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Disorder and Damage in CaLnZrNbO7 (Ln=La, Nd, Sm, Gd, Ho and Y)

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Acknowledgements

- **Peter Baldo, Ed Ryan, and Mark Kirk at IVEM-TANDEM**
- **Martin Mitchell and Sharon Ashbrook, University of St Andrews**
- **Engineering and Physical Sciences Research Council (EPSRC)**
- **DOE for funding the Electron Microscopy Centre, Argonne National Laboratory (EMC)**
- **Access to Major Facilities Research Programme (AMRFP), part of the International Science Linkages Programme (ISL)**

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Why $CaLnZrNbO_7$?

- **Model system**
  - II, III, IV, and V pyrochlore
- **A - site**
  - Ca^{2+} and Ln^{3+} (Ln = La, Nd, Sm, Gd, Ho, Yb and Y)
- **B - site**
  - Zr^{4+} and Nb^{5+} (plus Hf^{4+})
- **Earlier studies suggested pyrochlore - fluorite transition between Sm and Gd. [Sibi et al Solid State Ionics 180 1164]**
- **Provides a means by which damage/disorder can be examined.**
- **Can be used as a model for multicomponent pyrochlore based waste form.**

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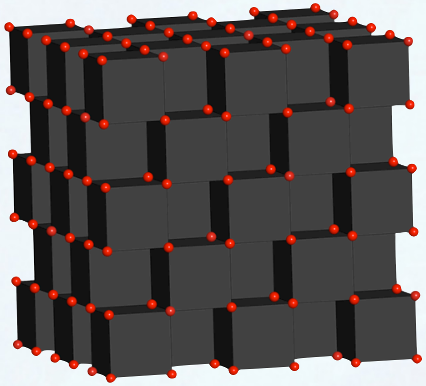
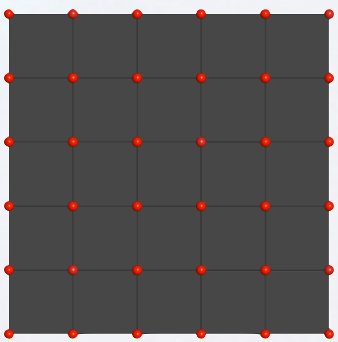
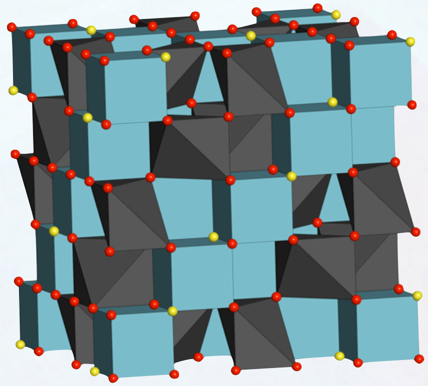
Fluorite - Pyrochlore



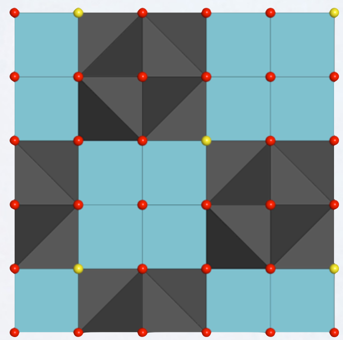
M_4O_8
$(A_2B_2O_8)$



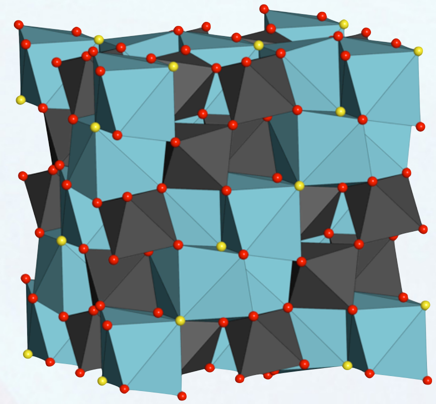
48f x = 0.375



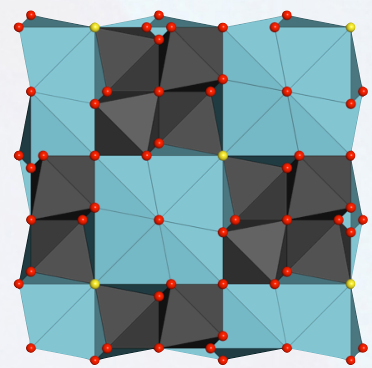
$A_2B_2O_7\square$
Unrelaxed



48f x = 0.375

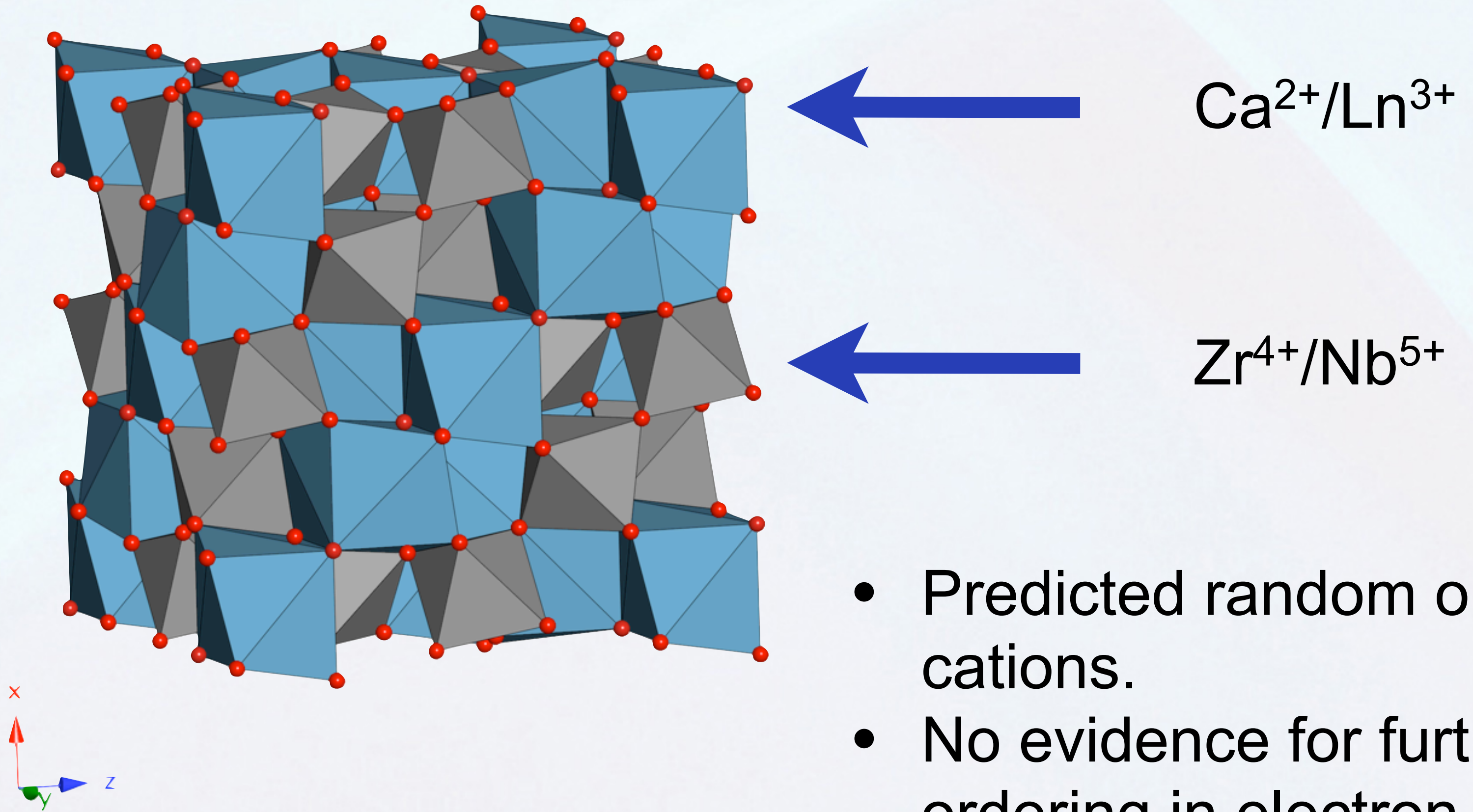


$A_2B_2O_7\square$
Relaxed



48f x = 0.421

$CaLnZrNbO_7$ - Pyrochlore



- Predicted random ordering of cations.
- No evidence for further ordering in electron diffraction

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Experimental

- **Oxides heated at 1500 ºC, 7 days.**
  - La, Nd, Sm, Gd, Ho, Yb and Y
  - Calcined as pellets (CIP)
- **XRD - Bruker D8**
- **^{89}Y MAS NMR**
  - $CaYZrNbO_7$ and $CaYHfNbO_7$
- **Neutron diffraction**
  - La, Nd, Ho, and Y - $CaLnZrNbO_7$
  - La, Y - $CaLnHfNbO_7$
- **Ion irradiation IVEM-TANDEM facility**
  - 1 MeV Kr^{2+}
  - Fluence ~6.25×10^{11} ions $cm^{-2}\,s^{-1}$
  - Ground samples dispersed on 'holey' carbon film
  - Temperature controlled environment

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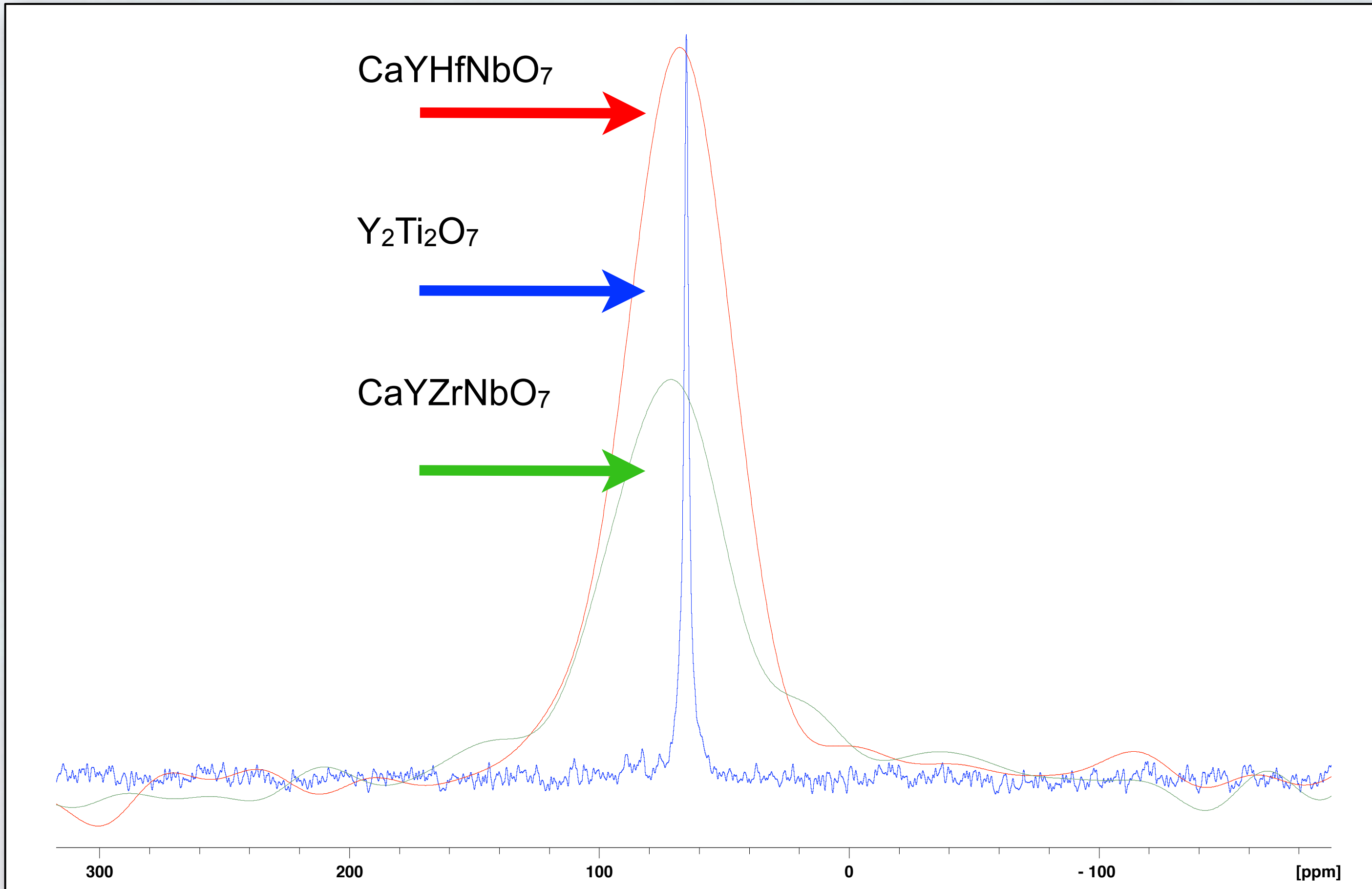
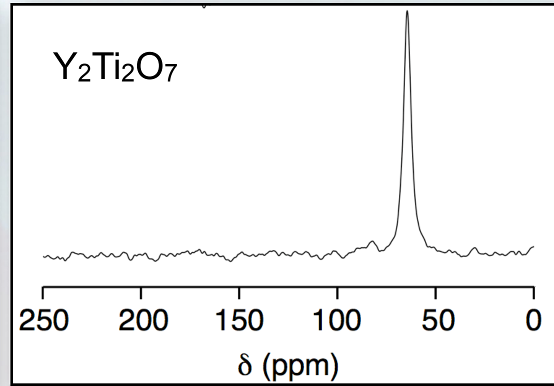
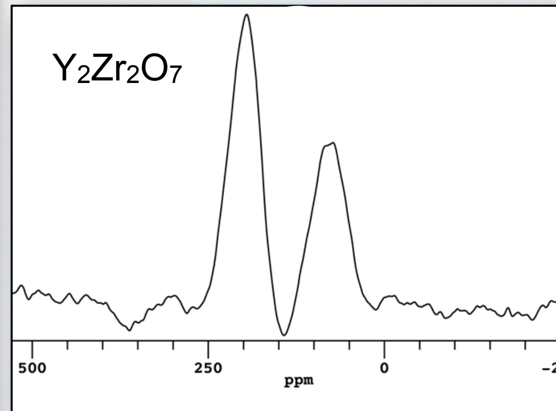
^{89}Y MAS NMR



CaYHfNbO7
Y2Ti2O7
CaYZrNbO7
300
200
100
0
- 100
[ppm]

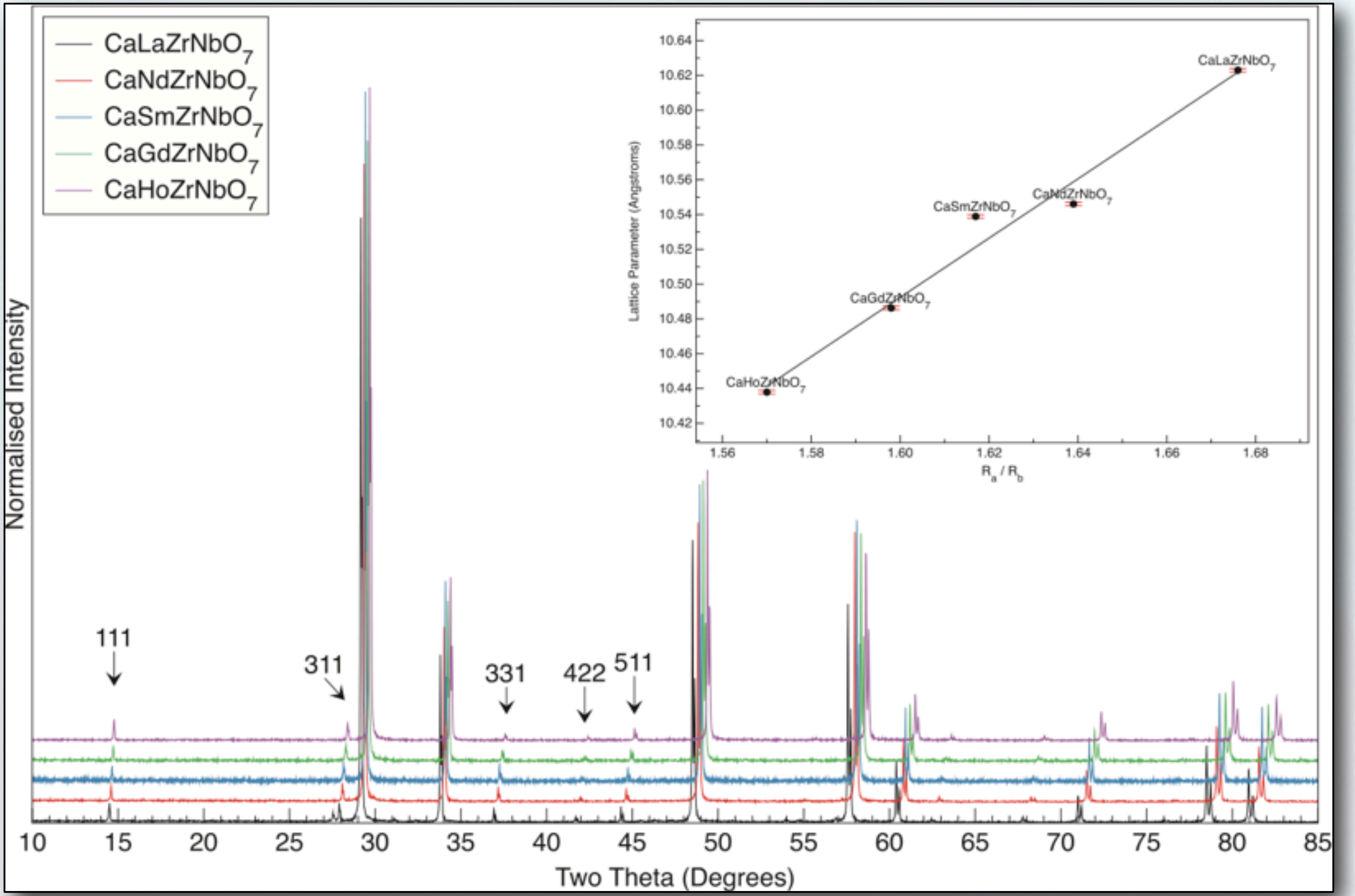


Y2Ti2O7
250
200
150
100
50
0
δ (ppm)



Y2Zr2O7
500
250
0
ppm

X-ray Diffraction



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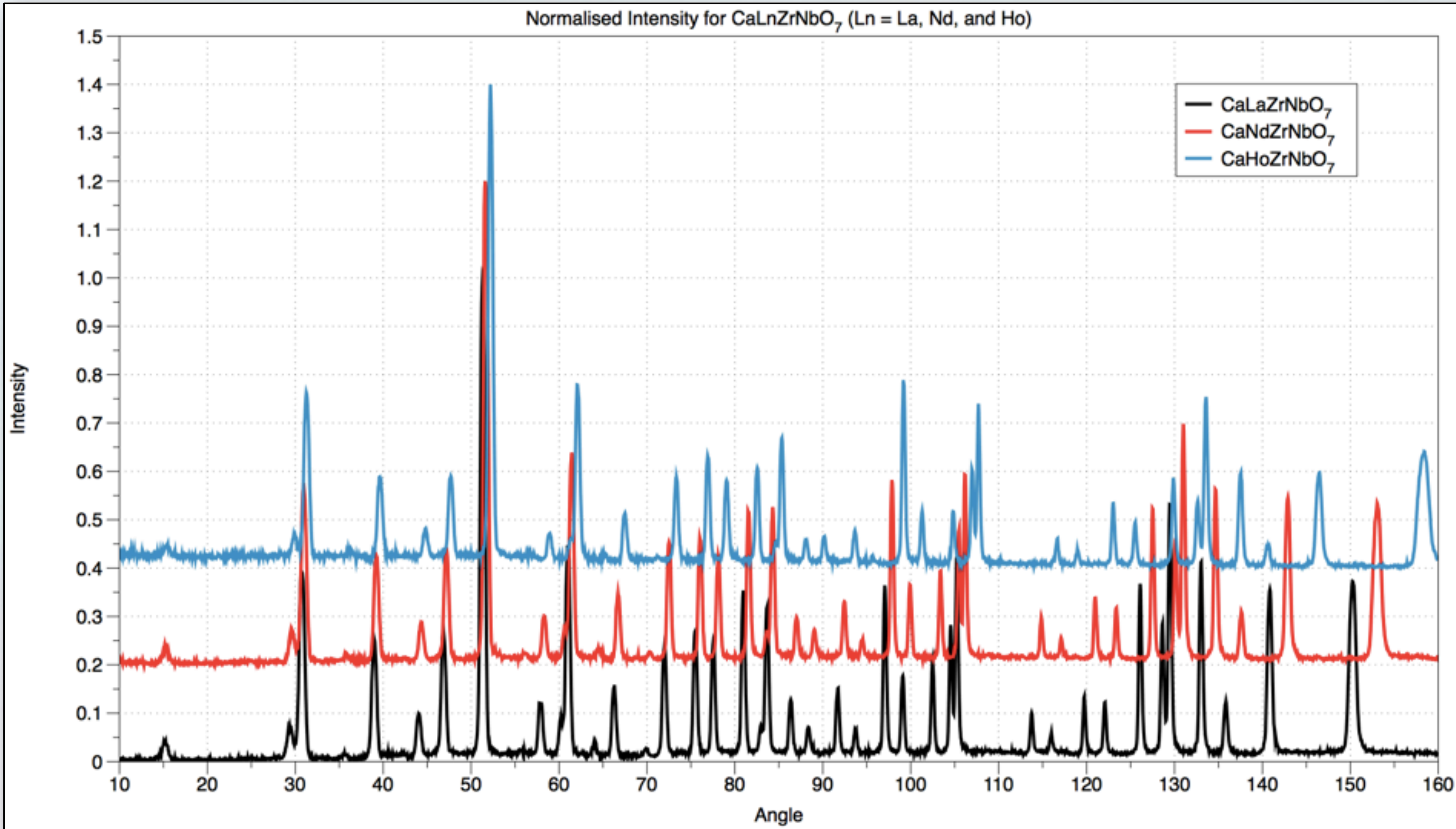
Neutron Diffraction



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Structure summary

- **Pyrochlore structure NOT fluorite**
  - superstructure present in all patterns
  - ionic radii suggests pyrochlore assuming Ca/Ln and Zr/Nb
  - no evidence for further ordering in electron diffraction
  - quick/nasty analysis shows 48f-x decreases from 0.427 to 0.420 (La to Ho)
- **Y^{3+} (Ln^{3+}) on the A-site**
  - ^{89}Y MAS NMR similar characteristics as $Y_2Ti_2O_7$
- **Ionic Radii**
  - Ca^{2+} / Ln^{3+} similar
  - Zr^{4+} / Nb^{5+} similar
- **Disorder to be confirmed**

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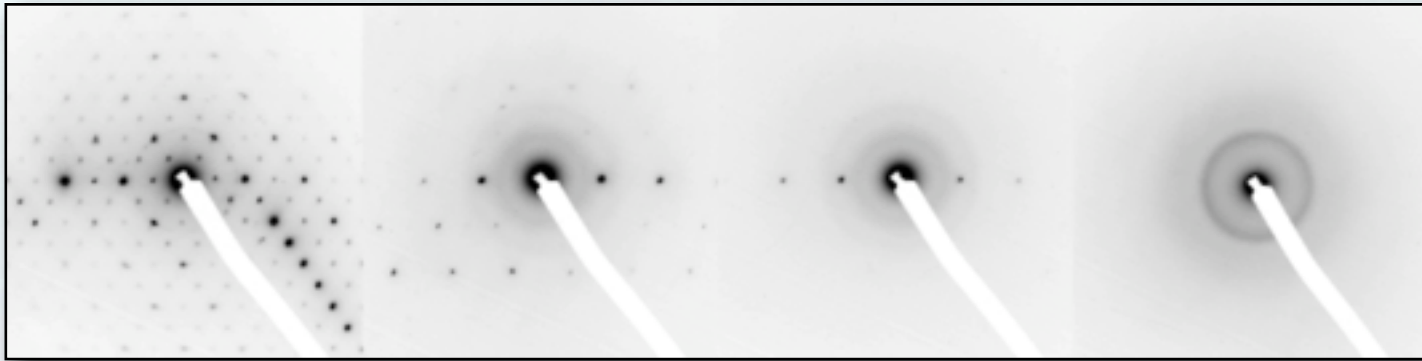
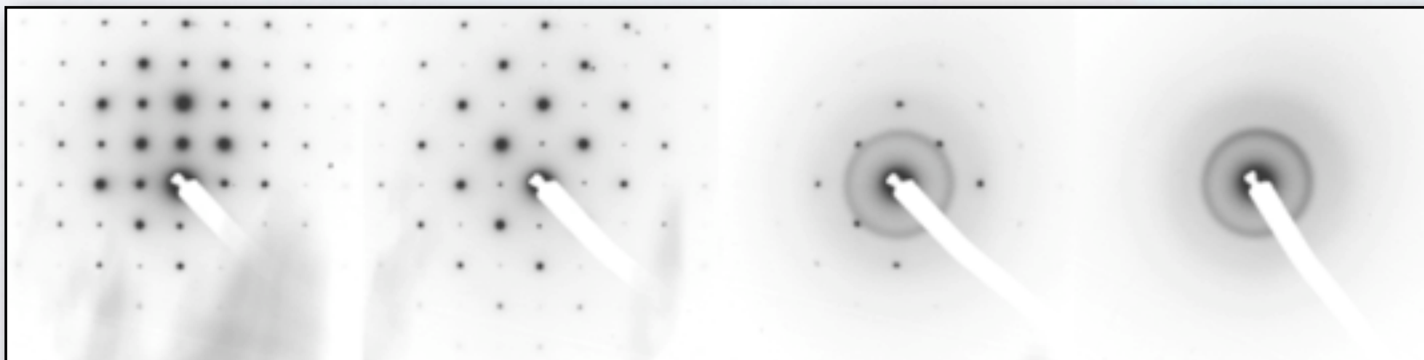
Irradiation

$Y_2Ti_{1.6}Sn_{0.4}O_7$
[111]



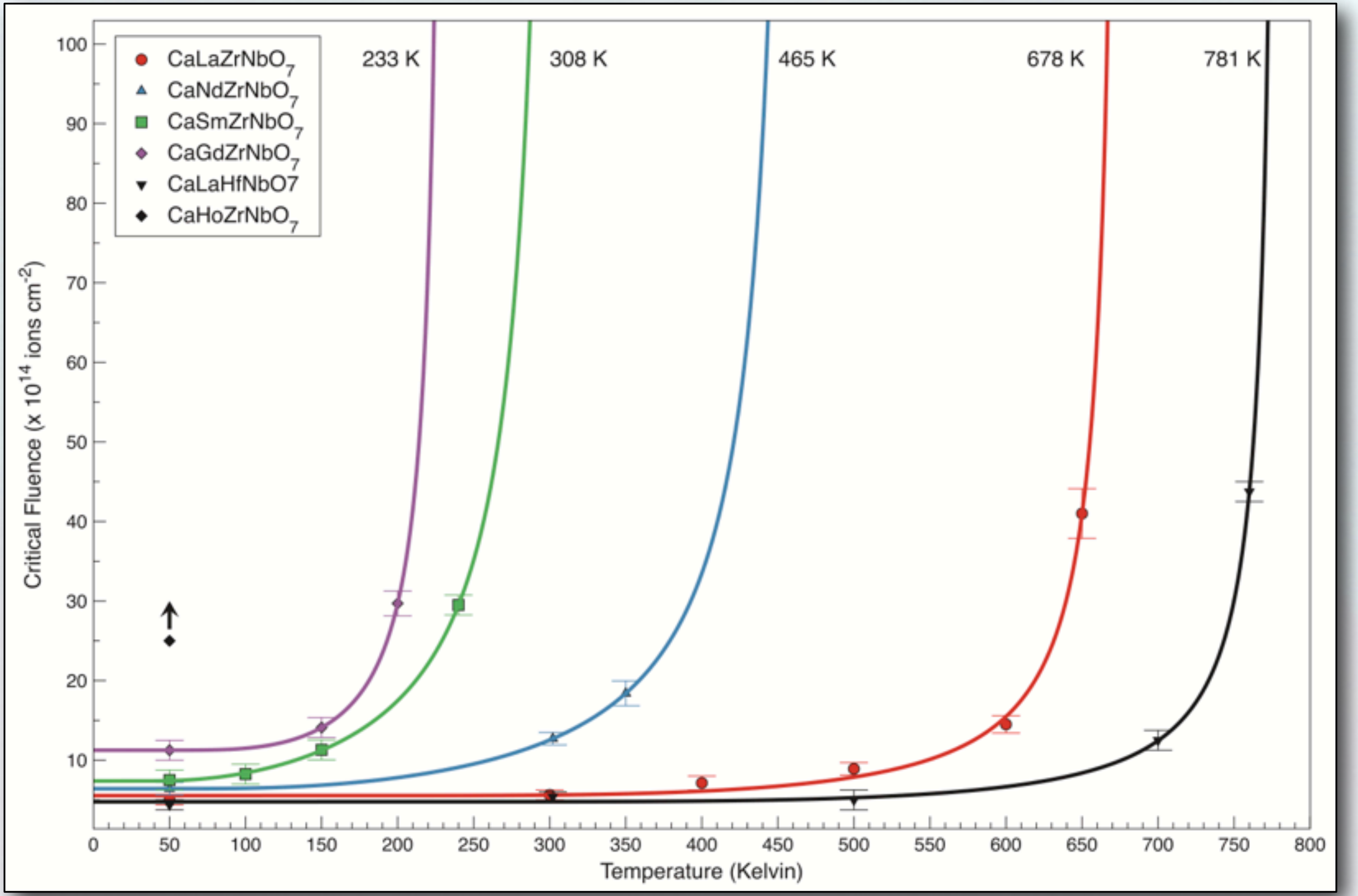
0 0.4 0.8 1.0

$Y_2Ti_{1.2}Sn_{0.8}O_7$
[100]



0 0.2 0.7 1.0

Ion Beam Irradiation



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Some Numbers....

System	Critical Temperature (K)	Critical Fluence at 0K (x 10^{14} ions cm^{-2})	Energy of Activation (eV)
$CaGdZrNbO_7$	230	11.2	0.7
$CaSmZrNbO_7$	310	7.4	0.93
$CaNdZrNbO_7$	465	6.4	1.38
$CaLaZrNbO_7$	678	6	2.08
$CaLaHfNbO_7$	780	4.8	2.30

Energy of activation for recovery

$$E_a = T_c\left[k_b \ln\left[\frac{F_{c0}\nu}{\phi}\right]\right]$$

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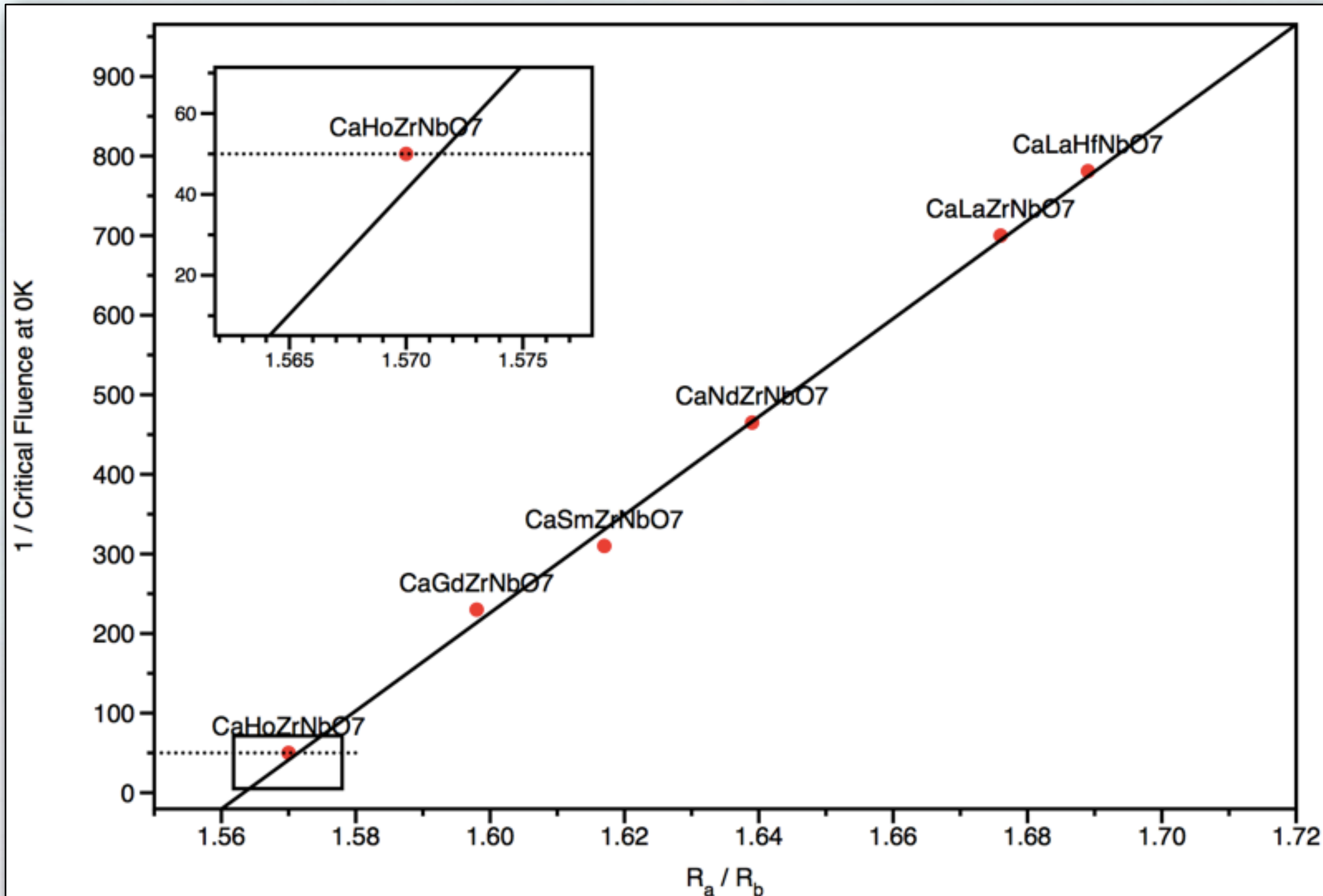

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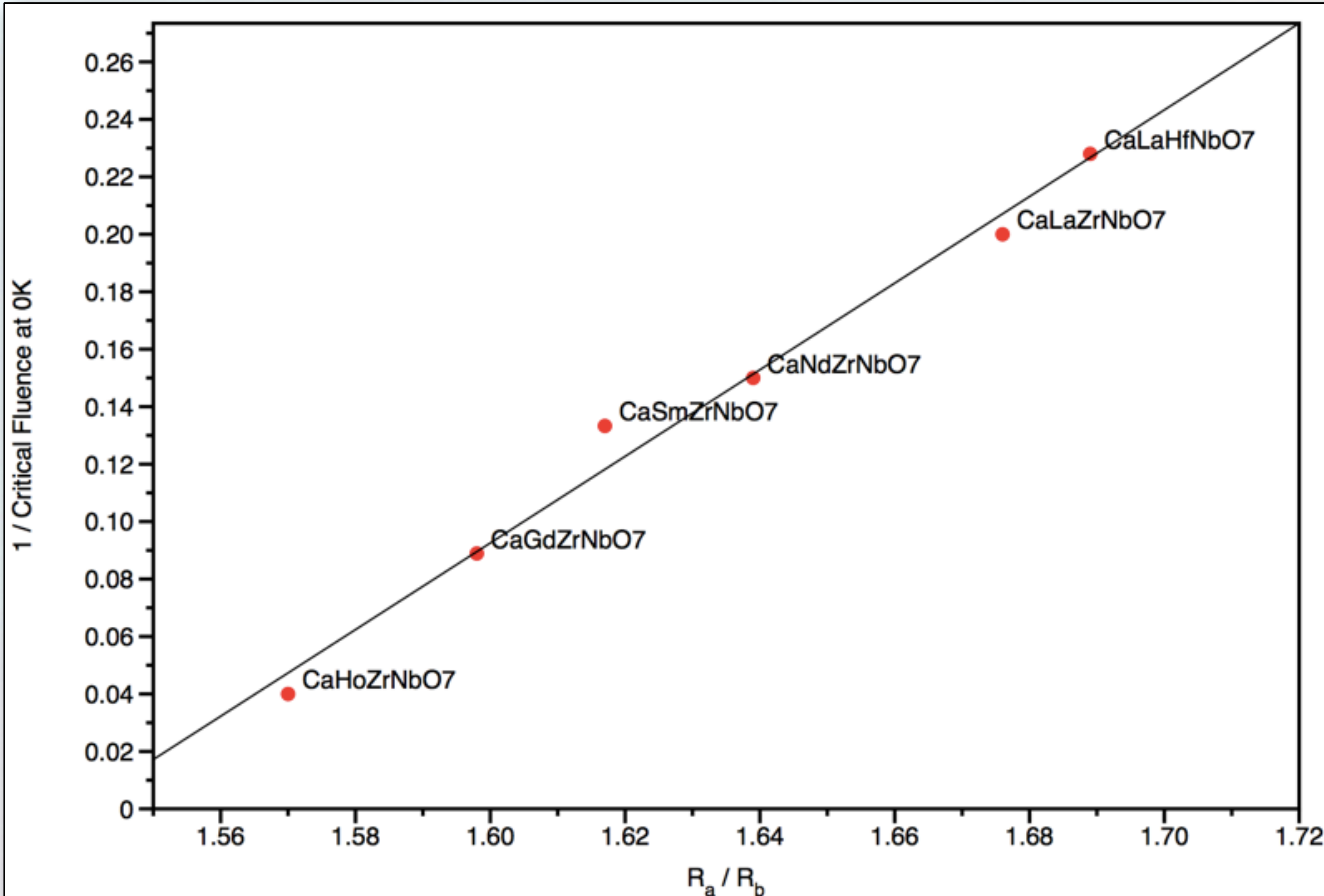

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So What is Happening?

- **Damage recovery rapid in some systems**
- **$CaYZrNbO_7$ & $CaHoZrNbO_7$ not amorphised at 50 K**
- **Pyrochlore-fluorite transition before amorphisation?**
  - No evidence to suggest this is happening
  - Absence of pyrochlore spots does not mean absence of superstructure!
- **Site disorder possible but unlikely**
  - Ionic radii mismatch - $Ca^{2+}/Ln^{3+} > Zr^{4+}/Nb^{5+}$
  - Ca^{2+}/Ln^{3+} on B-site induces strain in structure and vice versa

So What is Happening?

- **$Ln_2Ti_2O_7$ / $Ln_2Sn_2O_7$ / $Ln_2Zr_2O_7$**
  - Similar trend with decreasing T_c with change in Ln
  - Increase in tolerance - many explanations
    - radius ratio - simple
    - disordering energies - more complex
    - internal bonding structure - highly complex
- **$CaYbZrNbO_7$ - predicted to not amorphise at 0K**
- **Hf decreases tolerance of damage, increase in Tc of ~ 100K**
  - found in other systems with Hf for Zr ($La_2Zr_2O_7$/$La_2Hf_2O_7$ and $Ca_3Hf_2FeAlSiO_2$/$Ca_3Zr_2FeAlSiO_{12}$)

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Conclusion

- **$CaLnZrNbO_7$ - pyrochlore for all Ln**
- **Ca/Ln on A-site and Zr/Nb on B-site**
- **No evidence for ordering on A or B sites**
- **High degree of resistance to damage / rapid recovery from damage**

Further Work

- **Bulk surface irradiation to high levels of damage**
- **XTEM of damage / dislocations**
  - Amorphise, disorder ?
- **Confirm disorder using combined X-ray/neutron Rietveld refinements**
- **Damage simulation/recovery - MD/DFT/KMC**
- **$CaLnSnNbO_7$ - effect of Sn on tolerance**
  - Sn found to increase tolerance
  - decreases observed T_c

2011 MRS FALL MEETING

November 28-December 2 · Boston, MA

www.mrs.org/fall2011

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Abstract Deadline: June 21, 2011

REMINDER: In fairness to all potential authors, late abstracts will not be accepted.

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The recent renaissance in nuclear power has led to an increased need for research in new reactor, fuel, processing, and waste-form technologies. This symposium will address the key factors in the continued development of materials for fission/fusion technologies, e.g., AFCI, Gen IV, and ITER, and how they are linked. The symposium will be based on invited overviews, contributed talks giving the current state of research, and invited talks on future directions/opportunities for research. The symposium will bring together scientists from across the generations with a view to utilize all available expertise in a way that drives research forward.

Session topics will include:

- The current and future road maps for nuclear research worldwide, both fission and fusion based, e.g., Gen III, Gen IV, and ITER/DEMO
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  - Fuel and cladding development/performance
- Reactor materials
  - Structural materials
  - Fission/fusion core liners
  - Long-term radiation damage effects
- Materials behavior under extreme conditions
  - High temperature/pressures
  - Induced embrittlement
  - High-energy He irradiation
  - Damage tracks
  - Chemically driven degradation
- Applications of nuclear-derived research to new areas
  - Radioparagenesis/transmutation for synthesizing new novel materials
  - High-temperature oxides/carbides in non-nuclear areas, e.g., TRISO, SiC, and ZrC

A **tutorial** is tentatively planned on nuclear fuel, its development, and understanding performance. Further information will be included in the MRS Program that will be available online in September.

Invited speakers include:

Marie-France Barthe (CNRS-Orléans, France), **Kenneth Czerwinski** (Univ. of Nevada), **Phil Edmondson** (Oak Ridge National Lab), **Lyndon Edwards** (Australian Nuclear Science and Technology Org., Australia), **Mike Fitzpatrick** (Open University, United Kingdom), **Chris Grovenor** (Oxford Univ., United Kingdom), **Jonathan Hinks** (Univ. of Huddersfield, United Kingdom), **Djamel Kaoumi** (Univ. of South Carolina), **Matthias Krack** (Paul-Scherrer Inst., Switzerland), **Christopher Stanek** (Los Alamos National Lab), **Izabela Szlufarska** (Univ. of Wisconsin), **James Tulenko** (Univ. of Florida), **Brian Wirth** (Univ. of Tennessee), and **Thierry Wiss** (JRC-ITU, Germany).

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