Materials Science & Engineering

Investigation of MgO-Pyrochlore Composites and Spinel Compounds as Potential Inert Matrix Materials: ATR Experiment Overview and Results

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  - ATR-NSUF UF Experiment Contract 00077669

Outline

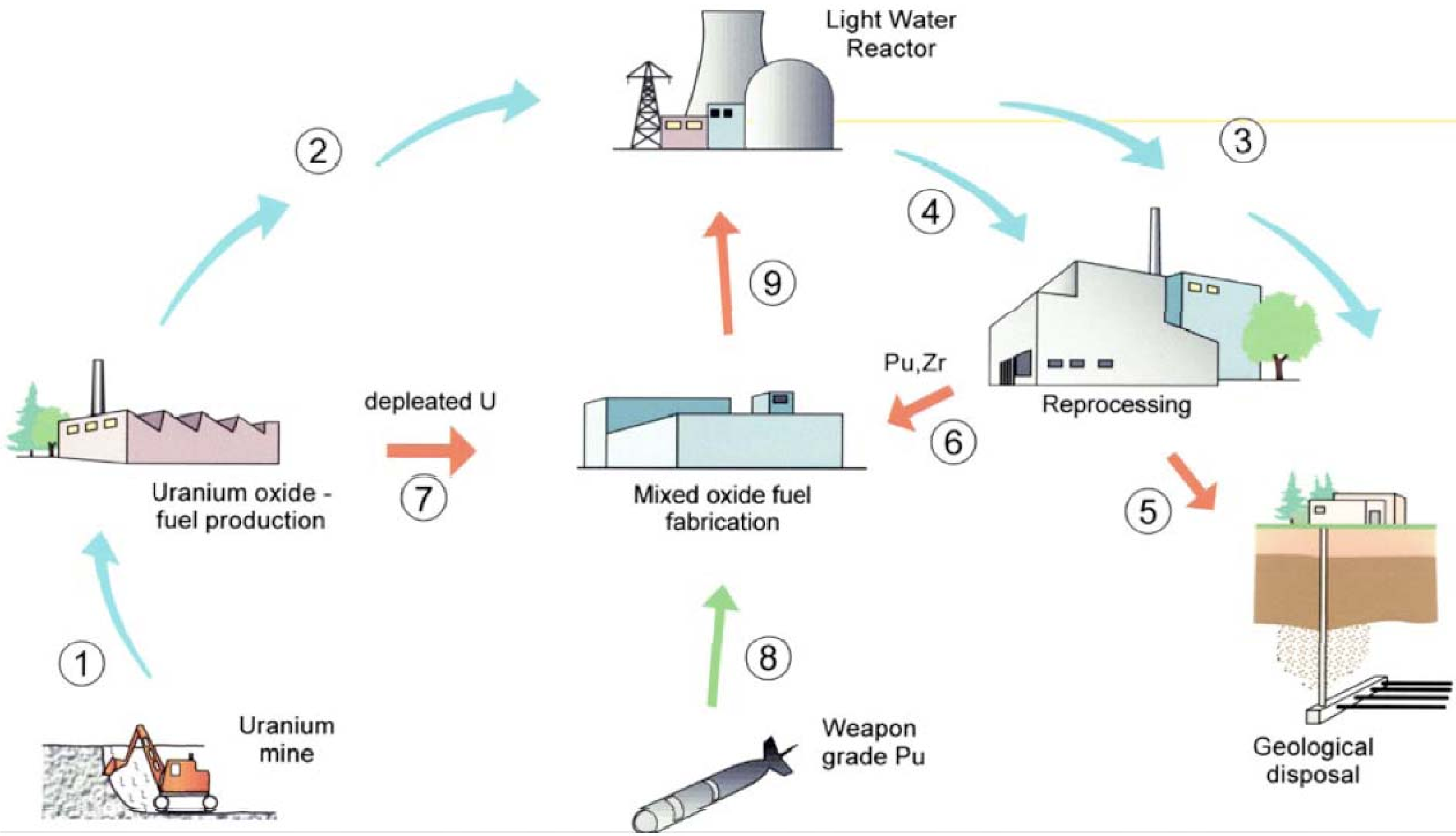
- Background and Motivation
- Materials Selection
- Summary of Prior Out-of-Pile Research
- ATR-NSUF Experiment Overview and Results
- Summary and Outlook

Background Problem

- Continuously increasing inventory of nuclear waste:
  - ~2000 mT of Pu created in nuclear reactors since 1941
  - 70-80 mT of new Pu from spent fuel added to the inventory each year
- Production of other minor actinides such as ^{237}Np, ^{241}Am, ^{243}Am, and ^{244}Cm

IAEA (2006)
IAEA (2007)

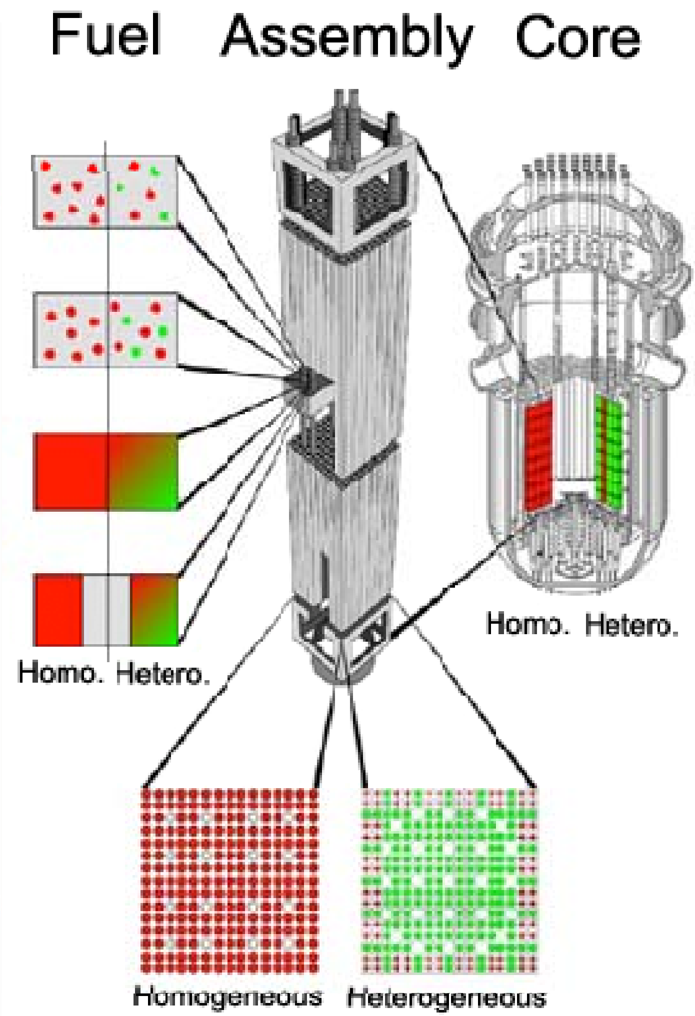
Nuclear Fuel Cycle



Courtesy IAEA

Opportunity

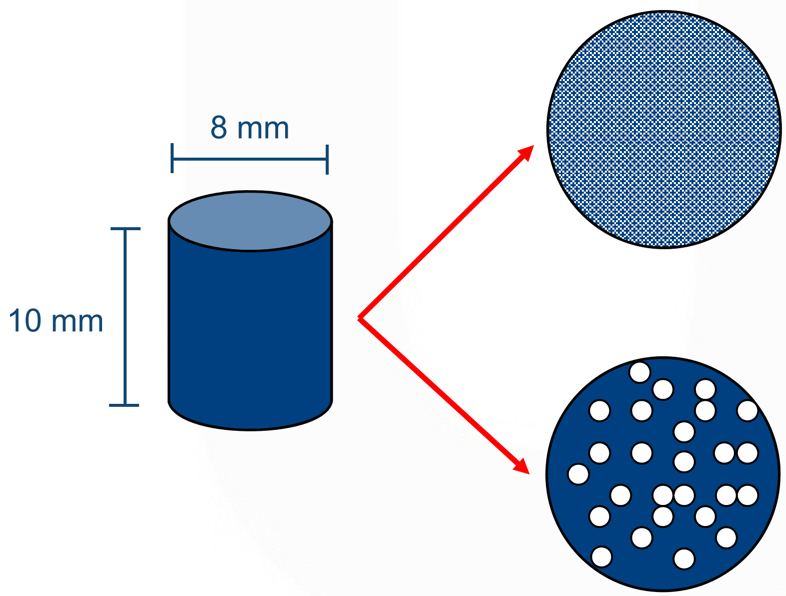
- Utilize light water reactors (LWRs) to burn or reduce Pu inventory by transmutation.
- While effective, MOX fuels lead to the production of new actinides.



Degueldre et al. *J. Nucl. Mater*. (1999).

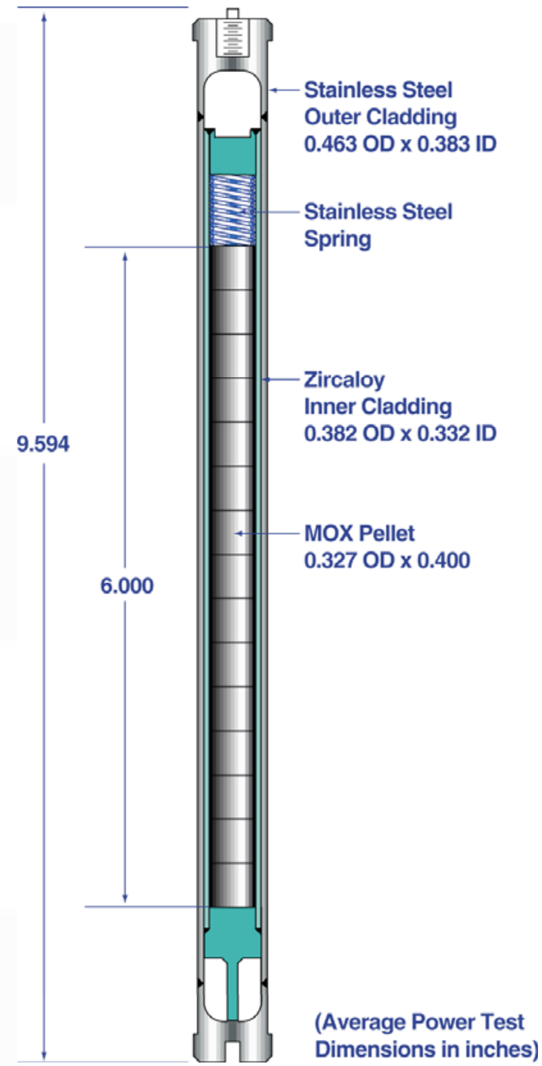
Inert Matrix Fuels

- Create a non-fertile matrix to support Pu or minor actinides in nuclear fuel
  - Metal or oxide
  - Single homogeneous phase or multi-phase heterogeneous material



<u>Single Phase</u>
(Microdispersion)

<u>Two-Phase Composite</u>
(Macrodispersion)



Courtesy J. Carmack, INL

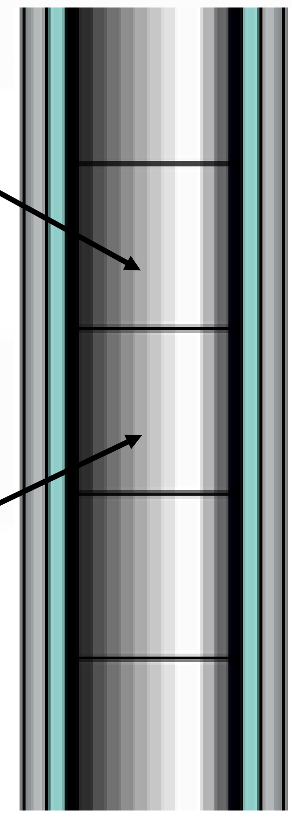
Inert Matrix Properties

Required IM Properties

- Neutron Transparency
- High Melting Point
- Good Irradiation Behavior
- High Temperature Phase Stability
- Cladding Compatibility
- Low Solubility in the Reactor Coolant

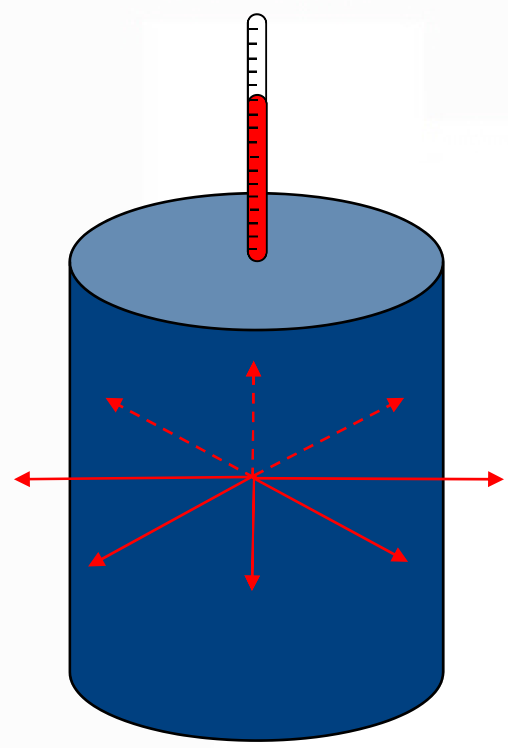
Desired IM Properties

- High Thermal Conductivity
- Soluble in Nitric Acid

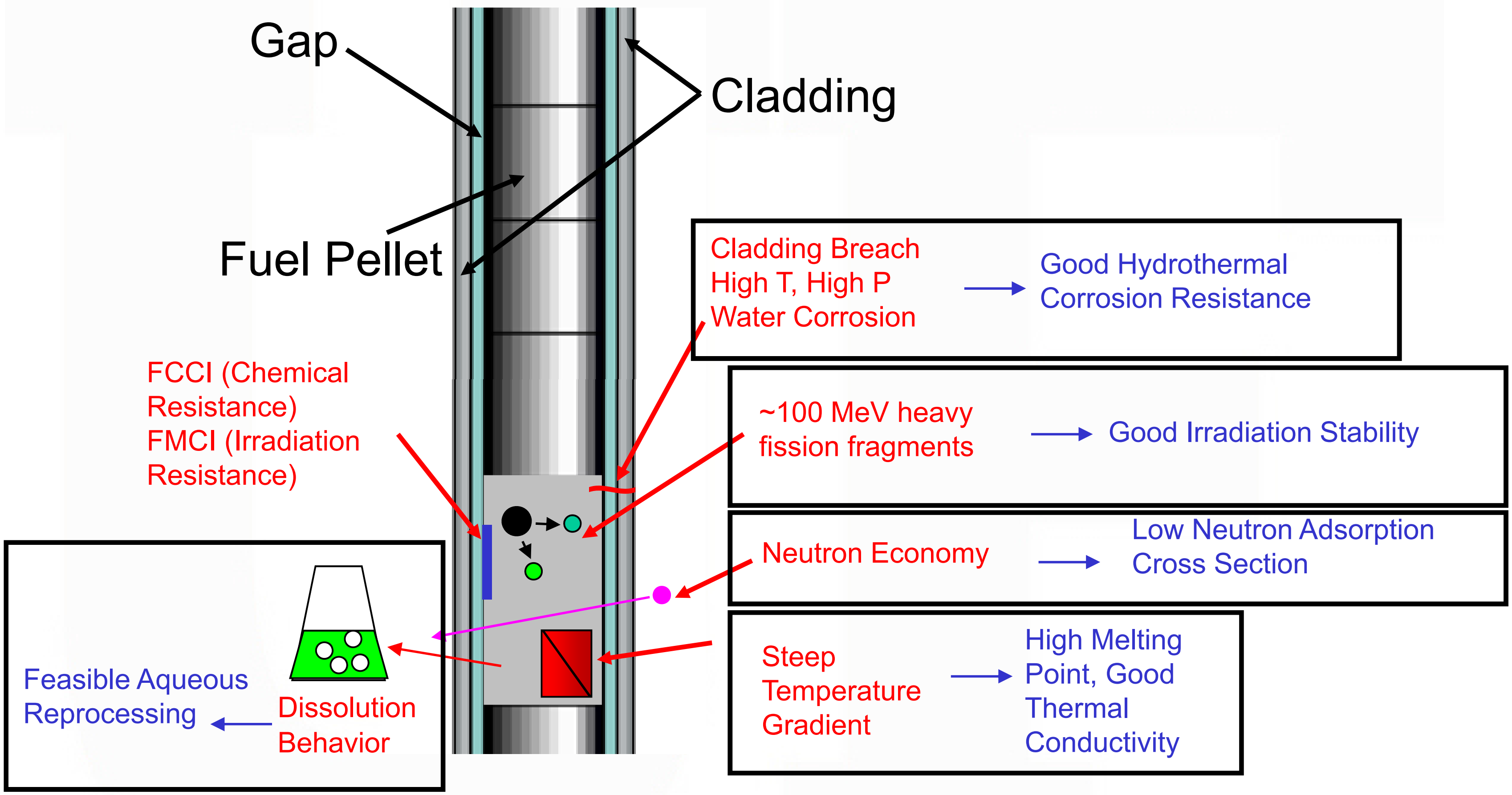


Thermal Conduction

- A viable IMF must possess a thermal conductivity to melting point ratio that meets or exceeds that of UO_2.
- More thermally conductive fuels decrease the centerline fuel temperature.



Inert Matrix Properties



H. Kleykamp, *J of Nucl Mater* **275** [1] 1-11 (1999).

IMF Candidate Materials

- IMF Candidate Materials [1]:
  - Fluorite: ZrO_2 (difficult to recycle, poor K_{th}), CeO_2
  - Corundum: Al_2O_3 (poor neutron irradiation behavior at high dpa)
  - Zircon: $ZrSiO_4$ (low dissolution temperature) [2]
  - Nitride: Si_3N_4
  - Carbide: SiC (difficult to recycle)
  - Pyrochlore: $Nd_2Zr_2O_7$ [3]
  - Spinel: $MgAl_2O_4$ (poor in-pile irradiation behavior)
  - Rocksalt: MgO (poor corrosion resistance)

New potential IM materials or strategies are needed…

[1] H. Matzke et al., *J Nucl Mater* **274** [1-2] 47-53 (1999).
[2] M. Burghartz, *Chimia* **51** [7] 414 (1997).
[3] S. Lutique et al., *J Nucl Mater* **319** 59-64 (2003).

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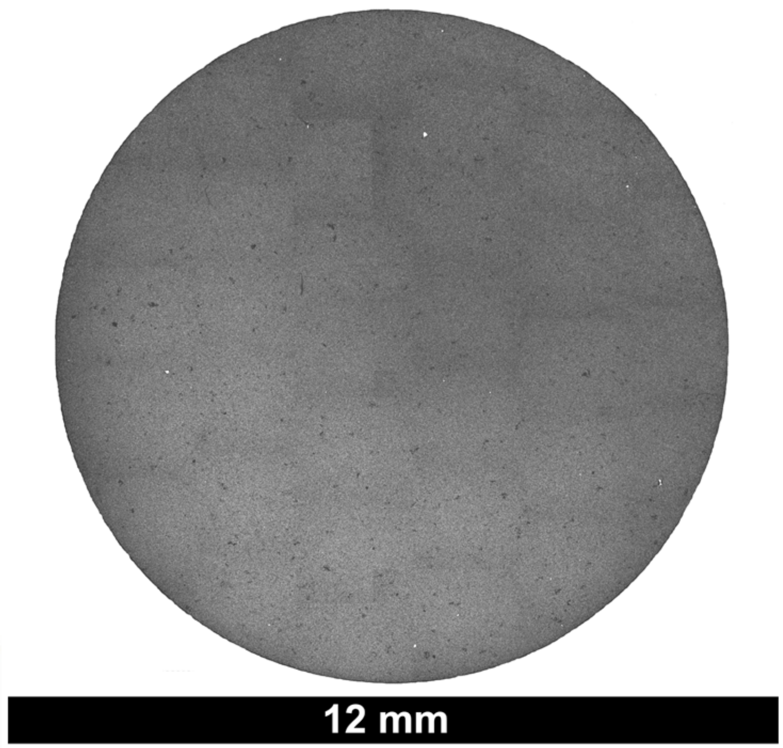
MgO-Pyrochlore Composites

Since IMFs are intended for LWRs they should perform as well or better than UO_2.

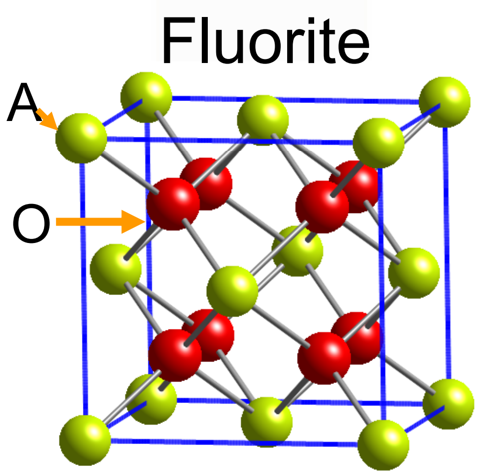
- YSZ is a primary IMF candidate.
  - Low thermal conductivity
  - Difficult to reprocess using conventional methods
- MgO is attractive but not stable in water.
- $MgO-ZrO_2$ composites were investigated at INL.



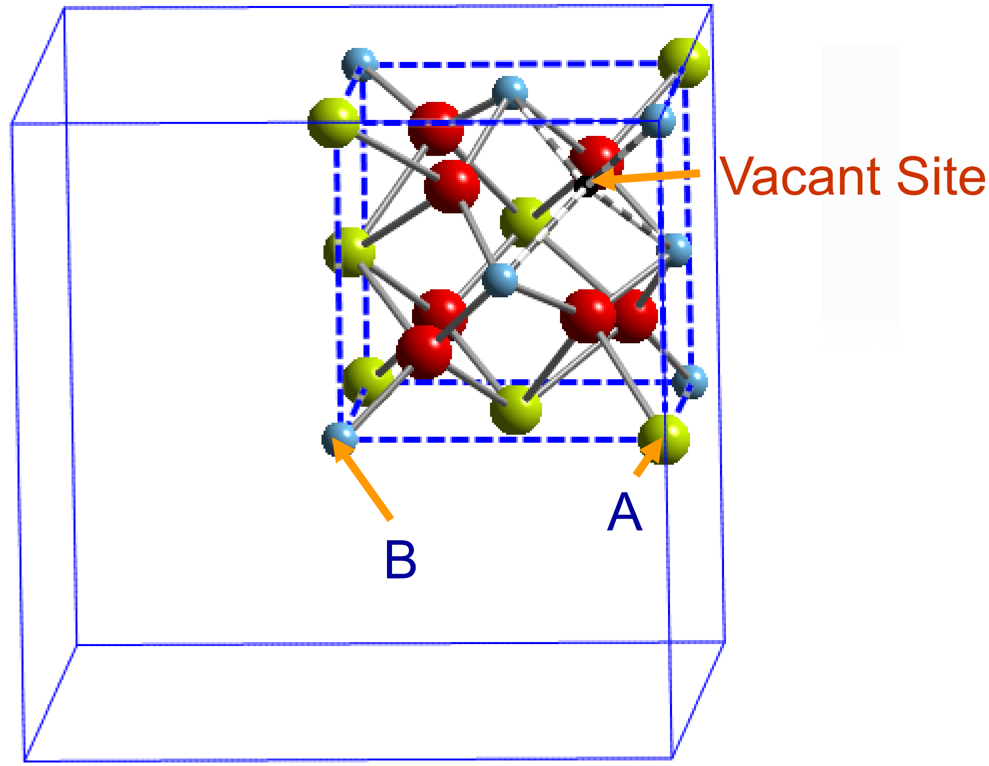
Prior work performed under
US DoE - DE-AC07-05ID14517

Fluorite➔ Pyrochlore

Lattice parameter
Fluorite: a
Pyrochlore: 2a



General formula: AO_2
Space group: $Fm\bar{3}m$



Pyrochlore
(1/8 unit cell)

General formula: $A_2B_2O_6O'$
Space group: $Fd\bar{3}m$
Wyckoff position:
8a for vacant site
48f for O
8b for O' (if B is origin)

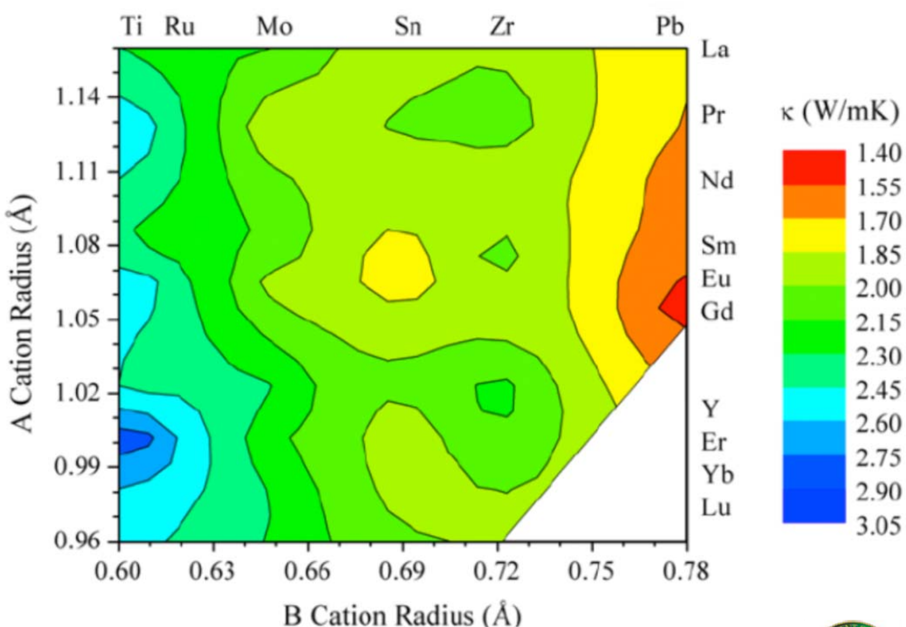
Prior work performed under
US DoE - DE-AC07-05ID14517

Pyrochlore Selection

Unacceptably large neutron absorption cross-sections eliminates pyrochlore compositions with the rare earth oxides:

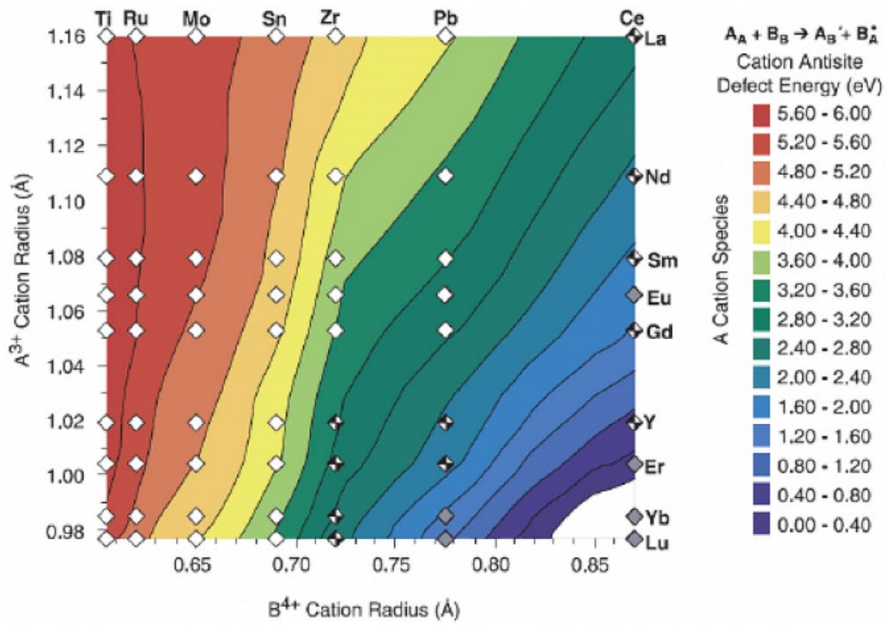
Gd_2O_3 Sm_2O_3 Eu_2O_3

Predicted Thermal Conductivity



Schelling, Phillpot, et.al. *Phil Mag Lett*. 2004.

Cation Antisite Defect Energy



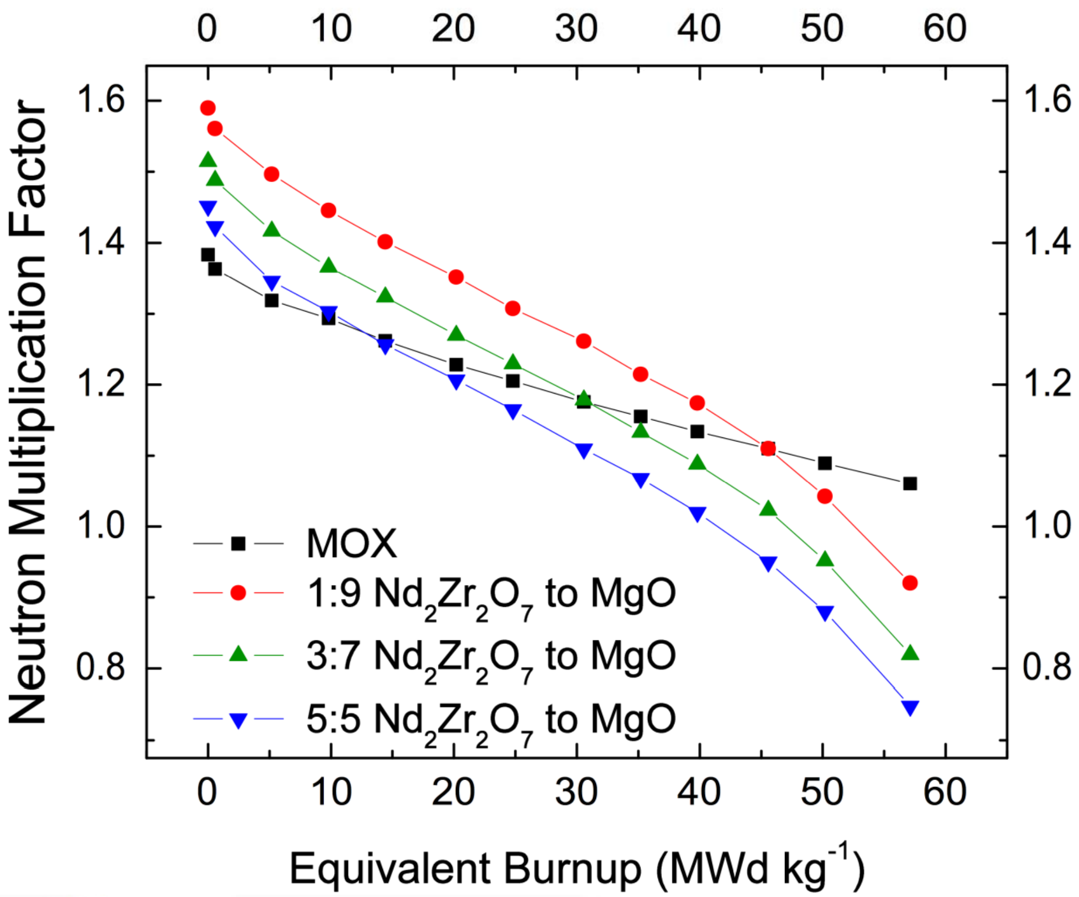
Sickafus, Minervini, Grimes, et.al. *Science*. 2000.

$Nd_2Zr_2O_7$ is down-selected from the remaining candidate pyrochlore compositions due to its better radiation tolerance.

Prior work performed under
US DoE - DE-AC07-05ID14517

Composite Composition

- Simulation based on 8 vol% weapons grade PuO_2 as fissile phase.
- Calculations show the best ratio of $Nd_2Zr_2O_7$ to MgO is 3:7.

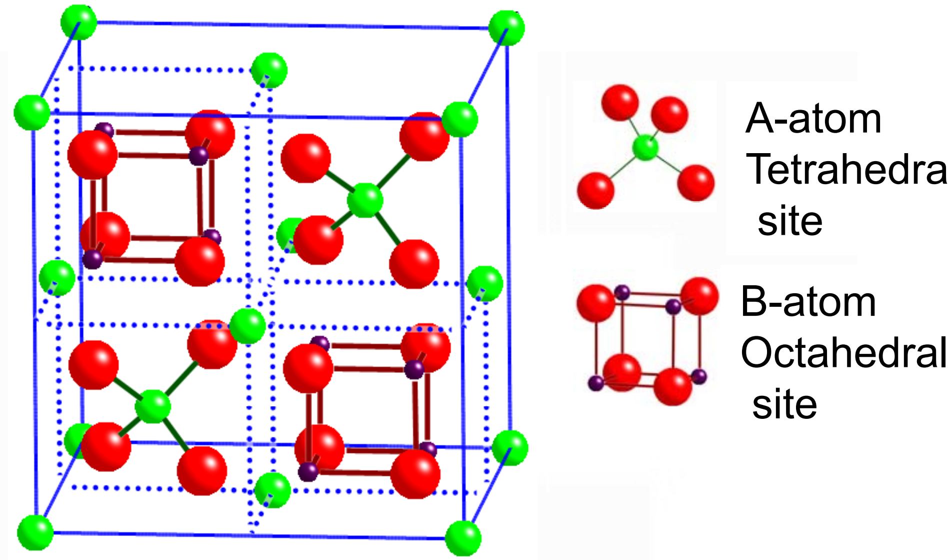


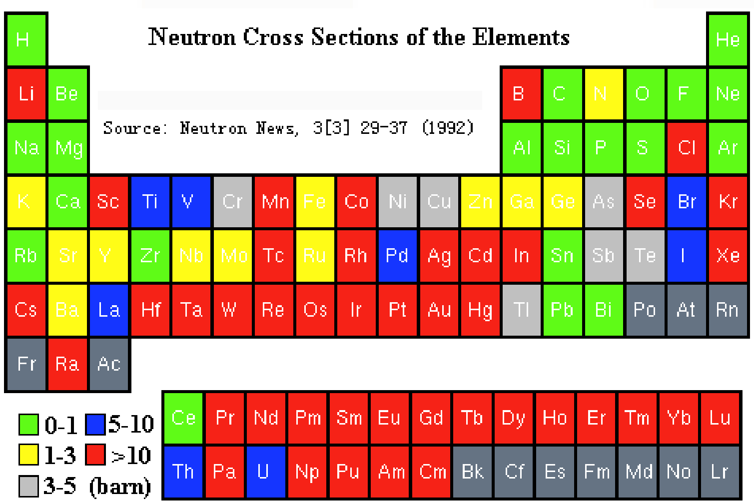
Yates, Xu, et al. *J. Nucl. Mater.* (2007).

Prior work performed under
US DoE - DE-AC07-05ID14517

Spinel Selection

- Versatile structure, over 200 spinel compounds reported.
- Good irradiation resistance
  - Anti-site cation disorder
  - Interstitial-vacancy recombination
  - Multi-component chemistry suppresses nucleation and growth of dislocation loops during irradiation





- Low neutron adsorption cross section
- Large, heavy ion
  - Magnesium stannate (Mg_2SnO_4)

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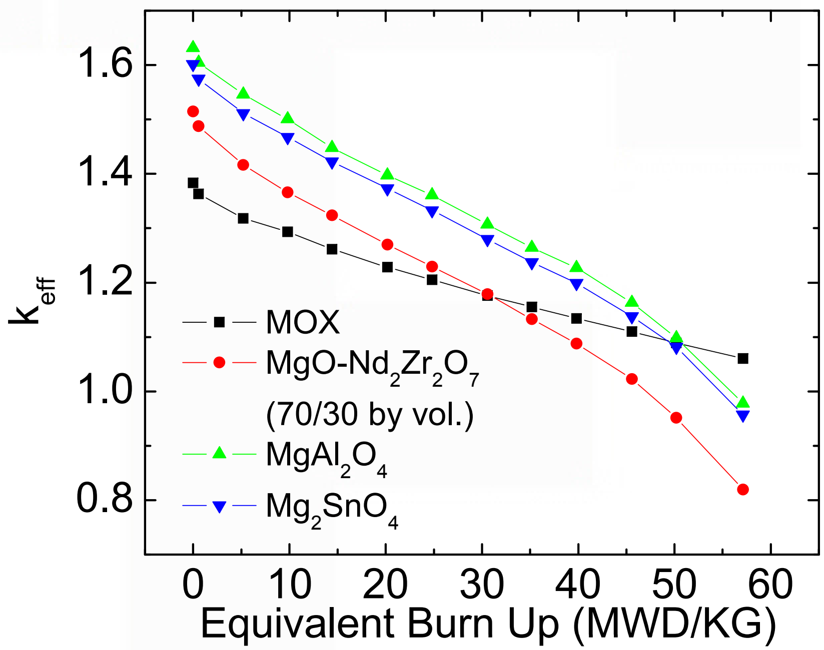
Spinel Selection

- $MgAl_2O_4$
  - Good irradiation resistance against neutrons and α-decay [1-3]
  - Poor in pile irradiation behavior: swelling due to fission fragment damage [4]
- Mg_2SnO_4
  - Low neutron adsorption cross section
  - Large, heavy ion



Prior work performed under
US DoE - DE-AC07-05ID14517

[1] K. E. Sickafus, et al., *Science* **289** 748 (2000).
[2] K. E. Sickafus, et al., *Nucl Instrum Meth B,* **106** 573 (1995).
[3] F. W. Clinard, et al., *J Nucl Mater* **108** 655 (1982).
[4] T. Wiss and H. Matzke, *Radiat Meas*, **31** [1-6] 507-14 (1999).

IM Materials

IM Candidate Materials:

- Spinel: $MgAl_2O_4$
- Off stoichiometric spinel: $MgO \bullet 1.5Al_2O_3$
- Rocksalt: MgO
- Inverse spinel: Mg_2SnO_4
- Pyrochlore: $Nd_2Zr_2O_7$
- Composite: $0.7MgO\text{-}0.3Nd_2Zr_2O_7$

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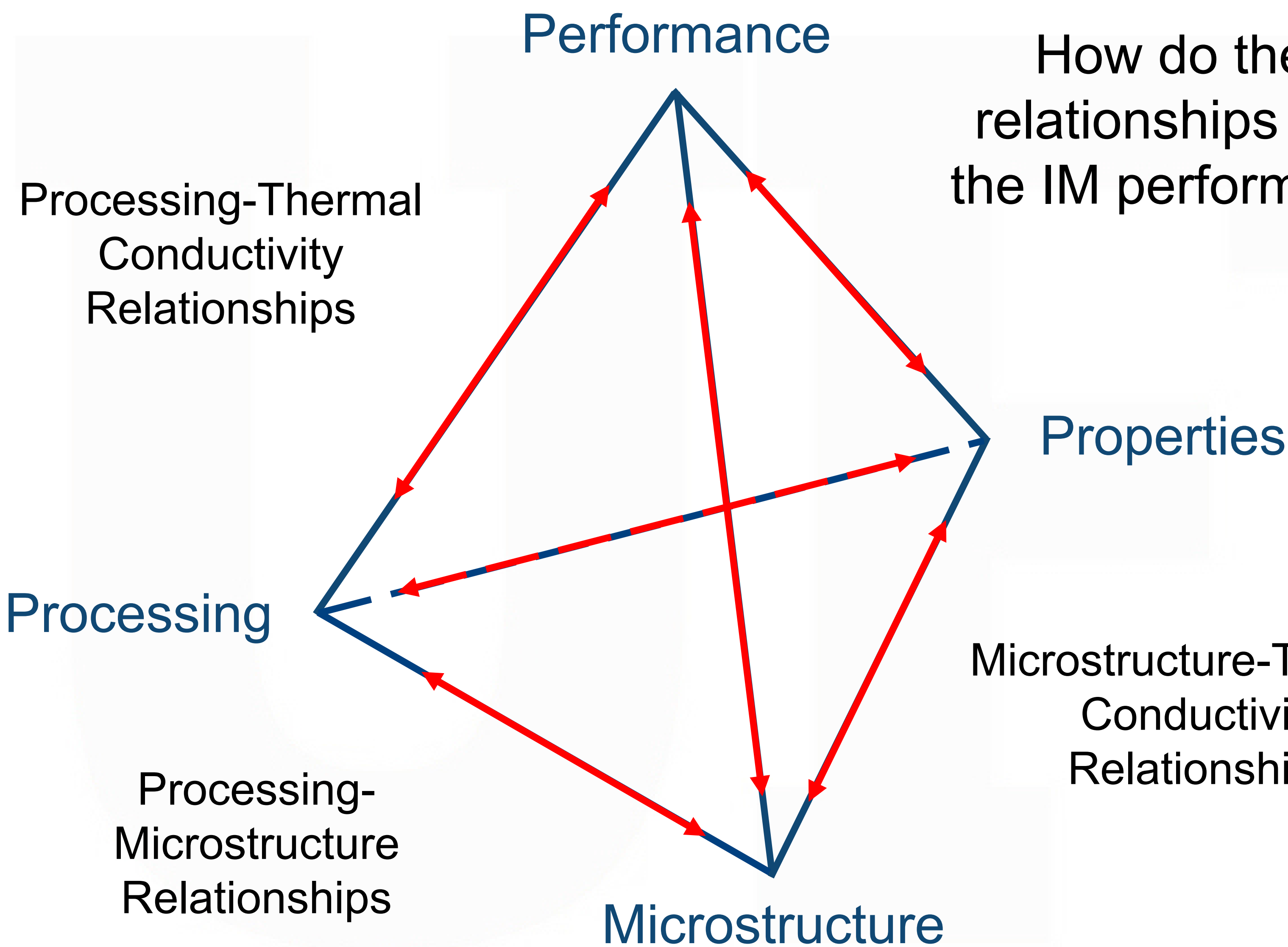
Approach



Processing-Thermal Conductivity Relationships

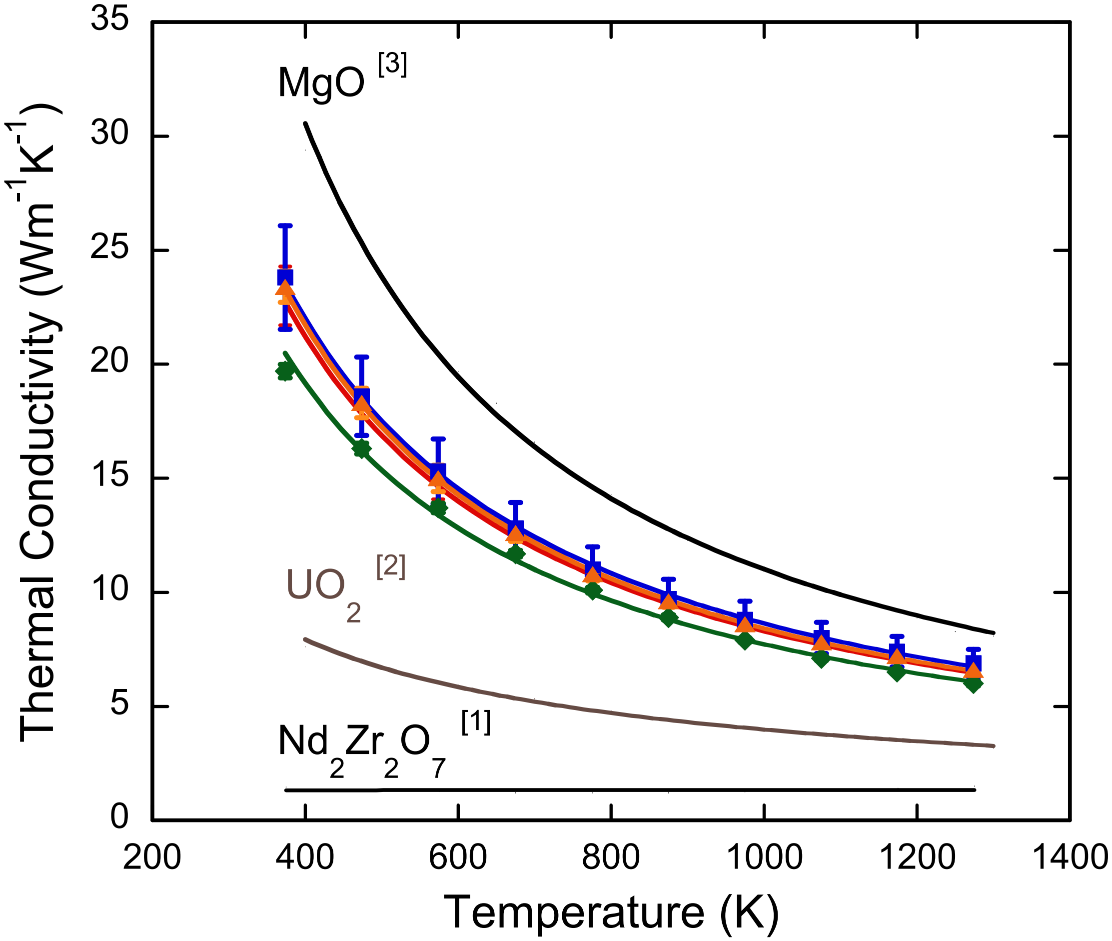
How do these relationships affect the IM performance?

Microstructure-Thermal Conductivity Relationships

Processing-Microstructure Relationships

Summary IM Thermal Conductivity

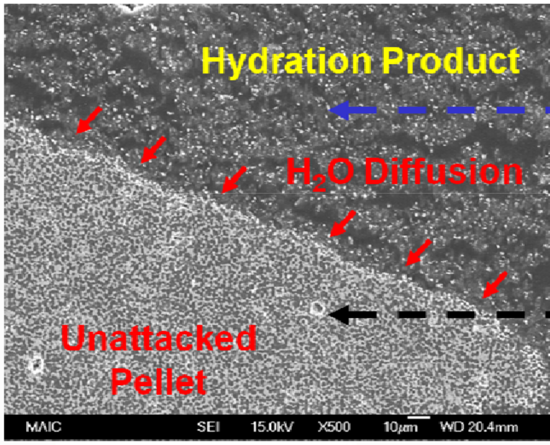
- The thermal conductivity of the composites exceeds that of UO_2.
- Ball-milling and SPEX blending yields the most consistent thermal conductivity.



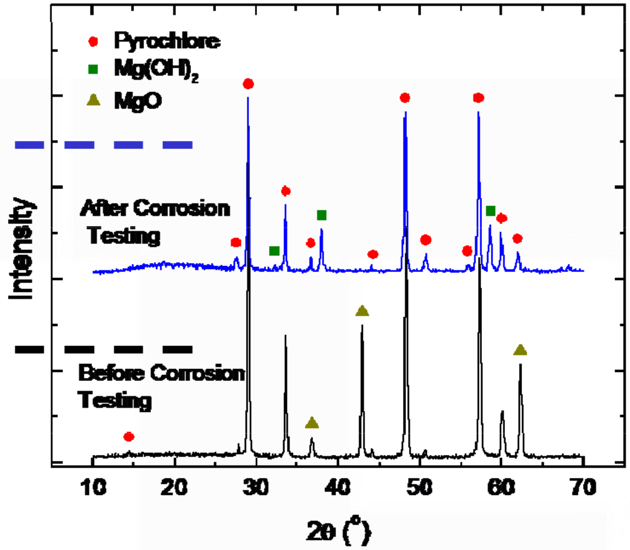
Prior work performed under
US DoE - DE-AC07-05ID14517

[1] Lutique, Konings, et al. *J. of Alloys and Compd.* (2003).
[2] Ronchi, Sheindlin, Musella, et al. *J. of Appl. Phys.* (1999).
[3] Slifka, Filla, Phelps. *J. of Res. NIST*. (1998).

Water Corrosion Summary



Cross-section of Hydrated Pellet



XRD Profile of Sintered Pellet and Hydrated Surface

- The water corrosion resistance of the $MgO\text{-}Nd_2Zr_2O_7$ composites is microstructure dependent. Due to high contiguity of MgO, the composite with 70 vol% of MgO could not survive in 300°C water
- Mg_2SnO_4 exhibited remarkable water corrosion resistance at 300°C with reduced mass loss and minimum volume change up to 30 days

Prior work performed under
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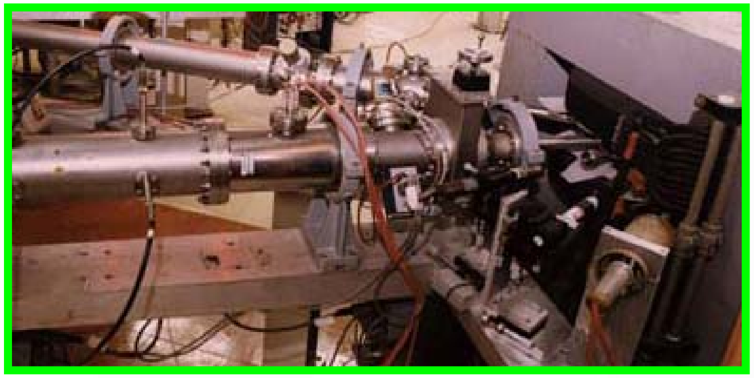
Irradiation Stability Experiments

IVEM-Tandem Facility
at Argonne National Lab
(ANL)



Ion Beam Target Area
650 kV NEC Ion Implanter
Ion source: 1 MeV Kr^{2+}
Flux: 10^{14} - 10^{16} $/m^2s$

Prior work performed under
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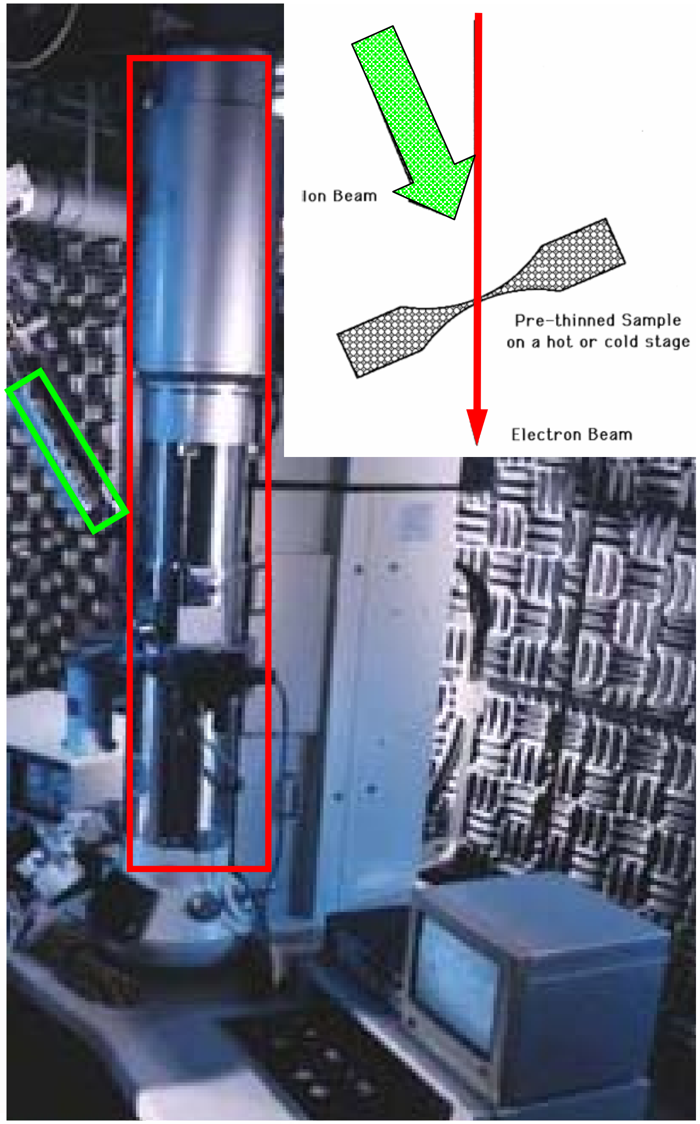

Irradiation Summary

- Mg_2SnO_4 can be amorphized at an ion dose of 5.5 dpa and 11.0 dpa at 50 K and 150 K
- Thermal annealing at room temperature is effective
- The average fuel temperature is above 1000 K; therefore, Mg_2SnO_4 may never become amorphous due to effective thermal annealing

Prior work performed under
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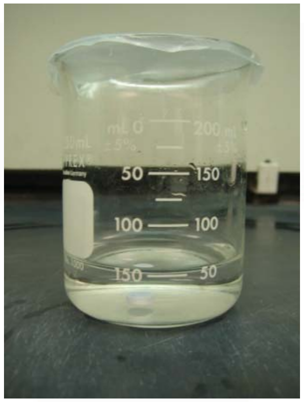
Dissolution Experiments



Static
(No agitation)

Dynamic
(Magnetic bar stirring)

Ultrasonic

Sample Collection

Inductively Coupled Plasma Atomic Emission Spectroscopy (Perkin-Elmer Plasma 3200)

Prior work performed under
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Summary on Dissolution

- Dissolution in HNO_3 resulted in a selective leaching of Mg^{2+} for both the $MgO-Nd_2Zr_2O_7$ composites and Mg_2SnO_4.
- Mechanical agitation such as magnetic bar stirring can enhance the mass transfer rate, resulting in a completed dissolution of Mg^{2+}, and the break up of the insoluble matrix into powder.
- $Nd_2Zr_2O_7$ can be dissolved in the boiling concentrated H_2SO_4.

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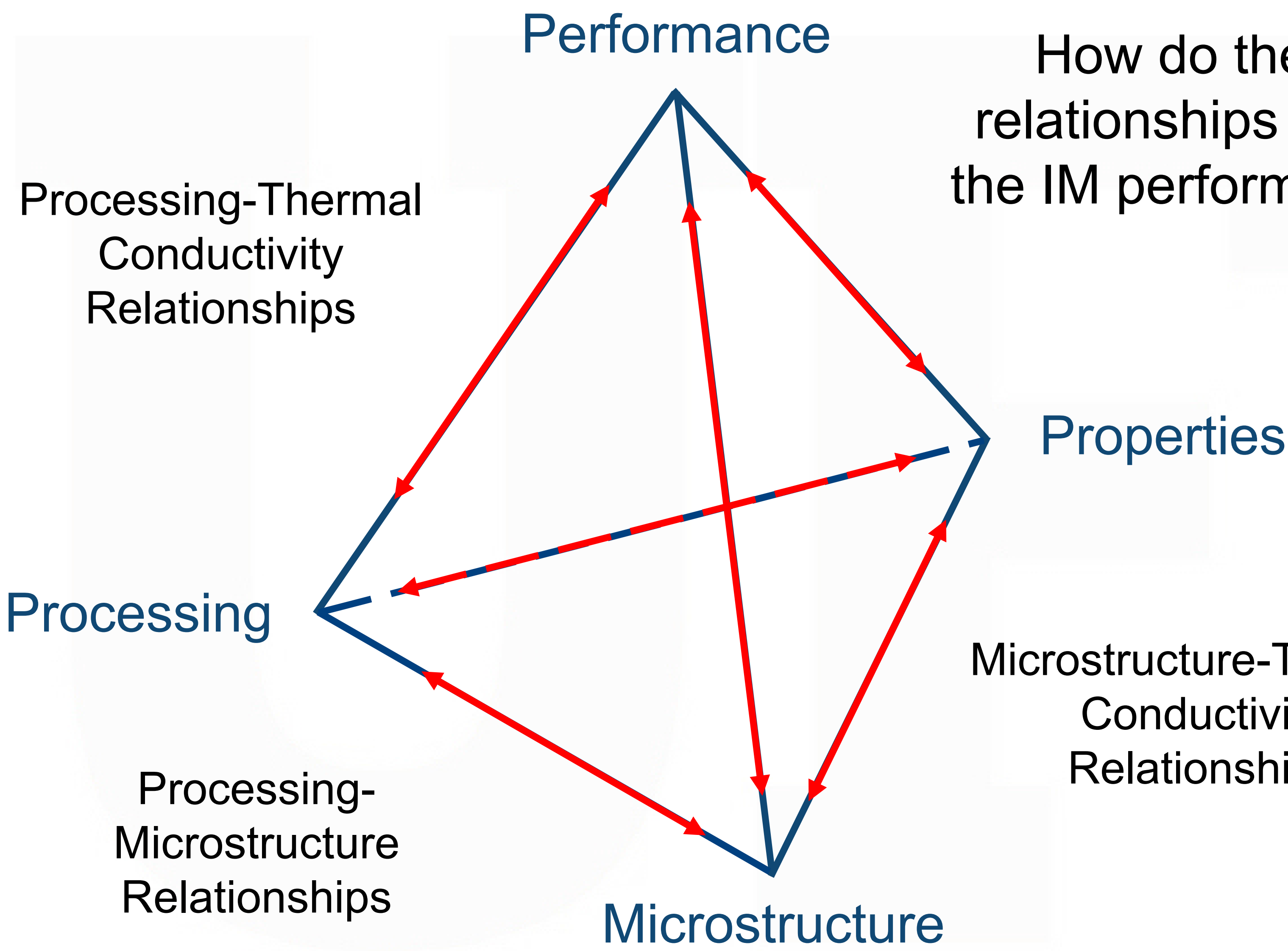

Processing-Thermal Conductivity Relationships

How do these relationships affect the IM performance?

Microstructure-Thermal Conductivity Relationships

Processing-Microstructure Relationships

ATR–NSUF UF Experiment

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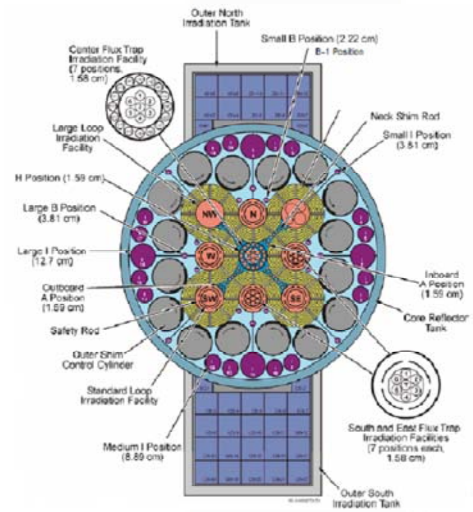
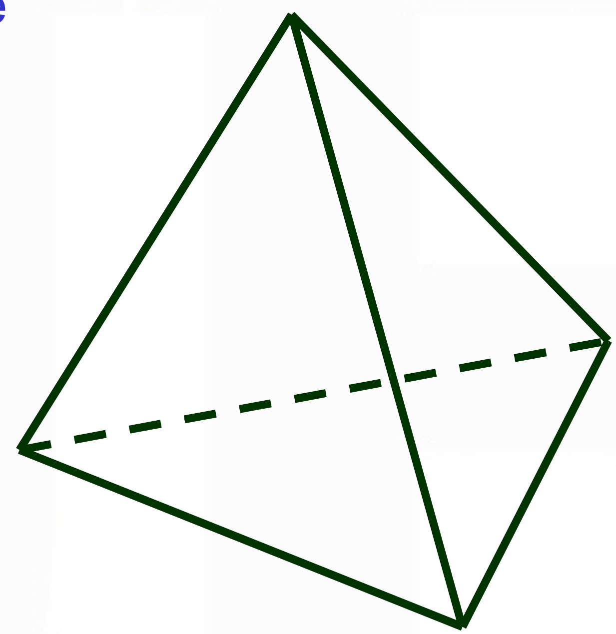


Calipers and Optical Microscope → Swelling, Cracks, etc.



Irradiation
350 and 700 °C
1 and 2 dpa

↑

ATR

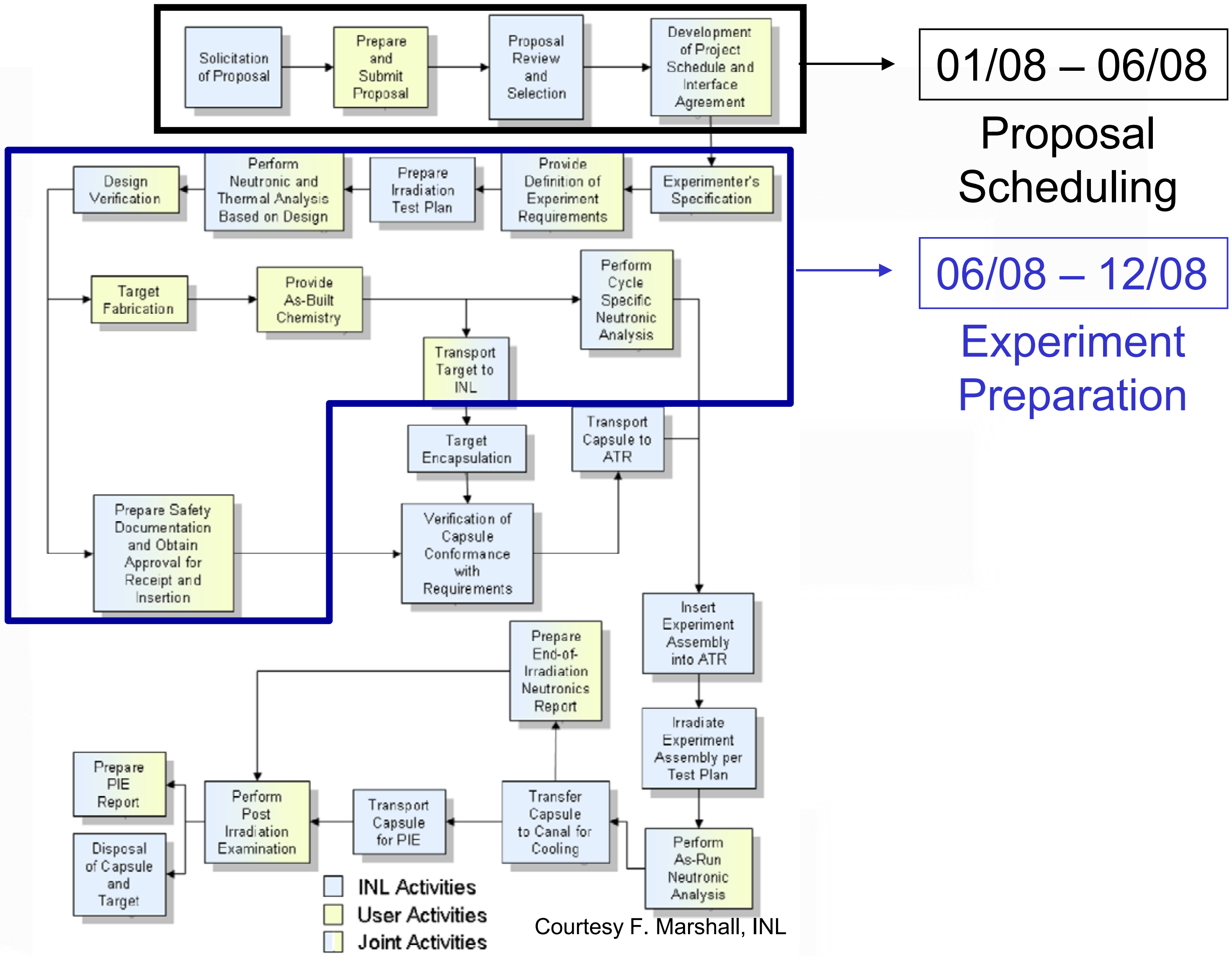
Properties
k_{th}

↑

Laser Flash

TEM and SEM → Crystal Structure Microstructure

ATR Experiment Roadmap



Courtesy F. Marshall, INL

ATR–NSUF UF Experiment

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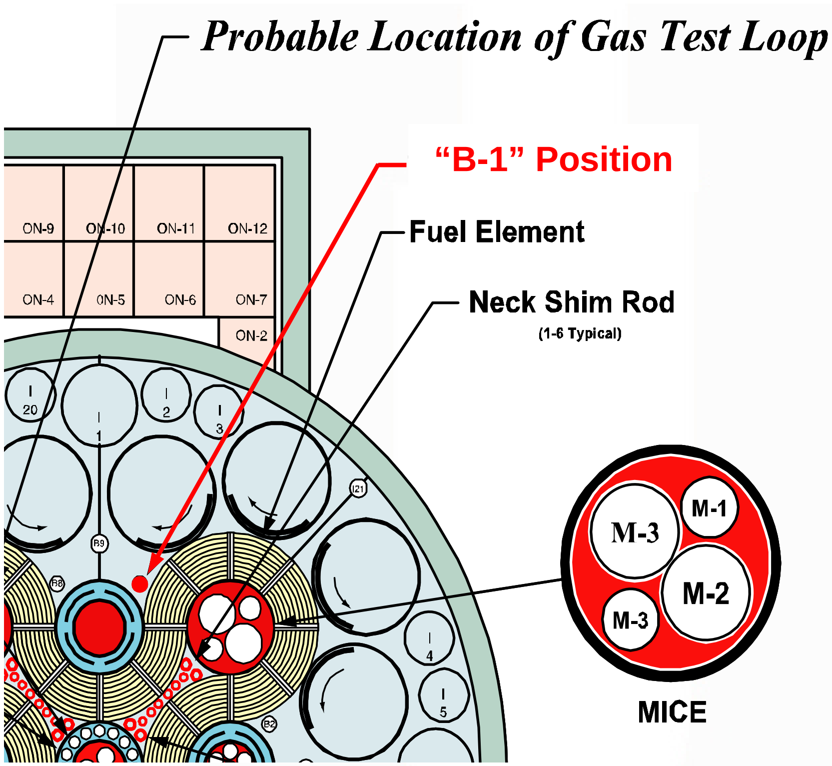
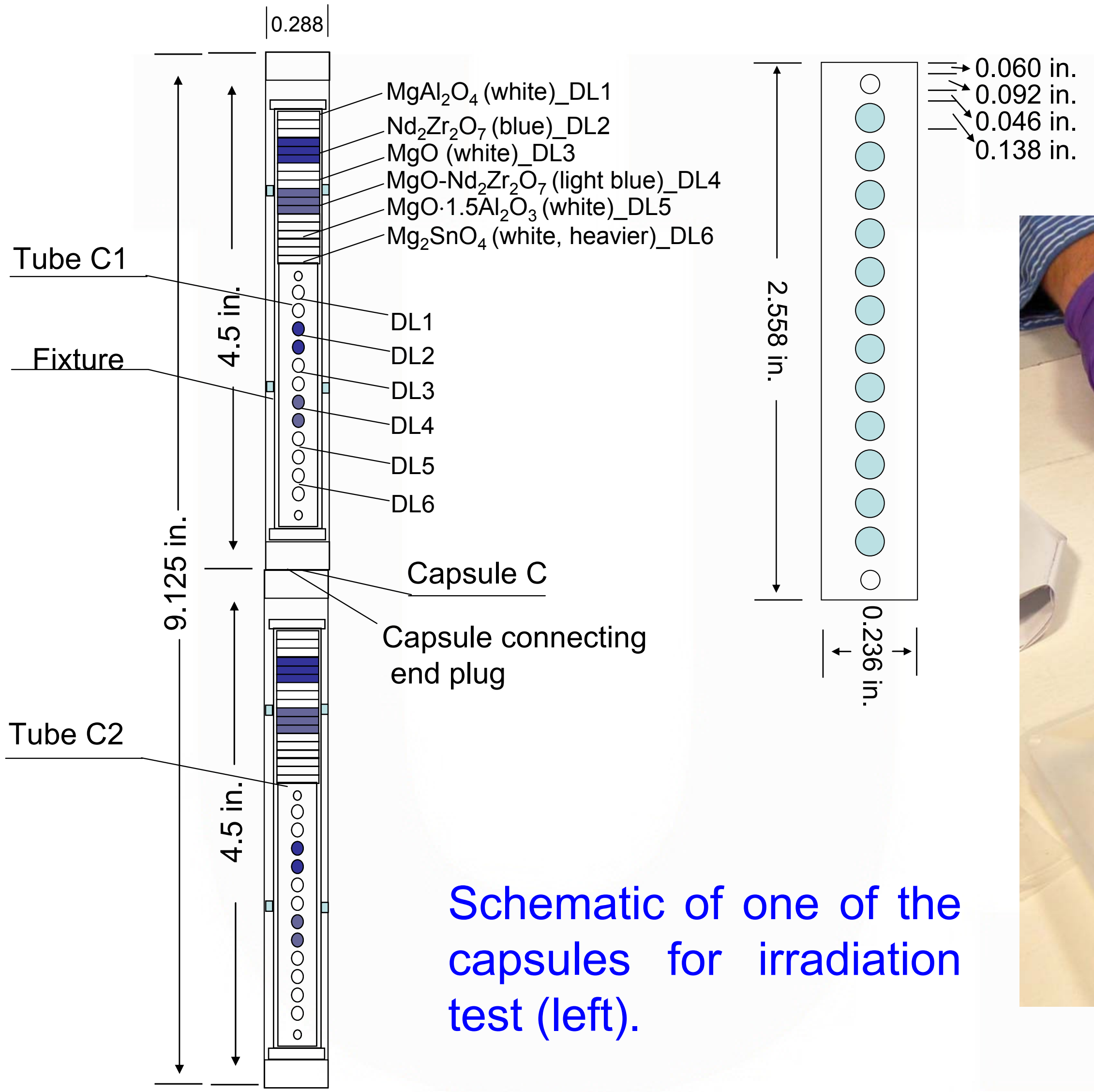


Six compositions were selected for irradiation tests in the ATR B-1 position. Three capsules were planned with two target doses (1 & 2 dpa) with insertion for the ATR cycle 144A .

Compositions
$MgO{\cdot}1.5Al_2O_3$
$MgAl_2O_4$
MgO
$Nd_2Zr_2O_7$
$0.7MgO\text{-}0.3Nd_2Zr_2O_7$
Mg_2SnO_4

UF Experiment Designation ID	Sample Type	Target Dose	Fast Neutron Fluence	Height (in.)	Temp. (C)
Capsule A2, B2	Diffusivity samples, TEM samples	1 dpa	1 x 10^{25} n/m^2	9	300, 700
Capsule C1,C2	Diffusivity samples, TEM samples	2 dpa	2 × 10^{25} n/m^2	9	300, 700

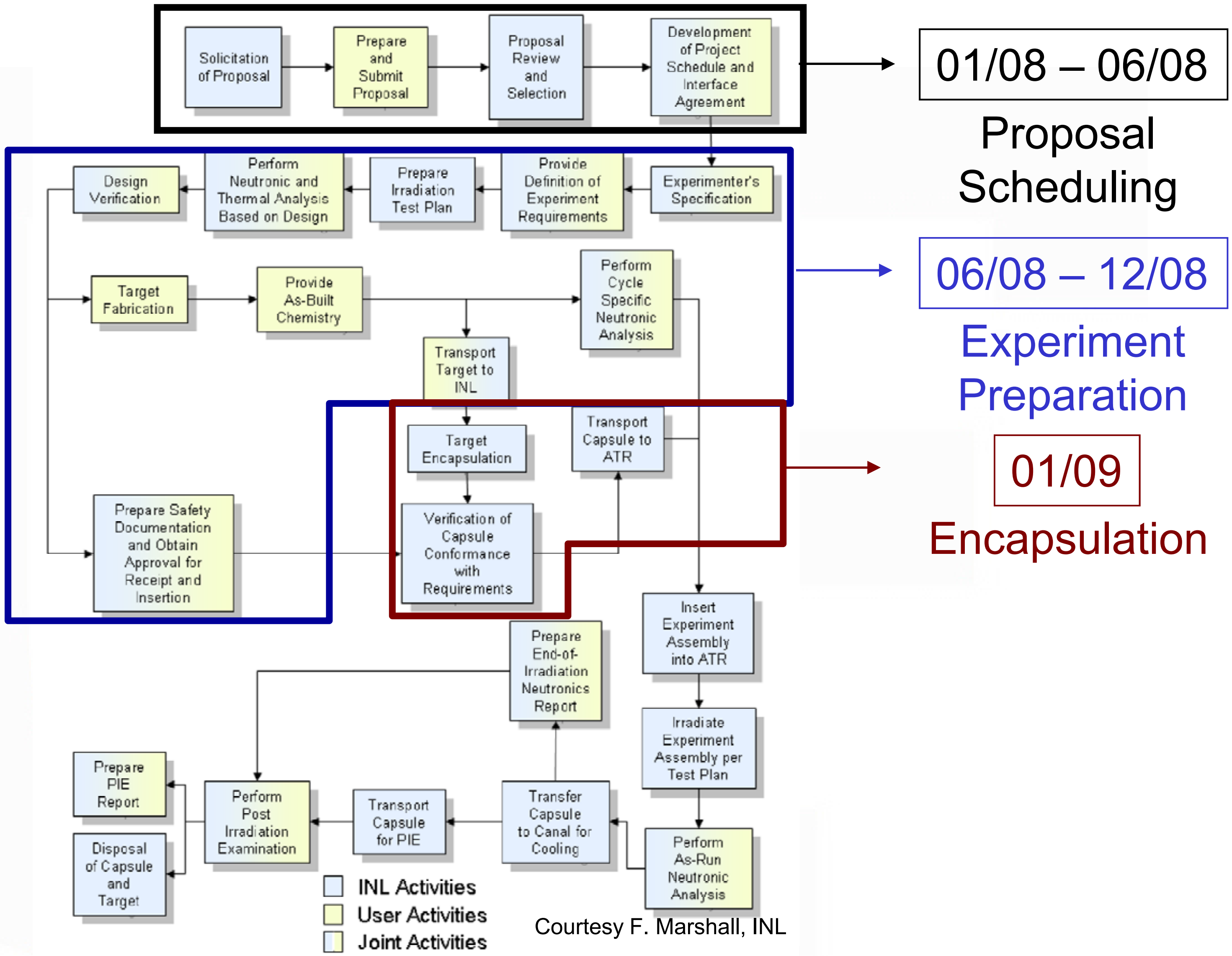
ATR–NSUF UF Experiment



Schematic of one of the capsules for irradiation test (left).

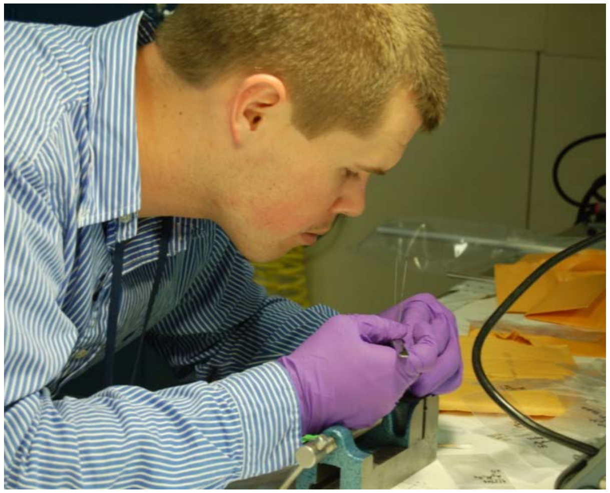
TEM fixture prior to loading

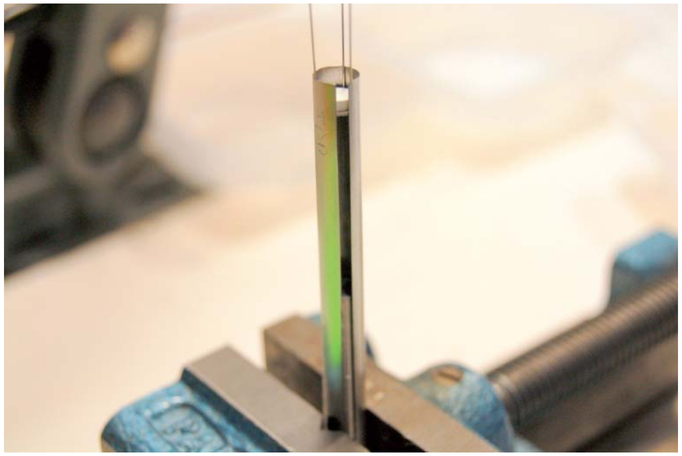
ATR Experiment Roadmap



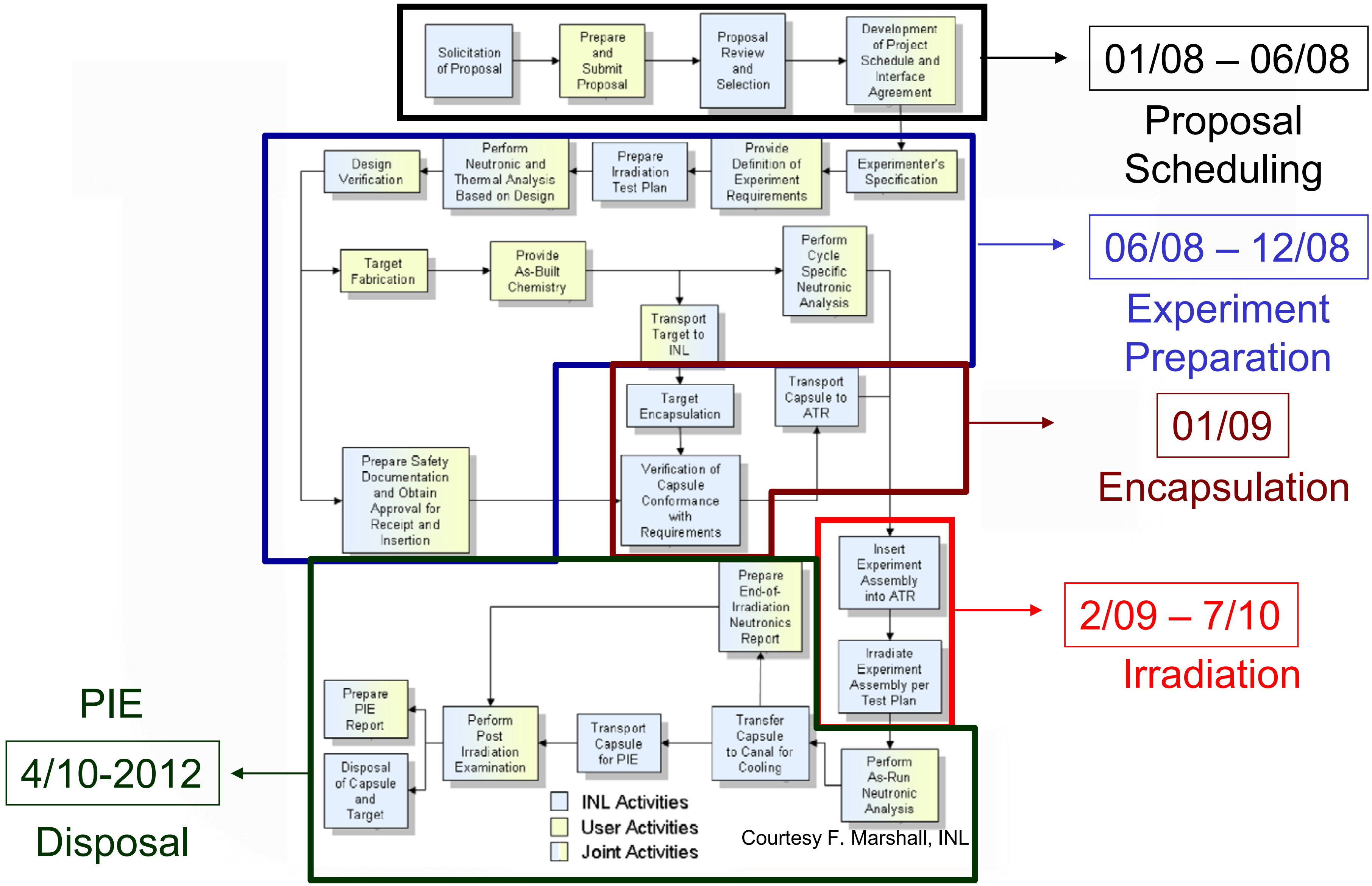
Courtesy F. Marshall, INL

Preparation

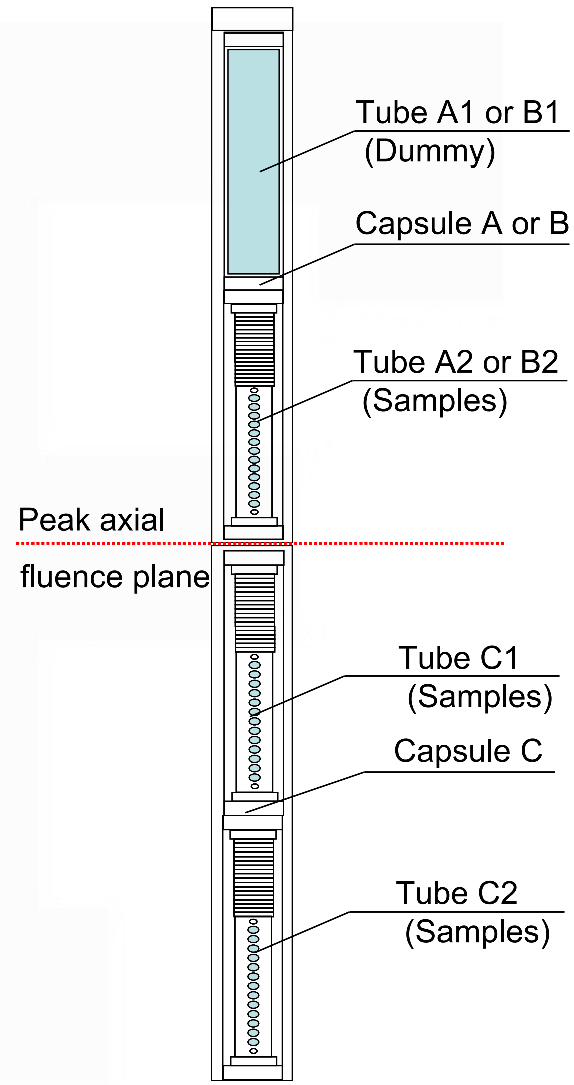
ATR Experiment Roadmap



Irradiation Conditions

- Temperature controlled by capsule backfill gas

Fast Neutron Fluence (n/m^2)	Irradiation Temperature	
	300°C	700°C
1×10^{25}	Capsule A2	Capsule B2
2×10^{25}	Capsule C1	Capsule C2



Current Status and PIE

- Capsule A is out of the reactor. The samples with low enough Rad level to begin work were moved to their respective labs.
- Capsules B and C came 07/10 and were shipped to HFEF the last quarter of 2010.

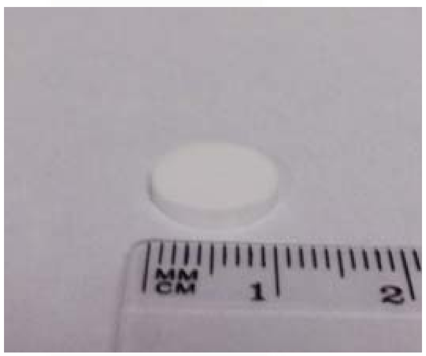
PIE

1) Measurement of sample volumetric change under irradiation. Quantification of swelling.
2) SEM microstructural characterization (grain size, micro cracks, voids, etc.)
3) Measurement of thermal diffusivity of irradiated samples.
4) TEM characterization of defect formation in materials under neutron irradiation.

Color Change

Nonirradiated (N) | Irradiated (I)

$MgAl_2O_4$



MgO

$MgO•1.5Al_2O_4$

Laser Flash Thermal Diffusivity

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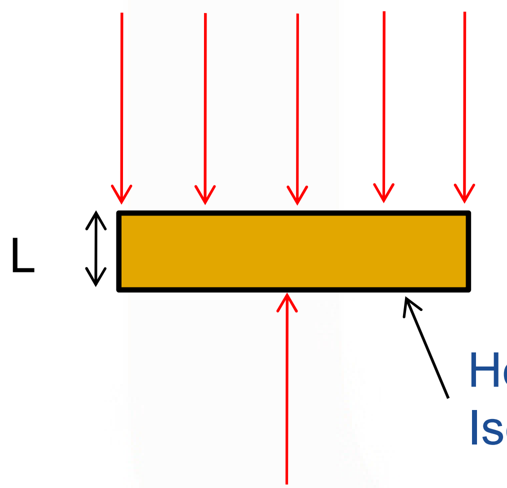
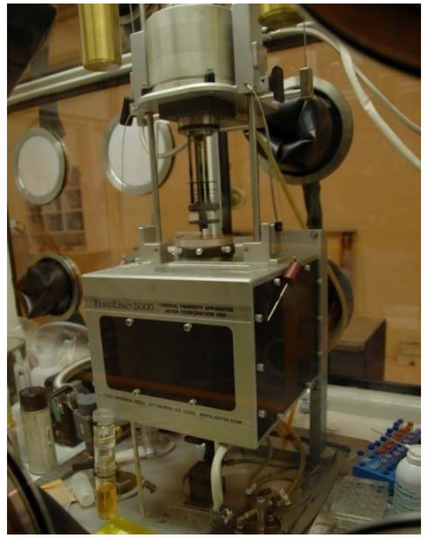
$$\kappa = \alpha \rho C_p$$

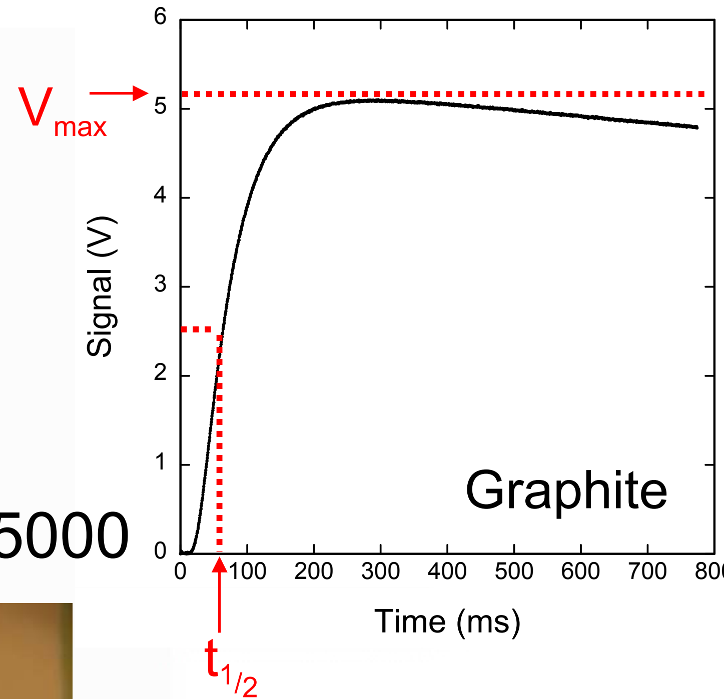
Laser Pulse



Measure To and ΔT

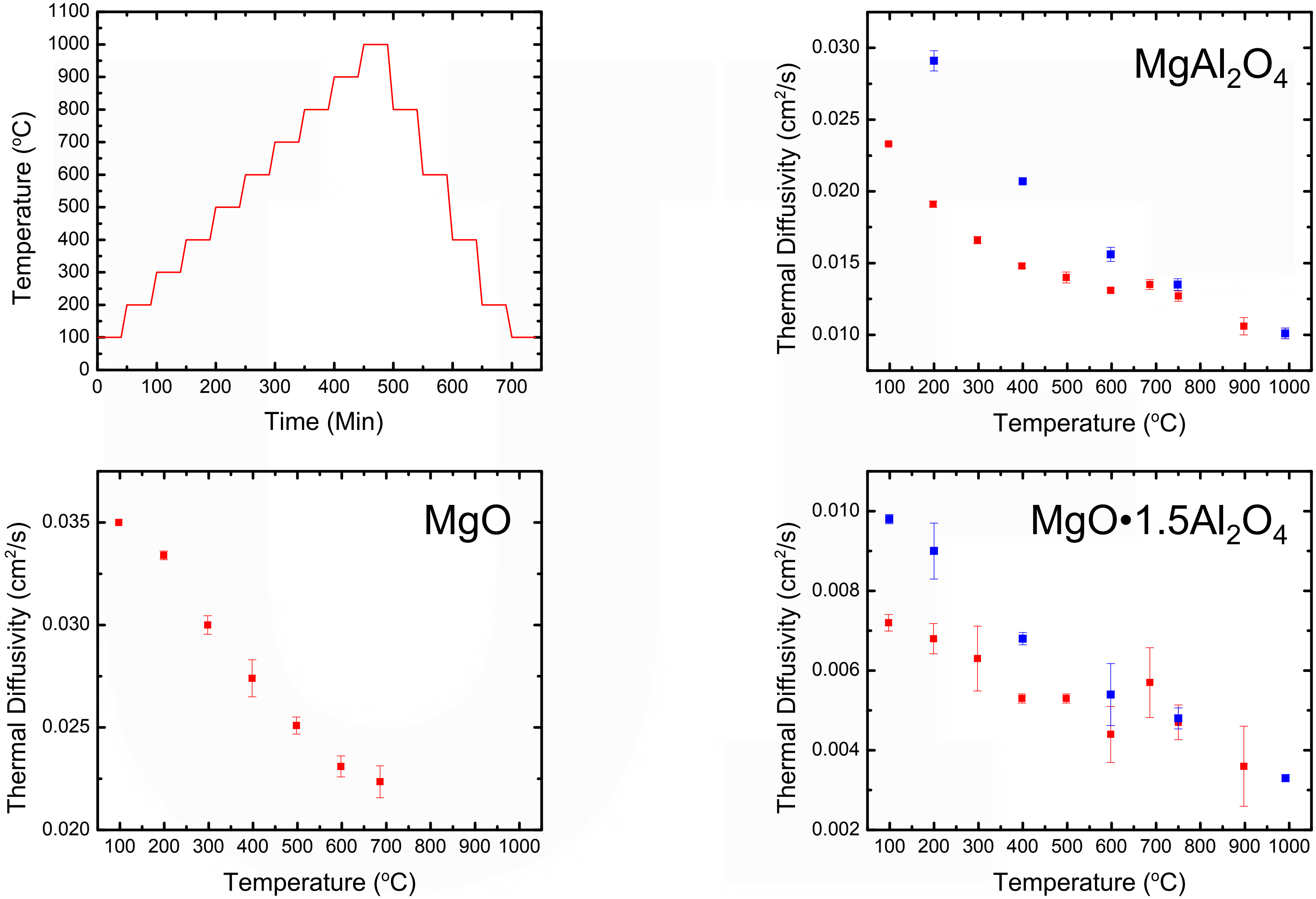


Anter Flashline 5000

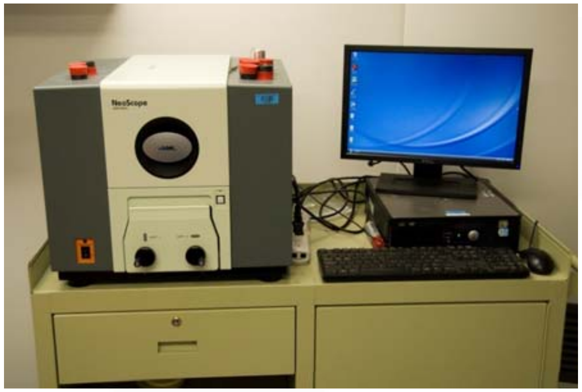


$$\alpha = 0.1388 L^2 / t_{1/2}$$

Thermal Diffusivity



Equipment



JOEL Neoscope

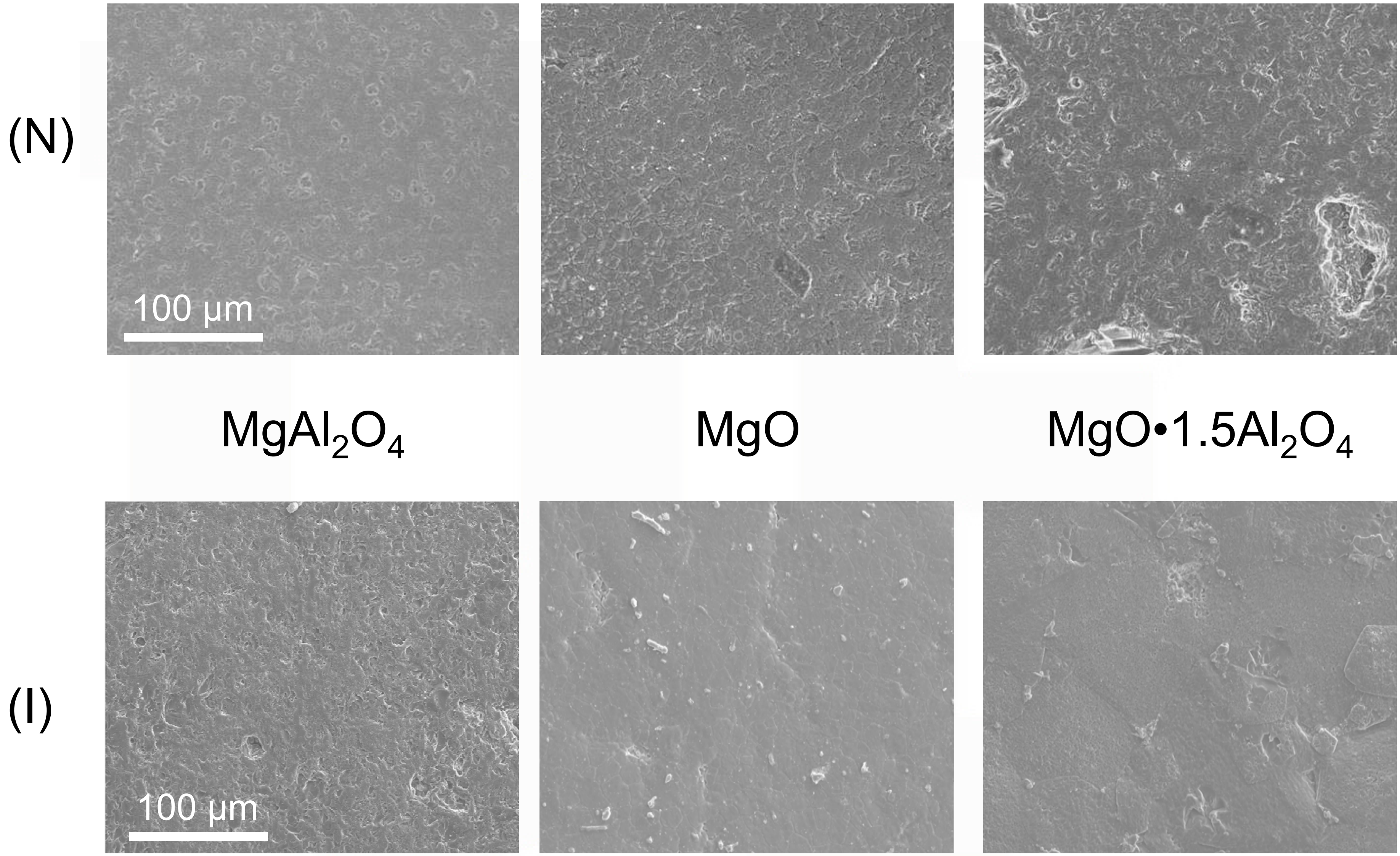
LEO 1455VP

JOEL 2010F

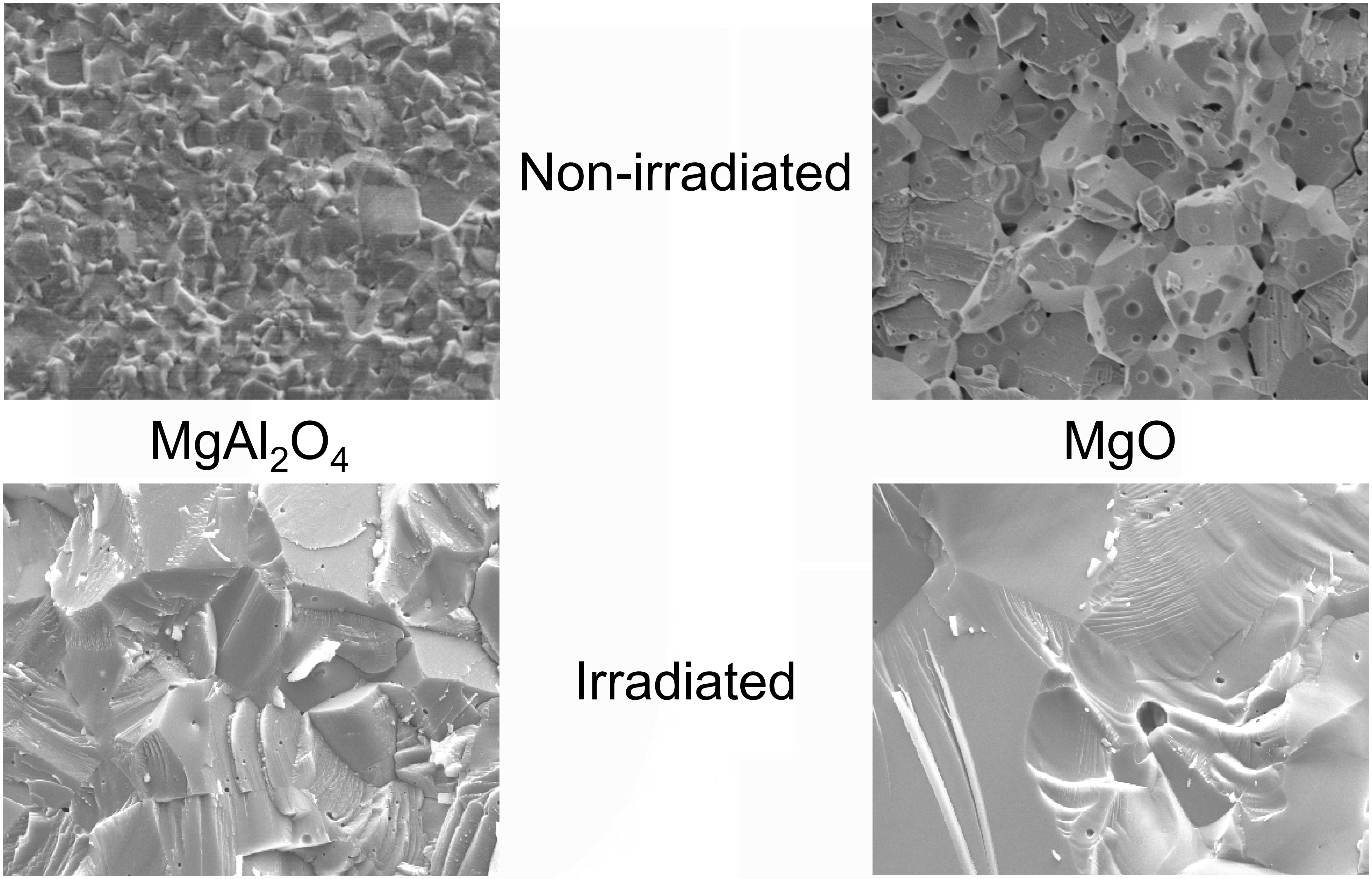
FEI Quanta 3D FEG

Inel Equinox 1000

(Untreated) Surface SEM



Fracture SEM



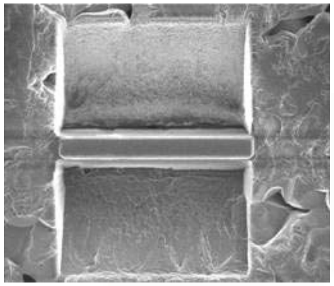
Non-irradiated

$MgAl_2O_4$

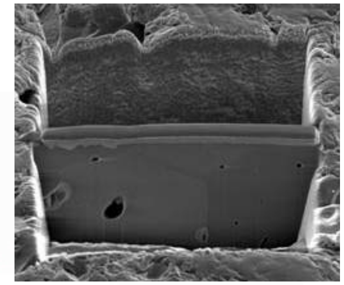
MgO

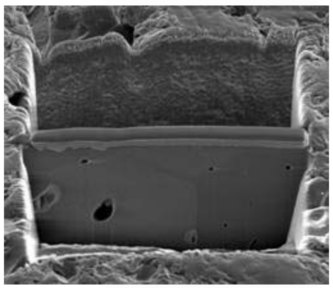
Irradiated

FIB Preparation

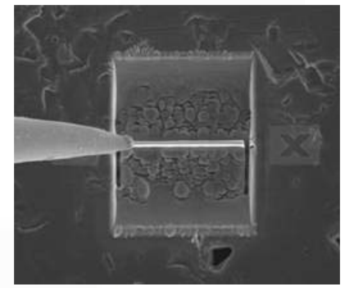


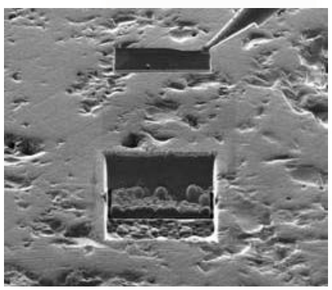
Deposit Pt and dig trenches using 30 kV Ga^{2+} ions → Thin to ~ 1μm



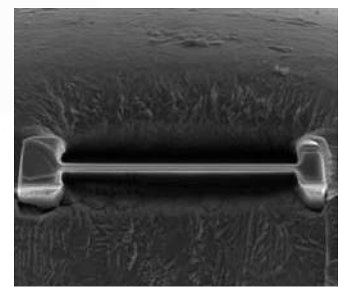


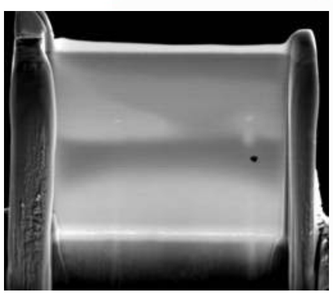
Cut around sample leaving supports on the top sides → Weld Omniprobe to sample and cut supports



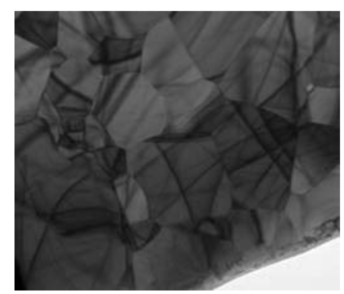


Lift sample out and Pt weld to TEM grid → Thin to ~ 200 nm

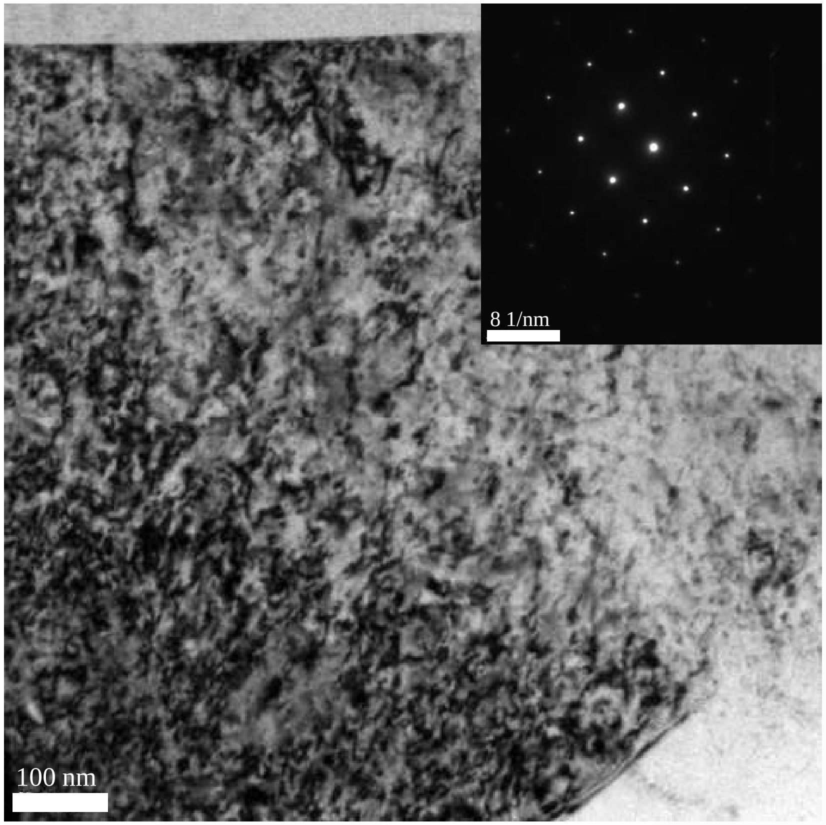




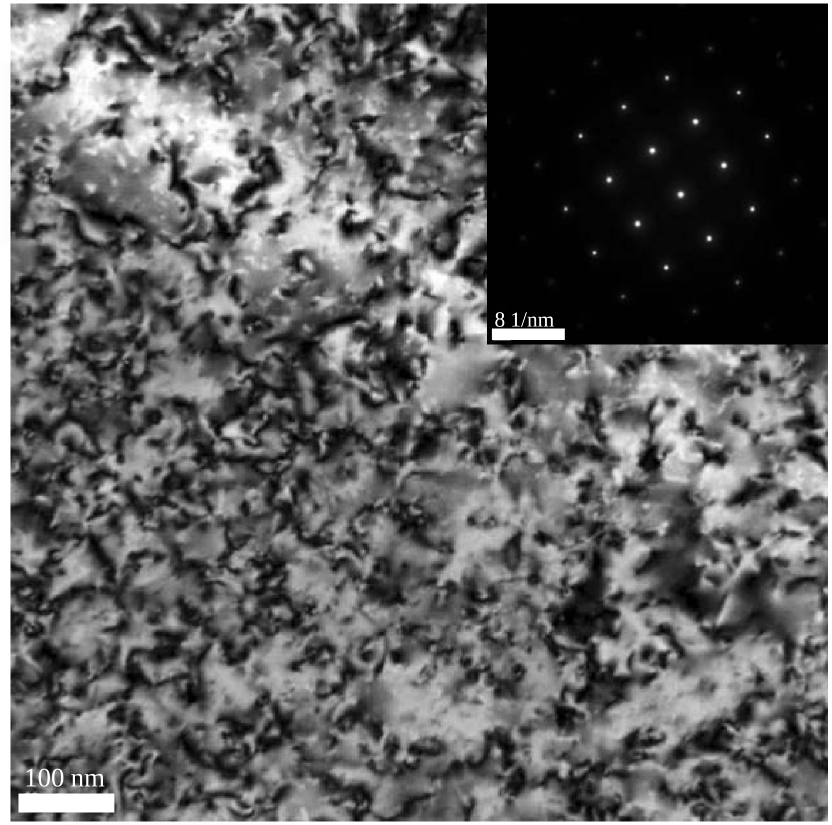
Clean sample surface with low energy beam → TEM



TEM of MgO

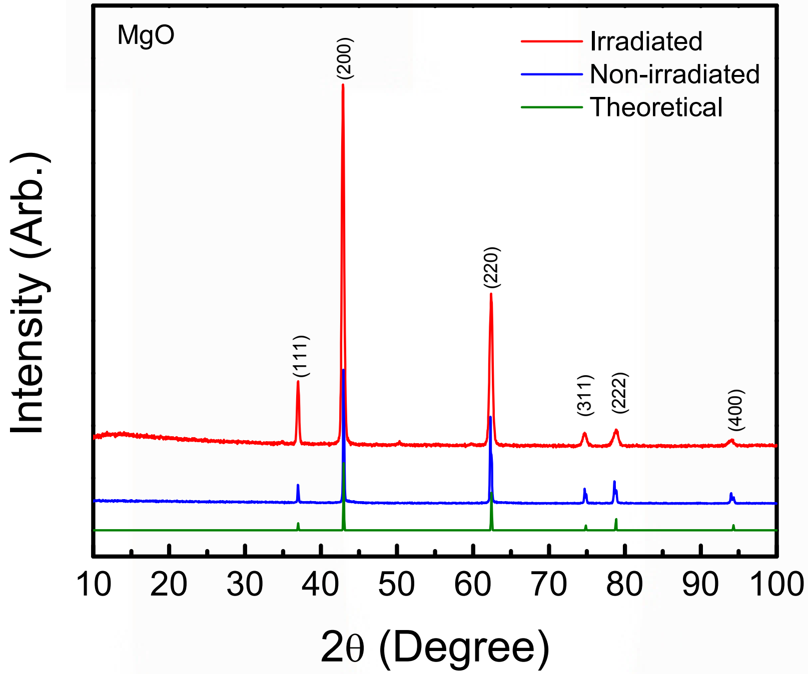


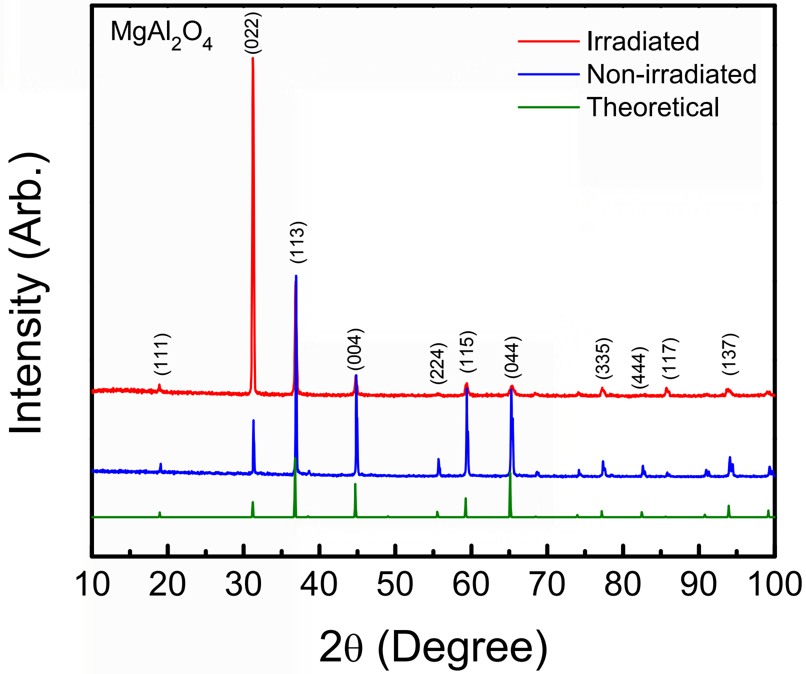
Non-irradiated MgO



Irradiated MgO

XRD


MgO
Irradiated
Non-irradiated
Theoretical
(111)
(200)
(220)
(311)
(222)
(400)
Intensity (Arb.)
10 20 30 40 50 60 70 80 90 100
2θ (Degree)


$MgAl_2O_4$
Irradiated
Non-irradiated
Theoretical
(111)
(022)
(113)
(004)
(224)
(115)
(044)
(335)
(444)
(117)
(137)
Intensity (Arb.)
10 20 30 40 50 60 70 80 90 100
2θ (Degree)

Outline

- Background and Motivation
- Materials Selection
- Summary of Prior Out-of-Pile Research
- ATR-NSUF Experiment Overview and Results
- Summary and Outlook

Summary

- Down-selection, synthesis, and processing optimization of inert matrix materials (i.e. MgO, $Nd_2Zr_2O_7$, $0.7MgO\text{-}0.3Nd_2Zr_2O_7$, $MgAl_2O_4$, Mg_2SnO_4, and $MgO{\cdot}1.5Al_2O_3$) was performed.
- The out-of-pile thermophysical properties (thermal diffusivity, thermal conductivity, contiguity, etc.) and in-service engineering parameters (water corrosion resistance, acidic dissolution, etc.) were characterized.
- Target samples (120) were successfully loaded (A2, B2, C1, C2) and inserted into ATR (B-1) during cycle 144A and PIE is ongoing

Summary of PIE

The following research was done on capsule A2:

- Density measurements and thermal diffusivity of gold coated $MgAl_2O_4$, MgO, and $MgO•1.5Al_2O_3$
- Collected XRD for $MgAl_2O_4$, MgO, and $MgO•1.5Al_2O_3$
- SEM of MgO, $MgAl_2O_4$, and $MgO•1.5Al_2O_4$
- Used FIB to make lamellae of MgO, $MgAl_2O_4$, and $MgO•1.5Al_2O_4$ then TEM

SEM, FIB, and TEM of nonirradiated samples

Summary of PIE

Initial pre v post irradiation observations:

- Irradiated samples exhibit significant accumulation of point (color change) and line (dislocations per TEM) defects.
- Irradiated $MgAl_2O_4$, MgO, and $MgO{\bullet}1.5Al_2O_3$ preserved macroscopic and overall crystallinity.
- Thermal conductivity of irradiated samples is lower than that of non-irradiated samples.
- Irradiated MgO, and $MgAl_2O_4$, show embrittlement consistent with observed grain growth (Hall-Petch effect).

Current Work

This summer we are focusing on the following tasks:

- SEM, TEM, and diffusivity measurements of MgO and $MgAl_2O_4$ from capsules C1 and C2
- SEM, TEM, and diffusivity measurements of $Nd_2Zr_2O_7$, MgO-$Nd_2Zr_2O_7$, and Mg_2SnO_4 from capsule A2
- Thermal diffusivity on pre-irradiated samples

Outlook

- Extract and evaluate integrity of capsules B and C
- Completion of PIE for all samples (over the next year and a half)
- Comparison of materials properties before and after irradiation
- Identification of mechanisms responsible for property degradation

Investigation of MgO-Pyrochlore Composites and Spinel Compounds as Potential Inert Matrix Materials: ATR Experiment Overview and Results

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