Analysis and Modeling of Microscopic Radiation Effects on Nuclear Waste Forms

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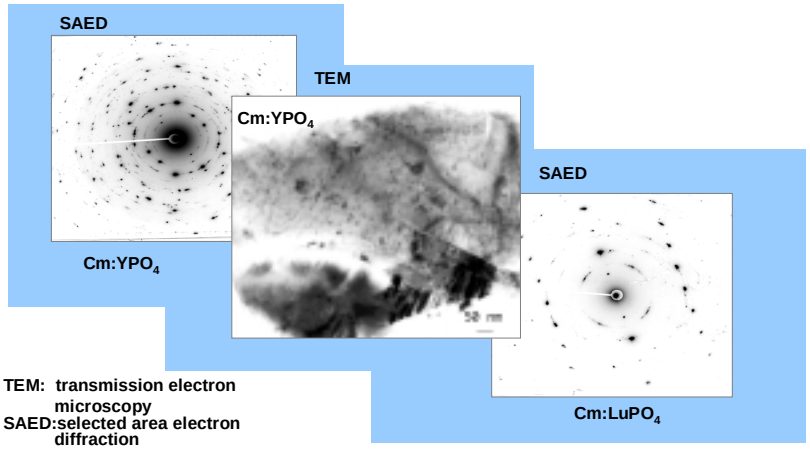
Objective

Investigate microscopic and long-term radiation effects on material properties. Achieve fundamental understanding of radiation effects for modeling and predicting performance of HLW forms and Pu immobilization phases.

Approach

- Actinide-incorporation
  - ^{244}Cm(1%):YPO_4, ^{244}Cm(1%):$LuPO_4$ (18-years old, ~ 5X10^{19} α-decay/g: same dose level as 2.4% ^{239}Pu stored for 10^4 years),
  - ^{244}Cm(1%), ^{249}Bk(1%) in borosilicate glass.
- Electron microscopy (SAED, TEM)
- Laser and X-ray spectroscopy (FLN, EXAFS)
- Computational modeling
  - Molecular dynamics (MD) and Monte Carlo simulations.



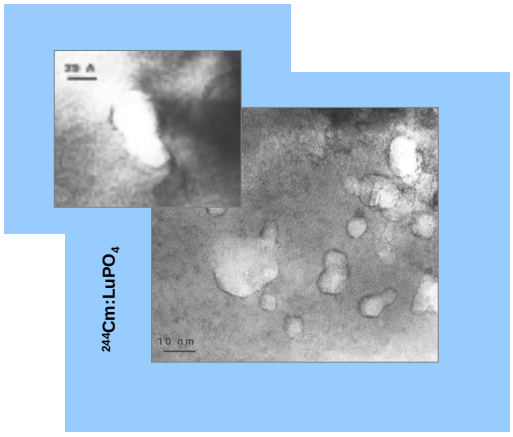
TEM: transmission electron microscopy
SAED: selected area electron diffraction

Long-term Radiation Effects

Crystalline phosphates: amorphization resistant

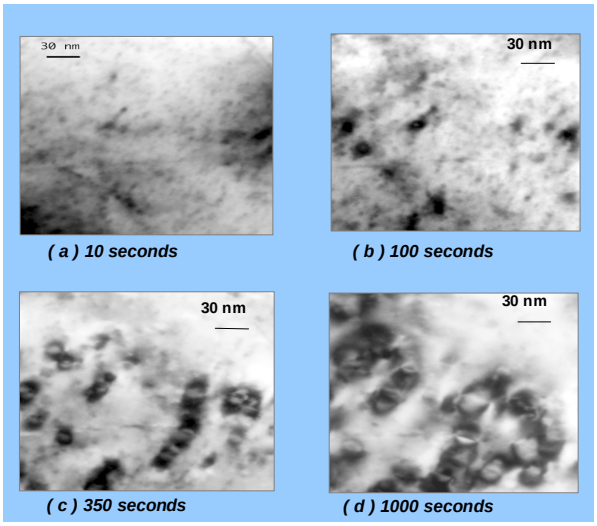
After 18-year accumulation of ~5x10^{19} α-decay/g damage, no amorphization but defect clusters and lattice distortion were observed in ^{244}Cm-doped phosphates: evidence of lattice recovery and defect aggregation at room temperature due to collective inter-atomic interactions.

Bubbles observed in 18-y old samples of phosphates doped with ^{244}cm: evidence of defect mobilization and aggregation



TEM images of ^{244}Cm:$LuPO_4$ showing the presence of bubbles embedded in crystalline lattice. The insert image shows an isolated bubble and its crystalline vicinity.

Formation and aggregation of defect clusters and helium bubbles in an 18-y old Cm:YPO_4 sample under TEM scope



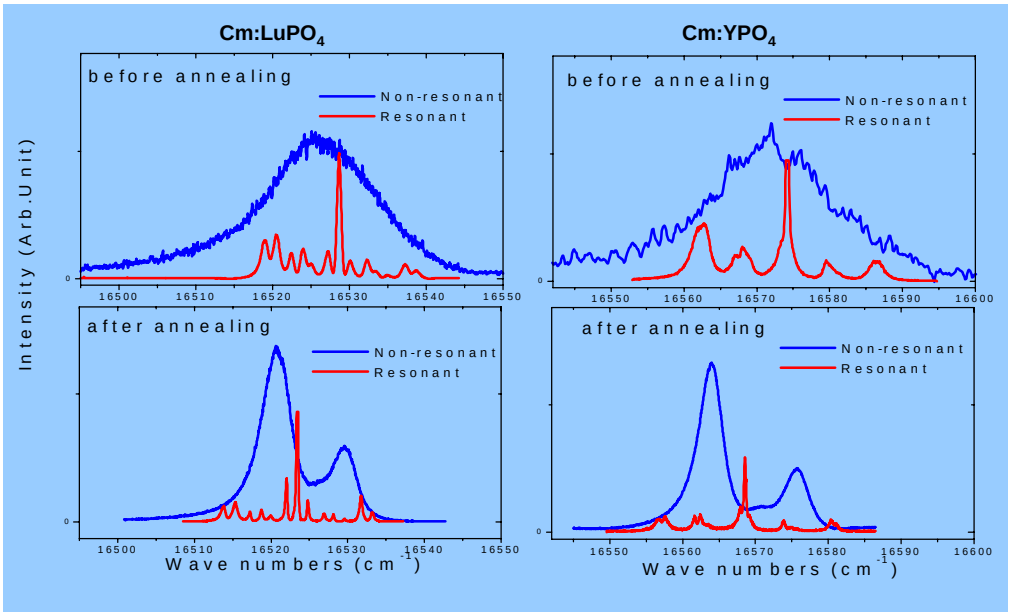
(a) 10 seconds *(b) 100 seconds* *(c) 350 seconds* *(d) 1000 seconds*

Mobility of radiation-induced defect clusters was enhanced by electron beam interaction. The electron energy was 200 keV and current density ~1.5x10^{-16} A/cm^2

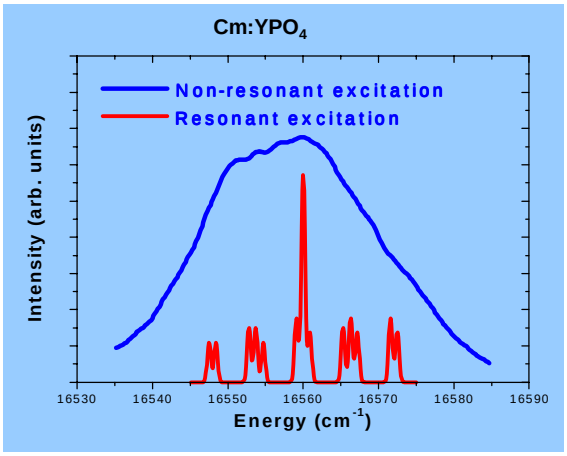
Laser Spectroscopic Probing and Monte Carlo Simulation of Radiation-Induced Lattice Disorder

- Monte Carlo simulation atom displacements induced by α-decay.
- Crystal-field calculation of ion-lattice interactions and local structure.
- Simulation of laser-induced fluorescence spectra.

Inhomogeneous broadening in optical spectra is very sensitive to local structure change. Laser-induced fluorescence spectra for the $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition of Cm^{3+} in $LuPO_4$ and YPO_4 were recorded for monitoring radiation-induced local structure change. Thermal annealing at 500 ^oC reduced line width from 20 cm^{-1} 5 cm^{-1}. The red curves are site-selected resonant excitation spectra. The sharp peaks are due to the Cm^{3+} ground state splitting.



Monte-Carlo simulation of the spectra before annealing suggests an average atom displacement ~ 1/20 diameter of a Cm ion.



Summary of Laser Experiments and Simulation:

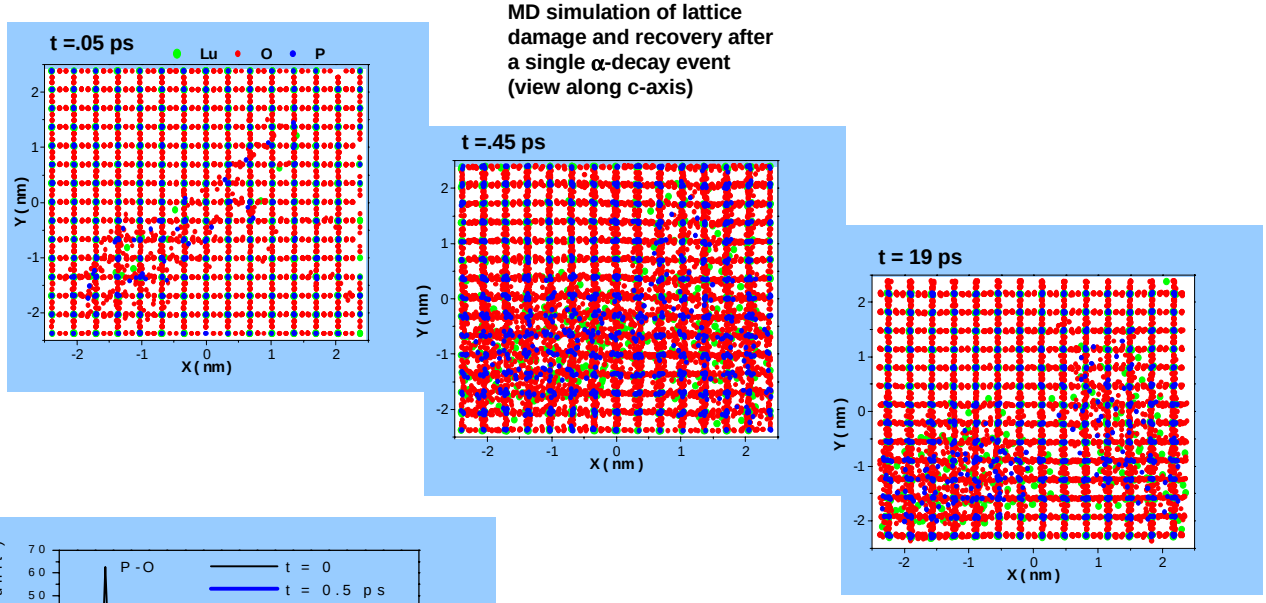
- No amorphization although disorder and defects exists.
- Inhomogeneous line-width measures distribution of lattice disorder. Crystal-field calculation provides a predictive understanding of laser-spectroscopic experimental results, and enables correlating electronic properties and structural disordering.
- Monte-Carlo simulation shows that the average atom displacements (in Gaussian distribution) is only 0.002 nm in both $^{244}Cm:LuPO_4$ and $^{244}Cm:YPO_4$, which have undergone α-decay damage for 18 years.
- Annealing at 500 ^oC removed most existing lattice disorder.

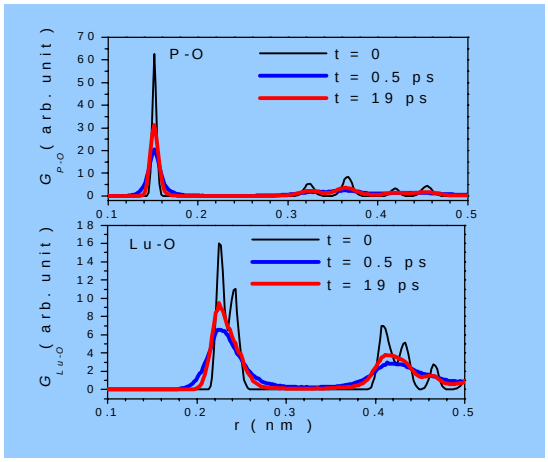
Molecular Dynamics Simulations of Radiation Damage in $LuPO_4$

— Understanding defect formation, aggregation, and annealing

- Two- and three-body inter-atomic potentials are included.
- Simulations of lattice structure and dynamics without radiation damage are confirmed by neutron and X-ray studies.
- Knock-on energy of 20 keV is launched at t = 0 on a Lu atom along [111] direction. 8232 atoms are simulated and taken into account in analyses of defect dynamics.
- The number of defects increases to a maximum at ~ 0.5 ps, then diminish.
- MD simulation has been performed up to 19 ps, and long-term effects will be further simulated using kinetic Monte Carlo methods.
- Analyses of defect dynamics are based on changes in Wigner-Seitz cells, partial radial distribution function, and distribution of interstitials and vacancies.

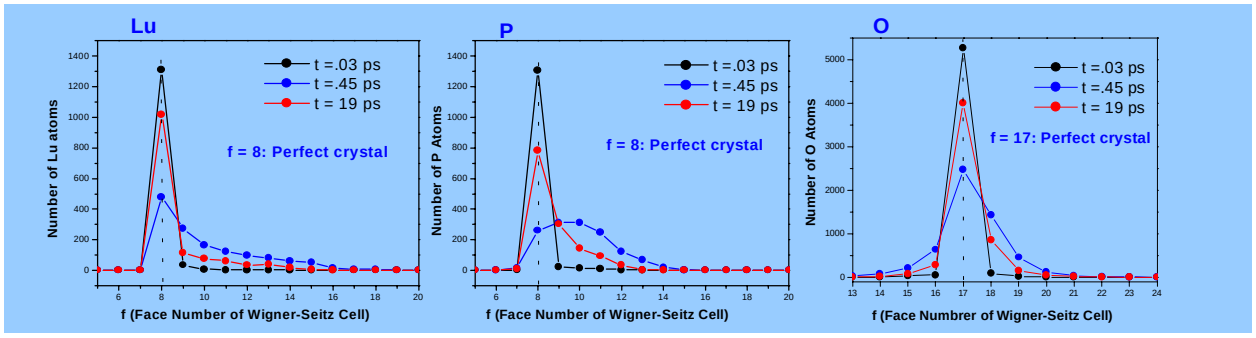
MD simulation of lattice damage and recovery after a single α-decay event (view along c-axis)





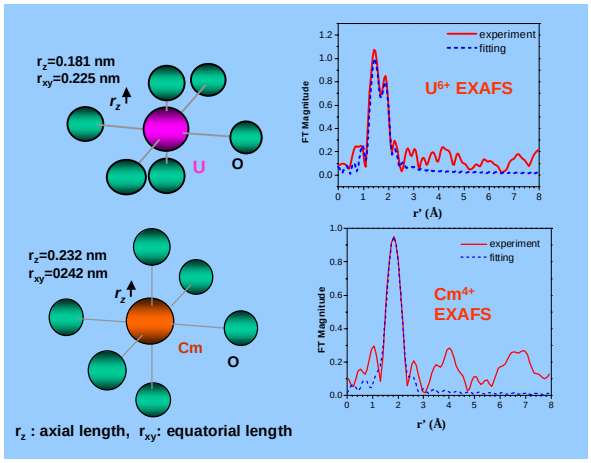
Partial radial distribution function for $LuPO_4$ before and after cascade collisions. Disorder reaches a maximum at ~ 0.5 ps, and damaged lattice recovers significantly within 20 ps after primary collision.

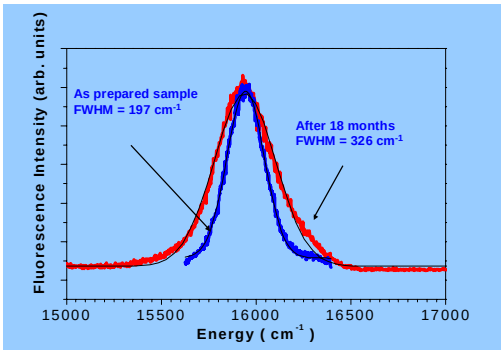
$LuPO_4$ Wigner-Seitz cell damage and recovery,



X-ray (EXAFS) and Laser Spectroscopic Probing of Actinide Structure and Radiation Damage in Borosilicate Glass

- Nearest-neighbor-ligand structure for U^{6+} and Cm^{3+} in borosilicate glass has determined from analyses of EXAFS spectra and laser excitation and fluorescence spectra.
- Electronic interaction between U (Cm) and O ligands were calculated and fit by experimental data in determination of symmetry and U-O (Cm-O) length.
- Radiation-damage-induced inhomogeneous line broadening of Cm^{3+} electronic transitions in ^{244}Cm-doped borosilicate glass: monitor of structural damage. Spectra of laser excitation and fluorescence and self-luminescence are being recorded periodically as the radiation dose increases.





FWHM: full width at half maximum intensity for Cm^{3+} ($^5D_{7/2}$ to $^8S_{7/2}$) fluorescence.

Summary

Microscopic effects of radiation damage induced by α-decay events in crystalline phosphates ($^{244}Cm:YPO_4$ and $^{244}Cm:LuPO_4$) for 18 years and radiation dose reached to ~$5x10^{19}$ α-decay/g:

Long-term radiation effects:

- no amorphization;
- residual lattice distortion after damage annealing and lattice recovery at room temperature.
- formation of isolated defect clusters and bubbles, which mobilize and aggregate;

Molecular dynamics simulation:

- reveals fundamental radiation effects – damage and recovery – based on collective inter-atomic interactions;
- after an α-decay-event, displacements reach a maximum in less than 1 ps, and most damage annealed within 20 ps.

Actinides in borosilicate glasses have ordered nearest neighbor ligands and radiation-induced structure damage has been monitored by using laser and X-ray spectroscopic methods.

Acknowledgement:

Work supported by DOE EMSP Program, 55367.