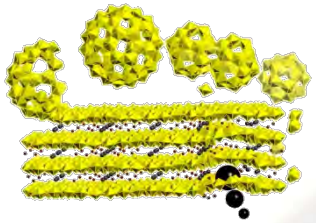
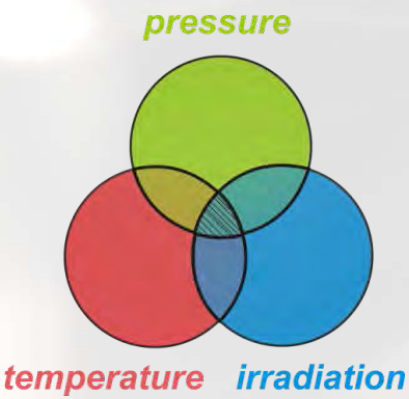
Materials Science of Actinides
Energy Frontier Research Center



U.S. DEPARTMENT OF ENERGY | Office of Science

STRUCTURAL TRANSFORMATIONS IN ACTINIDE AND ANALOGUE MATERIALS UNDER EXTREME CONDITIONS



Maik Lang

University of Tennessee
Department of Nuclear Engineering
Knoxville, TN, USA

THE UNIVERSITY of TENNESSEE KNOXVILLE

Extreme Environment Team

Stanford University

Rodney Ewing | Jiaming Zhang | Weixing Li | Sulgiye Park

University of Michigan

Fuxiang Zhang | Cameron Tracy | Alexander Cusick

University of Tennessee

Raul Palomares | Maik Lang

Collaborations:

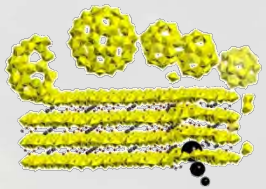
IONS

- Christina Trautmann – GSI Helmholtz Center (Germany)
- D. Severin, M. Bender – GSI Helmholtz Center (Germany)
- Vladimir Skuratov – Joint Institute Nuclear Research (Russia)

X-RAYS

- Vitali Prakapenka – Advanced Photon Source (GSECARS)
- C.Y. Park, D. Popov – Advanced Photon Source (HPCAT)
- Zhongwu Wang – Cornell Synchrotron Source (CHESS)
- Z.Q. Chen, S. Ghose – National Synchrotron Light Source (NSLS)

Support:



Energy Frontier Research Center

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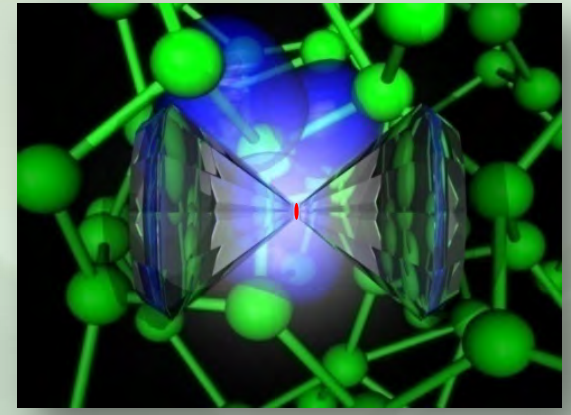
Motivation: Extreme Environments

DAC

P **~ 1 Mbar**

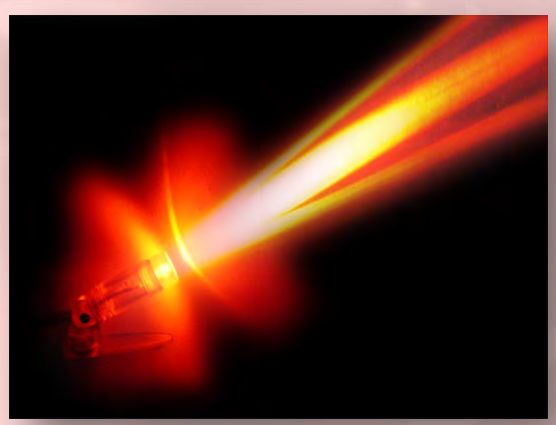


from: *www-pat.llnl.gov/Research/qsg/QSG.html*

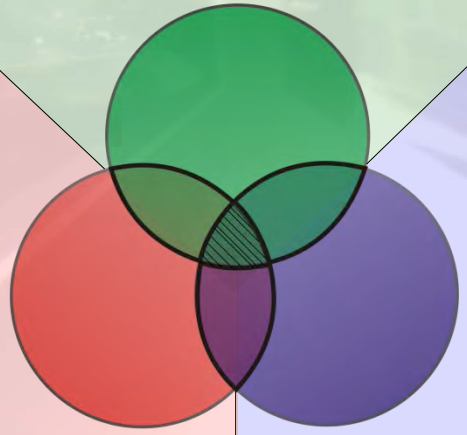
heating coils
laser heating
T **~ 4000 K**

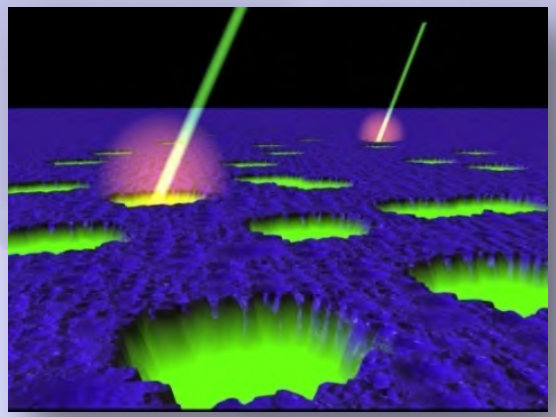
ion accelerator

ρ_E **~ eV/atom**



from: *www.sunbeamtech.com*

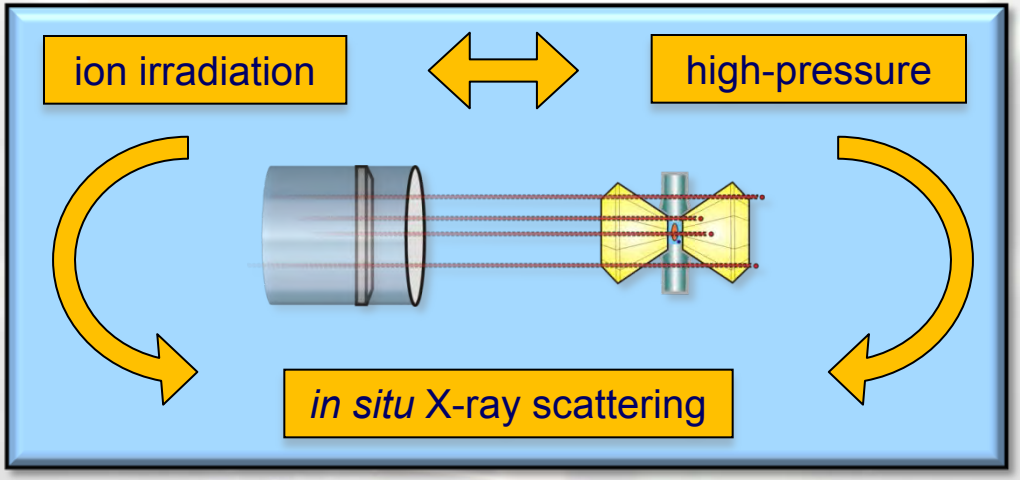




from: *www.simsworkshop.org*

Experiment Approach

ion accelerators

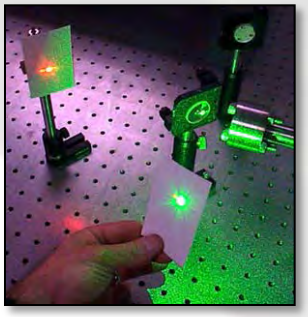


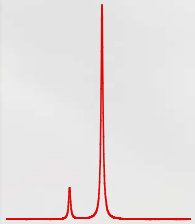
diamond-anvil cells, laser heating

transmission electron microscopy

synchrotron user facilities

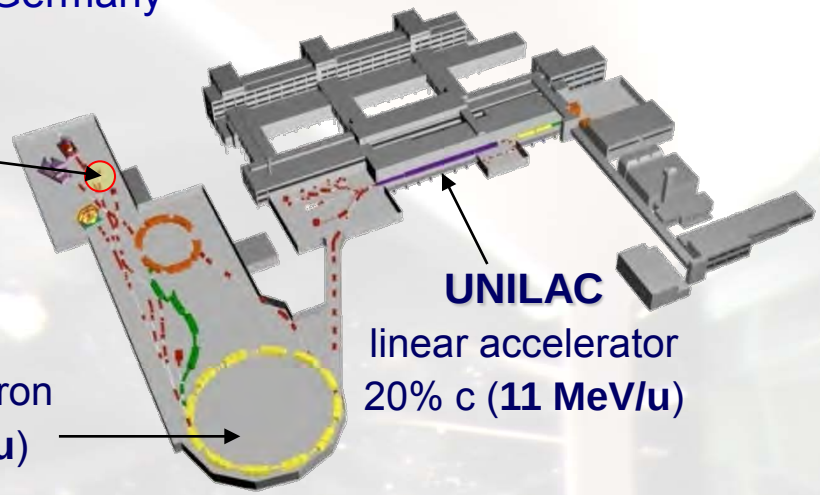
Raman spectroscopy

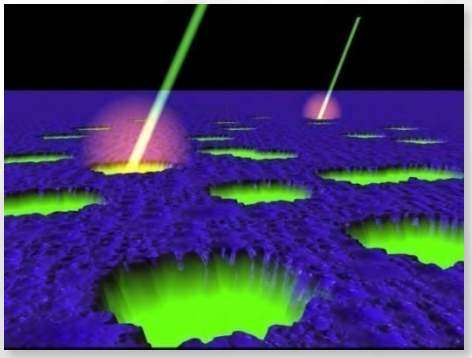




Swift Heavy Ions

Helmholtzzentrum für Schwerionenforschung GSI
Darmstadt, Germany

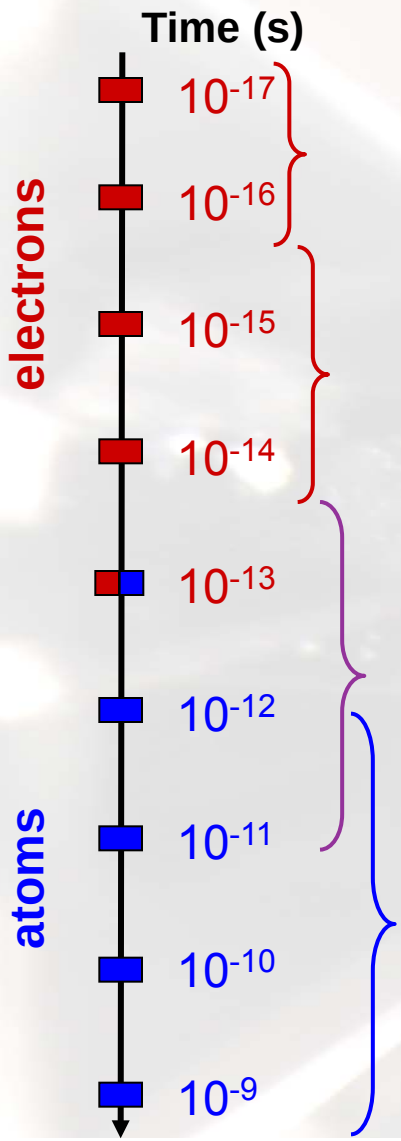




http://www.gsi.de

samples:	UO_2, ThO_2 and CeO_2
heavy ions:	^{132}Xe, ^{197}Au, ^{238}U
kinetic energy:	**160 MeV – 50 GeV**
energy loss:	10 – 55 keV/nm
ion dose:	up to 5×10^{13} ions/ cm^2

Swift Heavy Ions

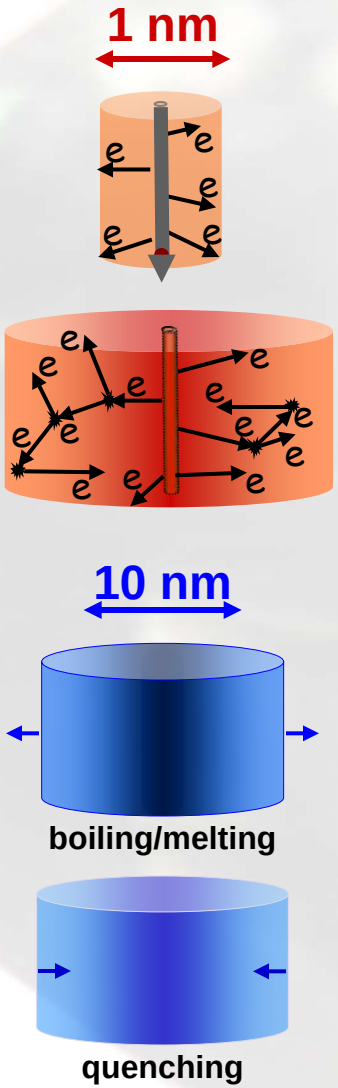


Stage 1: Energy deposition on electrons (e)
- generation of primary-electrons
- ionization
- creation of a Coulomb field

Stage 2: Plasma formation
- electron cascades
- screening of Coulomb field
- thermalization of electrons

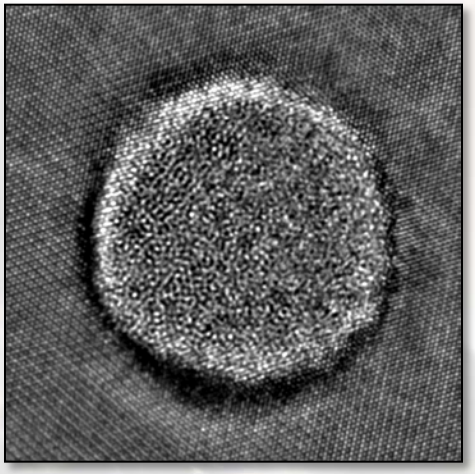
Stage 3: Electron relaxation
- self trapped excitons
- electron-phonon coupling
- thermal spike
- shock wave generation

Stage 4: Lattice processes
- exciton decay to Frenkel defects
- cooling of thermal spike
- radiative decay
- electron-hole recombination
- pressure relaxation

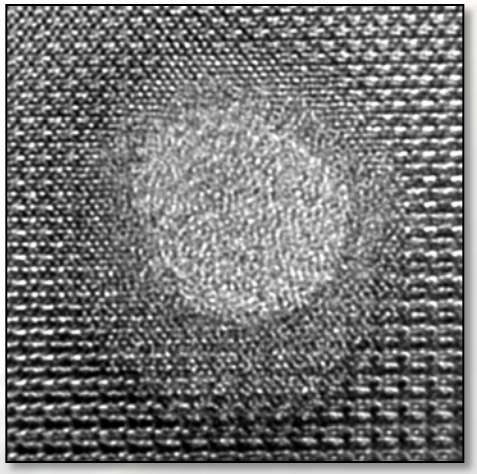


Swift Heavy Ion Tracks

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



changing
composition

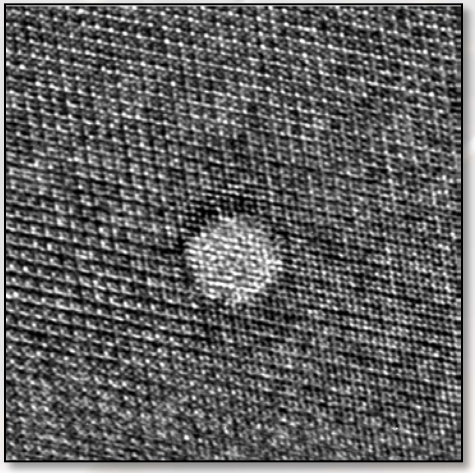


$Gd_2Ti_1O_5$
2.2-GeV ^{197}Au
40 keV/nm; RT

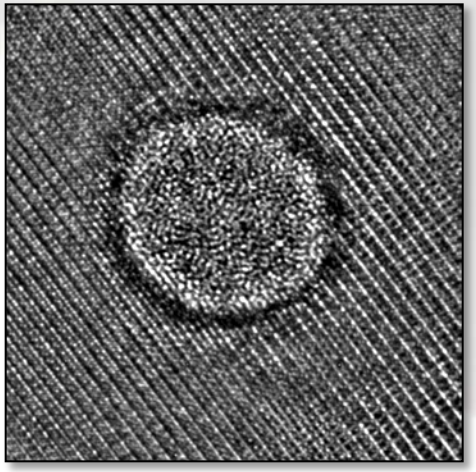
decreasing
energy density

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

Sample Holder for Irradiation and Analysis

50 – 200 µm holes

Electrical Discharge Machining (EDM)

20 MPa → ~50% theoretical density

hydraulic press

sample pellets

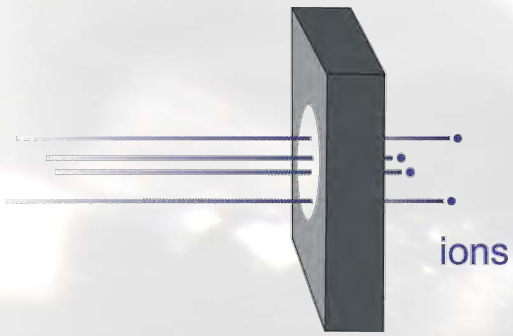
diameter: 50 – 200 µm

thickness: 12 – 50 µm

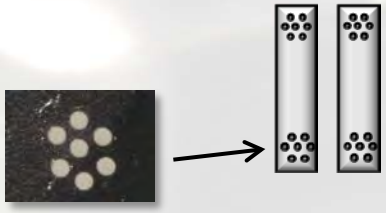
M. Lang, *et.al.* NIMB (2014)

Swift Heavy Ion Irradiation Experiment

irradiation of entire sample pellet → constant energy loss

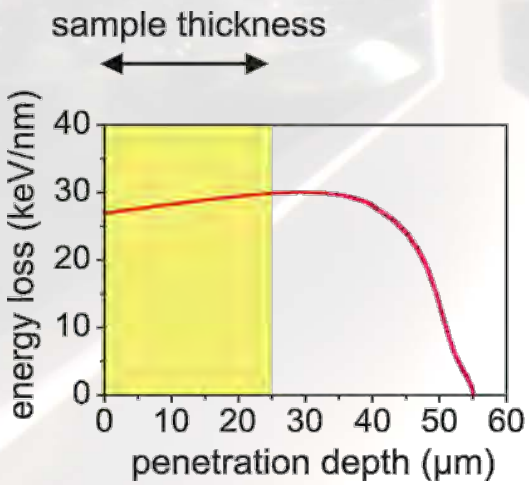


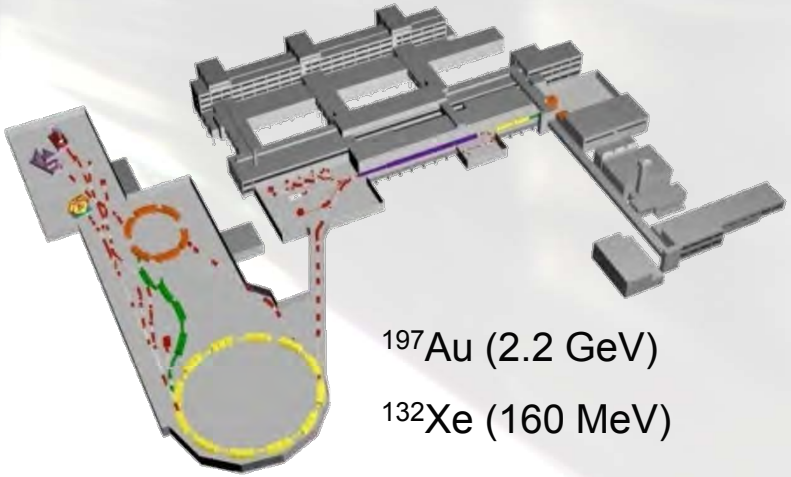
GSI Helmholtz Center (Germany) and
Joint Institute for Nuclear Research (Russia)



Sample chamber

diameter: 200 µm
thickness: 25 µm



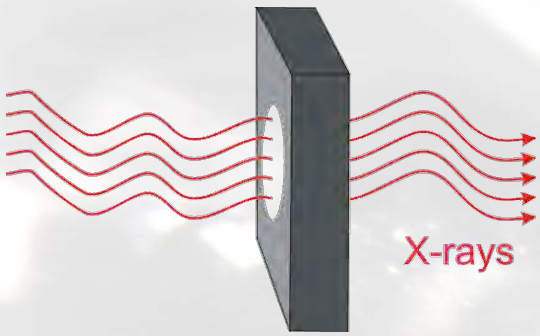


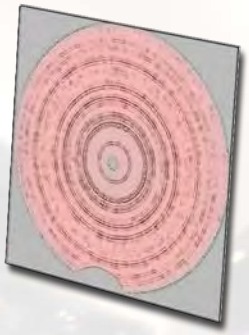
^{197}Au (2.2 GeV)

^{132}Xe (160 MeV)

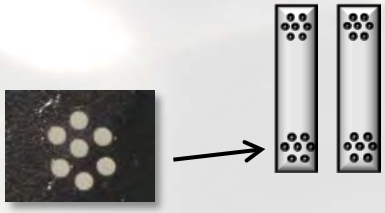
Synchrotron X-Ray Characterization

Synchrotron x-ray analysis in transmission mode

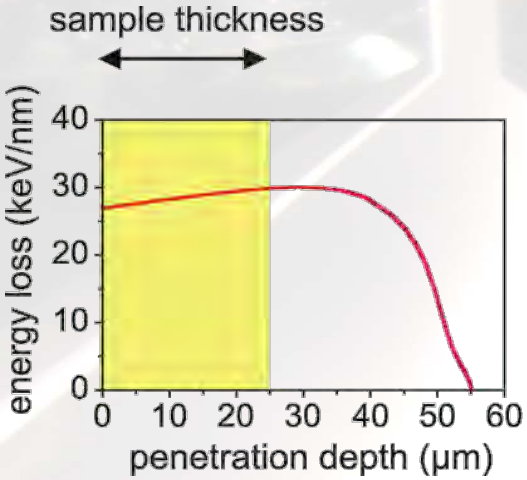




- diffraction experiments (XRD) and absorption spectroscopy (XAS)
- probing of entire sample thickness
- analyzing constant energy loss
- small sample volumes (actinides!)
- instant TEM-sample preparation
- samples available for further studies

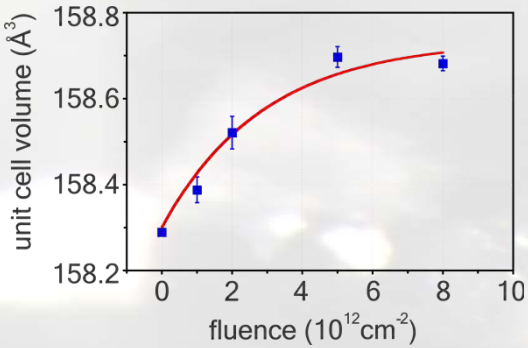


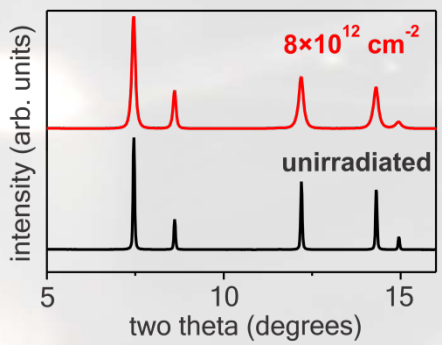
Sample chamber
diameter: 200 µm
thickness: 25 µm



Ion-Induced Material Modifications

defect formation swelling

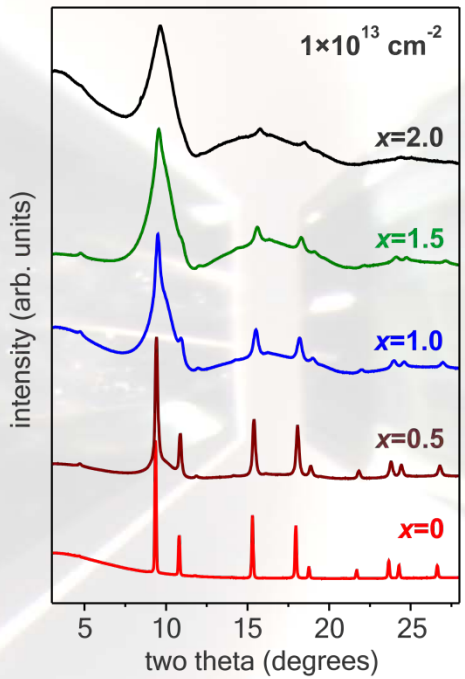




ThO_2

C.L. Tracy, *et al.*
Nucl. Instr. Meth. B (2014)

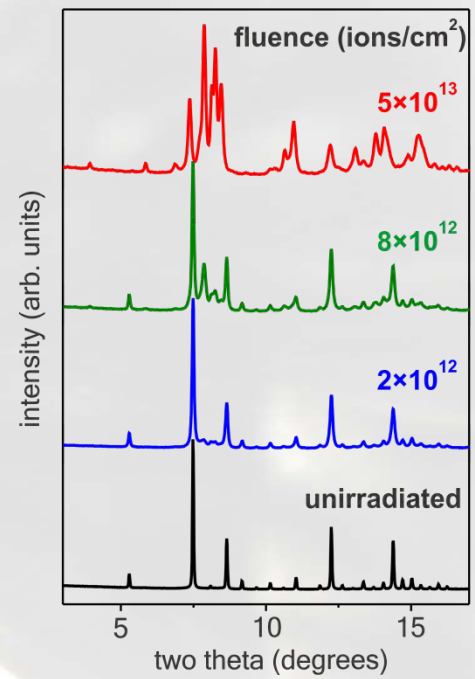
amorphization



$Gd_2Ti_xZr_{2-x}O_7$

M. Lang, *et al.*
Phys. Rev. B (2009)

phase transformation



Gd_2O_3

M. Lang, *et al.*
Nucl. Instr. Meth. B (2014)

Synchrotron X-Ray Experiments

X-rays

- ⇨ X-ray energy: 5 – 40 keV
- ⇨ flux at sample: ~10^{11}ph/s
- ⇨ beam-spot size: ~10 μm

Advanced Photon Source
Argonne National Laboratory

- HPCAT (XRD, XAS)
- GSECARS (XRD)

National Synchrotron Light Source
Brookhaven National Laboratory

- X17C (XRD)
- U2A (IR)

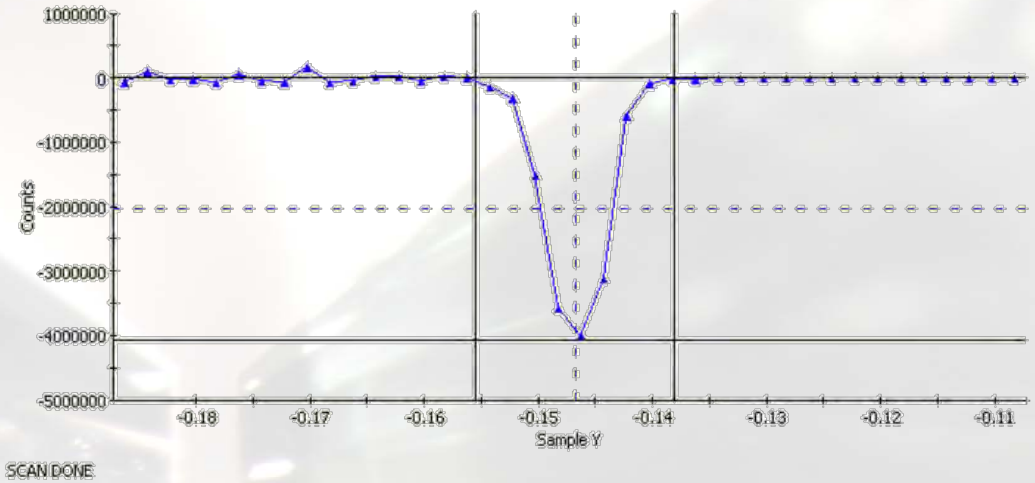
Synchrotron X-Ray Experiments

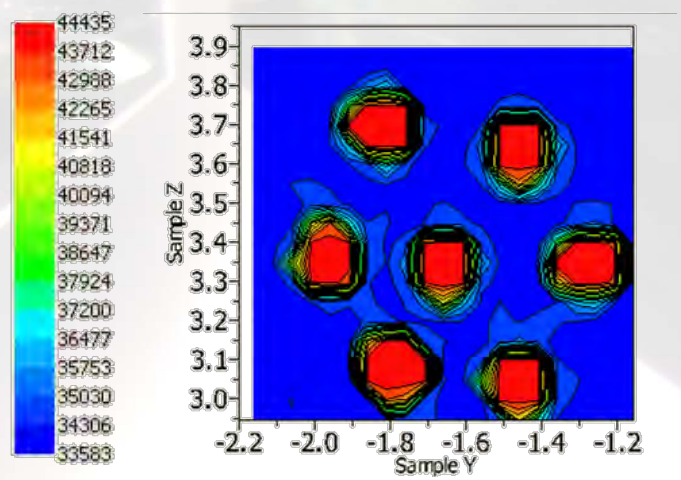
X-rays

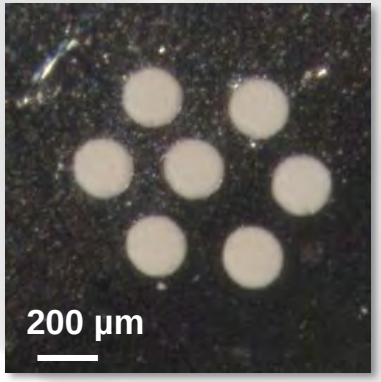
- ⇨ X-ray energy: 5 – 40 keV
- ⇨ flux at sample: ~10^{11}ph/s
- ⇨ beam-spot size: ~10 µm

sample positioning

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







X-Ray Diffraction and Spectroscopy

X-rays

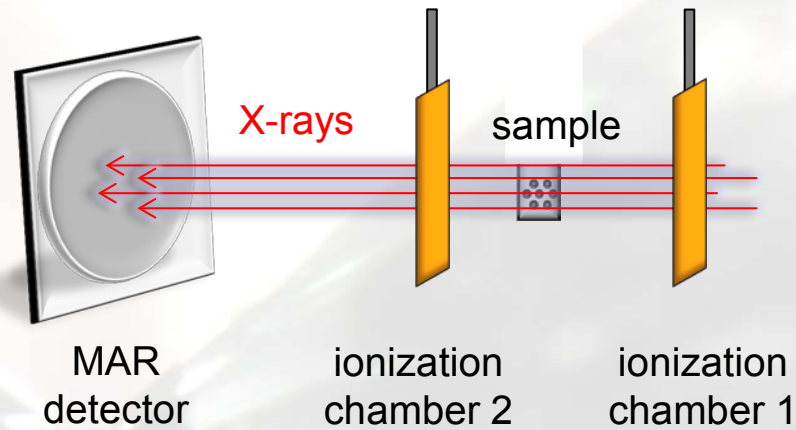
- ⇨ X-ray energy: 5 – 40 keV
- ⇨ flux at sample: ~10^{11}ph/s
- ⇨ beam-spot size: ~10 µm

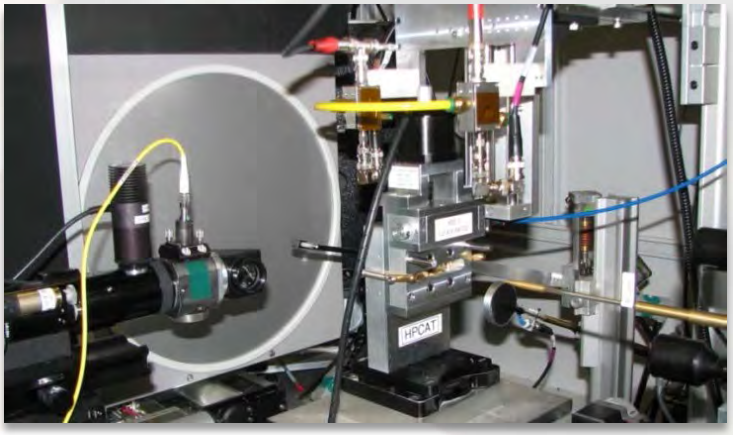
sample positioning

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

XRD and XAS measurements (HPCAT)

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



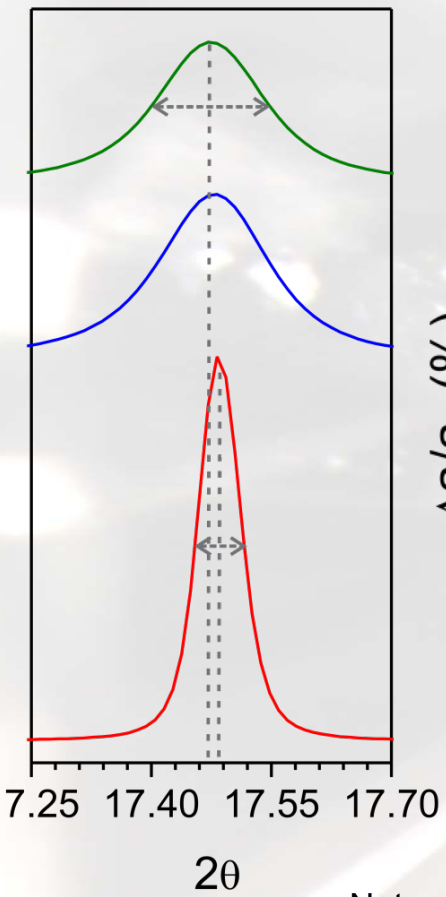


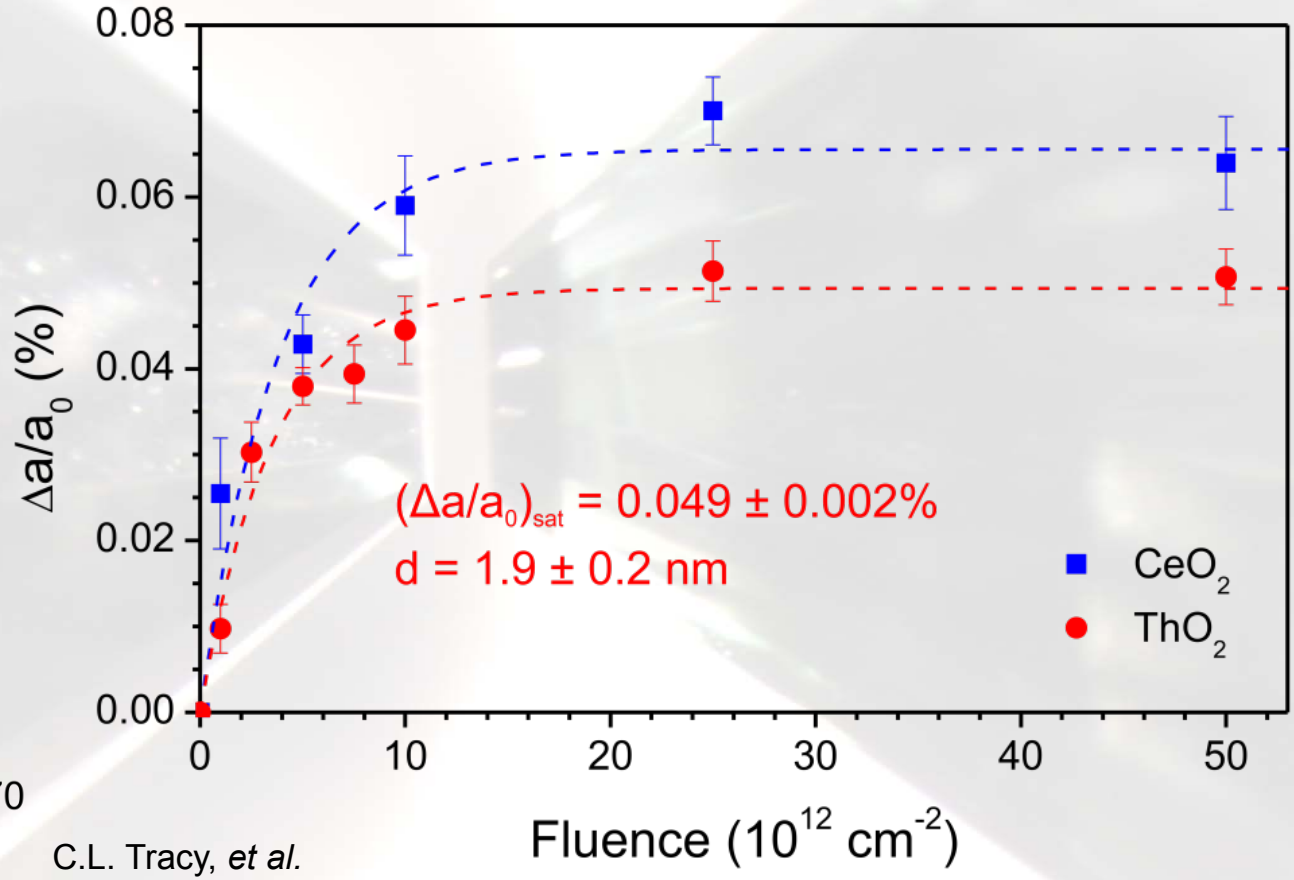
Information on structural (XRD) and electronic (XAS) properties at identical sample location

XRD: Defect Formation

CeO_2 and ThO_2

Peak shift → unit-cell expansion



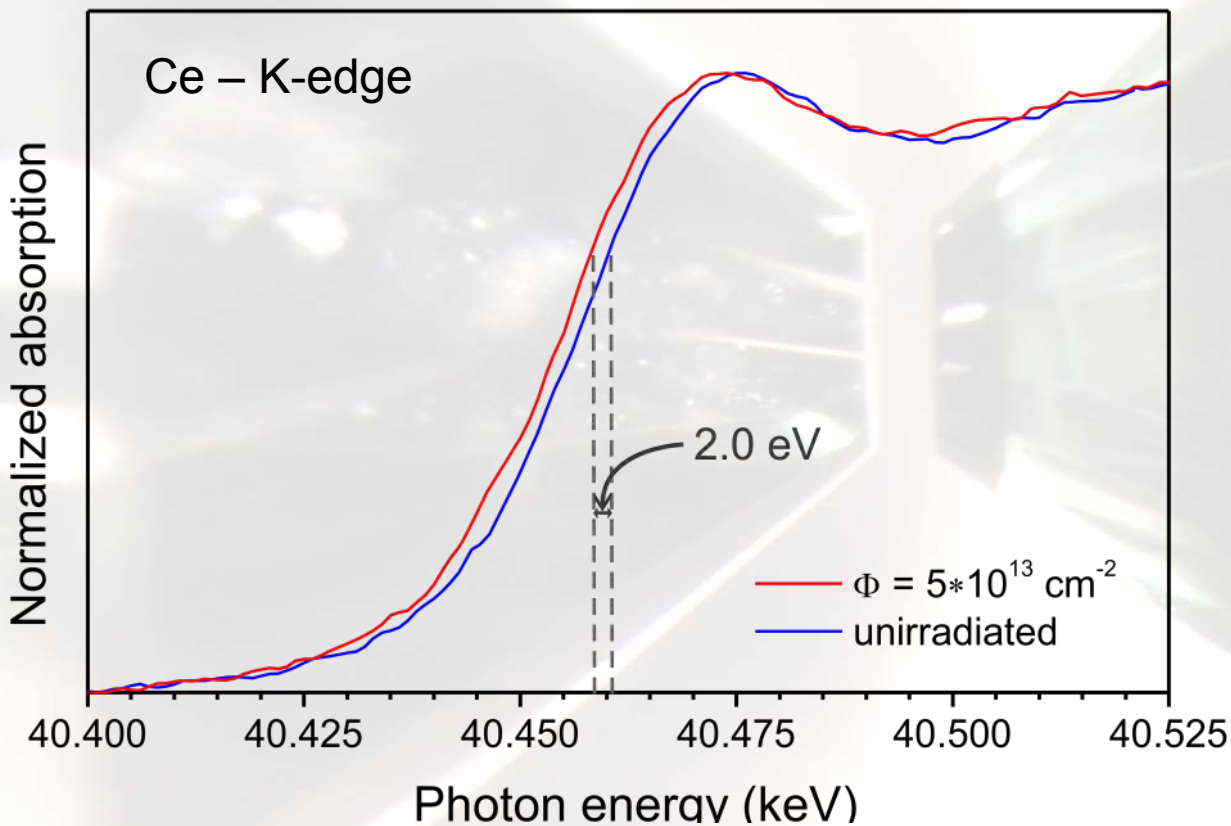


C.L. Tracy, *et al.*
Nature Materials (under review)

XAS: Change of Oxidation State

absorption-edge shift → change of oxidation state

CeO_2



ion-induced reduction of Ce: +4 → +3

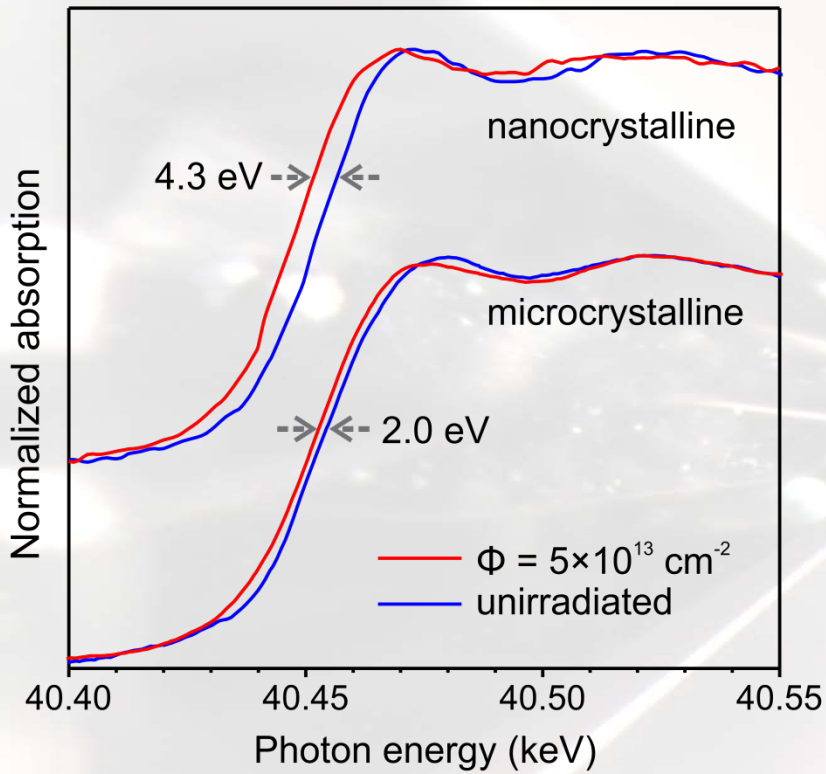
Structural modifications:

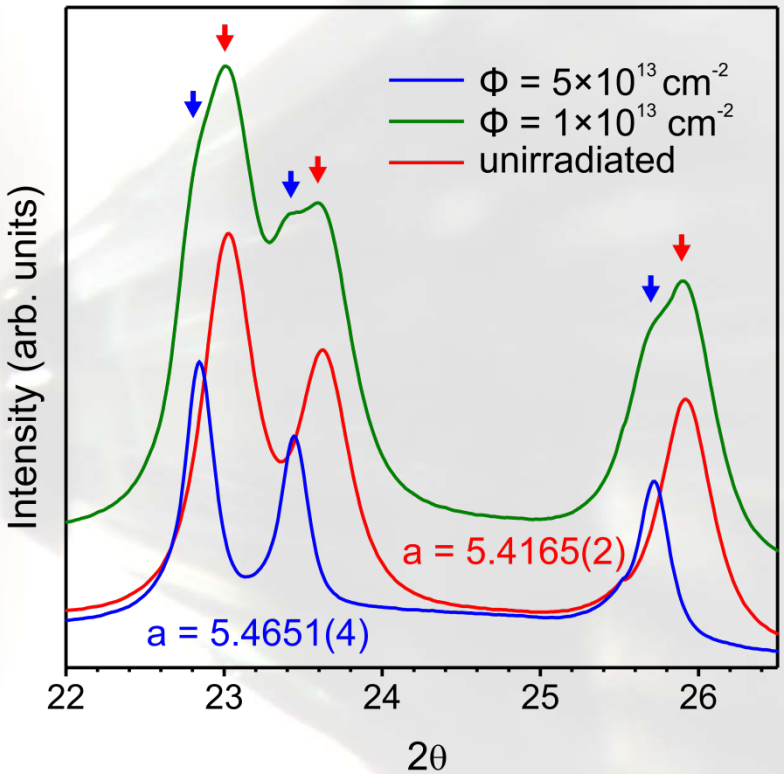
- Ce^{3+} is ~20% larger than Ce^{4+} Unit cell expansion
- Cation size mismatch → local structural distortion
- Full reduction: 7 eV shift

C.L. Tracy, *et al.*
Nucl. Instr. Meth. B (2014)

Effect of Grain Size: Nano-Materials

CeO_2

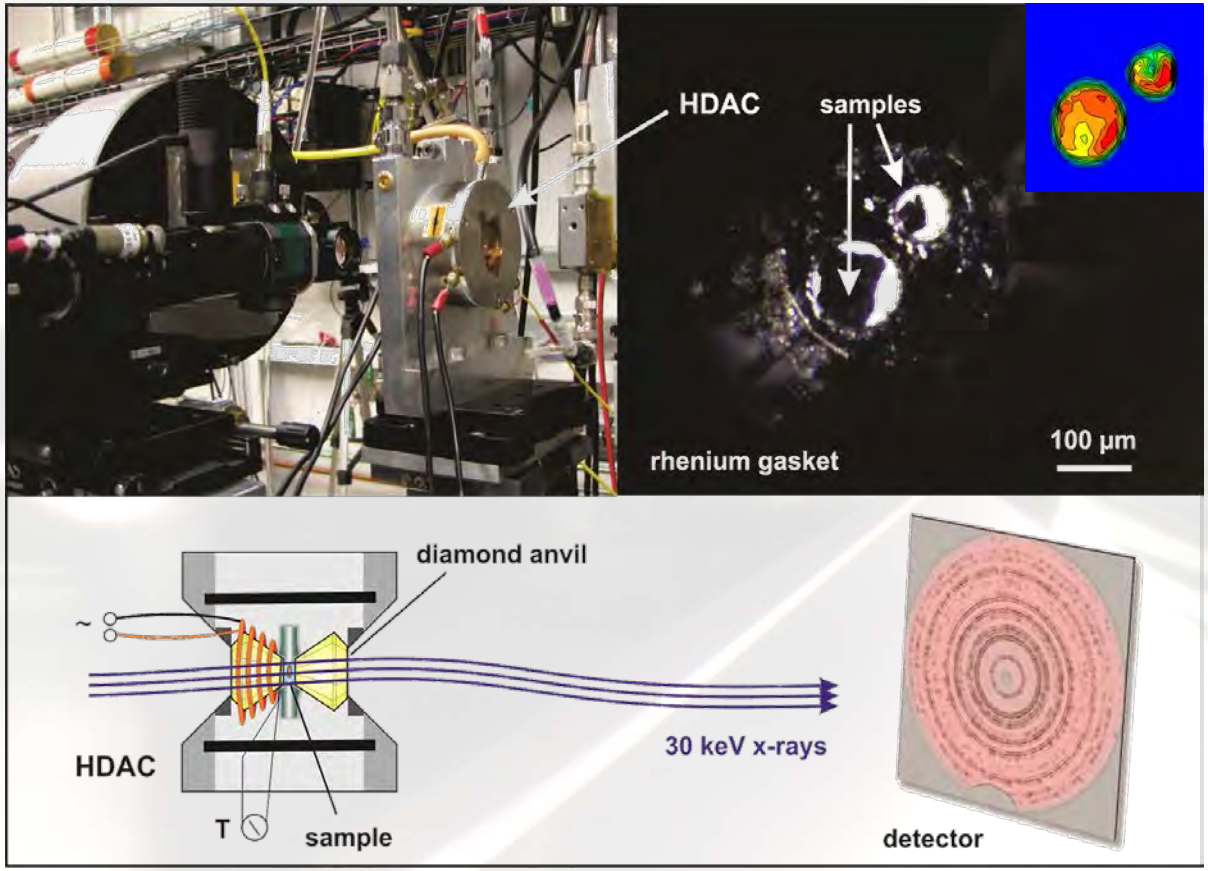


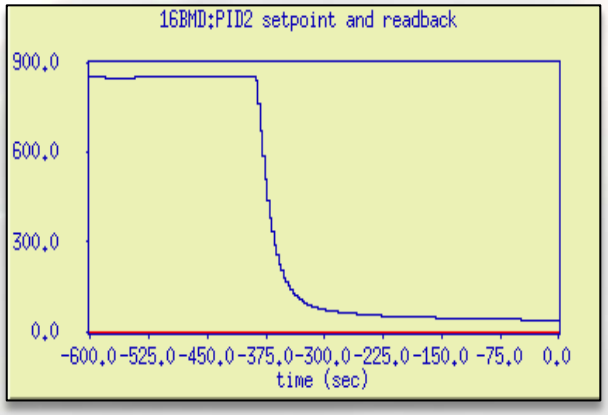


Nanocrystallinity enhances the efficiency of cerium reduction, leading to increased radiation damage (0.9% cell expansion).

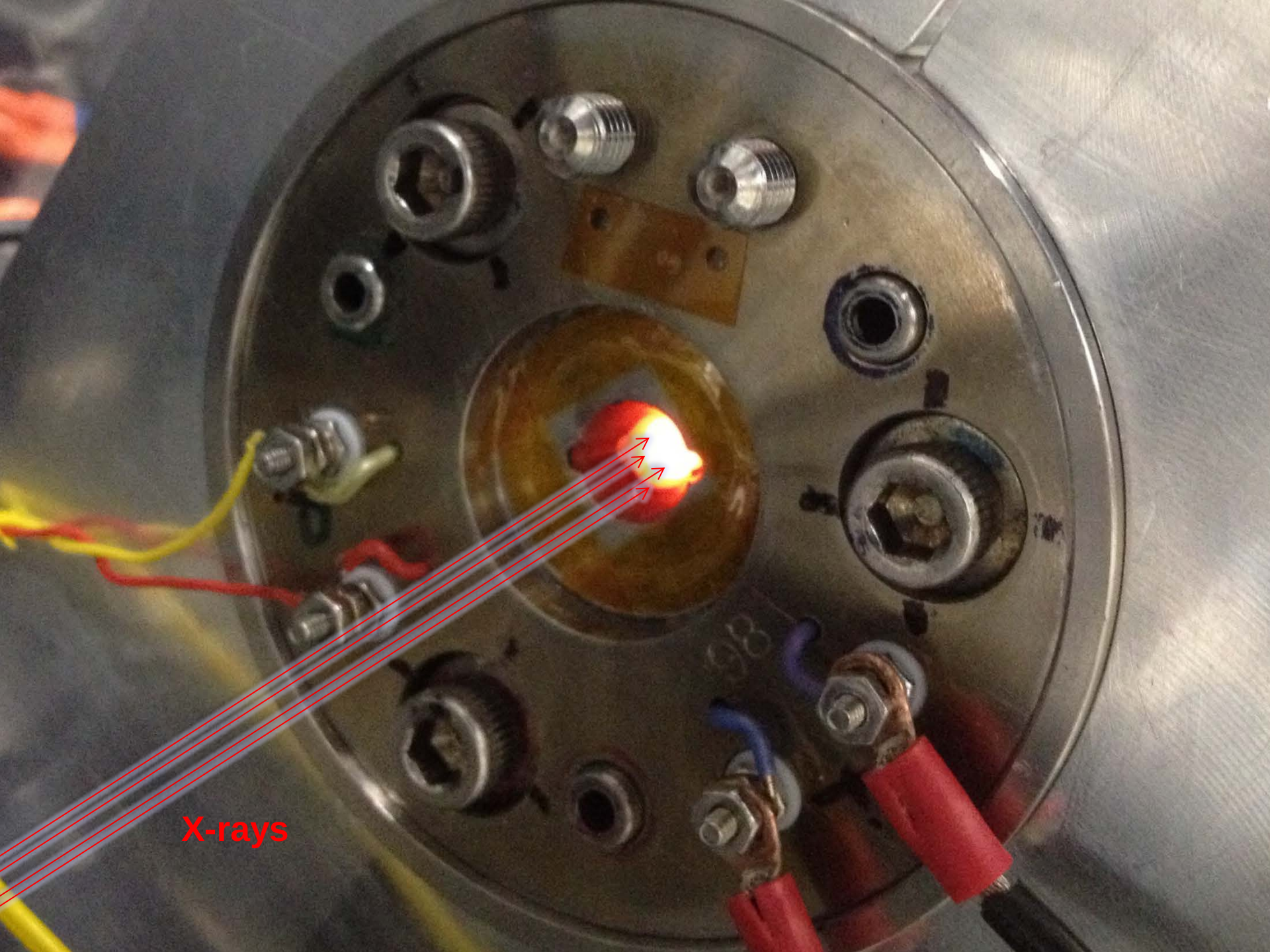
Defect Annealing and Synchrotron Radiation

Hydrothermal diamond anvil cell (HDAC)
as sample annealing device (up to 1000 ºC)



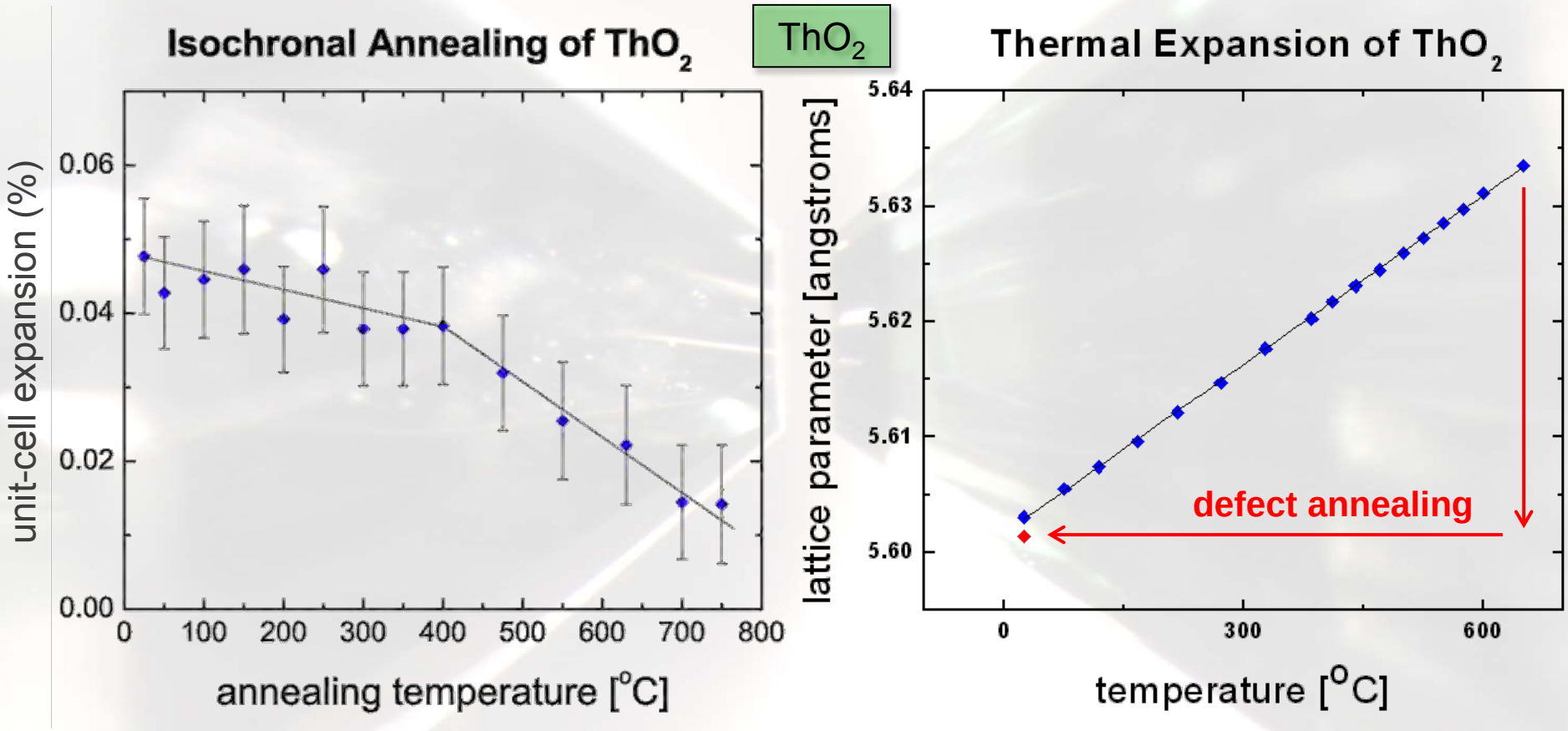


- ⇨ homogeneous heating
- ⇨ superior temperature control
- ⇨ microscopic sample volume
- ⇨ multiple samples
- ⇨ *in situ* access for X-rays
- ⇨ different atmospheres


X-rays

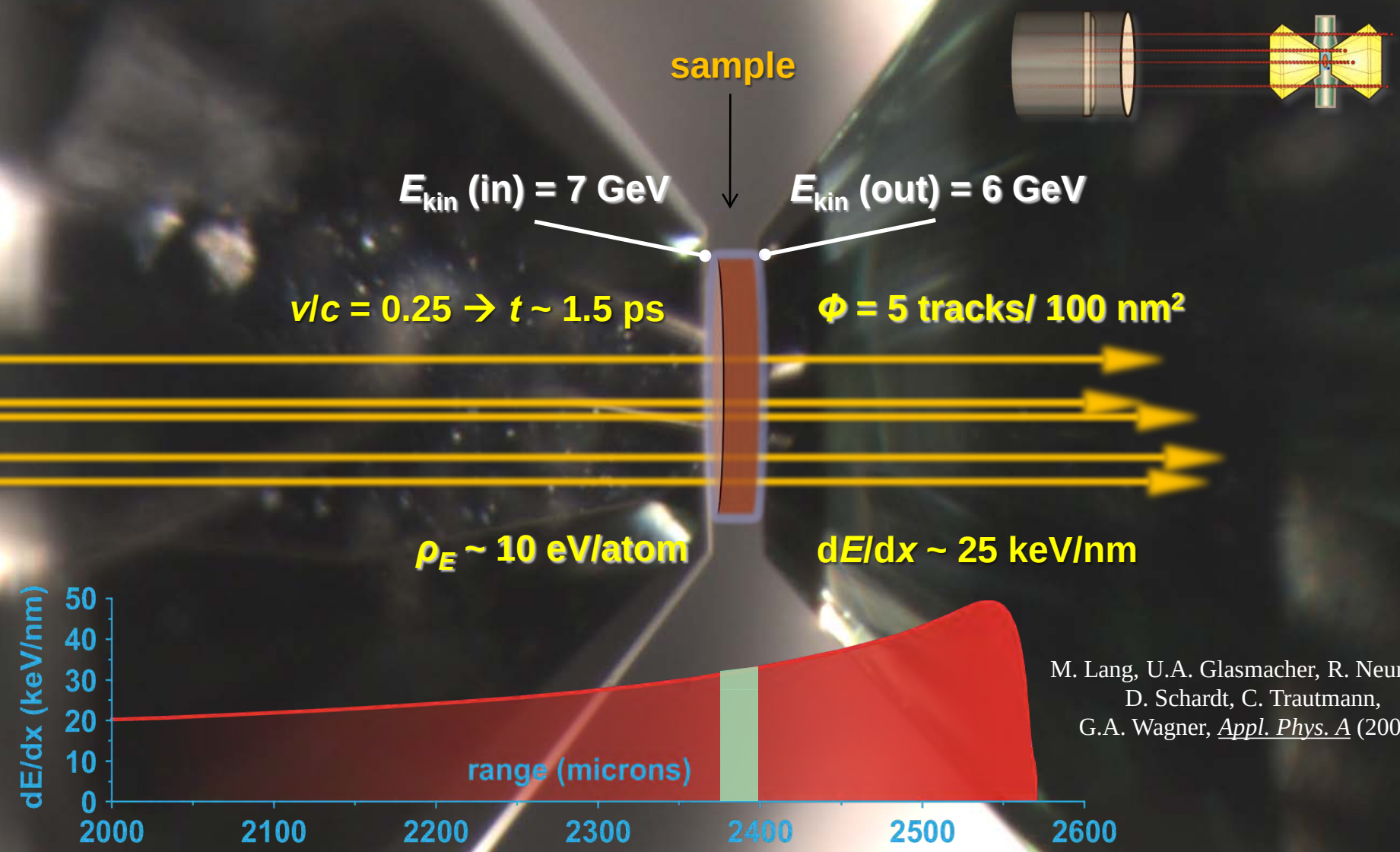
Defect Annealing in ThO_2

Synchrotron XRD : irradiated ThO_2 in heatable DAC up to 850 ºC



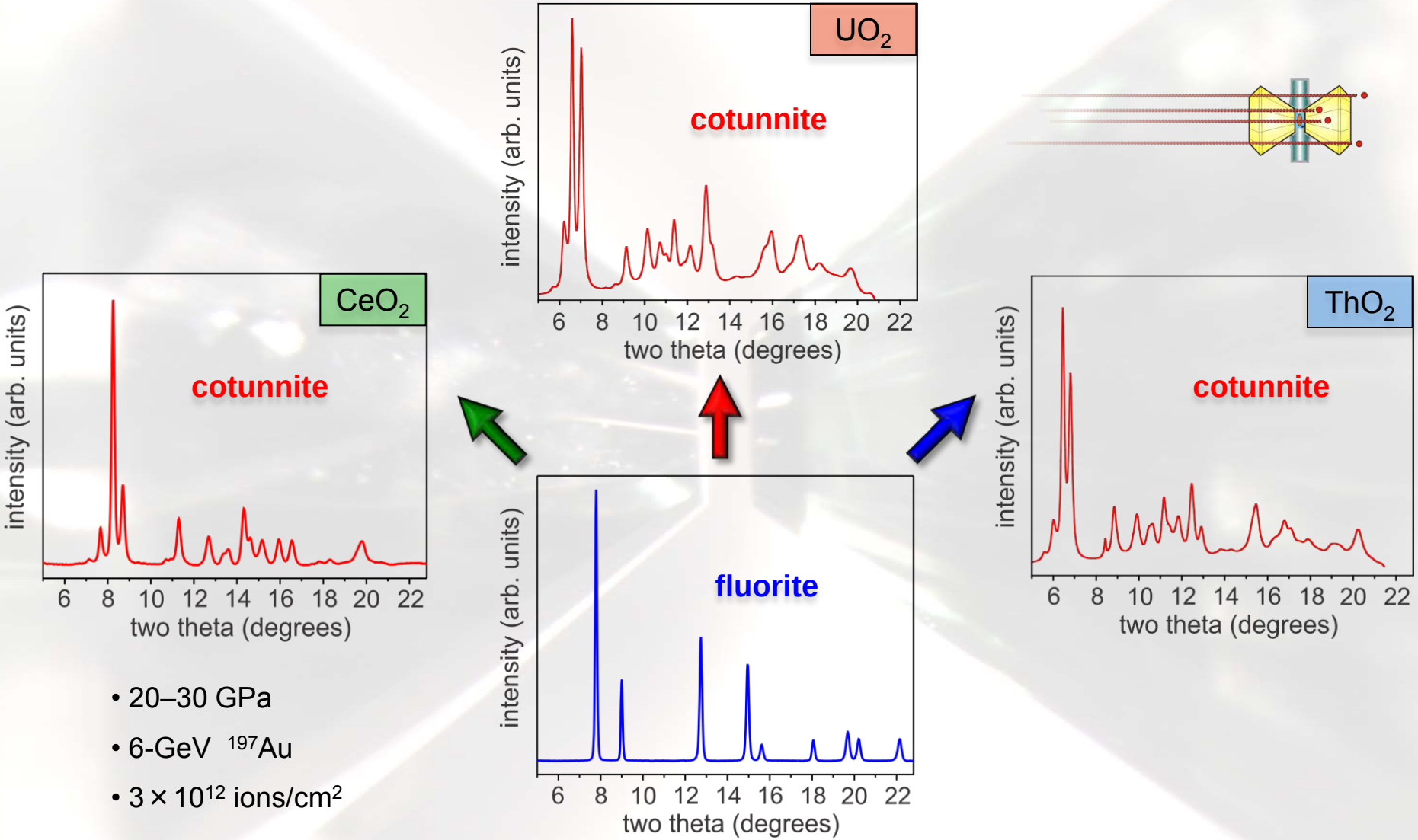
R.I. Palomares, *et al.* 2014 (in preparation)

Combined Pressure and Irradiation



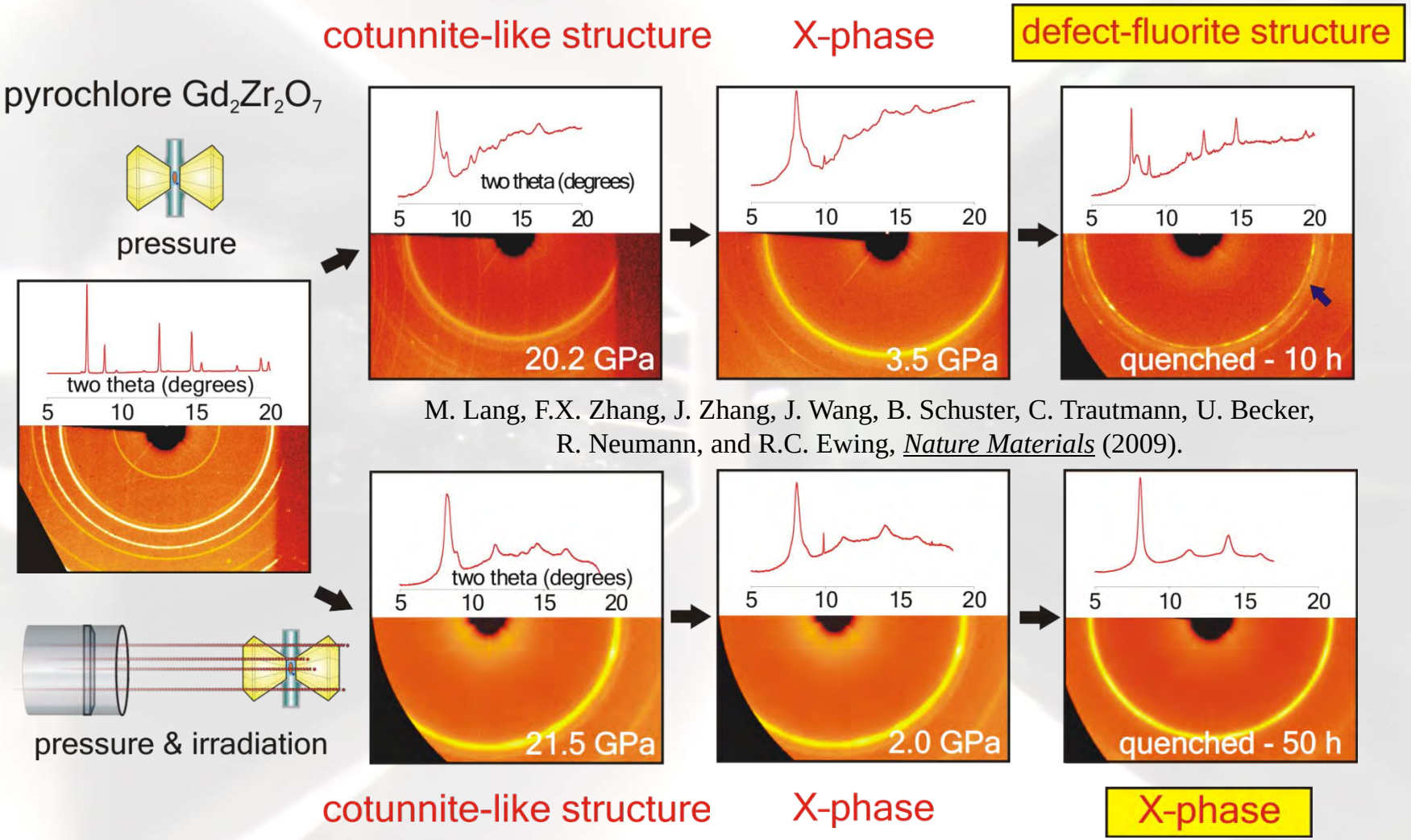
M. Lang, U.A. Glasmacher, R. Neumann, D. Schardt, C. Trautmann, G.A. Wagner, *Appl. Phys. A* (2005).

Combined Pressure and Irradiation: AnO_2



- 20–30 GPa
- 6-GeV ^{197}Au
- 3×10^{12} ions/cm^2

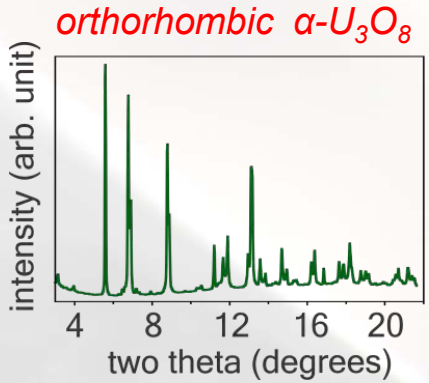
Radiation-Induced Stabilization: Pyrochlore

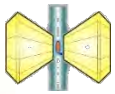


M. Lang, F.X. Zhang, J. Zhang, J. Wang, B. Schuster, C. Trautmann, U. Becker, R. Neumann, and R.C. Ewing, *Nature Materials* (2009).

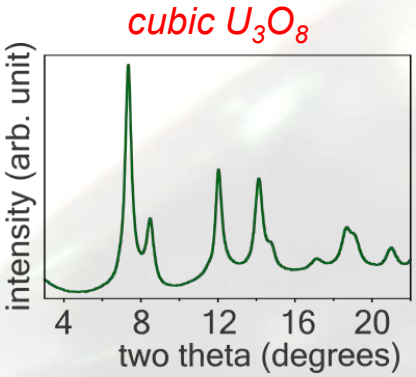
New Actinide Materials at Extremes

U_3O_8

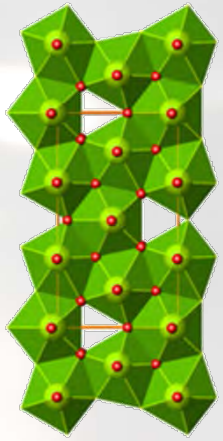


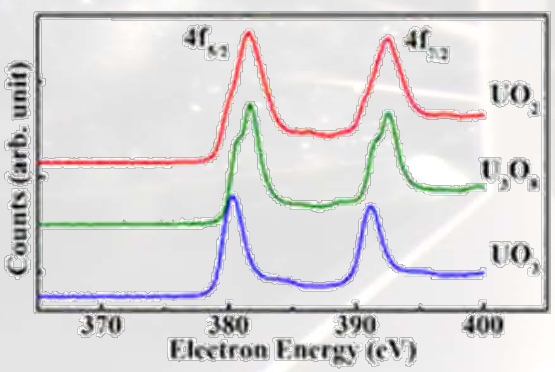


38 GPa

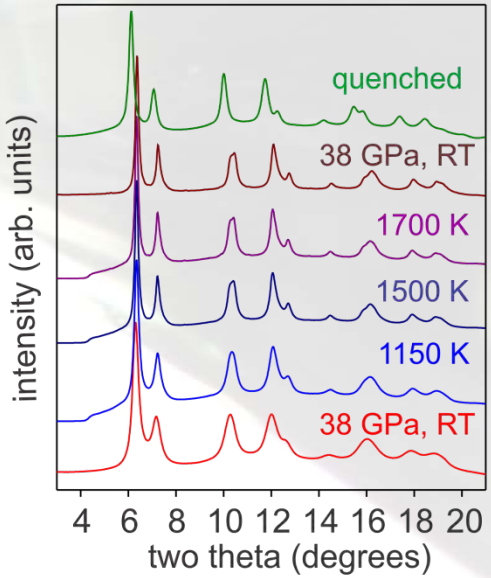


Fuxiang Zhang *et al*. to be submitted to *Phys. Rev. Lett.*





- ⇨ new cubic uranium-oxide material
- ⇨ recoverable to ambient conditions
- ⇨ remarkable structural stability



laser heating

Conclusions

- Synchrotron x-rays combined with high-pressure techniques is a powerful approach to study nuclear materials at extreme conditions:
  - defect formation and annealing, oxidation-state changes
  - crystalline-amorphous transformations
  - crystalline-crystalline phase transitions

- Redox chemistry of actinide materials influences significantly their radiation response:
  - ThO_2 ⇨ defect formation not affected by redox changes
  - CeO_2 ⇨ reduction by ionizing irradiation is major damage source
  - UO_3 ⇨ large extent of reduction leads to phase transformation

  ⇨ nanocrystallinity may negatively impact performance of nuclear materials!

  ⇨ doping with non-multivalent cations may improve radiation tolerance!

- Simultaneous combination of ion irradiation and high pressure is effective trigger for phase transformations (CeO_2, ThO_2, UO_2)

Thank you!