Joint ICTP-IAEA Workshop on Radiation Effects in Nuclear Waste Forms and their Consequences for Storage and Disposal

Trieste, Italy

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EXPERIMENTAL TECHNIQUES FOR RADIATION DAMAGE EFFECTS

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DEPARTMENT OF NUCLEAR ENGINEERING

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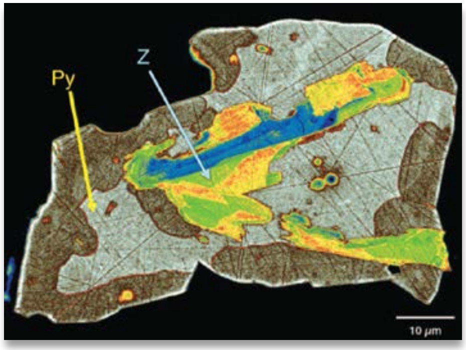
Durable Materials for Radionuclide Immobilization

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)

Advanced characterization techniques required to study radiation effects in nuclear waste forms and their consequences for storage and disposal

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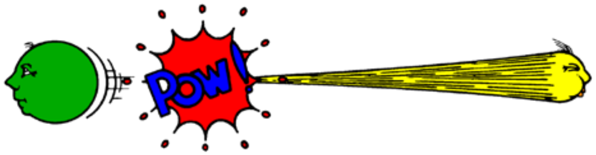
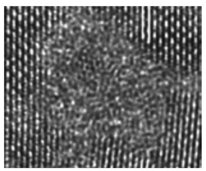
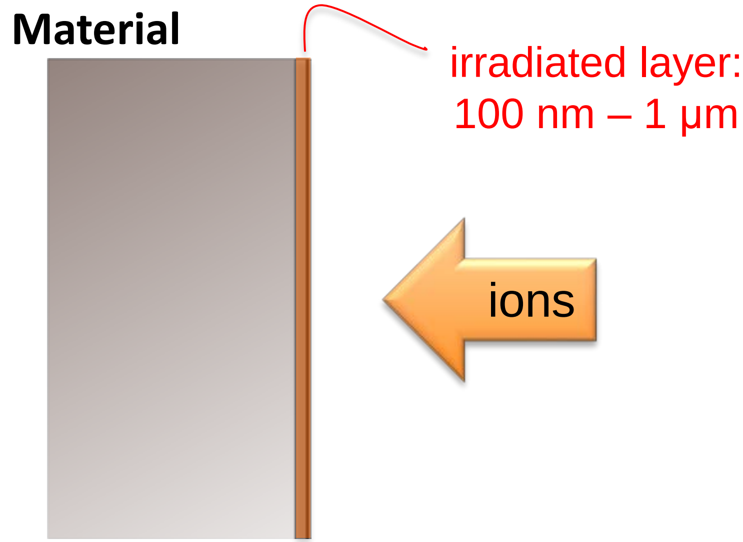
Simulation of Radiation Effects: Low Energy Ion Beams

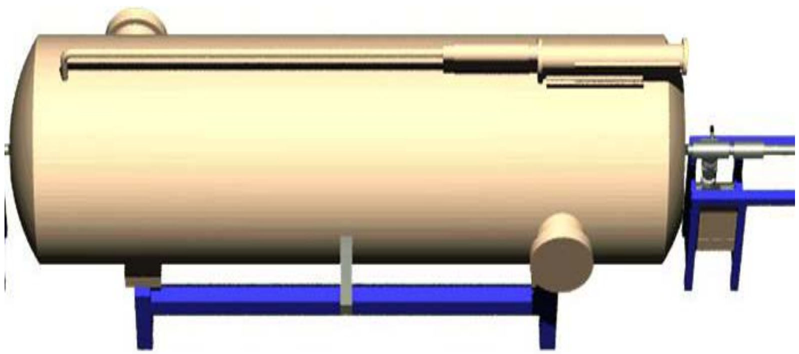
Alpha Decay





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

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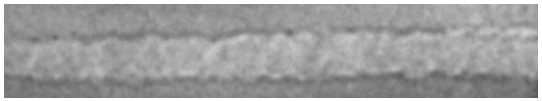
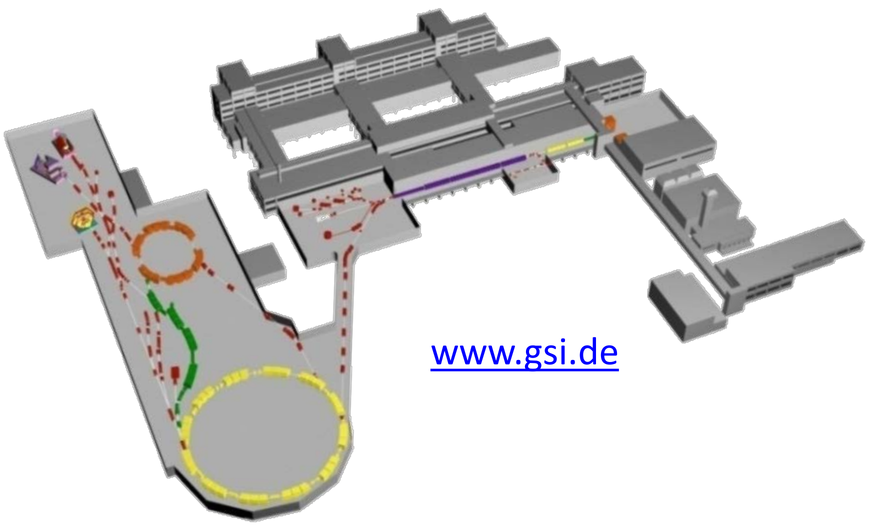
Simulation of Radiation Effects: High Energy Ion Beams

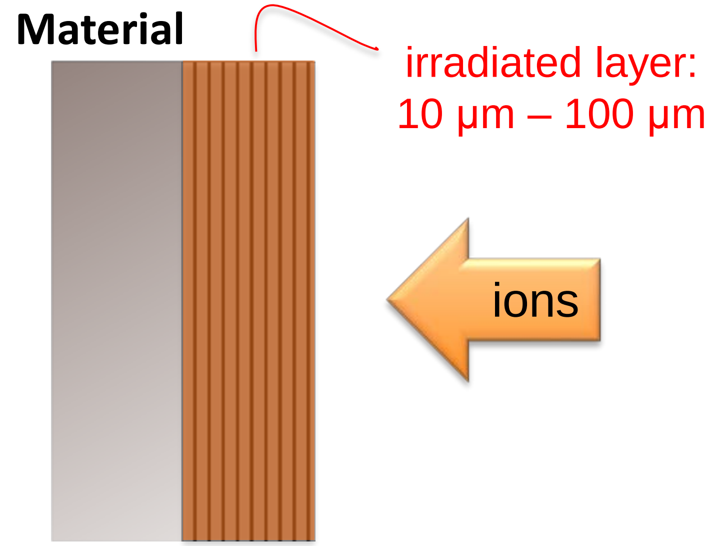
Spontaneous Fission

energy release:
~200 MeV





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



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

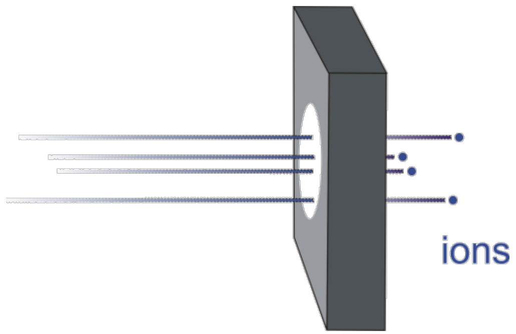
⇨ different ion-matter interactions (electronic d*E*/d*x*)

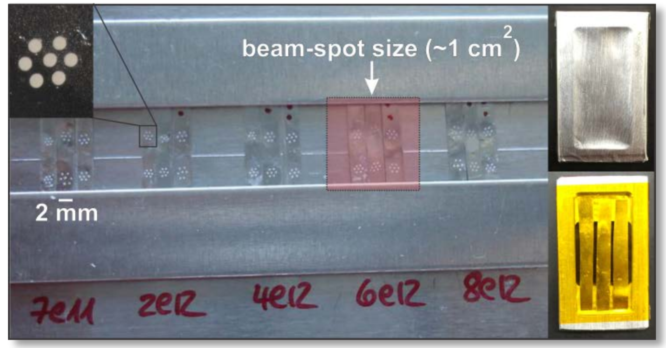
⇨ **large volume** of modified material

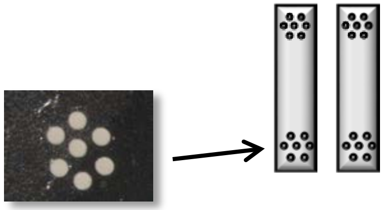
⇨ access to many bulk characterization techniques (e.g., X-ray and neutron scattering)

Swift Heavy Ion-Beam Irradiation Experiments

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





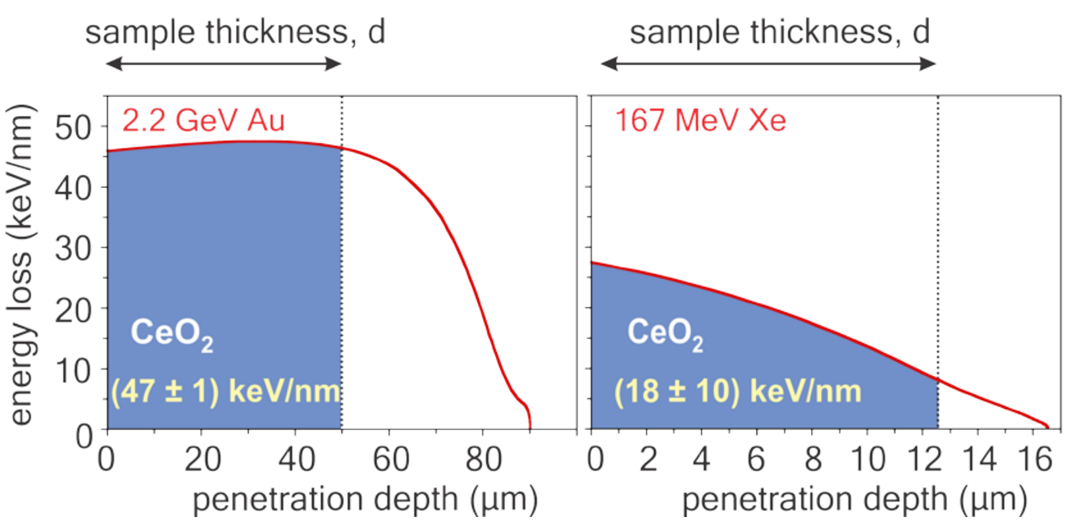


Sample chamber

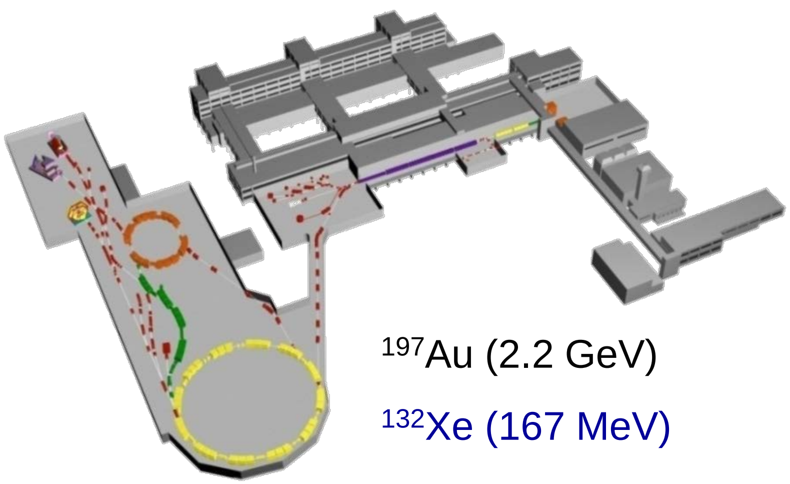
diameter: 100 µm

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)

Synchrotron X-ray Characterization

X-rays

- ⇨ X-ray energy: 5 – 100 keV
- ⇨ **flux at sample: ~10^{11} photons/s**
- ⇨ beam-spot size: ~10 µm

sample positioning

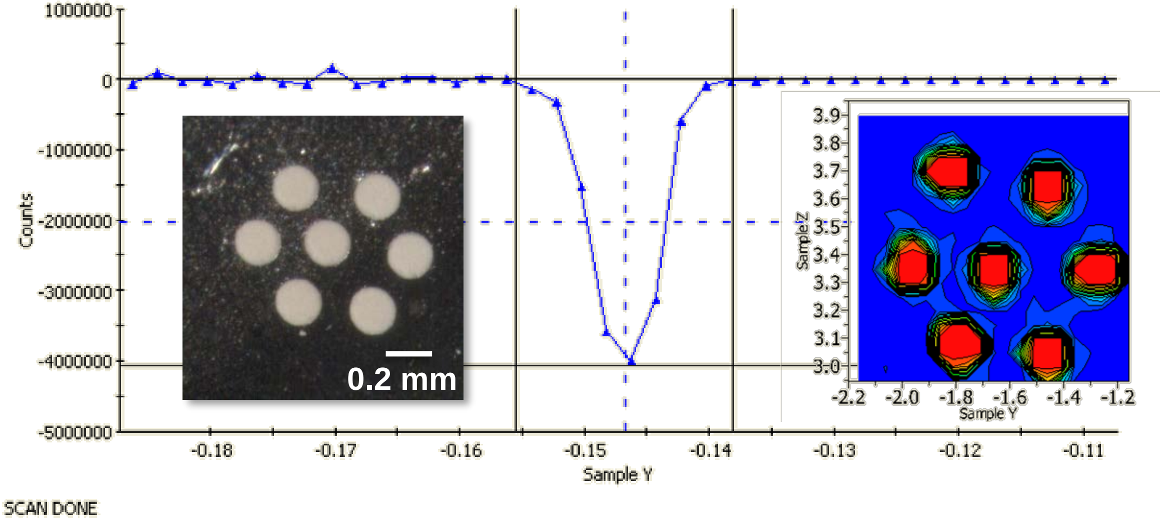
- ⇨ movable ionization chamber
- ⇨ 1d-scans and 2d-scans
- ⇨ ω-scans for precise sample-detector distance determination

XRD and XAS measurement

- ⇨ high-resolution detectors: MAR345 image plate, CCDs
- ⇨ ionization chambers
- ⇨ **exposure times: sec - min**

Advanced Photon Source
Argonne National Laboratory

National Synchrotron Light Source
Brookhaven National Laboratory



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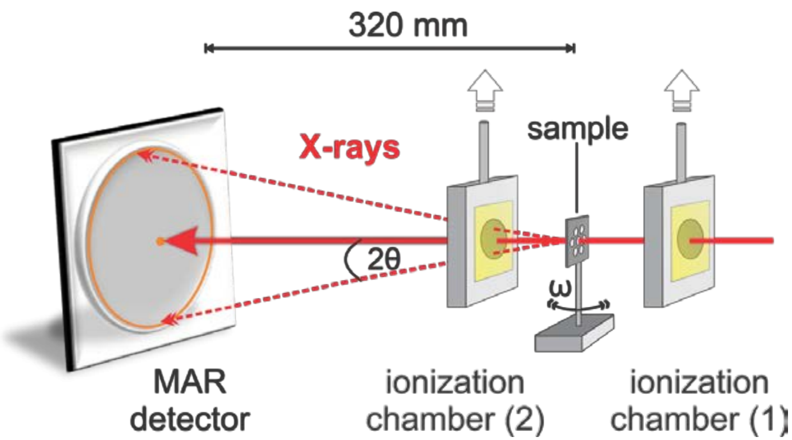
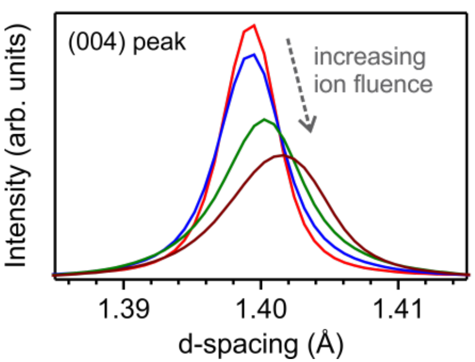
Synchrotron X-ray Characterization Techniques



Transmission geometry

XRD

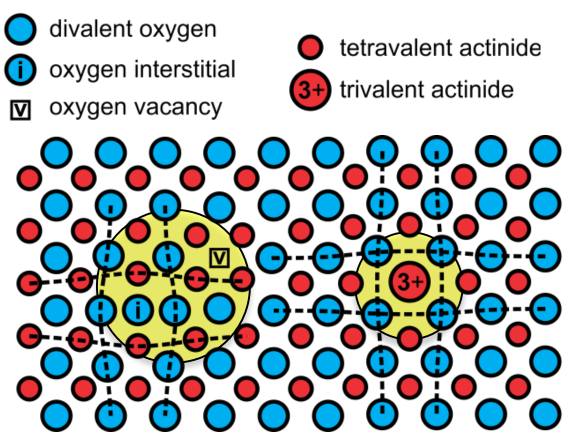
X-ray diffraction



Structural properties

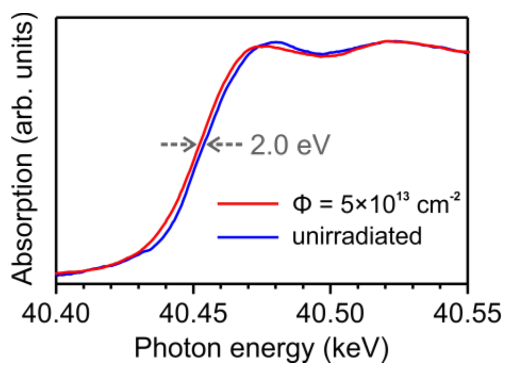
⇨ unit-cell parameter

⇨ microstrain



XAS

X-ray absorption spectroscopy

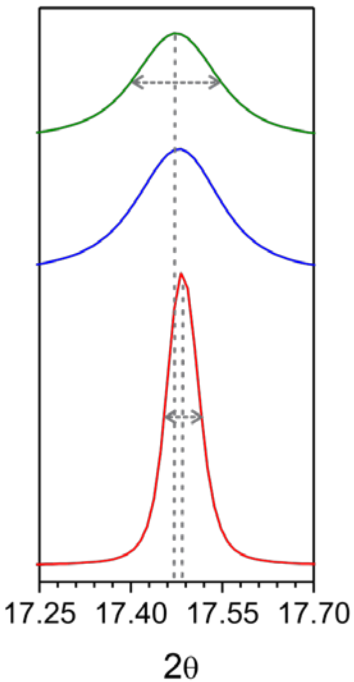


Electronic properties

⇨ oxidation state

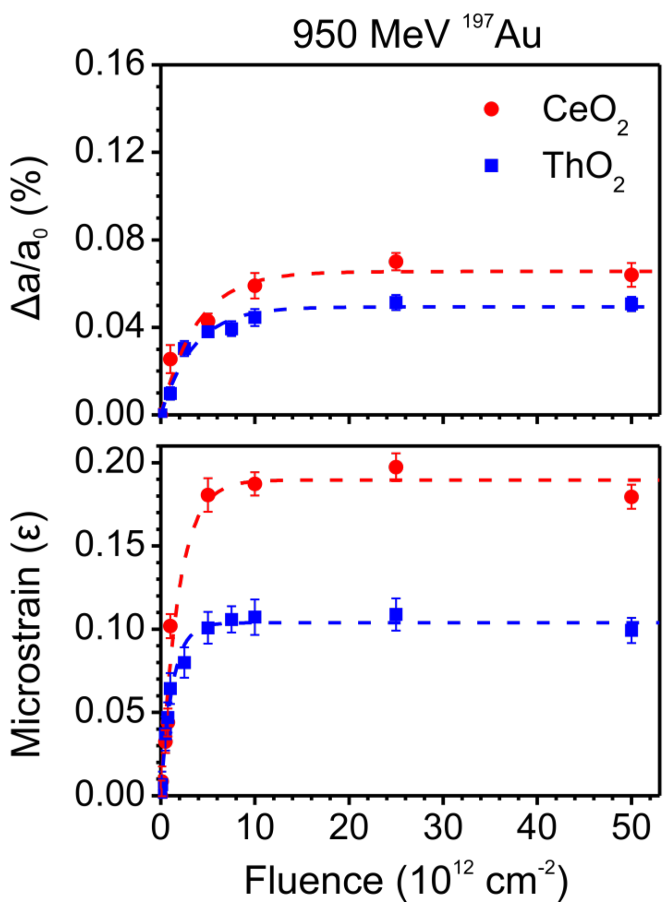
M. Lang, *et al.*, *Journal of Materials Research* (2015).

Redox Response of Actinide Oxides to Ion Irradiation



	f^0	f^1	f^2	f^3
	La 3+	Ce 3+ 4+	Pr 3+ 4+	Nd 3+
	Ac 3+	Th 4+	Pa 4+ 5+	U 4+ 5+ 6+

X-ray diffraction (XRD)



XRD patterns after irradiation:

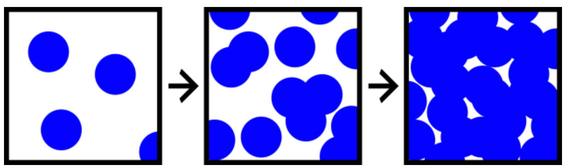
⇨ peak-intensity reduction
defects

⇨ peak shift
unit-cell expansion

⇨ peak broadening
strain, grain-size reduction

Single-impact behavior:

⇨ linear region followed by saturation due to track-overlap.



C.L. Tracy, *et al.*, Nature Communications **6** (2015).

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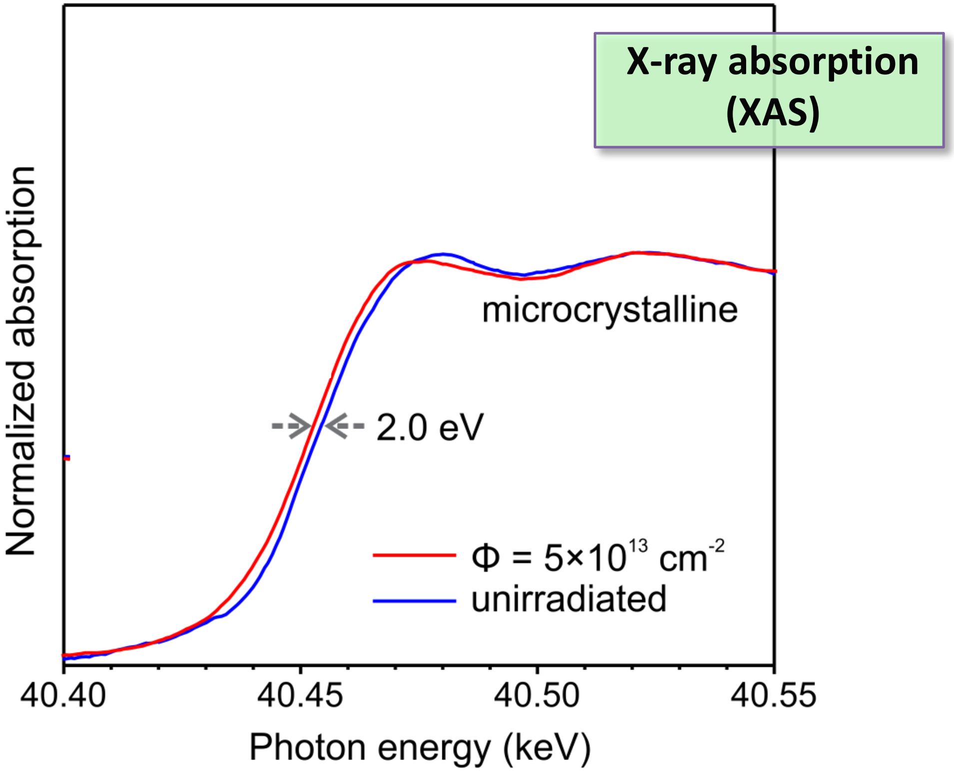
Redox Response of Actinide Oxides to Ion Irradiation



f^0	f^1	f^2	f^3
La 3+	**Ce** 3+ 4+	**Pr** 3+ 4+	**Nd** 3+
Ac 3+	**Th** 4+	**Pa** 4+ 5+	**U** 4+ 5+ 6+

Ce K-edge shift:

⇨ decreased core electron binding energy

⇨ increased electron screening

⇨ partial reduction from Ce^{4+} to Ce^{3+}

Structural modifications:

⇨ Ce^{3+} is ~20% larger than Ce^{4+} (unit-cell expansion)

⇨ cation-size mismatch (microstrain)

⇨ Cation valence reduction in CeO_2 leads to a fundamentally different radiation response as compared to ThO_2 (no reduction).

C.L. Tracy, *et al.*, Nature Communications **6** (2015).

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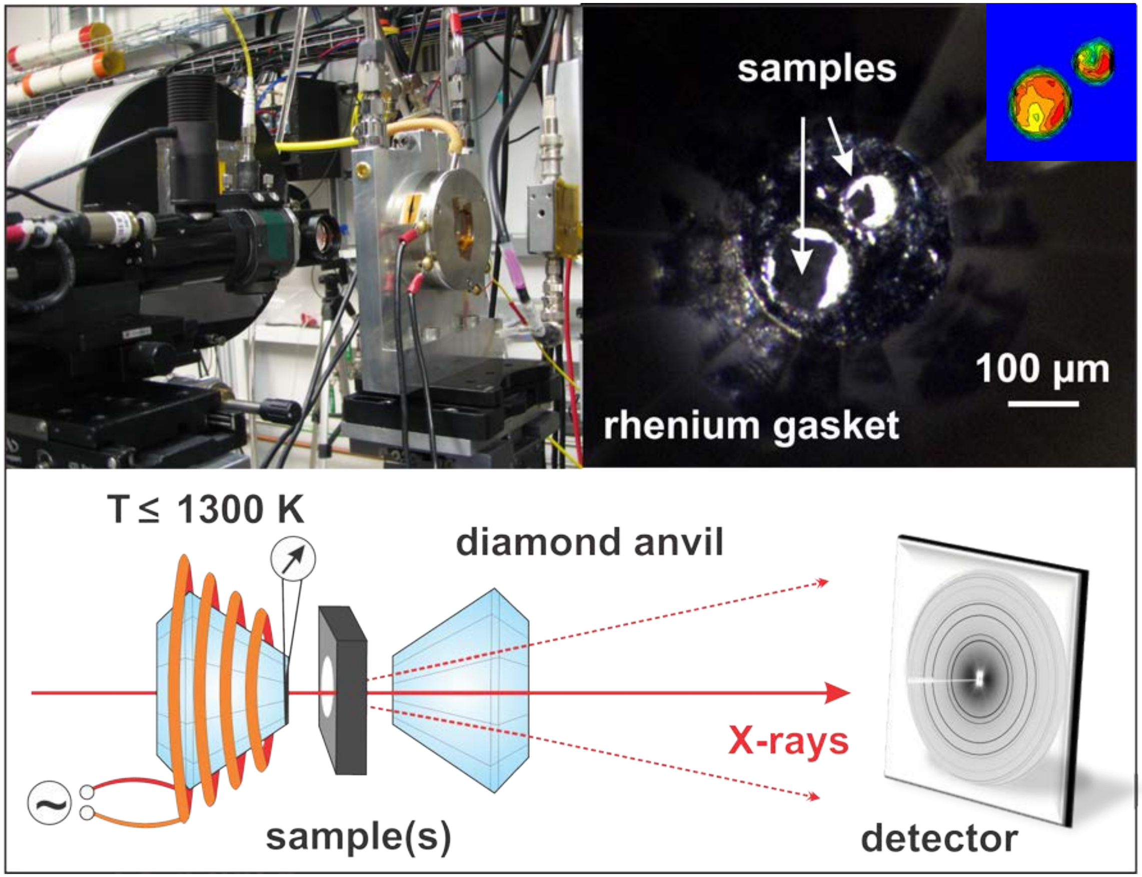
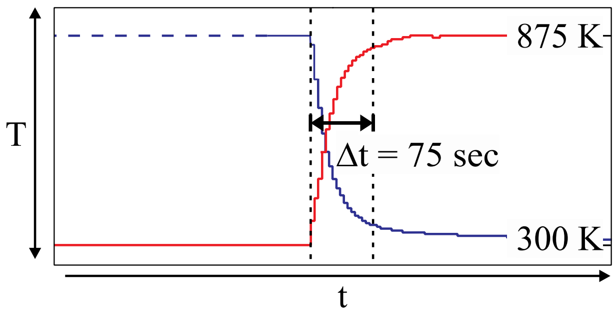
Defect-Annealing Studies at High Temperature

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

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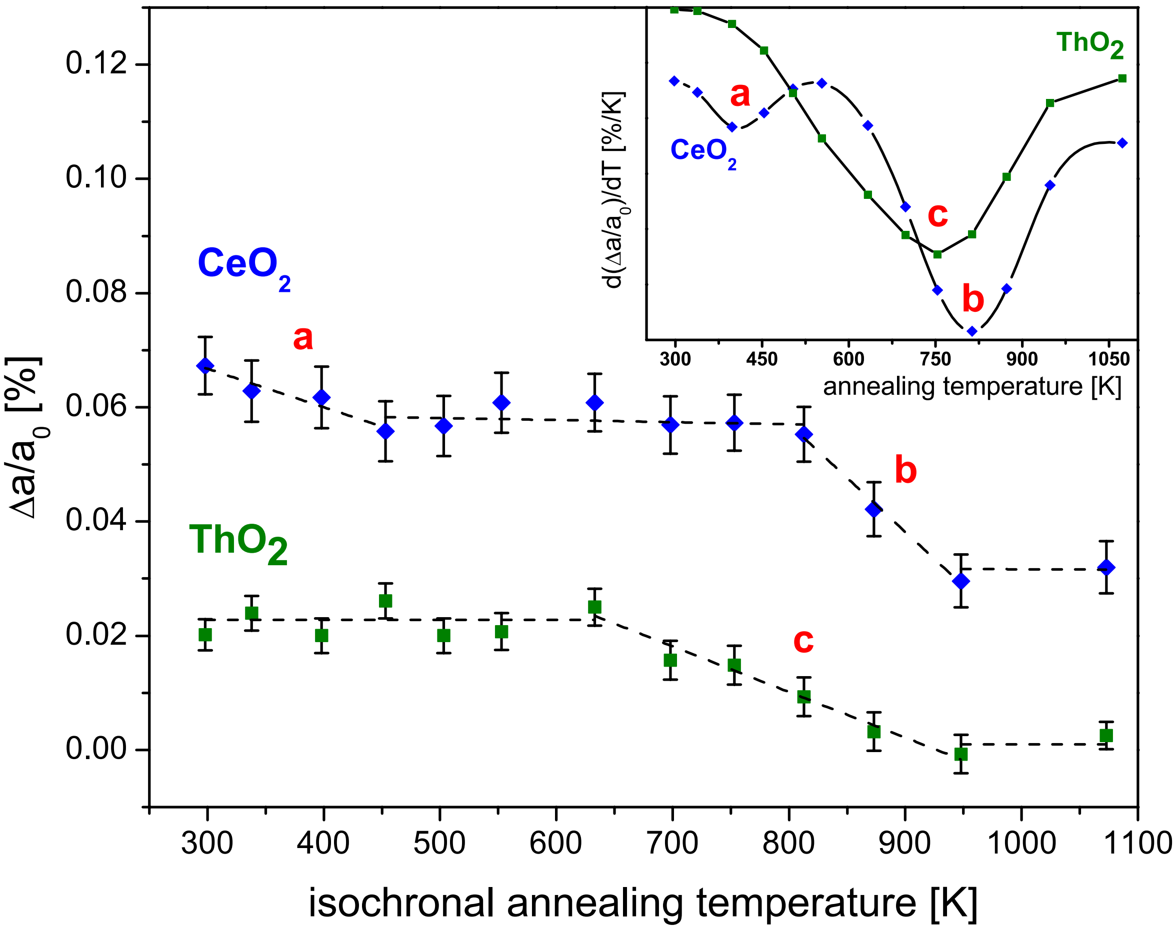
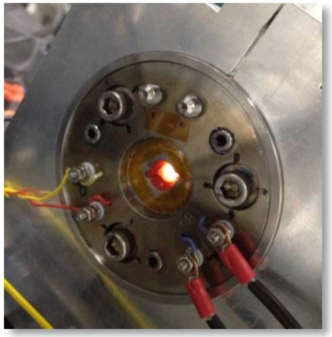
Defect-Annealing Studies at High Temperature

ThO_2 and **CeO_2** irradiated with **950 MeV ^{197}Au** annealed within an HDAC to **1070 K**



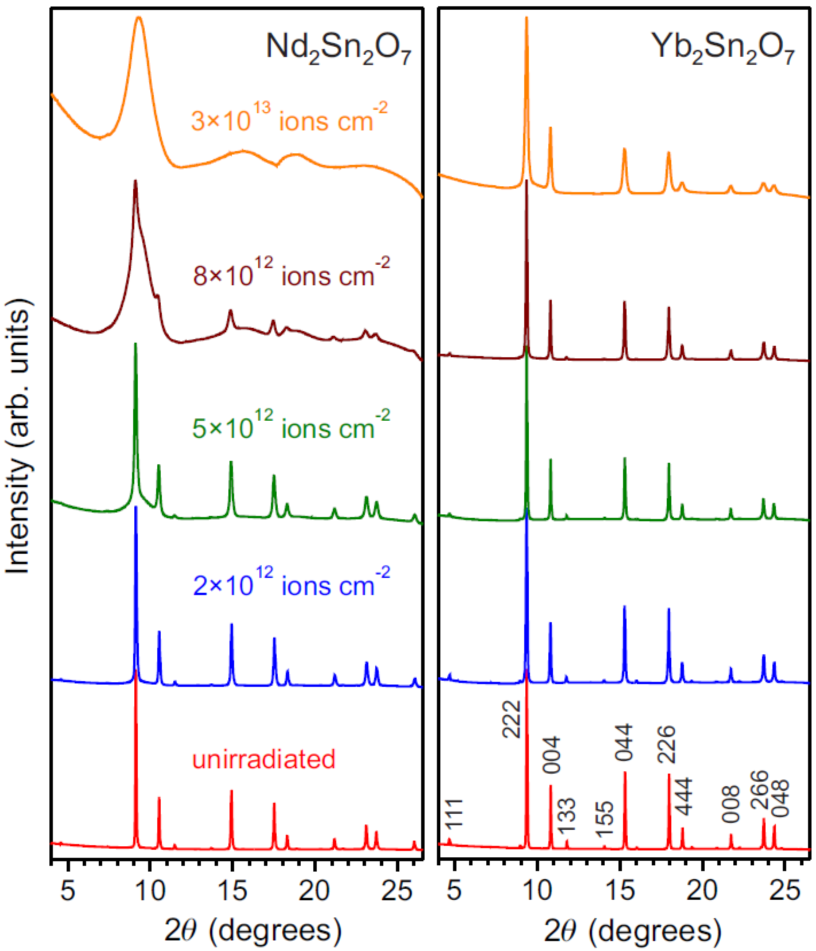


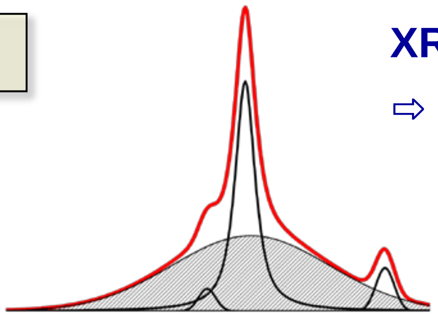
- ⇨ Defect annealing at high-*T*
- ⇨ Reduction of unit-cell parameter and microstrain
- ⇨ One-step process for ThO_2 two-step process for CeO_2 <u>(consistent with different defects)</u>
- ⇨ No full recovery up to 1070 K

R.I. Palomares, *et al.*, <u>*Journal of Applied Crystallography*</u> (2015).

Synchrotron XRD: Amorphization and Disordering

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

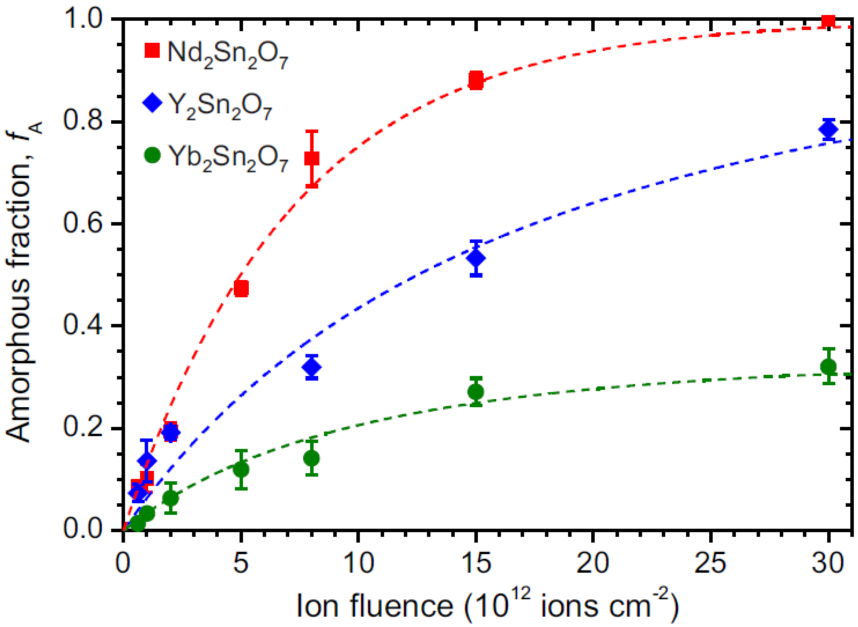




XRD peak deconvolution

⇨ amorphous fraction

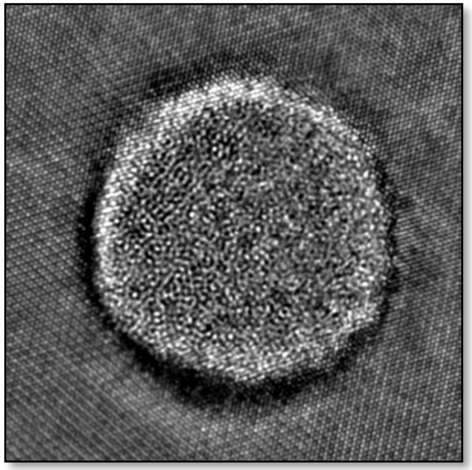
$$f_A(\Phi) = \frac{1 - e^{-\sigma_A \Phi + \sigma_D \Phi}}{1 - \left(\frac{\sigma_D}{\sigma_A}\right) e^{-\sigma_A \Phi + \sigma_D \Phi}}$$



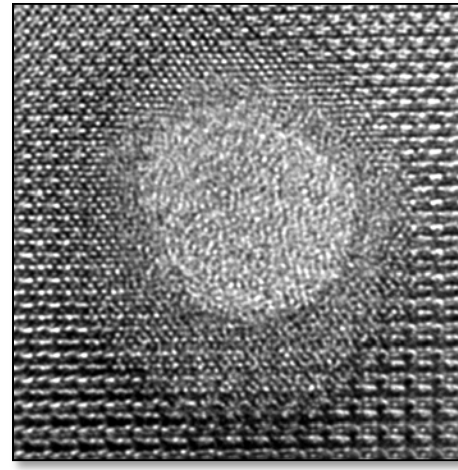
C.L. Tracy, *et al.*, PRB (2016) M. Lang, *et al.*, PRB (2009)

Transmission Electron Microscopy: Track Morphology

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



changing
composition



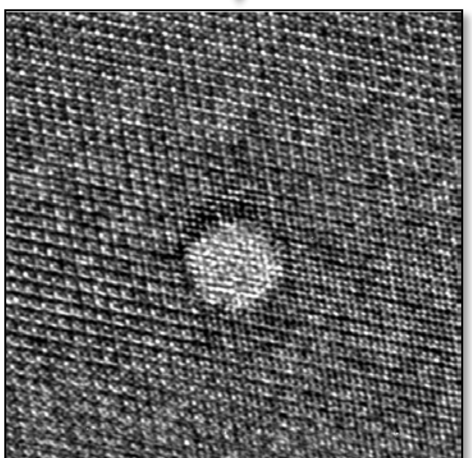
$Gd_2Ti_1O_5$
2.2-GeV ^{197}Au
40 keV/nm; RT

decreasing
energy density

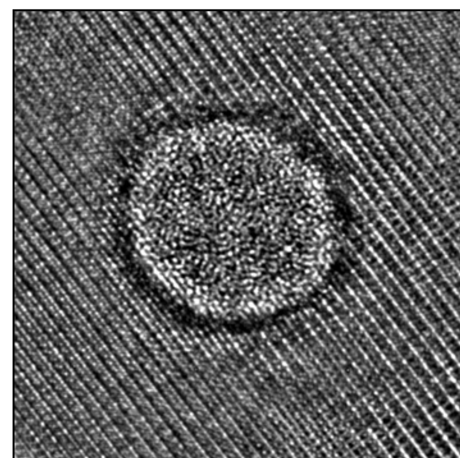
decreasing
temperature

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



5 nm



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

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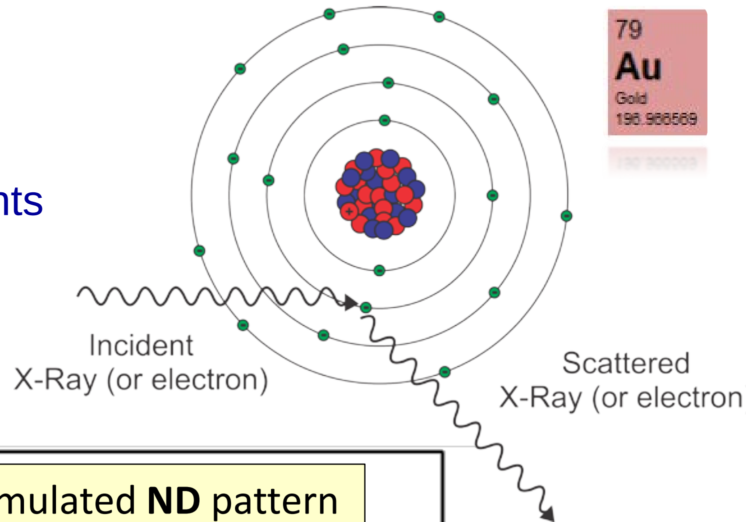
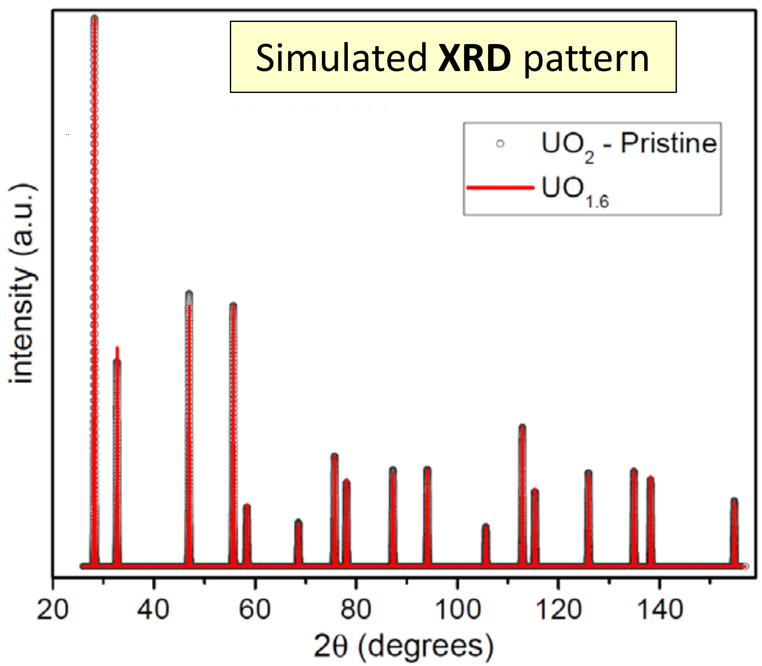
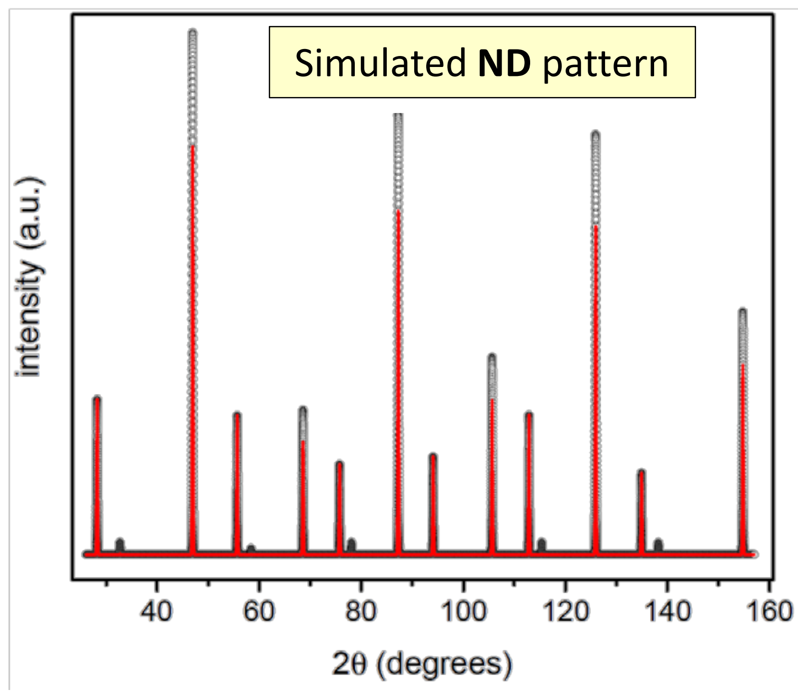
Limitation of Electron and X-ray Probes

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



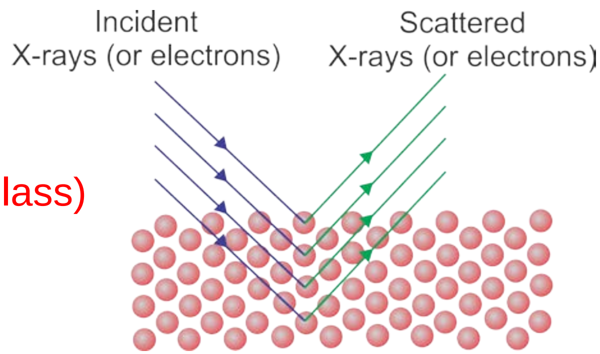


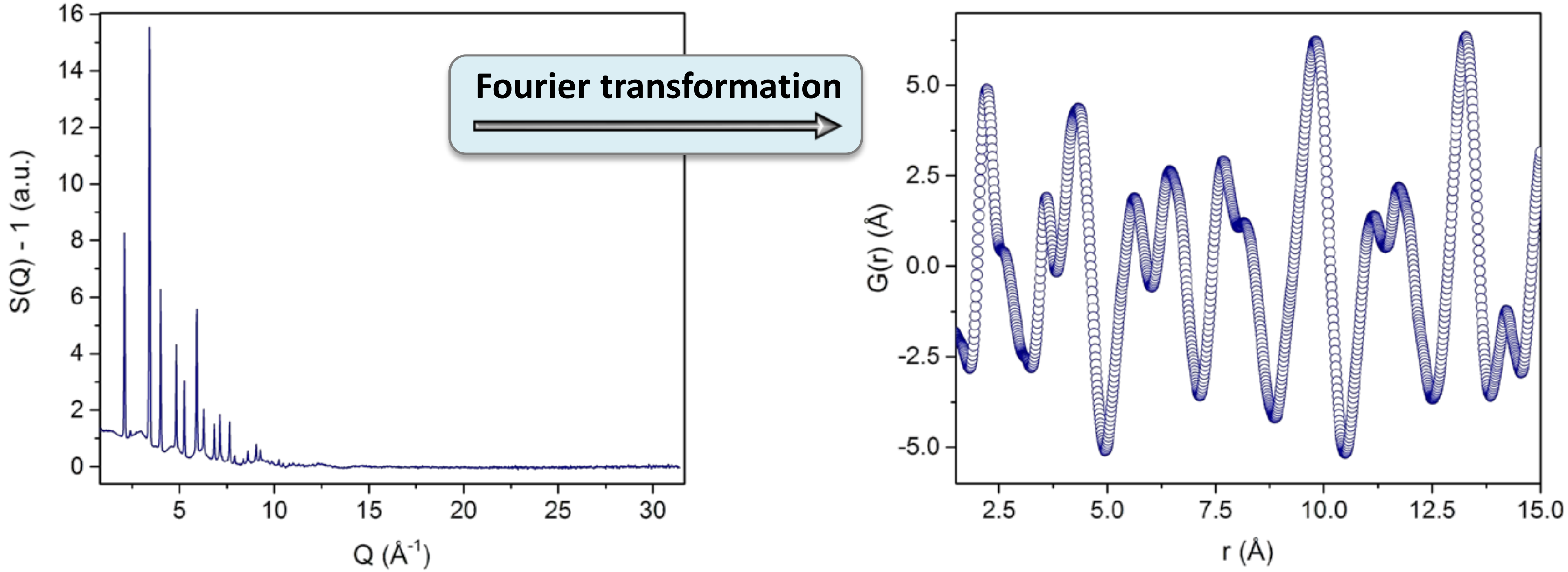


Limitation of Diffraction Experiments

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





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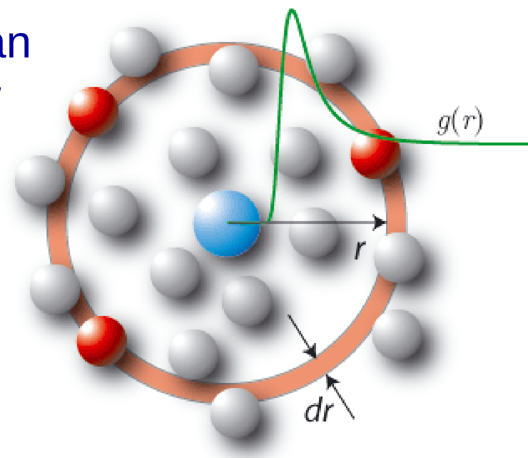
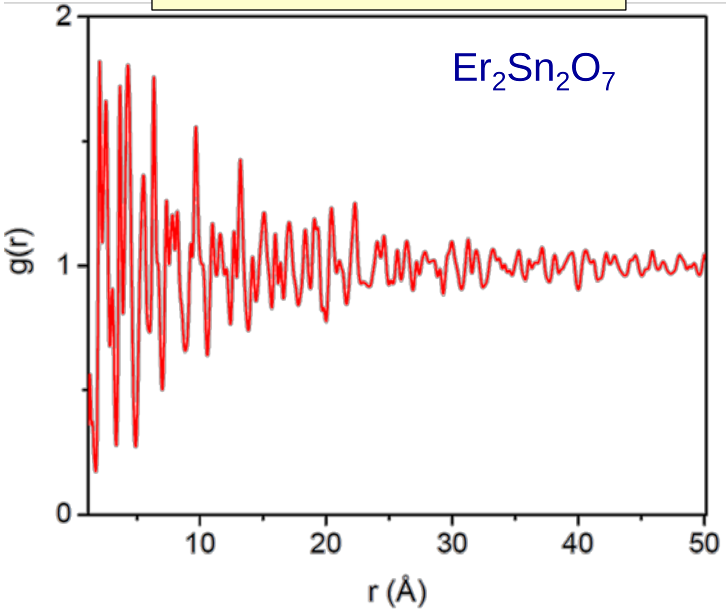
Pair Distribution Function (PDF) Analysis

- ⇨ *g*(*r*) is the probability of finding an atom pair at certain separation *r*
- ⇨ probability is high at low-*r* (intense peaks)
- ⇨ probability approaches unity at high-*r* due to atomic motion

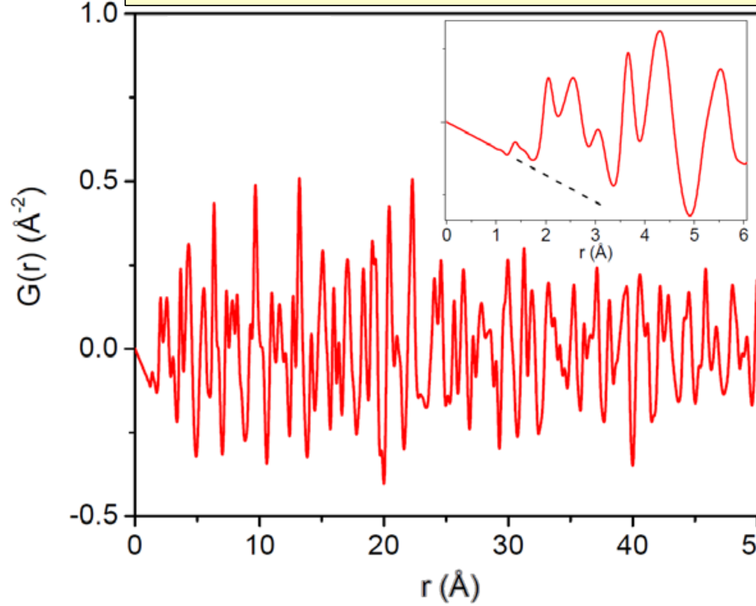


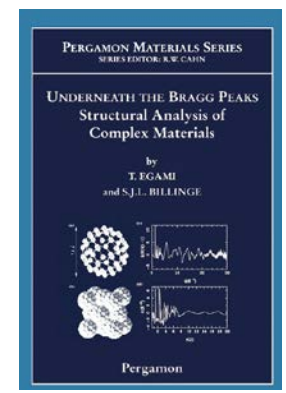
$$g(r) - 1 = \frac{G(r)}{4\pi r \rho_0} = \frac{\rho(r)}{\rho_0}$$

Pair distribution function



Reduced pair distribution function





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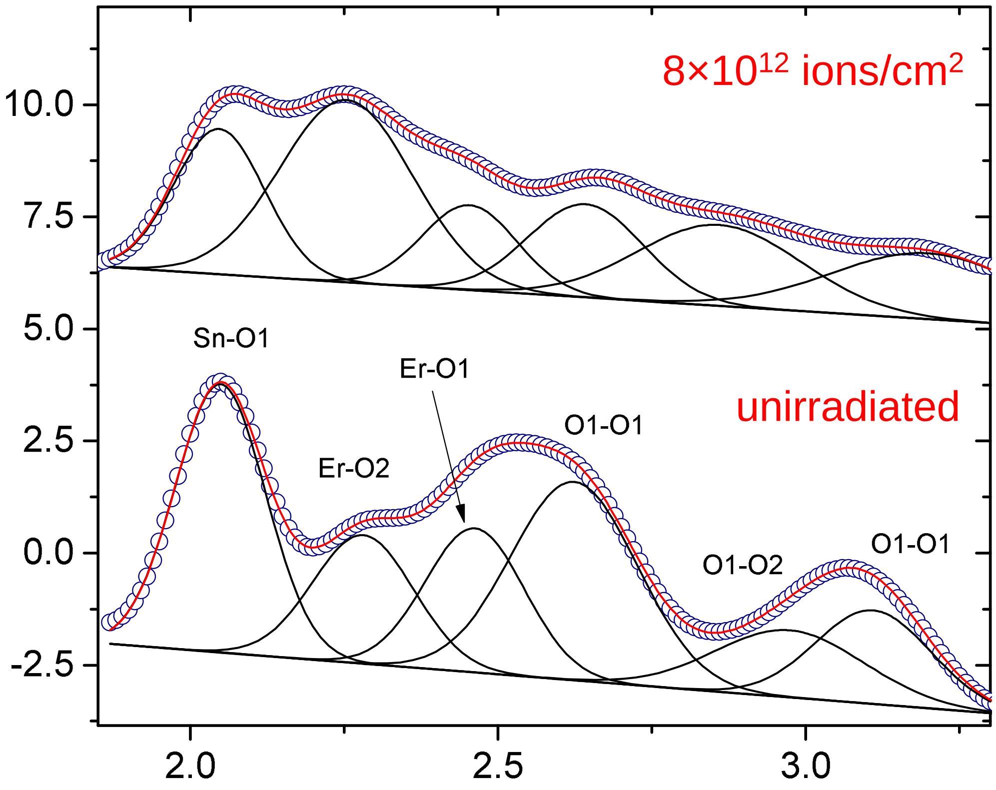
PDF Analysis of Radiation Effects in Materials

$Er_2Sn_2O_7$ irradiated with **2.2 GeV ^{197}Au ions**



Real-Space Refinement of PDFs:

⇨ peak position: bond lengths

⇨ peak area: coordination number

⇨ peak width: thermal motion/disorder

Neutron PDF Analysis:

⇨ sensitive to oxygen and other low-Z elements

⇨ detailed analysis of local defect structure

⇨ study of heterogeneous disorder that differs over lengthscales

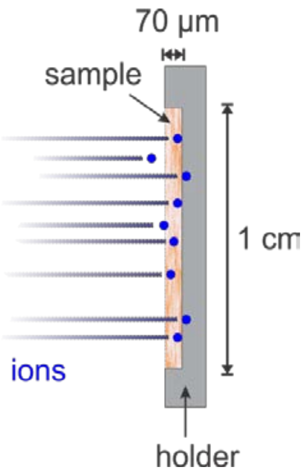
⇨ access to local order in non-crystalline materials (glasses)

Neutron Total Scattering Experiments at ORNL

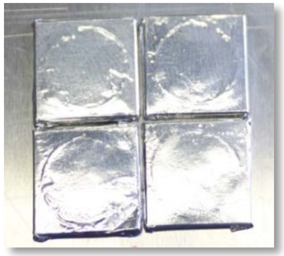
The Nanoscale-Ordered Materials Diffractometer (NOMAD)

- ⇨ 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: 150 mg**
- ⇨ post-calorimetry measurements

NOMAD detector



irradiation-sample holder

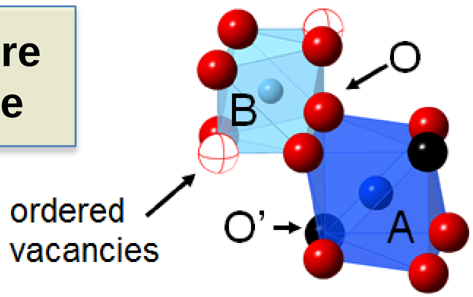


neutron-sample holder

⇨ high-energy ions (~1 GeV) essential for this approach

Order – Disorder Transformation in Pyrochlore Oxides

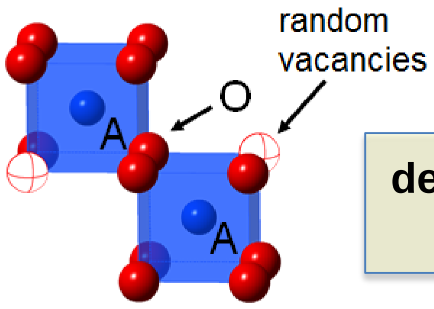
pyrochlore structure



$A_2B_2O_6O'$

disordering

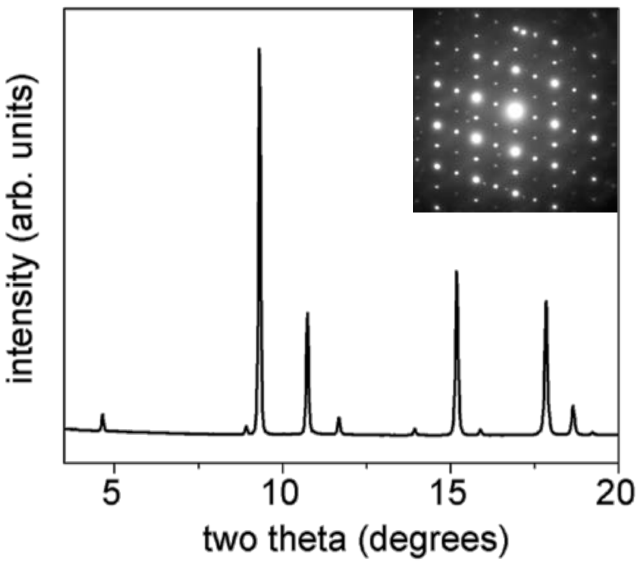
- irradiation
- temperature
- pressure
- composition



A_4O_7

defect-fluorite structure

$Ho_2Ti_2O_7$ – ordered

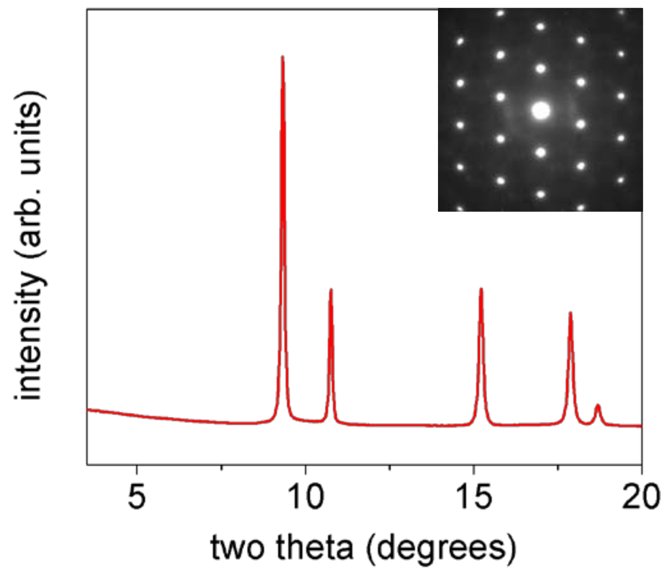


X-ray and electron diffraction:

▻ long-range structure

▻ cation sublattice

$Ho_2Zr_2O_7$ – disordered



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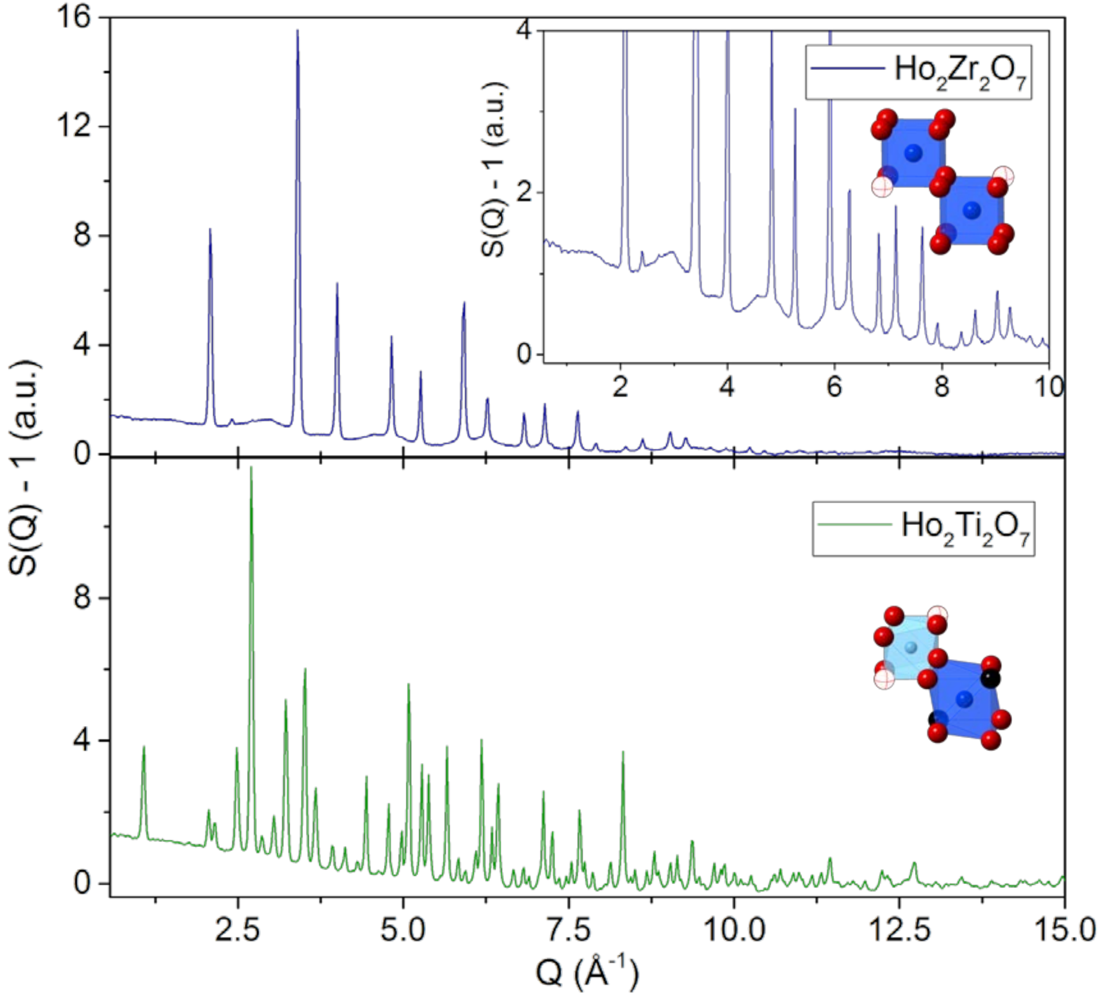
Order – Disorder Characterized by Neutron Scattering



$A_2Zr_2O_7$

terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70
Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**
158.93	162.50	164.93	167.26	168.93	173.04

disordered fluorite

Disorder *via* neutron diffraction:

- ⇨ lack of superstructure peaks
- ⇨ diffuse peaks emerge
- ⇨ analysis in real space required

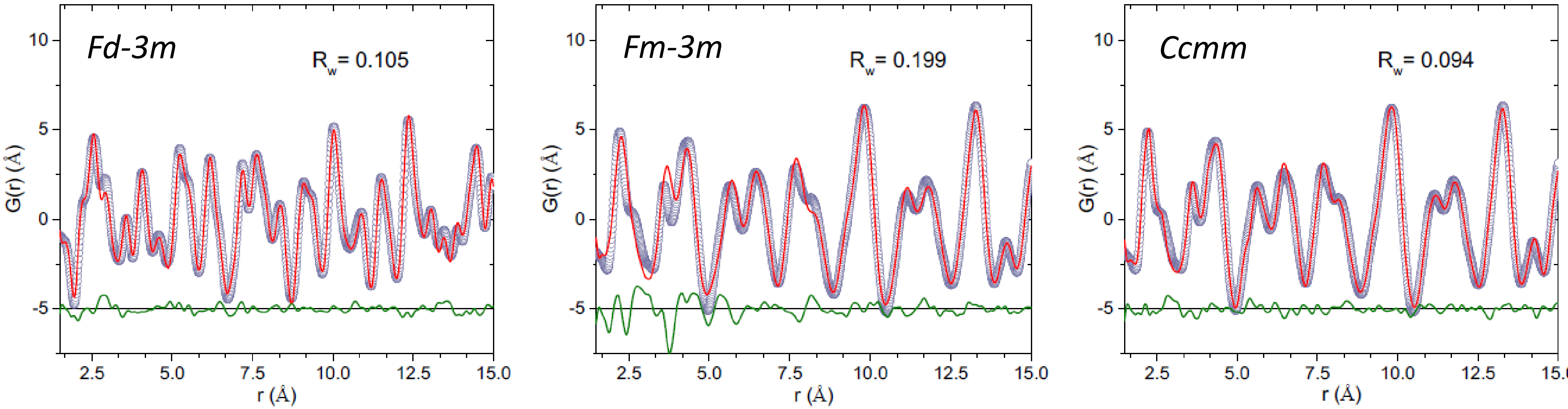
$A_2Ti_2O_7$

samarium 62	europium 63	gadolinium 64	terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70
Sm	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**
150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04

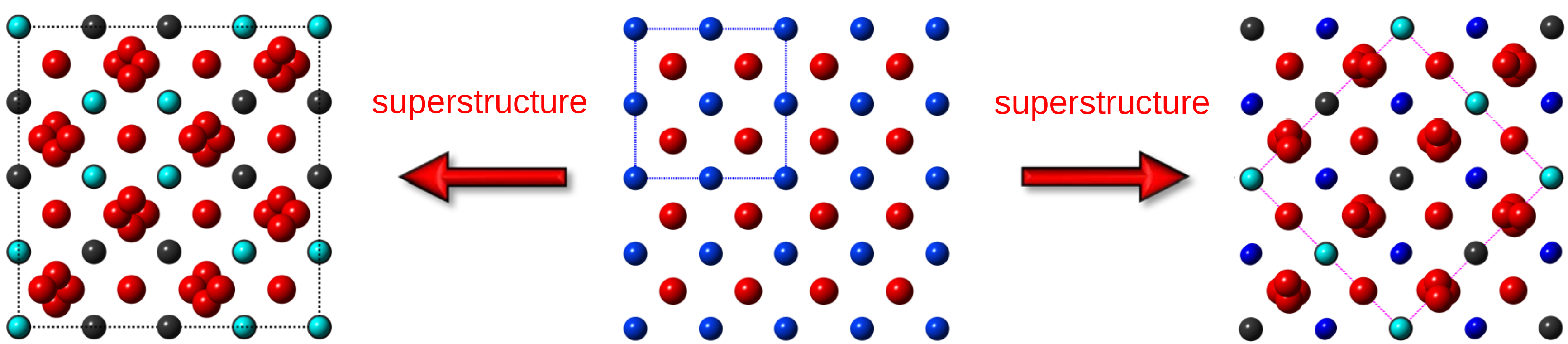
ordered pyrochlore

Order – Disorder Transformation in Pyrochlore Oxides

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



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



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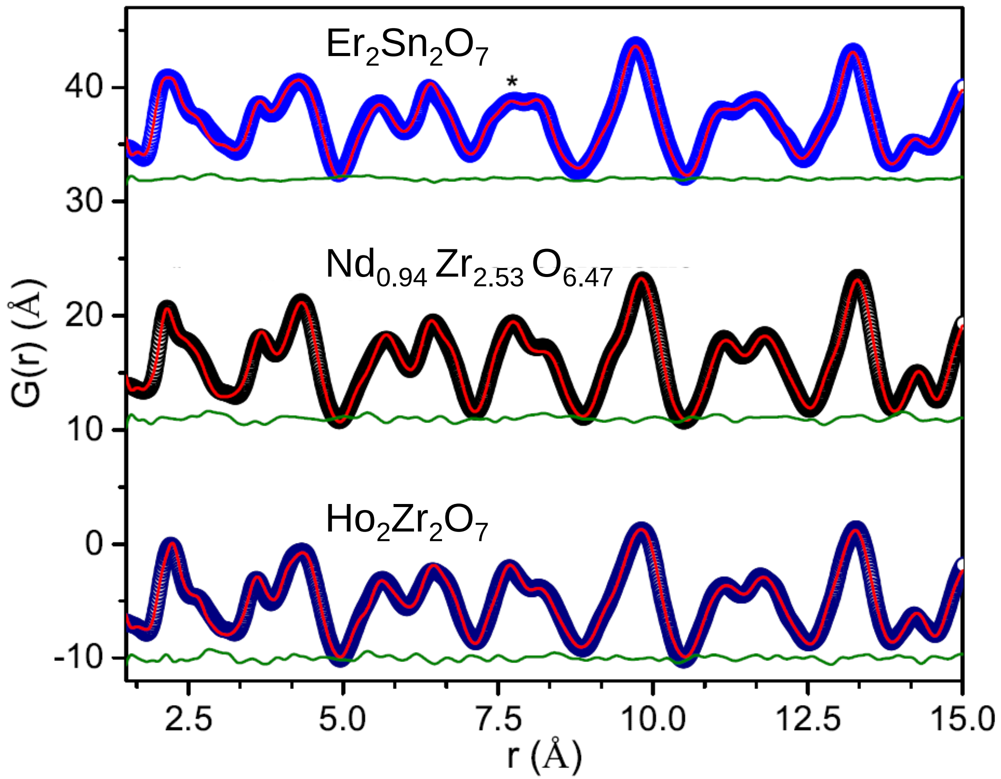
Order – Disorder Transformation in Pyrochlore Oxides

Real-space refinement of neutron PDF data:



Ion irradiation

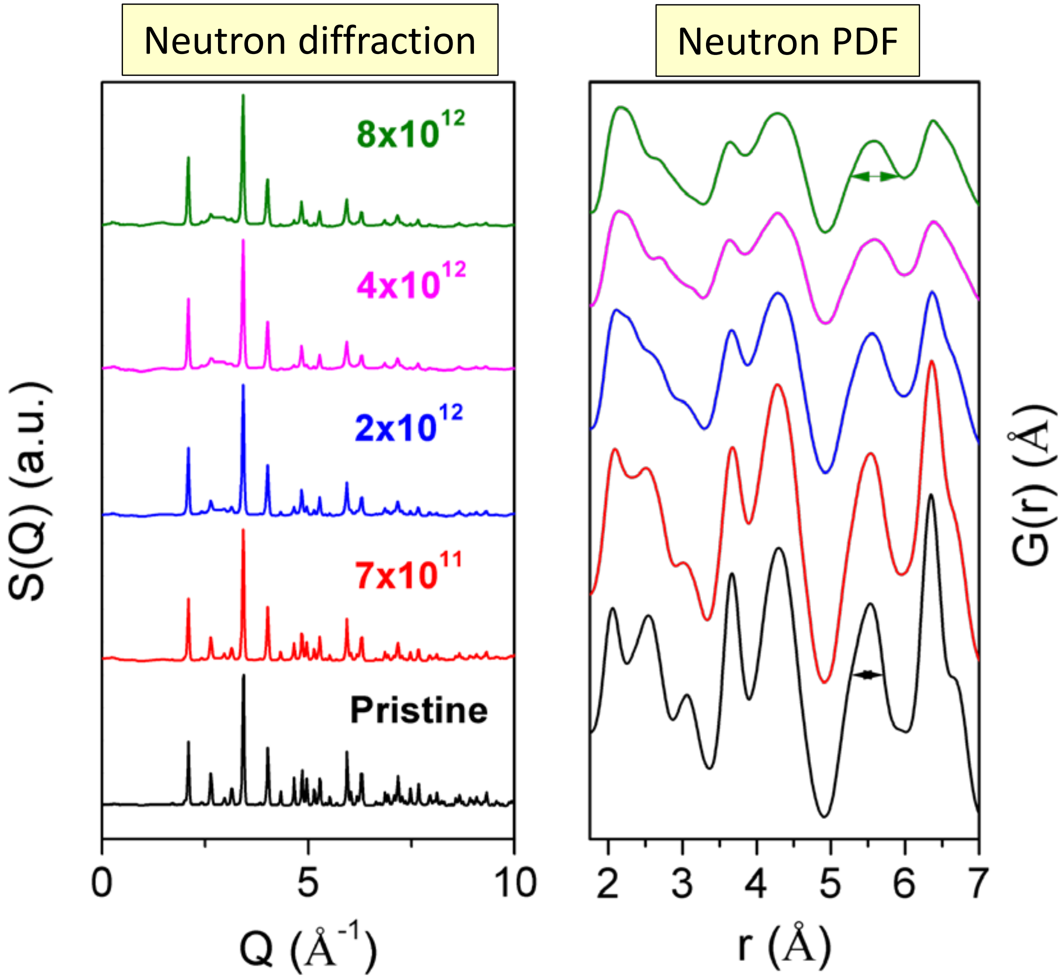
Non-stoichiometry

Chemical composition

⇨ local weberite and long-range defect fluorite in all cases

⇨ intrinsic and extrinsic disorder has same structural behavior

Damage Evolution in Irradiated Pyrochlore Oxides



$Er_2Sn_2O_7$ irradiated with **2.2 GeV ^{197}Au ions as function of fluence**

Average Structure (diffraction)

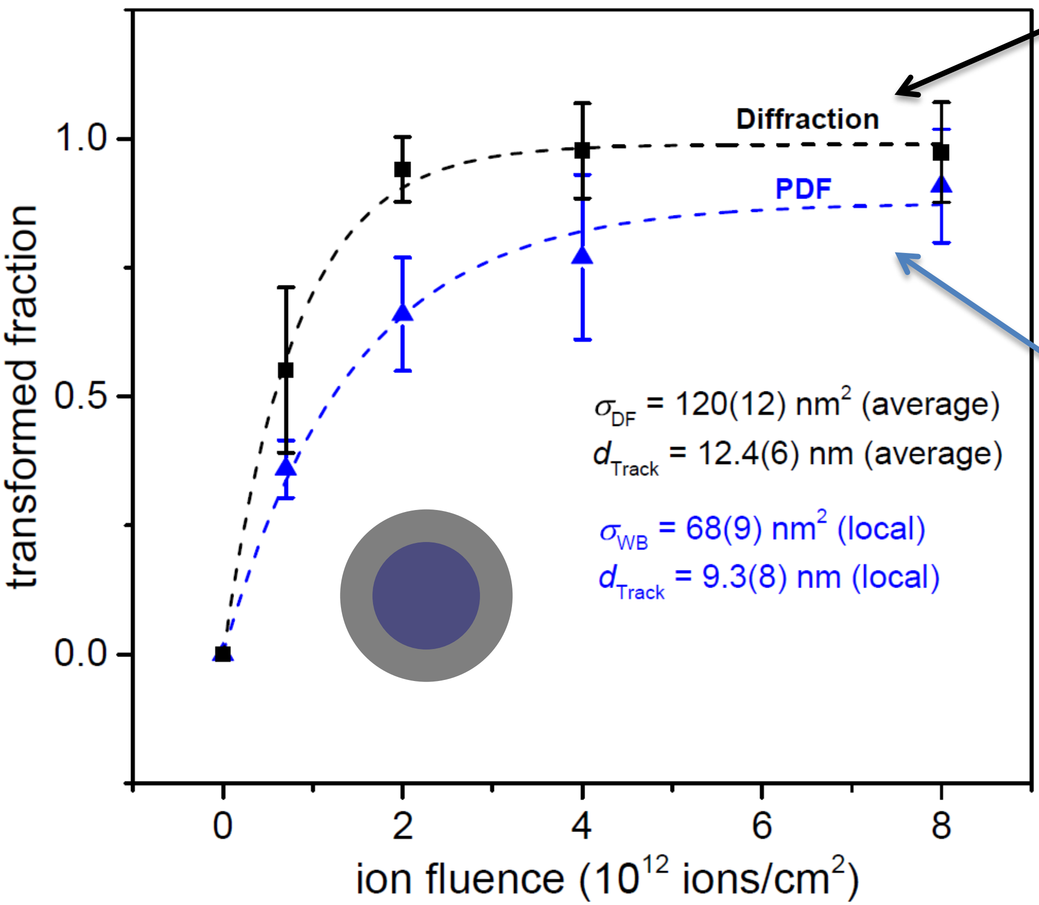
- ⇨ superstructure peaks disappear
- ⇨ no amorphization
- ⇨ pyrochlore-fluorite transformation (order-disorder)

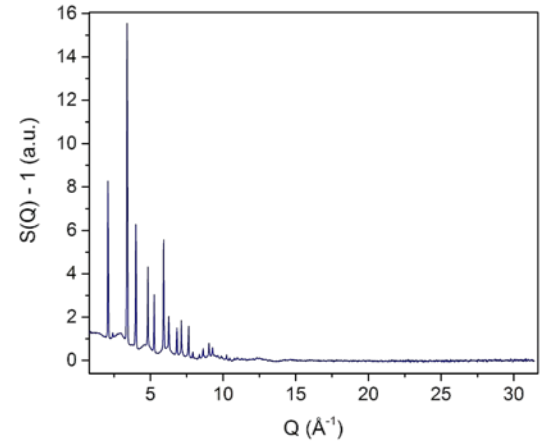
Local Structure (PDF)

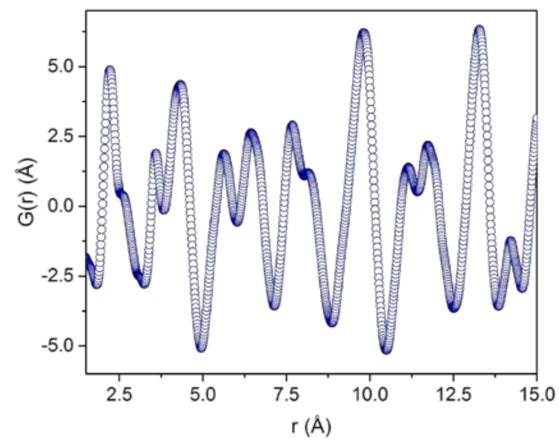
- ⇨ peak broadening
- ⇨ no loss of peak area at higher *r*
- ⇨ pyrochlore-weberite transformation

Damage Cross Sections in Irradiated Pyrochlore Oxides

$Er_2Sn_2O_7$ irradiated with **2.2 GeV ^{197}Au ions**

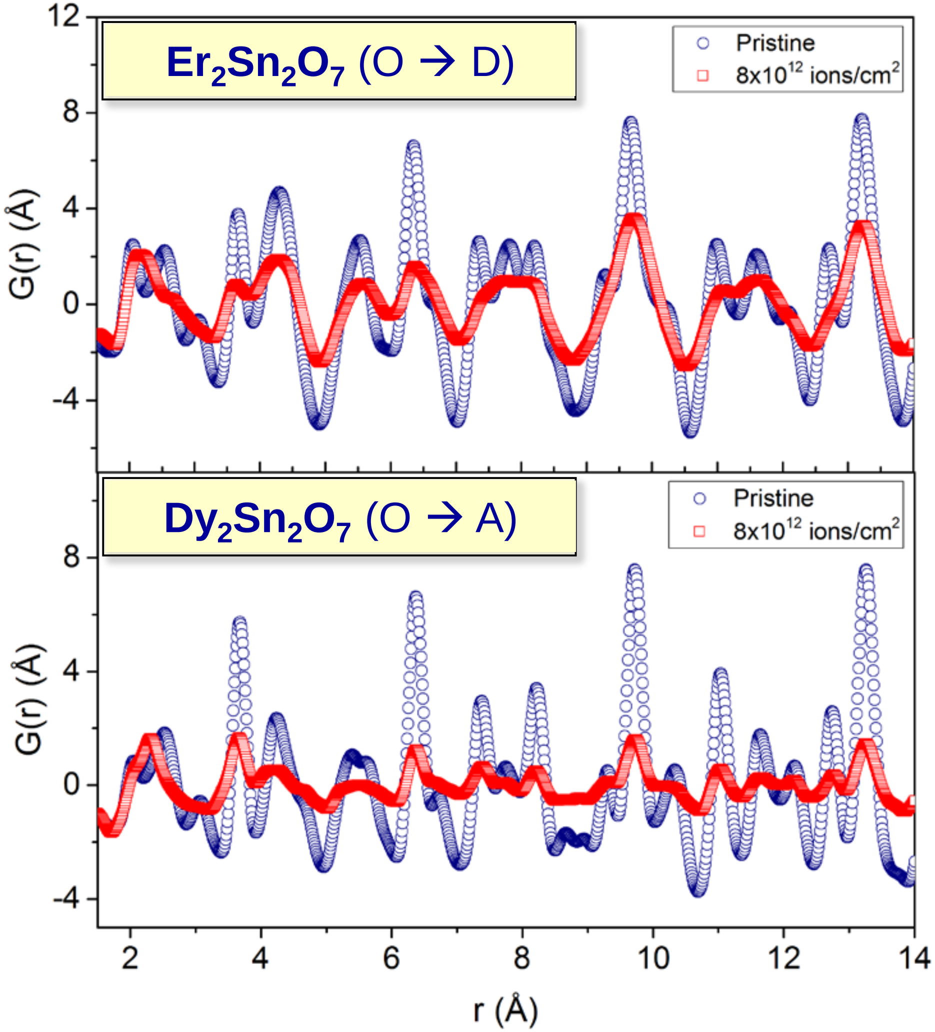






⇨ Defect behavior differs over range of length scales

Neutron PDF: Disordering *versus* Amorphization



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)

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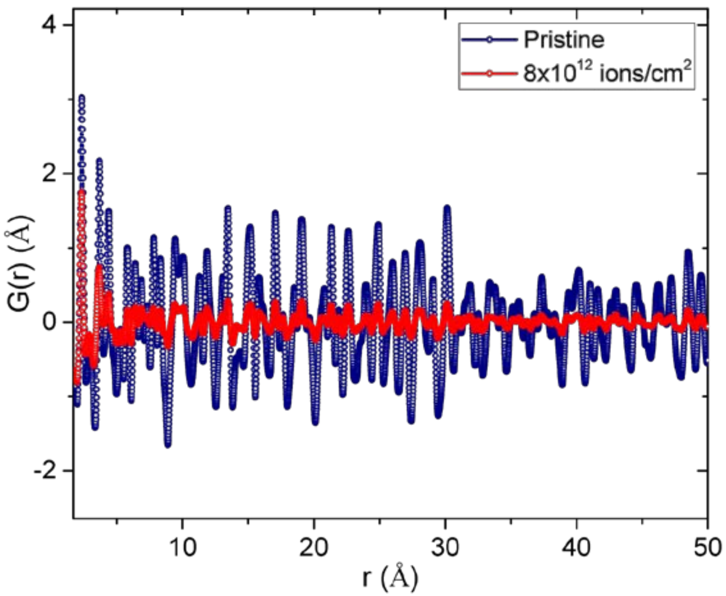
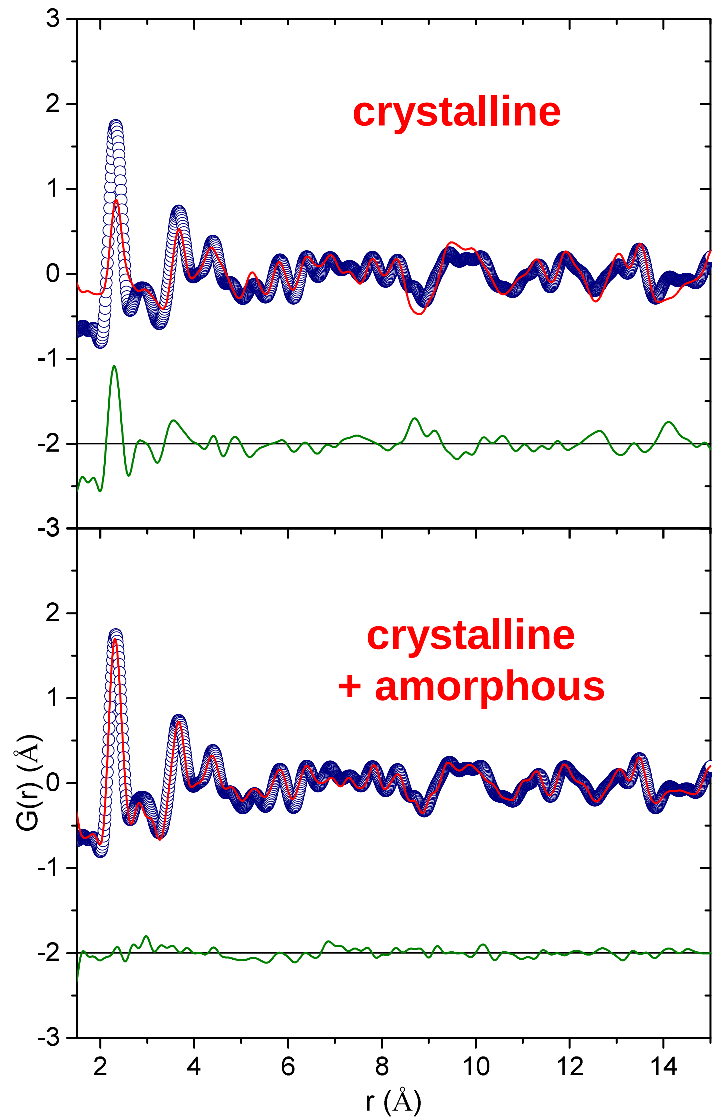
Radiation – Induced Amorphization in Complex Oxides

Dy_2TiO_5 irradiated with **2.2 GeV ^{197}Au ions**





Crystallinity → consistent short and long-range order

Amorphous → lack of long-range order

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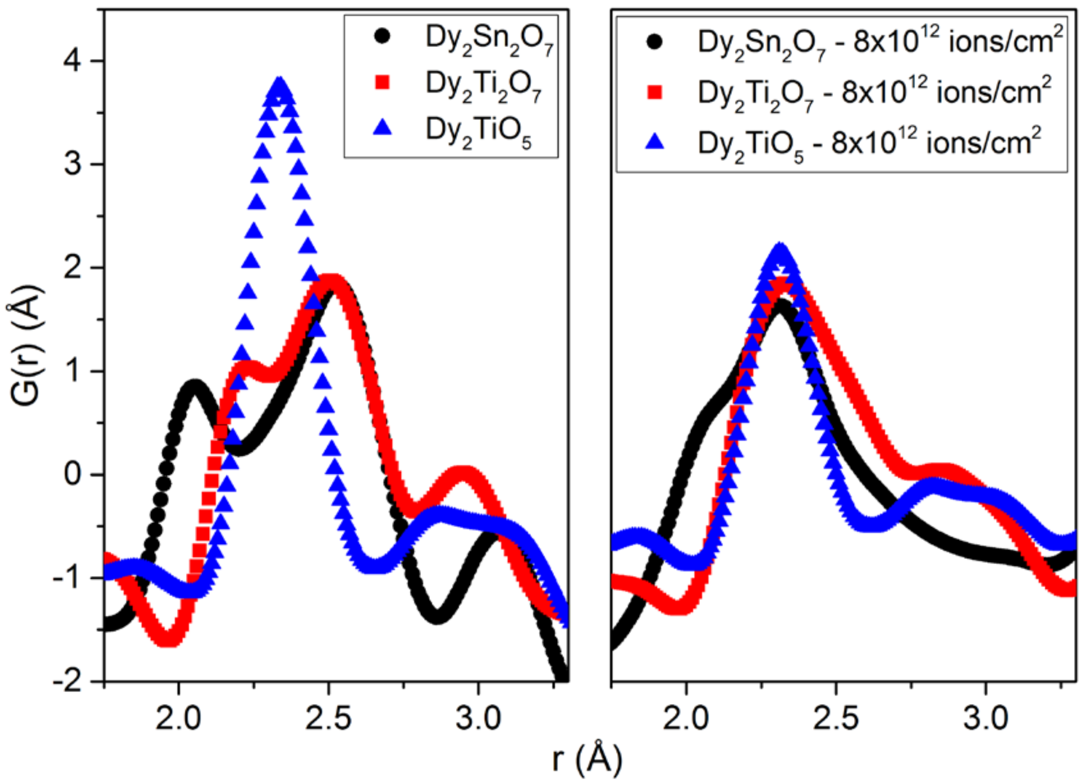
Radiation – Induced Amorphization in Complex Oxides

Complex oxides irradiated with **2.2 GeV ^{197}Au ions**



Ion-induced amorphization in different complex oxides:

- **$Dy_2Sn_2O_7$** isometric pyrochlore (more covalent bond character)
- **$Dy_2Ti_2O_7$** isometric pyrochlore (more ionic bond character)
- **Dy_2TiO_5** orthorhombic

⇨ Different complex oxides form very similar amorphous phase

Radiation Effects in (Waste) Glass

PRL **101,** 175503 (2008) PHYSICAL REVIEW LETTERS week ending 24 OCTOBER 2008

Fine Structure in Swift Heavy Ion Tracks in Amorphous SiO_2

P. Kluth,[1,*] C. S. Schnohr,[1] O. H. Pakarinen,[2] F. Djurabekova,[2] D. J. Sprouster,[1] R. Giulian,[1] M. C. Ridgway,[1] A. P. Byrne,[3] C. Trautmann,[4] D. J. Cookson,[5] K. Nordlund,[2] and M. Toulemonde[6]

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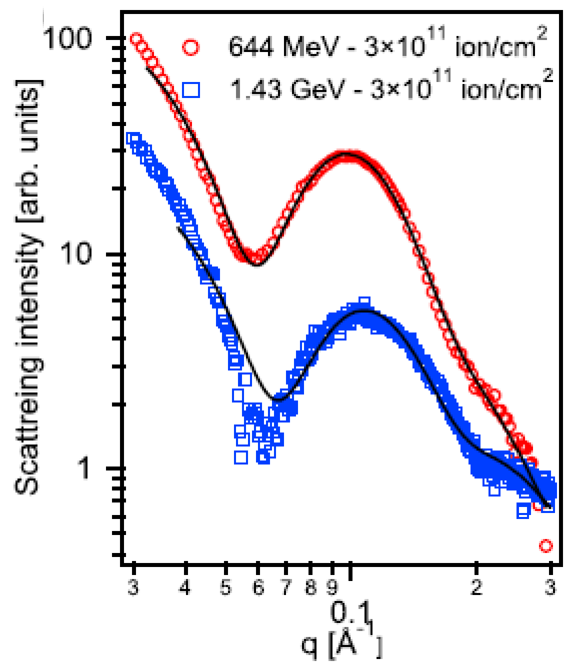
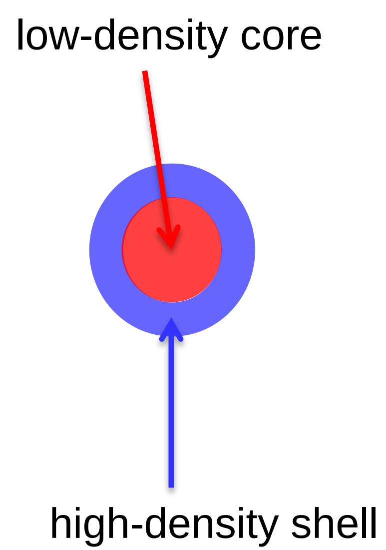
[6]*Centre interdisciplinaire de recherche sur les Ions, les MAtériaux et la Photonique (CIMAP), Caen, France*

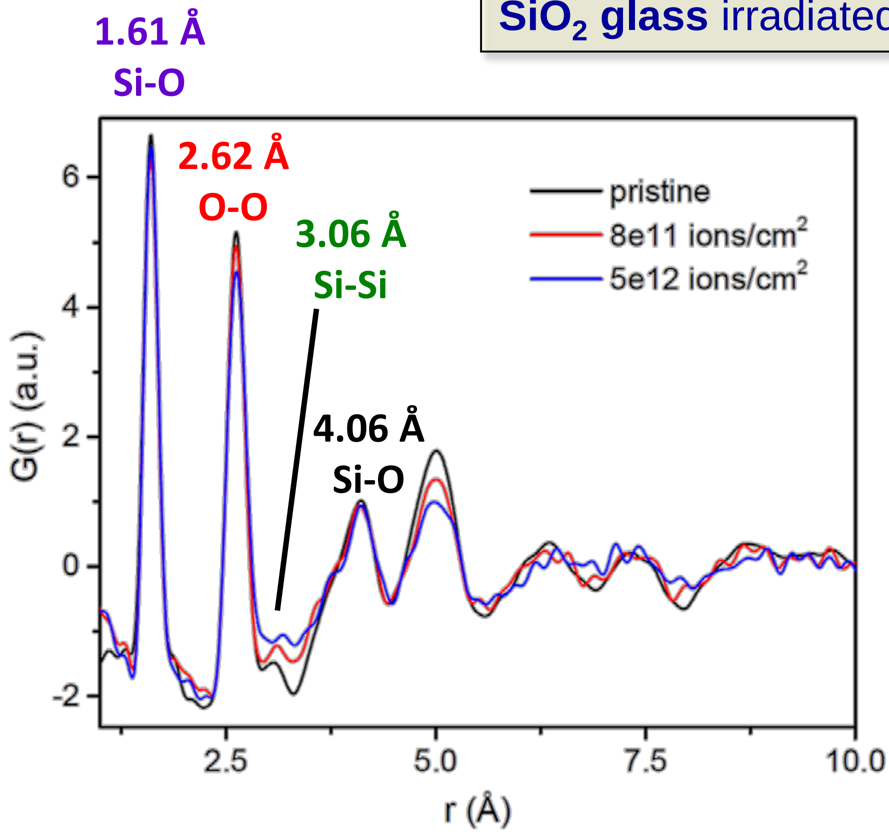
Small Angle X-ray Scattering (SAXS)

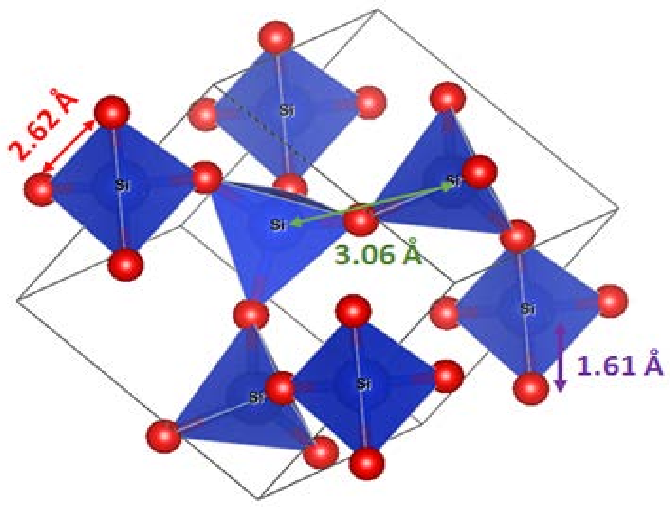




Radiation Effects in (Waste) Glass

SiO_2 glass irradiated with **2.2 GeV ^{197}Au ions**





local SiO_4-tetrahedra environment

⇨ **Neutron PDF-analysis:** SiO_4-tetrahedra remain intact but change their stacking/arrangement

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Conclusions

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

- Neutron PDFs provides insight into formation of local defect structure in irradiated crystalline and amorphous materials

- Disordering in pyrochlore is complex involving two distinct processes that occur over different length scales:
  - local transformation to weberite-type structure
  - aperiodic modulation of these local units to form average defect-fluorite structure

- Synchrotron XRD and XAS with intense X-ray beam can be used to measure radiation-induced structural and electronic modifications

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Research Team and Acknowledgement

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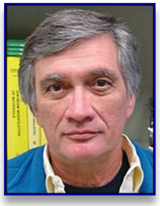
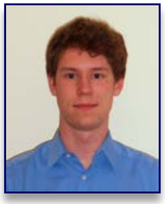


Rodney Ewing



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Thank you!