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Sandia National Laboratories

Designing High Entropy $RE_2Zr_2O_7$ Oxides

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Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications V

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U.S. DEPARTMENT OF ENERGY NNSA

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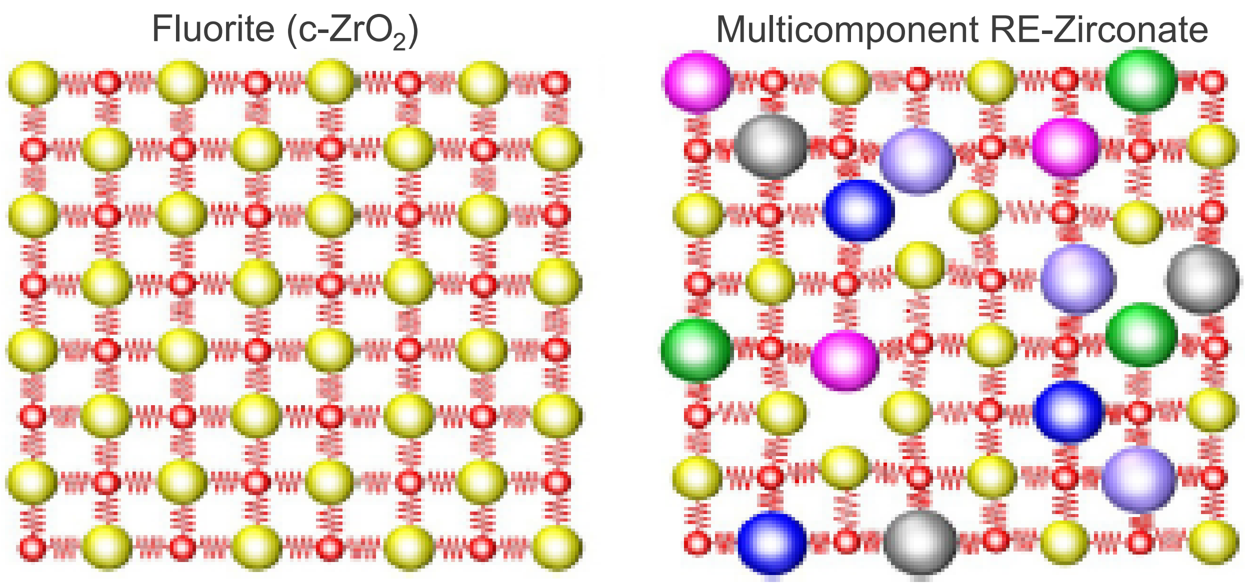
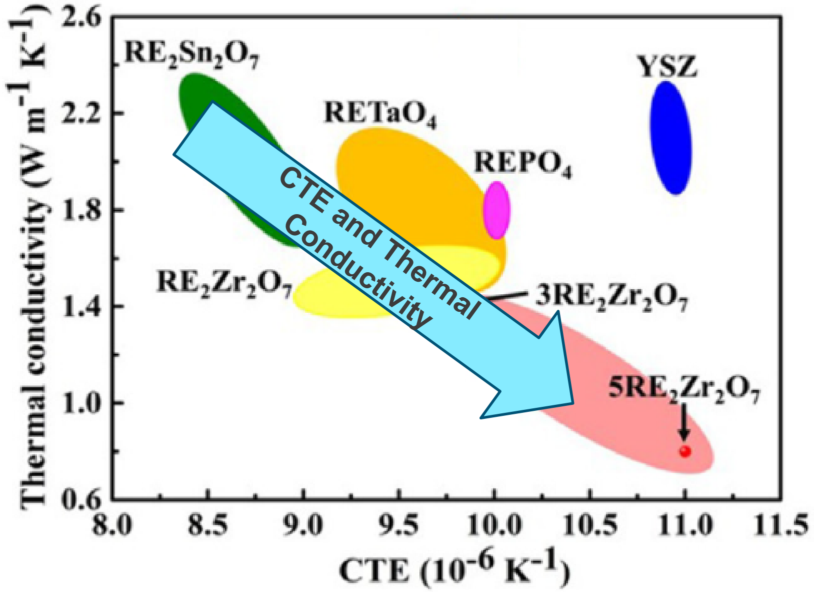
Outline

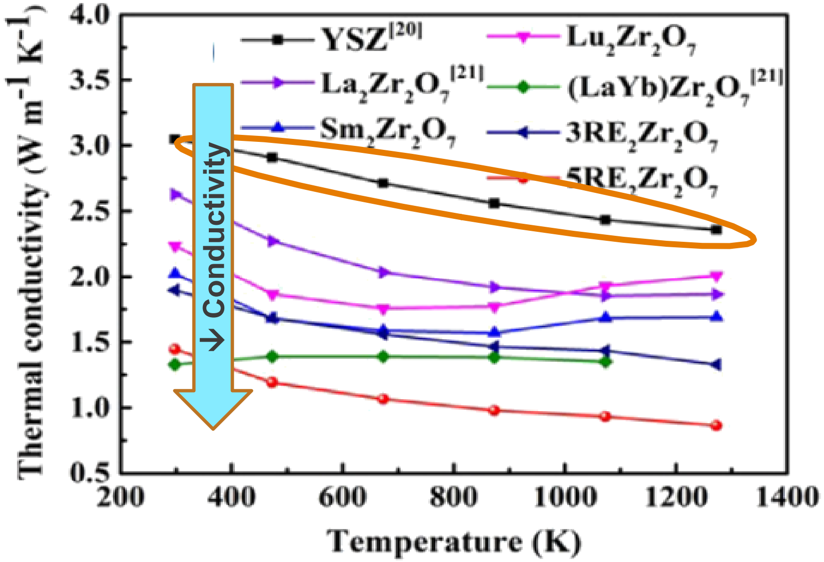
- Why high entropy materials?
- Predicting $RE_2Zr_2O_7$ structures: Pyrochlore vs Defect Fluorite
- Determination of phase composition and phase stability
- Tailorable thermal expansion
- Summary

High entropy $RE_2Zr_2O_7$ materials: Unique Properties



- 5 cation oxide = high entropy → ***tunable thermal and mechanical properties***
  - Thermal expansion
  - Specific heat
  - Thermal conduction
  - Elastic modulus
- Thermal barrier coatings
  - Need 2000 °C+ stability in oxidizing/inert conditions
  - State of the art YSZ is limited to 1400 °C





- $3RE_2Zr_2O_7$: $(SmEuDy)_2Zr_2O_7$
- $5RE_2Zr_2O_7$: $(SmEuTbDyLu)_2Zr_2O_7$

Ren Scripta Materialia 178 (2020) 382-386

Need predictable phase stability

$\gamma = \frac{r_{RE}}{r_{Zr}}$, Fluorite < γ=1.46 ($r_{RE} = 1.05$Å) < Pyrochlore

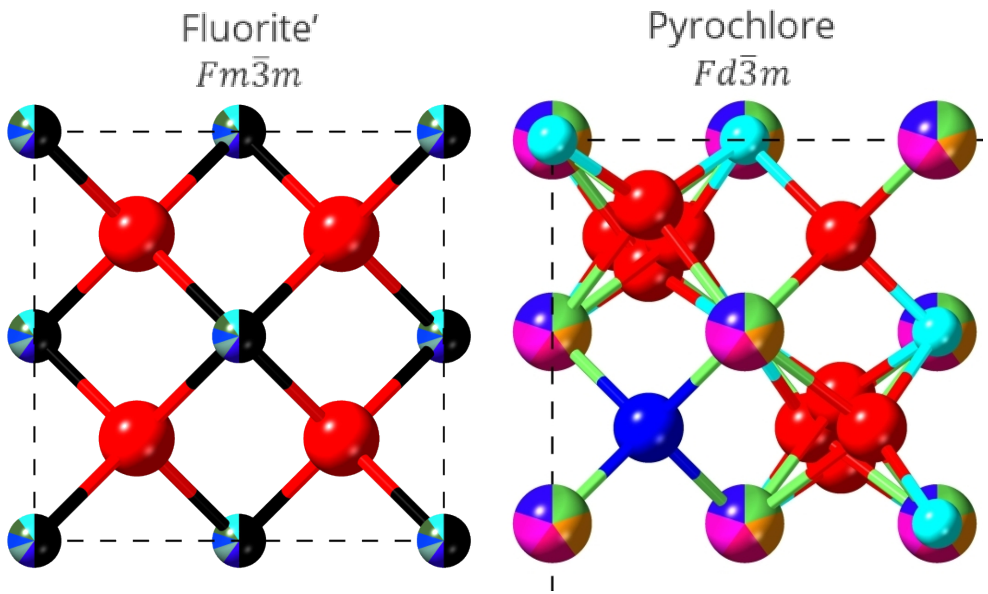
→ *extend to high entropy oxides*

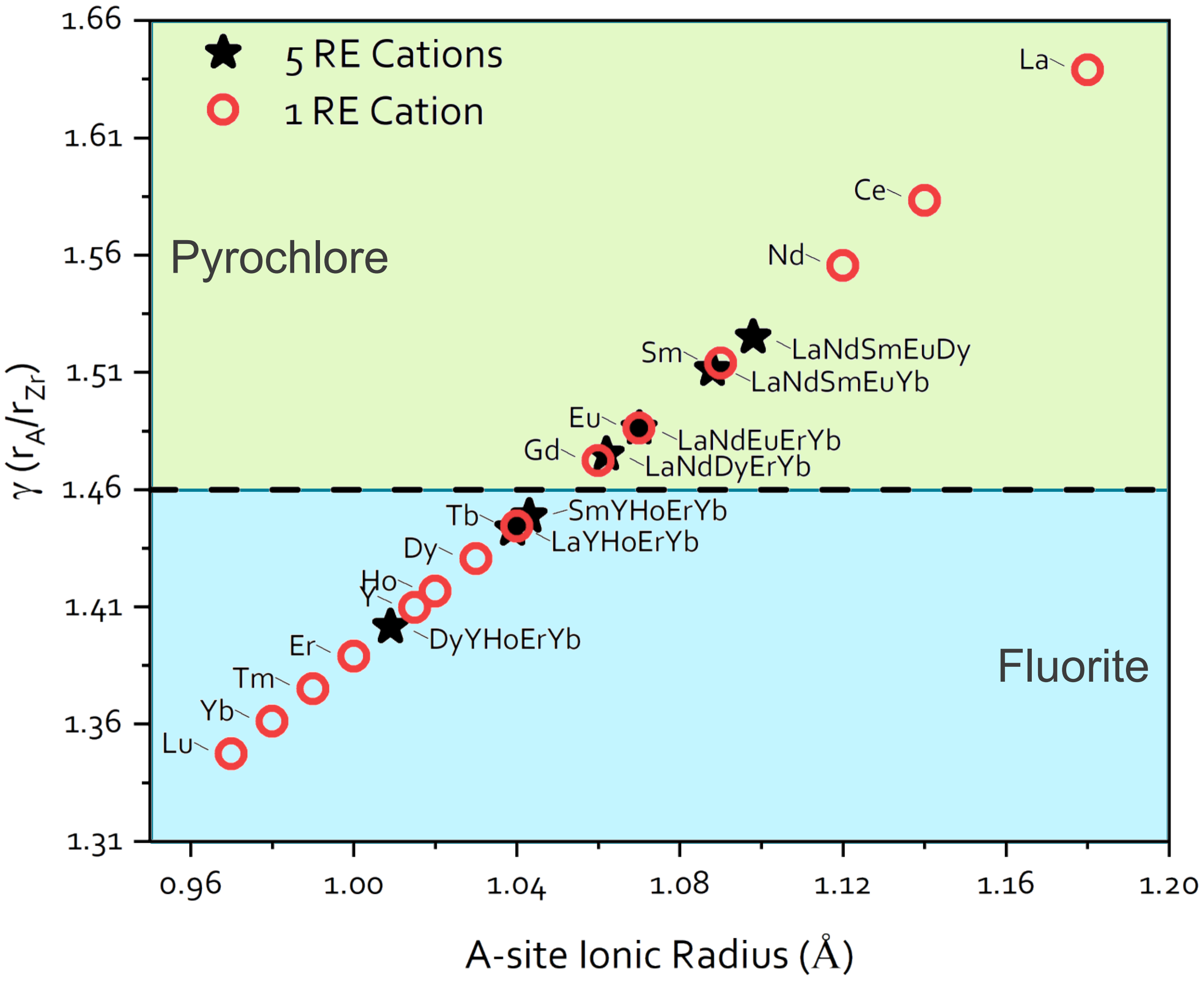
Property considerations

- **Large RE → High thermal expansion → Pyrochlores**
- Small RE → High thermal conductivity
- Desired to tailor thermal and physical properties through composition

Solid state synthesis

- Calcined at 1700°C for 24hrs

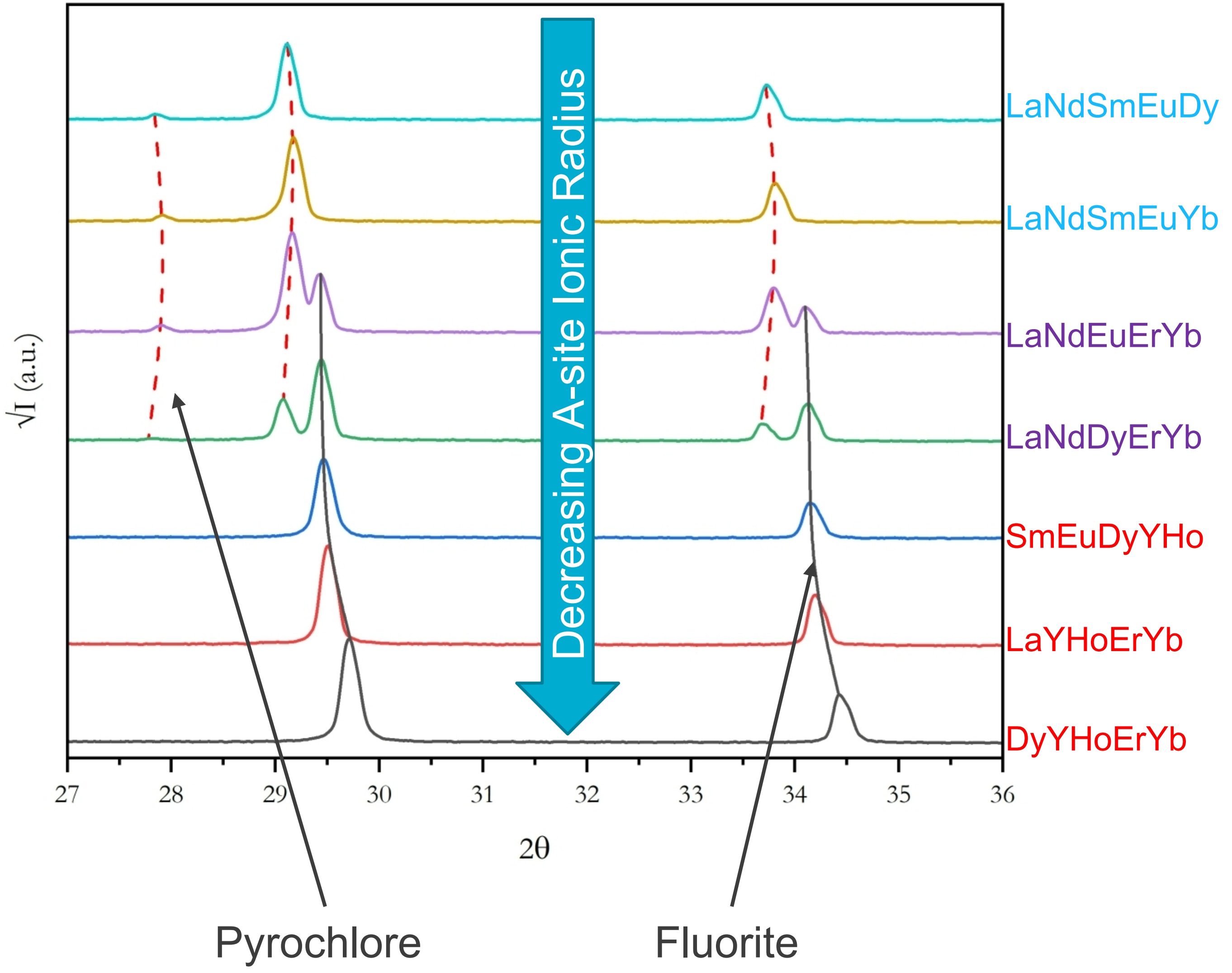


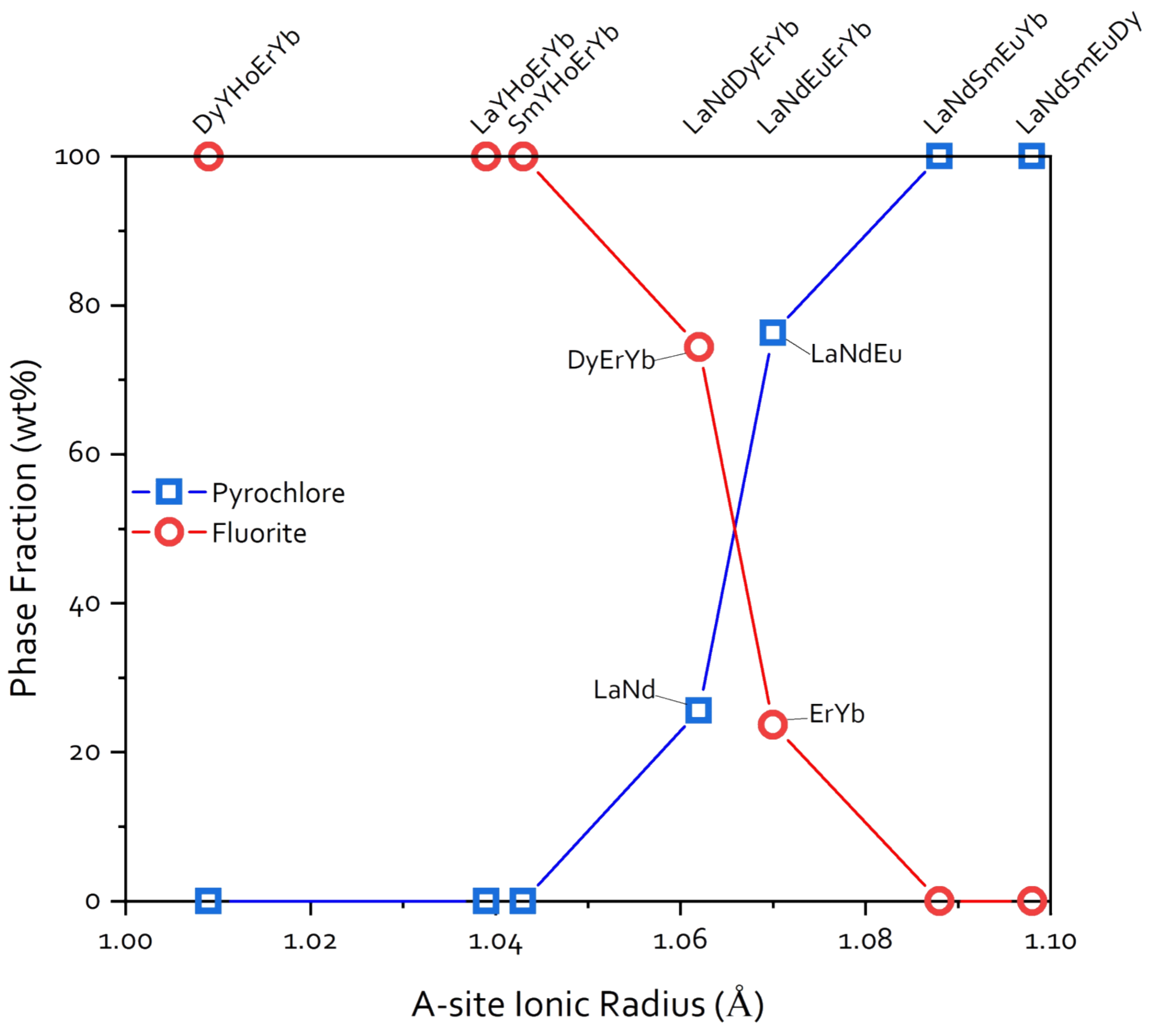


Popov, Journal of Alloys and Compounds 689 (2016) 669-679

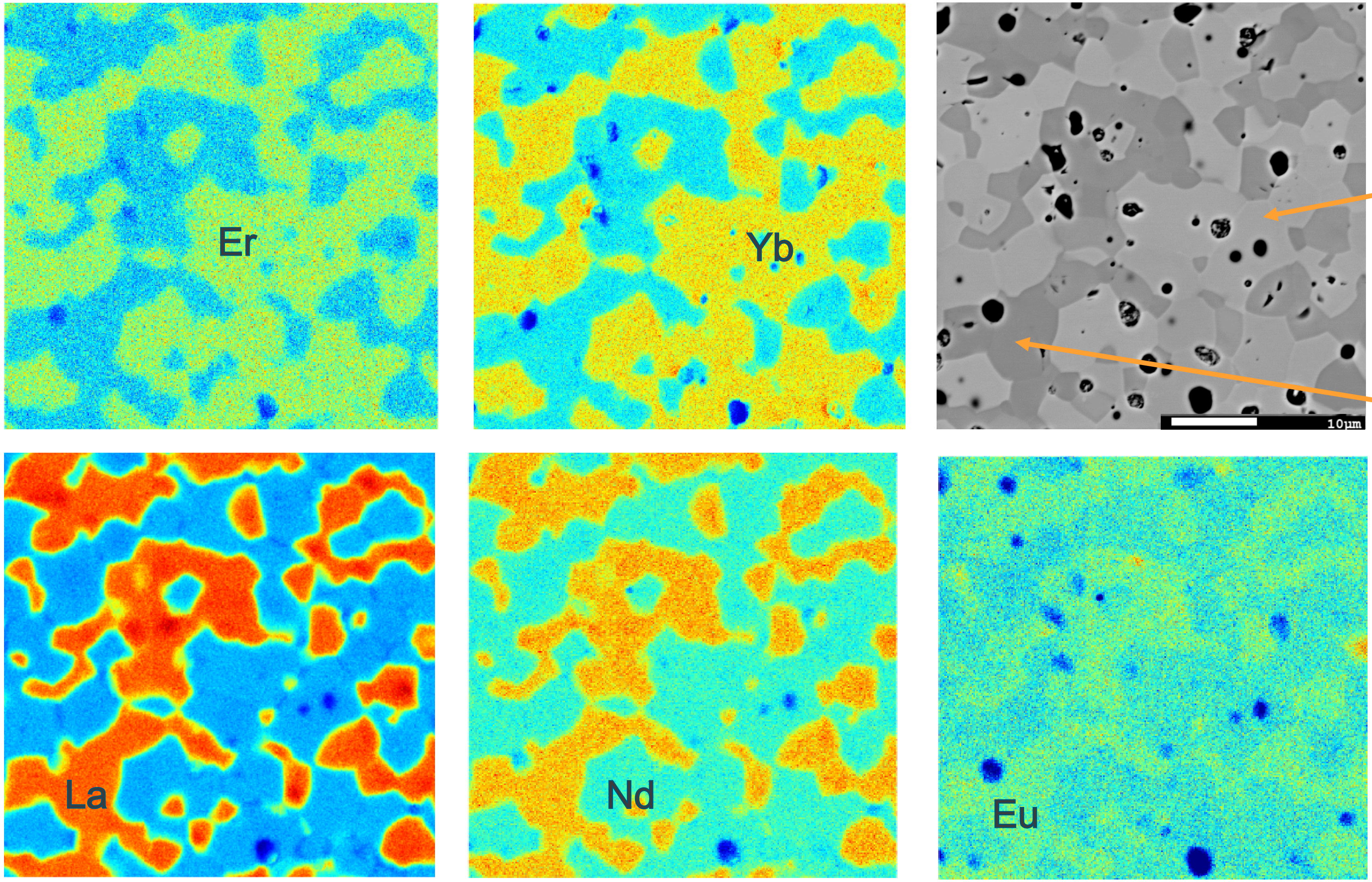
Shannon, Acta Crystallographica Section B 5 (1969) 925-

Observed phases match predictions except for intermediate radii





Element segregation into pyrochlore and fluorite phases



$(La_{0.12}Nd_{0.16}Eu_{0.19}\mathbf{Er_{0.29}Yb_{0.24}})_2Zr_2O_7$

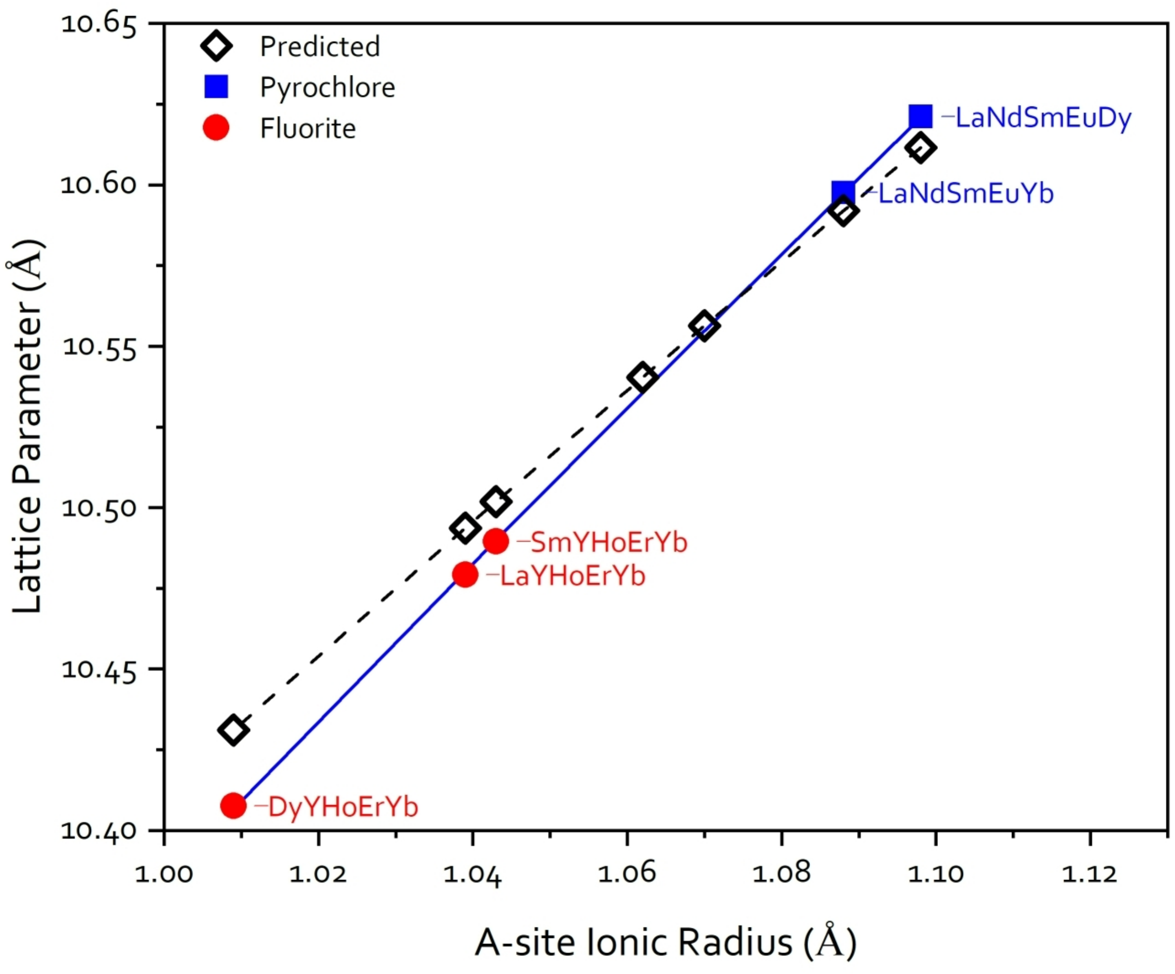
A = 1.049 Å → Fluorite

$(\mathbf{La_{0.26}Nd_{0.24}}Eu_{0.19}Er_{0.19}Yb_{0.12})_2Zr_2O_7$

A = 1.086 Å → Pyrochlore

Similar segregation observed in LaNdDyErYb

Revised lattice parameter prediction: 5 cation oxides!



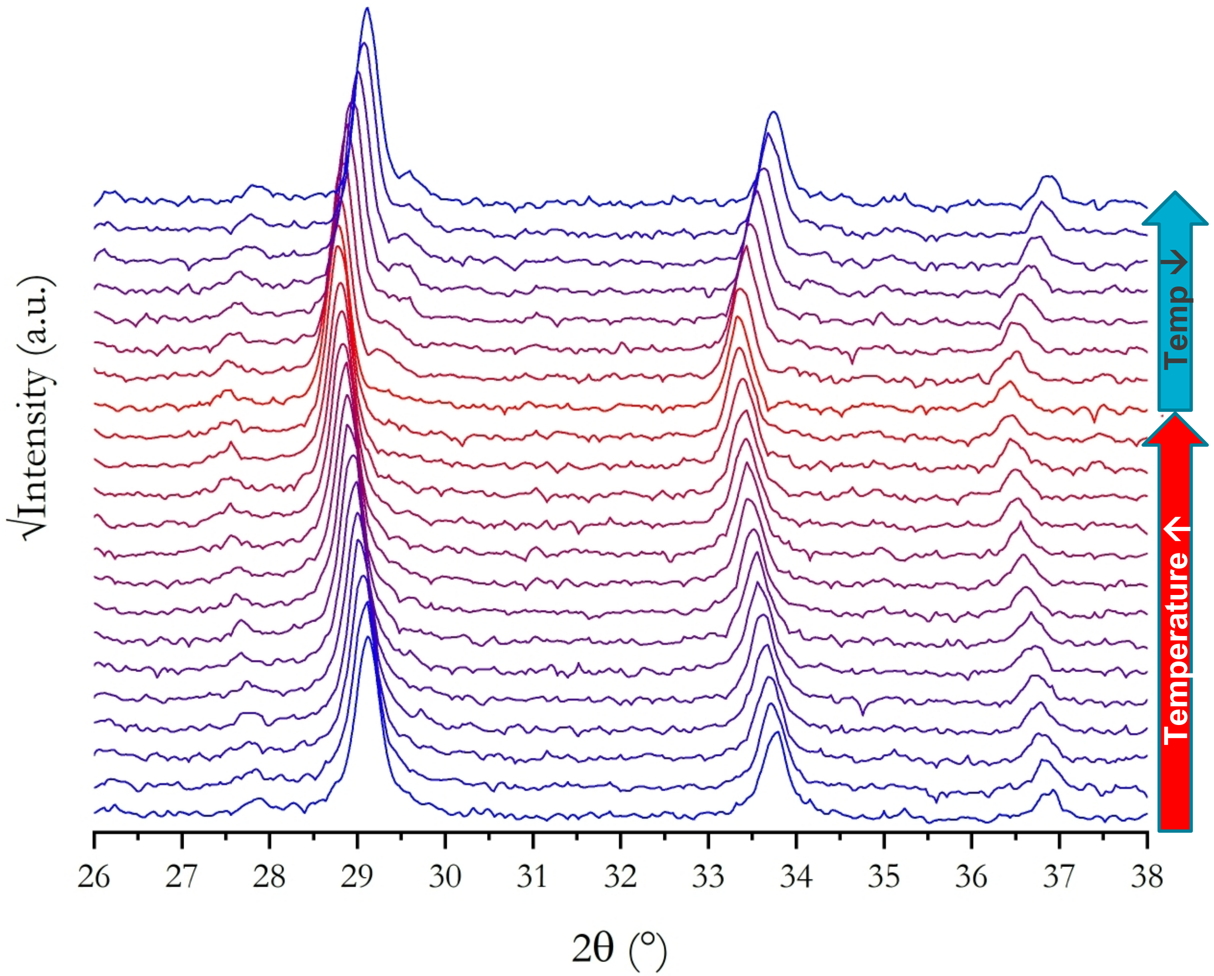
$$a_{Pyrochlore} = \frac{8}{\sqrt{3}}\left[1.43373(r_A + r_O) - 0.42931\left(\frac{(r_A + r_O)^2}{r_B + r_O}\right)\right]$$

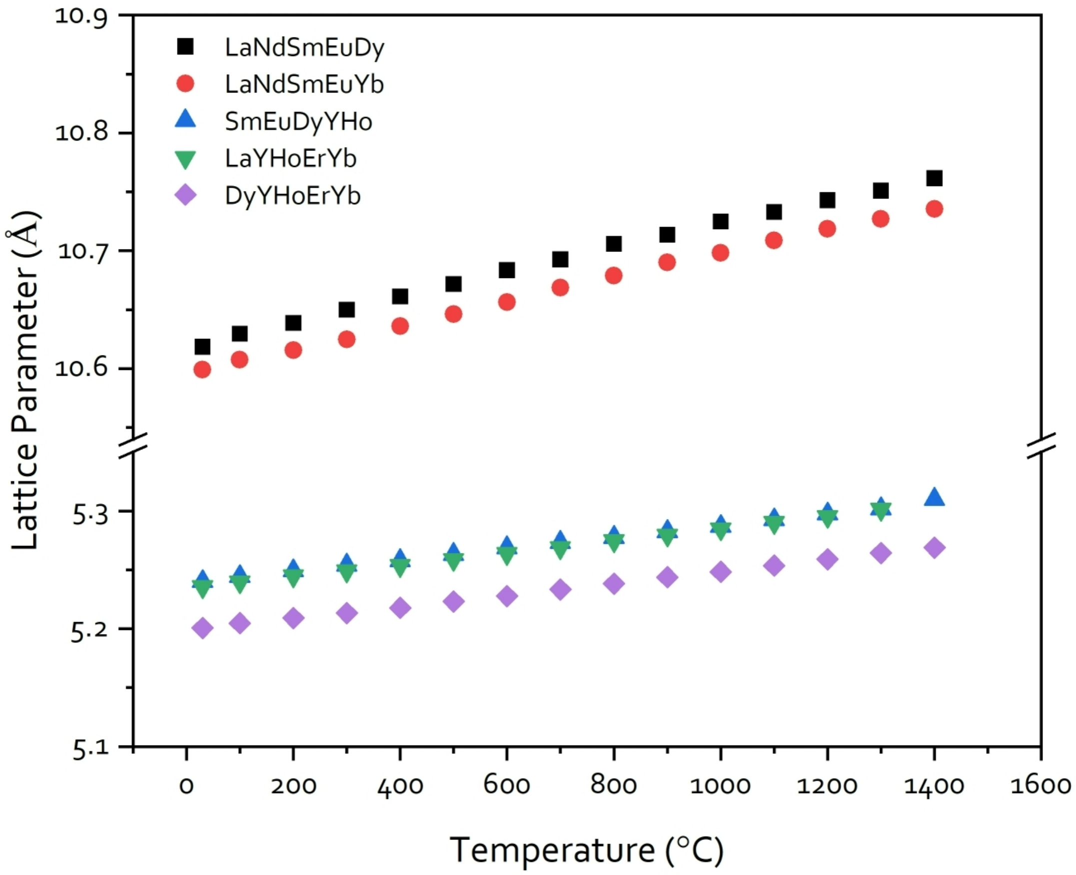
$$a_{Pyrochlore} = \frac{8}{\sqrt{3}}\left[1.35002(r_A + r_O) - 0.35768\left(\frac{(r_A + r_O)^2}{r_B + r_O}\right)\right]$$

- Measured 5 component RE oxide lattice parameters (solid) → predicted (hollow)
- Allows for prediction of additional properties
  - Thermal expansion
  - Thermal conductivity

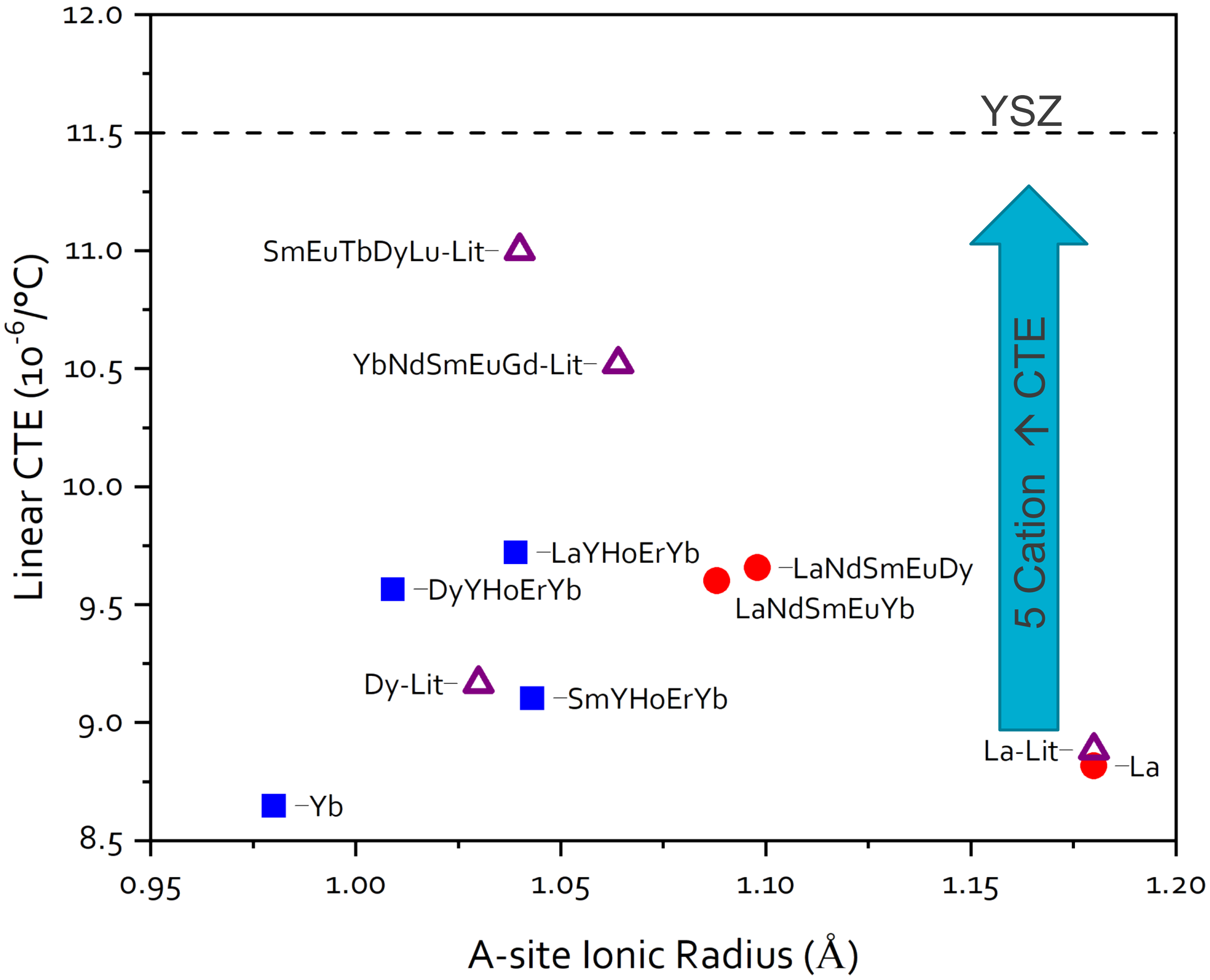
Mouta, Acta Crystallography B 69 (2013) 439-45

Linear thermal expansion observed up to 1500 °C with HTXRD





Effect of A-site composition on thermal expansion



- For 5RE compositions increasing A-site radius generally increased CTE
- Multicomponent compositions demonstrate higher CTE than single component

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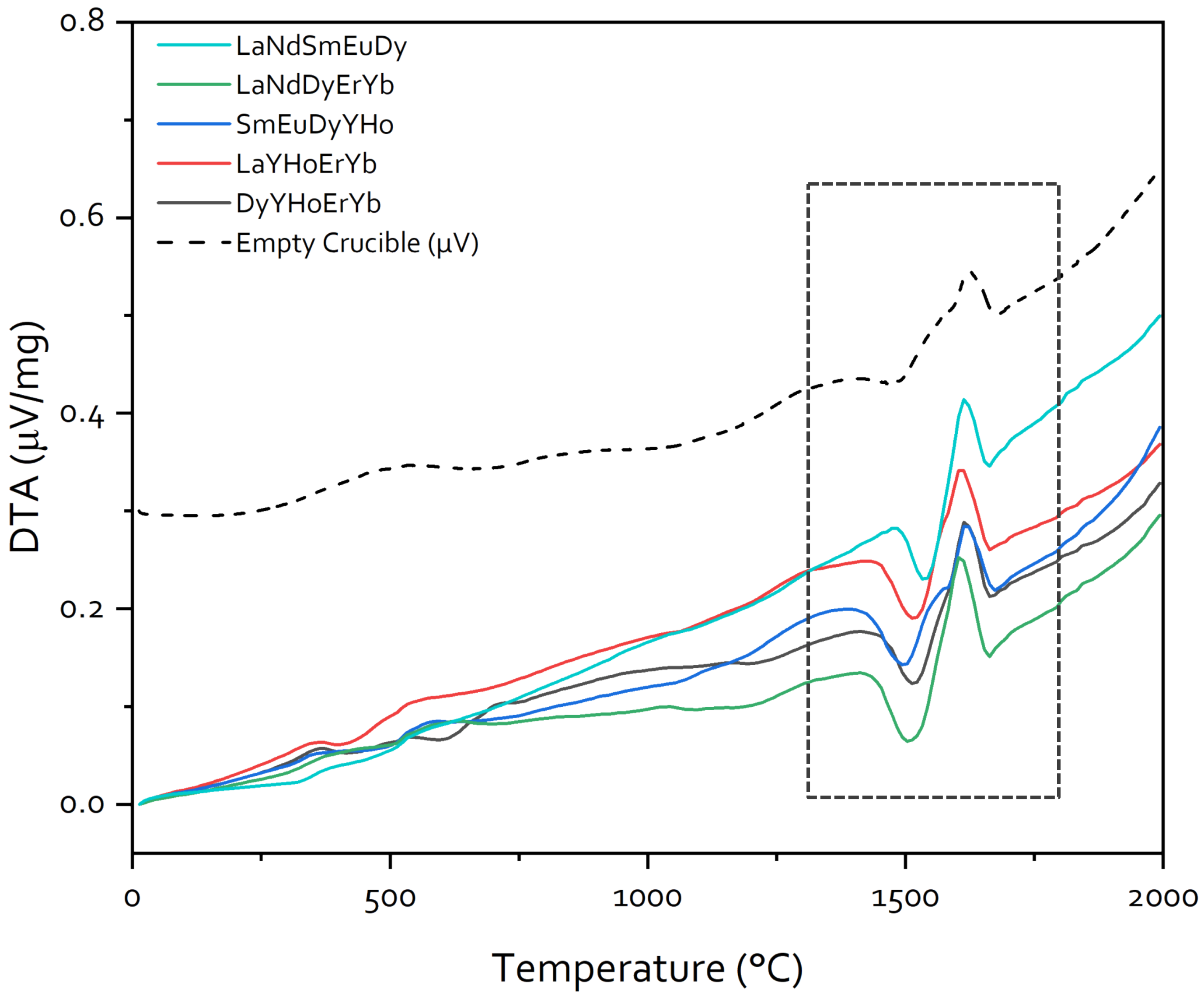
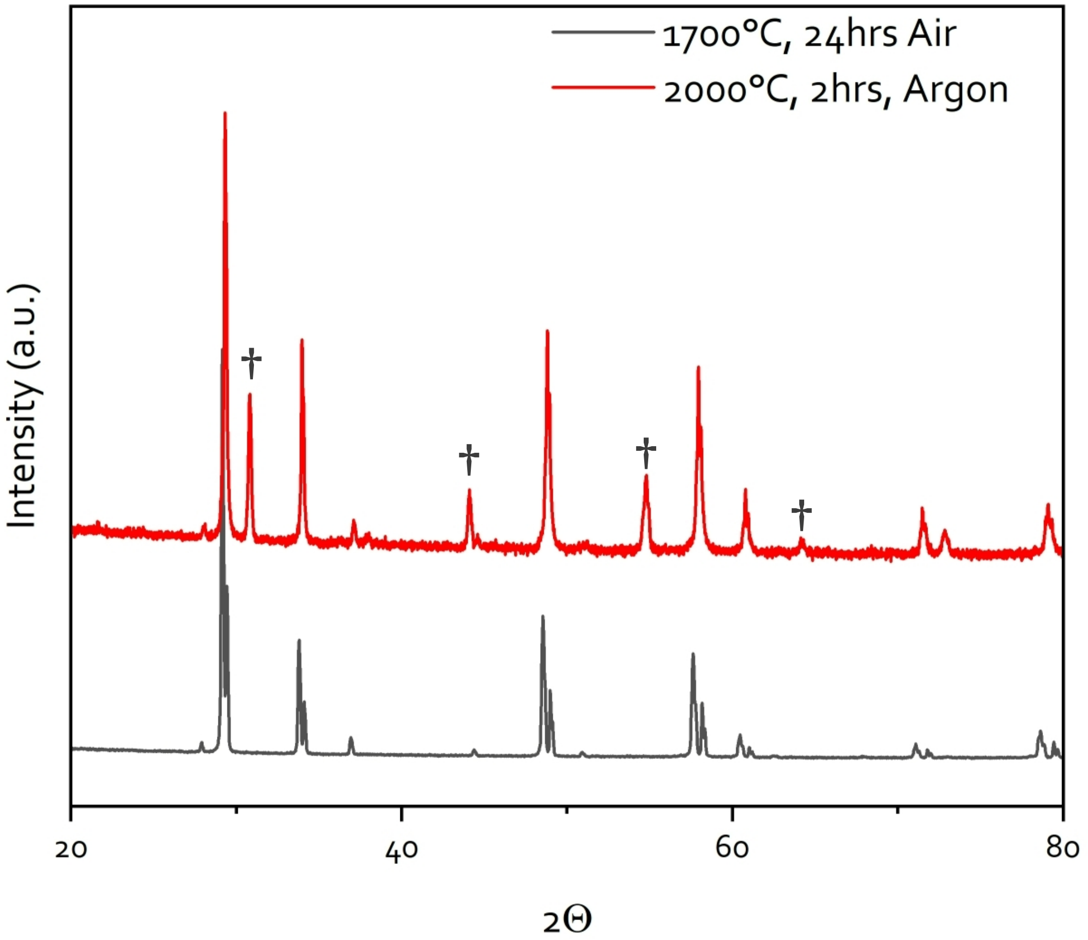
Luo JECerS 42 (2022)1391-2399

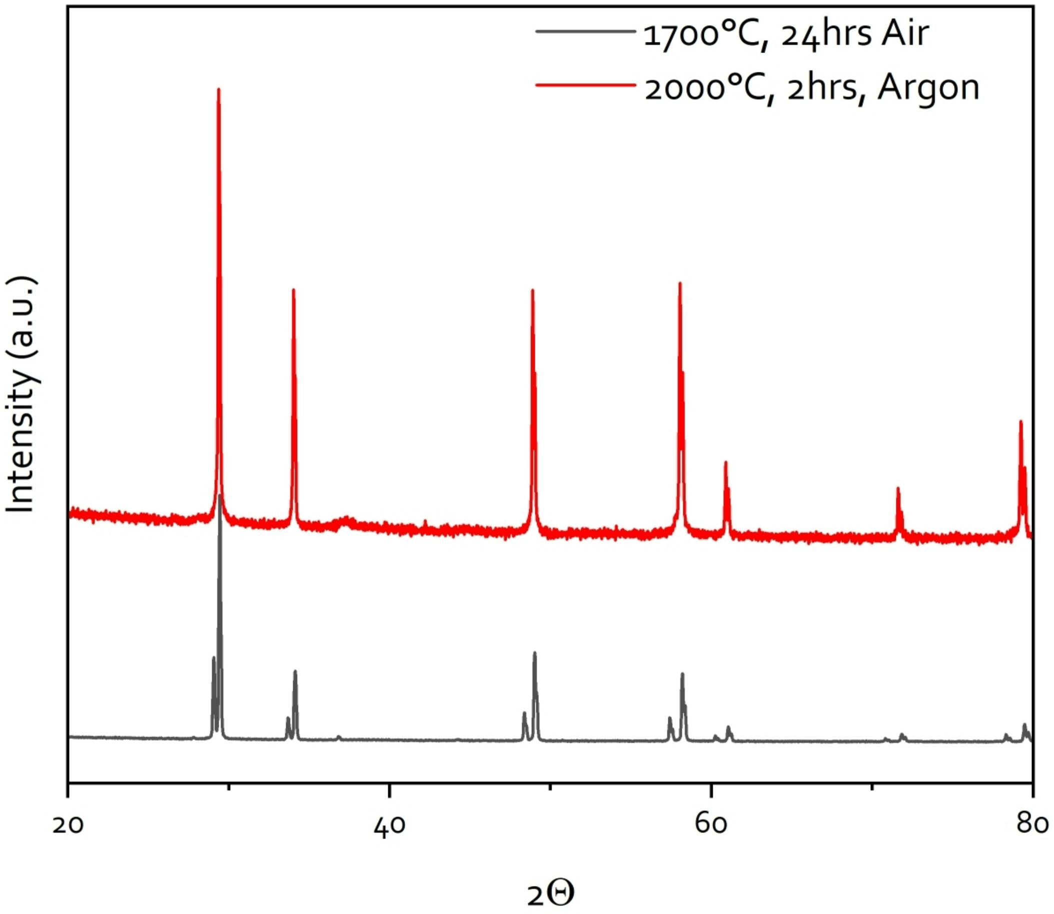
Phase stability up to 2000°C



- 15°C to 2000°C @ 25K/min
- Measured in He, $pO_2 \sim 10^{-13}$
- Boxed region → sample and ZrO_2 crucible reaction

Single phase achieved for intermediate radii at 2000°C!



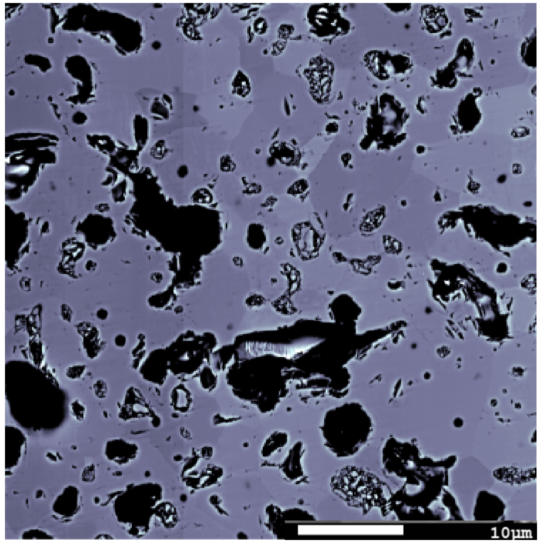


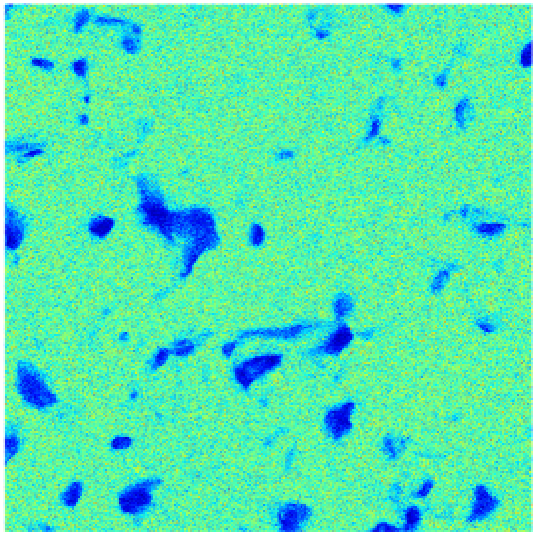
LaNd**Eu**ErYb → LaNdErYb pyrochlore + Eu metal

LaNd**Dy**ErYb → Single pyrochlore phase

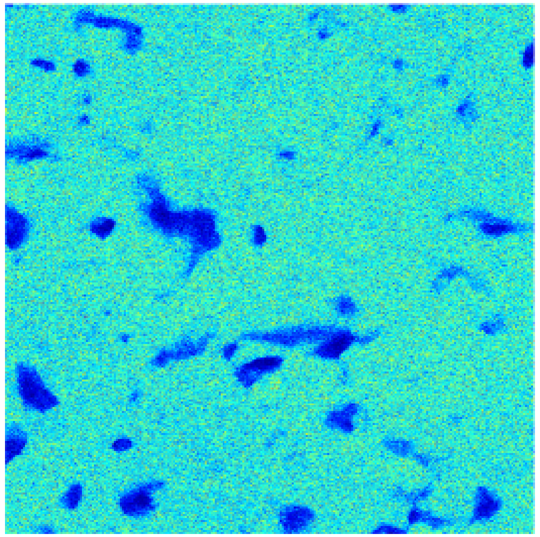
*pO_2 ~10^{-18}, ZrO_2 setter reduced

Single pyrochlore phase confirmed by microprobe ☺

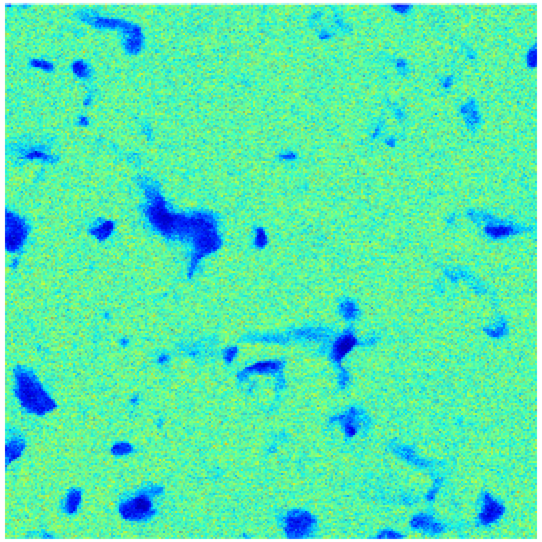




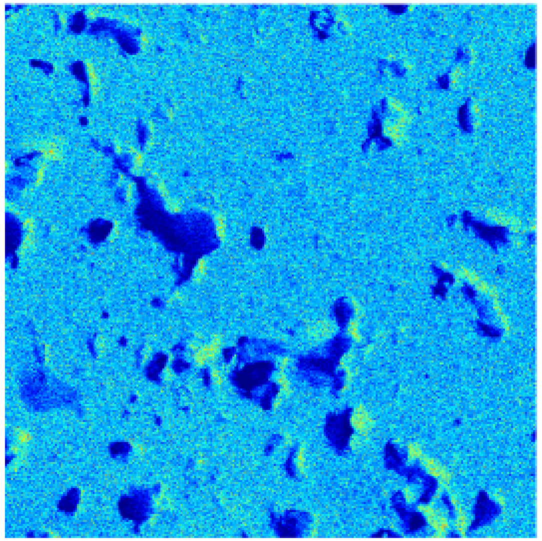
La



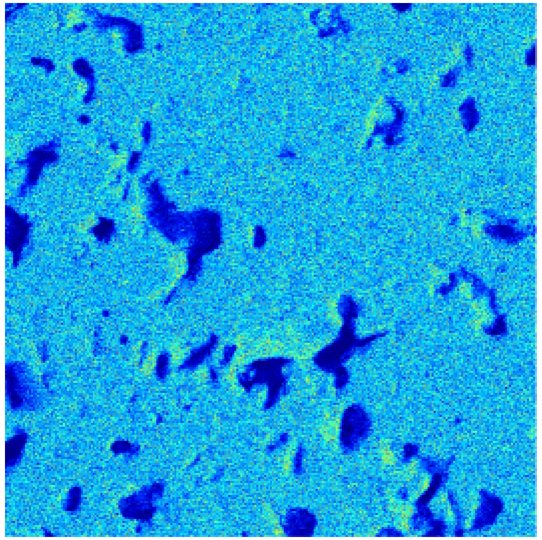
Nd



Dy



Er



Yb

Summary

- Revised relationship between ionic radius and phase stability
- Five element high-entropy RE oxides have a larger CTE than single-element RE oxides
  - Lower than previous literature
- Achieved single phase for intermediate radii
- Next steps
  - Improve densification
  - Determine the effect of ionic radius and cation selection on thermal conductivity
  - Determine the effect of ionic radius and cation selection on the elastic modulus

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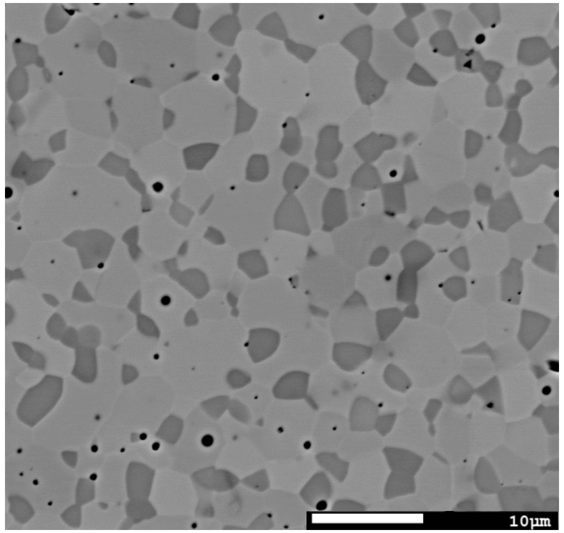
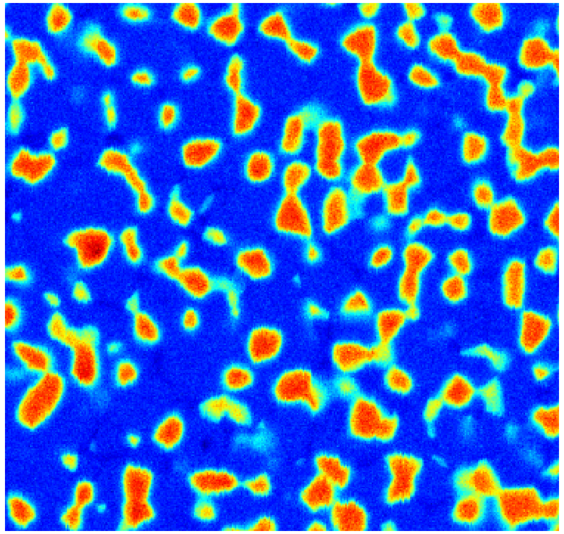
Elemental distribution of mixed phase compositions: $(LaNdDyErYb)_2Zr_2O_7$

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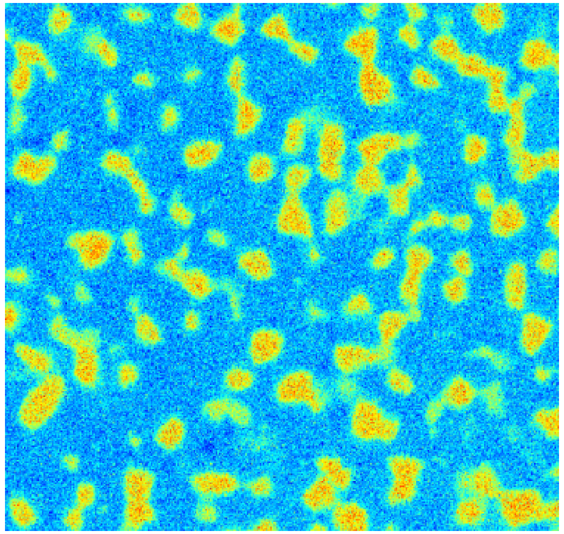
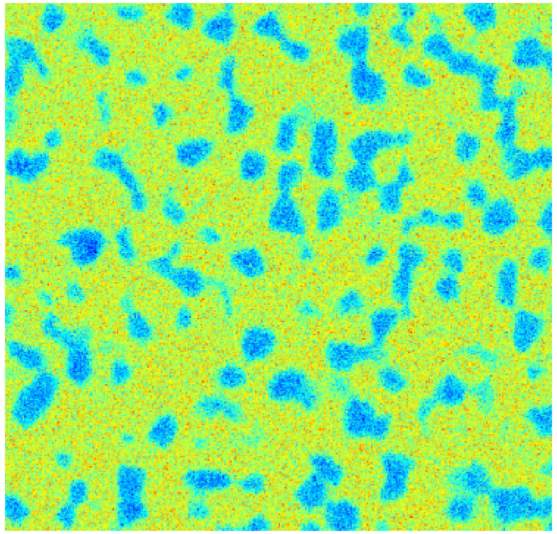

Nd

$(LaNd)_2Zr_2O_7$

Pyrochlore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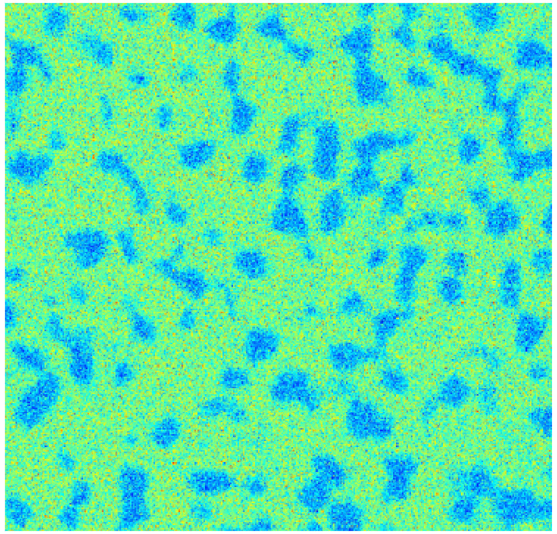
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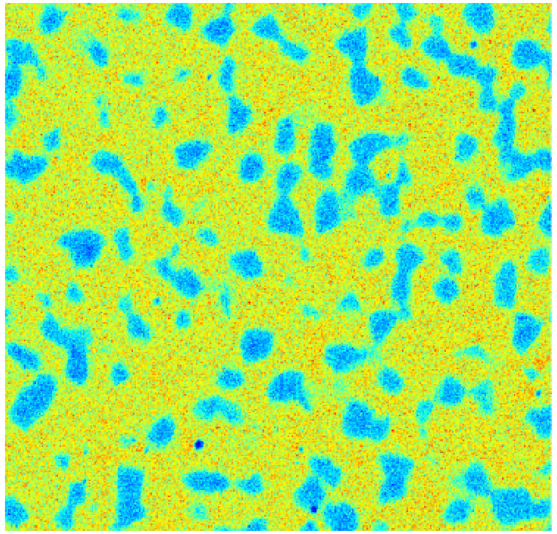
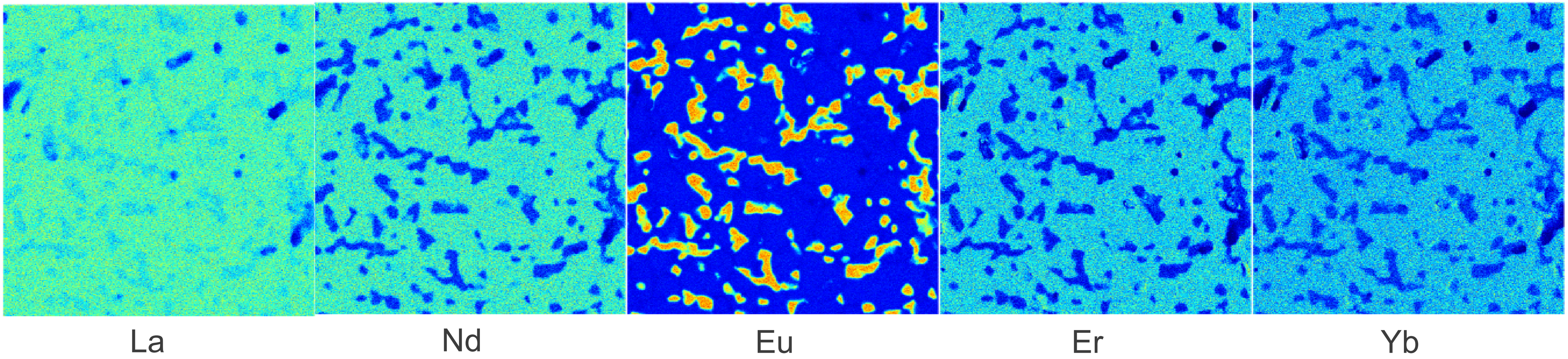

Yb

$(DyErYb)_2Zr_2O_7$

Defect Fluorite

Rare earth distribution of mixed phase compositions: 2000°C - 2hrs in Argon

$(LaNdEuErYb)_2Zr_2O_7$



$(LaNdDyErYb)_2Zr_2O_7$