LA-UR- 11-05528

Approved for public release; distribution is unlimited.

Title: Radiation Stability Study on Alternative Waste Forms for an Advanced Nuclear Fuel Cycle

Author(s): Ming Tang, Anna-Eden Kossoy-Simakov, Gordon Jarvinen
Los Alamos National Laboratory
Jarrod Crum, Laura Turo
Pacific Northwest National Laboratory
Kyle Brinkman, Kevin Fox, Amanda Billings, James Marra
Savannah River National Laboratory

Intended for: Presentation for MRS-2011 XXXV International Symposium "Scientific Basis for Nuclear Waste Management"

Los Alamos
NATIONAL LABORATORY
EST. 1943

Radiation Stability Study on Alternative Waste Forms for an Advanced Nuclear Fuel Cycle

Ming Tang, Anna-Eden Kossoy-Simakov, Gordon Jarvinen,
Los Alamos National Laboratory
Jarrod Crum, Laura Turo
Pacific Northwest National Laboratory
Kyle Brinkman, Kevin Fox, Amanda Billings, James Marra
Savannah River National Laboratory

A series of glass ceramic and crystalline ceramic waste forms are explored as an alternative waste form for glass, the current baseline, to be used for immobilizing alkaline/alkaline earth (Cs/Sr-CS) + lanthanide (LN) + transition metal (TM) fission product waste streams anticipated to result from nuclear fuel reprocessing. In this study, glass ceramics are fabricated using a borosilicate glass as matrix in which to incorporate CS/LN/TM combined waste streams, and the major phases in these multiphase materials are powellite, oxyaptite, pollucite, celsian, and durable residual glass phases; and Al_2O_3 and TiO_2 are combined with the same waste components to produce multiphase crystalline ceramics containing hollandite-type phases, perovskites, pyrochlores and other minor metal titanate phases. These alternative ceramic waste forms offer increased solubility of troublesome components in crystalline phases as compared to glass, leading to increased waste loading, and the crystalline network formed in these materials results in higher heat tolerance than glass.

For the radiation stability test, selected glass ceramic and crystalline ceramic samples are exposed to either low fluxes of high-energy (~3-5 MeV) protons and alphas generated by accelerator, or in-situ electron irradiations in a transmission electron microscope, to simulate the self-radiation in a waste form. Ion irradiation-induced microstructural modifications are examined using X-ray diffraction and transmission electron microscopy. The preliminary results show the very good radiation tolerance, especially the amorphization resistance, in these crystalline phases, but their stability may be rate dependent which may limit the waste loading that can be employed.

Keywords: glass ceramic, crystalline ceramic, waste form, radiation damage, TEM

- The MRS 2011 XXXV International Symposium “Scientific Basis for Nuclear Waste Managemen

Radiation Stability Study on Alternative Waste Forms for an Advanced Nuclear Fuel Cycle

Ming Tang, Anna Kossoy, Gordon Jarvinen

Los Alamos National Laboratory

Jarrod Crum, Laura Turo, and Brian Riley

Pacific Northwest National Laboratory

Kyle Brinkman, Kevin Fox, Amanda Billings, James Marra

Savannah River National Laboratory

Acknowledgements

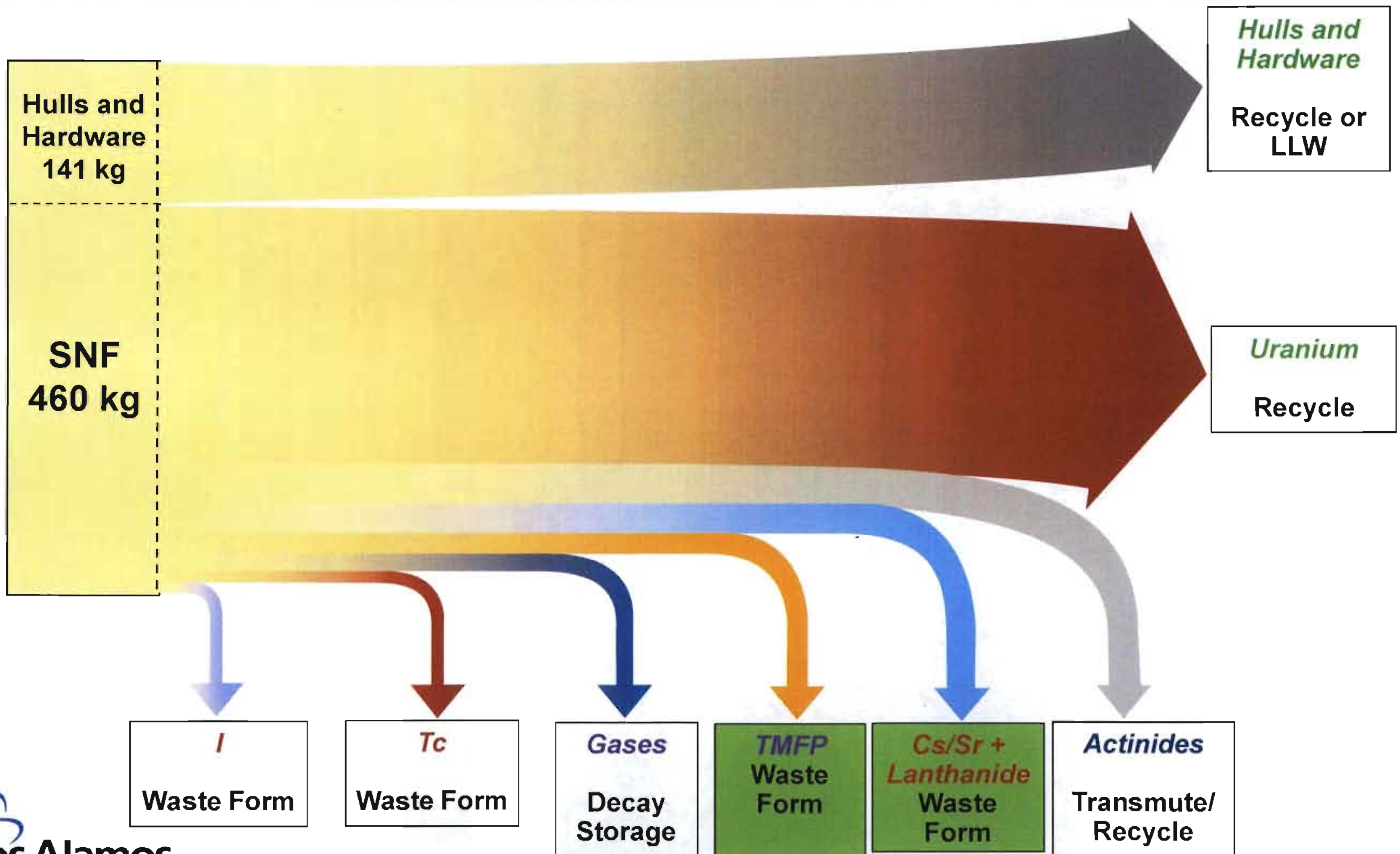
Research sponsored by U.S. DOE-NE

Fuel Cycle R&D Program

Waste Forms Campaign,

Alternative Waste Forms for Fission Products

Fuel Components (Typical LWR Assembly)



Ceramic Waste Form Concept

- **Immobilize major waste streams from aqueous processing:**
  - Cs/Sr/Ba/Rb (CS)
  - transition metals (TM)
  - lanthanides (LN)

- **Designed waste form with materials engineering approach to target specific phases**
  - –Pollucite $CsAlSiO_6$
  - –Celsian $(Ba,Sr)Al_2Si_2O_8$
  - –Oxyapatite $Sr_xNd_{(10-x)}Si_6O_{26}$
  - –Powellite $XMoO_4$, where X = mixture of lanthanides and alkaline earths
  - –Hollandite ($BaAlTi_5O_{14}$), Perovskite, Pyrochlore, Zirconolite
  - –Durable residual glass

Materials under study

1. Evaluate irradiation stability of glass-ceramic and crystalline ceramic, multi-phase specimens
2. Microstructure/phase composition of pristine and irradiated waste form

Two types of glass-ceramics from PNNL :

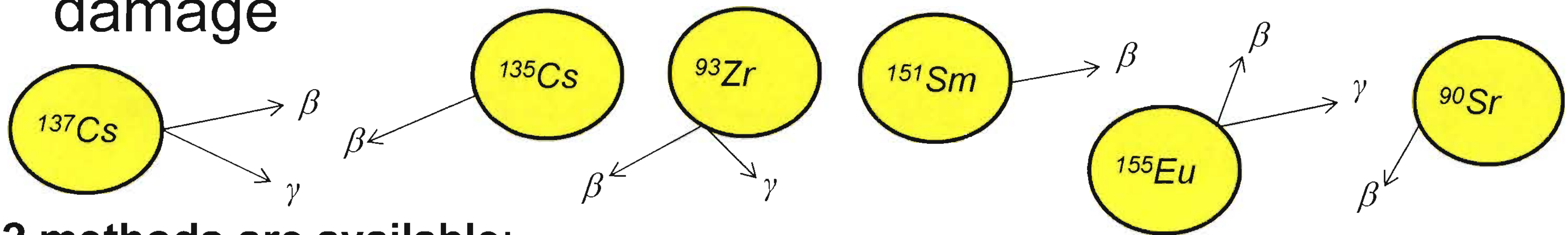
1) Waste loading 60 wt% (No Mo)+ Borosilicate glass-GC4
2) Waste loading 50 wt% (high Mo content 6.94 wt%) + Borosilicate glass-Mo-6.94%

Two types of crystalline ceramics from SRNL :

1) Waste loading 60 wt% (high Mo content 8 wt%) + TiO_2, Al_2O_3, CaO (CS/LN/TM Mo-2)
2) Waste loading 55 wt% (high Mo content 8 wt%) + TiO_2, CaO, Al_2O_3 (CS/LN/TM Mo-6)

Radiation types in waste forms

In waste-forms β, **γ-radiation** are main causes for damage



2 methods are available:

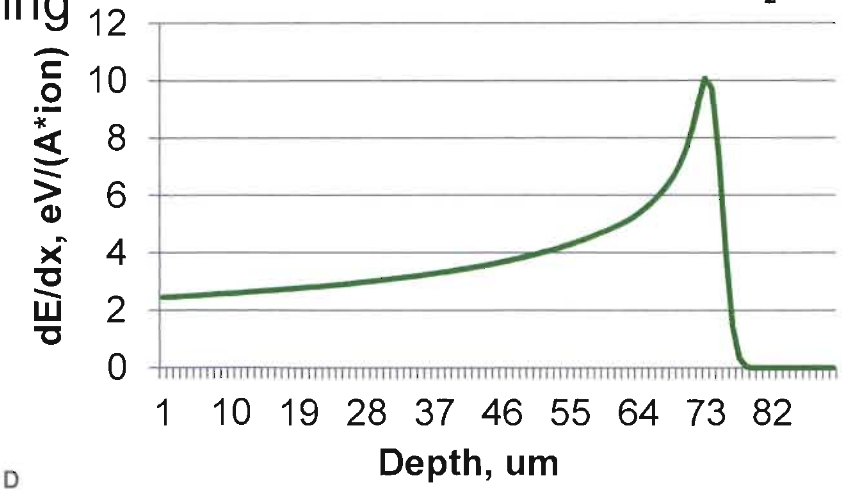
- electrons (in-situ TEM-300 kV)
- light ions (proton, alpha) - electronic stopping

Irradiation doses: 0.05-8.3 GGy

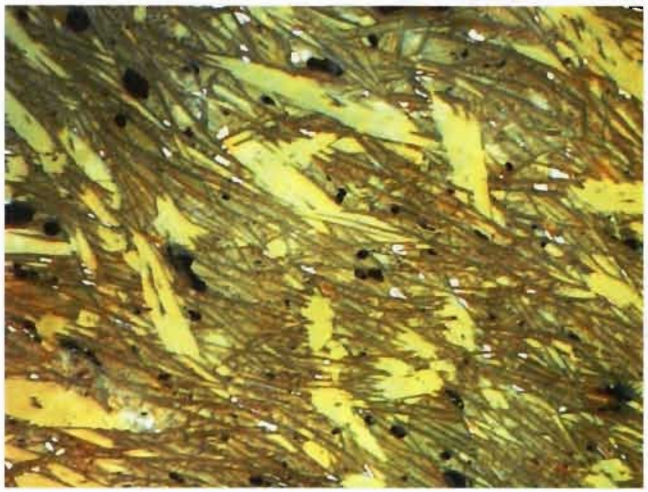
Irradiation energies: 2-5 MeV

Irradiation temperatures: 20-230 °C

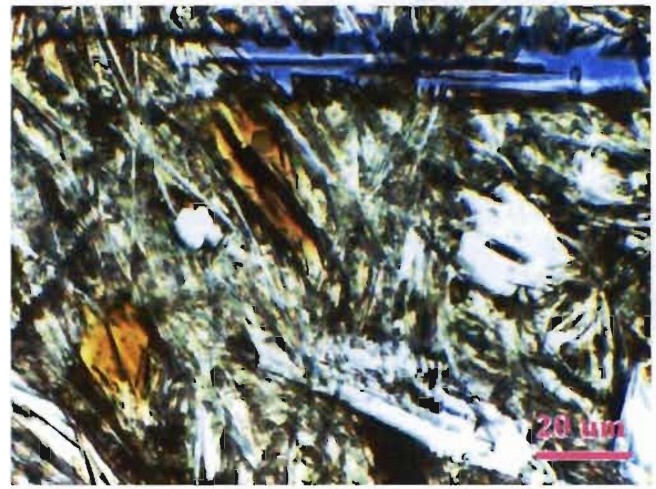
SRIM simulation: H^+ 3MeV in SiO_2



GC4

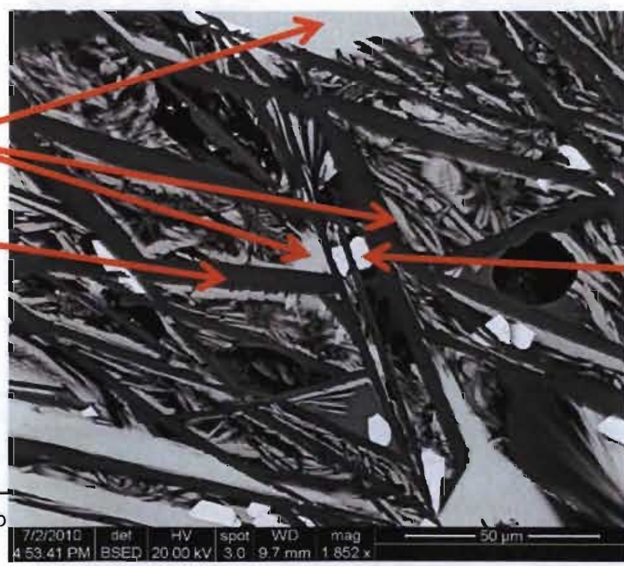


Bright Field in reflection, x200

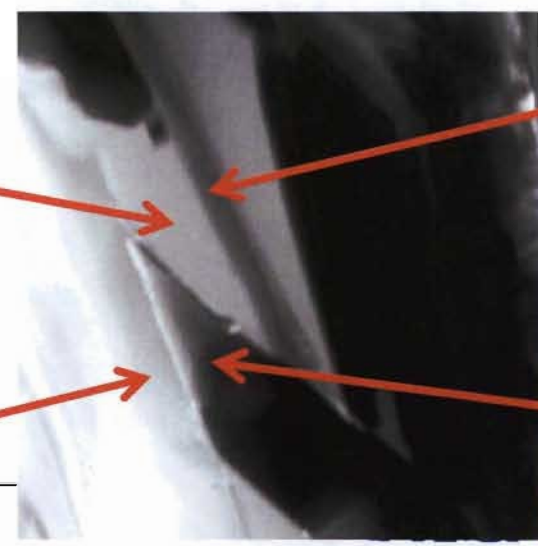


Petrographic image

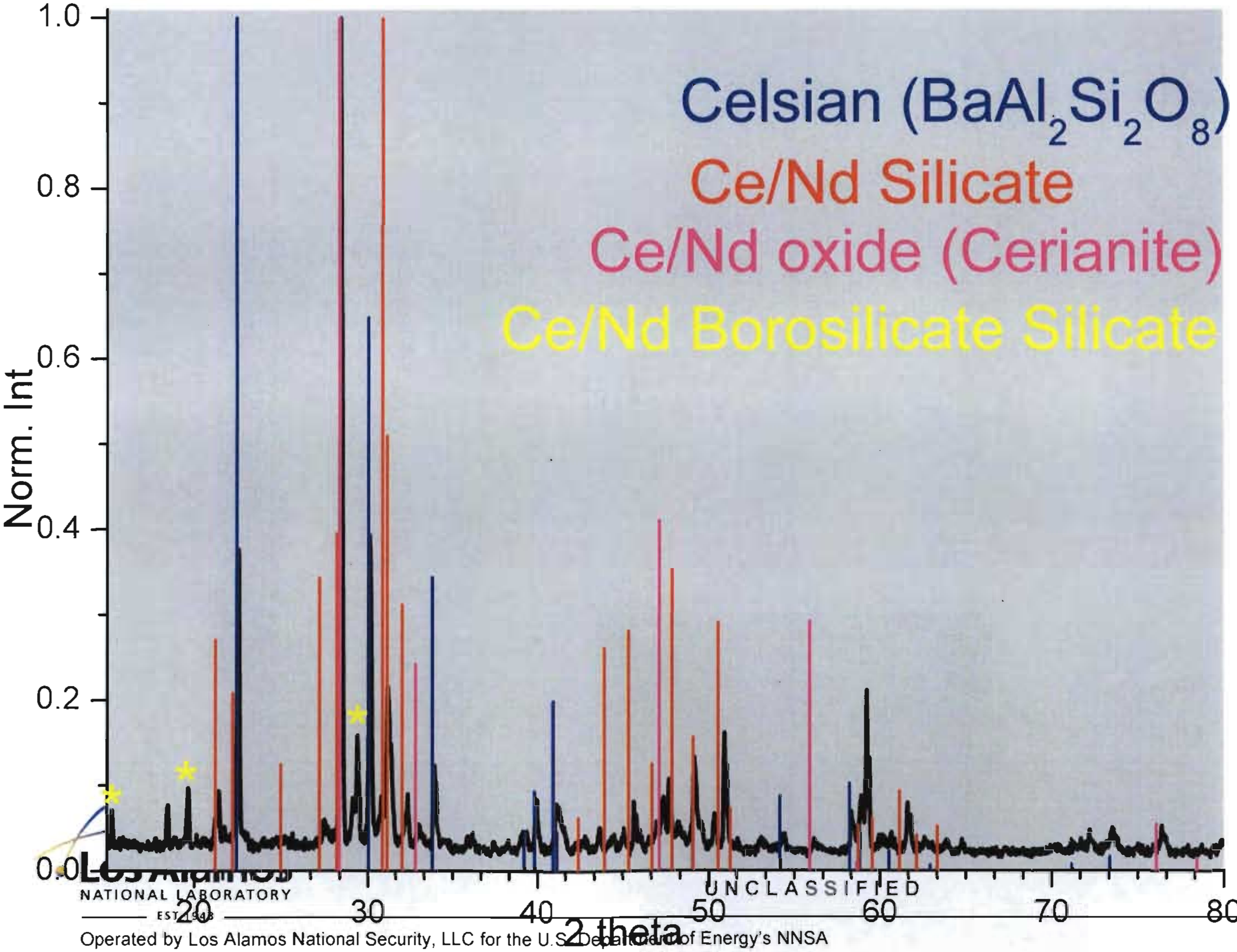
EDS (SEM):



EDS (TEM):



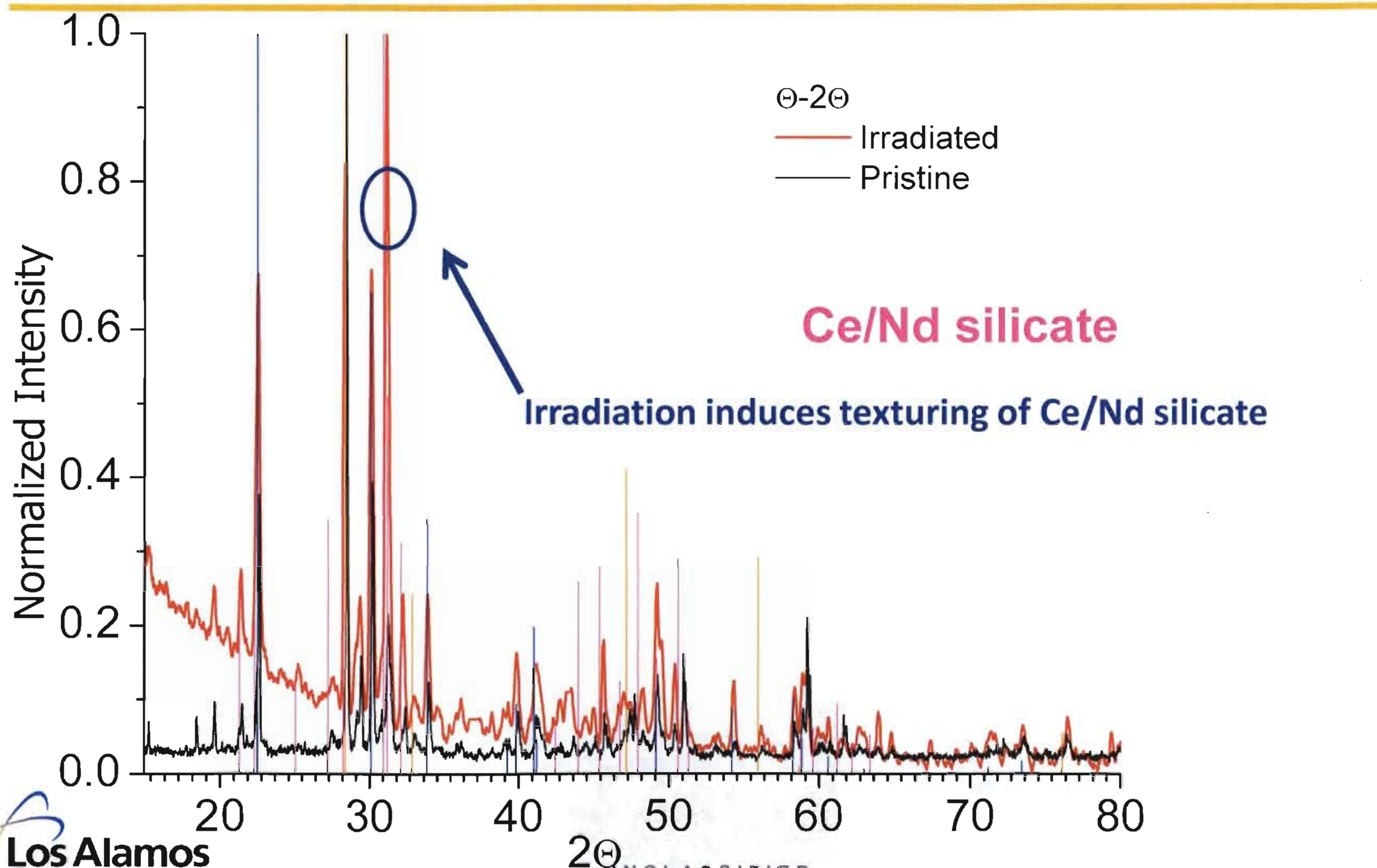
GC4: XRD



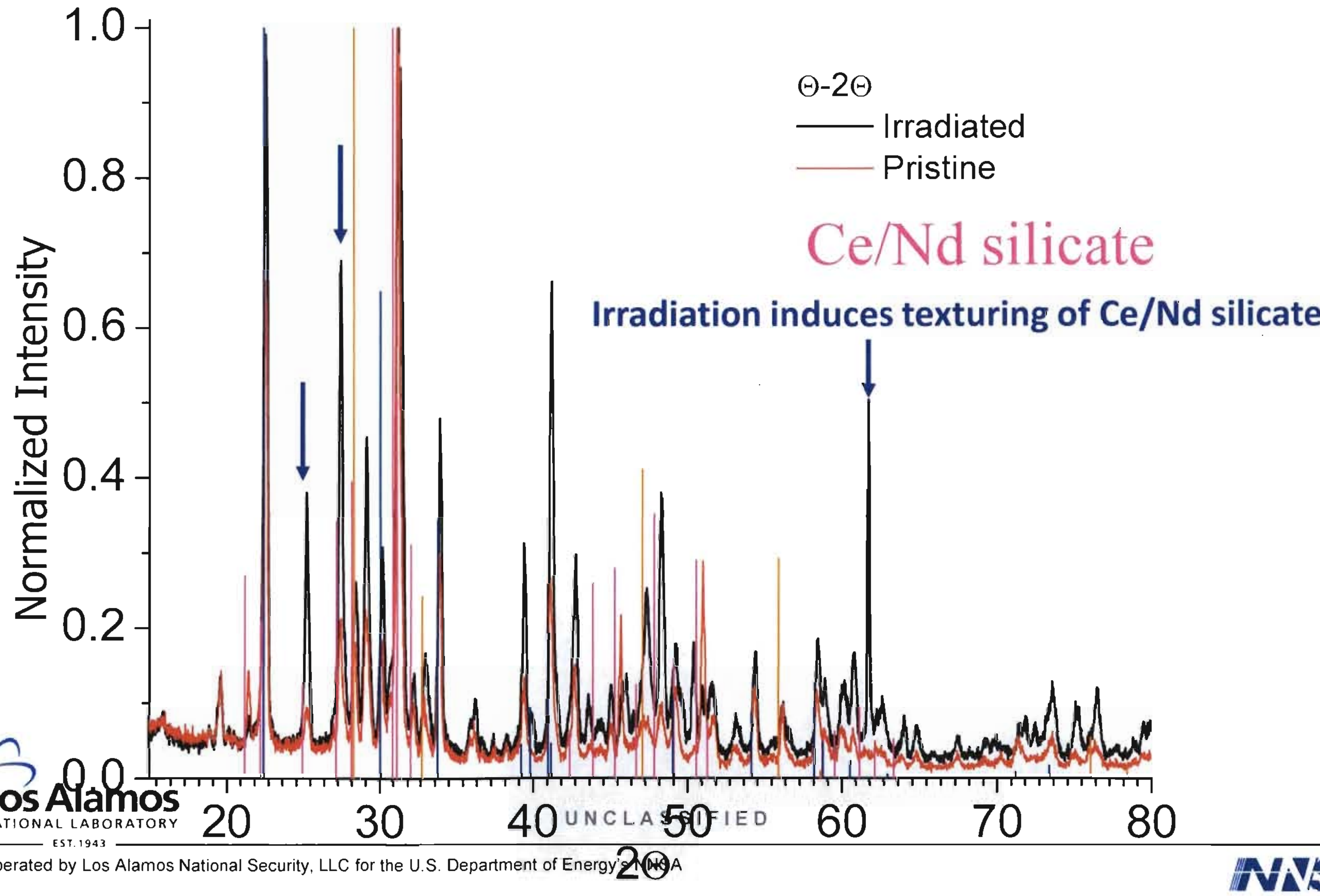
No amorphous phase

4 major phases

GC4: irradiated with 3 MeV protons (0.2 GGy)

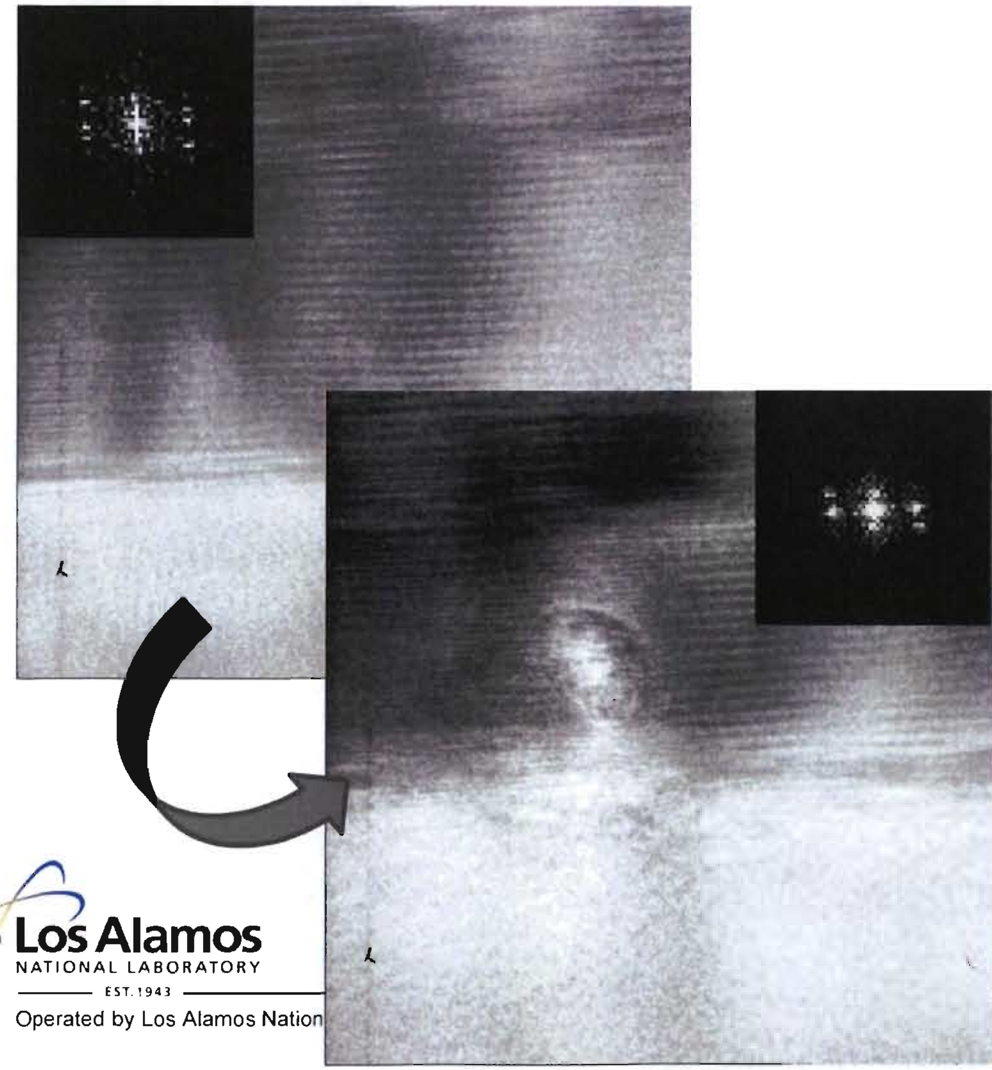


GC4: irradiated with 5 MeV alpha (8.3 GGy)

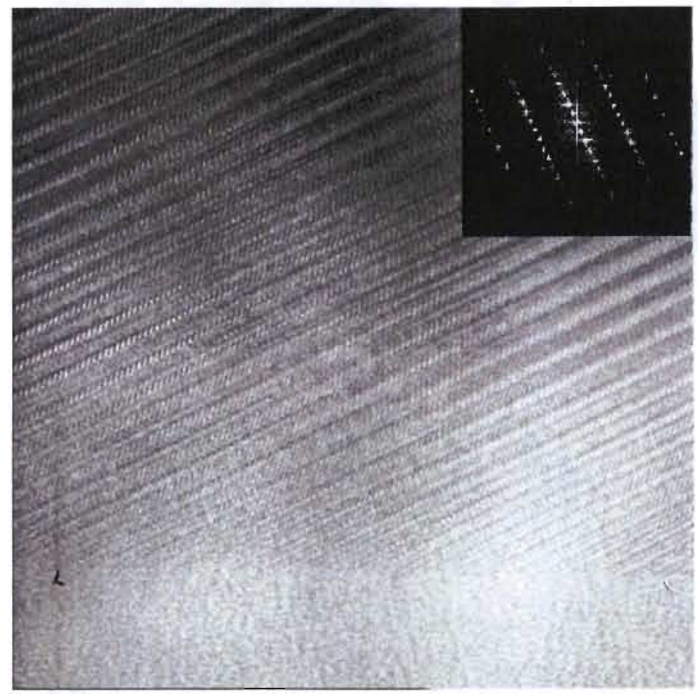


GC4: *in-situ* TEM electron irradiation (plan-view sample) @ ~1×10^{6} electrons/nm^{2}·s

Phase I : Si, Nd, Ce, O



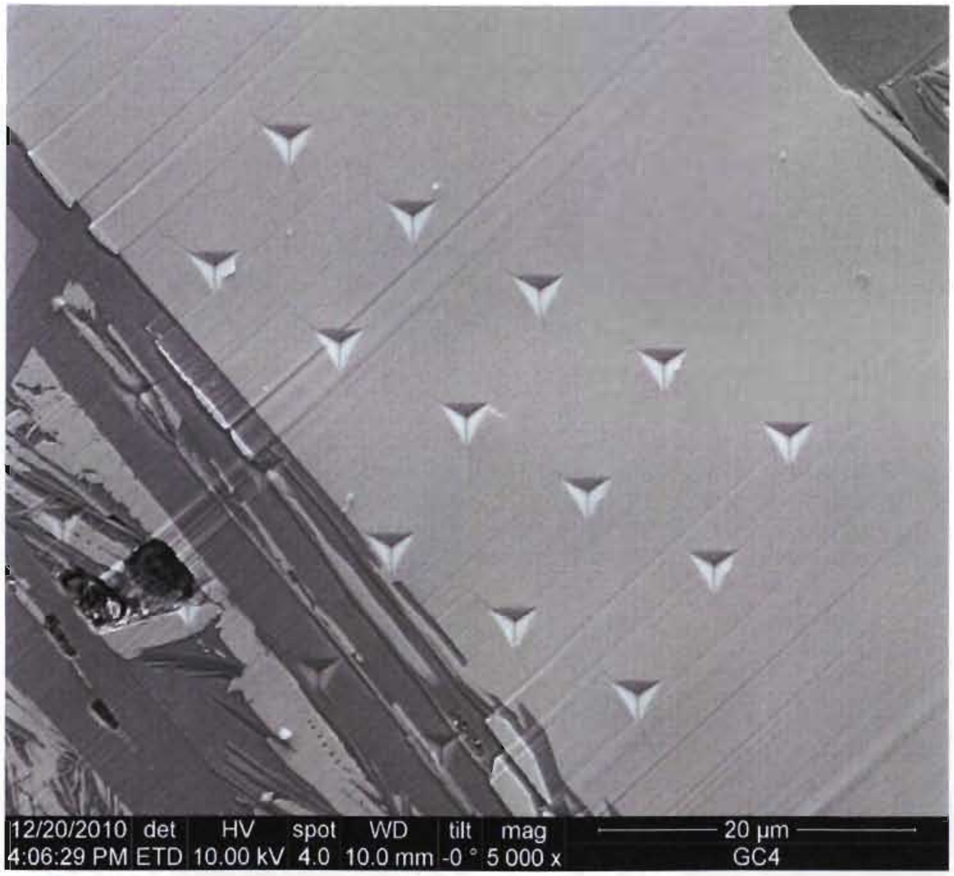
Phase II: Si, Al, O

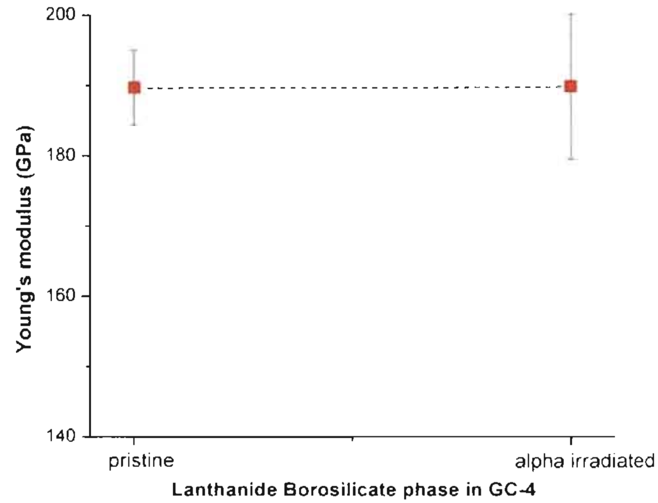


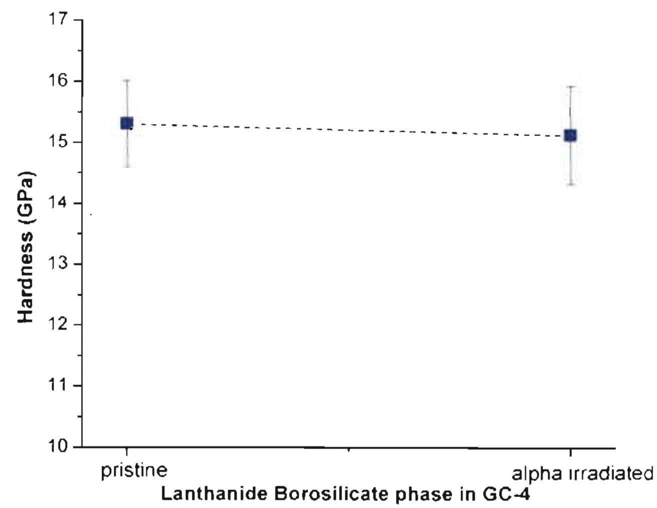
Phase I: C-C transformation due to e^{-} irradiation

Phase II: No change under electron irradiation

GC4: Mechanical properties determined by nano-indentation





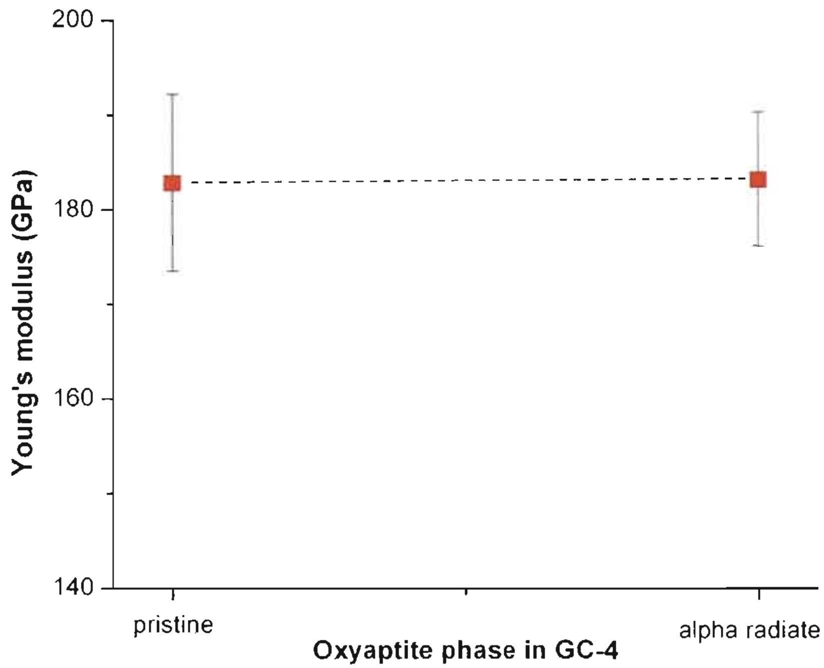


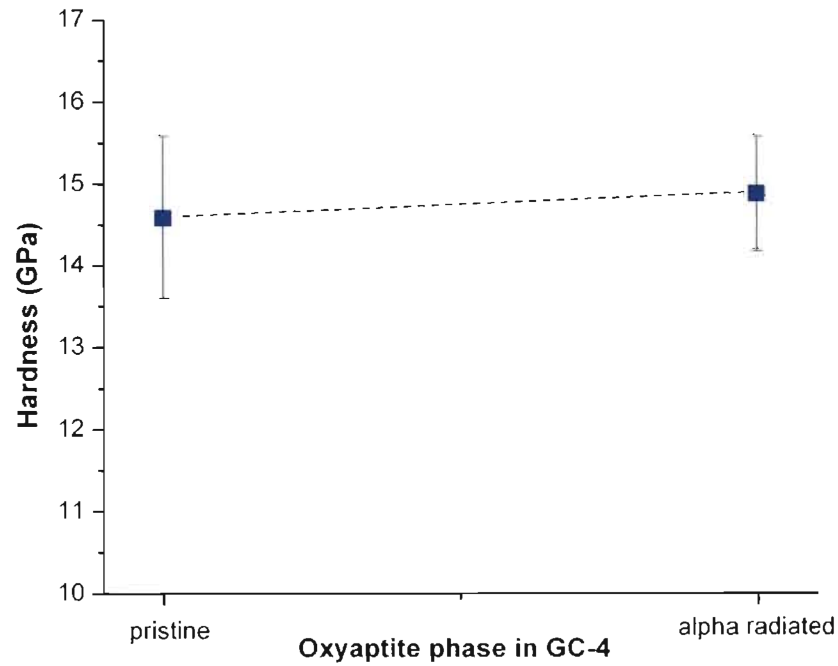
Los Alamos NATIONAL LABORATORY EST. 1943

UNCLASSIFIED

Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

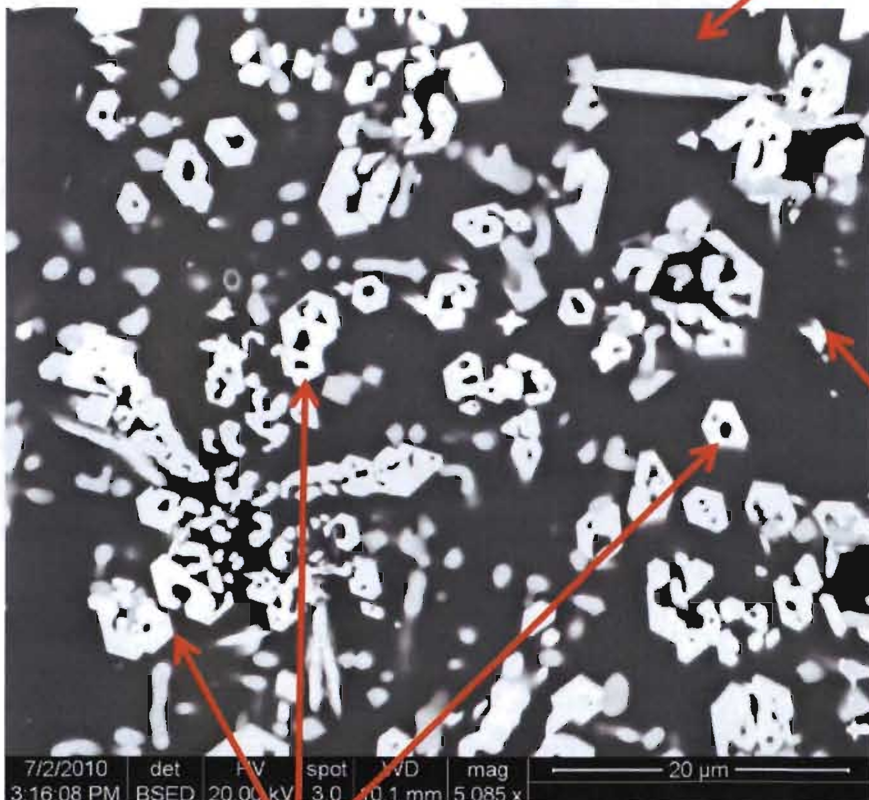
GC4: Mechanical properties determined by nano-indentation

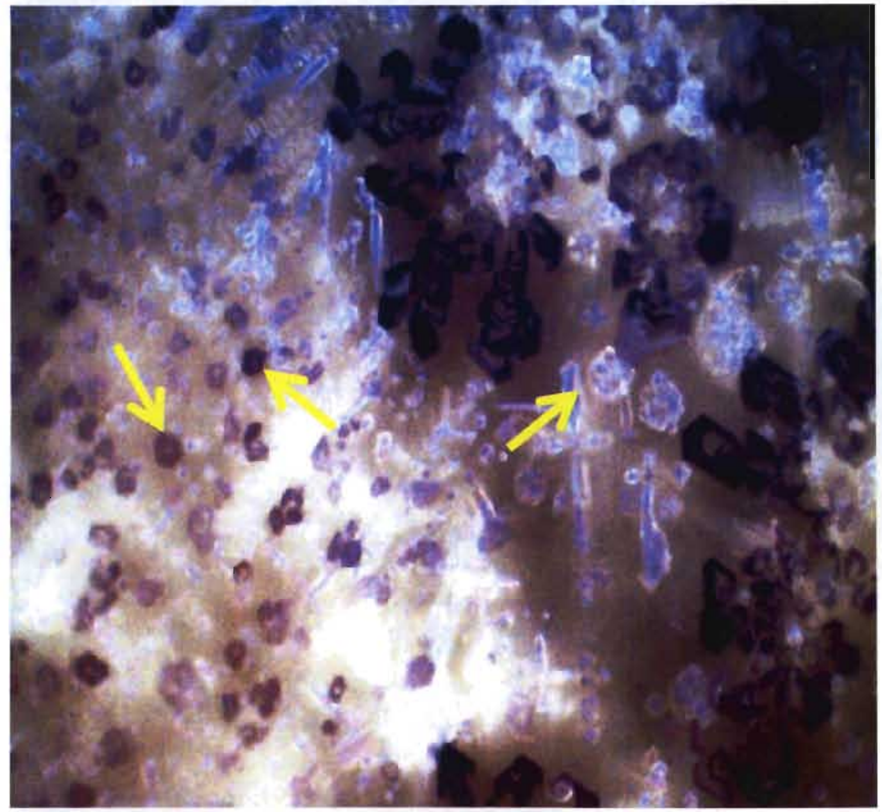




Oxyapatite-Si, Nd, Ce, O

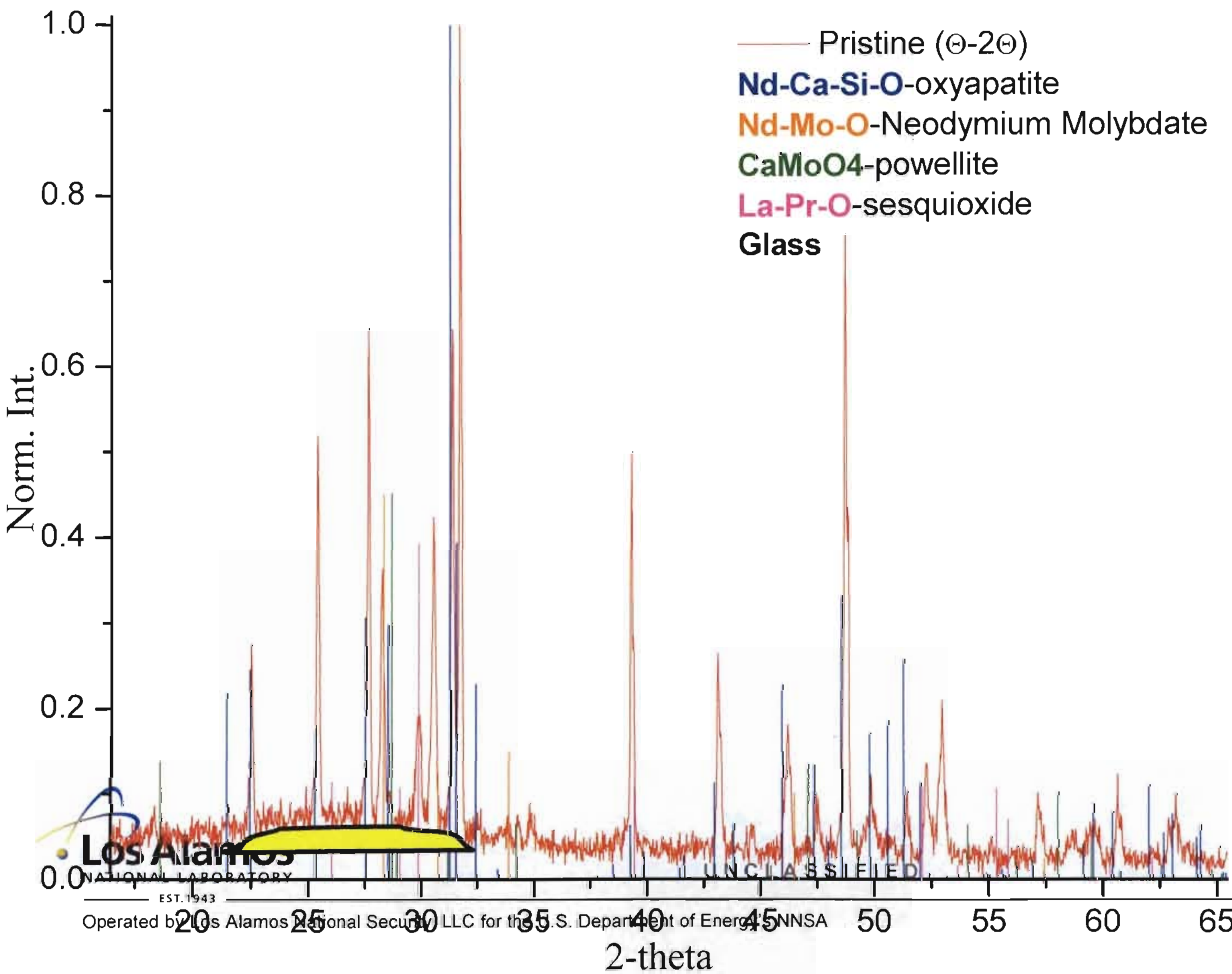
Mo-6.94%



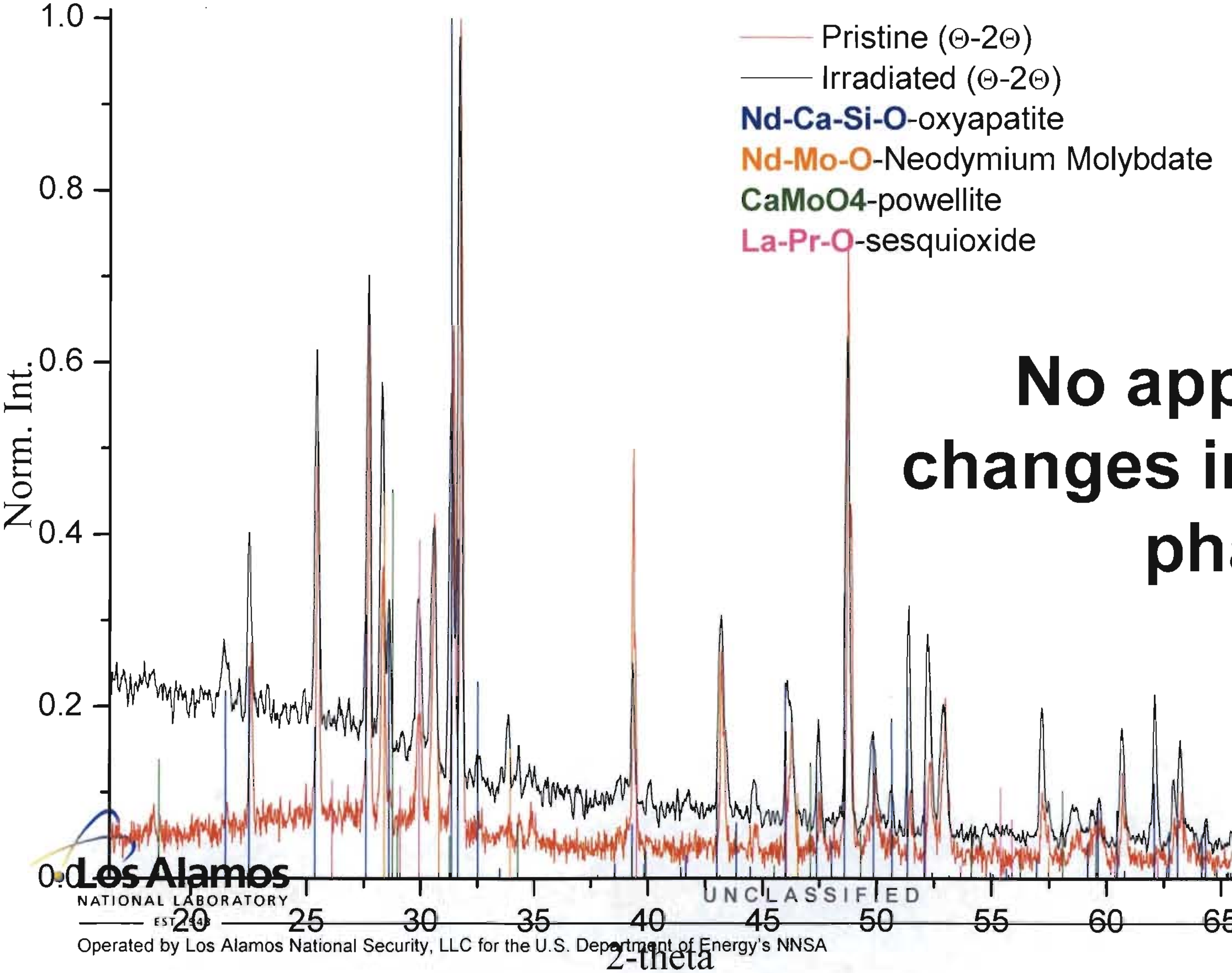


Polarized light, reflection, x1000

Mo-6.94%: XRD – 5 phases

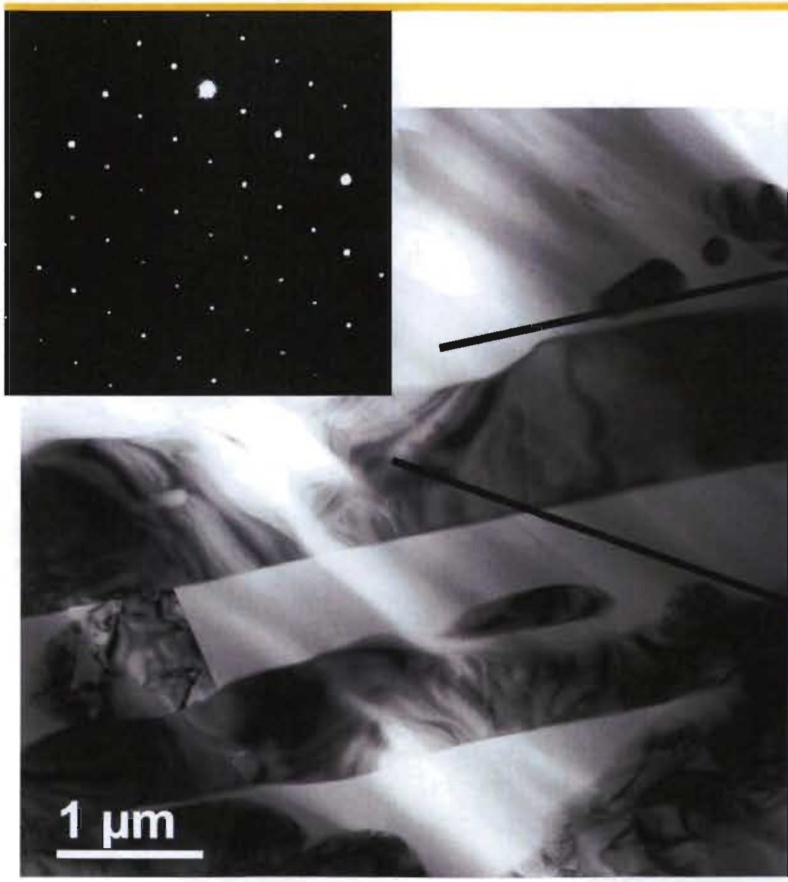


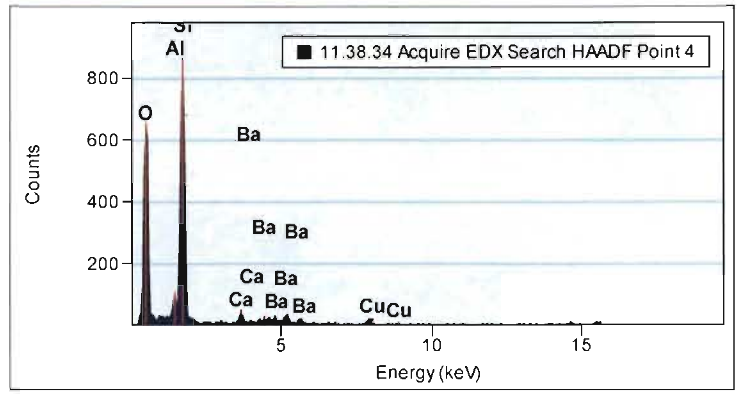
Mo-6.94%:irradiated with 3 MeV protons(0.2 GGy)



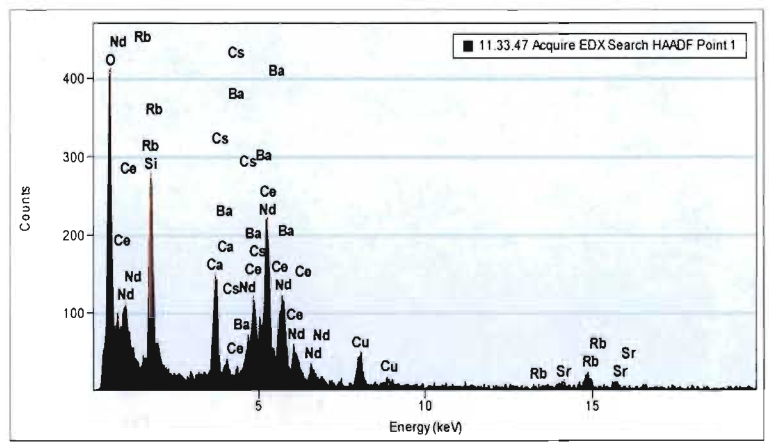
No appreciable changes in crystalline phases

Mo-6.94%: TEM (plan-view sample)





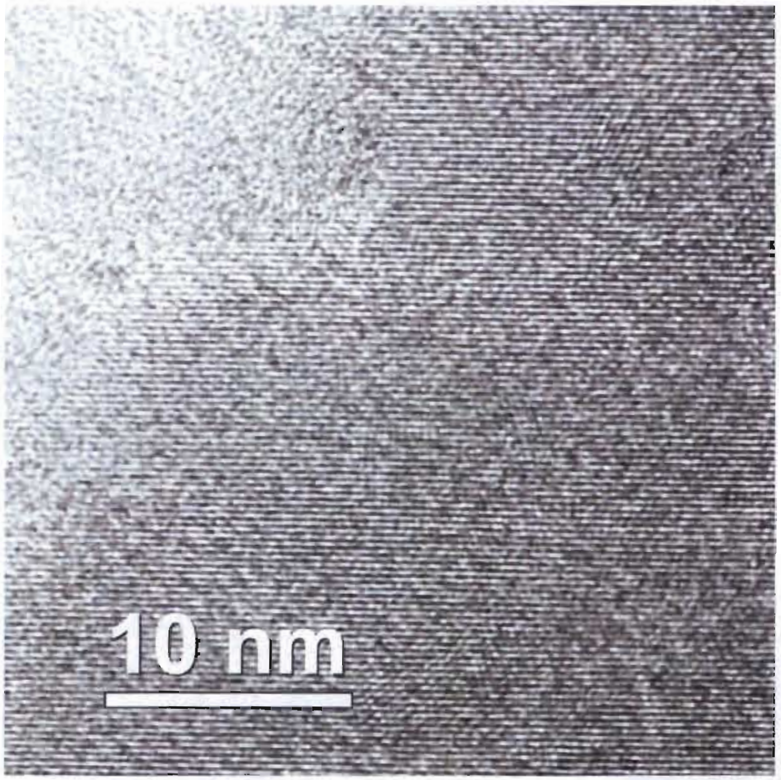
Glass-Si, Al, O



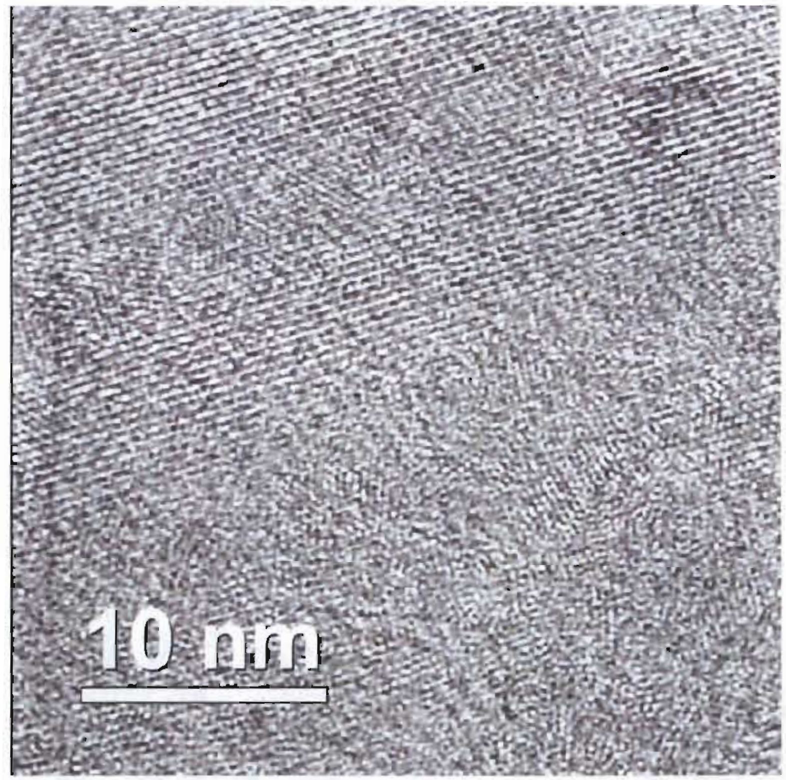
Oxyapatite-Si, Nd, Ca, O

Mo-6.94%: *in-situ* TEM electron irradiation (plan-view sample)- Oxyapatite-Si, Nd, Ca, O

start



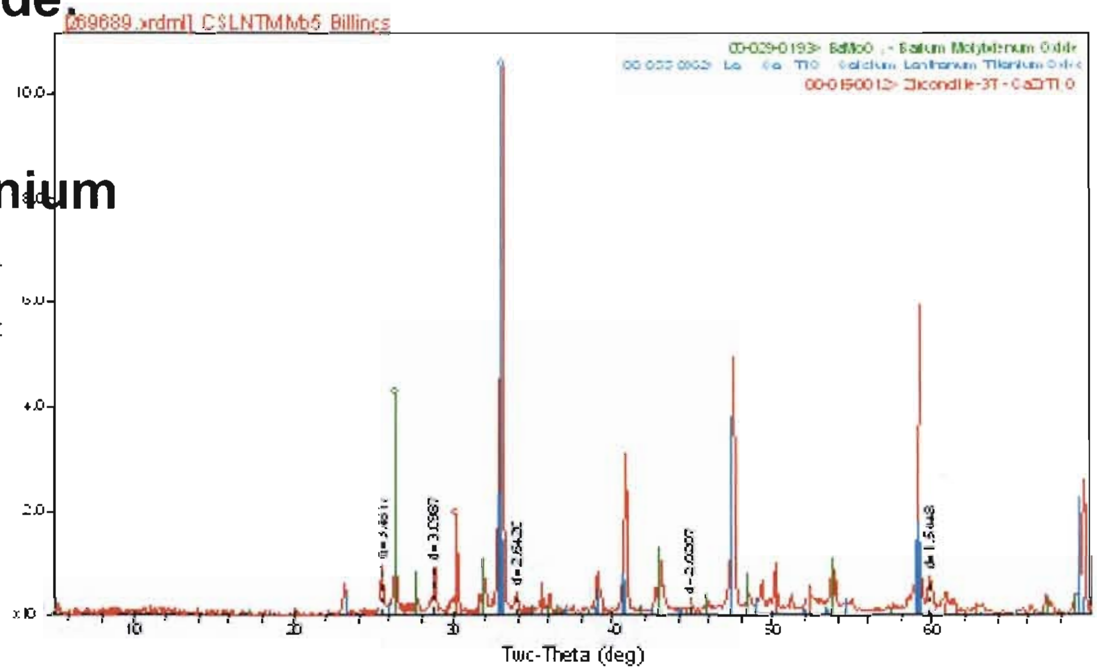
After 5 minutes



CS/LN/TM Mo-2: XRD

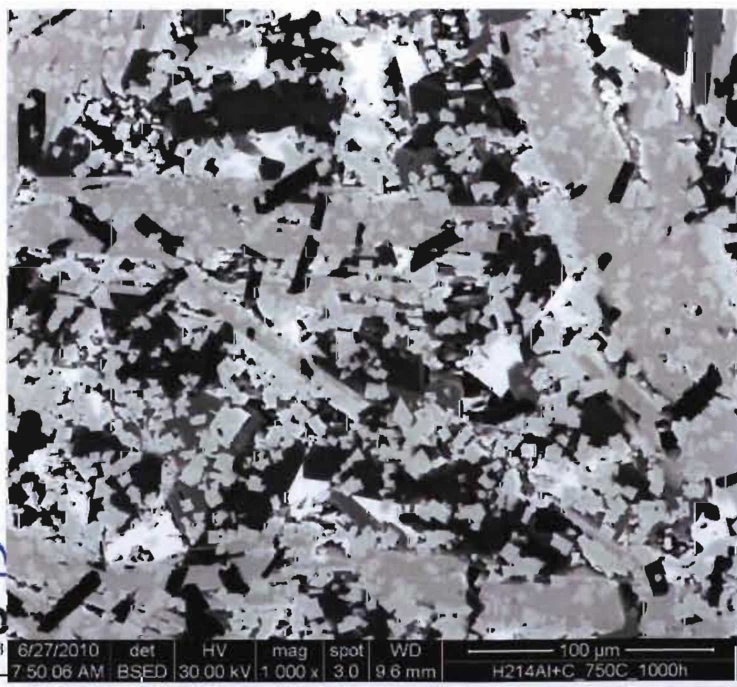
- Calcium Titanium Lanthanum Neodymium Oxide: $(CaTiO_3)_{0.4}(La_{0.33}Nd_{0.33}TiO_3)_{0.6}$
- Barium Molybdenum Oxide: $BaMoO_4$
- Calcium Lanthanum Titanium Oxide: $La_{0.13}Ca_{0.8}TiO_3$
- Zirconolite: $CaZrTi_2O_7$
- Other unidentified peaks

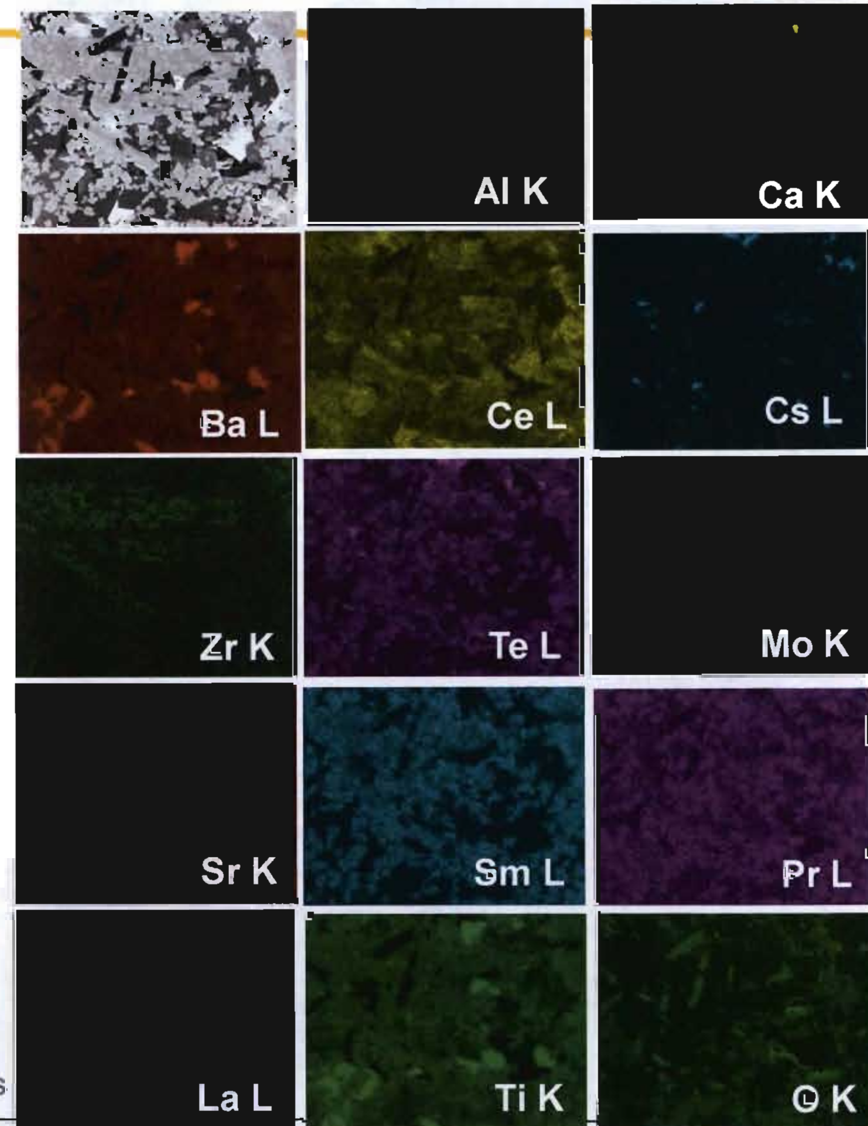
CS/LN/TM Mo - 2



CS/LN/TM Mo-2: SEM & EDX

- Unreacted Al_2O_3 evident
- $BaMoO_4$
- Identifiable perovskite, zirconolite and pyrochlore phases

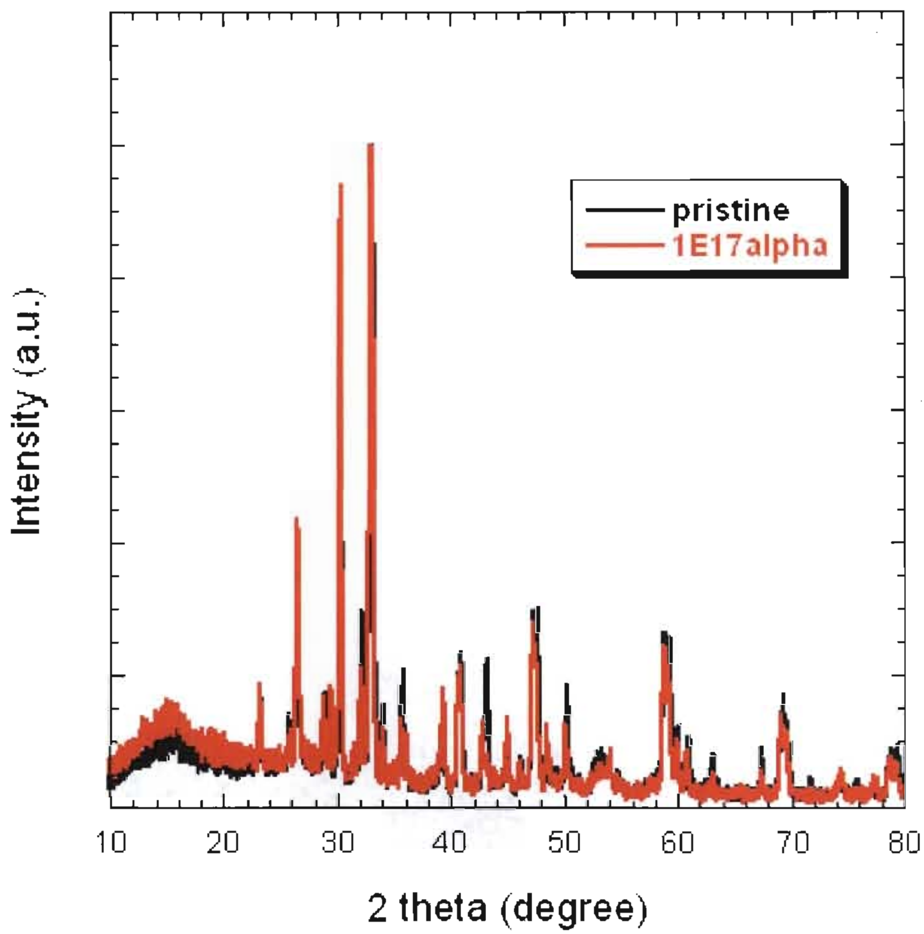




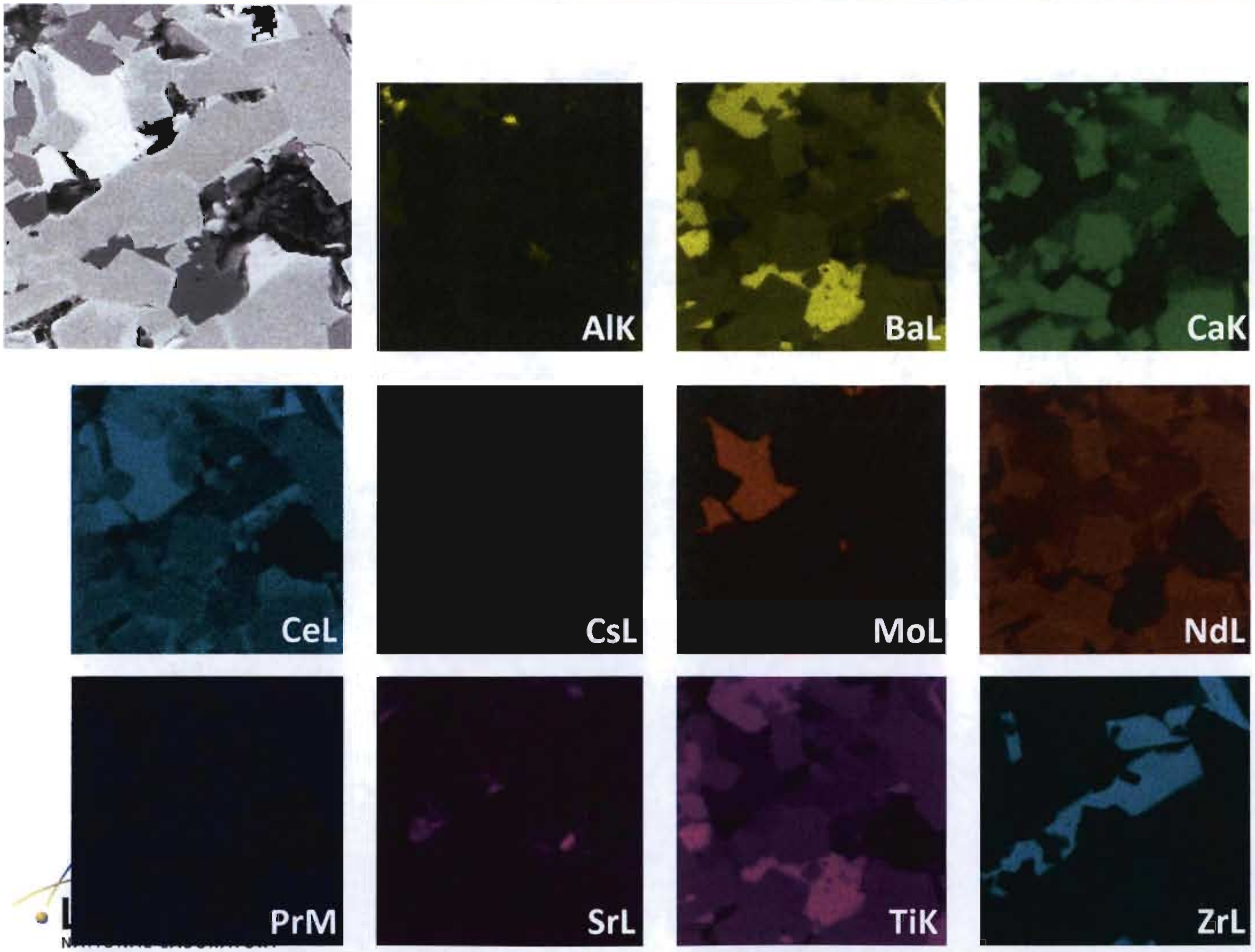
CS/LN/TM Mo-2: irradiated with 5 MeV alpha (8.3 GGy)

Little difference in XRD patterns before and after irradiation → preliminary evidence to suggest good radiation resistance

CS/LN/TM Mo-2 sample before & after 5 MeV Alpha irradiation at room temperature



CS/LN/TM Mo-6: SEM & EDX

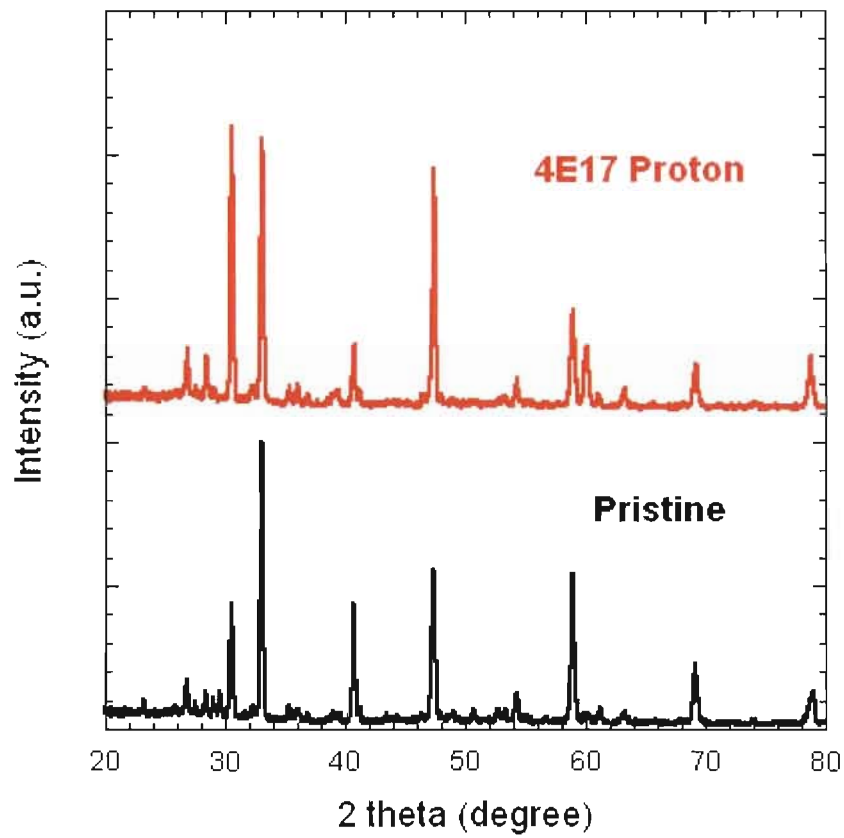


- $BaMoO_4$
- Identifiable hollandite, zirconolite and pyrochlore phases

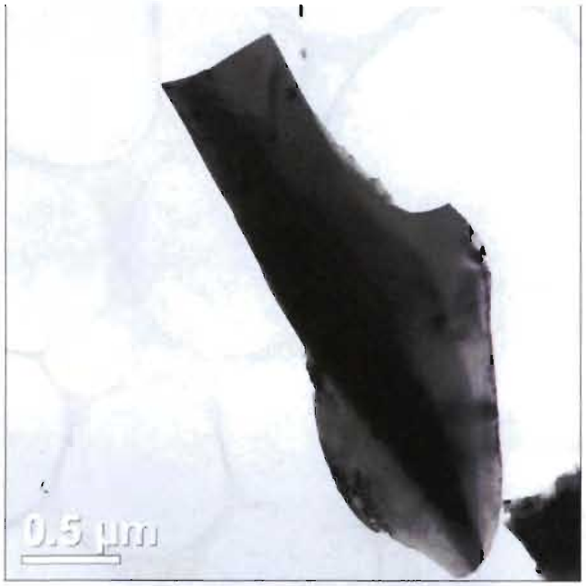
CS/LN/TM Mo-6: irradiated with 2 MeV protons (8 GGy)

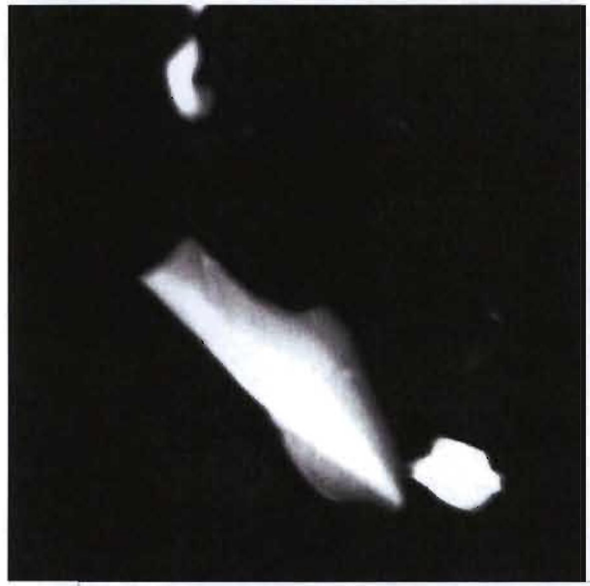
No appreciable changes in crystalline phases

CS/LN/TM Mo-6 sample before & after 2 MeV Proton irradiation at room temperature

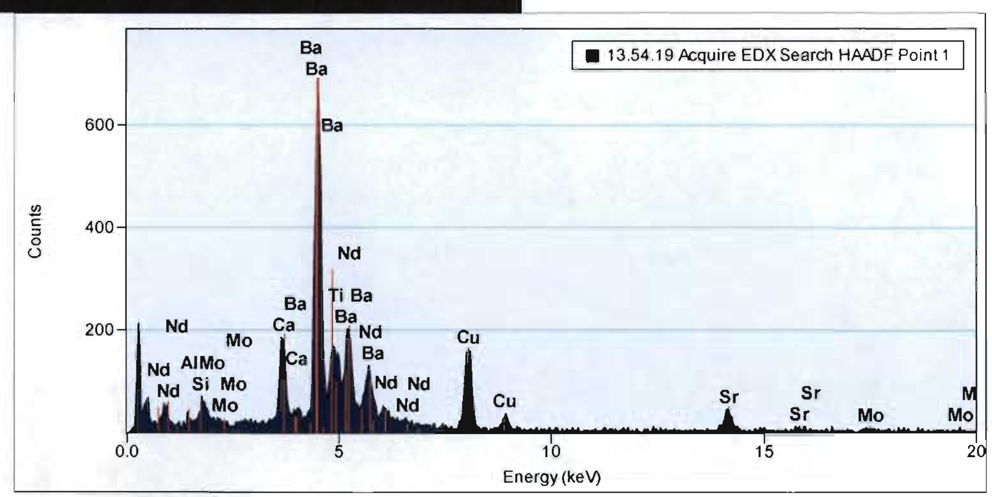


CS/Ln/TM Mo-06: TEM (powder sample)



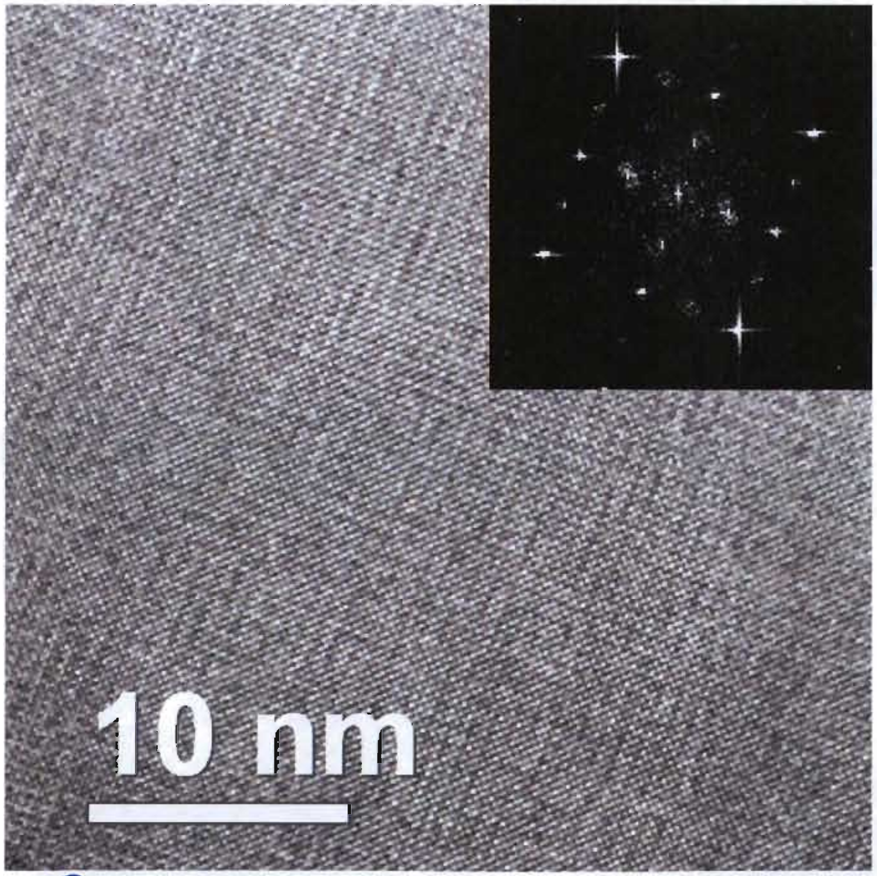


Ba, Ca, Ti, Nd, Sr, O

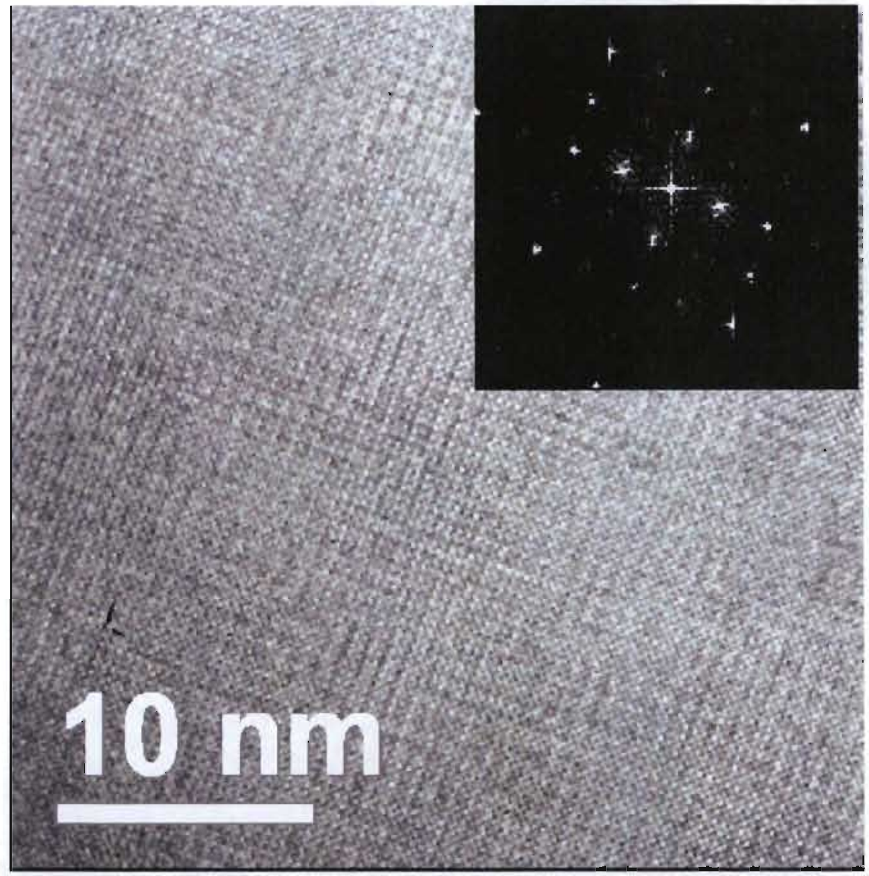


CS/Ln/TM Mo-06: *in-situ* TEM electron irradiation (powder sample)

start



After 5 minutes



Conclusions

- Successful collaboration was initiated to work on the FCR&D program to study advanced waste forms.
- Samples exhibited promising irradiation stability – no amorphization and phase separation observed.