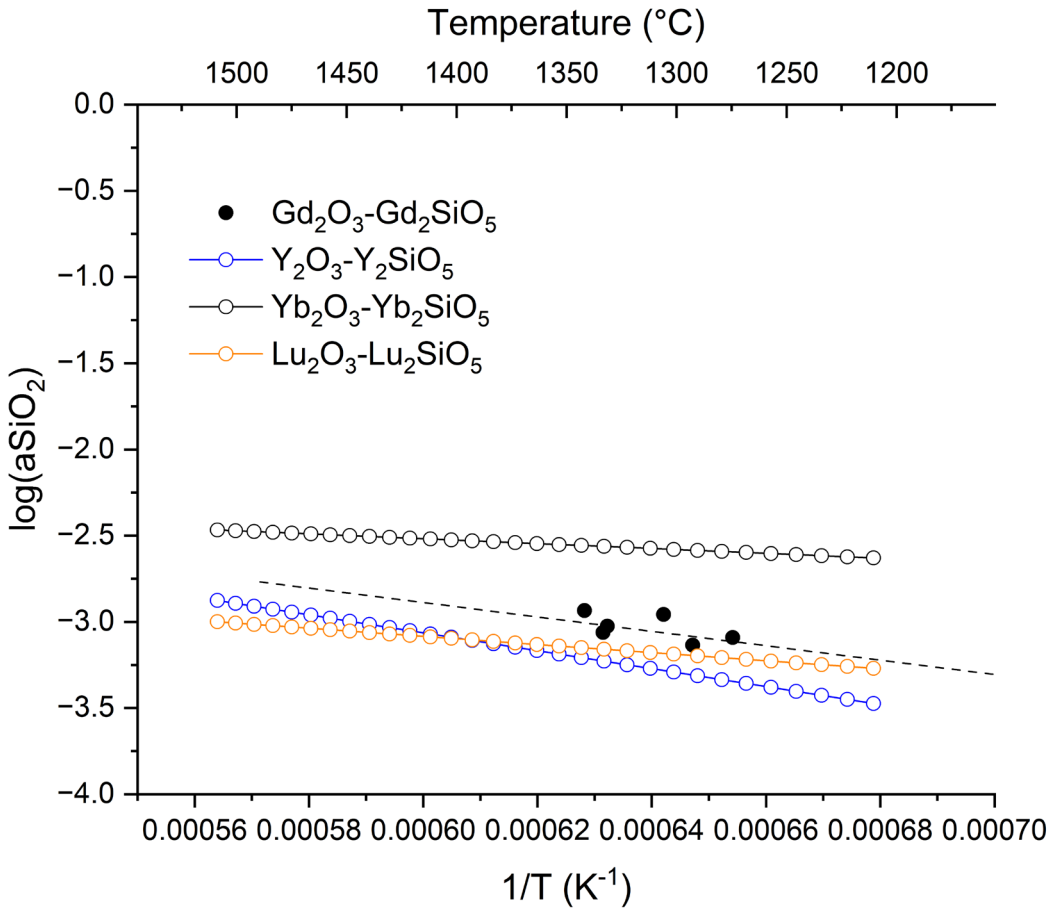
	Temperature (°C)	Intercept
1	1255.5	4.5342
2	1272.0	4.3896
3	1284.3	4.2845
4	1308.6	4.0813
5	1310.4	4.0657
6	1318.6	3.9989

$$P_{sio} = \frac{k I_{sio} T}{\sigma_{sio}(E)}$$

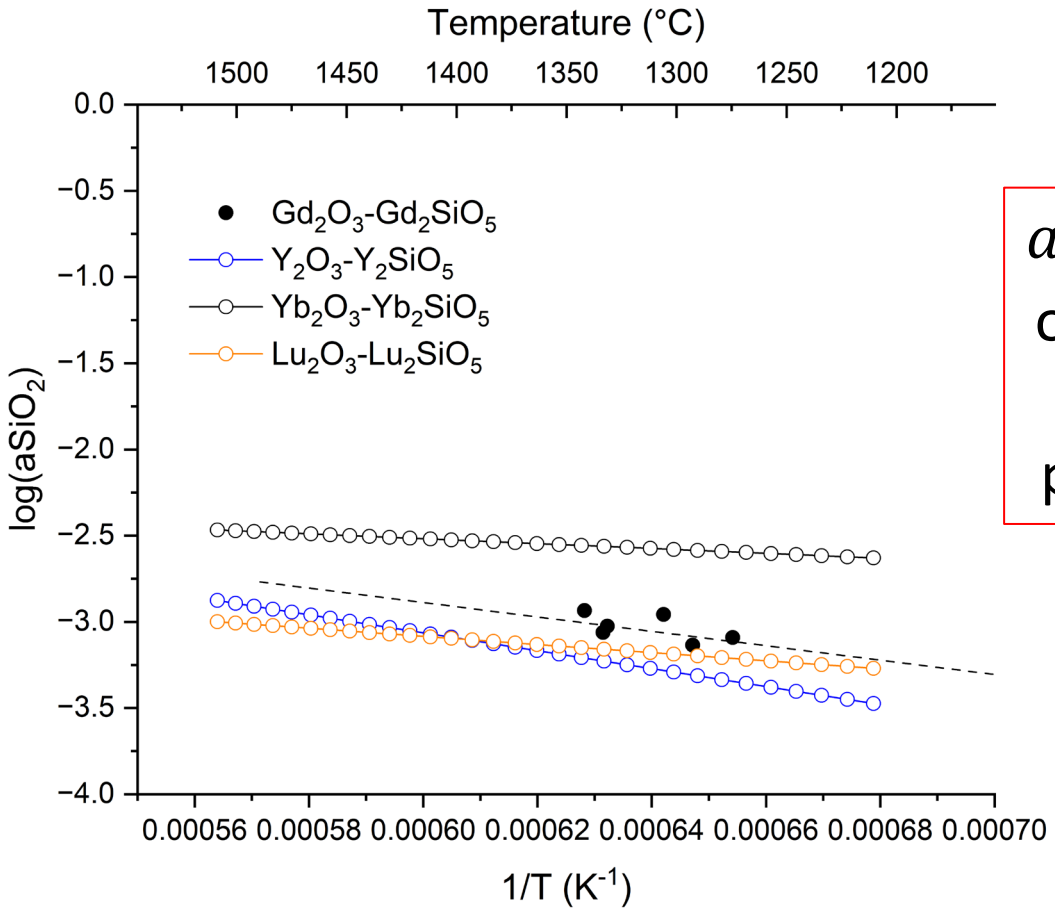
Results: Gd_2O_3 + Gd_2SiO_5 (+Ta)



Results: Comparing RE_2O_3 + RE_2SiO_5 (+Ta)

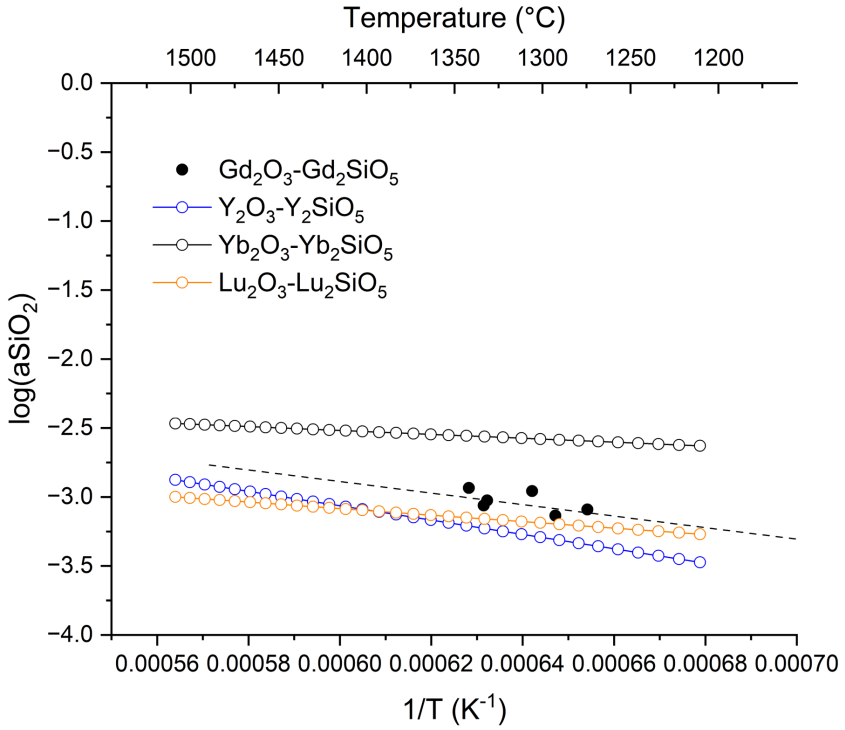


Results: Comparing RE_2O_3 + RE_2SiO_5 (+Ta)



a_{SiO_2} values are on the order of 0.001 – 0.005 for RE_2O_3-RE_2SiO_5 phase field at 1500°C.

Results: Comparing RE_2O_3 + RE_2SiO_5 (+Ta)



$$\Delta H_f^{ox}(RE_2SiO_5)@T = slope \times R \times 2.303$$

Jacobson. *J. Am. Ceram. Soc.* (2014).

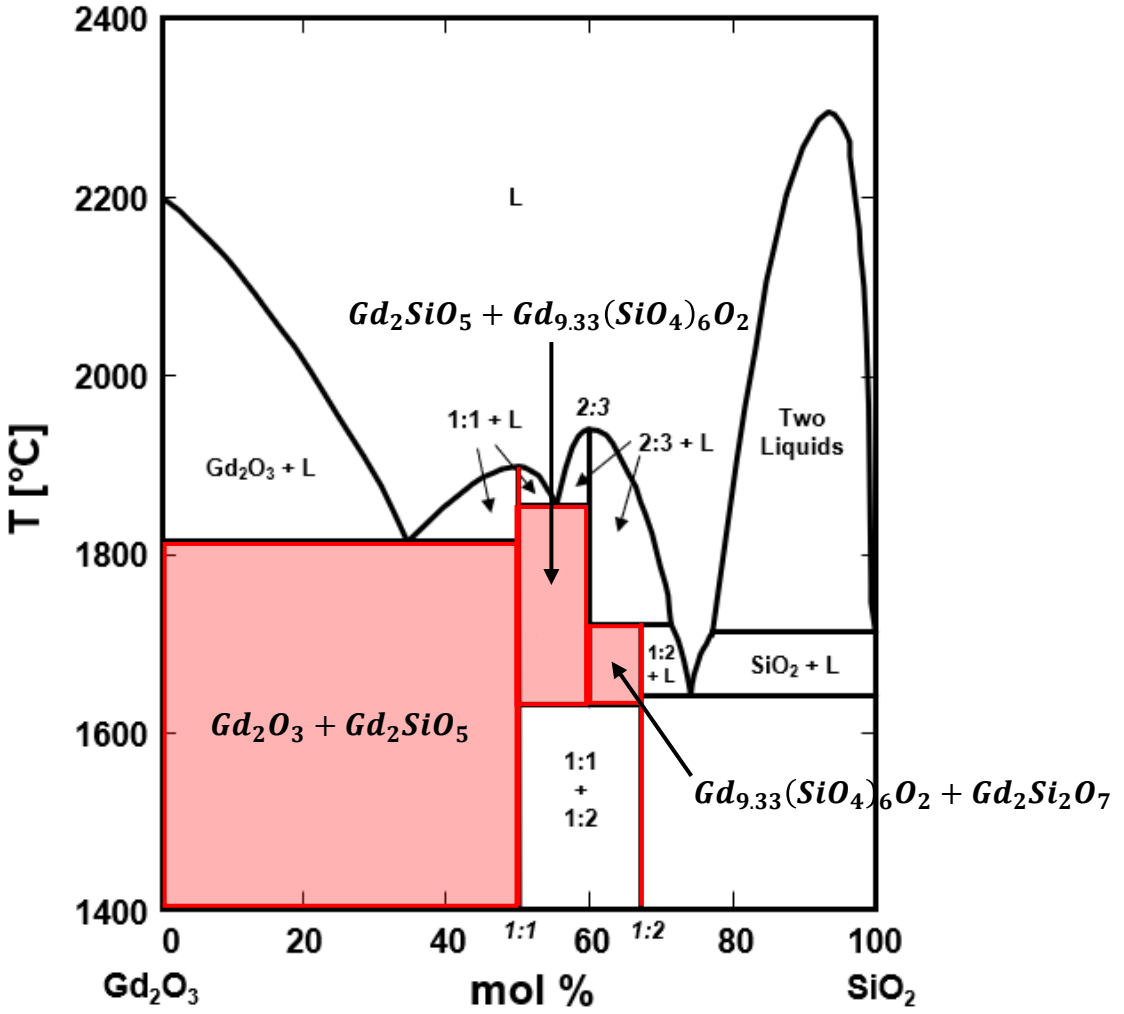
Costa and Jacobson. *J. Eur. Ceram. Soc.* (2015).

Kowalski et al. *J. Chem. Thermodyn.* (2021).

	RE = Gd	**RE = Y**	**RE = Yb**	**RE = Lu**
ΔH_f^{ox} (RE_2SiO_5; kJ/mol) @ T	-86.5 (Ta, 1565 K)	-99.6 ± 5 (Ta, 1600 K)	-27.0 ± 2 (Ta, 1562 K)	-45.0 ± 3 (Ta, 1550 K)
ΔH_f^{ox} (RE_2SiO_5; kJ/mol) @ 298 K	-98	-93.8	-56.9	-46.1
ΔH_f^{el} (RE_2SiO_5; kJ/mol) @ 298 K	-2825.7	-2904 ± 16	-2774 ± 11	-2831.1 ± 12

Results: Predominance of apatite phase

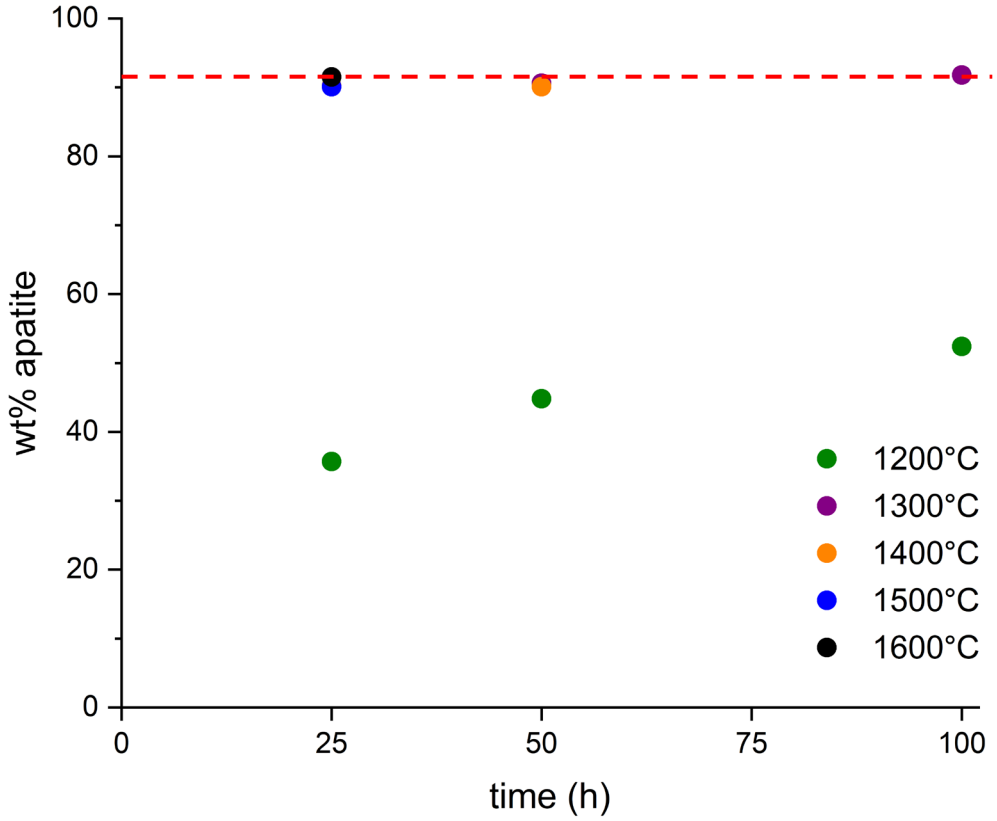
- Gd_2SiO_5 + $Gd_2Si_2O_7$ phase mixture was not able to be prepared
- Gd_2SiO_5 + $Gd_{9.33}(SiO_4)_6O_2$ and $Gd_{9.33}(SiO_4)_6O_2$ + $Gd_2Si_2O_7$ formed within temperature region of interest instead

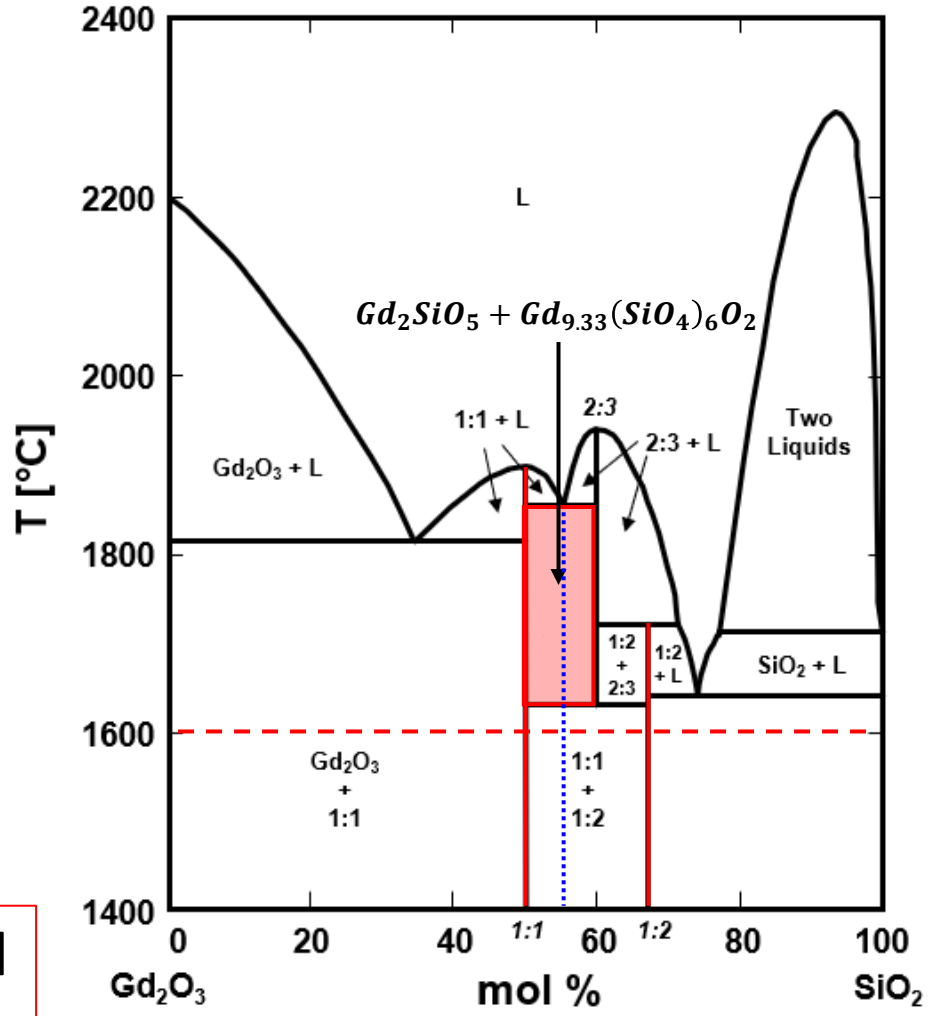


Results: Predominance of apatite phase

- Gd_2O_3-SiO_2 mixtures within the Gd_2SiO_5 + $Gd_{9.33}(SiO_4)_6O_2$ and $Gd_{9.33}(SiO_4)_6O_2$ + $Gd_2Si_2O_7$ phase regions prepared and heat treated between 1200 and 1600°C for up to 100 h
- X-ray diffraction (XRD) performed to determine phases

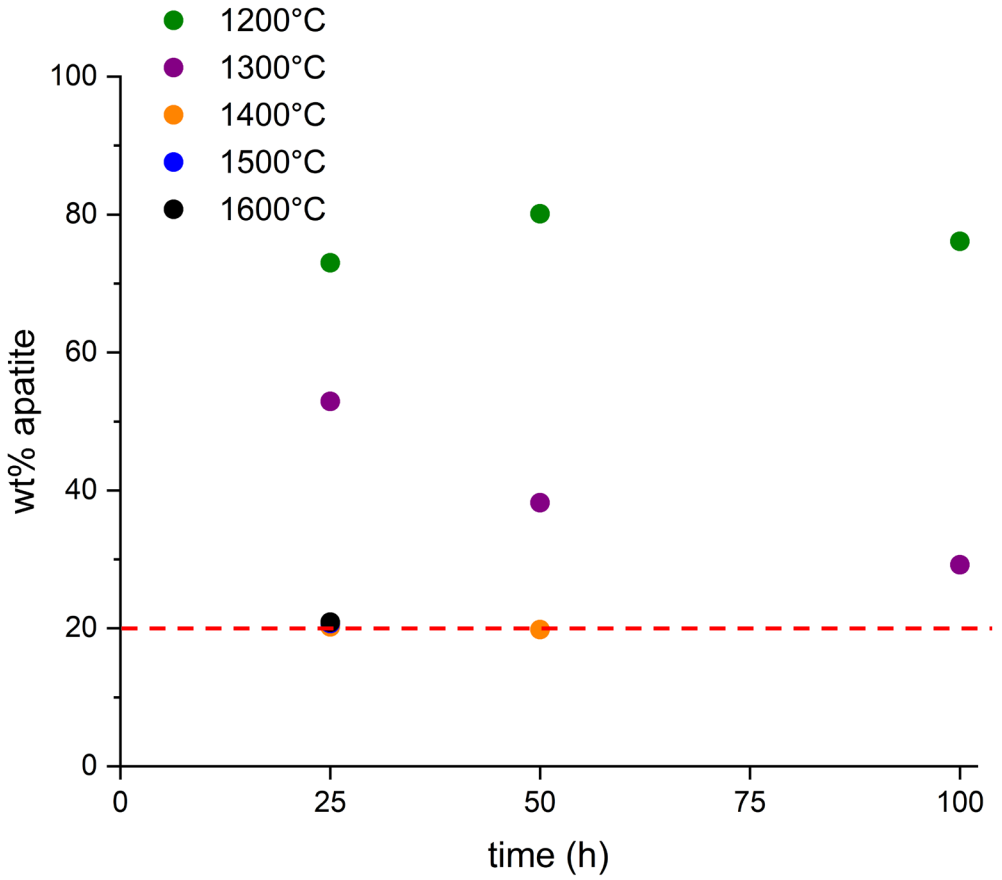
Results: Predominance of apatite phase

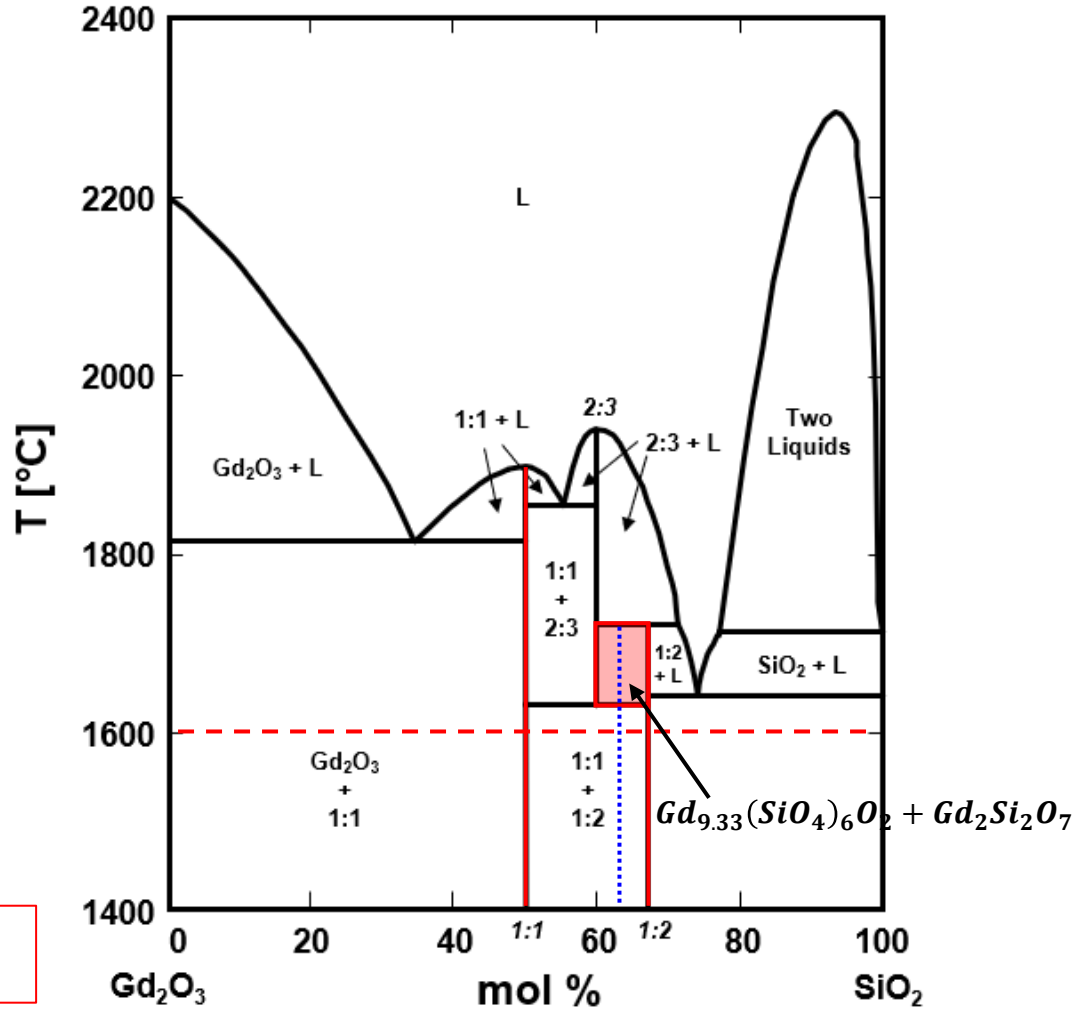




$Gd_2SiO_5 + Gd_{9.33}(SiO_4)_6O_2$ phase equilibrium reached by 1300°C, 25 h.

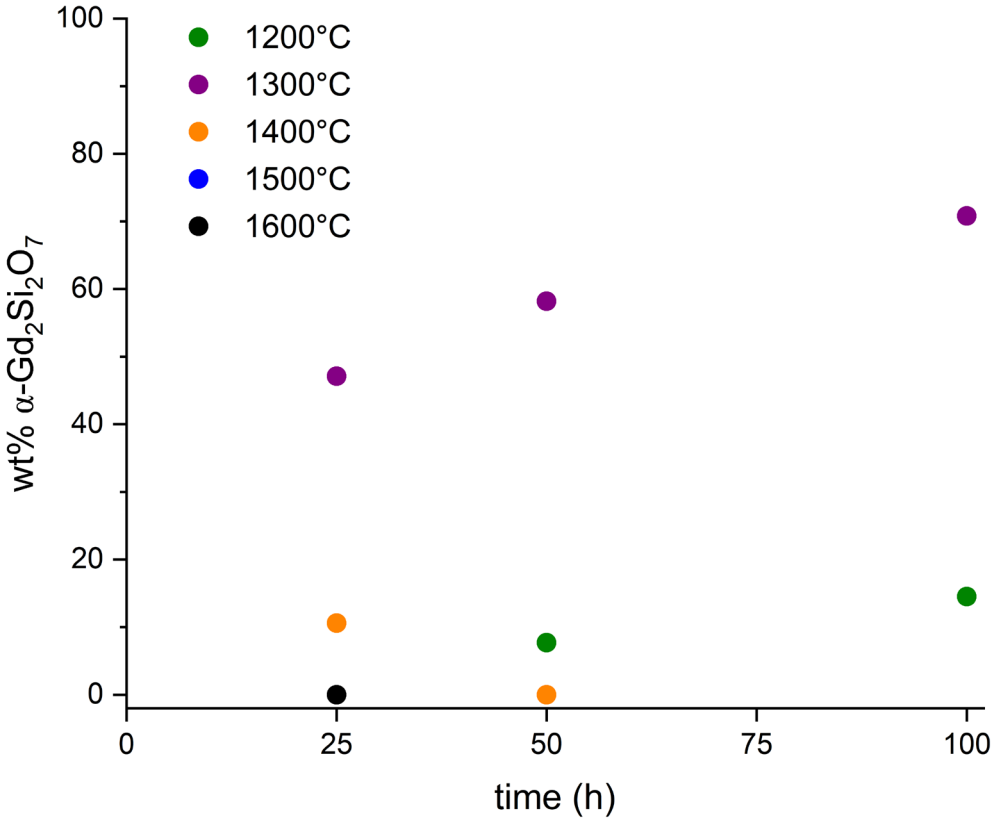
Results: Predominance of apatite phase

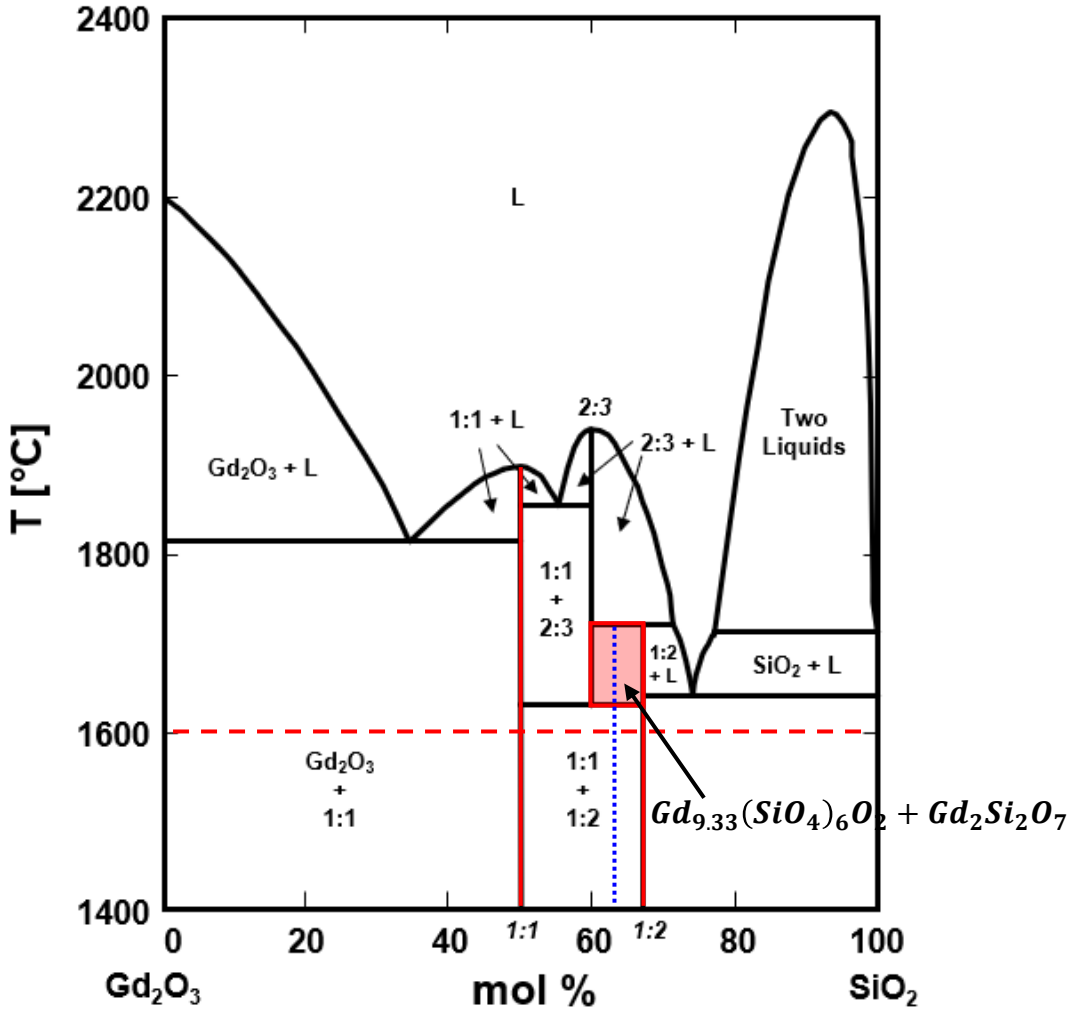




$Gd_{9.33}(SiO_4)_6O_2$ content stabilizes by 1400°C, 25 h.

Results: Predominance of apatite phase





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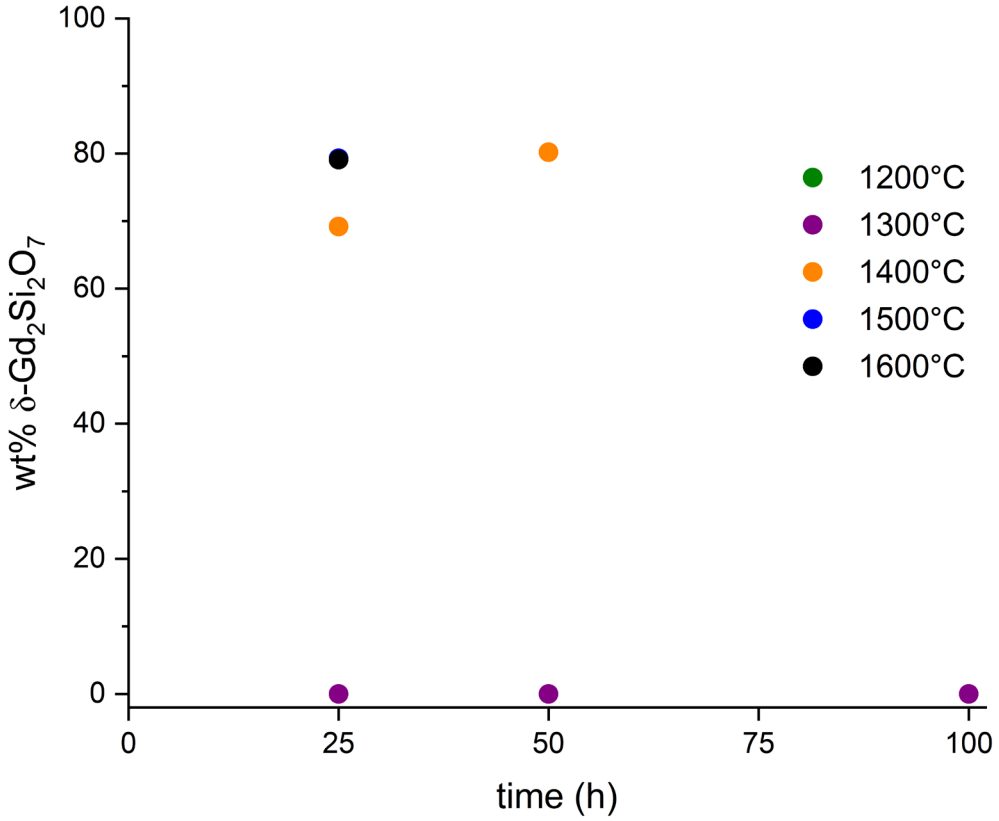
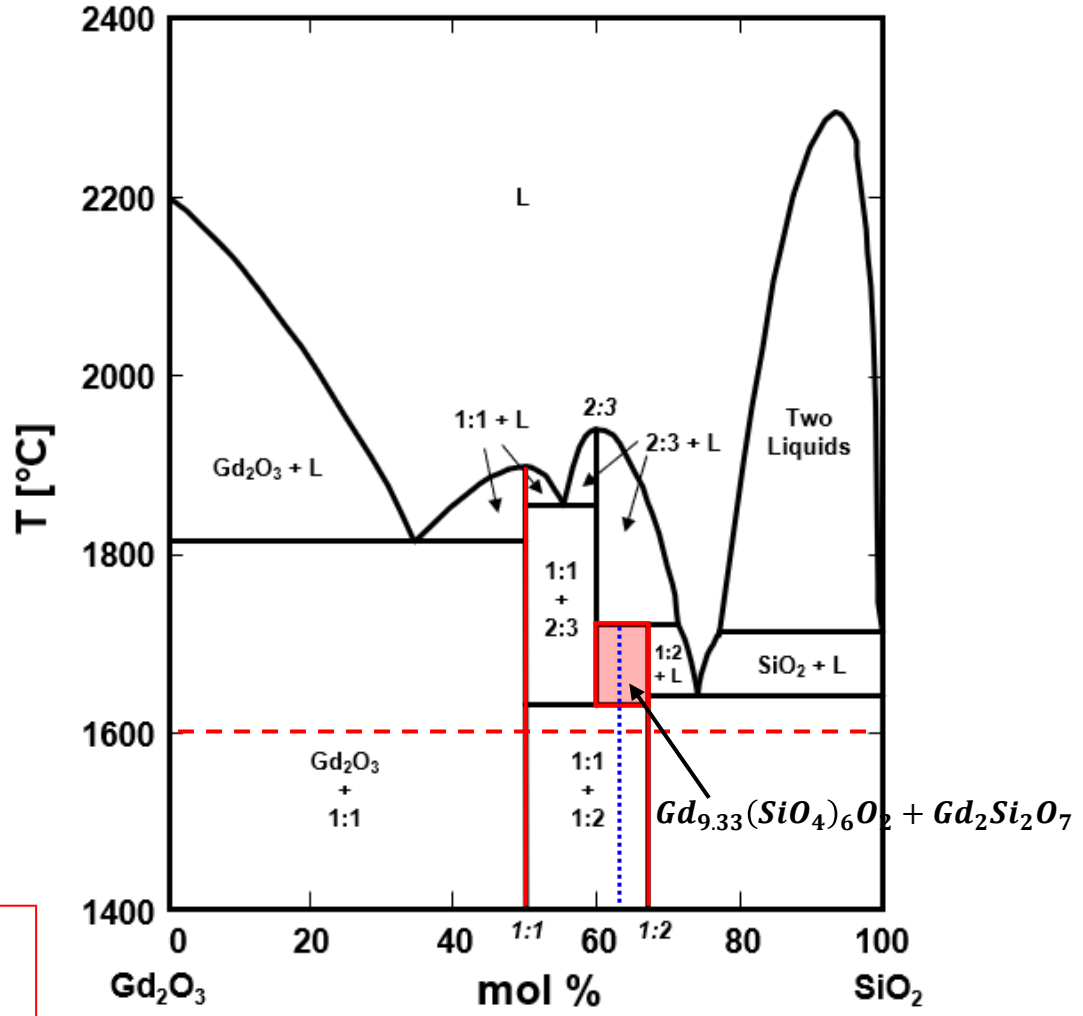
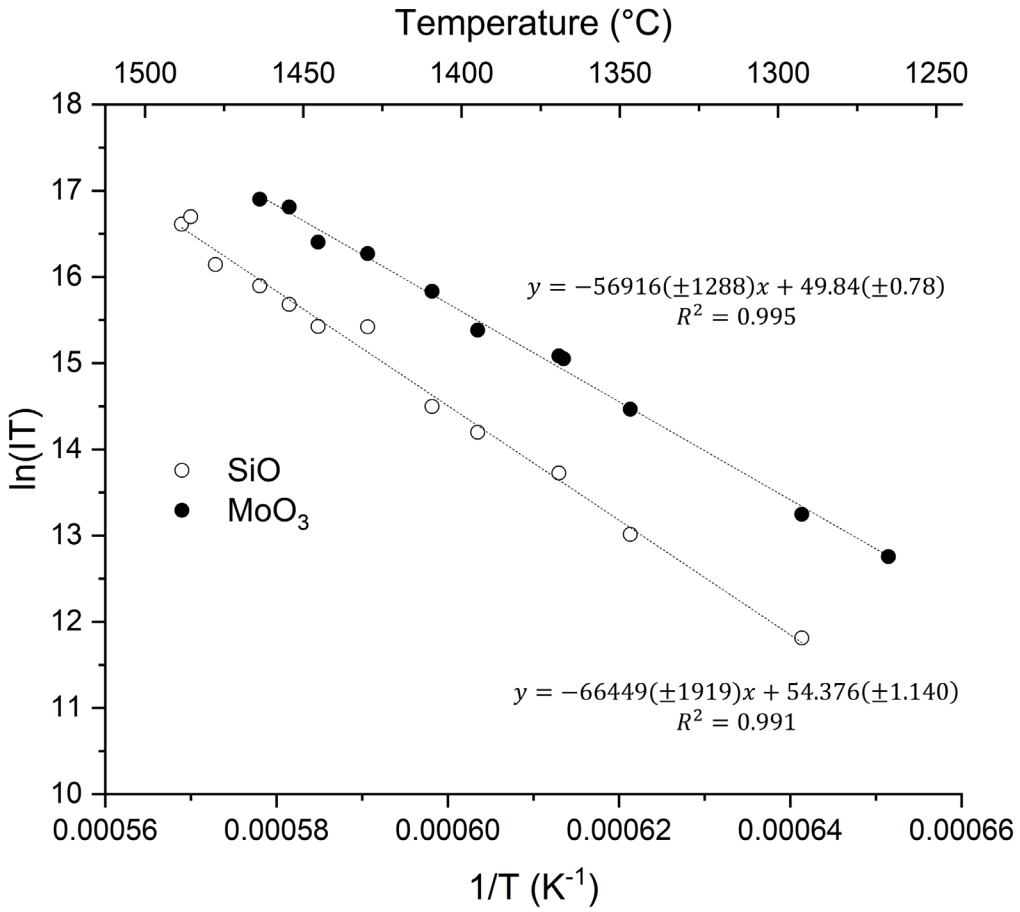




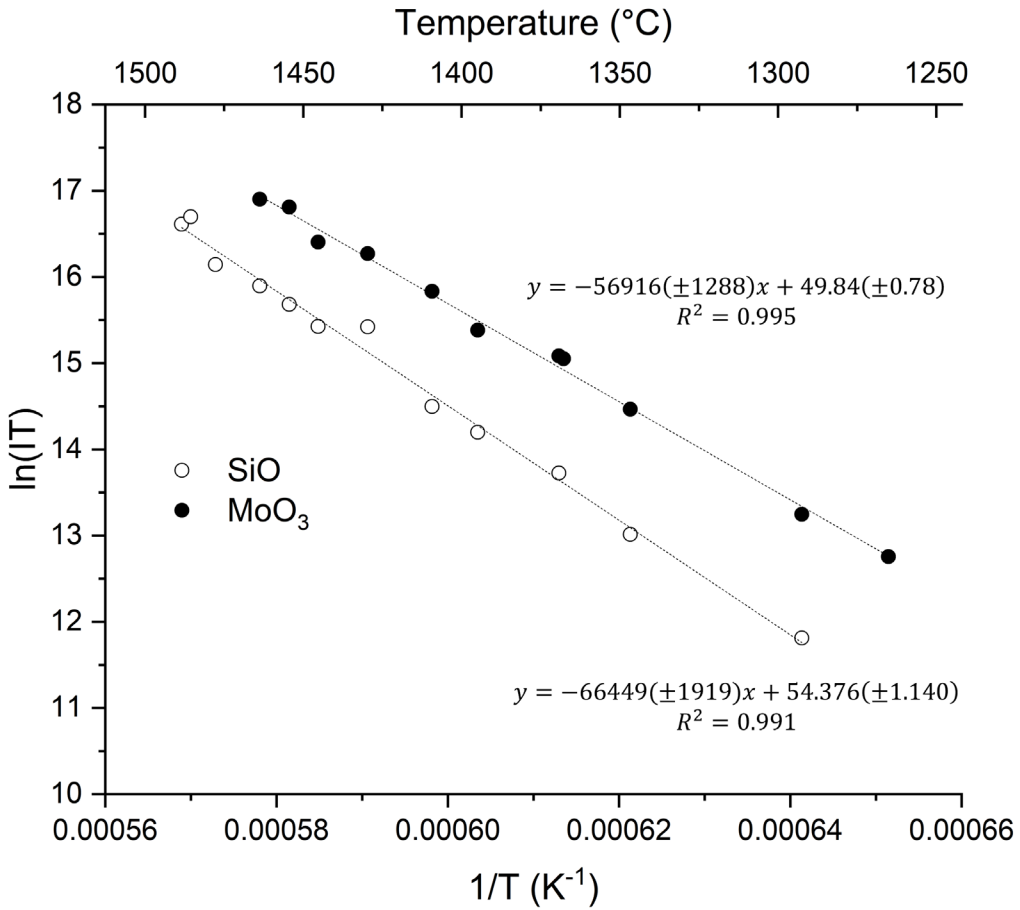
α-$Gd_2Si_2O_7$ fully converts to δ-$Gd_2Si_2O_7$ by 50 h, 1400°C.

Results: Gd_2SiO_5 + $Gd_{9.33}(SiO_4)_6O_2$ (+Mo)

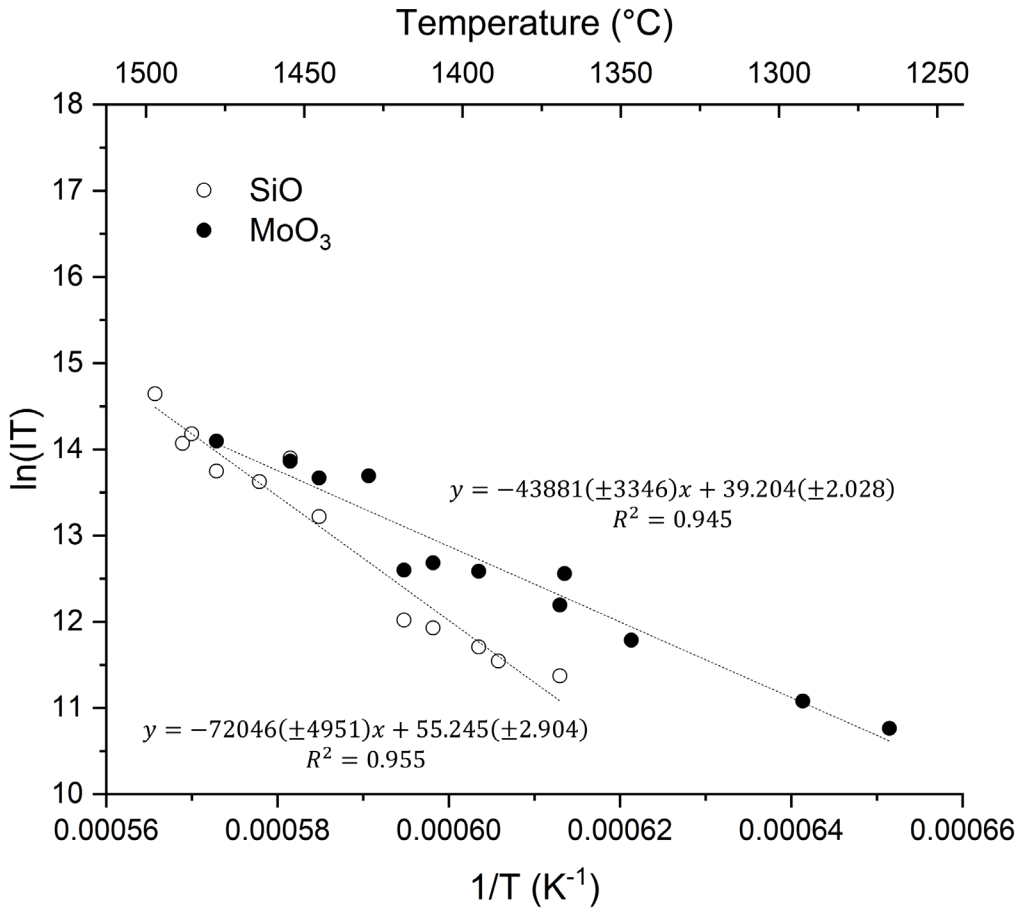


SiO_2

Results: Gd_2SiO_5 + $Gd_{9.33}(SiO_4)_6O_2$ (+Mo)



SiO_2



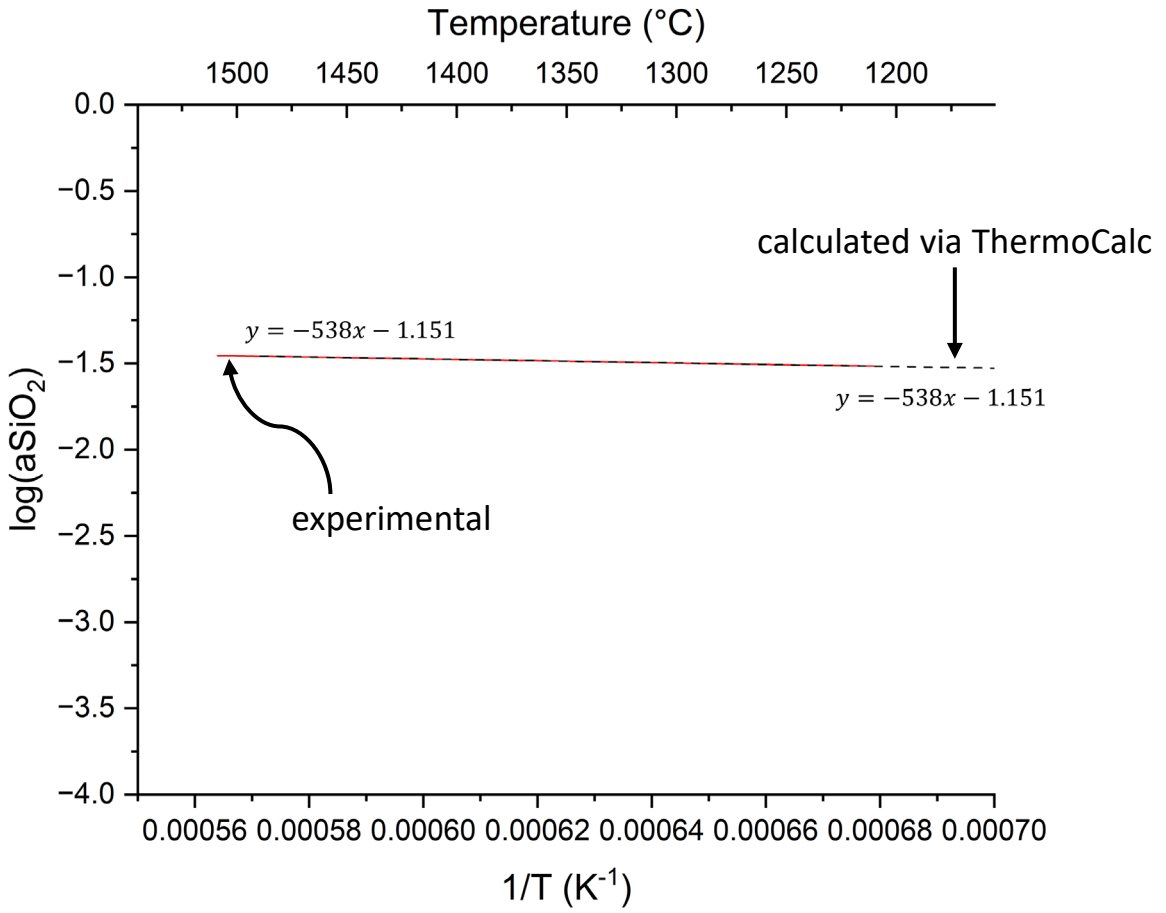
sample

Results: Gd_2SiO_5 + $Gd_{9.33}(SiO_4)_6O_2$ (+Mo)

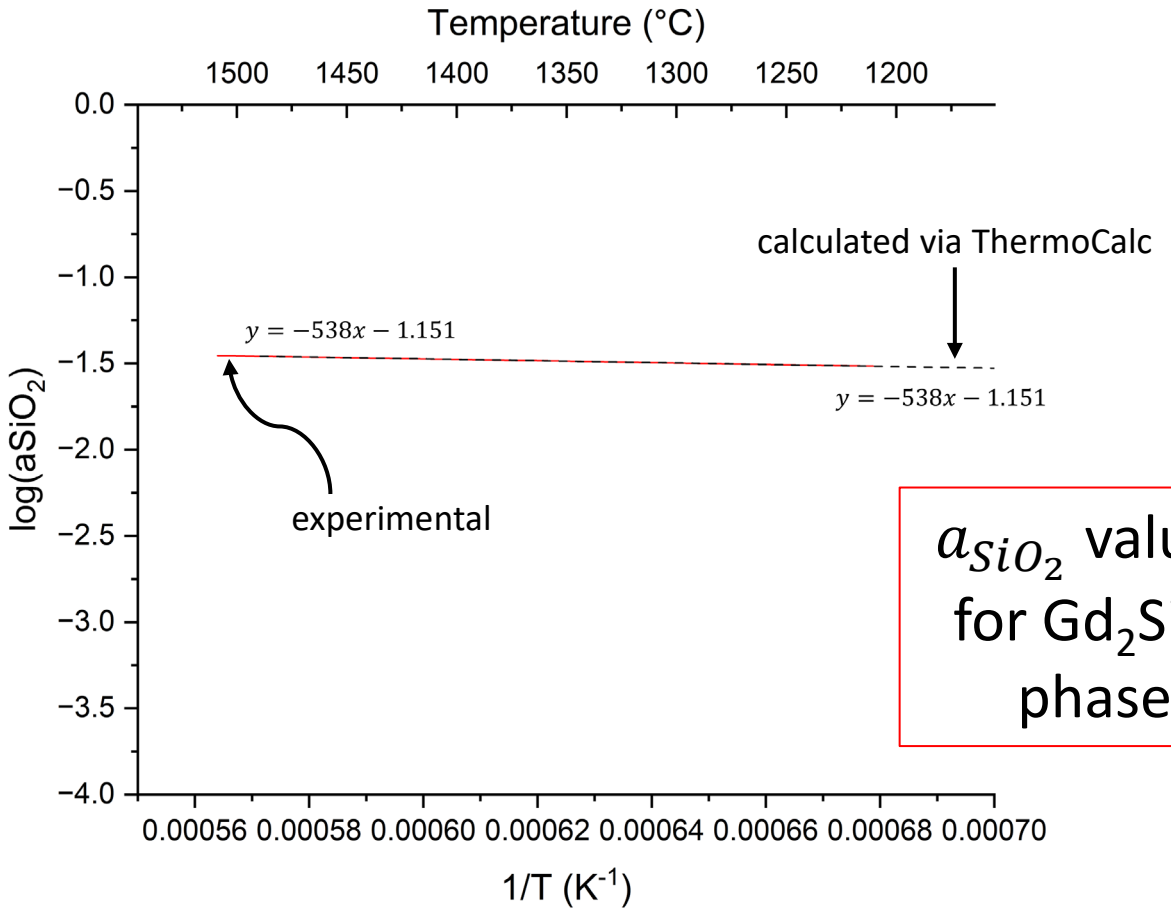
$$a_{SiO_2} = \left\{ \frac{\left(exp^{-72046 \times \frac{1}{T} + 55.245} \right)^3 \times \left(exp^{-43881 \times \frac{1}{T} + 39.204} \right)}{\left(exp^{-66449 \times \frac{1}{T} + 54.376} \right)^3 \times \left(exp^{-56916 \times \frac{1}{T} + 49.84} \right)} \right\}^{0.33}$$

$$a_{SiO_2} = \left\{ \frac{[I^*_{SiO}]^3 [I^*_{MoO_3}]}{[I^\circ_{SiO}]^3 [I^\circ_{MoO_3}]} \right\}^{\frac{1}{3}}$$

Results: Gd_2SiO_5 + $Gd_{9.33}(SiO_4)_6O_2$ (+Mo)

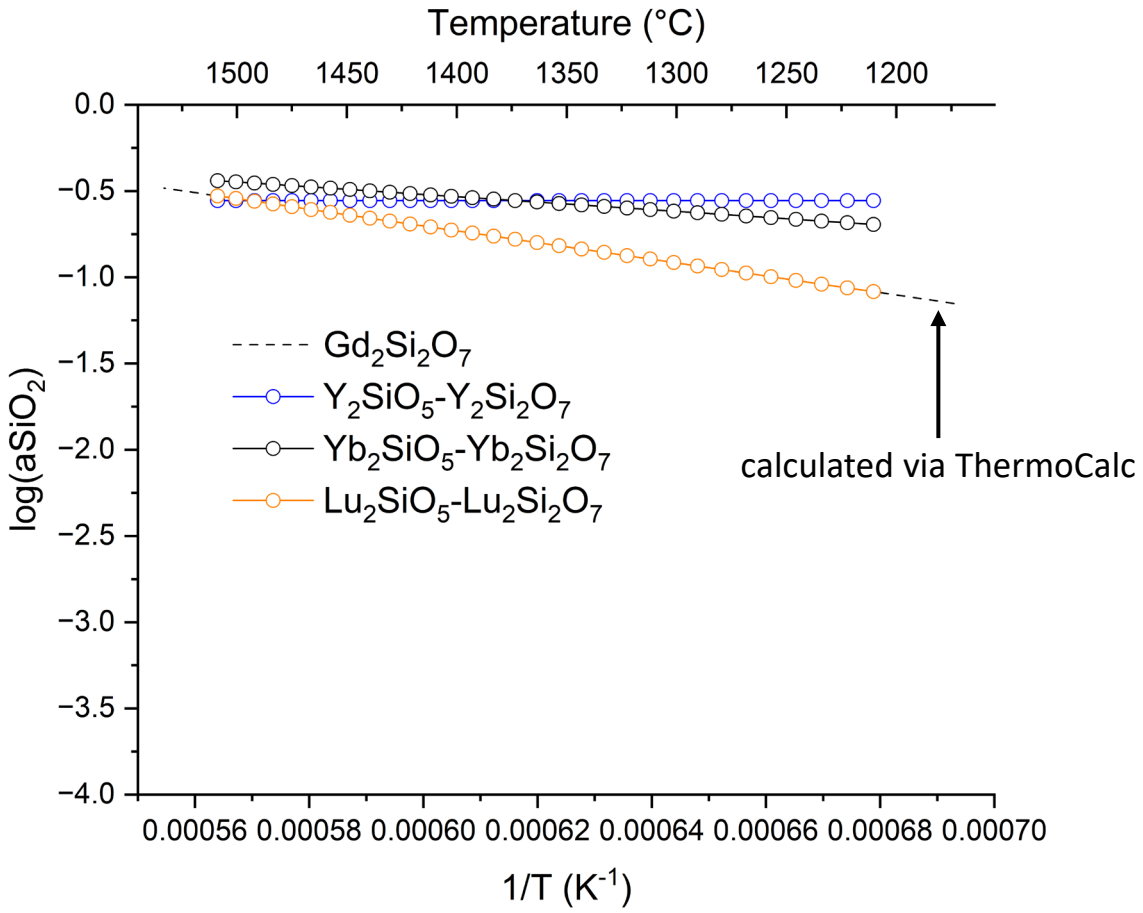


Results: Gd_2SiO_5 + $Gd_{9.33}(SiO_4)_6O_2$ (+Mo)

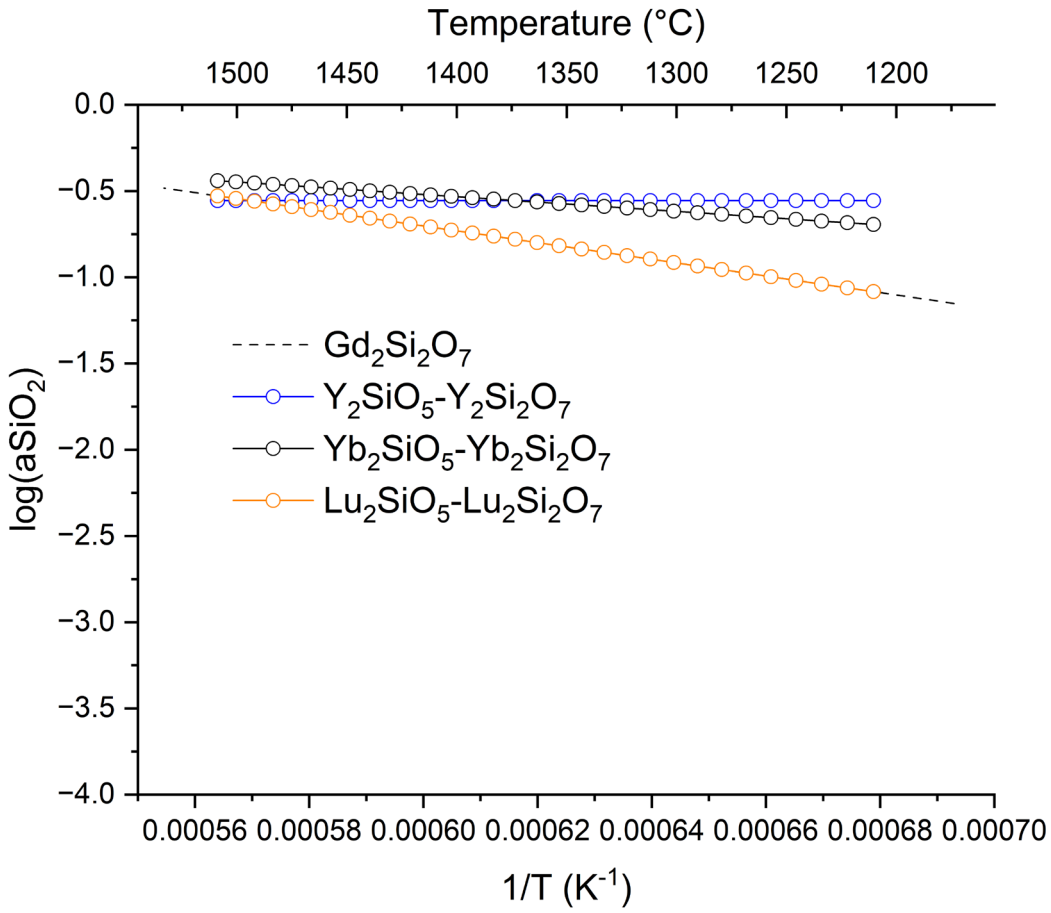


a_{SiO_2} value is equal to 0.039 for Gd_2SiO_5-$Gd_{9.33}(SiO_4)_6O_2$ phase field at 1500°C.

Results: $Gd_2Si_2O_7$

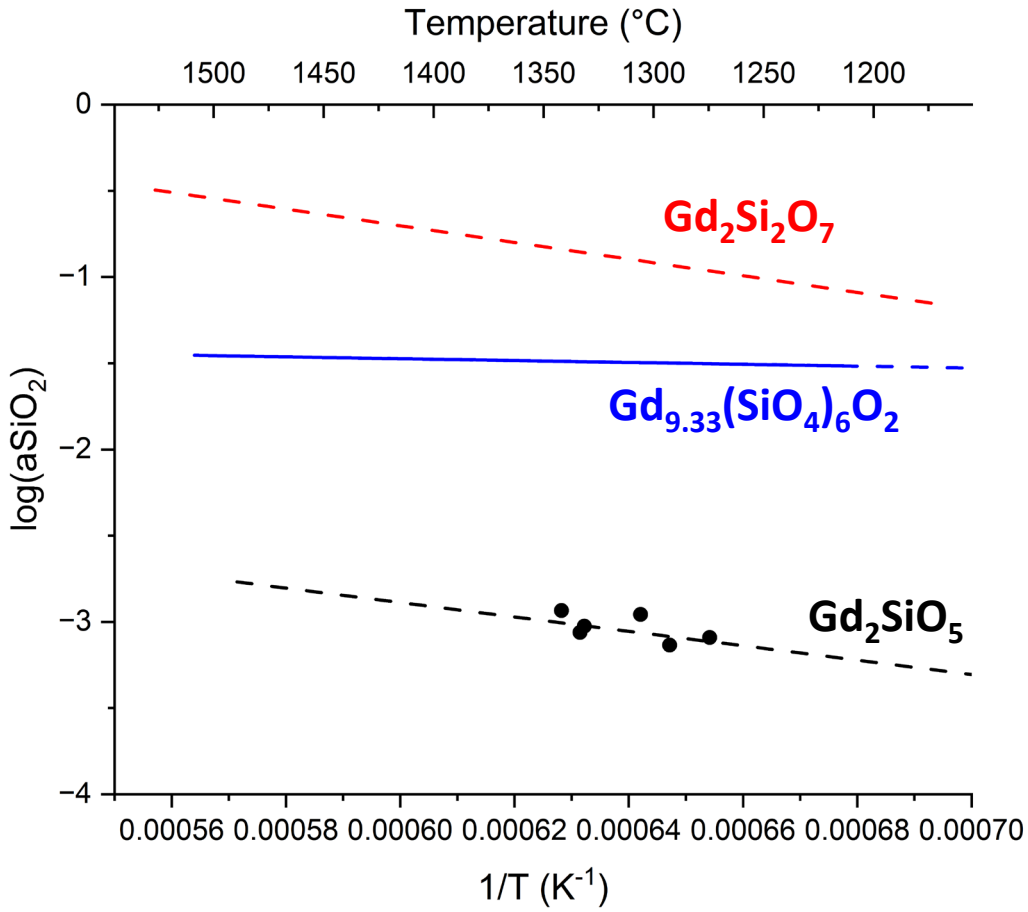


Results: Comparing $RE_2Si_2O_7$



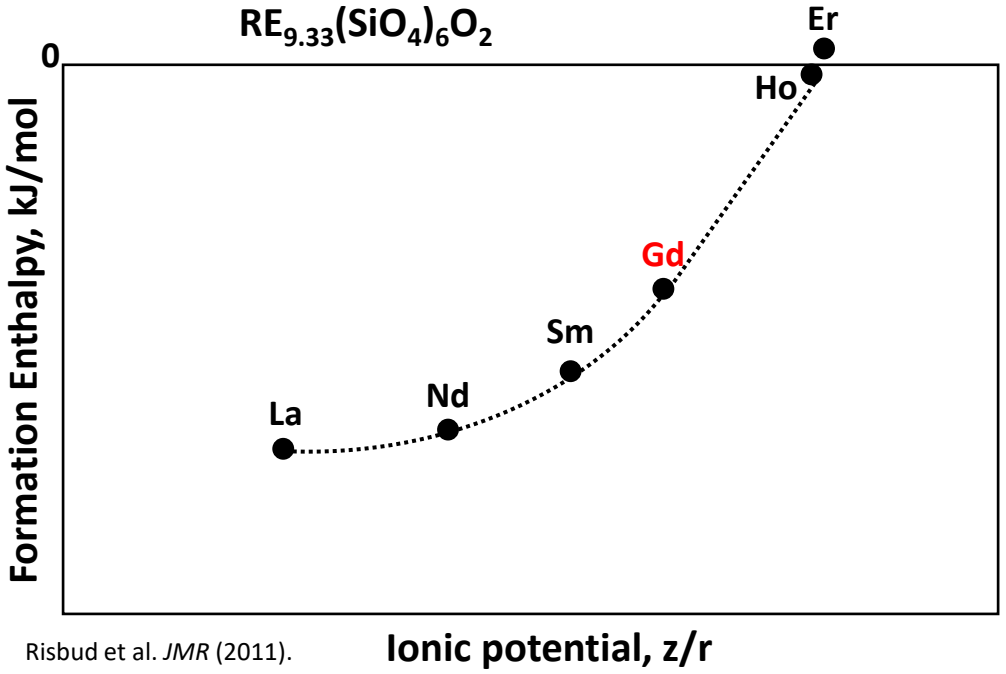
a_{SiO_2} values are on the order of 0.29 – 0.36 for $RE_2Si_2O_7$ at 1500°C.

Results: Comparing Gd silicates



Summary and conclusions

- Unlike that observed for RE_2O_3-SiO_2 (RE = Lu, Yb, Y) apatite ($RE_{9.33}(SiO_4)_6O_2$) forms at much lower temperatures than expected in the Gd_2O_3-SiO_2 system



Risbud et al. *JMR* (2011).

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- a_{SiO_2} increases Gd_2SiO_5 < $Gd_{9.33}(SiO_4)_6O_2$ < $Gd_2Si_2O_7$
  - Gd_2SiO_5 would be considered most “recession-resistant” material

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