Materials Science of Actinides
Energy Frontier Research Center

RADIATION DAMAGE IN CRISTALLINE WASTEFORMS

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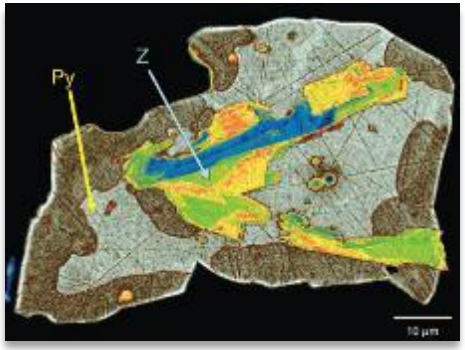
Durable Materials for Radionuclide Immobilization

Performance in extreme environments:

- intense radiation
- elevated temperature
- changing chemical composition
- long-term disposal in changing environment



Intergrowth of natural pyrochlore (Py) and zirconolite (Z)

G.R. Lumpkin, *Elements* (2006)

Complex structural and chemical modifications:

- simple defects and defect clusters
- order-disorder and crystalline-amorphous transformations
- partial recrystallization of waste glasses
- defect mobility and damage recovery at high temperature

Ion track in $Gd_2Zr_2O_7$ (12-MeV C_{60})

J.M. Zhang *et al.*, *J. Appl. Phys.* (2010)

Crystalline Wasteforms:

- chemical durable (very low leach rates)
- compatibility for geological disposal
- large intake of actinides
- concern: radiation effects and crystalline-to-amorphous transformation

Crystalline Wasteforms for Radionuclide Immobilization

simple oxides:	*zirconia*	ZrO_2
complex oxides:	*pyrochlore*	$(Na,Ca,U)_2(Nb,Ti,Ta)_2O_6$
	murataite	$(Na,Y)_4(Zn,Fe)_3(Ti,Nb)_6O_{18}(F,OH)_4$
	zirconolite	$CaZrTi_2O_7$
	perovskite	$CaTiO_3$
silicates:	*zircon**	$ZrSiO_4$
	*thorite**	$ThSiO_4$
	*garnet**	$(Ca,Mg,Fe^{2+})_3(Al,Fe^{3+},Cr^{3+})_2(SiO_4)$
	britholite	$(Ca,Ce)_5(SiO_4)_3(OH,F)$
	titanite	$CaTiSiO_5$
phosphates:	*monazite**	$LnPO_4$
	*apatite**	$Ca_{4-x}Ln_{6+x}(PO_4)_y(O,F)_2$
	*xenotime**	YPO_4

*durable heavy minerals

Pyrochlores: Important Group of Materials

Applications

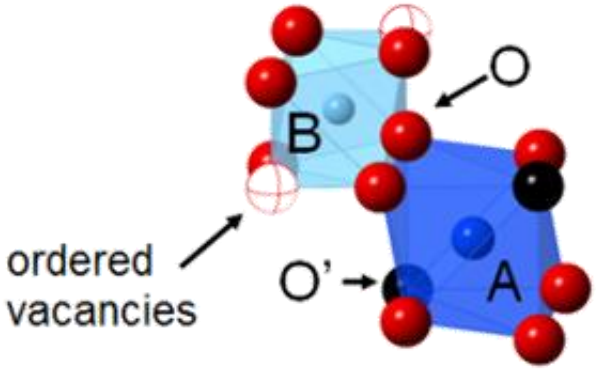
- ⇨ Exotic magnetic properties
- ⇨ Fast ionic conductors
- ⇨ Thermal barrier coatings
- ⇨ Actinide immobilization

spin ice state

$Ho_2Ti_2O_7$

Structure

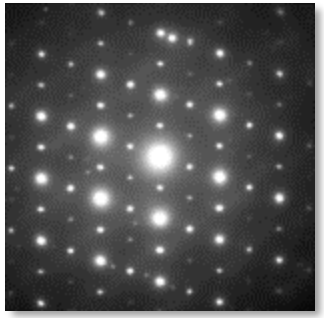
- ⇨ $A_2B_2O_6O'$
- ⇨ 2x2x2 supercell of fluorite
- ⇨ 5 crystallographic sites

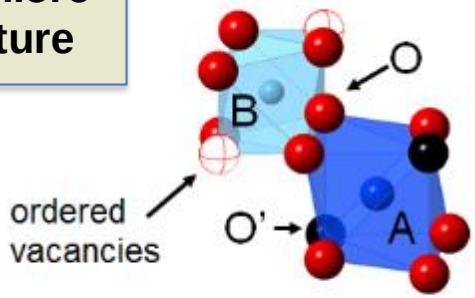


$A_2B_2O_6O'$

Disordering of Pyrochlore under Extreme Conditions

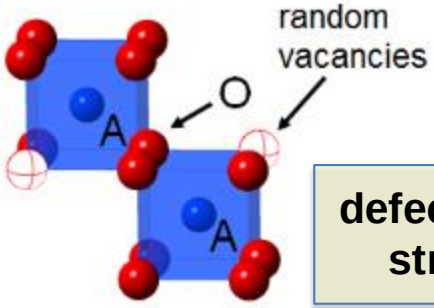
pyrochlore structure





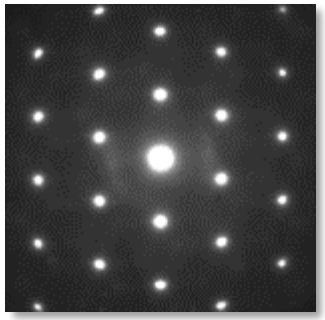
$A_2B_2O_6O'$

disordering



A_4O_7

defect-fluorite structure

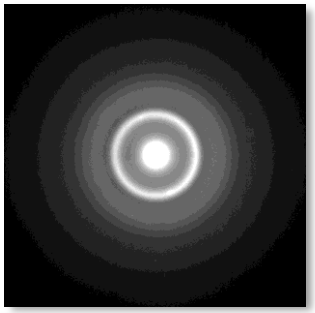


$Gd_2Zr_2O_7$

$A_2B_2O_7$

r_A/r_B

amorphization

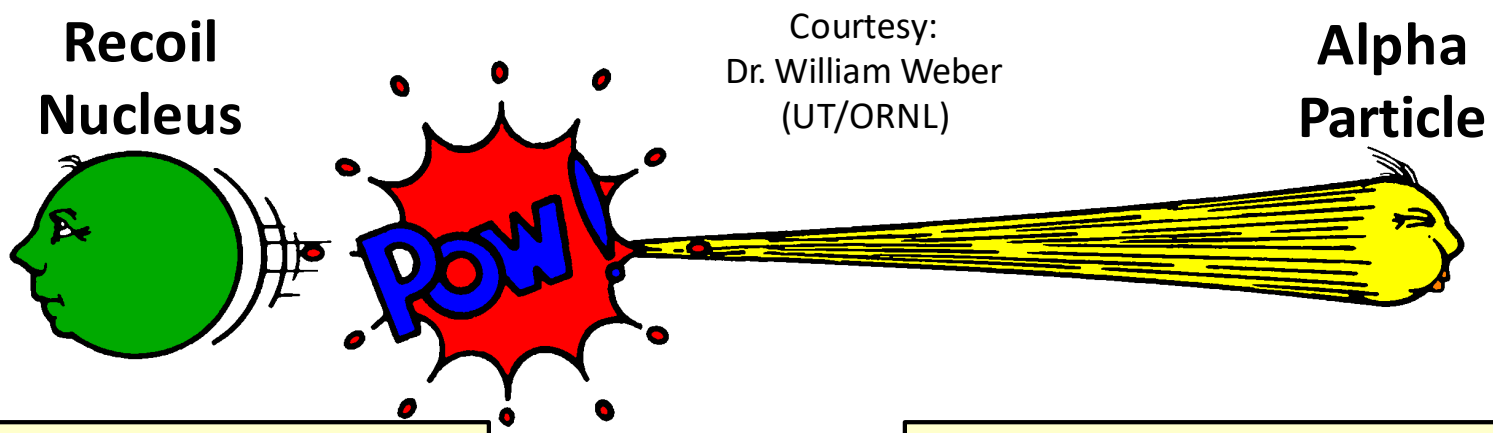


$Gd_2Ti_2O_7$

- ▹ cation and anion disorder
- ▹ retaining crystallinity

- ▹ loss of crystallinity

Radiation Effects in Actinide-Bearing Wasteforms



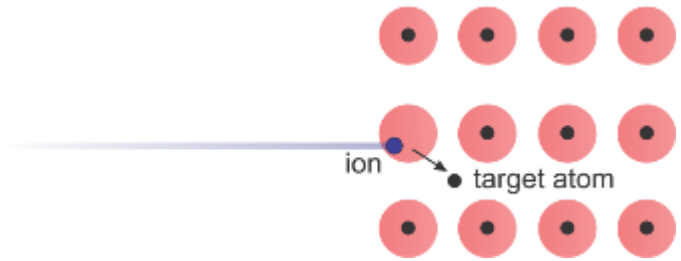
Courtesy:
Dr. William Weber
(UT/ORNL)

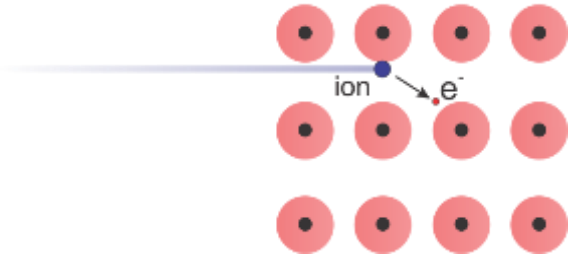
Alpha-Recoil Nucleus

- 70 - 100 keV **ion**
- 30 - 40 nm Range
- Creates More Damage (~2000 Displaced Atoms)

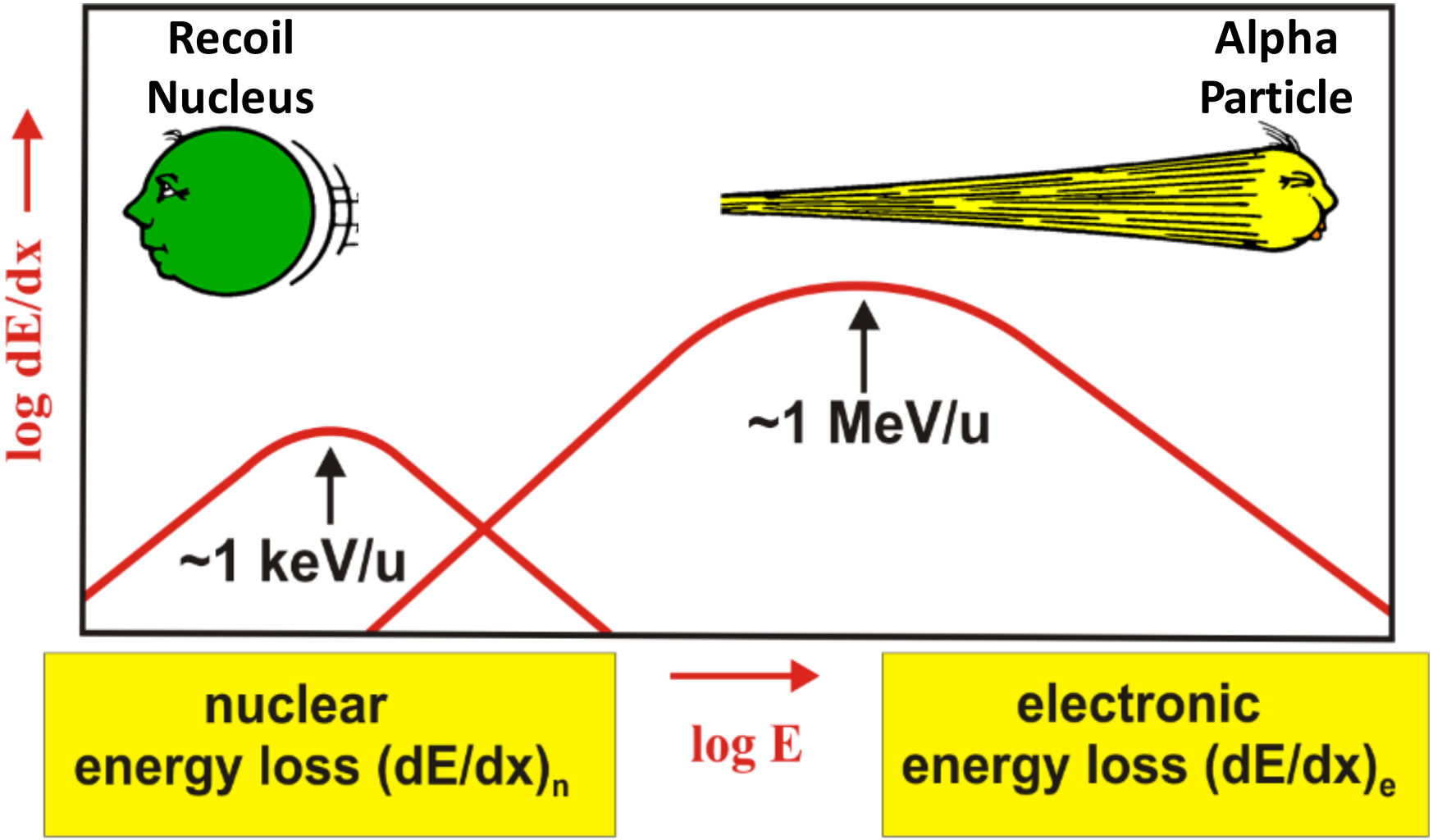
Alpha-Particle

- 4.5 - 5.8 MeV **ion**
- 16 - 22 μm Range
- Creates Less Damage (~350 Displaced Atoms)

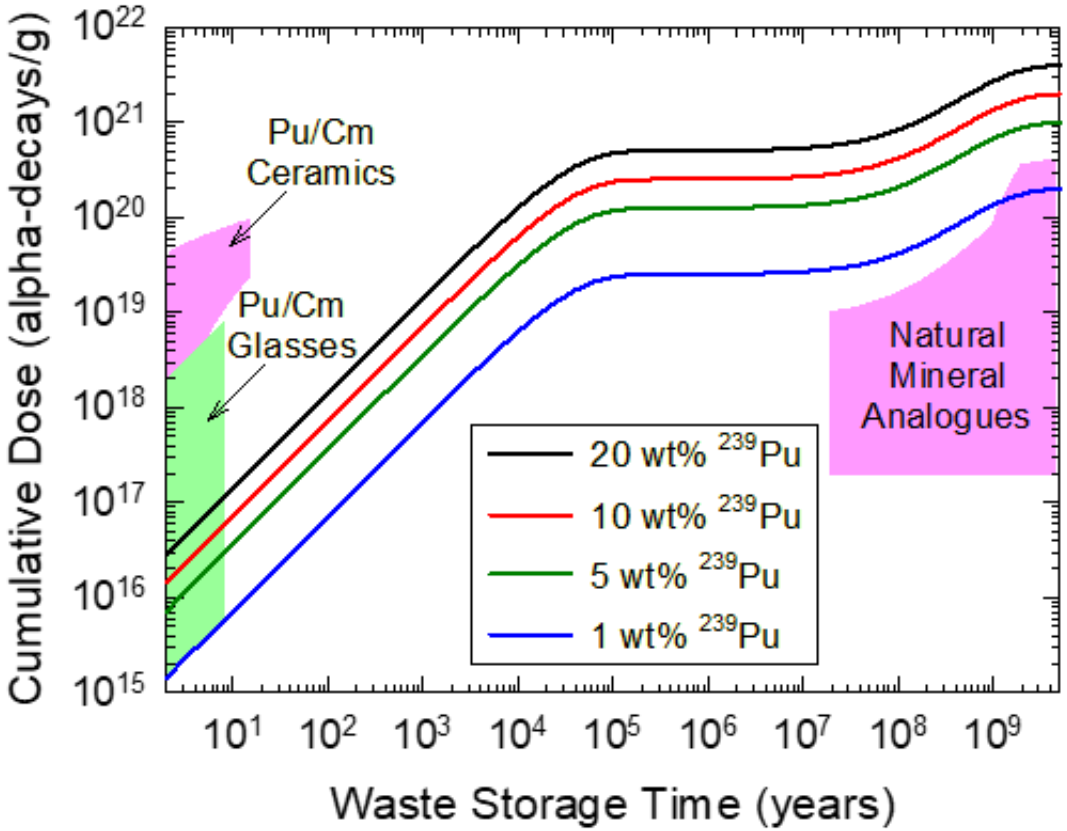


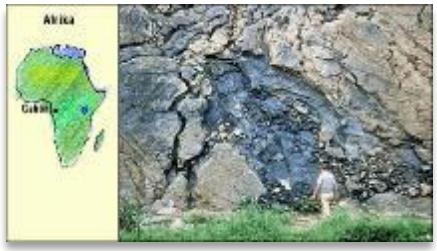


Radiation Effects in Actinide-Bearing Wasteforms



Radiation Effects in Nuclear Wasteforms





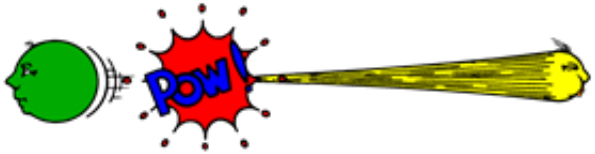
Courtesy:
Dr. William Weber
(UT/ORNL)

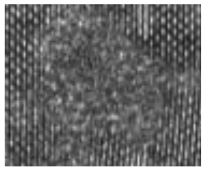
Ion Irradiation & Computer Simulation provide way to bridge Time Gap (Dose Rate Effects) between Laboratory Studies and Geologic Time Scales

W.J. Weber et al., *J. Mater. Research* **13** (1998) 1434-1484

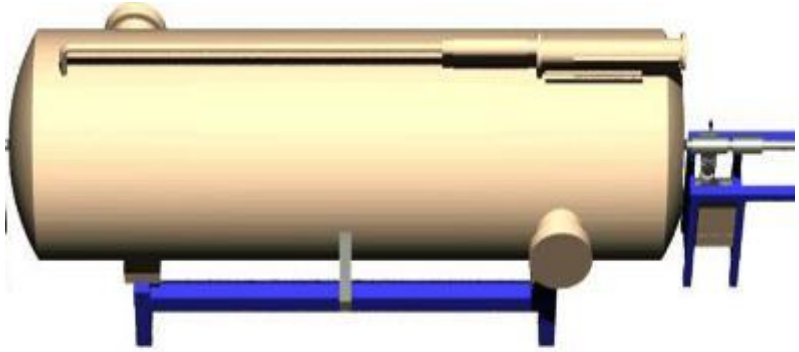
Simulation of Alpha-Recoil Damage in Waste Forms

Alpha Decay

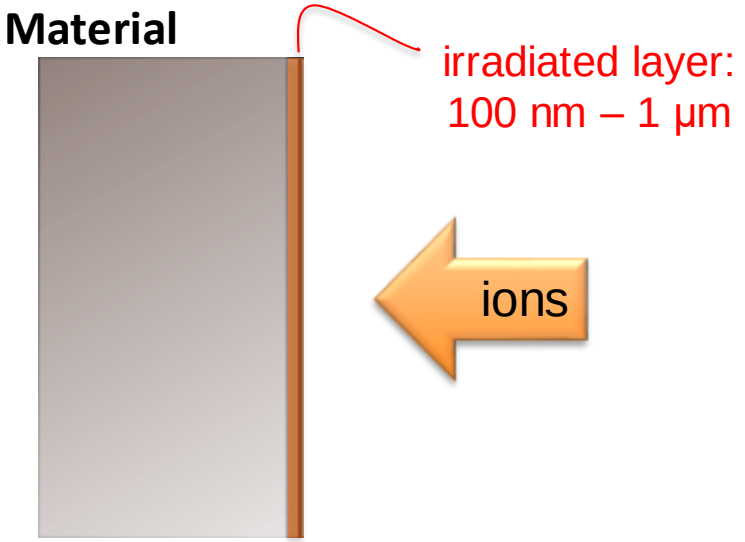




energy release:
~5 MeV



Tandem Accelerator (E < 25 MeV)
available in many laboratories



<u>Ion-beam experiments: MeV energies</u>

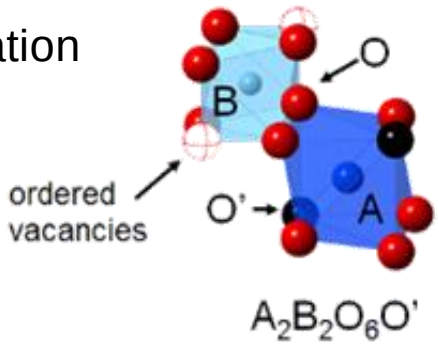
- ⇨ more realistic simulation of radiation effects (nuclear d*E*/d*x*)
- ⇨ **small volume** of modified material
- ⇨ many bulk characterization techniques are not applicable

Low-Energy Irradiation Effects in Pyrochlore Oxides

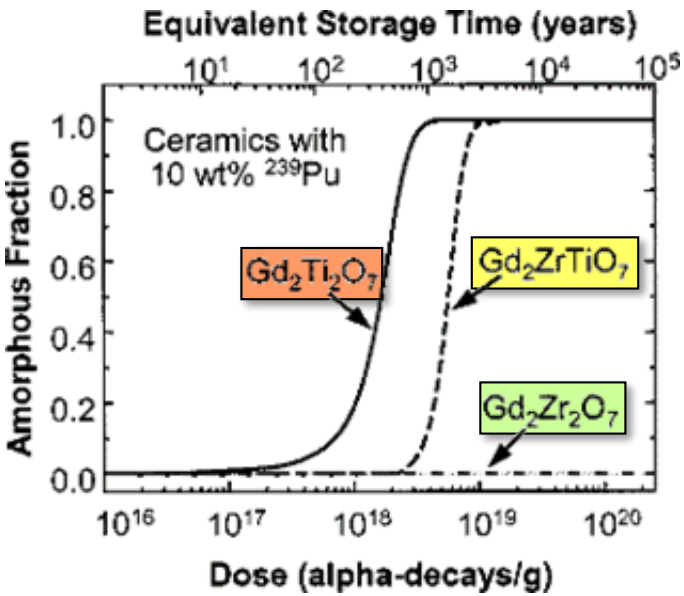
Actinide decay in complex oxides

⇨ damage accumulation from self-irradiation

R. Ewing, W.J. Weber, and J. Lian, *J. Appl. Phys.* 95 (2004)



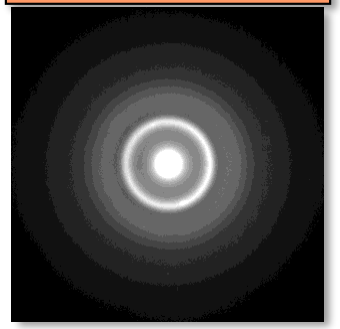
pyrochlore



S.X. Wang *et al.*, *J. Mater. Res.* (1999)
B.D. Begg *et al.*, *J. Nucl. Mater.* (2001)

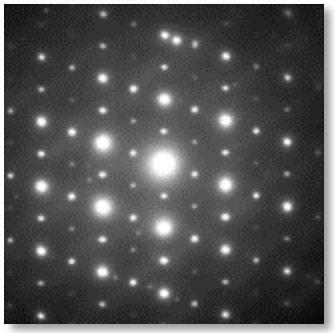
J. Lian *et al.*, *Phys. Rev. Lett.* (2001)

$Gd_2Ti_2O_7$



amorphous

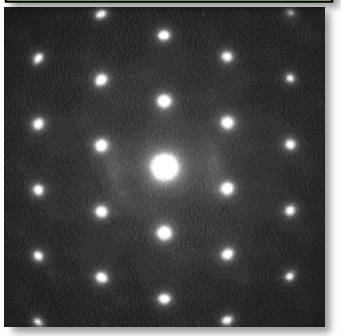
1-MeV Kr ions



pyrochlore

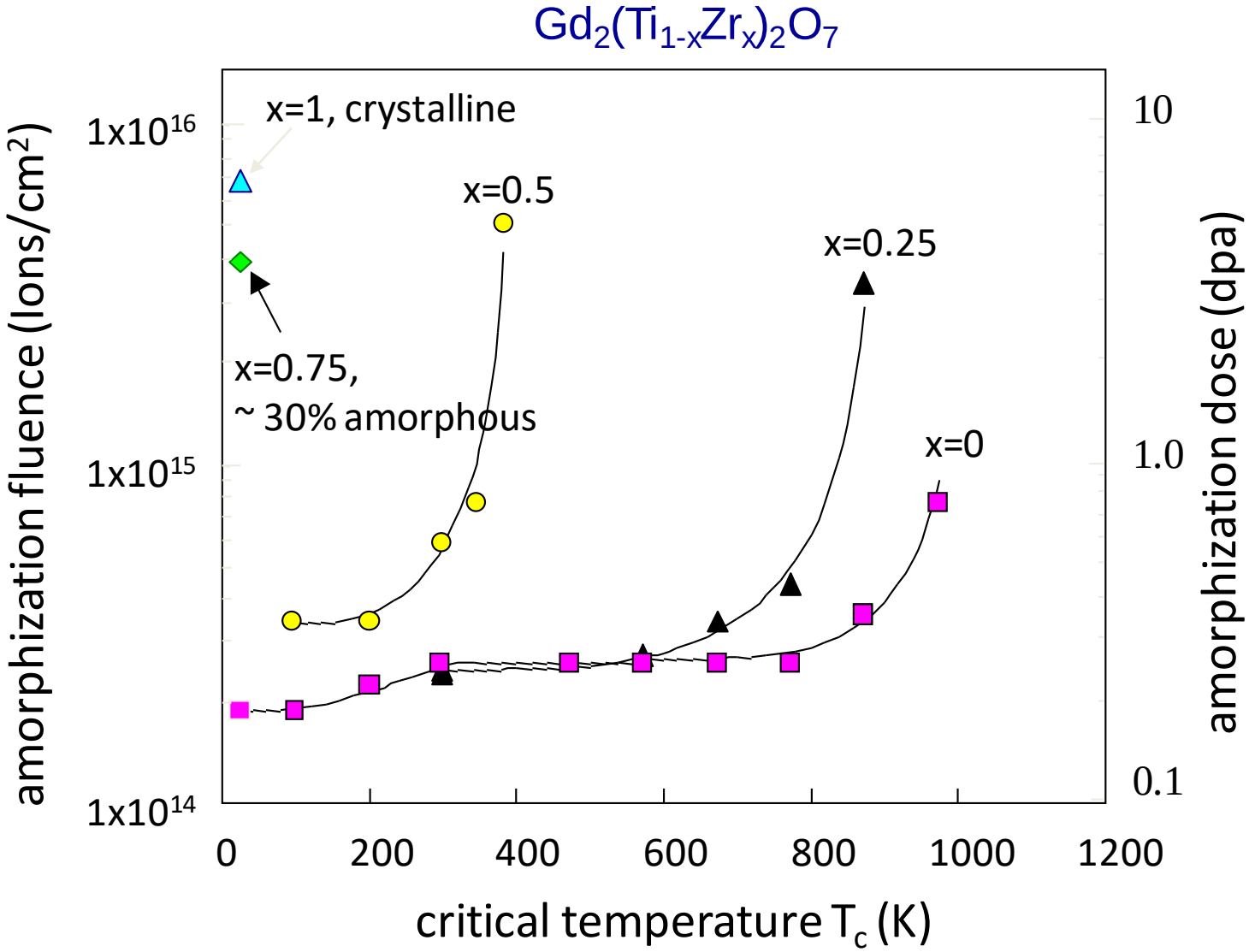
1-MeV Kr ions

$Gd_2Zr_2O_7$



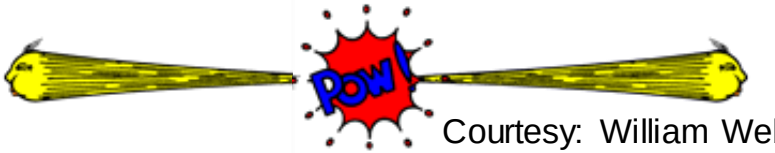
defect fluorite

Critical Temperature of Amorphization in Pyrochlore



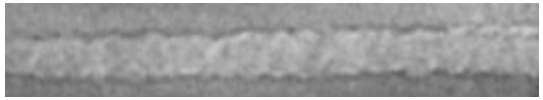
Simulation of Radiation Effects with Swift Heavy Ions

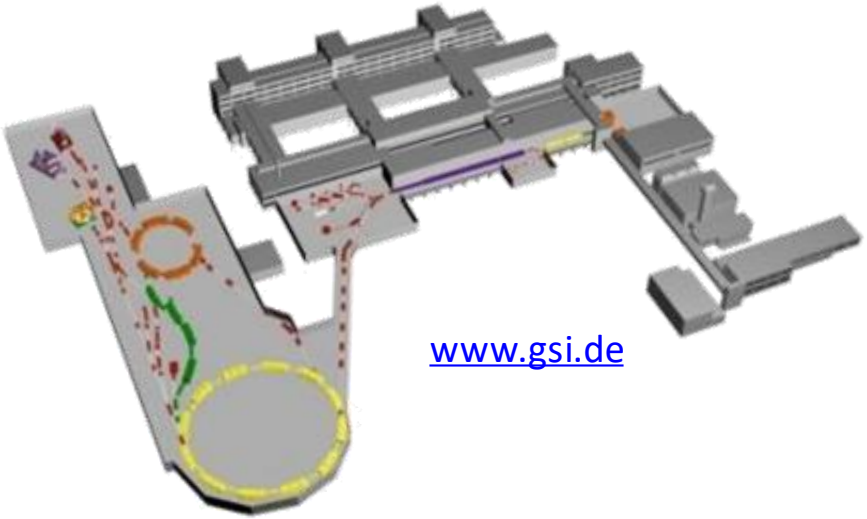
Spontaneous Fission



Courtesy: William Weber (UT)

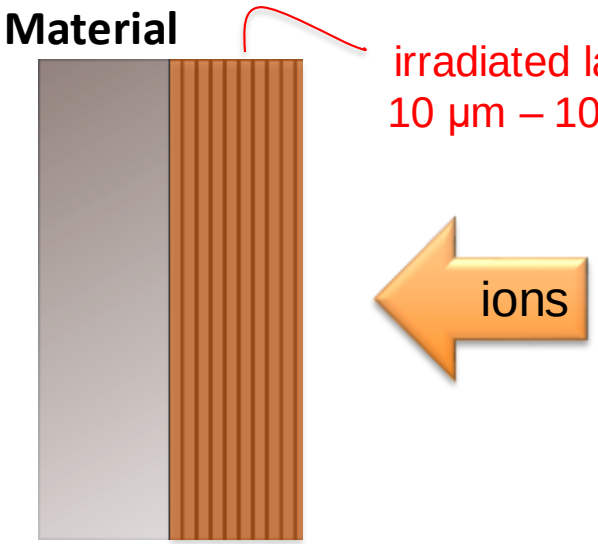
energy release:
~200 MeV





www.gsi.de

Linear and ring accelerators (E ~1 GeV) available at large user facilities



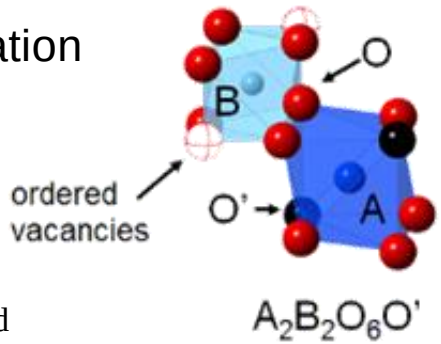
<u>Ion-beam experiments: GeV energies</u>

- ⇨ different ion-matter interactions (electronic d*E*/d*x*)
- ⇨ **large volume** of modified material
- ⇨ access to many bulk characterization techniques (e.g., X-ray and neutron scattering)

High-Energy Irradiation Effects in Pyrochlore Oxides

Actinide decay in complex oxides

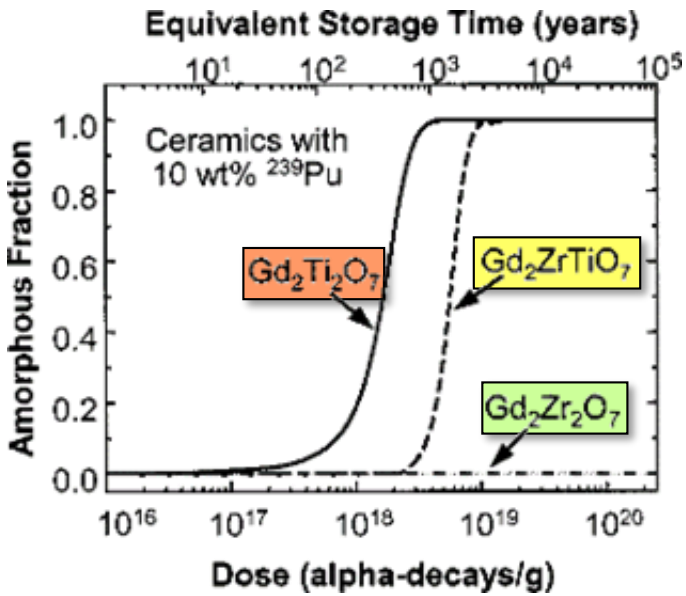
⇨ damage accumulation from self-irradiation



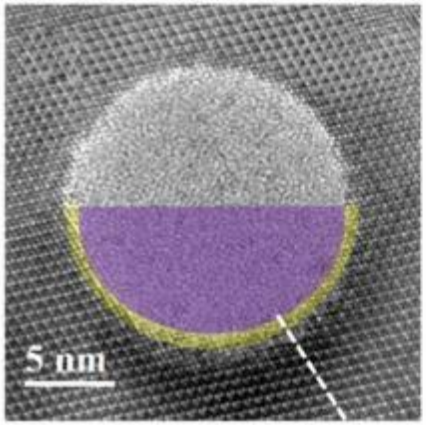
$A_2B_2O_6O'$

pyrochlore

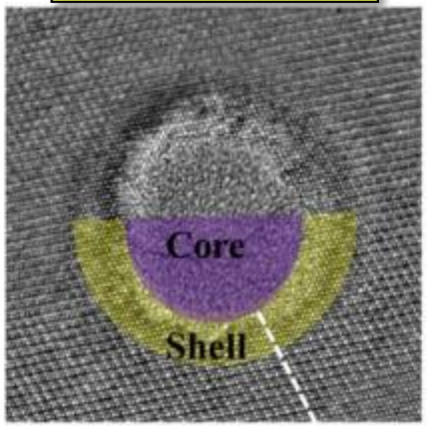
R. Ewing, W.J. Weber, and J. Lian, *J. Appl. Phys.* *95* (2004)



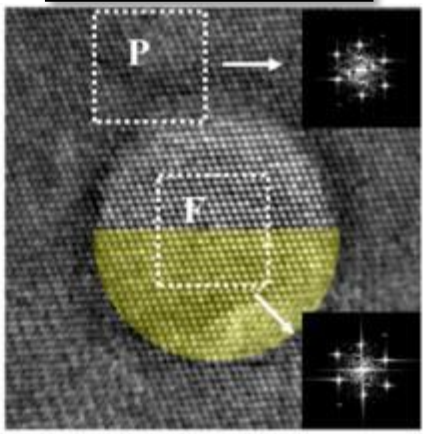
$Gd_2Ti_2O_7$



Gd_2TiZrO_7



$Gd_2Zr_2O_7$

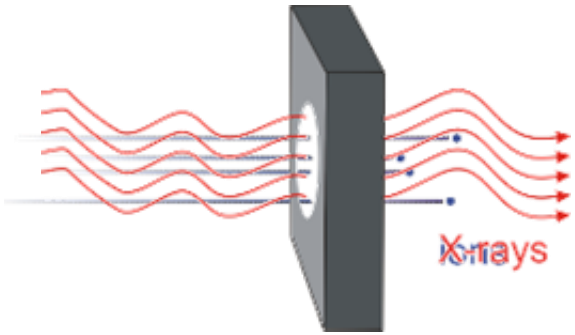


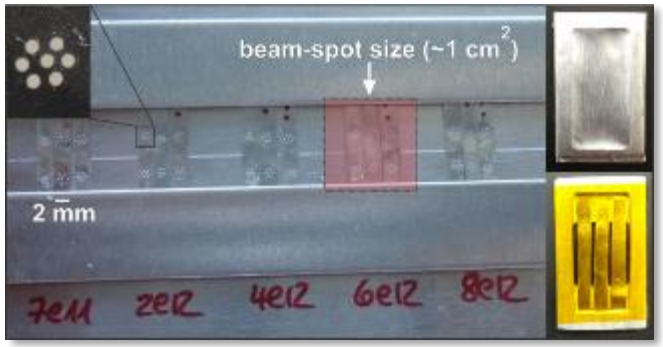
30-MeV C_{60} ions

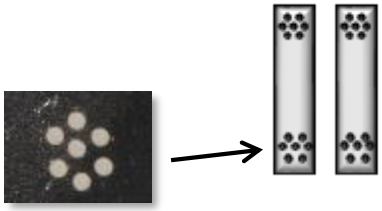
J. Zhang, M. Toulemonde, M. Lang, J.Costantini, S. Della-Negra, R. Ewing, *J. Mater. Res.* *30* (2015)

Radiation Effects: Synchrotron X-Ray Characterization

M. Lang, *et al.*, *Journal of Materials Research* (2015).





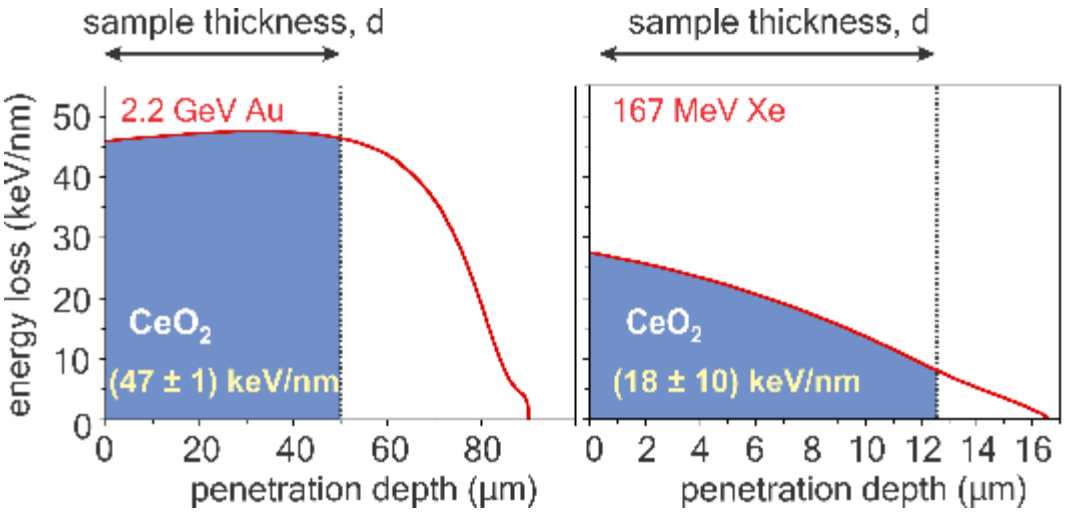


Sample chamber

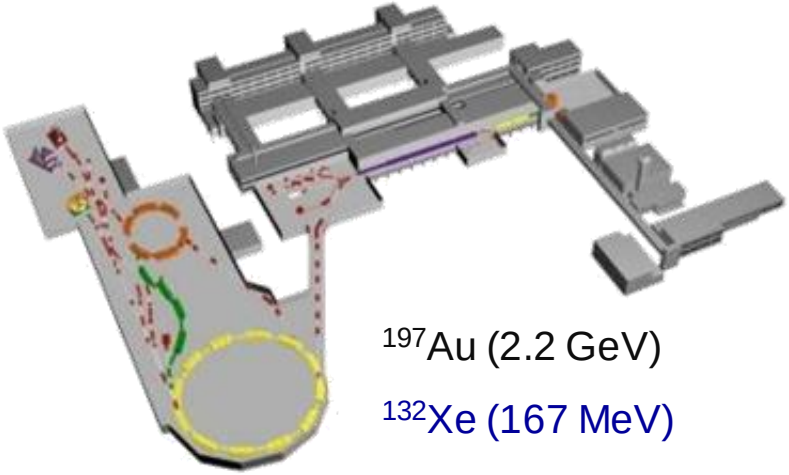
diameter: 100 µm

thickness: 50 µm

thickness: 12.5 µm



GSI Helmholtz Center (Germany) and
Joint Institute for Nuclear Research (Russia)

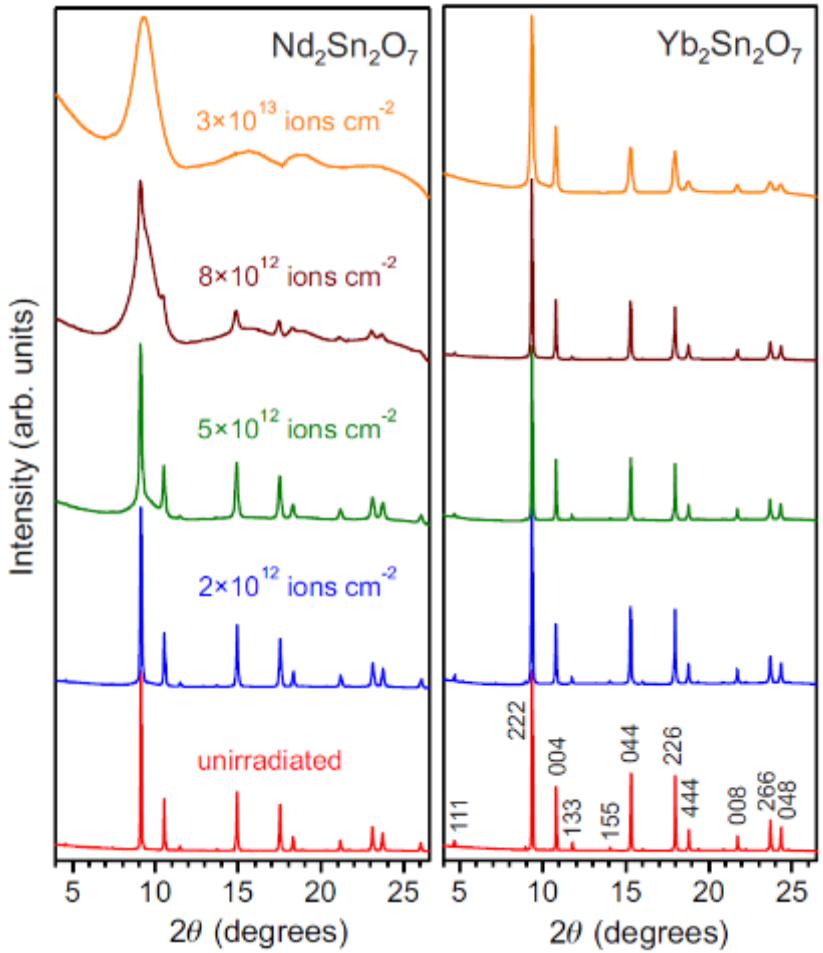


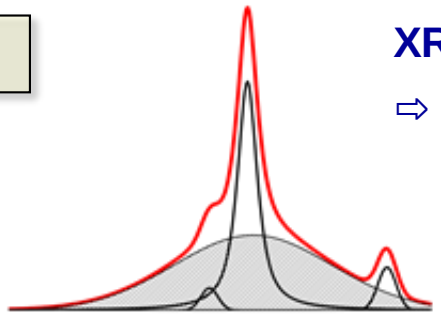
^{197}Au (2.2 GeV)

^{132}Xe (167 MeV)

Radiation Effects in Complex Oxides: X-Ray Diffraction

$A_2Sn_2O_7$ irradiated with **2.2 GeV ^{197}Au**

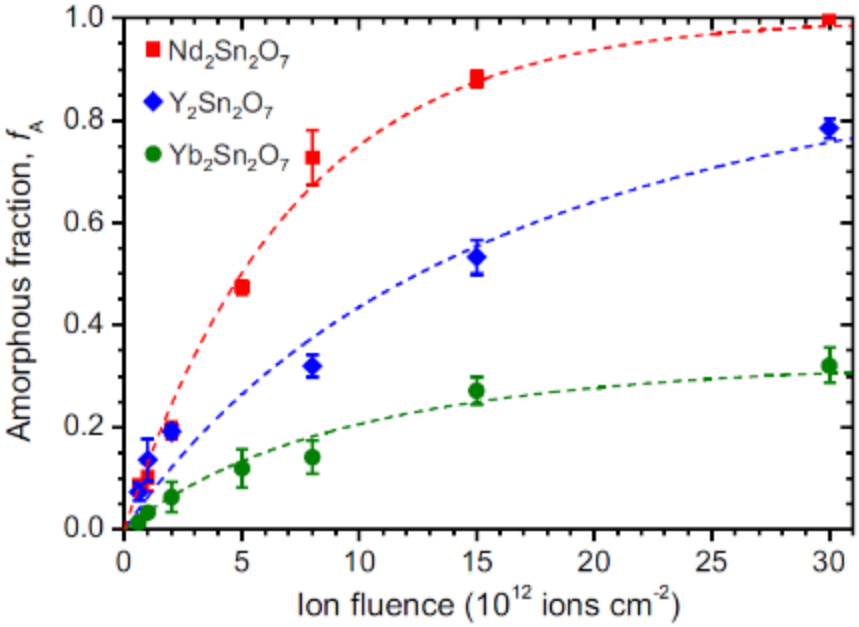




XRD peak deconvolution

⇨ amorphous fraction

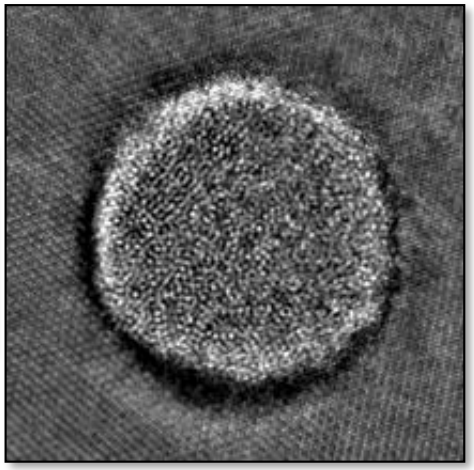
$$f_A(\Phi) = \frac{1 - e^{-\sigma_A\Phi + \sigma_D\Phi}}{1 - \left(\frac{\sigma_D}{\sigma_A}\right)e^{-\sigma_A\Phi + \sigma_D\Phi}}$$



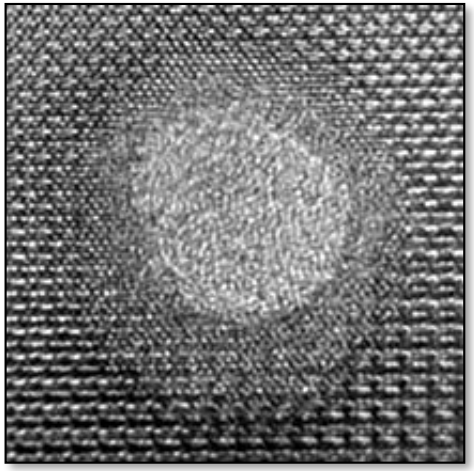
C.L. Tracy, *et al.*, *PRB* (2016) M. Lang, *et al.*, *PRB* (2009)

Transmission Electron Microscopy: Track Morphology

$Gd_2Ti_2O_7$
2.2-GeV ^{197}Au
40 keV/nm; RT



changing
composition

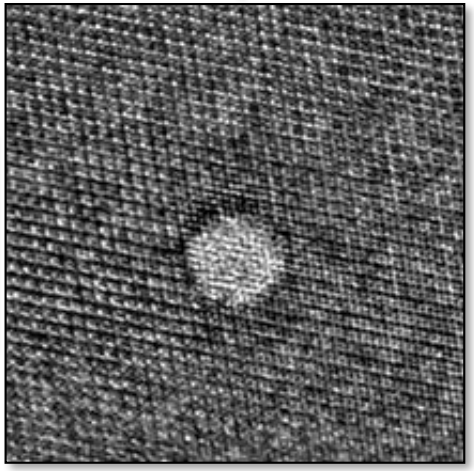


$Gd_2Ti_1O_5$
2.2-GeV ^{197}Au
40 keV/nm; RT

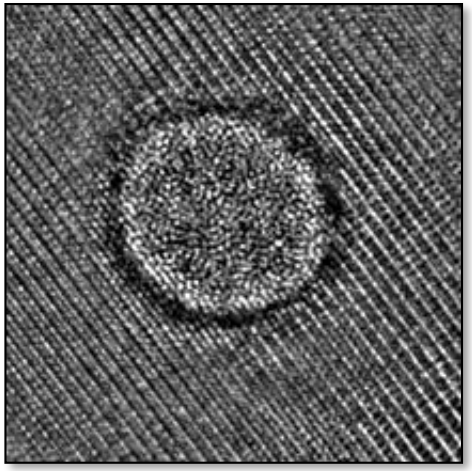
decreasing
energy density

J. Zhang, M. Lang, M. Toulemonde, R. Devanathan, R.C. Ewing, W.J. Weber, *J. Mater. Res.* (2010).

$Gd_2Ti_2O_7$
1.1-GeV ^{101}Ru
20 keV/nm; RT



decreasing
temperature



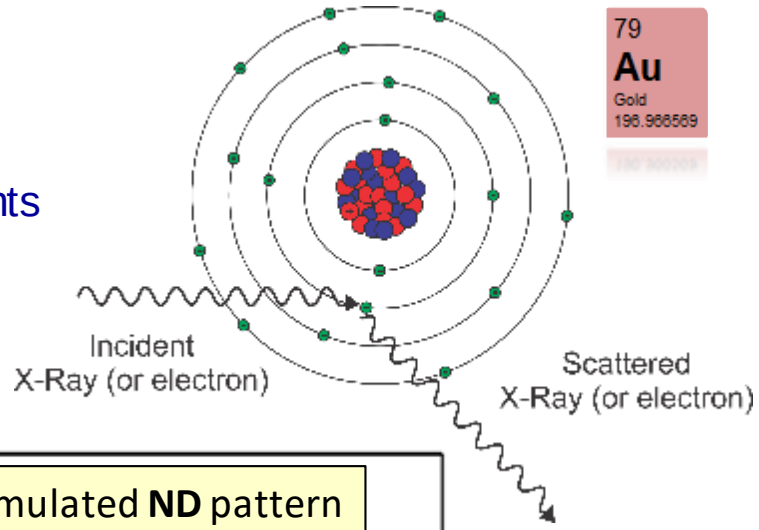
$Gd_2Ti_2O_7$
2.2-GeV ^{197}Au
40 keV/nm; **8 K**

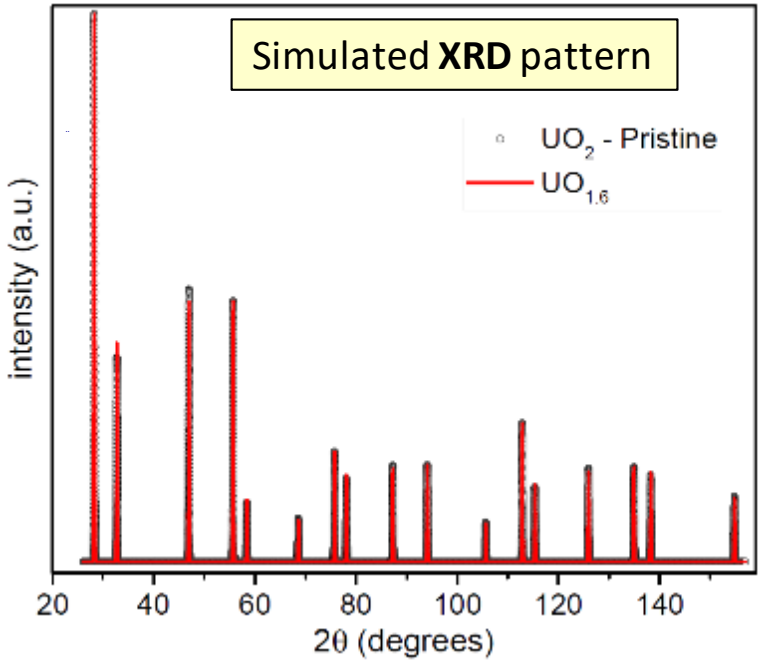
5 nm

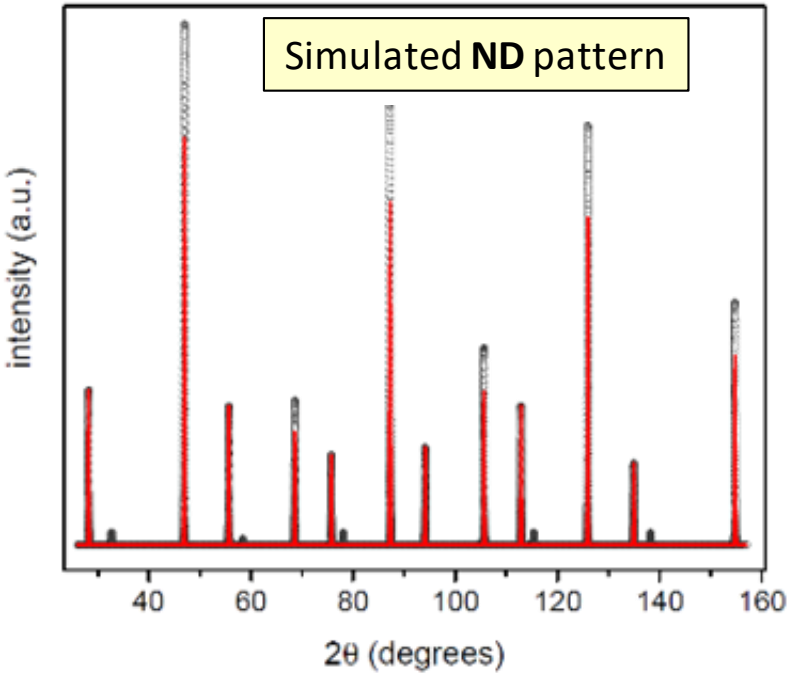
Limitation of X-ray and Electron Probes

Z-dependence of X-ray (electron) interactions:

- ▷ X-rays (electrons) scatter off atomic electrons
- ▷ very small scattering contributions from low-Z elements
  - ⇨ oxygen sublattice basically inaccessible for oxides
- ▷ elements with comparable Z contribute equally
  - ⇨ atomic positions of similar cations indistinguishable



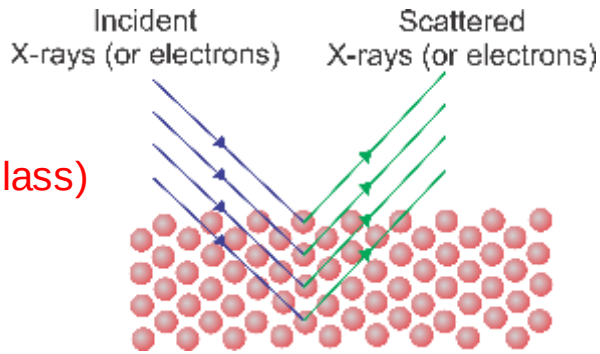




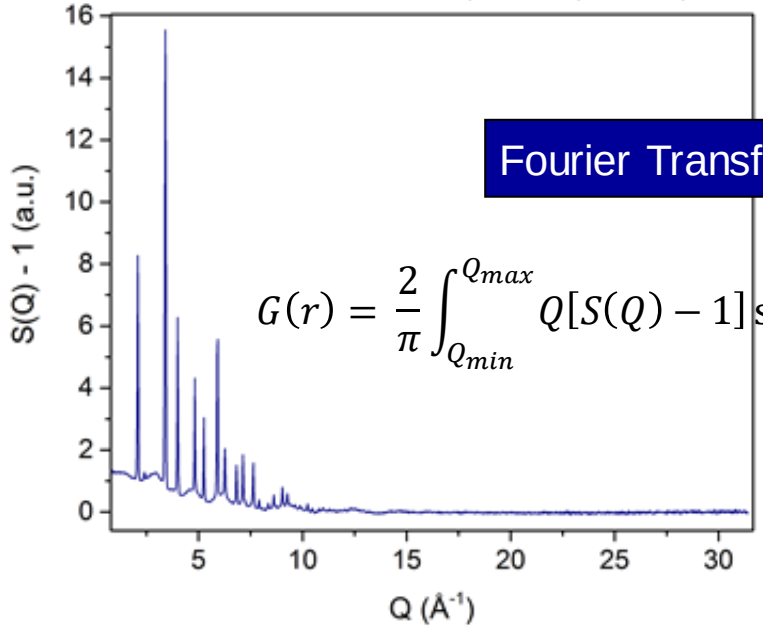
Limitation of Diffraction Experiments

Diffraction experiments:

- ▷ access to long-range structure of crystalline materials
- ▷ no information of medium-range and short-range order
  - ⇨ no structural information from amorphous solids (e.g., wasteglass)
- ▷ diffuse scattering discarded during structural refinement
  - ⇨ local defect structure and disorder inaccessible



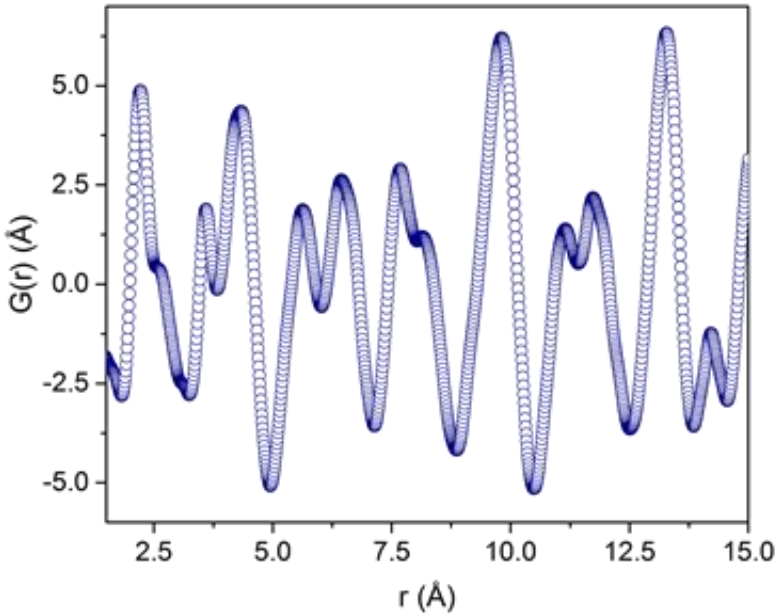
Total Scattering: long range



Fourier Transform

$$G(r) = \frac{2}{\pi}\int_{Q_{min}}^{Q_{max}} Q[S(Q)-1]\sin(Qr)\,dQ$$

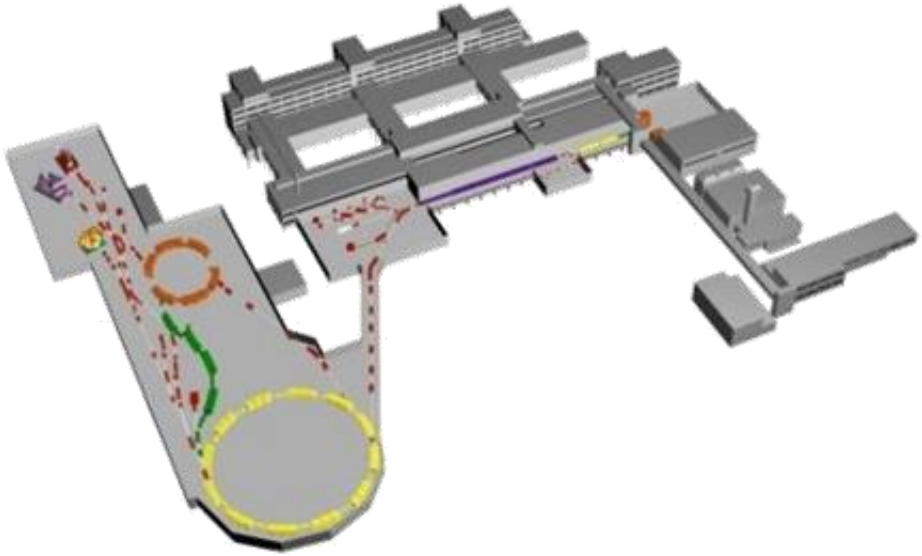
PDF: short range



Neutron Total Scattering Experiments at ORNL

Large Ion Accelerator Facility

simulation of radiation effects



Spallation Neutron Source

structural characterization

maximization of irradiated sample mass

swift heavy ions (large range)

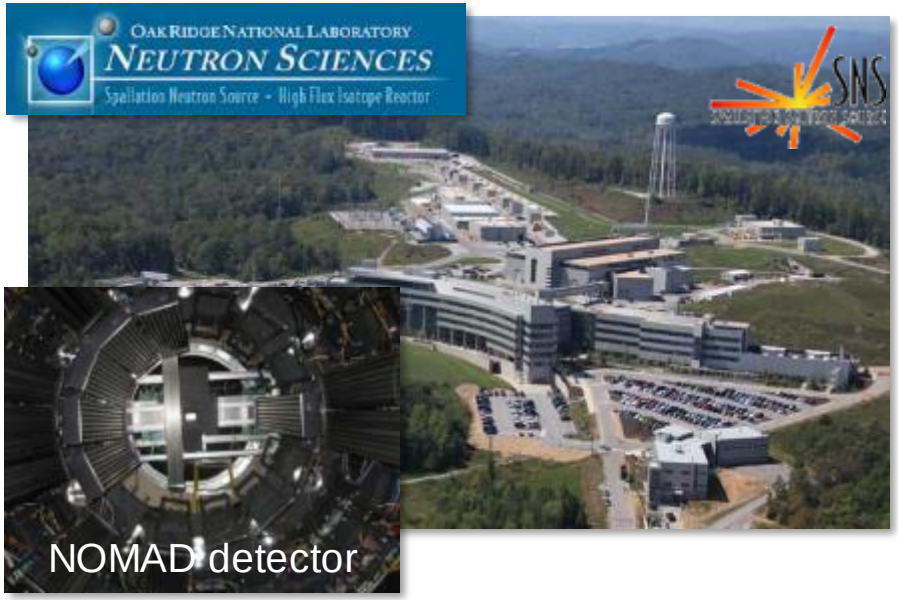
minimization of required sample mass

intense neutron beam (10^8 $cm^{-2} \cdot sec^{-1}$)

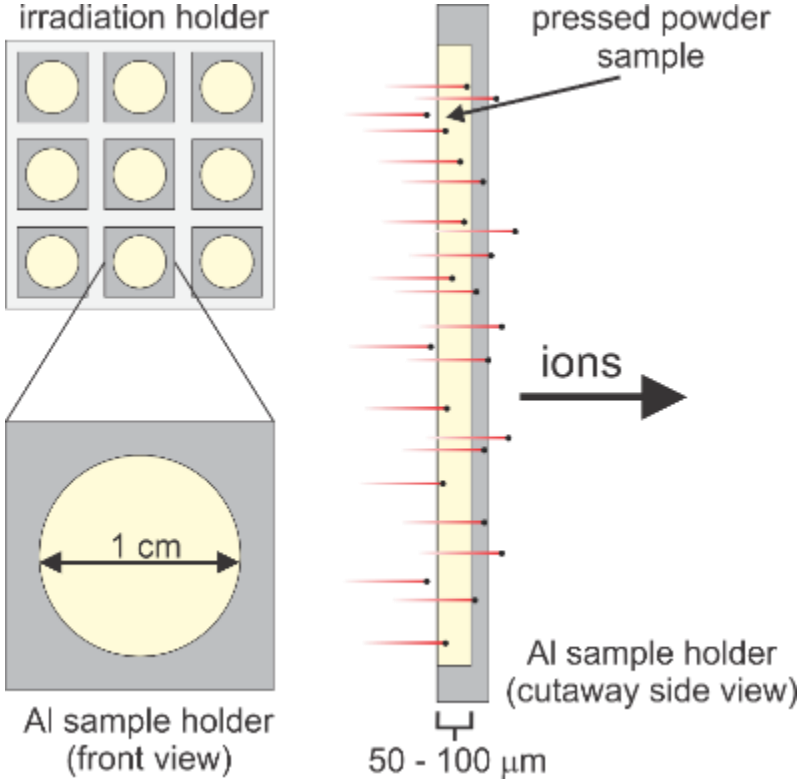
~100 mg

⇨ **investigation of radiation effects by neutron total scattering**

Neutron Total Scattering Experiments at ORNL

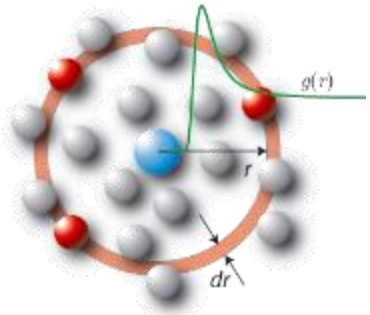


The Nanoscale-Ordered Materials Diffractometer (NOMAD)

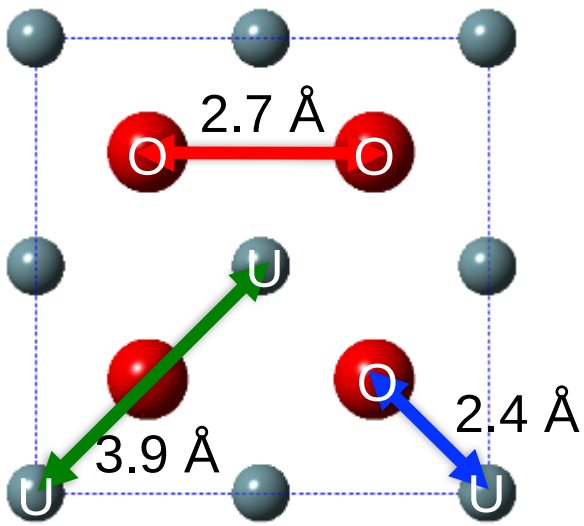


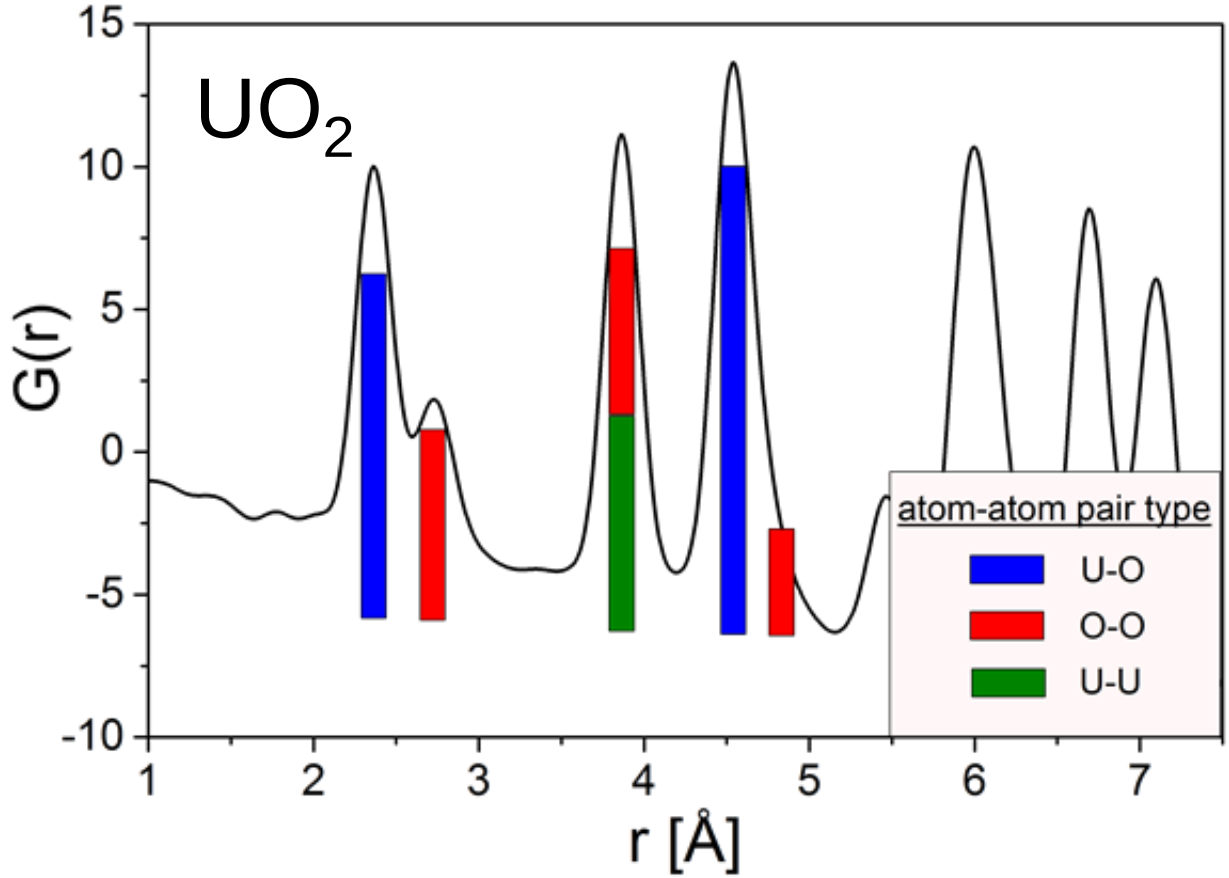
- ⇨ neutron wavelength: 0.1 – 3 Å
- ⇨ flux on sample: 10^8 $cm^{-2} \cdot sec^{-1}$
- ⇨ large detector coverage
- ⇨ high-resolution pair distribution function (PDF)
- ⇨ defects and local disorder
- ⇨ **sample mass: 100 mg**

Pair Distribution Function (PDF) Analysis



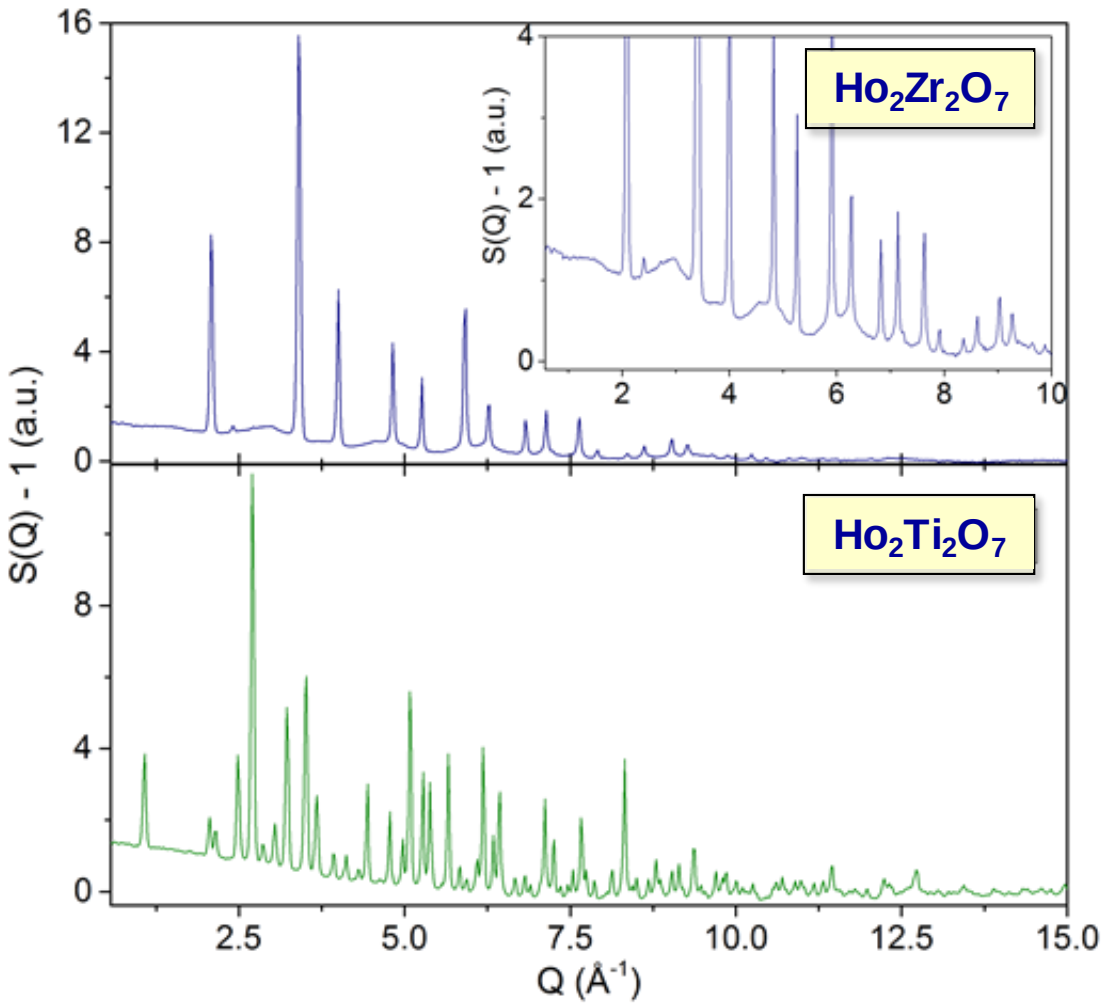
- more intuitive real-space representation
- pairwise interatomic distances





- position = interatomic distance
- intensity ∝ coordination number
- width = spread in interatomic distances

Neutron Diffraction: Order – Disorder Transformations



$A_2Zr_2O_7$

65	66	67	68	69	70
Tb	Dy	Ho	Er	Tm	Yb

disordered fluorite

order-disorder transformation

- ⇨ antisite defects (cations)
- ⇨ randomization of oxygen vacancies

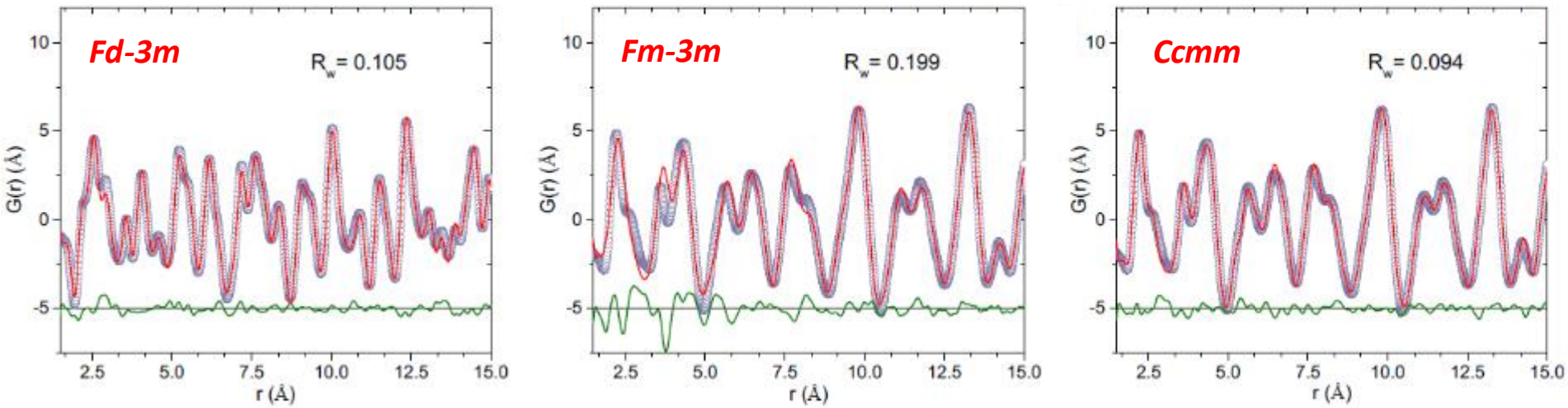
$A_2Ti_2O_7$

62	63	64	65	66	67	68	69	70
Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb

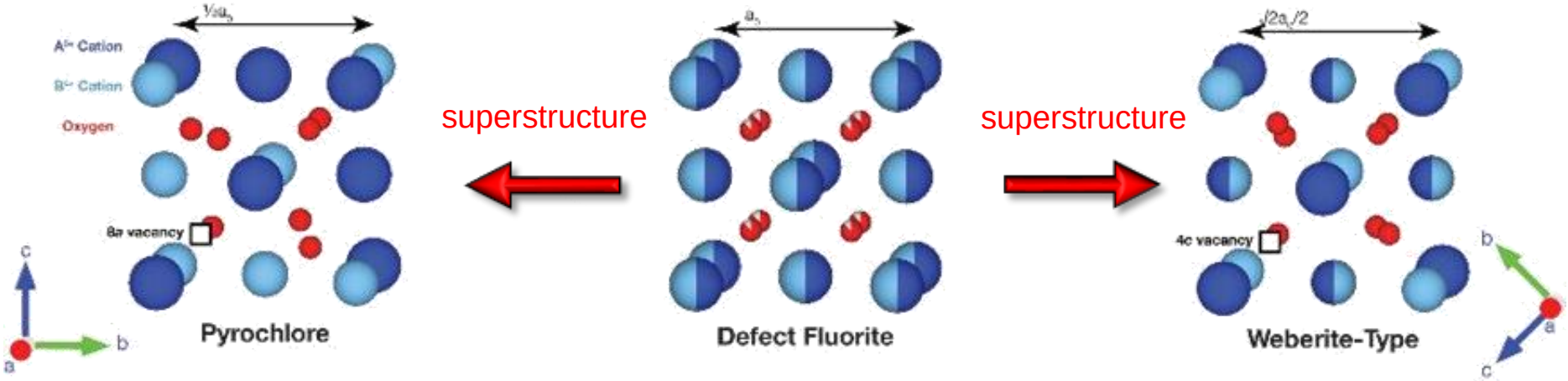
ordered pyrochlore

Neutron PDF: Order – Disorder Transformations

$Ho_2Ti_2O_7$ (pyrochlore) | **$Ho_2Zr_2O_7$** (fluorite) | **$Ho_2Zr_2O_7$** (weberite)

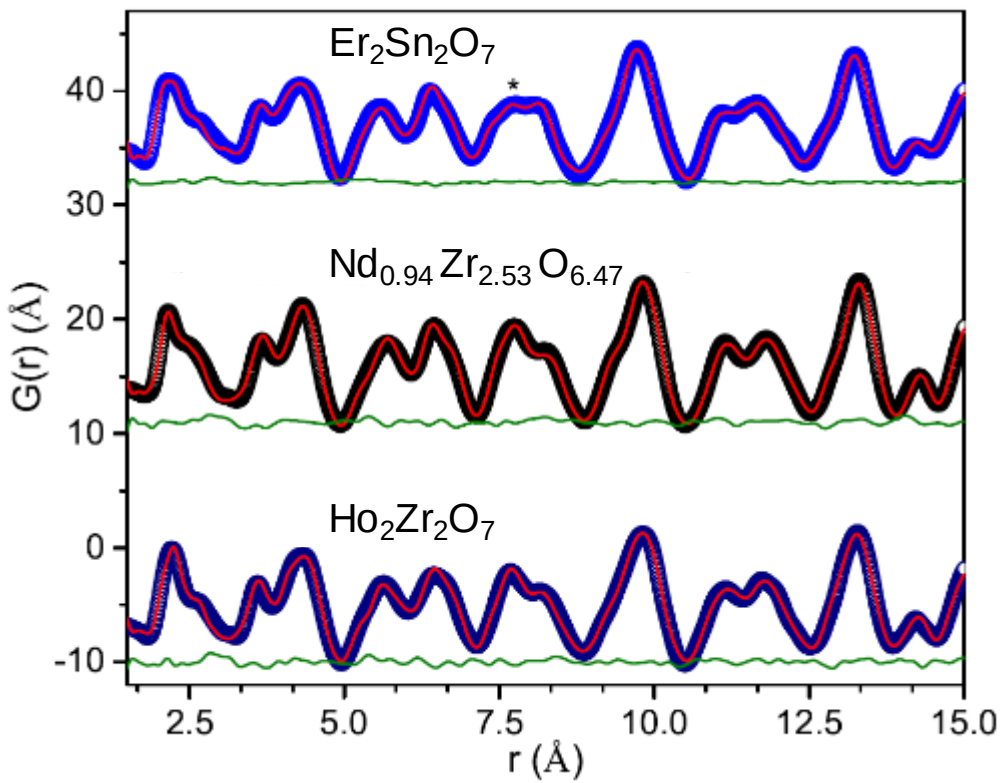


J. Shamblin, *et al.*, *Nature Materials*, 15, 507-511 (2016).



Complex Disordering Mechanism in Pyrochlore

J. Shamblin, *et al.*, *Nature Materials*, 15, 507-511 (2016)



Ion irradiation

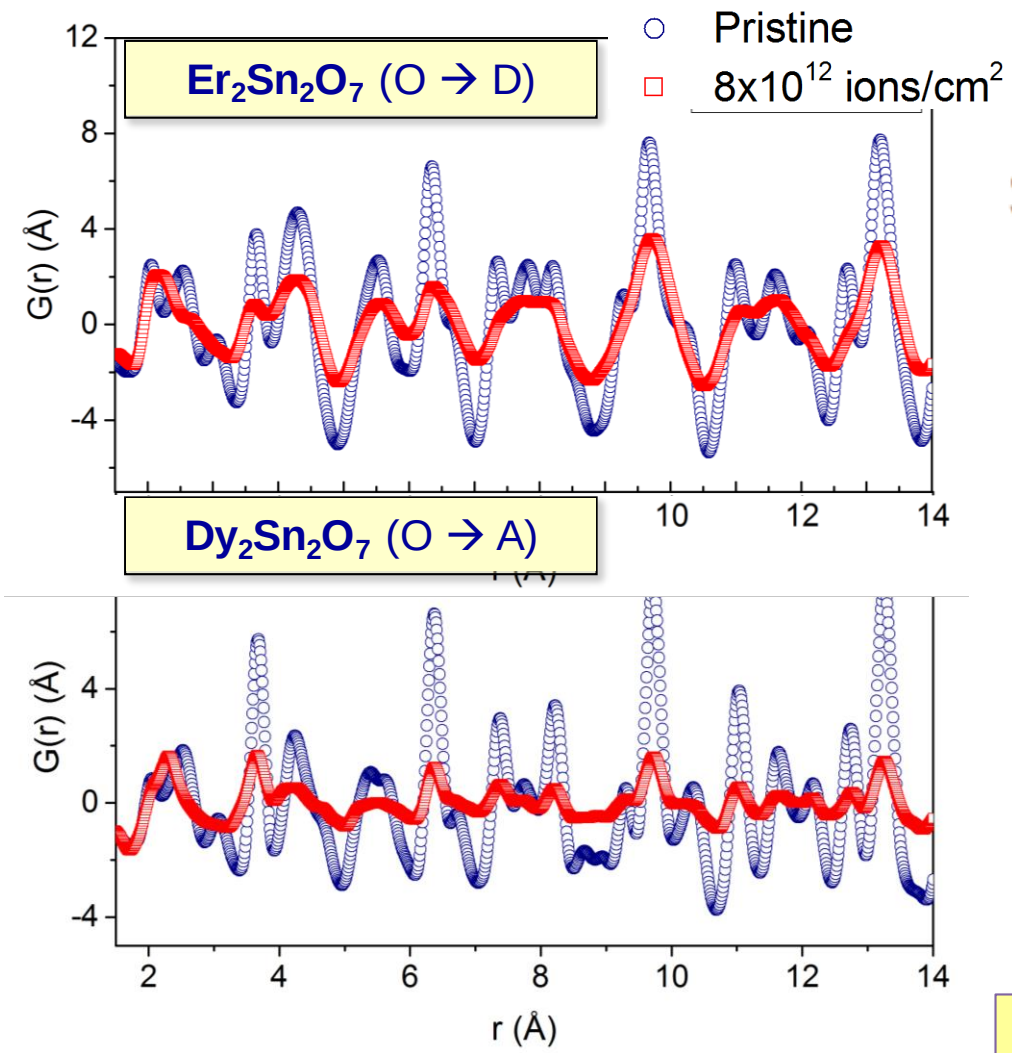
Non-stoichiometry

Chemical composition

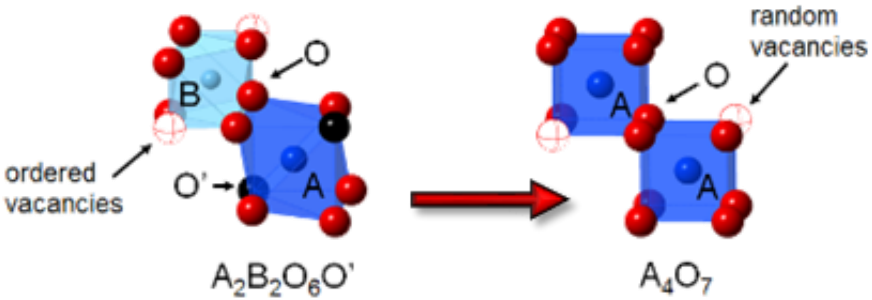
⇨ short-range weberite-like and long-range defect fluorite in all cases

⇨ intrinsic and extrinsic disorder has same structural behavior

Neutron PDF: Disorder *versus* Amorphization



Jacob Shamblin, *et al.*, Acta Materialia (2017)



Disorder

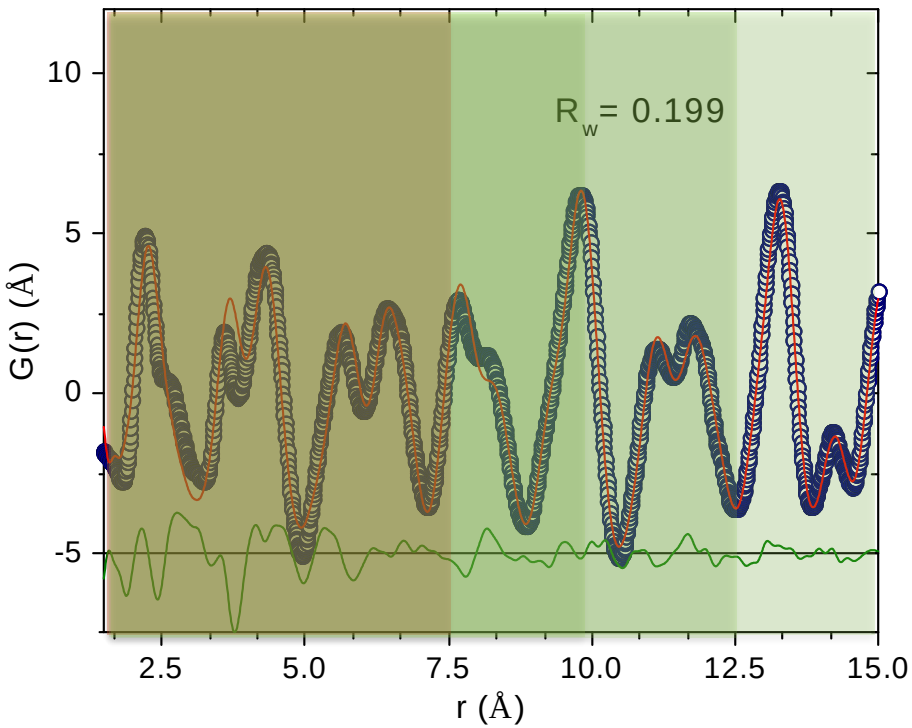
- ⇨ peak broadening at higher-*r*
- ⇨ *r* > 8 Å structure is fluorite-like

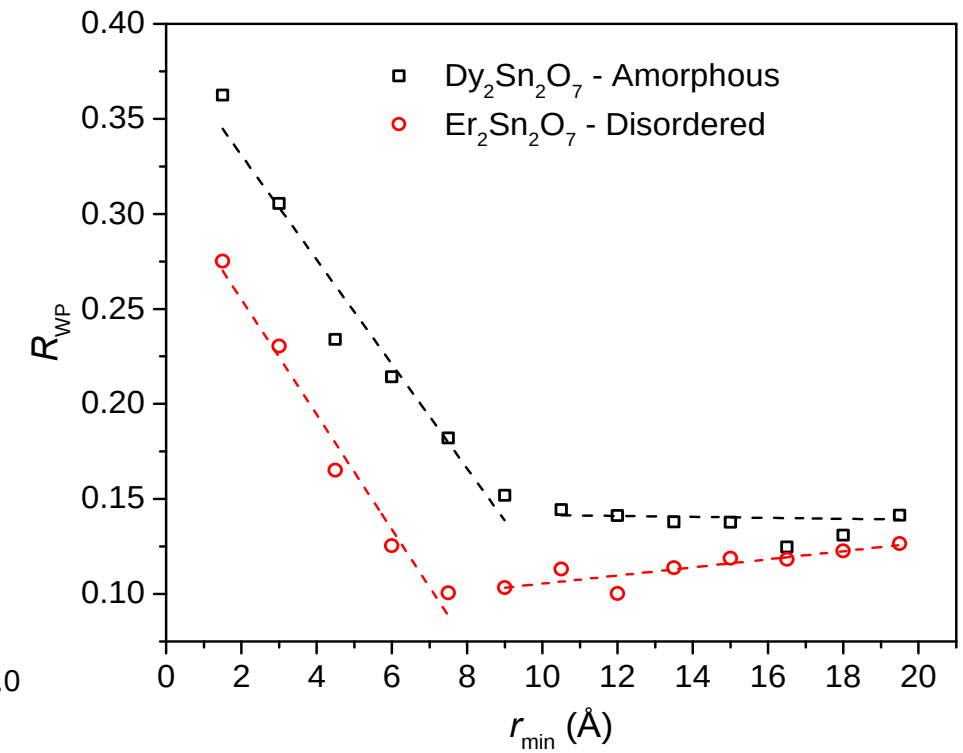
Amorphization

- ⇨ reduced peak intensity at higher-*r*
- ⇨ minimal peak broadening
- ⇨ *r* > 8 Å structure is pyrochlore-like (undamaged matrix)

⇨ same local structure after irradiation

Spatial Extent of Local Order in Disordered Materials





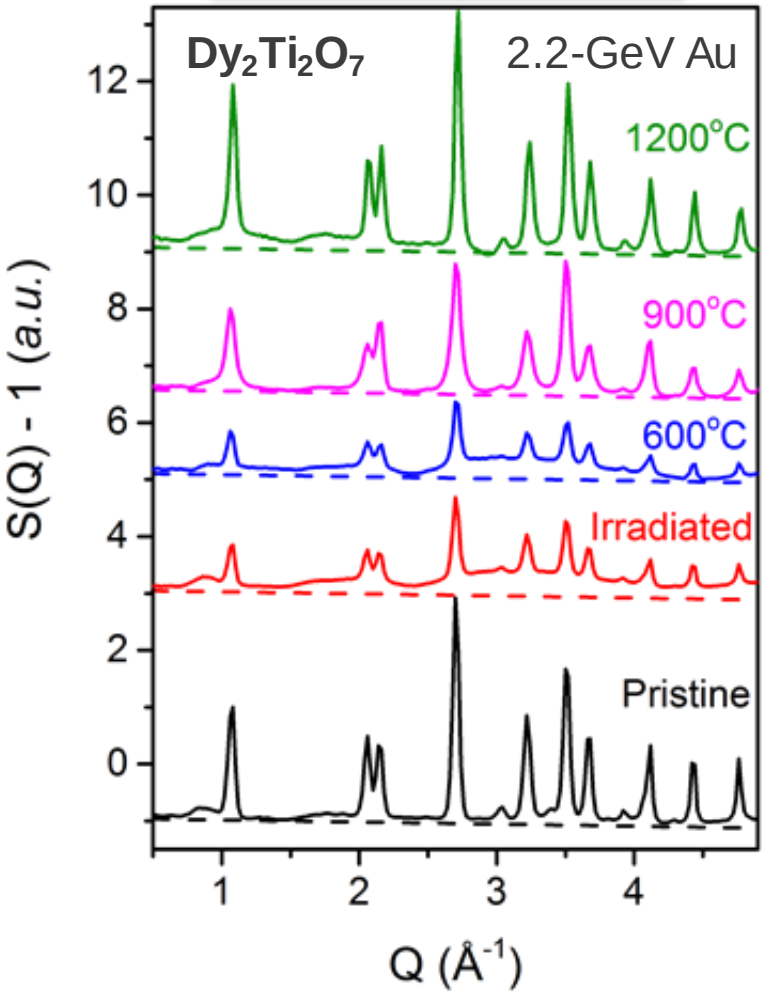
Disorder *versus* Amorphization (box-car refinement)

- ⇨ Spatial extent of weberite-type structural units from quality of fit (R_W)
- ⇨ Similar size of local order in disordered and amorphous pyrochlore

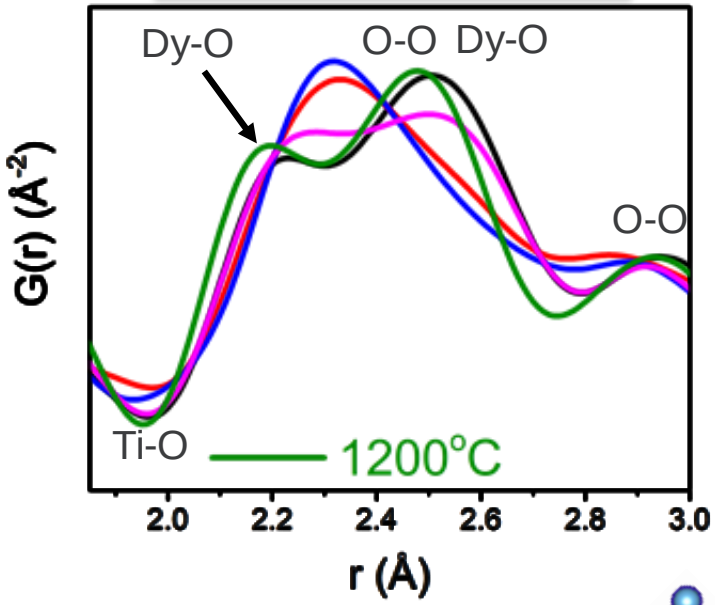
Jacob Shamblin, *et al.*, Acta Materialia (2017)

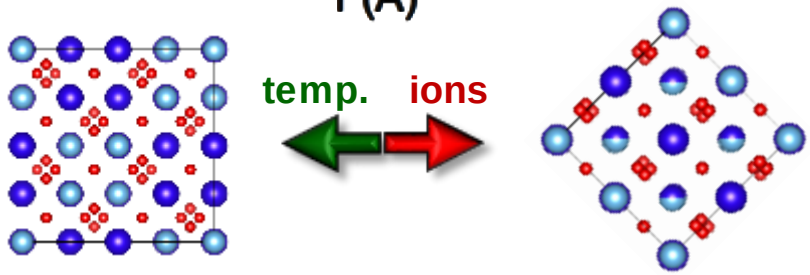
Neutron Total Scattering: Amorphization in Pyrochlore

Neutron diffraction
(long-range structure)



Neutron PDF
(short-range structure)

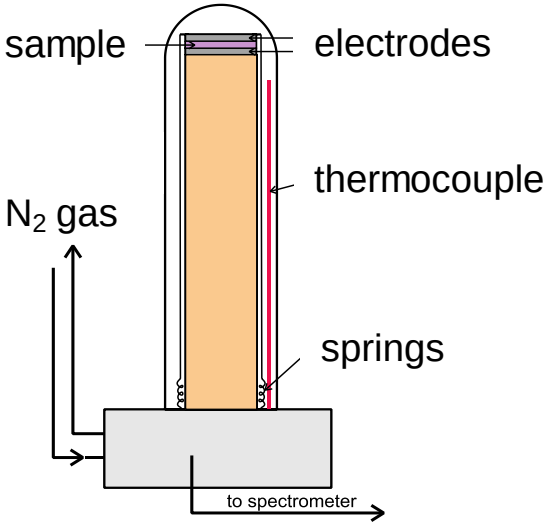




pyrochlore
(ordered)

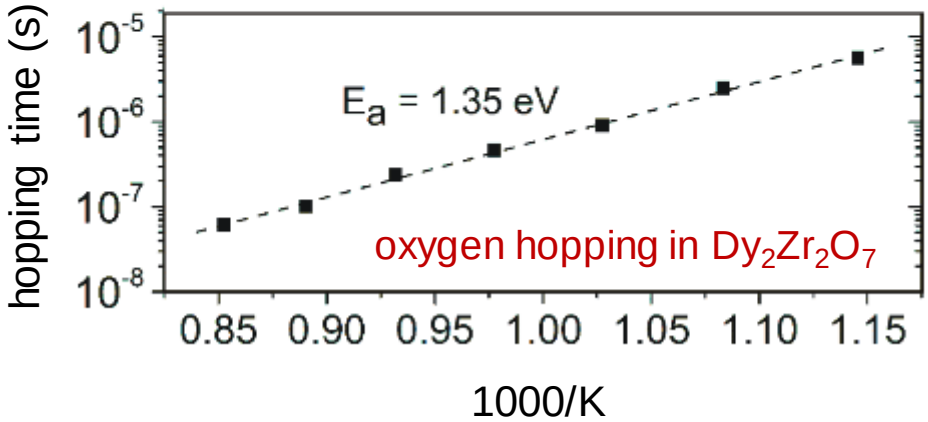
weberite-like
(local distortions)

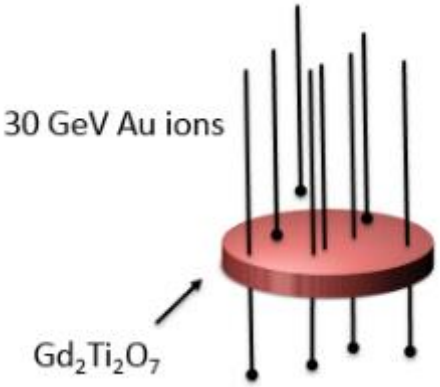
Analyzing Radiation Effects by Dielectric Spectroscopy



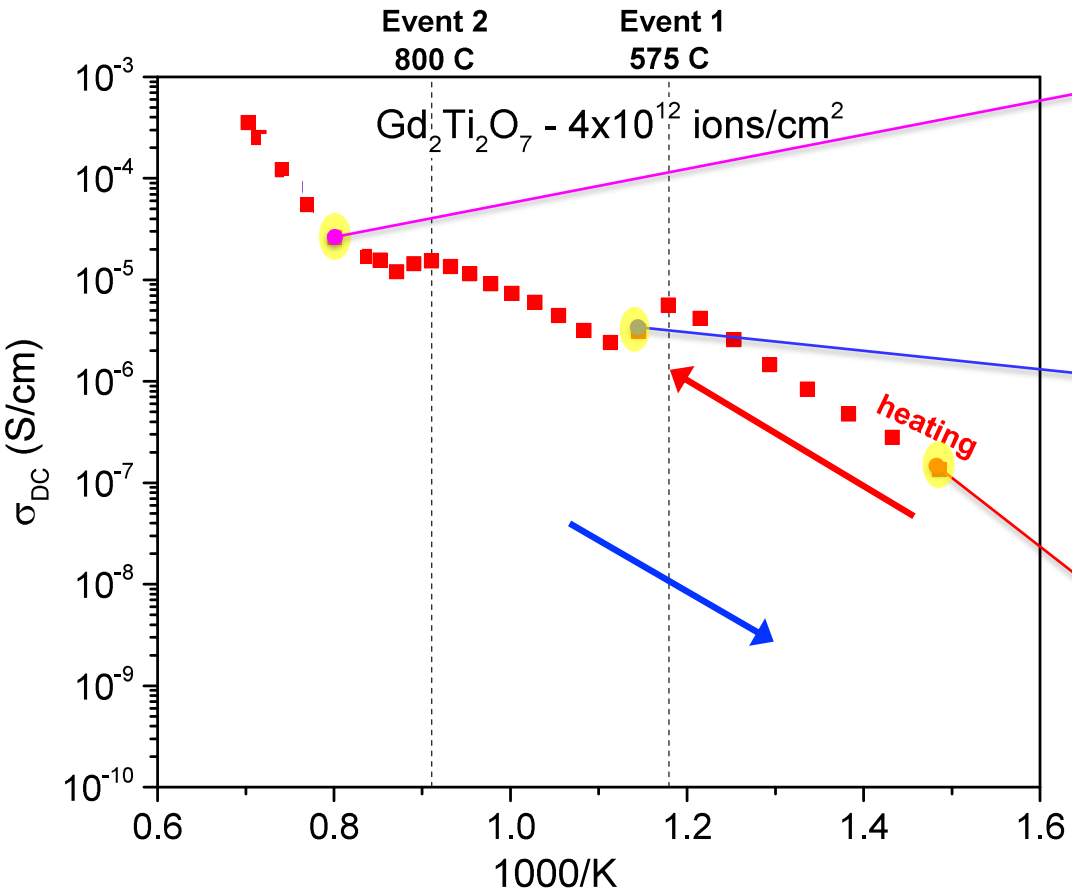
Broadband Dielectric Spectroscopy

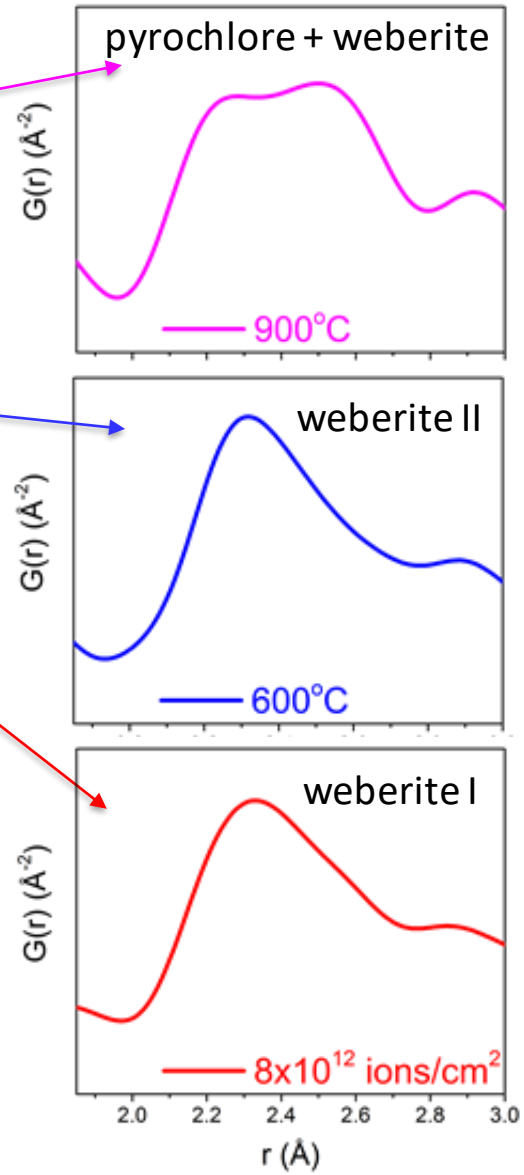
- ⇨ conductivity from µHz to MHz
- ⇨ from room temperature up to 1400 °C
- ⇨ under controlled atmosphere
- ⇨ information on damage recovery and defect dynamics





Impedance Spectroscopy: Amorphization in Pyrochlore



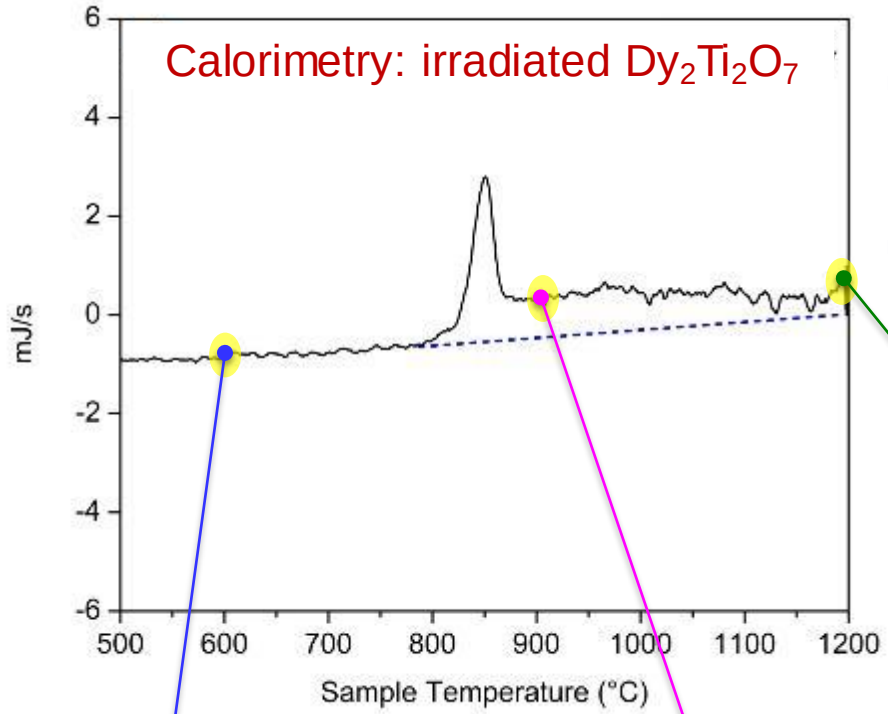


⇨ two distinct damage recovery events

⇨ 250 fold increase in ionic conductivity

Advanced Calorimetry: Amorphization in Pyrochlore

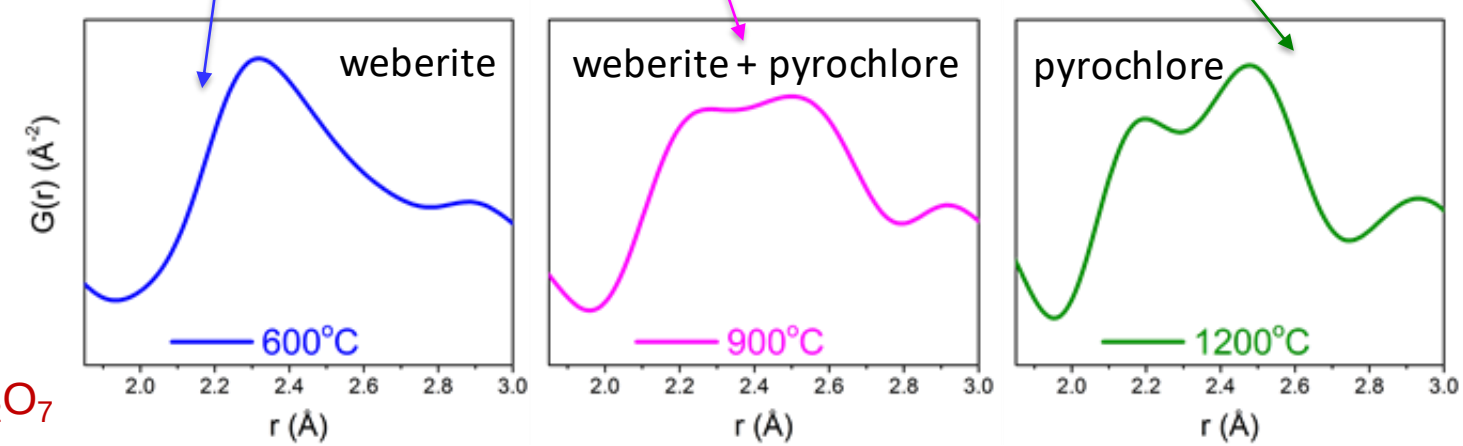
In collaboration with
Alex Navrotsky
(UC Davis)



⇨ sharp exothermic event (recrystallization)

⇨ broad exothermic event (local re-ordering)

Kai Cheng, *et al.*, *Acta Materialia* (2018)



Neutron PDF: irradiated $Dy_2Ti_2O_7$

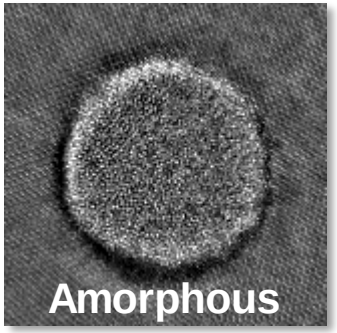
Amorphization and Recrystallization in Pyrochlore

PDF = pair distribution function
BDS = dielectric spectroscopy
DSC = scanning calorimetry

PDF + BDS
rearrangements within amorphous phase

PDF + DSC
decoupled long- and short-range damage recovery with
(i) recrystallization at 800 °C and
(ii) local recovery at higher temperature

Ion-beam irradiation



T = 580 ºC

Thermal annealing

T_{crit} = 800 ºC

T = 1200 ºC

PDF + BDS
remaining local order (orthorhombic distortions) with 250 fold increase in ionic conductivity

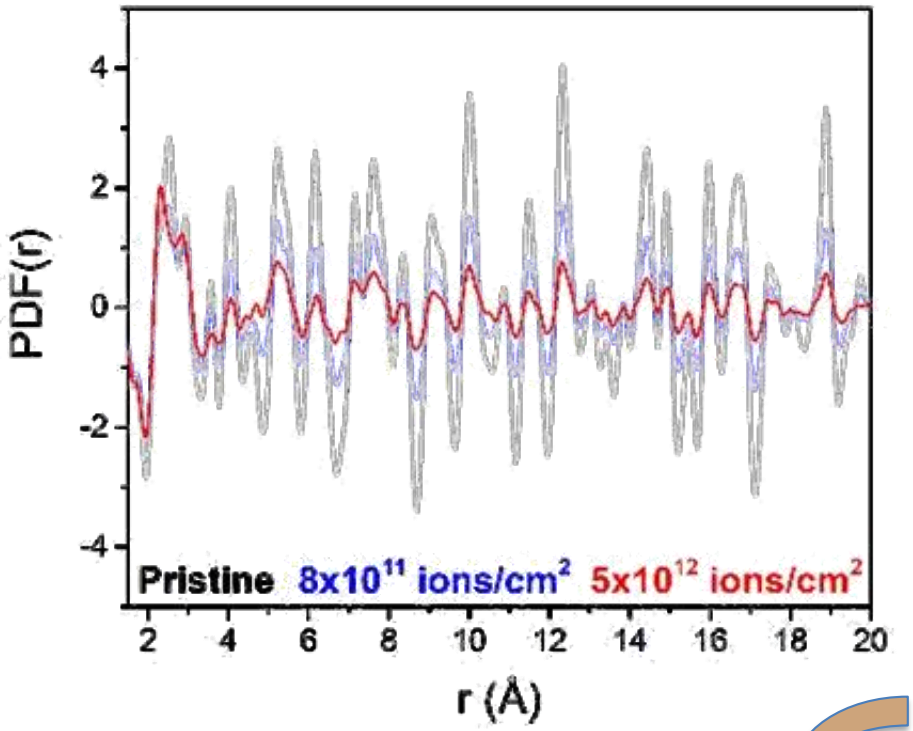
PDF + DSC + BDS
only 50% of local distortions are recovered at 1200 °C and 50% of energy still stored in system

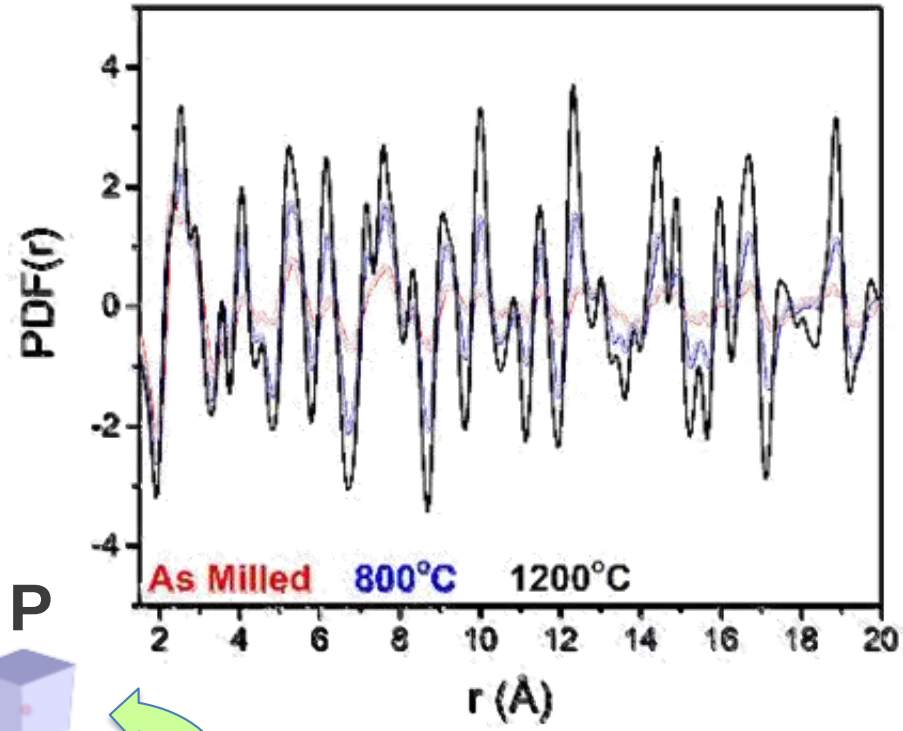
Disorder in High Energy Ball Milled Pyrochlore

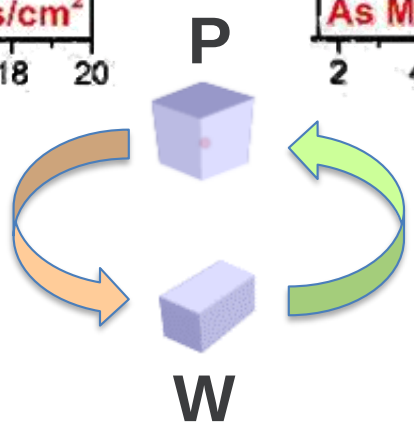
In collaboration with Antonio Fuentes

$Er_2Ti_2O_7$ pyrochlore

Eric O'Quinn, *et al.*, in preparation





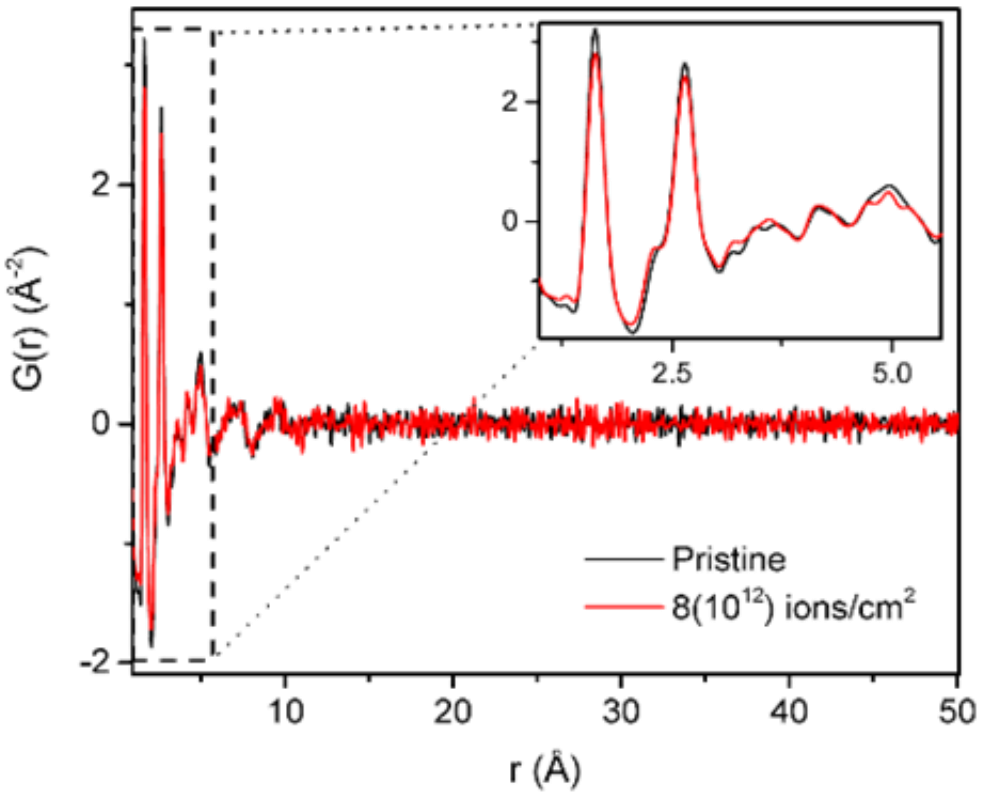


Ion irradiation as a function of fluence

Heating after mechano-chemical synthesis

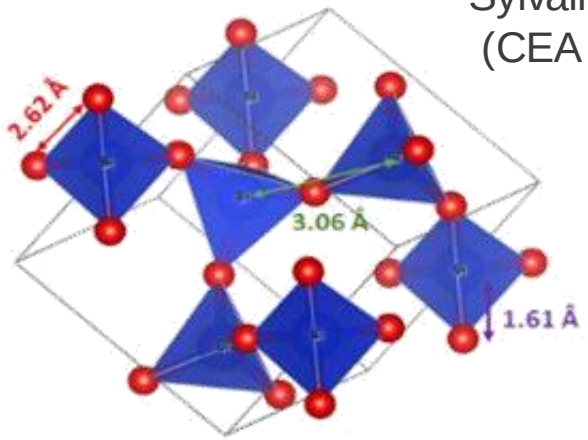
Neutron PDF Analysis: Radiation Effects in Waste Glass

waste glass irradiated with **2.2 GeV ^{197}Au ions**



	%wt oxide	%wt element	%mol oxide	%mol element
SiO_2	54.4	25.4	57.4	18.4
Na_2O	35.5	26.3	36.3	23.2
Al_2O_3	10.1	5.3	6.3	4.0
O		42.9		54.4
total	100	100	100	100

in collaboration with Sylvain Peuget (CEA France)



local SiO_4-tetrahedra environment

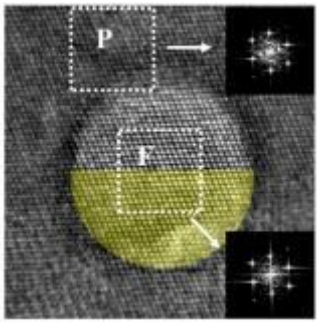
⇨ irradiation causes changes in the local glass framework (now investigated by RMC)

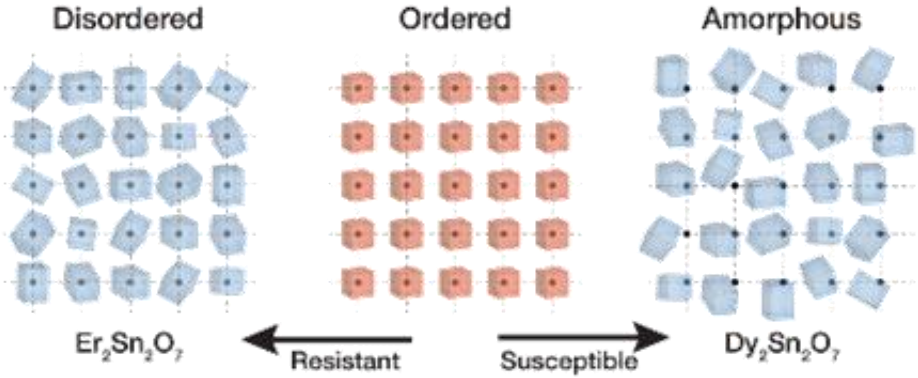
Conclusions

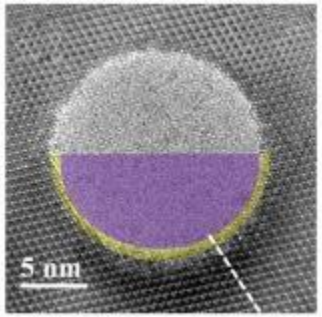
- Use of very high energy ions provide sufficient sample mass to apply advanced bulk materials characterization techniques

- Neutron total scattering with pair distribution function analysis (PDF) is suitable to characterize various radiation effects in oxide materials:
  - cation and anion sublattices (low-Z elements)
  - average (long-range) structure through diffraction experiments
  - local (short-range) structure through PDF analysis

- Amorphization and recrystallization in pyrochlore is complex involving two distinct processes that occur over different length scales







Extreme Environment Team

University of Tennessee

Stanford University







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Vladimir Skuratov – Joint Institute Nuclear Research (Russia)

Vitali Prakapenka – Advanced Photon Source (GSECARS)
C.Y. Park, D. Popov – Advanced Photon Source (HPCAT)

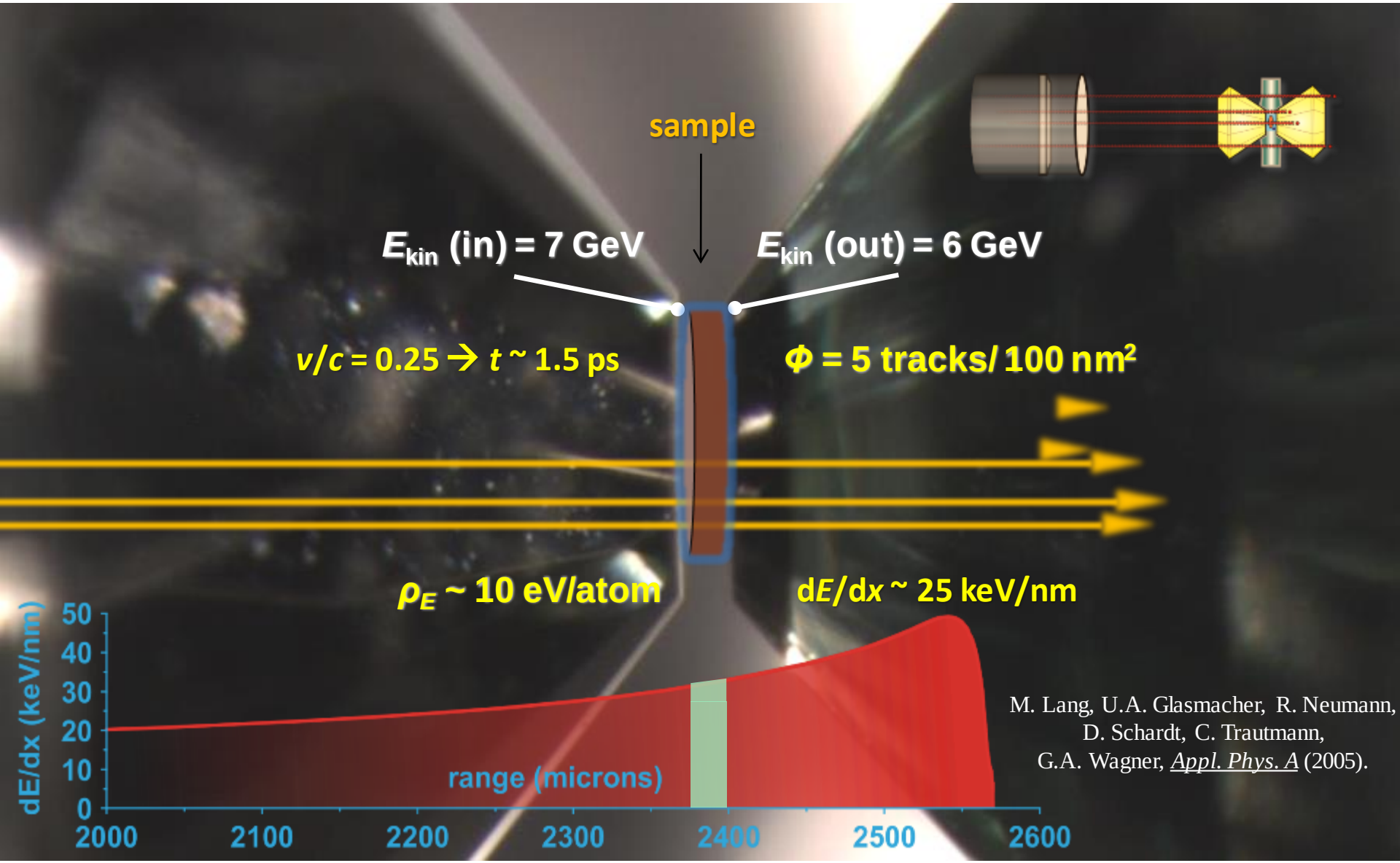
Jörg Neuefeind – Spallation Neutron Source (NOMAD)
Mikhail Feygenson – Spallation Neutron Source (NOMAD)

Support:

Pu U Np Th Am Cm MSA
Materials Science of Actinides
Energy Frontier Research Center

Los Alamos
U.S. DEPARTMENT OF ENERGY | Office of Science

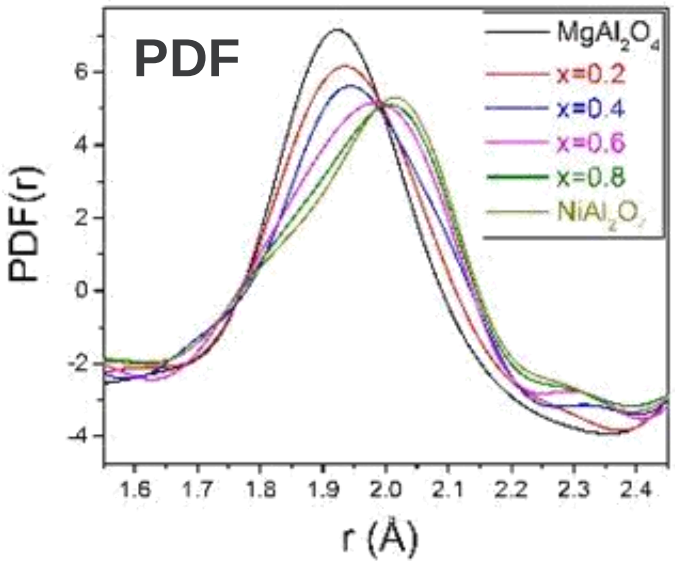
Irradiations at High Pressure

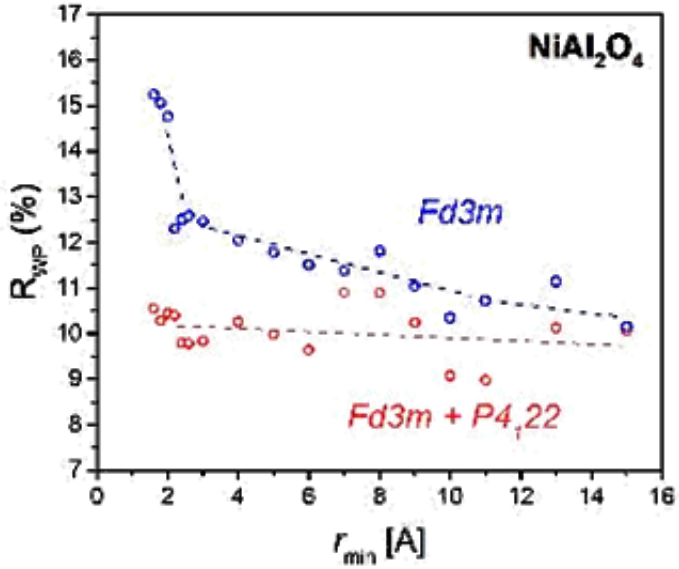


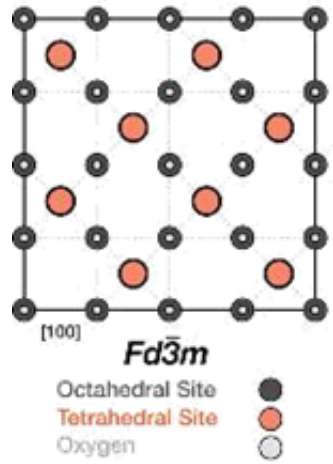
M. Lang, U.A. Glasmacher, R. Neumann, D. Schardt, C. Trautmann, G.A. Wagner, *Appl. Phys. A* (2005).

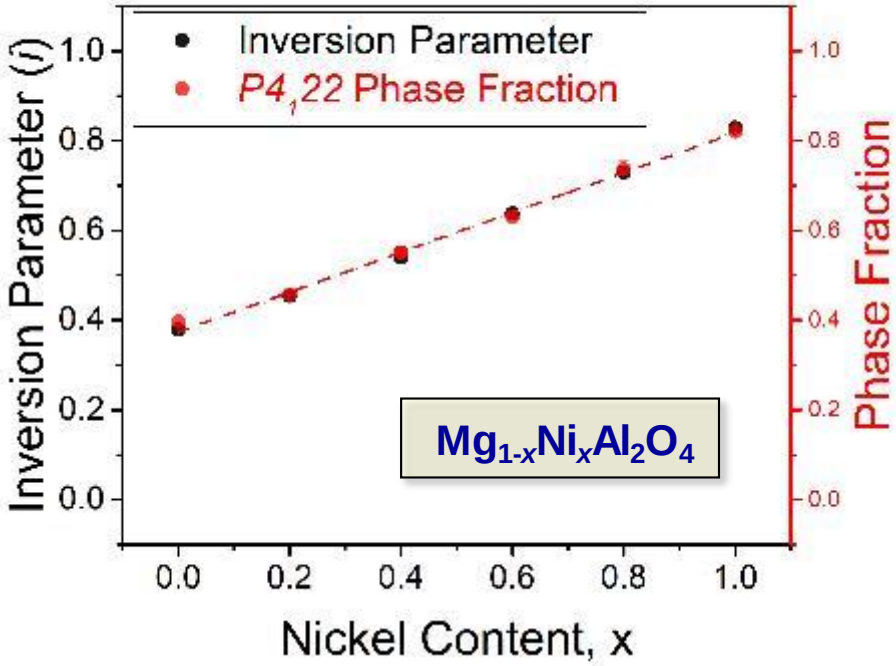

Thanks!

Inversion in Spinel: Local Phase Transition



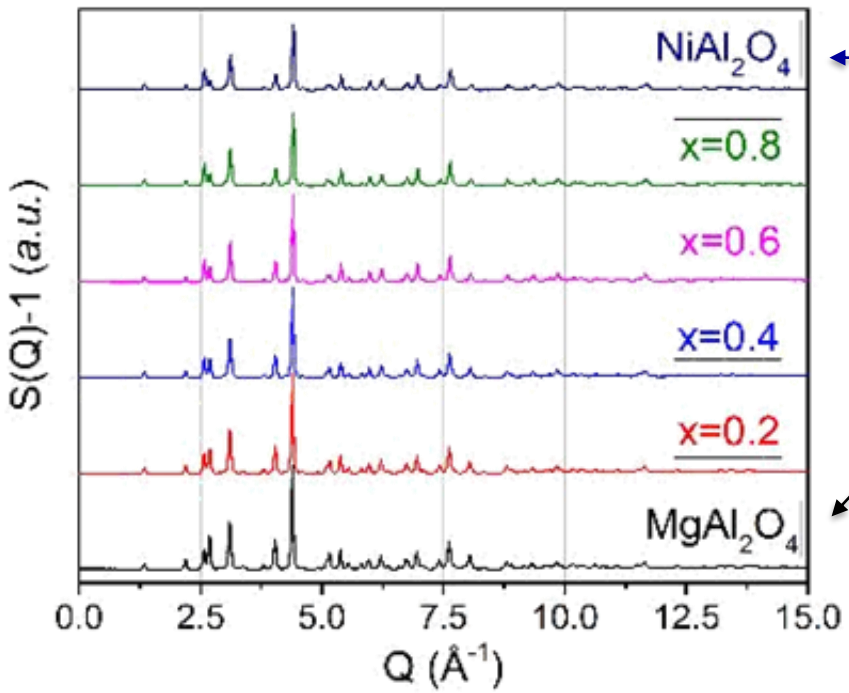






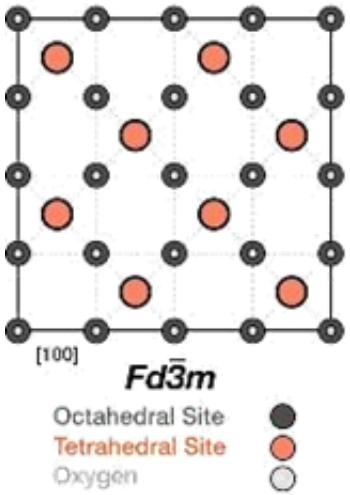
Neutron PDF: Disorder in Spinel (Inversion)

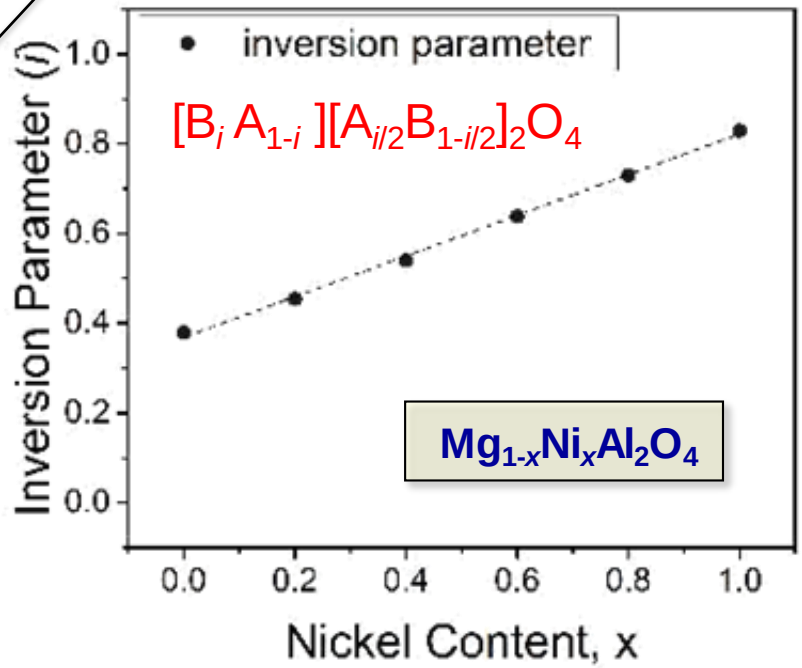
Neutron Diffraction



"inverse" spinel

"normal" spinel





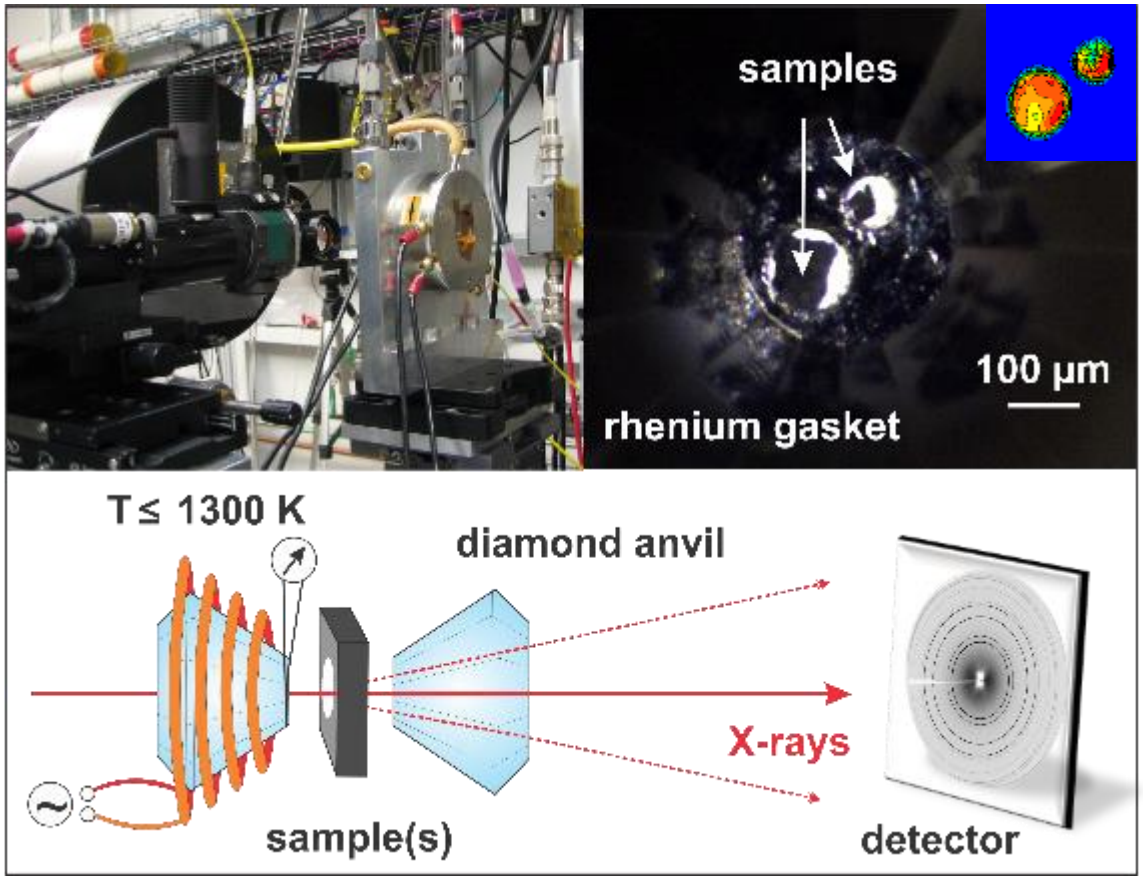
Inversion

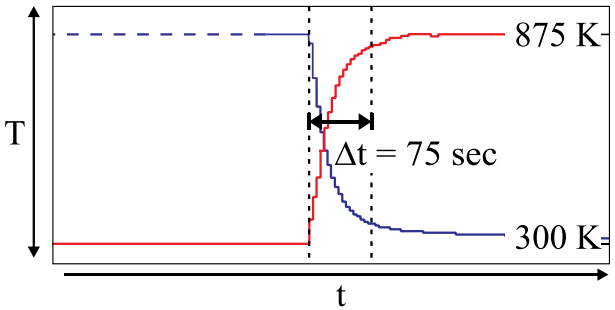
- ⇨ Exchange of A- and B-site cations
- ⇨ Increased inversion for Ni-rich spinels

Eric O'Quinn, *et al.*, *J. Am. Chem. Soc.* (2017)

Recrystallization Studies at High Temperatures

Hydrothermal diamond anvil cell (HDAC)
⇨ Sample-annealing chamber for nuclear materials (up to 1300 K)

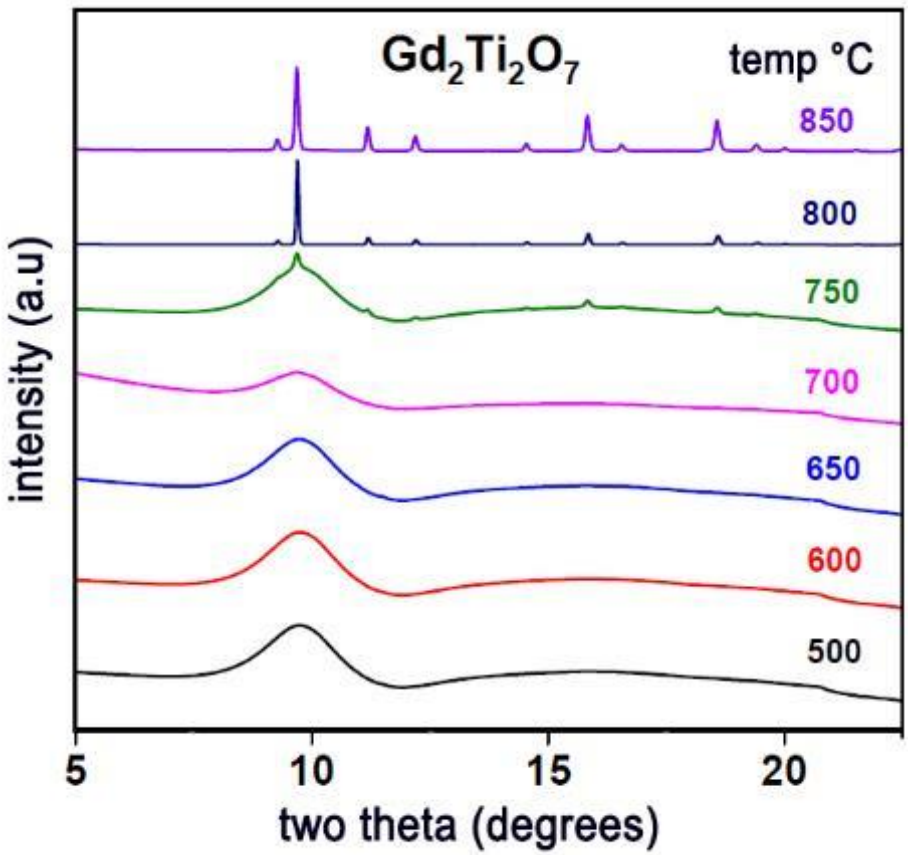


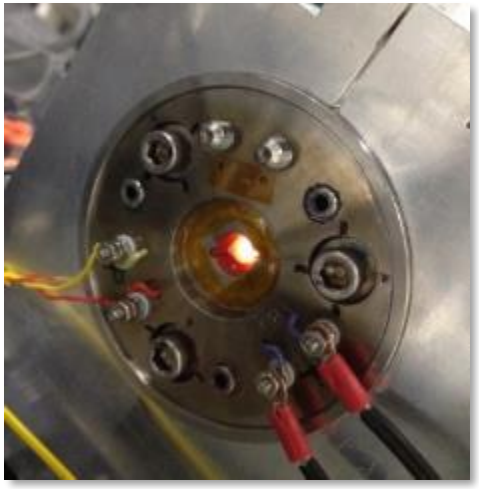


- ⇨ isochronal and isothermal annealing studies
- ⇨ homogeneous heating
- ⇨ superior temperature control
- ⇨ microscopic sample volume
- ⇨ multiple samples in parallel
- ⇨ *in situ* access for X-rays
- ⇨ different atmospheres

Recrystallization Studies at High Temperatures

$Gd_2Ti_2O_7$ irradiated with **2 GeV ^{181}Ta** annealed within an HDAC to **850 °C**





- ⇨ Recrystallization at high-*T*
- ⇨ Critical temperature depends on pyrochlore composition
- ⇨ Full recovery at 850 °C

Sulgiye Park, *et al.*, *Acta* Materialia (2015).