Calorimetric Measurements of the Thermodynamic Properties of RE-Silicate Coating Materials

Gustavo Costa[1,2], Bryan Harder[1], Michael Kulis[1], Benjamin Kowalski[1], Narottam Bansal[1], Jamesa Stokes[1]

[1]NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH, 44135, USA

[2] Vantage Partners, LLC, 3000 Aerospace Pkwy, Brookpark, OH, 44142

Thermodynamics Genome of Environmental Barrier Coatings

- Thermodynamic properties of rare – earth silicate based coatings including their reaction products with silicate debris will be measured
- Integral thermodynamic quantities: High Temperature Reaction Calorimetry

- Rare-earth silicates ($RE_xSi_yO_z$)
- RE - mono and disilicates (Y, Nd, Gd, Dy, Er, Yb and Lu)

- Calcium rare – earth apatites
- $CaRE_4Si_3O_{13}$ (Y, Nd, Sm, Gd, Dy, Er, and Yb)

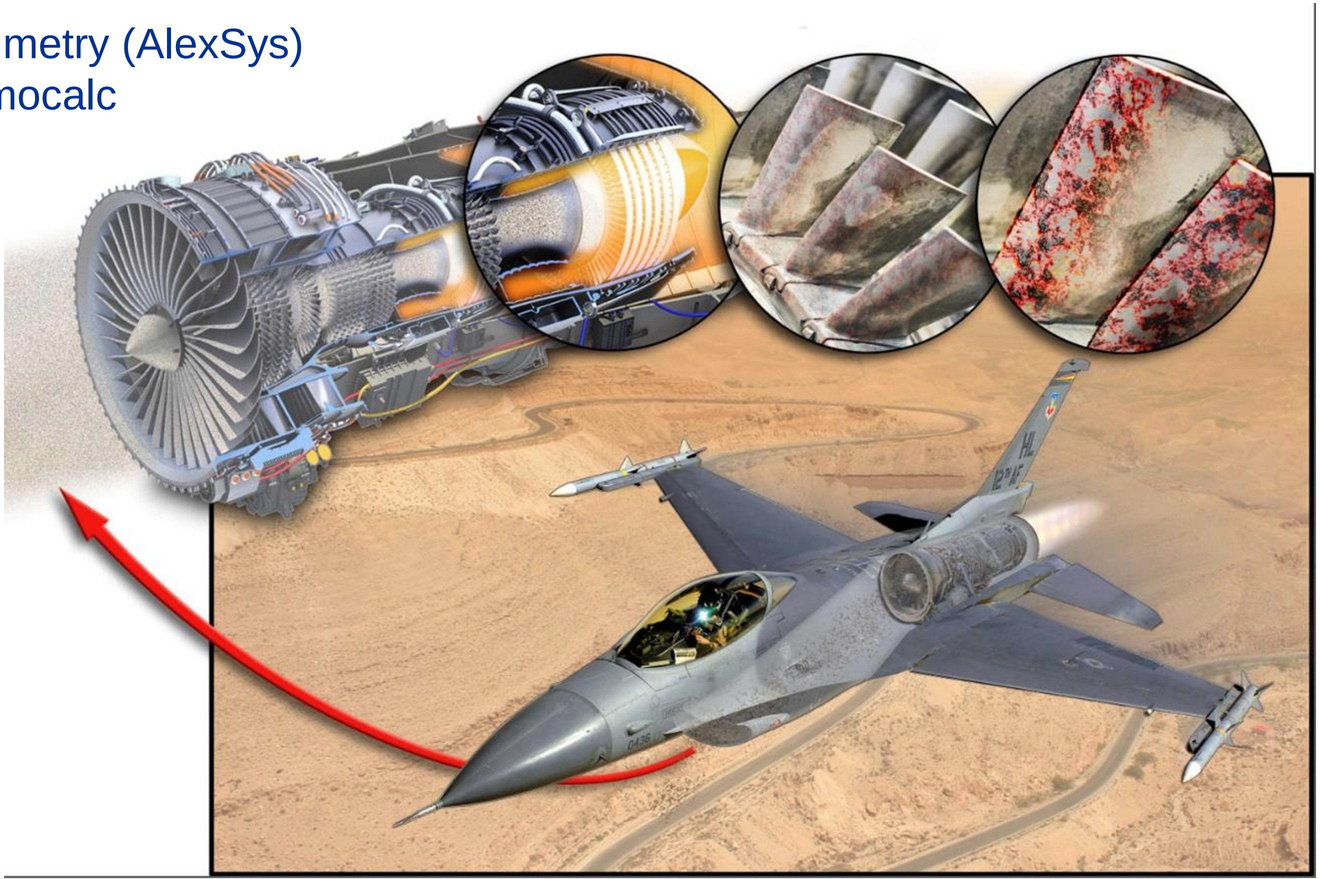
$$RE_2Si_2O_{7(xl)} + 0.5CaO_{(CMAS)} = 0.5CaRE_4Si_3O_{13(xl)} + 0.5SiO_{2(CMAS)}$$

$$RE_2SiO_{5(xl)} + 0.5CaO_{(CMAS)} + 0.5SiO_2 = 0.5CaRE_4Si_3O_{13(xl)}$$

Chemical Interactions of RE Silicates Coating Materials in Extreme Environments

  - Corrosive agents: e.g. Water vapor; deposits: salts, volcanic ash, desert sands
- Understanding Chemical reactions at high temperatures
  - Thermodynamics

-High Temperature Calorimetry (AlexSys)
-Codes: FactSage, Thermocalc

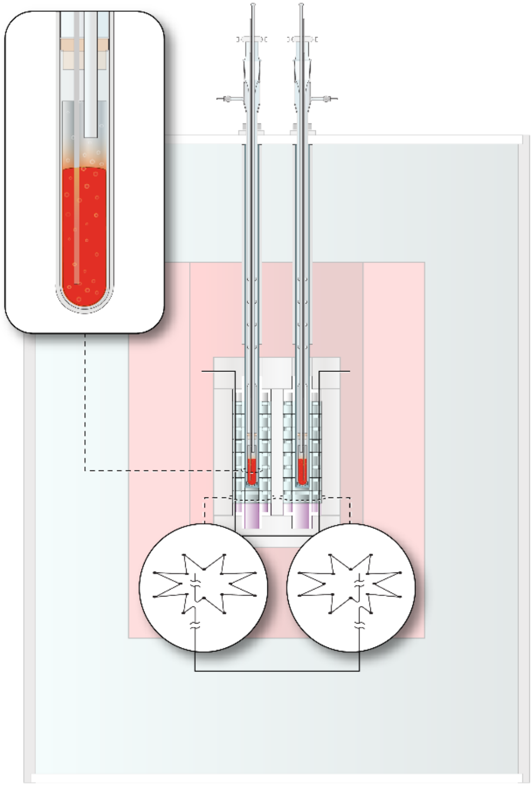


Costa et al, J. Am. Ceram Soc. 2018.

High Temperature Calorimetry

Formation enthalpies of Silicate Materials

Drop Solution Calorimetry



- Drop in molten lead borate solvent
- Determine the formation enthalpies for RE Silicates (EBCs) and Oxyapatites (CMAS-EBCs reaction product)

Understanding the interplay between energetic stability and structural properties
Input into thermodynamic codes

Thermodynamic Quantities

Limited thermodynamic data for designing coatings materials for gas turbine applications

- Input for thermodynamic codes (FactSage, ThermoCalc)
- Rare earth silicates and reaction products with CMAS
- Enthalpy of formation (ΔHf)
- Heat capacity (Cp) from almost 0 to 1600 ºC
- Enthalpy of fusion (ΔHfusion)

Energetics of Calcium Rare-earth Silicate Oxyapatites

Corrosion product of Ceramic Coatings

$Ca_2RE_8Si_6O_{26}$ (Y, Nd, Sm, Gd, Dy, Er, and Yb)

Rare – earth silicates (EBCs) + silicate debris (CMAS) = Rare-earth silicate oxyapatites

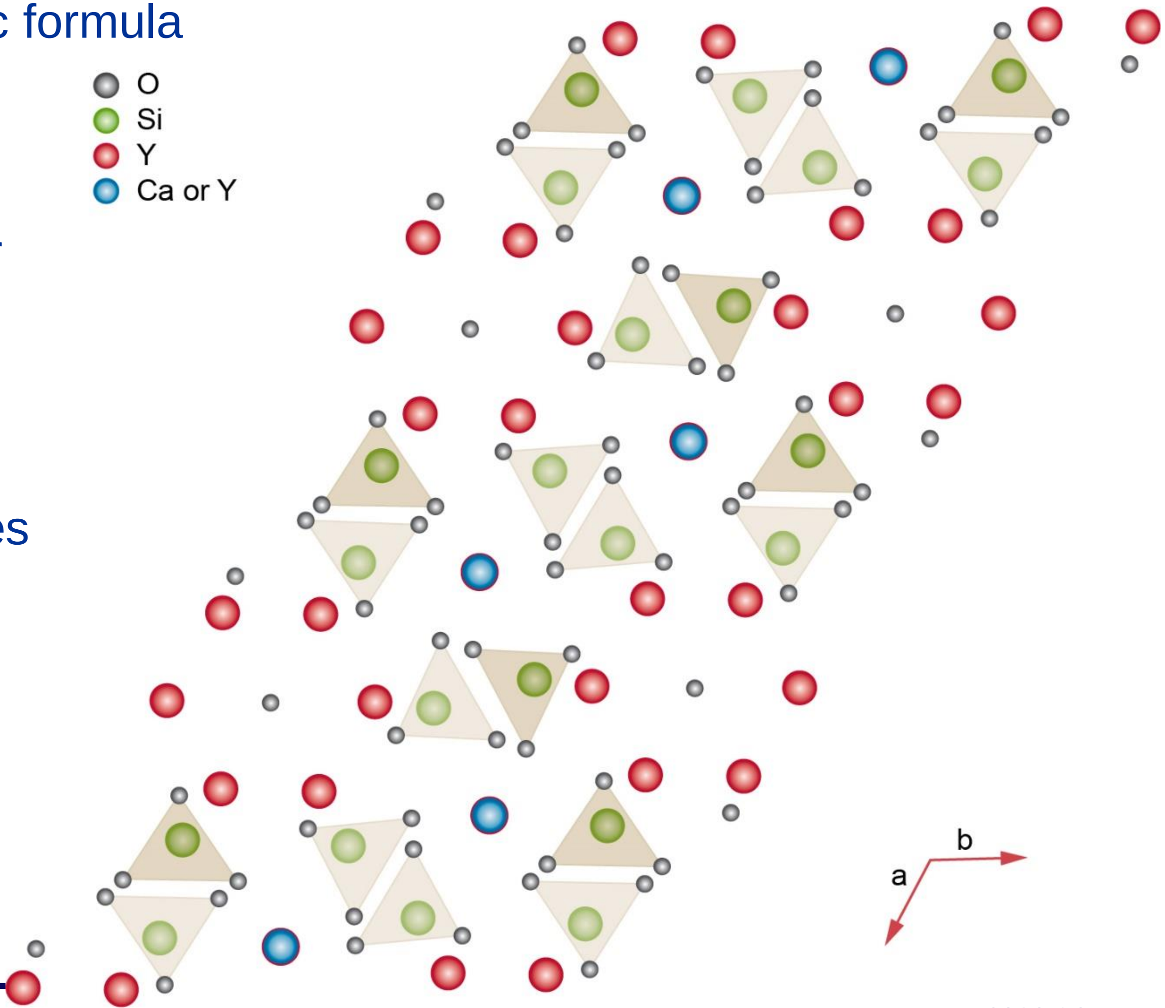
${}^{IX}M(1)_4{}^{VII}M(2)_6({}^{IV}TO_4)_6X_2$ – generic formula

M – Rare-earth or alkaline earth

X – mono or divalent anions

T – p - block element

Superscript – coordination number



$RE_{10}Si_6O_{27}$ – interstitial oxygen

$RE_{9.33}\square_{0.67}Si_6O_{26}$ – cation vacancies

$RE_8AE_2Si_6O_{26}$ – stoichiometric

AE – alkaline earth

Costa et al, J. Am. Ceram Soc. 2019.

High Temperature Drop Solution Calorimetry

$$\Delta H_{ds} = \Delta H_{TTD} + \Delta H_{s}$$

1 -$Ca_2RE_8Si_6O_{26(xl,\ 25\ °C)} = Ca_2RE_8Si_6O_{26(sol,\ 800\ °C)}$

2 - $4RE_2O_{3(xl,\ 25\ °C)} = 4RE_2O_{3\ (sol,\ 800\ °C)}$

3 - $6SiO_{2(xl,\ 25\ °C)} = 6SiO_{2(sol,\ 800\ °C)}$

4 - $2CaO_{(xl,\ 25\ °C)} = 2\ CaO_{(sol,\ 800\ °C)}$

5 - $2CaO_{(xl,\ 25\ °C)} + 6SiO_{2(xl,\ 25\ °C)} + 4RE_2O_{3(xl,\ 25\ °C)}$

$= Ca_2RE_8Si_6O_{26\ (xl,\ 25\ °C)}$

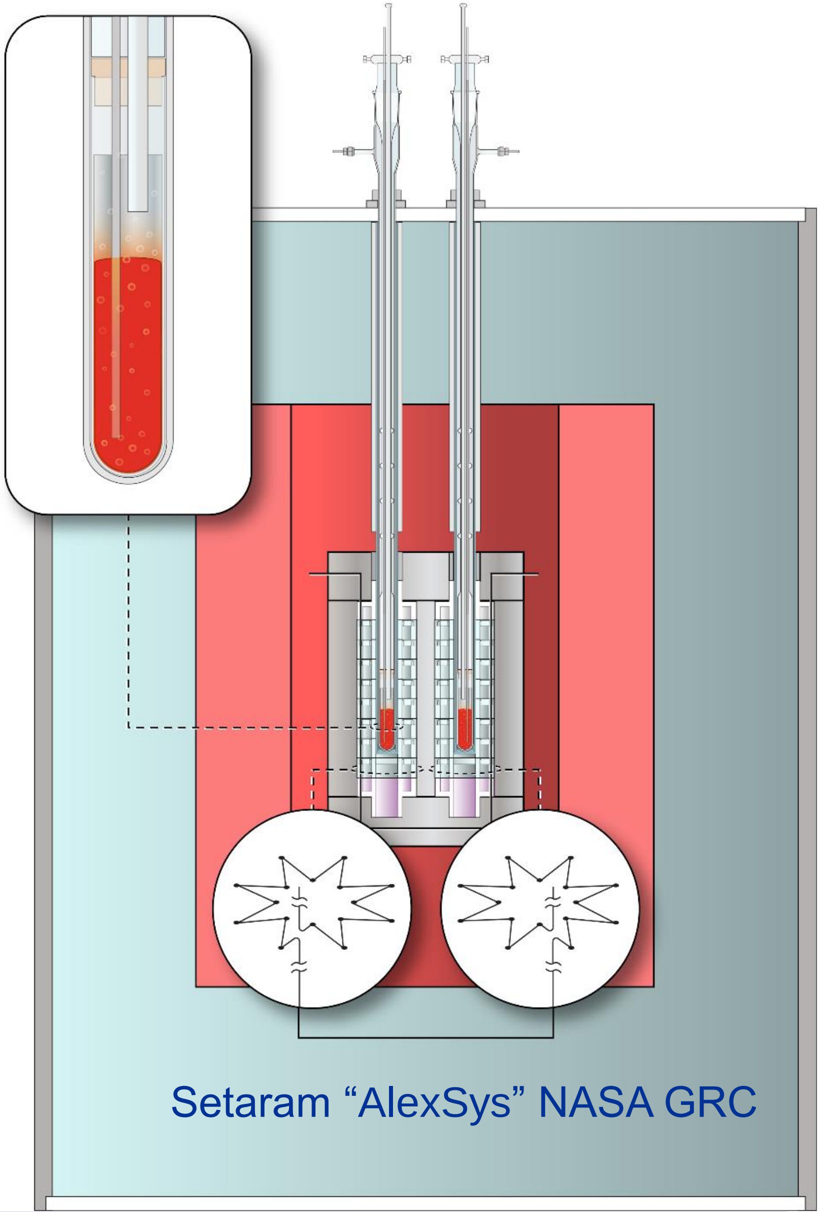
$\Delta H_1 = -\Delta H_{ds\ (calcium\ RE\ oxyapatites)}$

$\Delta H_2 = 4\Delta H_{ds\ (RE\ oxides)}$

$\Delta H_3 = 6\Delta H_{ds\ (quartz)}$

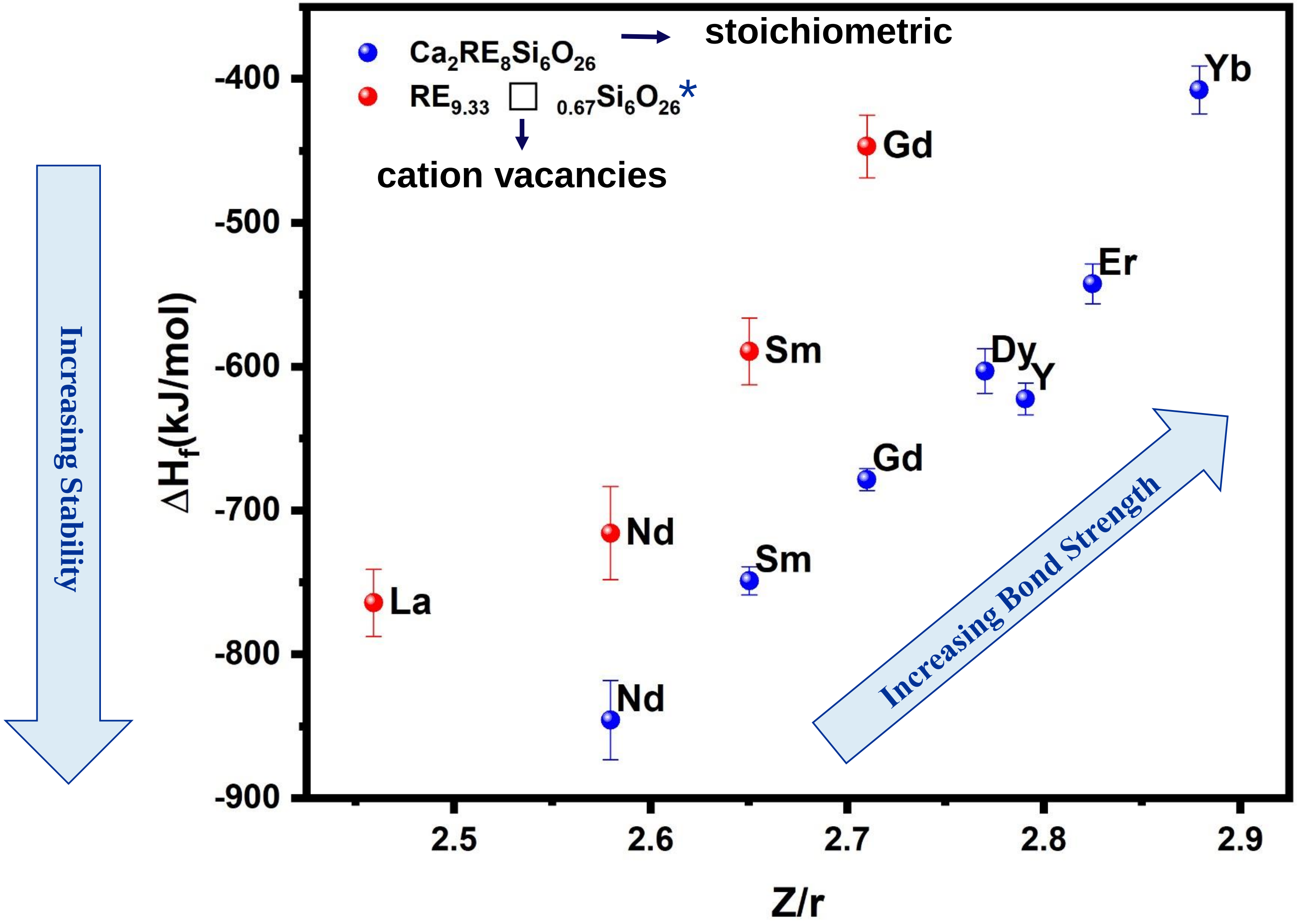
$\Delta H_4 = 2\Delta H_{ds\ (lime)}$

$\Delta H_5 = \Delta H_{f,\ ox\ (calcium\ RE\ oxyapatites)}$



Setaram “AlexSys” NASA GRC

Calorimetric Results

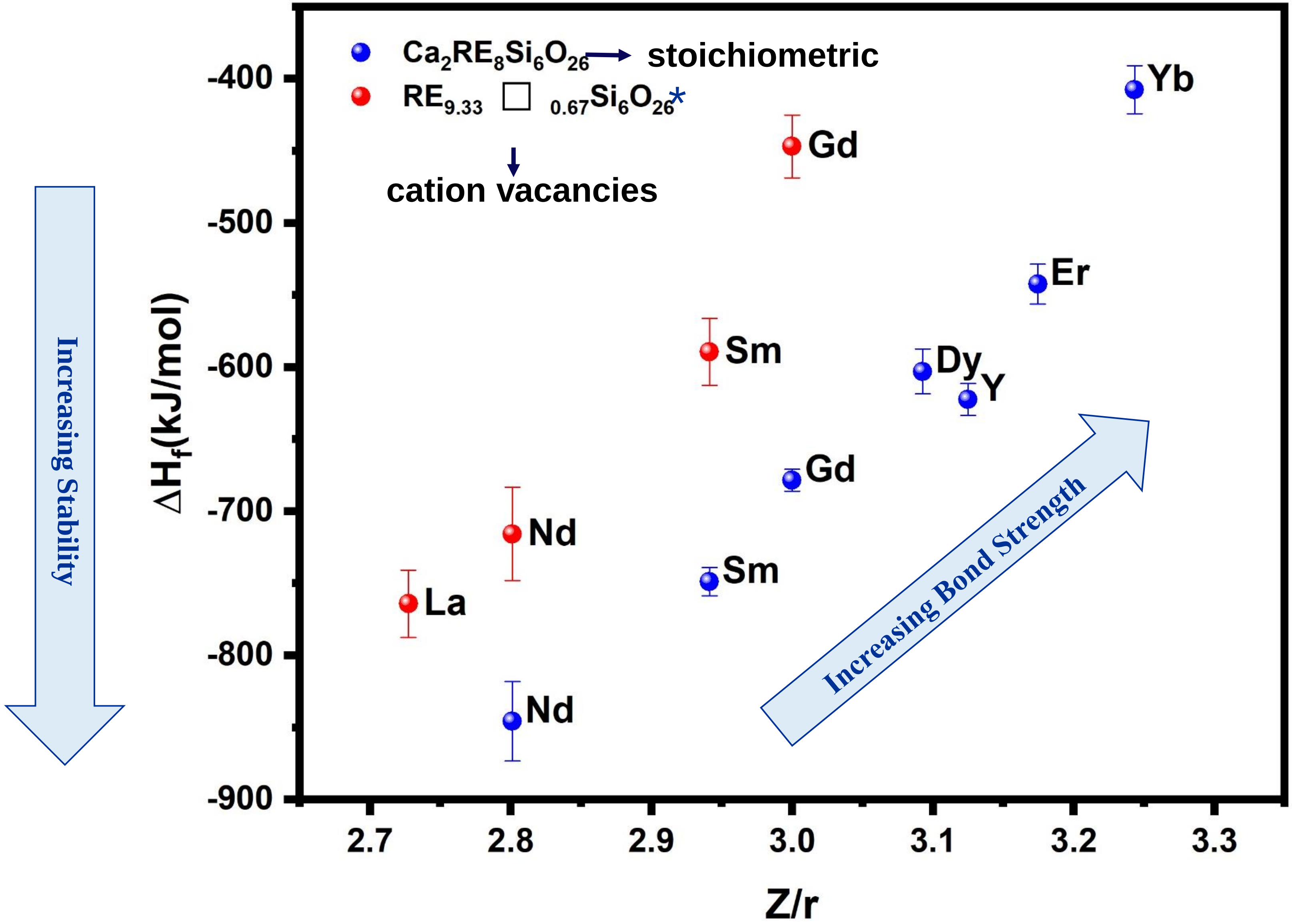


Enthalpy of formation of oxyapatites Versus their ionic potential (Z/r) in the M(1) sites. $RE_{9.33}\square_{0.67}Si_6O_{26}$ from an earlier study*

Costa et al, J. Am. Ceram Soc. 2019.

*Risbud et al J. Mater. Res. 2001.

Calorimetric Results

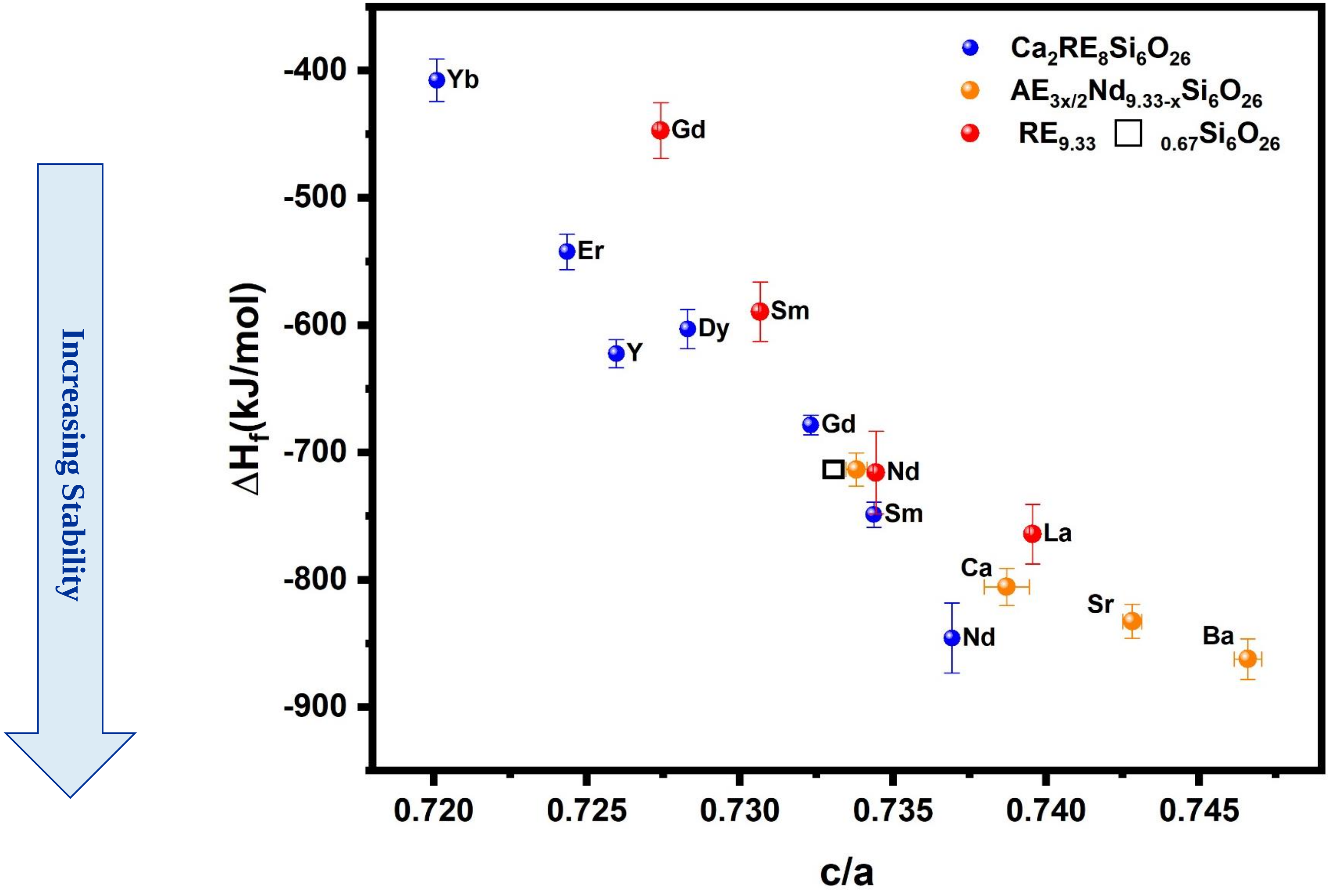


Enthalpy of formation of oxyapatites Versus their ionic potential (Z/r) in the M(2) sites.
$RE_{9.33}\square_{0.67}Si_6O_{26}$ from an earlier study*

Costa et al, J. Am. Ceram Soc. 2019.

*Risbud et al J. Mater. Res. 2001.

Calorimetric Results



Enthalpies of formation of the oxyapatites from the oxides versus the c/a. Enthalpies of formation of $RE_{9.33}\square_{0.67}Si_6O_{26}$ and $AE_{3x/2}Nd_{9.33-x}Si_6O_{26}$ (AE = Ca, Sr and Ba, X = 0 and 1.33) are from an earlier studies

*Hosseini et al J. Am. Ceram. Soc. 2013.

*Risbud et al J. Mater. Res. 2001.

Summary

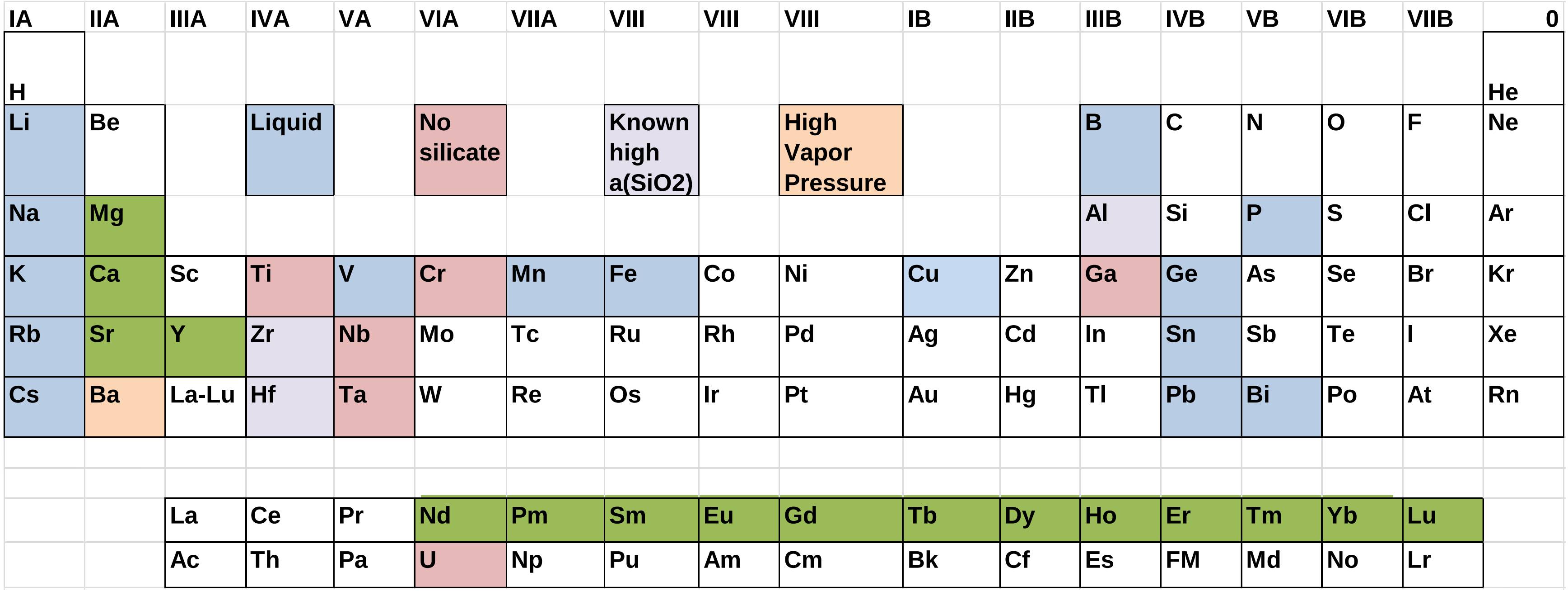
Calcium Rare-earth Silicate Oxyapatites

- Oxyapatites are significantly more stable relative to their binary oxides.
- Oxyapatites becomes more stable when achieving fully stoichiometric composition.
- Oxyapatites stability increases with decreasing ionic potential of the rare-earths in the M(1) and M(2) sites and ionic field strength, meaning that stability increases with their ionic radius.

Thermodynamics of Rare-earth Silicates

Periodic Table of Solid Binary Silicates Opila, UVa

Coating Materials Candidates



IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
H																	He
Li	Be		Liquid		No silicate		Known high a(SiO2)		High Vapor Pressure			B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	FM	Md	No	Lr	

- Rare earth silicates: Limited thermodynamic data
- Input for thermodynamic codes (FactSage, ThermoCalc)
- YMS, YDS and YbMS (measured: thermodynamic activities, ΔHf, ΔHvaporization and Cp)
- On going work:
  - **ΔHf** and Cp measured by calorimetry: Nd, Gd, Dy, Er, Yb and Lu disilicates
  - ΔHfusion: Y and Yb disilicate
  - Thermodynamic activities and ΔHvaporization also measured for LuMS-DS by KEMS

High Temperature Drop Solution Calorimetry

$$\Delta H_{ds} = \Delta H_{TTD} + \Delta H_{s}$$

1 - $RE_2Si_2O_{7(xl,\ 25\ °C)} = RE_2Si_2O_{7\ (sol,\ 800\ °C)}$

2 - $RE_2O_{3(xl,\ 25\ °C)} = RE_2O_{3\ (sol,\ 800\ °C)}$

3 - $2SiO_{2(xl,\ 25\ °C)} = 2SiO_{2(sol,\ 800\ °C)}$

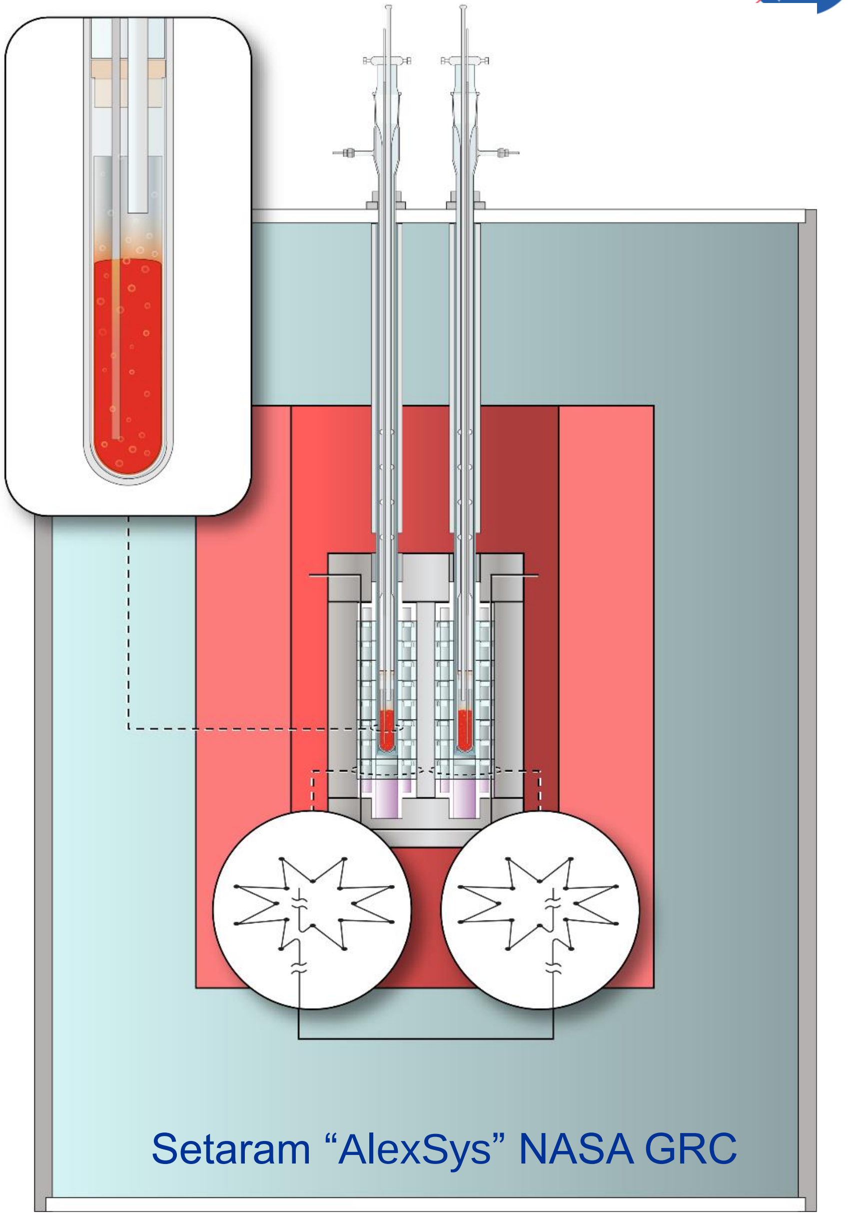
4 - $RE_2O_{3(xl,\ 25\ °C)} + 2SiO_{2(xl,\ 25\ °C)} = RE_2Si_2O_{7\ (sol,\ 800\ °C)}$

$\Delta H_1 = -\Delta H_{ds\ (RE\ disilicates)}$

$\Delta H_2 = \Delta H_{ds\ (RE\ oxides)}$

$\Delta H_3 = 2\Delta H_{ds\ (quartz)}$

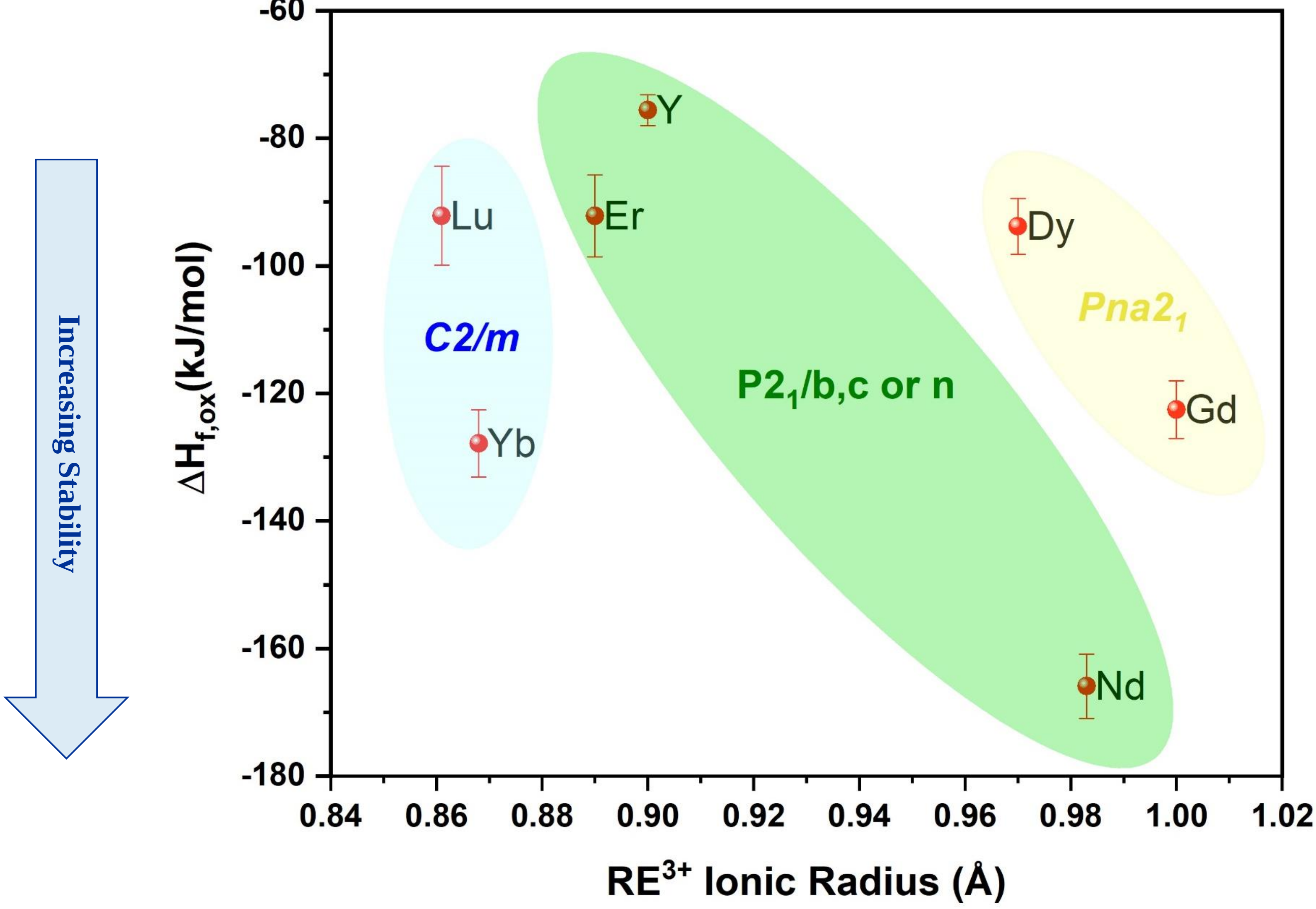
$\Delta H_4 = \Delta H_{f,\ ox\ (RE\ disilicates)}$



Setaram “AlexSys” NASA GRC

Calorimetric Results

High Temperature Drop Solution Calorimetry

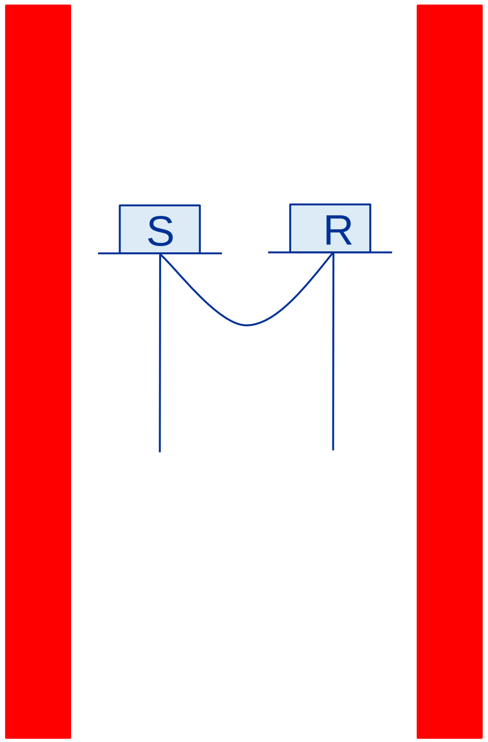


Enthalpy of formation of RE disilicates Vs RE^{3+} ionic radius.

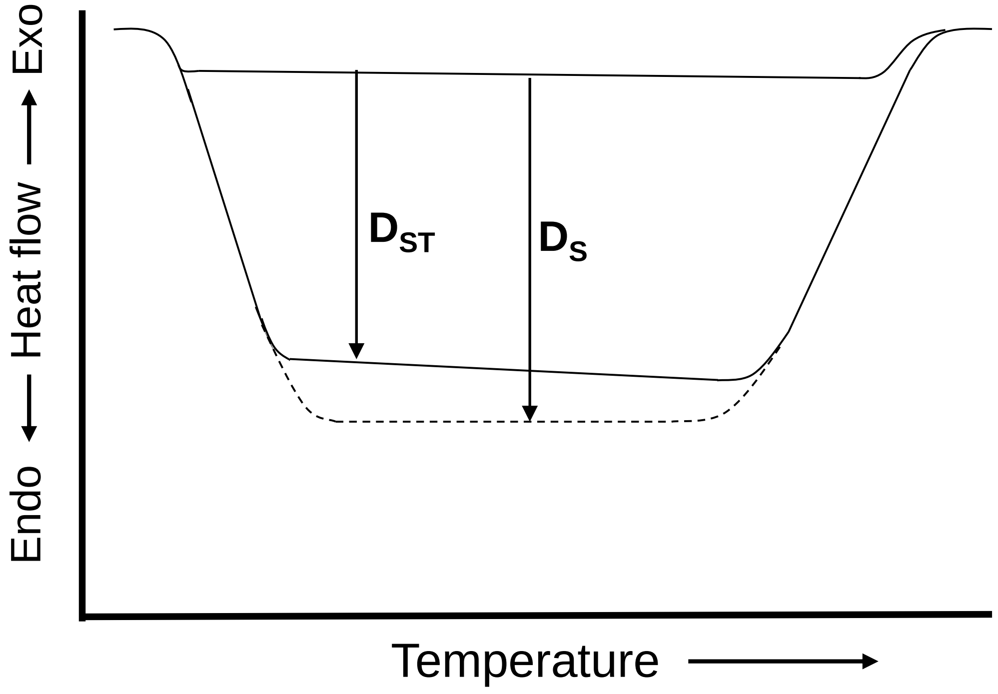
Differential Scanning Calorimetry - Specific Heat Capacity

Netzsch – DSC F1 Pegasus®

- 3 measurements required: empty (baseline), sapphire (standard) and sample.
- ASTM E1269.



DSC furnace side view
(S – sample and R –reference)



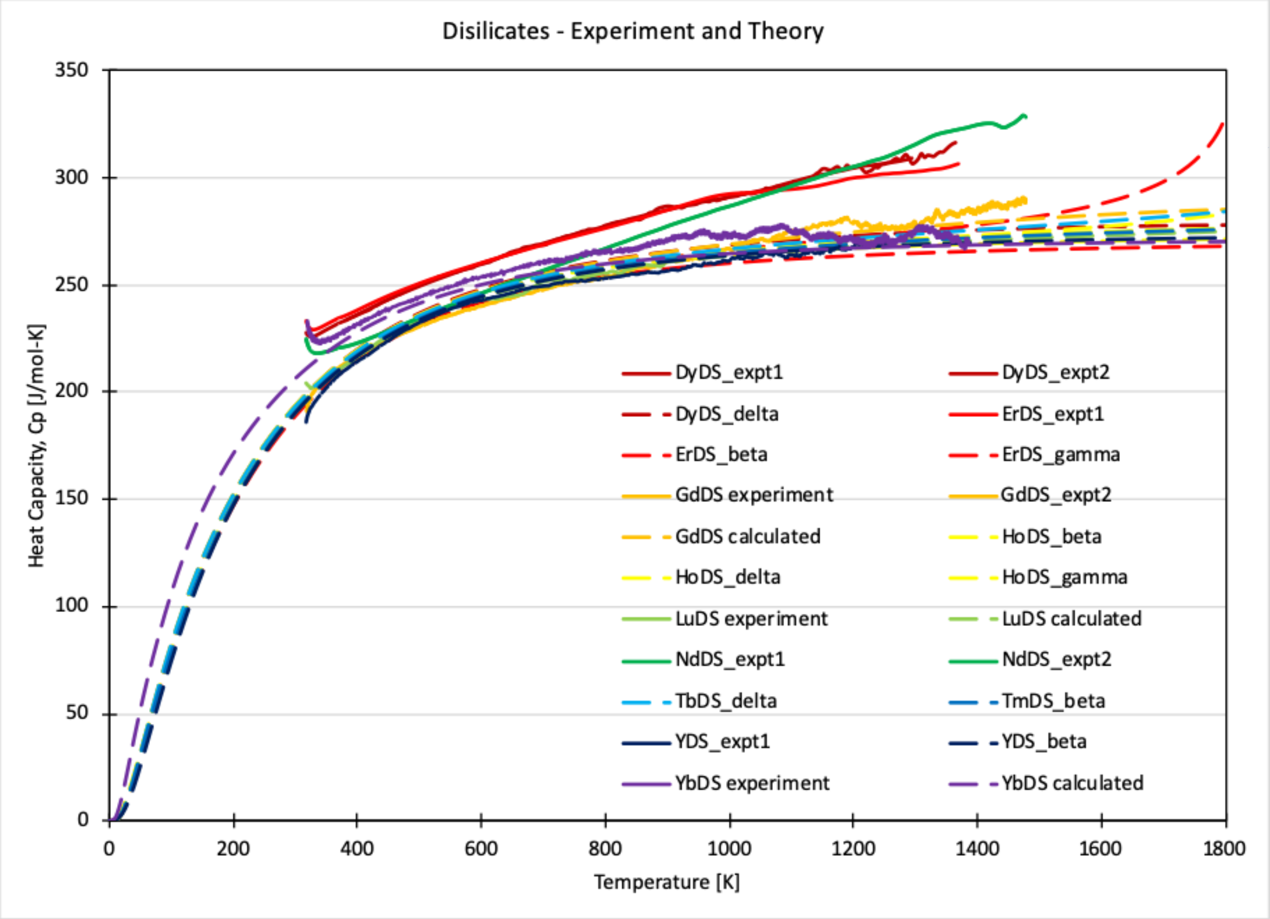
$$Cp(S) = Cp(ST)\frac{D_S \cdot W_{ST}}{D_{ST} \cdot W_S}$$

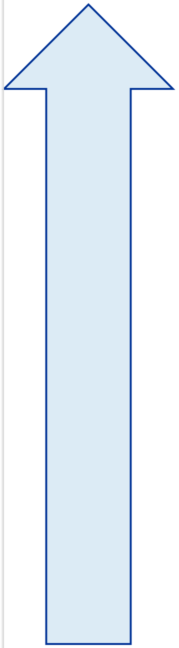
D – displacement
W – mass

S – sample
ST - sapphire

Calorimetric Results

Differential Scanning Calorimetry





Increasing
RE^{3+} ionic radius

- Good agreement with DFT – based Cp calculations! Cameron Bodenschatz

Heat capacity (Cp) of RE disilicates Vs temperature.

Summary

Rare-earth Disilicates

- Rare-earth disilicates stability increases with increasing RE ionic radius considering the same crystal structure.

- Heat capacity of rare-earth disilicates increases with increasing RE ionic radius except for yttrium and gadolinium disilicates.