X-ray and neutron diffraction on laser heated levitated samples: successes and challenges

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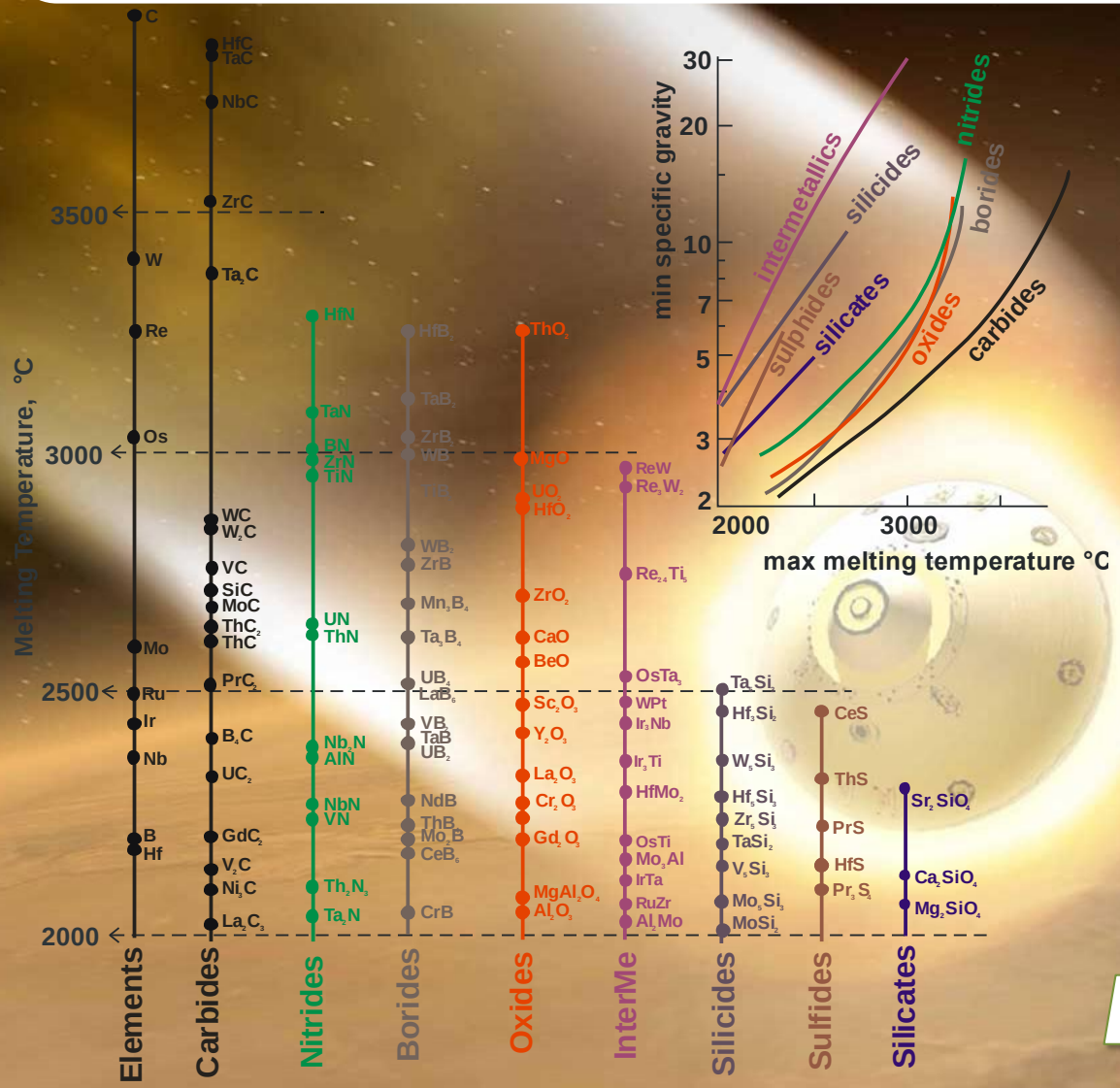
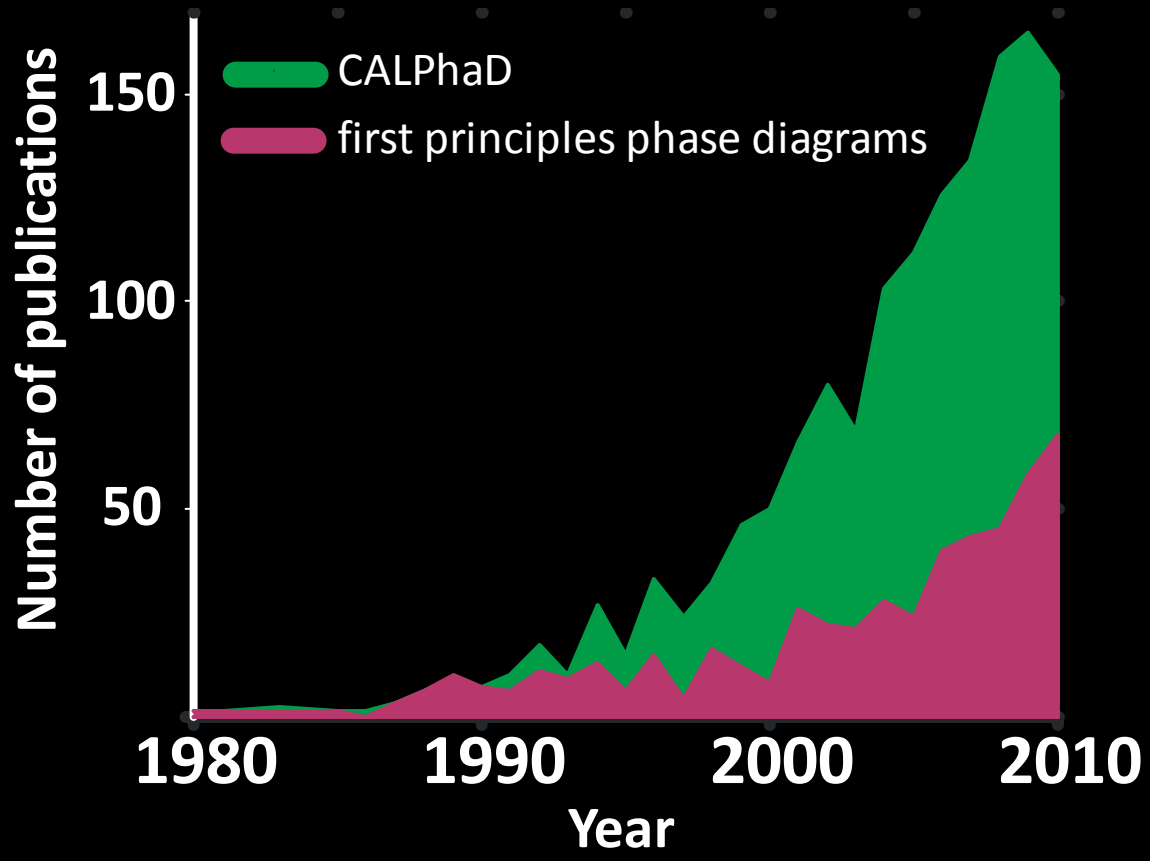
High temperature ceramics for aerospace and nuclear applications



MOTIVATION

Calculation of Phase Diagrams (CALPHAD) methods rely on thermodynamic data for compounds and their alloys / solid solutions



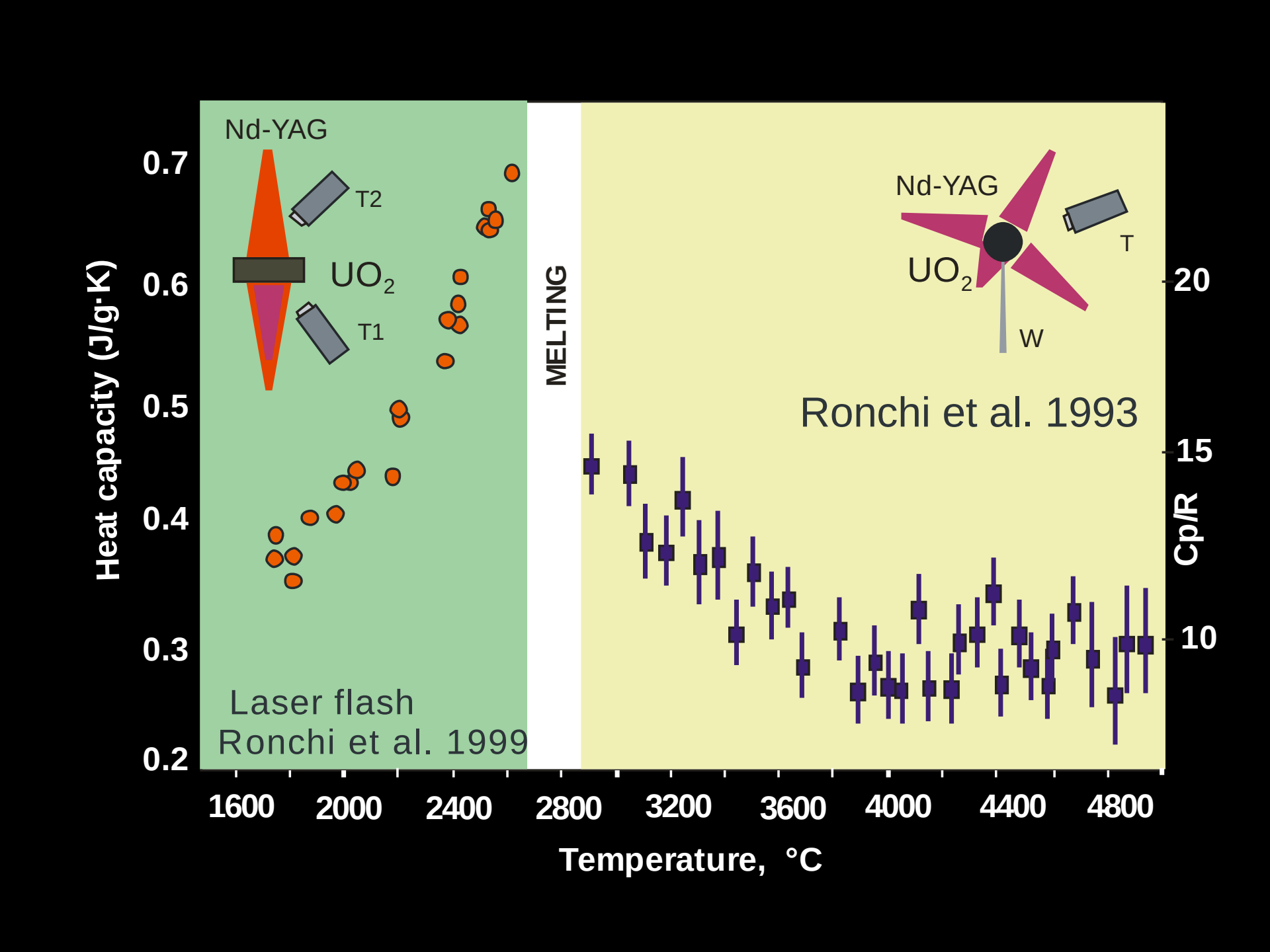
FactSage,
MTDATA,
PANDAT,
MatCalc,
JMatPro,
Thermo-Calc

MOTIVATION

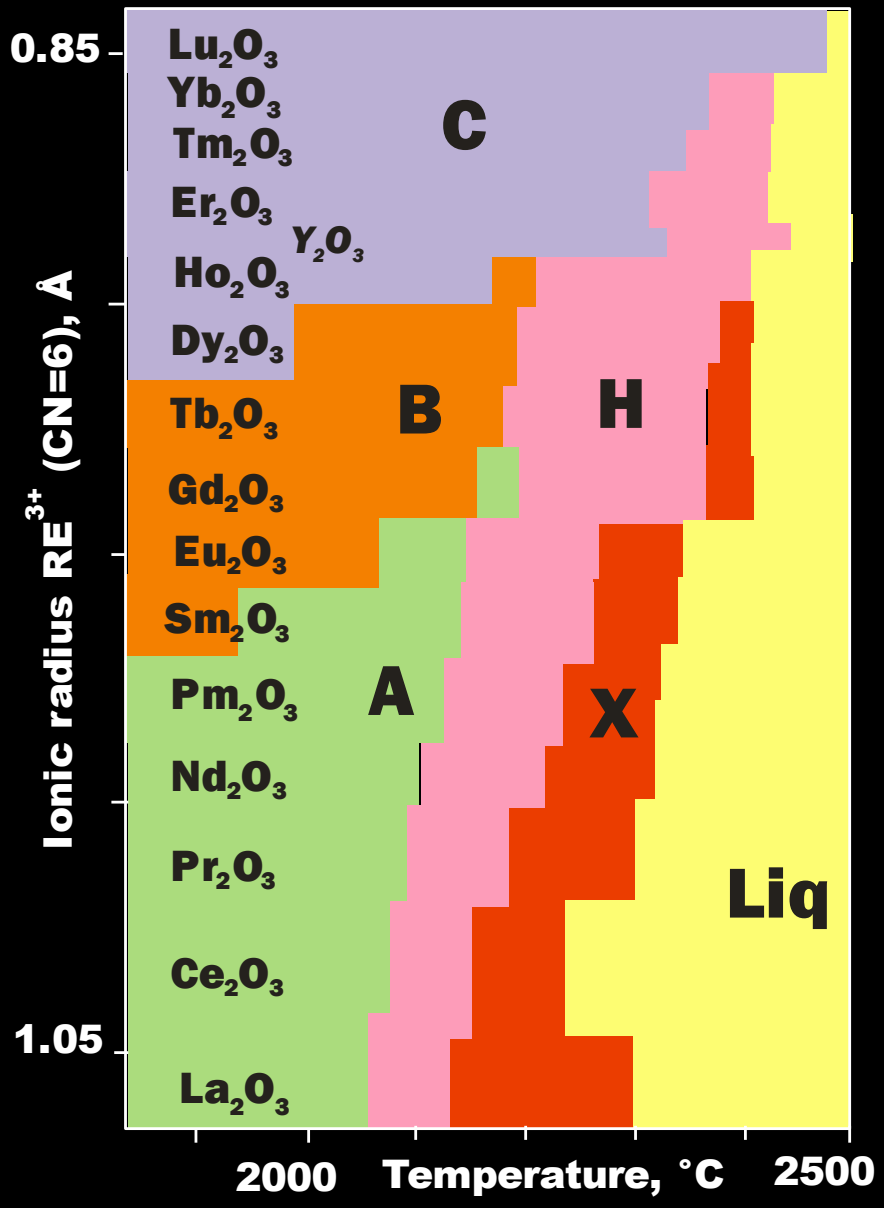
Thermodynamic data from high-T diffraction

- Molar volumes as a function of temperature
- ΔV for solid state phase transitions
- ΔS_c for order - disorder transitions
- *In situ* phase diagram determination

MOTIVATION


Nd-YAG
T2
UO2
T1
Laser flash
Ronchi et al. 1999
MELTING
Nd-YAG
T
UO2
W
Ronchi et al. 1993
Heat capacity (J/g·K)
0.7
0.6
0.5
0.4
0.3
0.2
Cp/R
20
15
10
1600
2000
2400
2800
3200
3600
4000
4400
4800
Temperature, °C

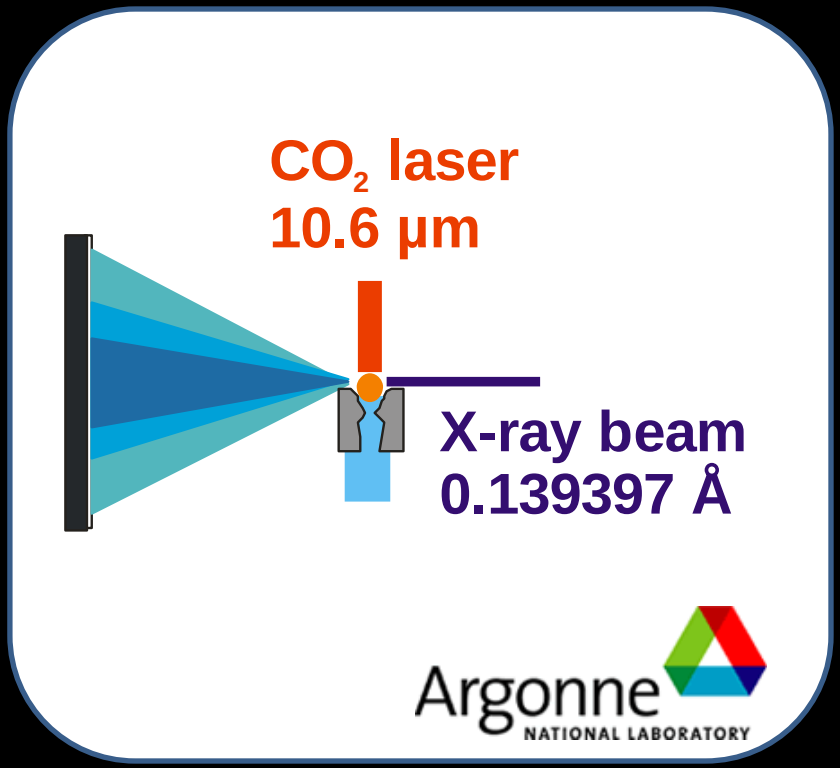
Phase transitions in RE_2O_3



NSF DMR 1506229
Phase Transitions
in RE_2O_3 above 2000 °C

Aerodynamic levitators with laser heating

APS 6-ID-D



Chris Benmore

SNS NOMAD BL1B

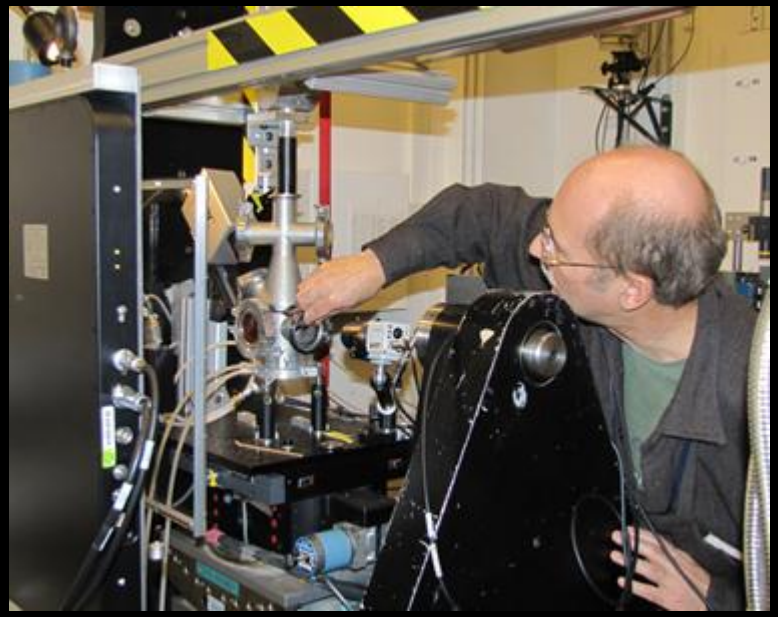
Richard Weber

Joerg Neuefeind

METHOD

Aerodynamic levitators with laser heating

APS 6-ID-D



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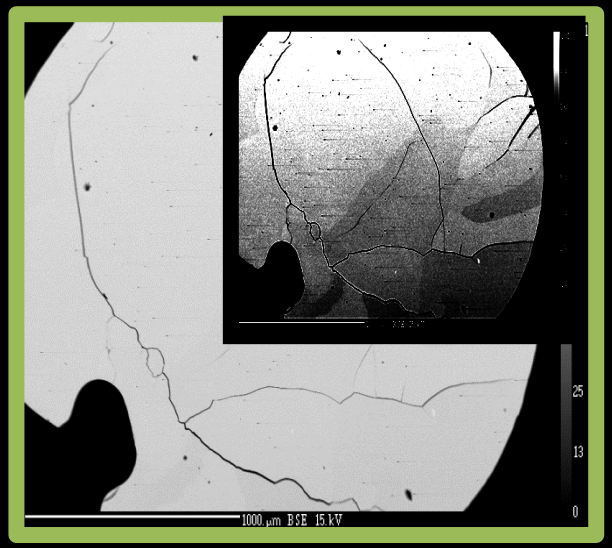
Samples preparation

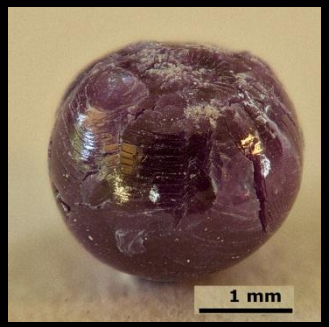
Powder melting

Levitation

Microprobe

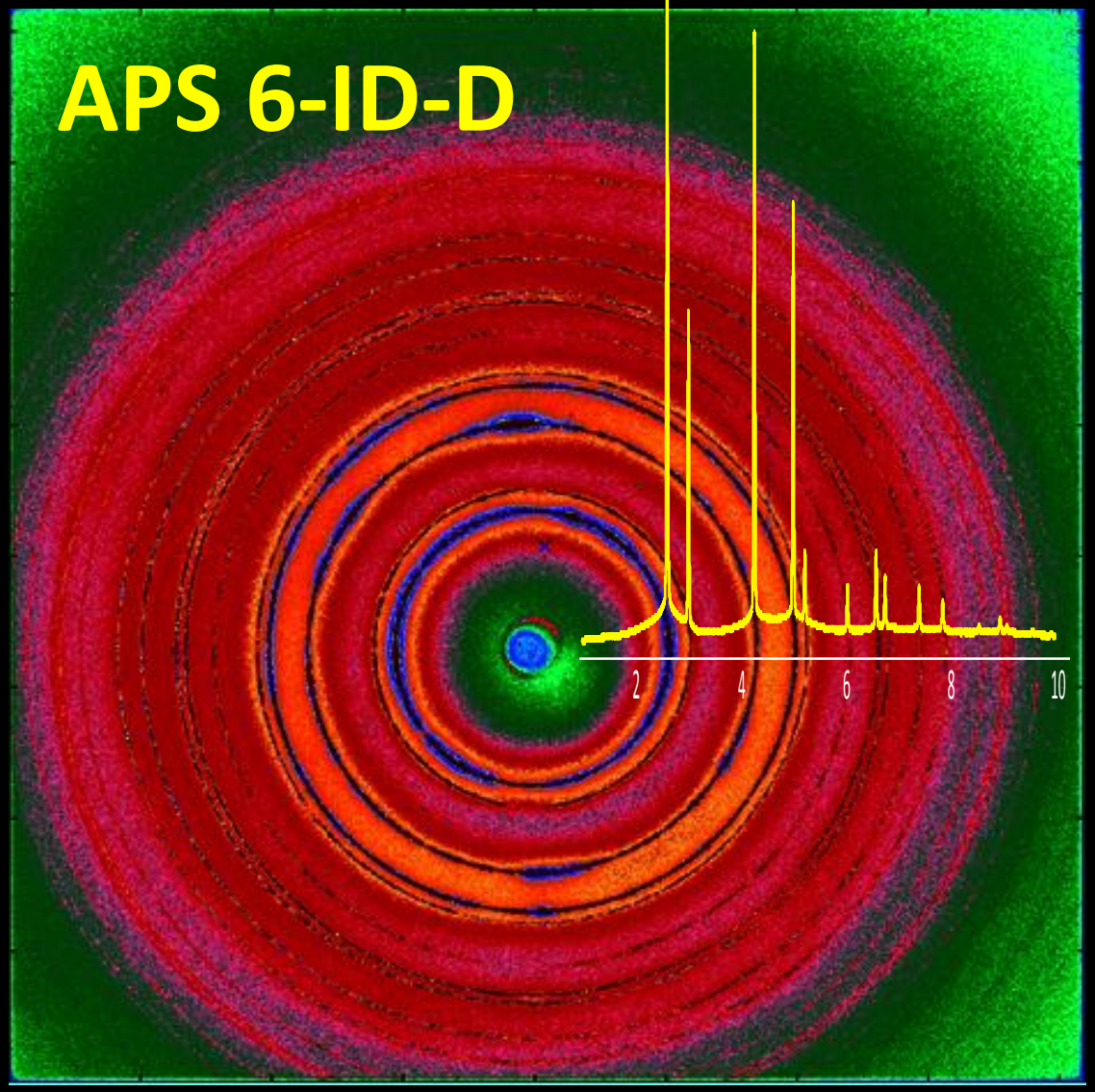


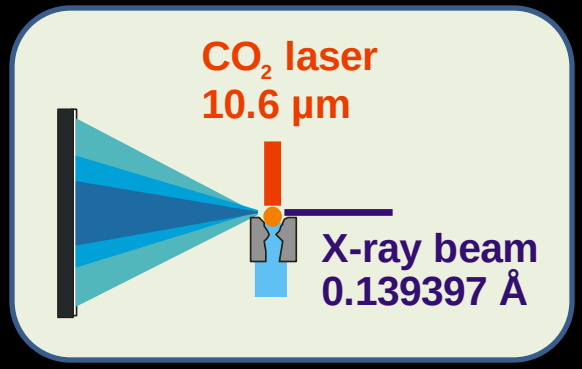
Er_2O_3



Nd_2O_3

XRD data collection





6 seconds collection

0.1 s exposure time
60 summed exposures

Cubic ZrO_2
T app = 2900 °C
a = 5.283 Å

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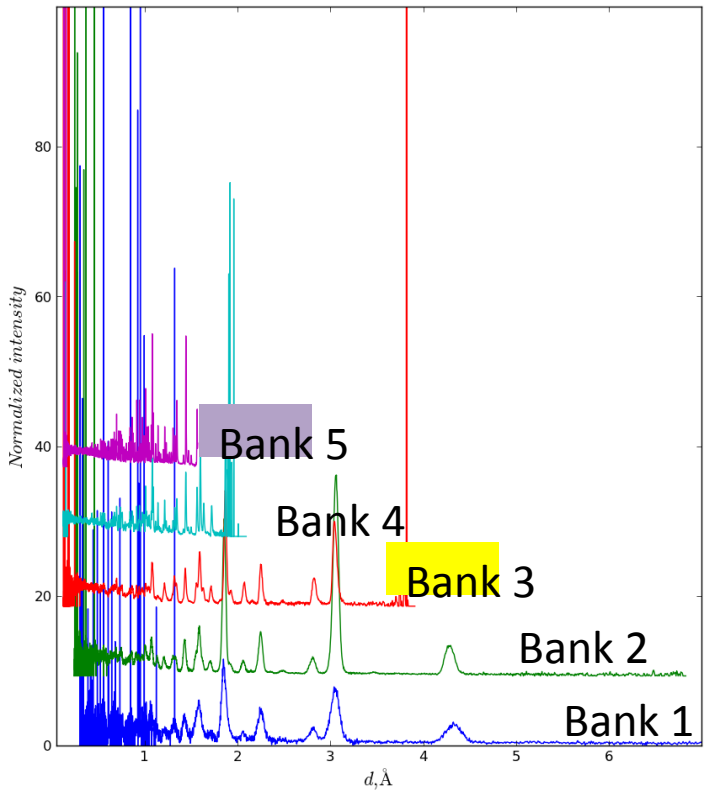
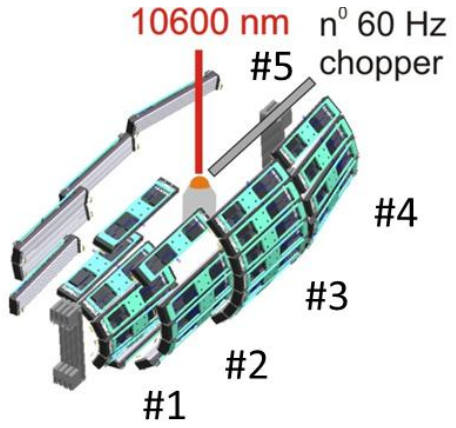
ND data collection





SNS NOMAD BL1B

Levitated Y_2O_3 at RT
30 minutes

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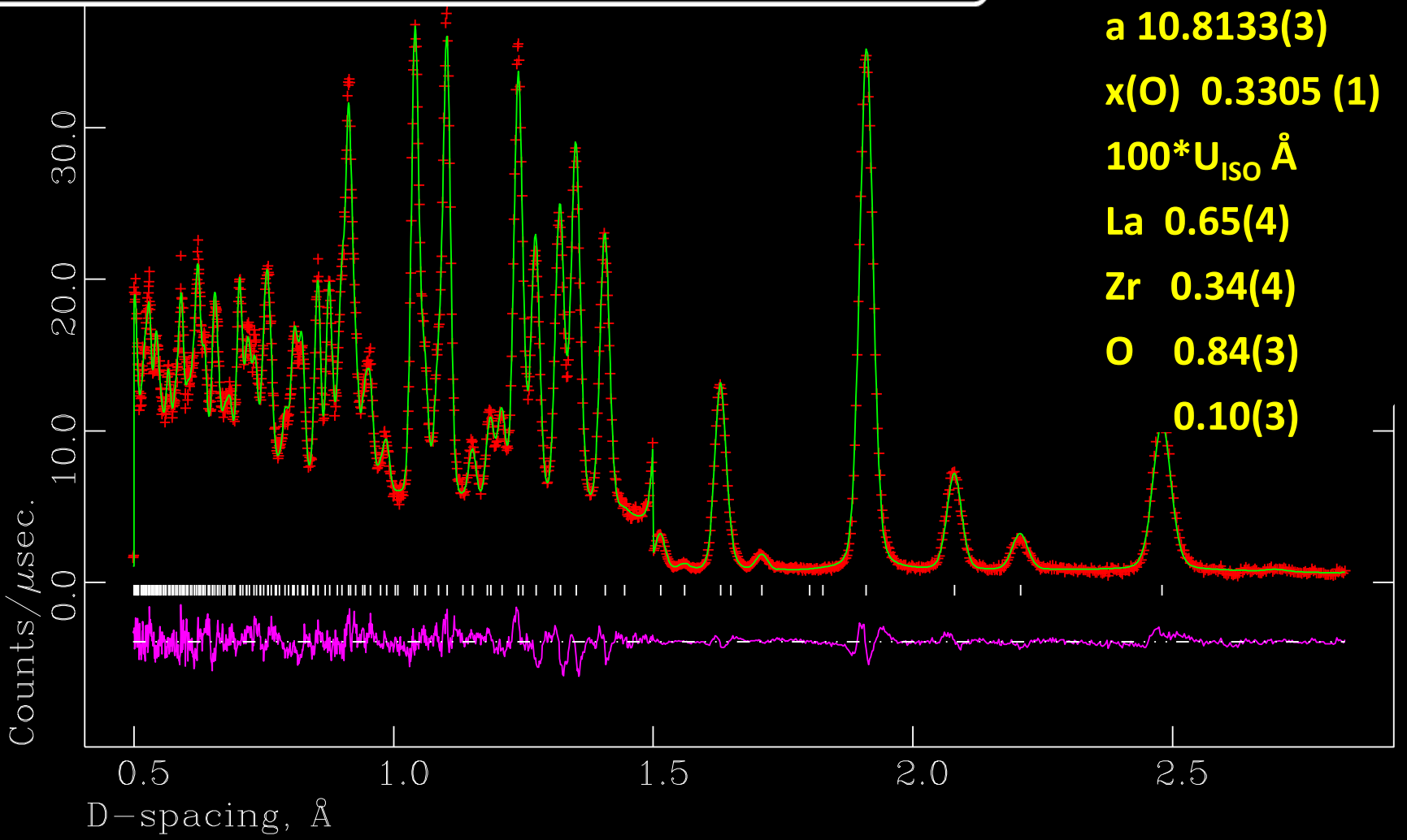
Data Processing

- Calibration at RT for every levitating bead
- Integration with FIT2D, refinement with GSAS/ExpGUI, FullProf, GSAS-II
- Le Bail refinement of cell parameters for high temperature H phases in Y_2O_3, Er_2O_3, Ho_2O_3
- Refinement of room temperature structures on levitated samples to validate the method

ND of levitated $La_2Zr_2O_7$ at RT, BANK 3, Rietveld fit

χ^2 2.75
R_{wp} 4.8%
R_F^2 4.3 %

a 10.8133(3)
x(O) 0.3305 (1)
100*U_{ISO} Å
La 0.65(4)
Zr 0.34(4)
O 0.84(3)
0.10(3)



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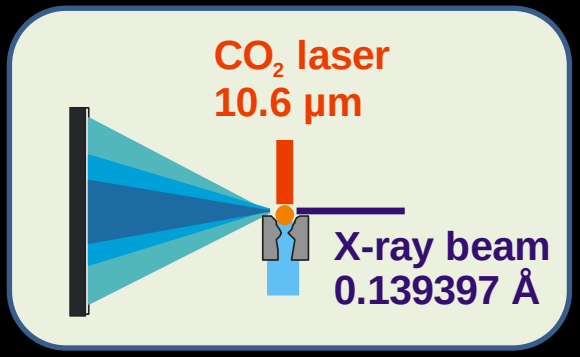
Results from 3 days of diffraction experiments on levitator at APS (June 15-17, 2011)



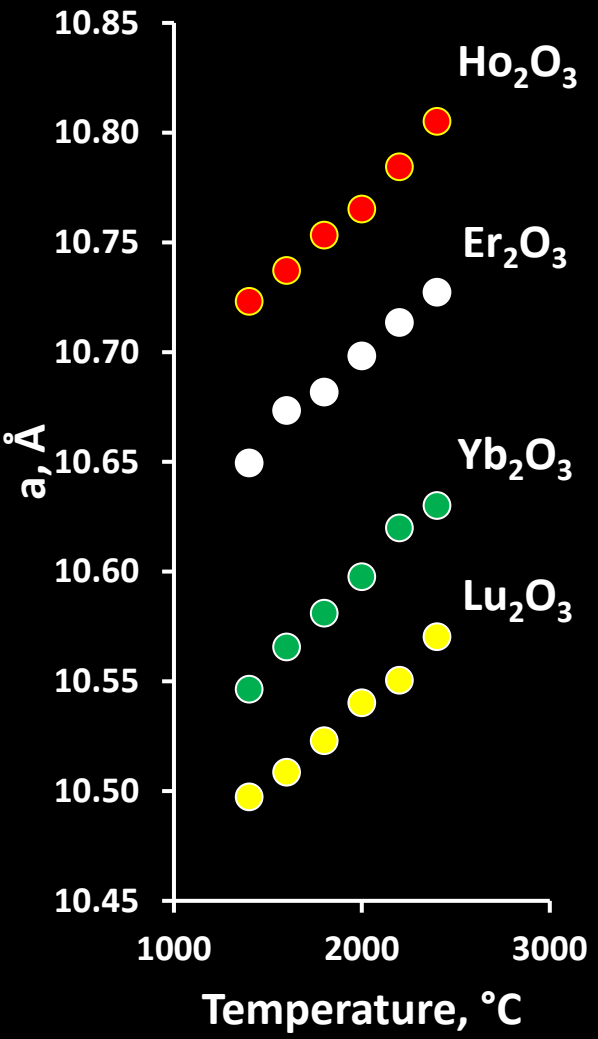
- **Y_2O_3 transforms in H-type before melting in Ar and O_2. Volume reduction on C-H phase transition was refined.**
- **Pyrochlore structure of $La_2Zr_2O_7$ persists to the melting temperature. Thermal expansion was used to validate high temperature *ab initio* calculations.**
- **Thermal expansion of Eu_2O_3-ZrO_2 DF solid solutions and anti-site occupancies on pyrochlore-DF phase transition in $Eu_2Zr_2O_7$ were refined.**

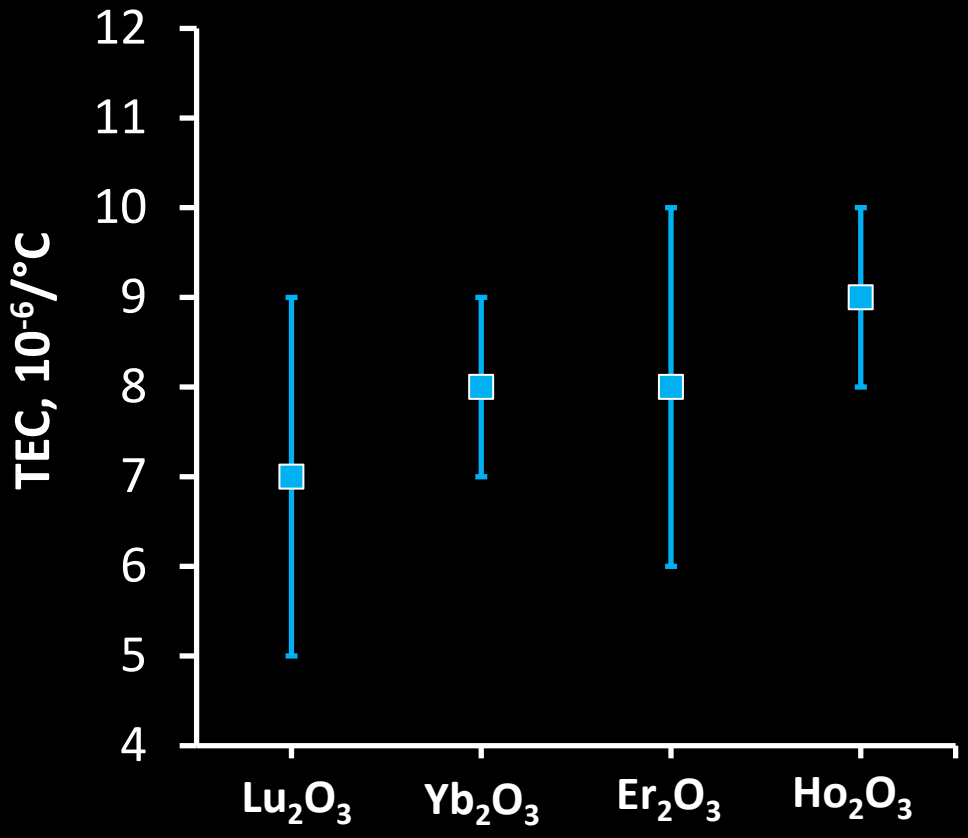
Maram PS, Ushakov SV, Weber RJK, Benmore CJ, & Navrotsky A (2015) *J. Am. Ceram. Soc.* 98 (4), 1292

Hong Q-J, Ushakov SV, Navrotsky A, & van de Walle A (2015) *Acta Mater.* 84, 275

Ushakov SV & Navrotsky A (2012) *J. Am. Ceram. Soc.* 95, 1463

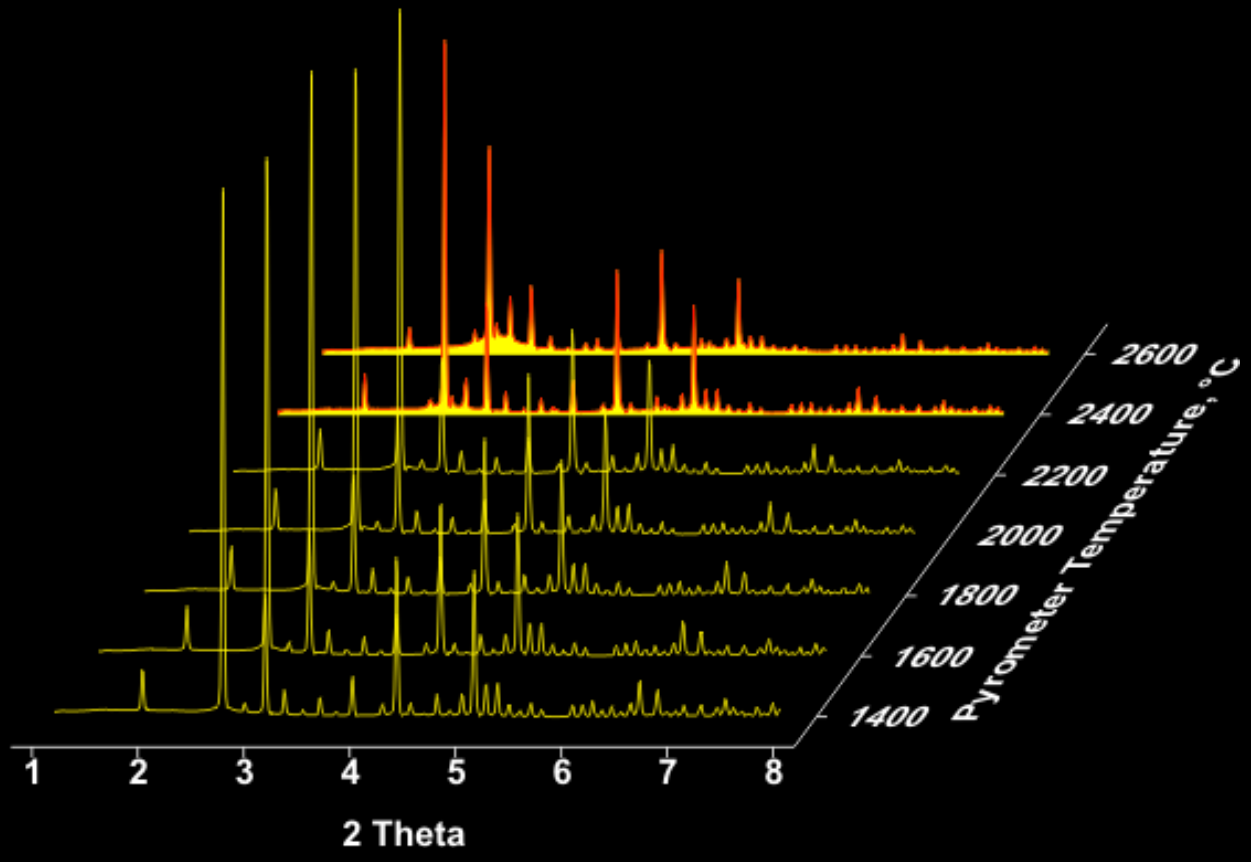
Thermal expansion of C-type RE_2O_3 in Oxygen flow





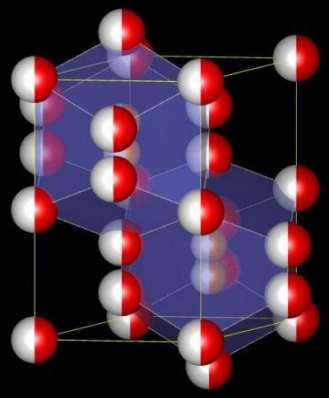
Alfred Pavlik, Summer 2015

C-H pre-melting phase transitions RE_2O_3

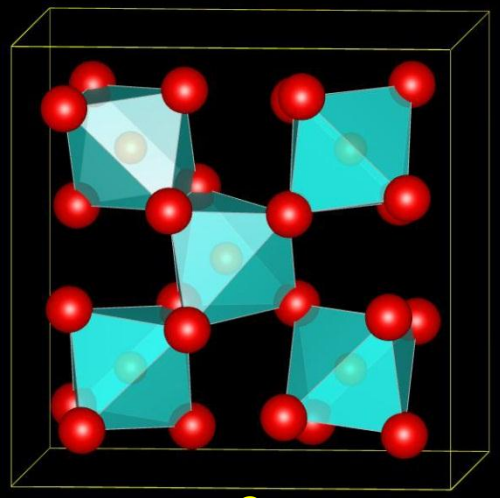


Pre-melting C-H phase transition in Er_2O_3 in Ar

H-type Z=1

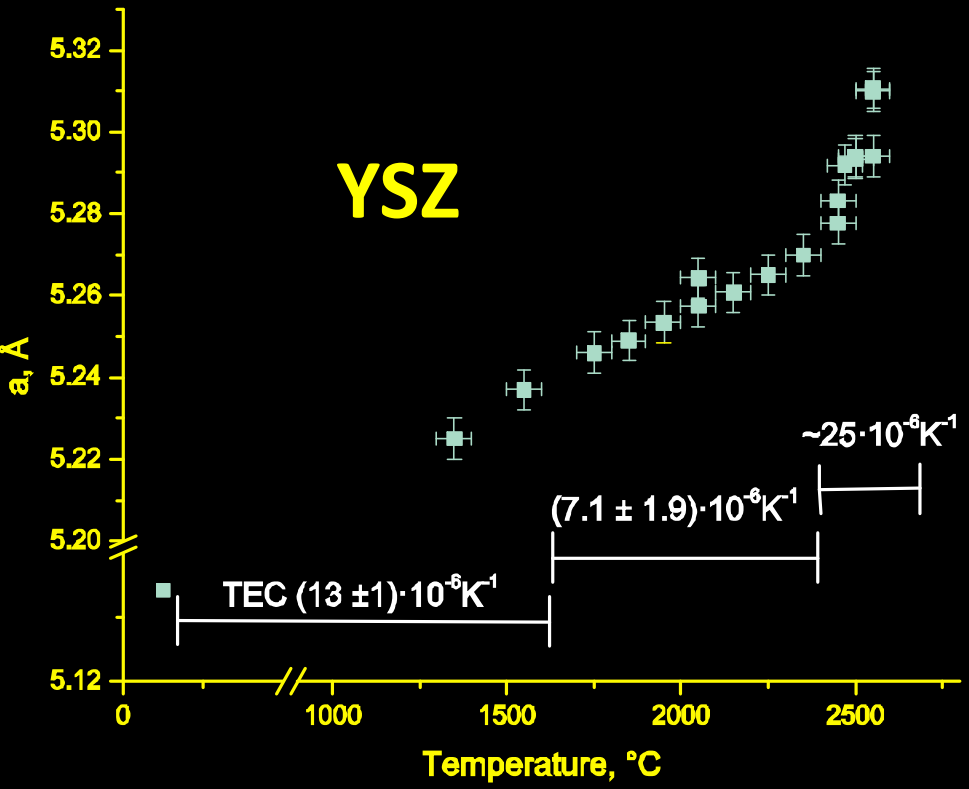


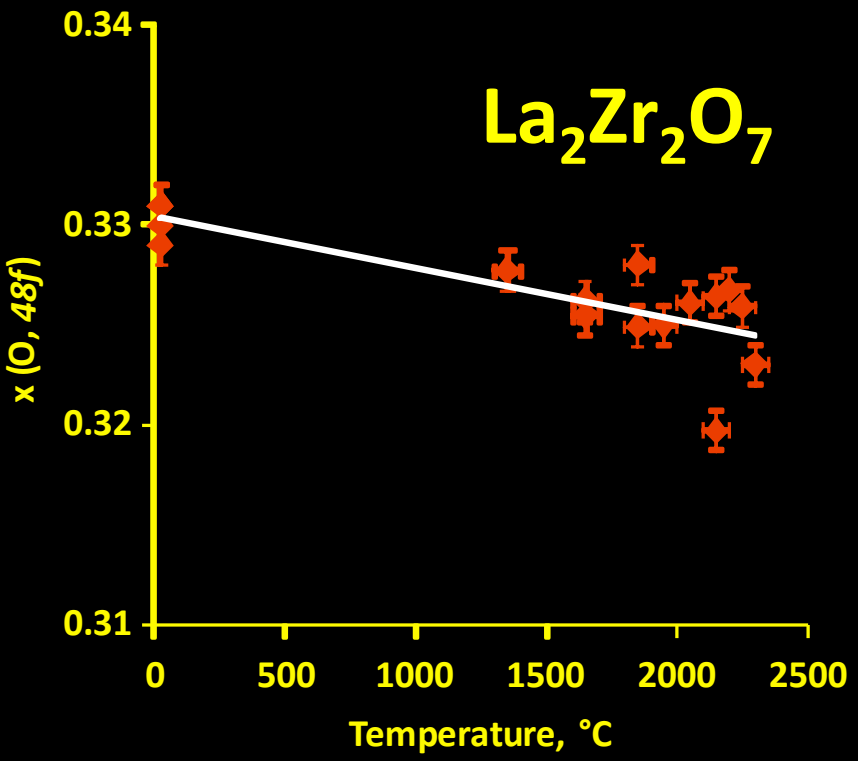
Y_2O_3 ΔV -3.1%
Er_2O_3 ΔV -3.4%
Ho_2O_3 ΔV -3.9%



C-type Z=16

Neutron Diffraction results (Aug 23-29, 2014)





Ushakov, S. V., Navrotsky, A., Weber, R. J. K. and Neuefeind, J. C. (2015), Structure and Thermal Expansion of YSZ and $La_2Zr_2O_7$ Above 1500°C from Neutron Diffraction on Levitated Samples. J. Am. Ceram. Soc., 98: 3381

Conclusion

Refinement of high temperature structures is possible from X-ray and neutron diffraction on laser heated levitated samples using existing instruments at APS 6-ID-D and SNS NOMAD*

*Thermal gradient of ~150 °C in diffraction volume

UC Davis workshop on

Structure and Thermodynamics of oxides at High Temperature

October 18-21, 2016

(before MS&T 2016 and ACerS 118th meeting in Salt Lake City)

Confirmed Invited speakers:

Dario Manara, ITU
Richard Weber, MDI
Elizabeth Opila, University of Virginia
Lawrie Skinner, Stony Brook

http://thermo.ucdavis.edu/

Questions ?