Radiation Damage in Crystalline Wasteforms

Maik Lang
University of Tennessee
Department of Nuclear Engineering
Knoxville, TN, USA
mlang2@utk.edu
Durable Materials for Radionuclide Immobilization

Performance in extreme environments:
- intense radiation
- elevated temperature
- changing chemical composition
- long-term disposal in changing environment

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

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

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

Ion track in $\text{Gd}_2\text{Zr}_2\text{O}_7$ (12-MeV $\text{C}_{60}$)
## Crystalline Wasteforms for Radionuclide Immobilization

**simple oxides:**
- zirconia: $\text{ZrO}_2$

**complex oxides:**
- pyrochlore: $(\text{Na},\text{Ca},\text{U})_2(\text{Nb},\text{Ti},\text{Ta})_2\text{O}_6$
- murataite: $(\text{Na},\text{Y})_4(\text{Zn},\text{Fe})_3(\text{Ti},\text{Nb})_6\text{O}_{18}(\text{F},\text{OH})_4$
- zirconolite: $\text{CaZrTi}_2\text{O}_7$
- perovskite: $\text{CaTiO}_3$

**silicates:**
- zircon*: $\text{ZrSiO}_4$
- thorite*: $\text{ThSiO}_4$
- garnet*: $(\text{Ca},\text{Mg},\text{Fe}^{2+})_3(\text{Al},\text{Fe}^{3+},\text{Cr}^{3+})_2(\text{SiO}_4)$
- britholite
- titanite: $\text{CaTiSiO}_5$

**phosphates:**
- monazite*: $\text{LnPO}_4$
- apatite*: $\text{Ca}_{4-x}\text{Ln}_{6+x}(\text{PO}_4)_y(\text{O},\text{F})_2$
- xenotime*: $\text{YPO}_4$

* durable heavy minerals
Pyrochlores: Important Group of Materials

Applications

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

Structure

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

spin ice state

$\text{Ho}_2\text{Ti}_2\text{O}_7$
Disordering of Pyrochlore under Extreme Conditions

- pyrochlore structure

- ordered vacancies

- A₂B₂O₆O’

- disordering

- amorphization

- A₂B₂O₇

- rₐ/rₐ

- Gd₂Zr₂O₇

- > cation and anion disorder

- > retaining crystallinity

- ➤ loss of crystallinity

- Gd₂Ti₂O₇

- defect-fluorite structure
Radiation Effects in Actinide-Bearing Wasteforms

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)

Courtesy: Dr. William Weber (UT/ORNL)
Radiation Effects in Actinide-Bearing Wasteforms

- Recoil Nucleus
- Alpha Particle

- Nuclear energy loss \( (dE/dx)_n \)
- Electronic energy loss \( (dE/dx)_e \)

- \( \log \frac{dE}{dx} \)
- \( \log E \)

- \( \sim 1 \text{ keV/}u \)
- \( \sim 1 \text{ MeV/}u \)
Ion Irradiation & Computer Simulation provide way to bridge Time Gap (Dose Rate Effects) between Laboratory Studies and Geologic Time Scales

Simulation of Alpha-Recoil Damage in Waste Forms

**Alpha Decay**

- Energy release: ~5 MeV

**Material**

- Irradiated layer: 100 nm – 1 μm

**Ion-beam experiments: MeV energies**

- More realistic simulation of radiation effects (nuclear dE/dx)
- Small volume of modified material
- Many bulk characterization techniques are not applicable

**Tandem Accelerator (E < 25 MeV)**

Available in many laboratories
Low-Energy Irradiation Effects in Pyrochlore Oxides

**Actinide decay in complex oxides**

⇒ damage accumulation from self-irradiation


Gd$_2$Ti$_2$O$_7$

Gd$_2$Zr$_2$O$_7$

1-MeV Kr ions

amorphous

pyrochlore

defect fluorite
Critical Temperature of Amorphization in Pyrochlore

$Gd_2(Ti_{1-x}Zr_x)_2O_7$

Critical temperature $T_c$ (K) vs. amorphization fluence ($I_{ions/cm^2}$) and amorphization dose (dpa).

- $x=1$, crystalline
- $x=0.75$,~ 30% amorphous
- $x=0.5$
- $x=0.25$
- $x=0$

Maik Lang – University of Tennessee
Spontaneous Fission

energy release:
~200 MeV

Material

Irradiated layer:
10 μm – 100 μm

ion-beam experiments: GeV energies

⇒ different ion-matter interactions
   (electronic dE/dx)

⇒ large volume of modified material

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

Linear and ring accelerators (E ~ 1 GeV)
available at large user facilities
High-Energy Irradiation Effects in Pyrochlore Oxides

Actinide decay in complex oxides

⇒ damage accumulation from self-irradiation


30-MeV C\textsubscript{60} ions
Radiation Effects: Synchrotron X-Ray Characterization


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

\[ A_2Sn_2O_7 \text{ irradiated with } 2.2 \text{ GeV } ^{197}Au \]

XRD peak deconvolution
\[ f_A(\Phi) = \frac{1 - e^{-\sigma_A \Phi + \sigma_D \Phi}}{1 - (\frac{\sigma_D}{\sigma_A})e^{-\sigma_A \Phi + \sigma_D \Phi}} \]

C.L. Tracy, et al., *PRB* (2016)  
Transmission Electron Microscopy: Track Morphology


Gd$_2$Ti$_2$O$_7$

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

Gd$_2$Ti$_1$O$_5$

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

Gd$_2$Ti$_2$O$_7$

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

Gd$_2$Ti$_2$O$_7$

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

**Decreasing energy density**

**Changing composition**

**Decreasing temperature**

**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

Simulated XRD pattern

Simulated ND pattern
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

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

Total Scattering: long range

PDF: short range
Neutron Total Scattering Experiments at ORNL

Large Ion Accelerator Facility

- simulation of radiation effects

- maximization of irradiated sample mass
  - swift heavy ions (large range)

Spallation Neutron Source

- structural characterization

- minimization of required sample mass
  - intense neutron beam ($10^8 \text{ cm}^2 \cdot \text{sec}^{-1}$)

⇒ investigation of radiation effects by neutron total scattering
Neutron Total Scattering Experiments at ORNL

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

The Nanoscale-Ordered Materials Diffractometer (NOMAD)
Pair Distribution Function (PDF) Analysis

- more intuitive real-space representation
- pairwise interatomic distances

\[ \text{position} = \text{interatomic distance} \]
\[ \text{intensity} \propto \text{coordination number} \]
\[ \text{width} = \text{spread in interatomic distances} \]
Neutron Diffraction: Order – Disorder Transformations

\[ A_2Zr_2O_7 \]

- disordered fluorite

\[ A_2Ti_2O_7 \]

- ordered pyrochlore

- order-disorder transformation
  - antisite defects (cations)
  - randomization of oxygen vacancies

\[ \text{Ho}_2\text{Zr}_2\text{O}_7 \]

\[ \text{Ho}_2\text{Ti}_2\text{O}_7 \]
Neutron PDF: Order – Disorder Transformations

\[ \text{Ho}_2\text{Ti}_2\text{O}_7 \text{ (pyrochlore)} \]  \[ \text{Ho}_2\text{Zr}_2\text{O}_7 \text{ (fluorite)} \]  \[ \text{Ho}_2\text{Zr}_2\text{O}_7 \text{ (weberite)} \]

\( Fd-3m \)  \( Fm-3m \)  \( Ccmm \)

Complex Disordering Mechanism in Pyrochlore


- **Ion irradiation**
- **Non-stoichiometry**
- **Chemical composition**

\[ \Rightarrow \text{short-range weberite-like and long-range defect fluorite in all cases} \]

\[ \Rightarrow \text{intrinsic and extrinsic disorder has same structural behavior} \]
Neutron PDF: Disorder 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)
- same local structure after irradiation

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

Neutron Total Scattering: Amorphization in Pyrochlore

**Neutron diffraction**
(long-range structure)

**Neutron PDF**
(short-range structure)

Dy$_2$Ti$_2$O$_7$

2.2-GeV Au

1200°C

900°C

600°C

Irradiated

Pristine

\[ S(Q) - 1 \text{ (a.u.)} \]

\[ Q \text{ (Å}^{-1}) \]

\[ G(r) \text{ (Å}^2) \]

\[ r \text{ (Å)} \]

Dy-O

O-O

Dy-O

Ti-O

1200°C

temp. ions

pyrochlore
(ordered)

weberite-like
(local distortions)
Analyzing Radiation Effects by Dielectric Spectroscopy

Broadband Dielectric Spectroscopy

- conductivity from $\mu$Hz to MHz
- from room temperature up to 1400 °C
- under controlled atmosphere
- information on damage recovery and defect dynamics

Oxygen hopping in $\text{Dy}_2\text{Zr}_2\text{O}_7$

$$E_a = 1.35 \text{ eV}$$

1000/K
Two distinct damage recovery events

250 fold increase in ionic conductivity
Advanced Calorimetry: Amorphization in Pyrochlore

In collaboration with Alex Navrotsky (UC Davis)

Calorimetry: irradiated Dy$_2$Ti$_2$O$_7$

- sharp exothermic event (recrystallization)
- broad exothermic event (local re-ordering)


Neutron PDF: irradiated Dy$_2$Ti$_2$O$_7$

- weberite
- weberite + pyrochlore
- pyrochlore

Maik Lang – University of Tennessee
Amorphization and Recrystallization in Pyrochlore

PDF + BDS
rearrangements within amorphous phase

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

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

T = 580 °C
T_{crit} = 800 °C
T = 1200 °C

Ion-beam irradiation

Amorphous

Thermal annealing

Recrystallized

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$_2$Ti$_2$O$_7$ 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**

<table>
<thead>
<tr>
<th></th>
<th>%wt oxide</th>
<th>%wt element</th>
<th>%mol oxide</th>
<th>%mol element</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>54.4</td>
<td>25.4</td>
<td>57.4</td>
<td>18.4</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>35.5</td>
<td>26.3</td>
<td>36.3</td>
<td>23.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>10.1</td>
<td>5.3</td>
<td>6.3</td>
<td>4.0</td>
</tr>
<tr>
<td>O</td>
<td>42.9</td>
<td></td>
<td>54.4</td>
<td></td>
</tr>
<tr>
<td><strong>total</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

- Irradiation causes changes in the local glass framework (now investigated by RMC)

- Local SiO$_4$-tetrahedra environment

In collaboration with Sylvain Peuget (CEA France)
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

Jacob Shamblin  Raul Palomares  Eric O’Quinn  Jessica Bishop  Will Cureton  Igor Gussev  Maik Lang

Stanford University

Rodney Ewing  Sulgi Park  Cameron Tracy

Collaborations:

Christina Trautmann  –  GSI Helmholtz Center (Germany)
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:
Irradiations at High Pressure

\[ E_{\text{kin}} \text{(in)} = 7 \text{ GeV} \]
\[ E_{\text{kin}} \text{(out)} = 6 \text{ GeV} \]
\[ \frac{v}{c} = 0.25 \rightarrow t \sim 1.5 \text{ ps} \]
\[ \Phi = 5 \text{ tracks/100 nm}^2 \]
\[ \rho_E \sim 10 \text{ eV/atom} \]
\[ \frac{dE}{dx} \sim 25 \text{ keV/nm} \]

Thanks!
Inversion in Spinel: Local Phase Transition

PDF

$Mg_{1-x}Ni_xAl_2O_4$

Inversion Parameter

$P4_{22}$ Phase Fraction

Nickel Content, $x$
Neutron PDF: Disorder in Spinel (Inversion)

Inversion

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

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$_2$Ti$_2$O$_7$** 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