materials design

SRNL

WEBINAR

From National Security to Energy Security: How Computational Chemistry is Defining Science at SRNL

Lindsay Roy, Ph.D.
Principal Scientist, Savannah River National Laboratory, USA

© Materials Design, Inc. 2020

Materials Design UGM

materials design

SRNL

WEBINAR

From National Security to Energy Security: How Computational Chemistry is Defining Science at SRNL

Lindsay Roy, Ph.D.
Principal Scientist, Savannah River National Laboratory, USA

© Materials Design, Inc. 2020

UGM Plenary Session Speakers

Lindsay Roy, Ph.D

Principal Scientist, SRNL

Katherine Hollingsworth

khollingsworth@materialsdesign.com

Dr. Taylor Juran

tjuran@materialsdesign.com

© Materials Design 2020

Materials Design UGM Plenary Sessions

- Share the plenary sessions with your colleagues!
  - Registration details

    https://www.ugm.materialsdesign.com
- We will be recording this session
  - Upcoming sessions are posted on the UGM site
  - Watch any of our earlier webinars anytime

    www.materialsdesign.com/webinars
- Brief survey
  - Take a 2-minute brief survey at the end of this webinar!

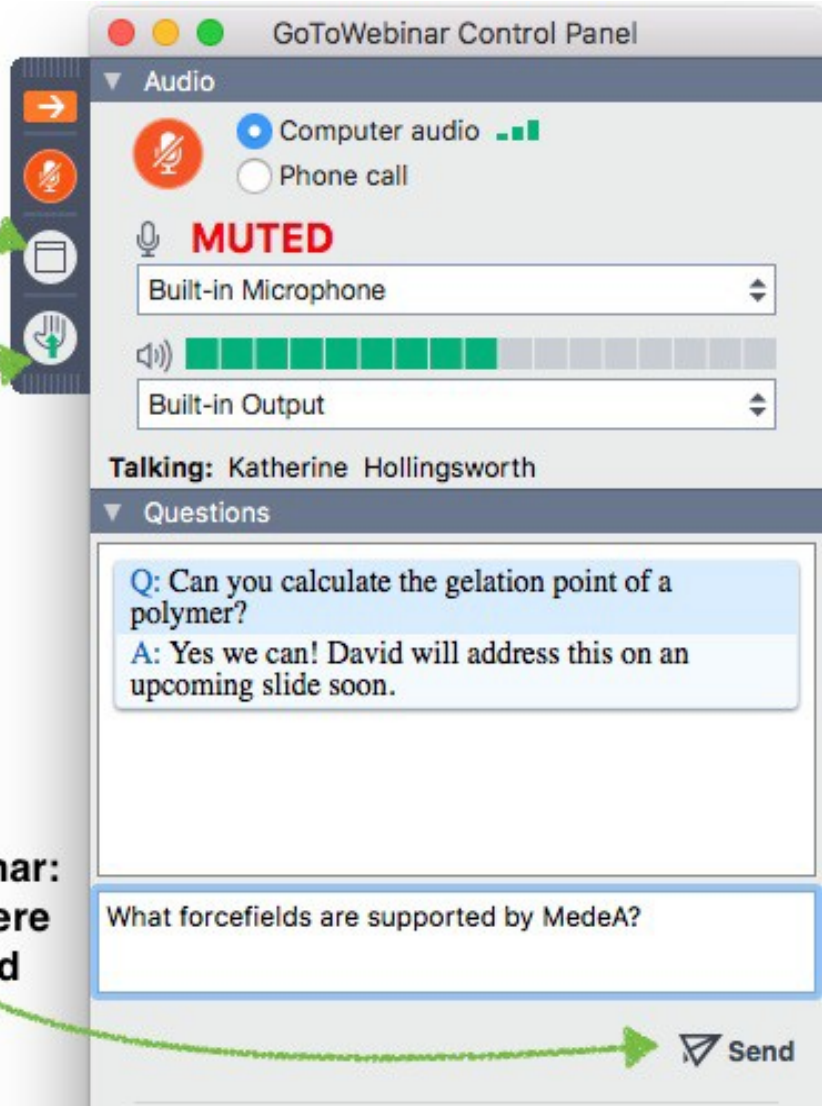
Please Ask Questions

full screen

during discussion:

Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send



Savannah River National Laboratory®

From National Security to Energy Security: How Computational Chemistry is Defining Science at SRNL

Dr. Lindsay Roy
Principal Scientist, Savannah River National Laboratory

Materials Design UGM 2020

October 1, 2020

This work has been supported by the U.S. Department of Homeland Security (DHS), Domestic Nuclear Detection Office (DNDO), Defense Threat Reduction Agency (DTRA), and Savannah River National Laboratory – Laboratory Directed Research and Development program (LDRD). This support does not constitute an express or implied endorsement on the part of the Government.

SRNL-STI-2020-00411

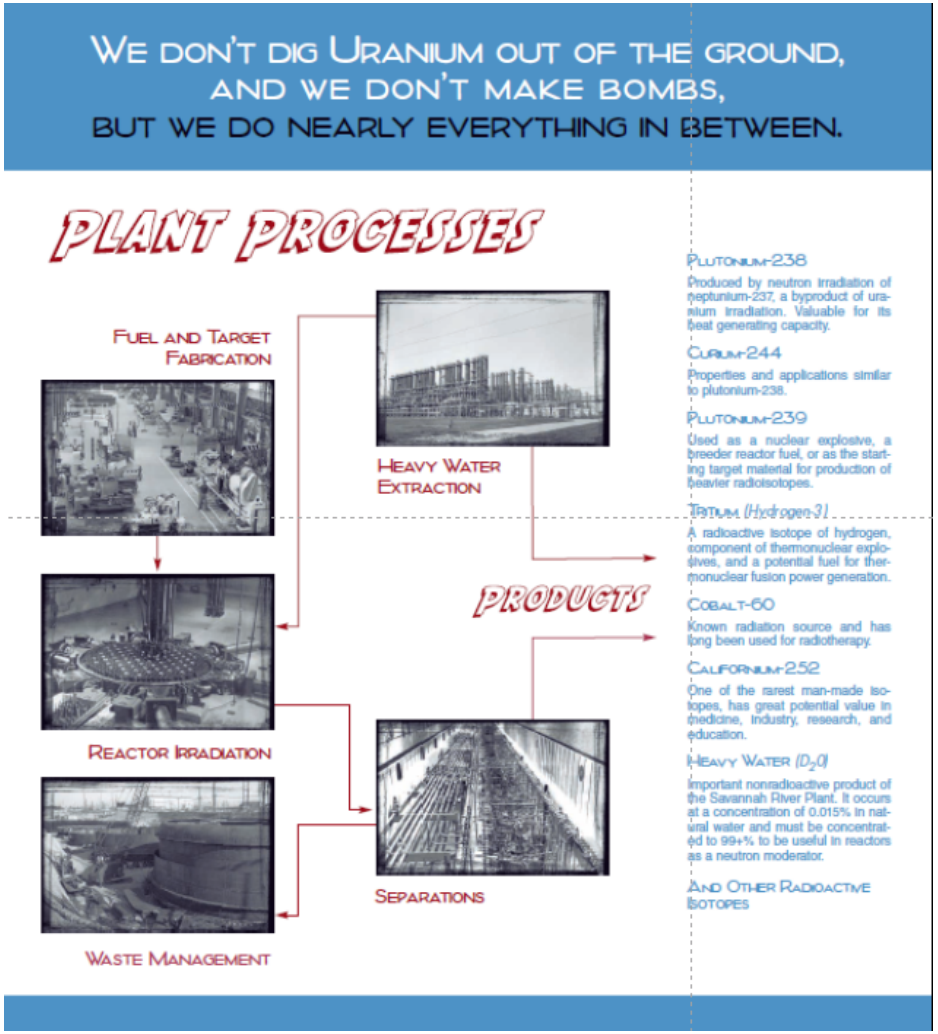
Contributors and Collaborators

- **Plutonium Processing (DHS)**
  - Si Young Lee (SRNL)
  - Jeff Pike (SRNL)
  - Chaitanya Deo (Ga Tech)
  - Anh Tam Masterson (SRNS – HB-Line)
  - Jeff Schaade (SRNS – Mission Development)
  - Chris South (SRNL Postdoc)
  - Eric Hoar (SRNL Postdoc)
  - Minority Serving Institutions Partnership Program (MSIPP) Interns
- **Ag-Zeolite (DTRA)**
  - Maria Kriz (SRNL)
  - Omar Rivera (SRNL)
  - Kaitlin Lawrence (SRNL)
  - Chris South (SRNL Postdoc)
  - Eric Hoar (SRNL Postdoc)
- **Li-LLZO (LDRD)**
  - Dale Hitchcock (SRNL)
  - Brenda Garcia-Diaz (SRNL)
  - Kyle Brinkman (Clemson)
  - Lindsay Shuller-Nickles (Clemson)
  - Akihiro Ishii (Clemson Postdoc)
  - Changlong Li (Clemson student)

DOE National Laboratory System

Overview – Savannah River National Laboratory

- Since the early 1950s, the Savannah River Site (SRS) has provided knowledge, technology and integrated solutions for our most pressing national needs.
  - Five reactors, two chemical separations plants, heavy water extraction plant, nuclear fuel and target fabrication facility, waste management, laboratory/analytical facilities
- Scientific and engineering R&D are a natural complement to our core business
  - Morphologies of PuO_2 from various Pu flowsheets
  - Environmental effects on PuO_2
  - Labs: PNNL, LANL
  - Universities: Colorado School of Mines, Clemson, Ga Tech



SRNL at a Glance

We protect our nation by applying science to international security, the environment and the energy economy

Core Competencies

- Environmental Remediation and Risk Reduction
- Tritium Processing, Storage and Gas Transfer Systems
- Nuclear Materials Processing and Disposition
- Nuclear Detection, Characterization and Assessments

Location: Aiken, SC
Type: Multiprogram
Year Founded: 1951
Director: Dr. Vahid Majidi
Contractor: Savannah River Nuclear Solutions

Multi-Program Laboratory

1,000 Staff

$290M

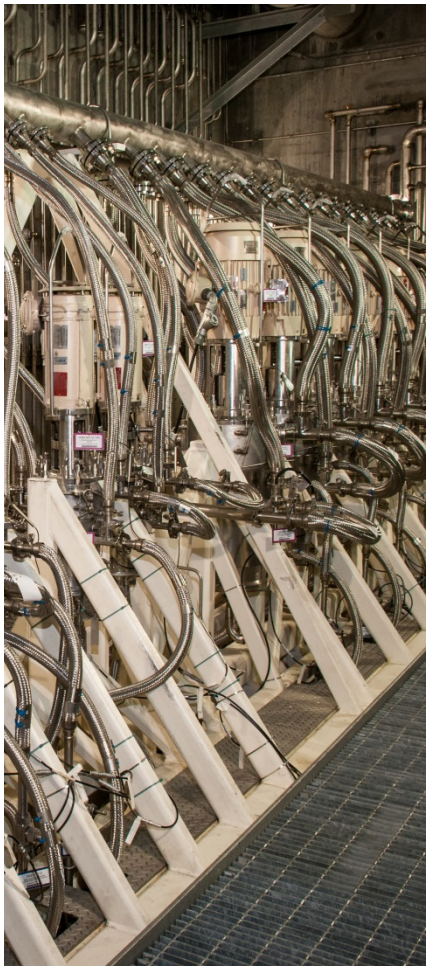
FY19 Programmatic Lab Budget*

*Does not include $55M in operations & facilities budget

Program Areas

- Chemical & Environmental Sciences 20%
- National Security 45%
- Nuclear Materials Management 31%
- Energy Materials Science 4%

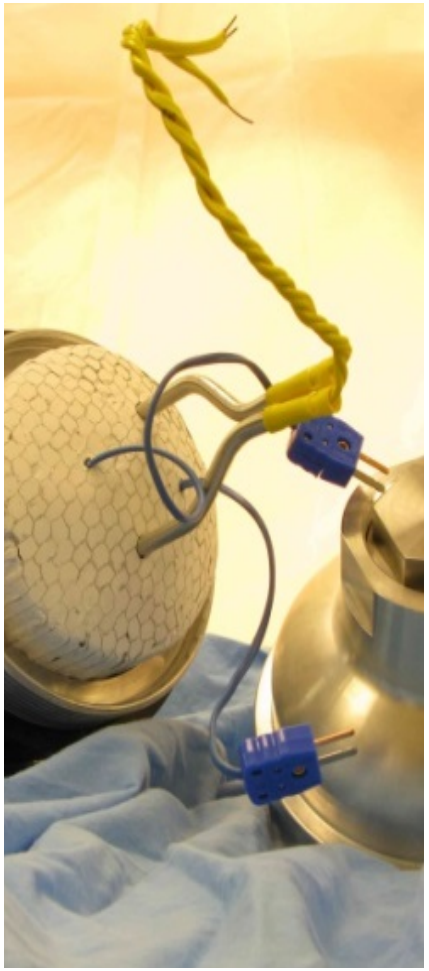
SRNL Core Areas



Chemical & Engineering Science

National Security

Nuclear Materials Management



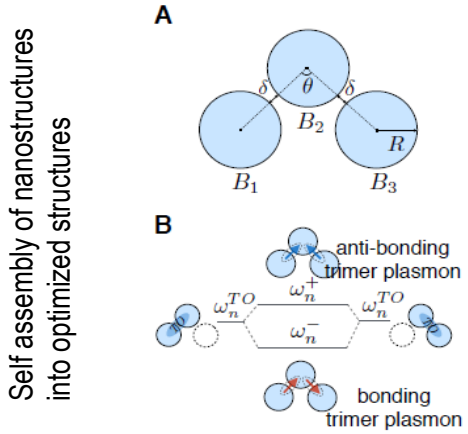
Energy Security

Building an Enduring Foundation for Fundamental Scientific Advances

- **New Discovery Science Program, funded by LDRD, begins in FY20**

Quantum Fields on Driven Plasmonic Nanostructures

Scientific Question: What new material properties will be discovered by modeling and observing nanoparticle (NP) interactions in macro-molecular arrays?

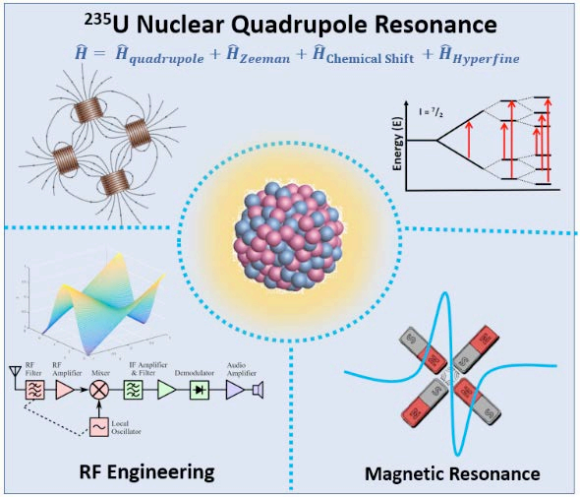


Approach:

- Develop models to explore physics of NP interactions in large assemblies
- Determine how EM fields can be used to control the NP properties
- Construct large self-assembled NPs using newly acquired SEM-FIB
- Investigate new phenomena in the interaction of light with NP arrays

Nuclear Quadrupole Resonance (NQR) Spectroscopy of U-235

Scientific Question: Can high-frequency nuclear quadrupole resonance be used to detect U-235 in solid materials?



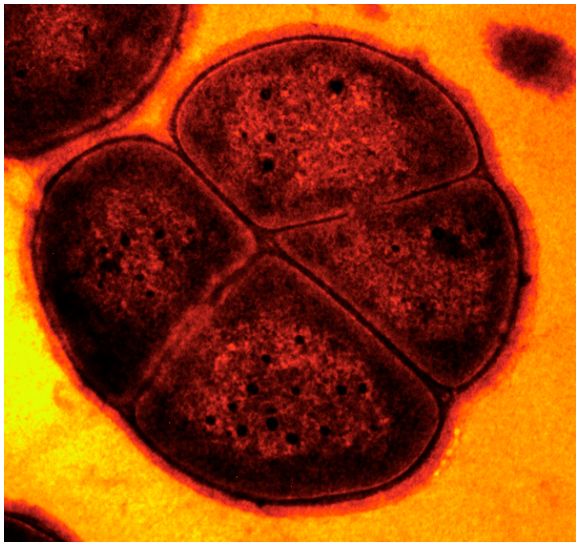
Approach:

- Develop nuclear quadrupole spectrometer
- Synthesize uranium-fluoride crystals with different enrichments
- Perform NQR measurements of reference materials and U-235 samples
- Demonstrate the effect of U-235 enrichment on ^{19}F NMR in solids

Cellular Responses to Radiation Exposure

Principal Objectives:

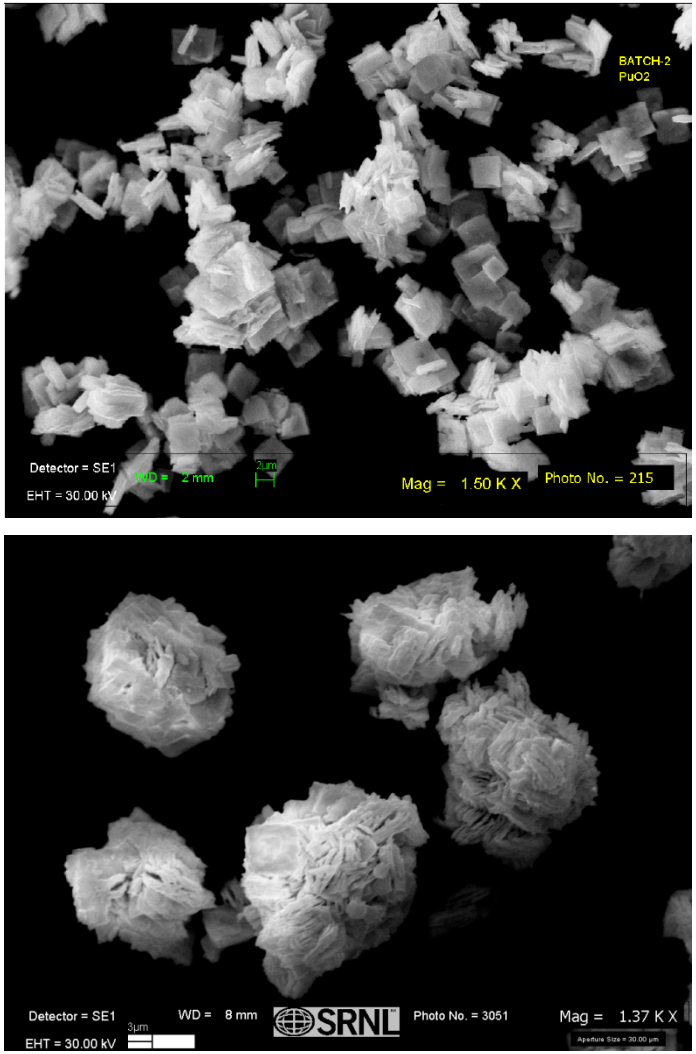
- Identify key genomic signatures and byproducts responsible for survival in rad environments
- Investigate microbial metabolic systems through proteomics to understand epigenetic response to exposure
- Determine metagenomic and molecular markers involved in radioprotection by studying radiation resistant bacteria



This Talk – National and Energy Security (and Science)

- **Multi-scale Modeling of Plutonium Processing – PreCalc**
  - Calcination Reaction Pathway from $Pu(C_2O_4)_2$ to PuO_2
- **Probing Ag-Zeolite Adsorbents**
  - Silver Cluster Formation in Ag-Chabazite
- **Materials Development of Doped $Li_7La_3Zr_2O_{12}$ (LLZO) Structures**
  - Li-ion mobility in Ga- and Ta-Doped LLZO

Motivation for Multi-Scale Modeling of Pu Processing

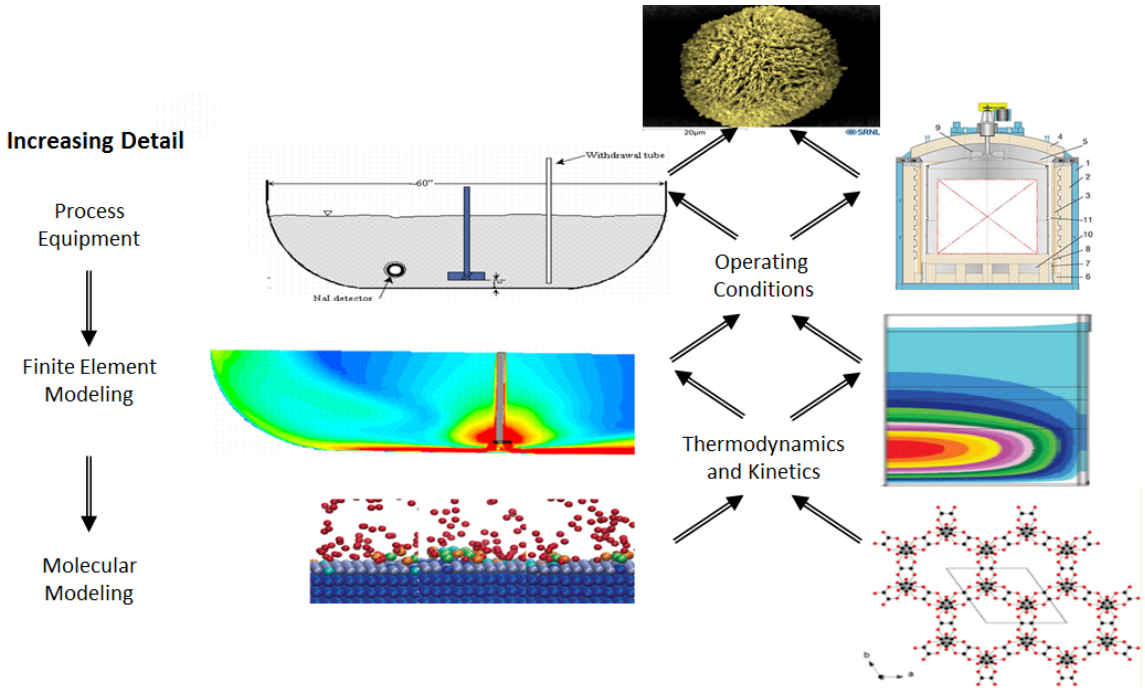


Laboratory- (1g, top) and plant-scale (1 kg, bottom) SEM images of PuO_2.

- **Fundamental relationships between morphological and physicochemical properties from a PuO_2 production facility are understood at an empirical level**
  - Laboratory-scale phenomena do not translate linearly to plant-scale
    - *Inhomogeneous temperature and pressure gradients complicate macroscopic prediction of global kinetics*
- **Multi-scale, multi-physics models can provide a basis for prediction of specific properties**
  - Approach must capture the atomistic features of nonequilibrium dynamic phenomena at finite temperatures while remaining relevant at the process scale

What is the PreCalc Project?

- **Development of a software framework that will integrate multiple models at various time/length scales to provide a description of the precipitation and calcination dynamics of PuO_2 from a production facility**
  - Challenge: Linking together the different types of sub-models



- **Goal: Provide a description of the agglomeration phenomenon for the plutonium oxalate precipitation and the calcination mechanism**

Where to start? Chemistry

- **For Pu(IV) nitrate conversion to oxide:**

$$Pu(NO_3)_4 + 2H_2C_2O_4 + 6H_2O \rightarrow Pu(C_2O_4)_2 \cdot 6H_2O\downarrow + 4HNO_3$$

$$Pu(C_2O_4)_2 \cdot 6H_2O \xrightarrow{\Delta} PuO_2 + 2CO\uparrow + 2CO_2\uparrow + 6H_2O\uparrow$$

Precipitation Conditions:

- Nitric acid concentration
- Plutonium concentration
- Oxalic acid concentration
- Oxalic acid feed
- Strike temperature
- Digestion time
- Agitation speed
- Vessel size/shape

Calcination Conditions:

- Calcination temperature
- Calcination atmosphere (Air/Ar)
- Hold temperature prior to calcination

Variations of these factors allow for the control of important particle properties

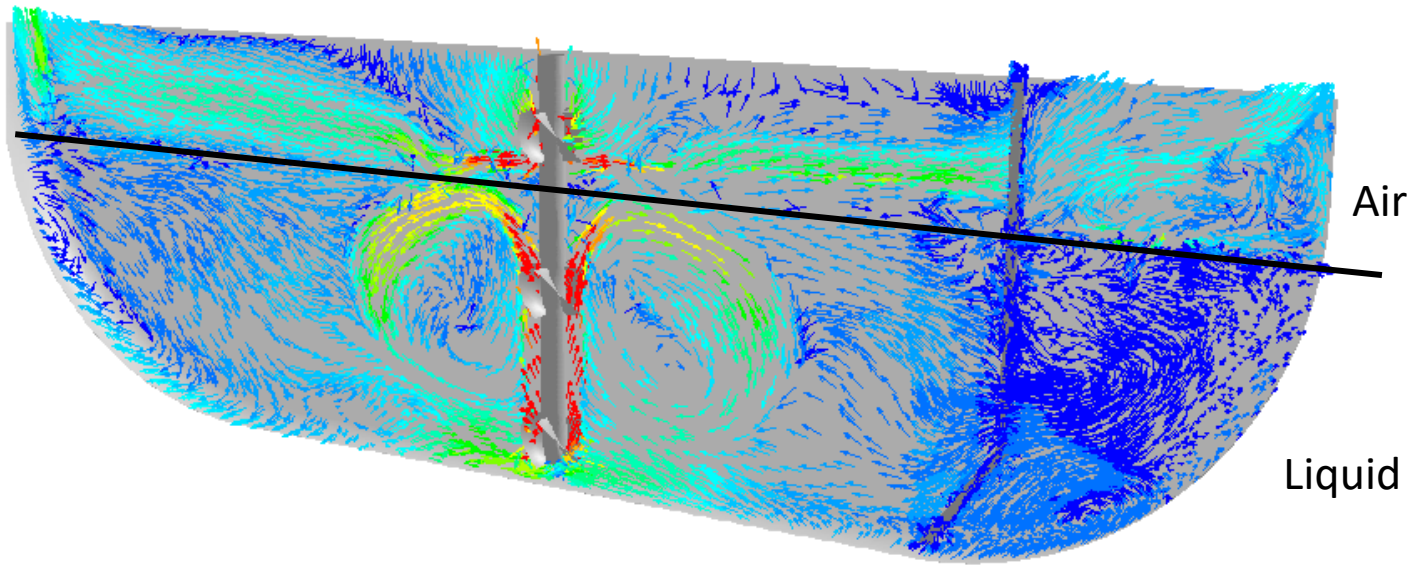
Precipitation

Determination of the supersaturation ratio:

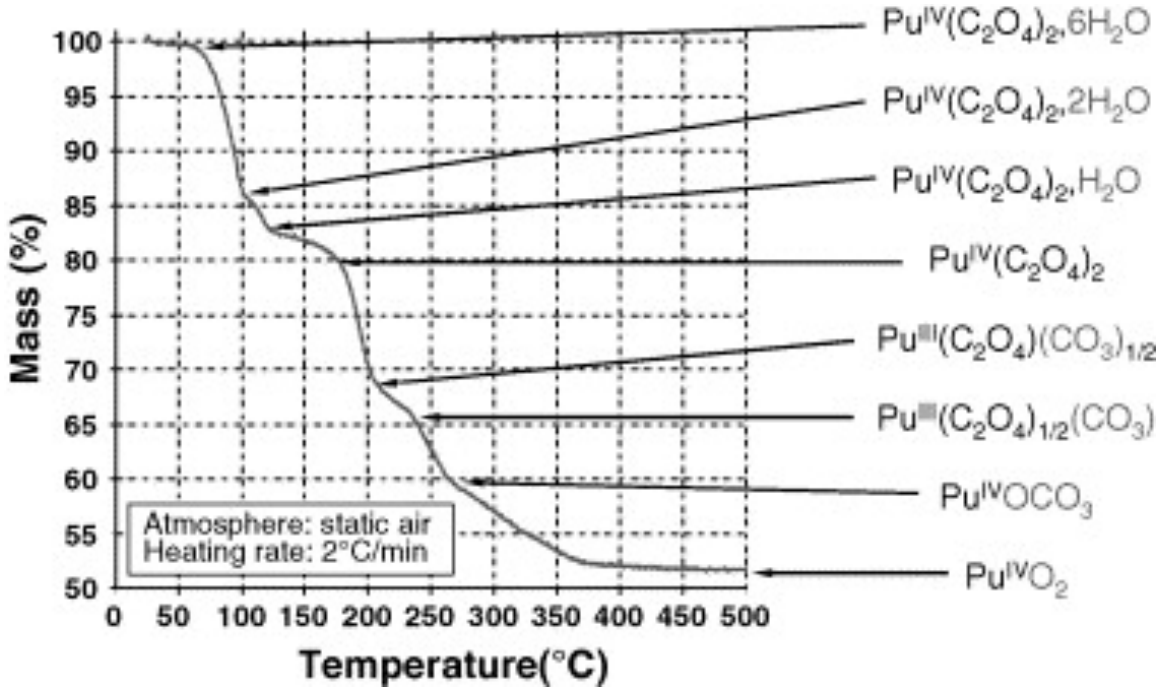
$$S=(2)^{\frac{1}{3}}\frac{1}{K_{sp}^{\frac{1}{3}}}\left[C_{Pu,0}-6\frac{\phi_V\rho_C}{M_C}\frac{R_N}{G}(G\tau)^4\right]$$

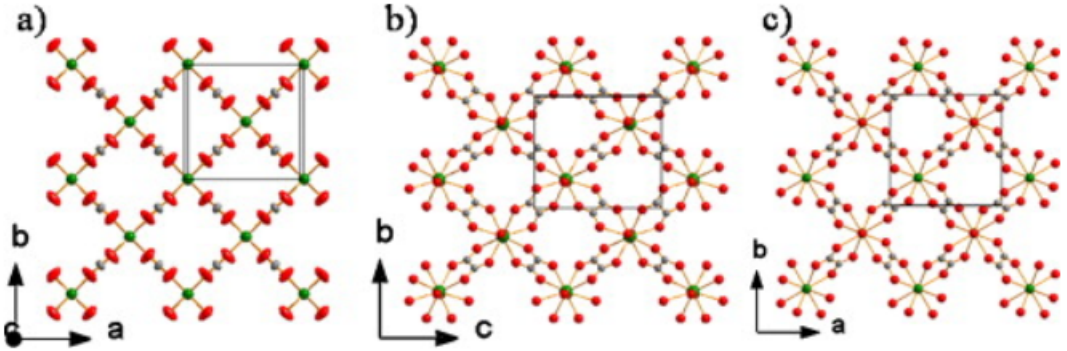
Agglomeration kernel:

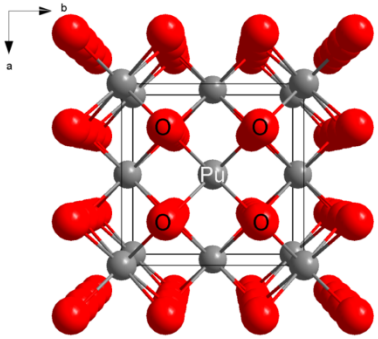
Mechanism	$\beta_0 \times f(L,\lambda)$
Brownian motion	$\beta_0(L+\lambda)(L^{-1}+\lambda^{-1})$
Gravitational	$\beta_0(L+\lambda)^2\lvert L-\lambda\rvert$
Shear	$\beta_0(L+\lambda)^3$
Particle Inertia	$\beta_0(L+\lambda)^2\lvert L^2-\lambda^2\rvert$



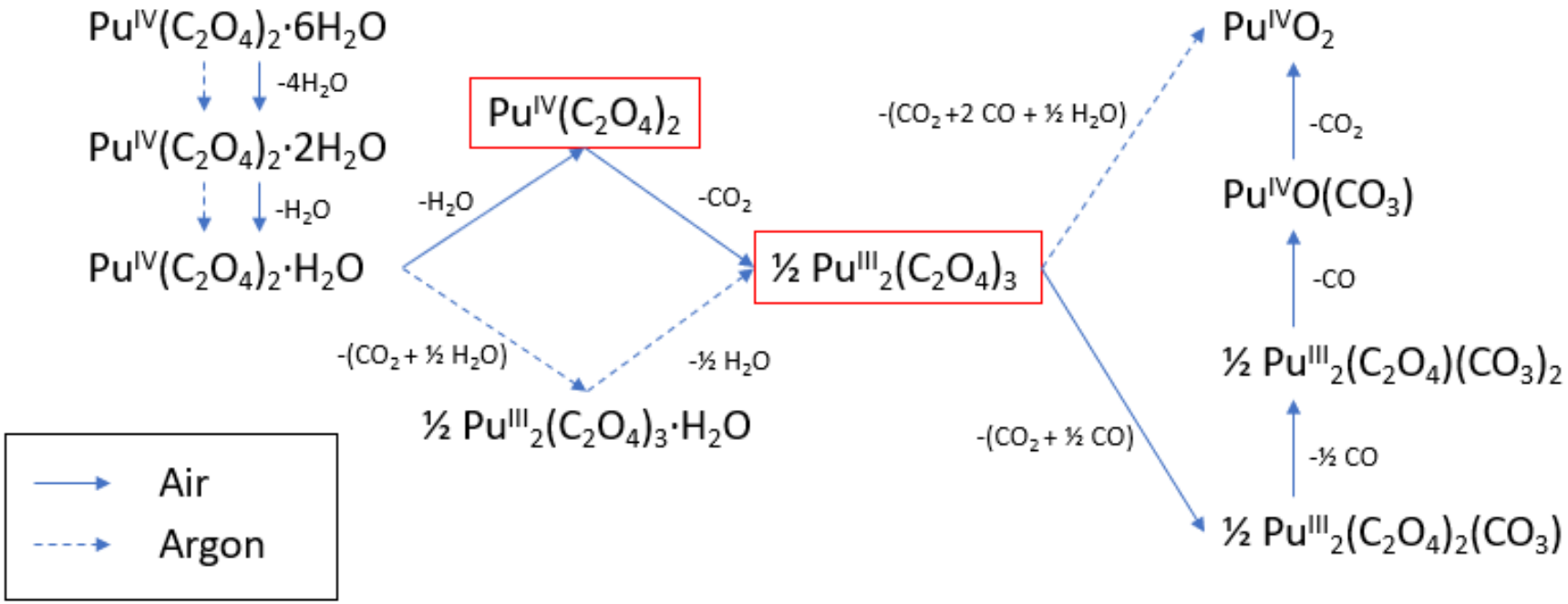
Calcination – Bumpy Road to Oxide Conversion



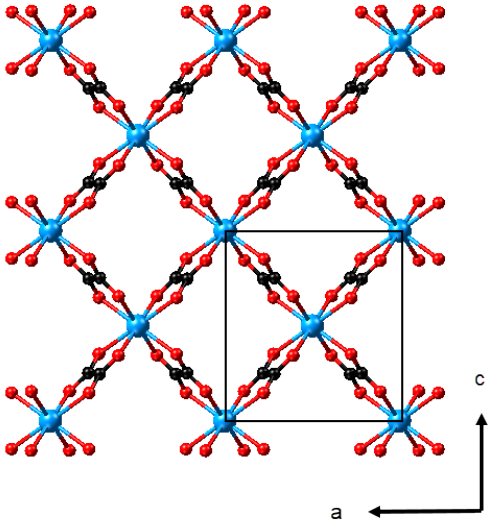


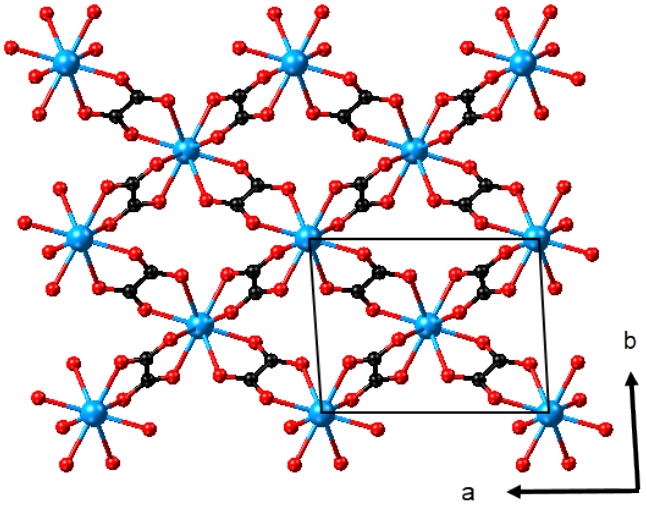


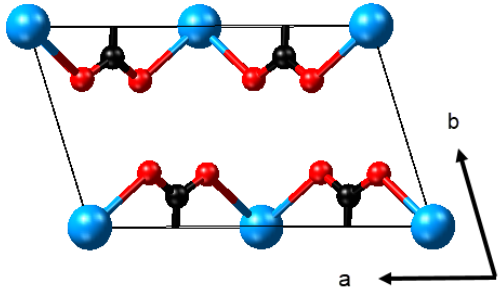
Proposed Reaction Pathway

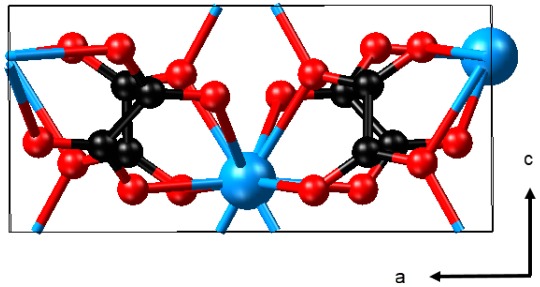


Optimized Structures of $Pu^{IV}(C_2O_4)_2$





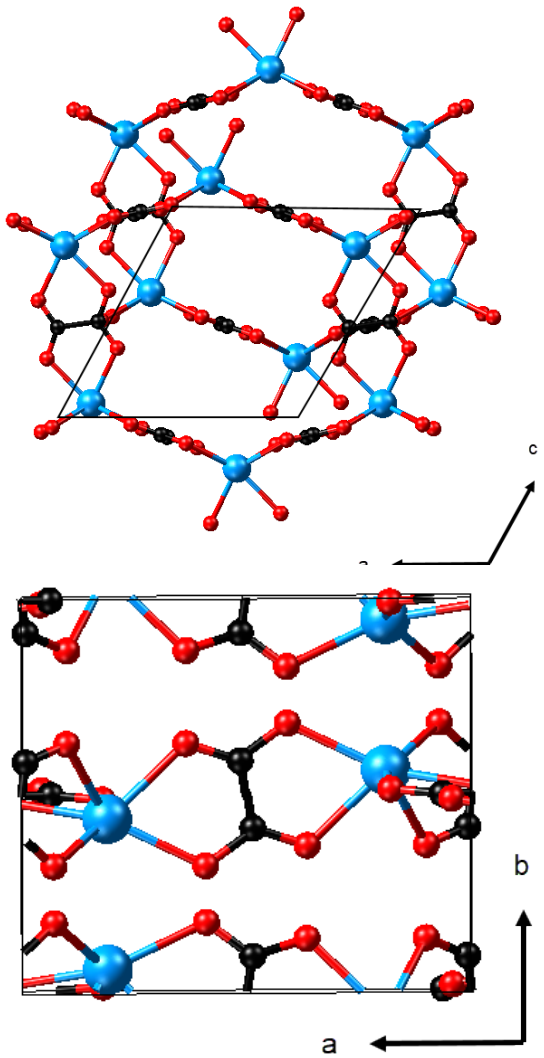




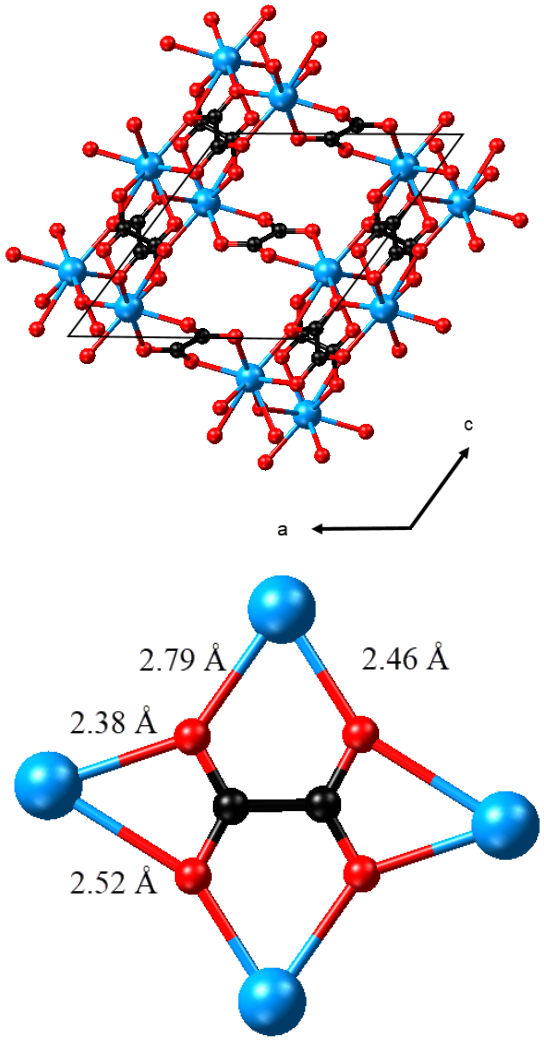
Pu(IV)Ox-1

Pu(IV)Ox-2

Optimized Structures of $Pu^{III}_2(C_2O_4)_3$



Pu(III)Ox-1



Pu(III)Ox-2

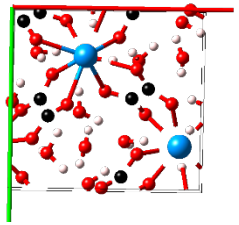
Calculated Reaction Energies

- **Pu(IV)Ox-1 predicted to be the preferred structure at PBE-D3+U level**
  - Lower in energy by only ~8.2 kJ/mol
- **Pu(III)Ox-1 shown to be the lowest energy structure**
  - More stable by ~54.6 kJ/mol
- **Preferred reaction pathway determined to be Pu(IV)Ox-1 to Pu(III)Ox-1**
  - Total reaction energy of -134.4 kJ/mol
  - Energy of Pu(IV)Ox-2 to Pu(III)Ox-1: -142.6 kJ/mol
    - *DFT is not accurate enough to distinguish these two reactions*

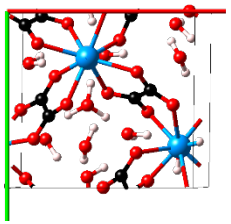
$$Pu(IV)Ox \rightarrow Pu(III)Ox + CO_2$$

Absolute Energies	
Molecule	Energy (kJ/mol)
Pu(IV)Ox-1 PBE-D3+U	-10827.733
Pu(IV)Ox-2 PBE-D3+U	-10819.529
Pu(III)Ox-1 PBE-D3+U	-17490.980
Pu(III)Ox-2 PBE-D3+U	-17436.324
CO_2 PBE-D3	-2216.686

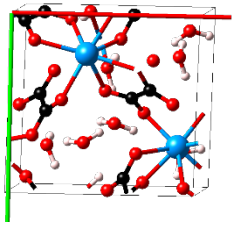
Identified intermediate species



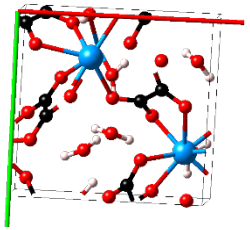
$PuOx_2 \cdot 6H_2O$



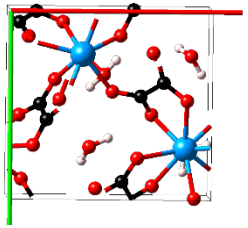
$PuOx_2 \cdot 5H_2O$



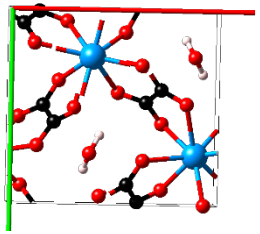
$PuOx_2 \cdot 4H_2O$



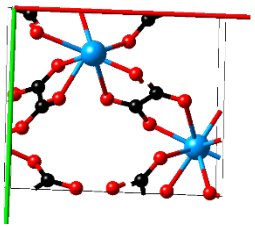
$PuOx_2 \cdot 3H_2O$



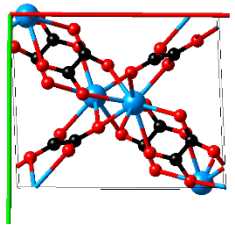
$PuOx_2 \cdot 2H_2O$



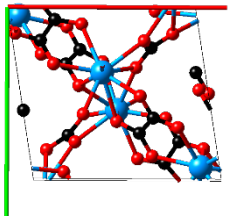
$PuOx_2 \cdot H_2O$



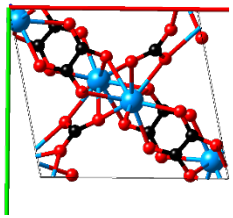
$PuOx_2$



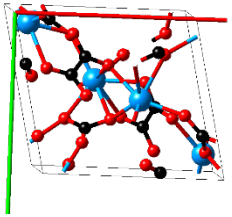
Pu_2Ox_3



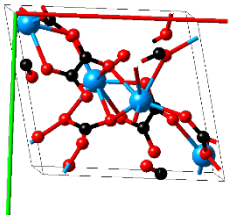
Pu_2Ox_3 rearr



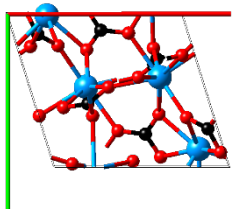
$Pu_2Ox_2CO_3$



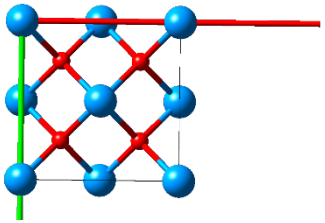
$Pu_2Ox_2CO_3$ rearr



$Pu_2Ox(CO_3)_2$



$Pu_2(CO_3)_3$



PuO_2

Band Gaps

- **Without strong correlation, all compounds optimize metallic/semi-metallic**
- **HSE06 predicts all compounds to be antiferromagnetic insulators**
  - Band gaps for hydrates within ~ 2.5 – 3.1 eV from single point calculations
  - PuO_2 shows a band gap of ~ 2.1 eV
    - *Experiment[2]: 2.8 eV*
    - *HSE06 at FCC geometry[3]: ~ 2.7*
- **PBE-D3+U obtains band gaps from 1.5 to 2.1 eV for the $PuOx_2$ hydrates**
  - PuO_2 shows a band gap of 2.5 eV

Band Gaps		
Molecule	HSE06 (eV)	PBE-D3+U (eV)
$PuOx_2 \cdot 6\ H_2O$	2.955	2.074
$PuOx_2 \cdot 5\ H_2O$	3.076	
$PuOx_2 \cdot 4\ H_2O$	2.521	1.524
$PuOx_2 \cdot 3\ H_2O$	2.694	1.469
$PuOx_2 \cdot 2\ H_2O$	2.505	1.528
$PuOx_2 \cdot H_2O$	2.728	1.756
$PuOx_2$	2.861	1.587
PuO_2	2.150	2.500

[2]McCleskey, T. M.; Bauer, E.; Jia, Q.; Burrel, A. K.; Scott, B. L.; Conradson, S. D.; Mueller, A.; Roy, L.; Wen, X.; Scuseria, G. E.; Martin, R. L. *J. Appl. Phys.* **2013,** *013515*, 013515

[3]Prodan, I. D.; Scuseria, G. E.; Martin, R. L. *Phys. Rev. B.* **2007,** *76*, 033101

Table of Reaction Free Energies

Free Energies				
Energy	PBE (kJ/mol)	HSE06 (kJ/mol)	PBE-D3 (kJ/mol)	PBE-D3+U (kJ/mol)
1st dehydration	387.258	64.774	86.420	
2nd dehydration	-249.839	68.897	82.322	
3rd dehydration	-132.555	31.820	52.556	43.313
4th dehydration	232.163	53.707	65.768	84.922
5th dehydration	31.006	44.198	42.045	72.639
5th dehydration alt	-84.934	43.896	82.116	
6th dehydration	22.308	24.436	36.611	89.954
6th dehydration alt	138.248	24.738	-3.460	
1st CO_2 elimination	-312.580		-0.680	-326.844
1st rearrangement	132.546		85.376	22.556
1st CO elimination	-43.169		-15.815	141.094
2nd rearrangement	165.407		162.113	-34.068
2nd CO elimination	-42.384		-27.946	320.970
3rd rearrangement	114.702		90.598	-139.890
3rd CO elimination	-121.981		-111.706	-89.444
4th CO elimination	509.751		267.256	426.496
2nd CO_2 elimination	-78.904		-80.755	-72.974

Free Energies

- **HSE06, PBE-D3, and PBE-D3+U all predict hydration energies to be endothermic**
  - PBE alone, does not
  - Dispersion and strong correlation important
- **PBE and PBE-D3 predict same trends for calcination**
- **1st CO_2 elimination is spontaneous**
  - Consistent with experimental observations
- **Reaction energies larger than expected in most cases**
  - 1st CO elimination, 4th dehydration, and 4th CO elimination
- **4th CO elimination energy far too endothermic**
  - Should be visible in IR, but not observed experimentally
  - All tested methods show this large barrier height

Future Work

- **Complete the modeling of the remainder of the reaction pathway using PBE-D3+U**
  - Construct the energy profile as a function of reaction coordinate
- **Calculate barrier heights for kinetic data and reaction rates**
- **Determine the effect of O_2 on the pathway and on its effects on the kinetics and thermodynamics of calcination**
  - Catalyst or reagent?

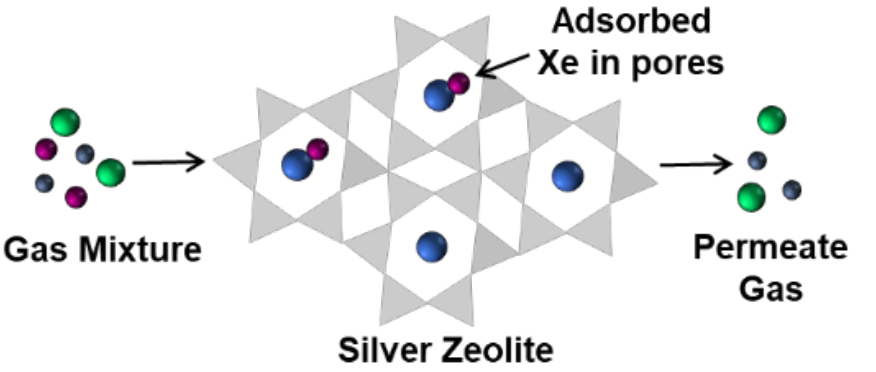
This Talk – National and Energy Security (and Science)

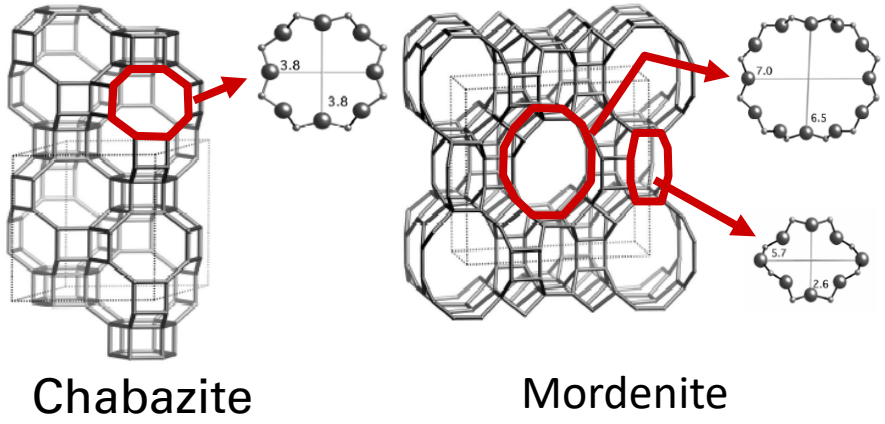
- **Multi-scale Modeling of Plutonium Processing – PreCalc**
  - Calcination Reaction Pathway from $Pu(C_2O_4)_2$ to PuO_2
- **Probing Ag-Zeolite Adsorbents**
  - Silver Cluster Formation in Ag-Chabazite
- **Materials Development of Doped $Li_7La_3Zr_2O_{12}$ (LLZO) Structures**
  - Li-ion mobility in Ga- and Ta-Doped LLZO

Probing Ag-Zeolite Adsorbants: Insights for Material Design

Objective: To use a combined experimental/theoretical approach to rationalize trends in Xe uptake in Ag-exchanged zeolites and develop a basis for designing novel, low-cost adsorbents with improved performance.

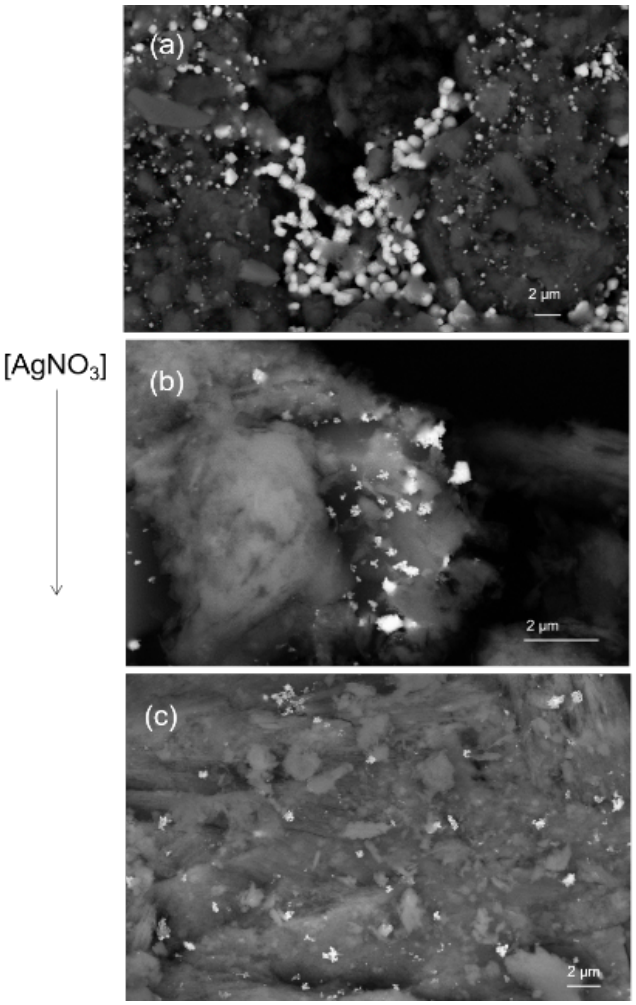
Relevance: Anthropogenic noble gases are a key indicators of nuclear activity.





Best performer for Xe uptake: silver-exchanged zeolites

Experimental Results – Ag loading on Zeolite



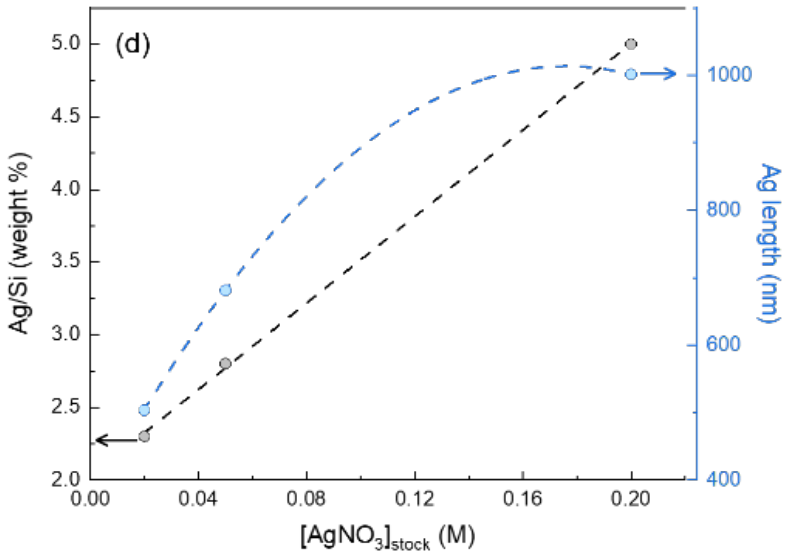
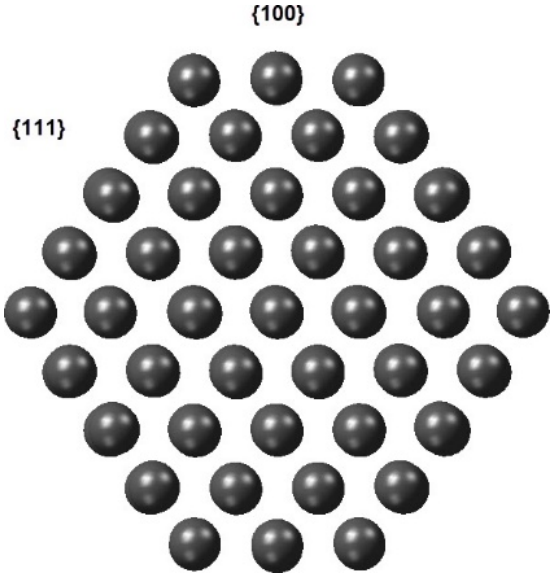


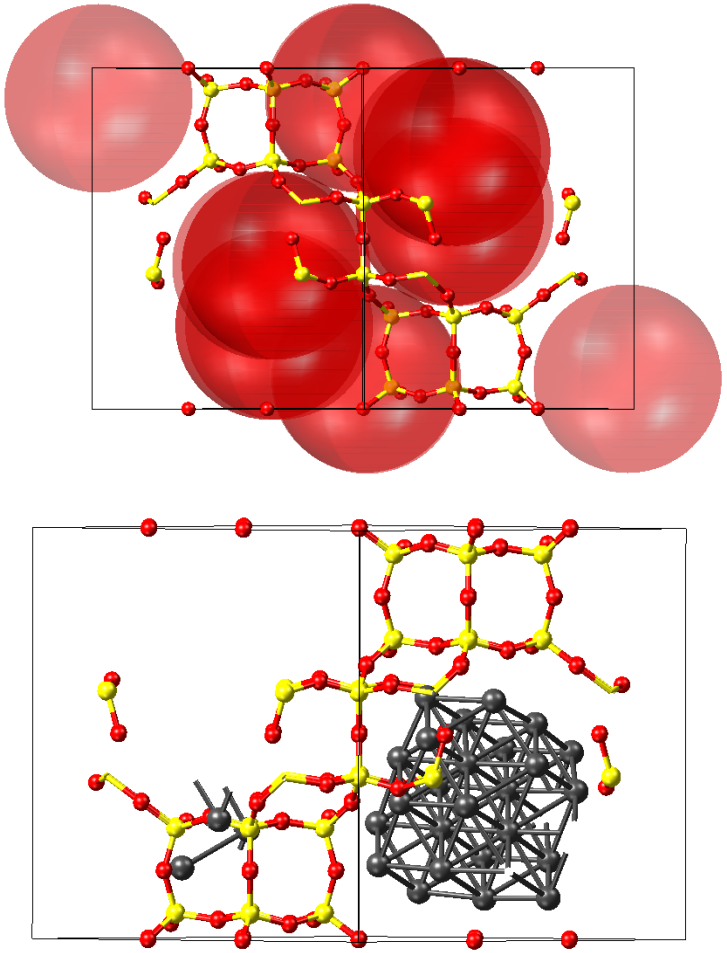
Figure 5: Effect of concentration on silver loading and surface morphology on Ag-cabsorb

Initial Computational Work



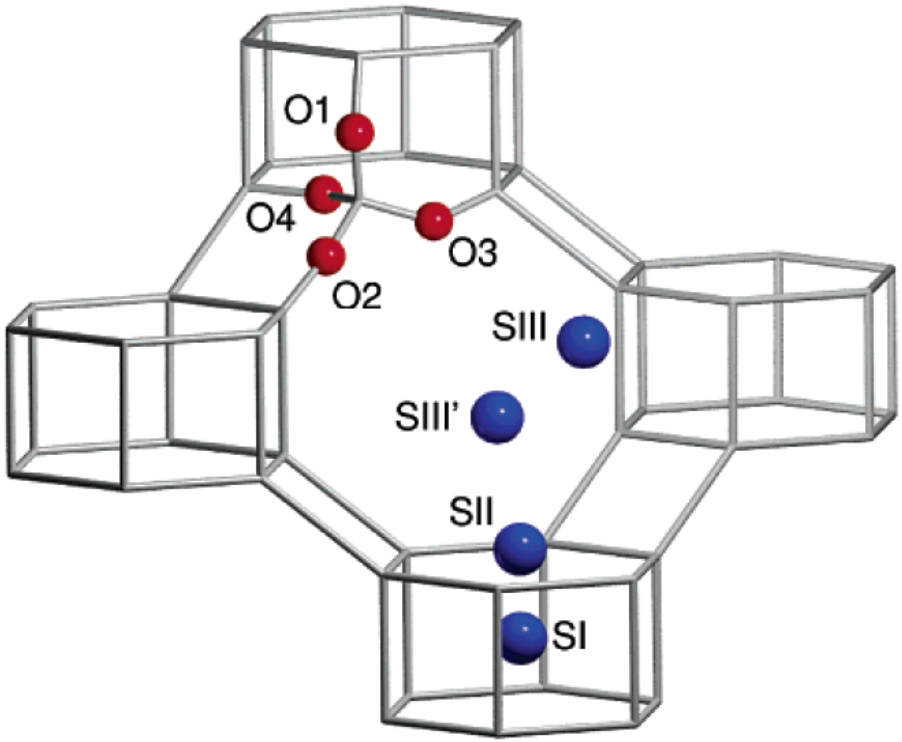
Number of Atoms	Diameter (nm)
28	0.8
43	1.1
68	1.3
140	1.5
176	1.6
201	2.0
405	2.5
586	2.7
807	3.0

Low-Index Facet Evaluation



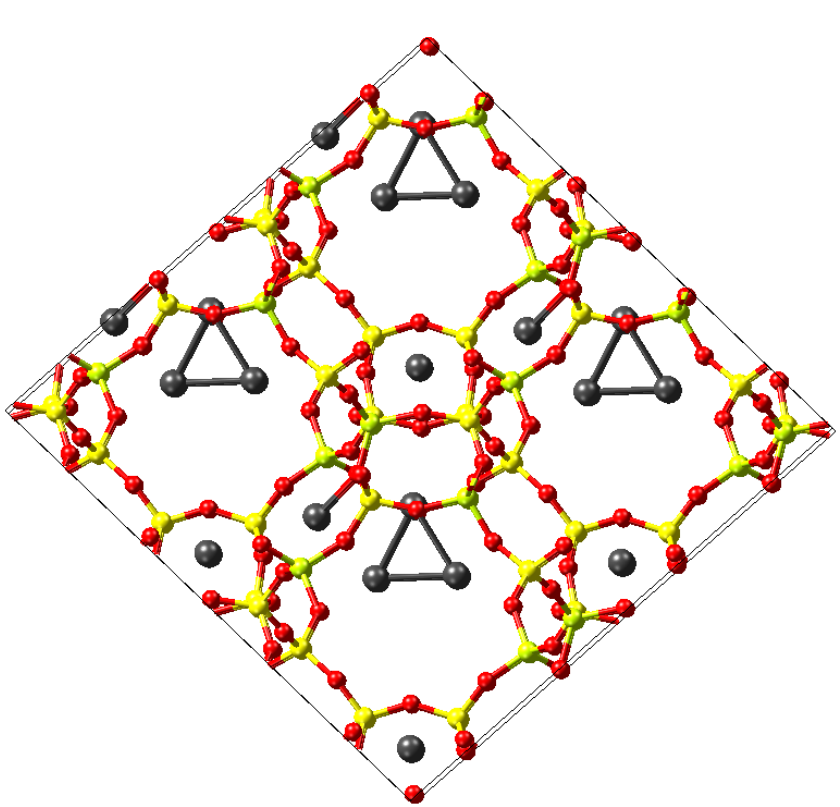
Chabazite Optimization + 28 atom AgNP

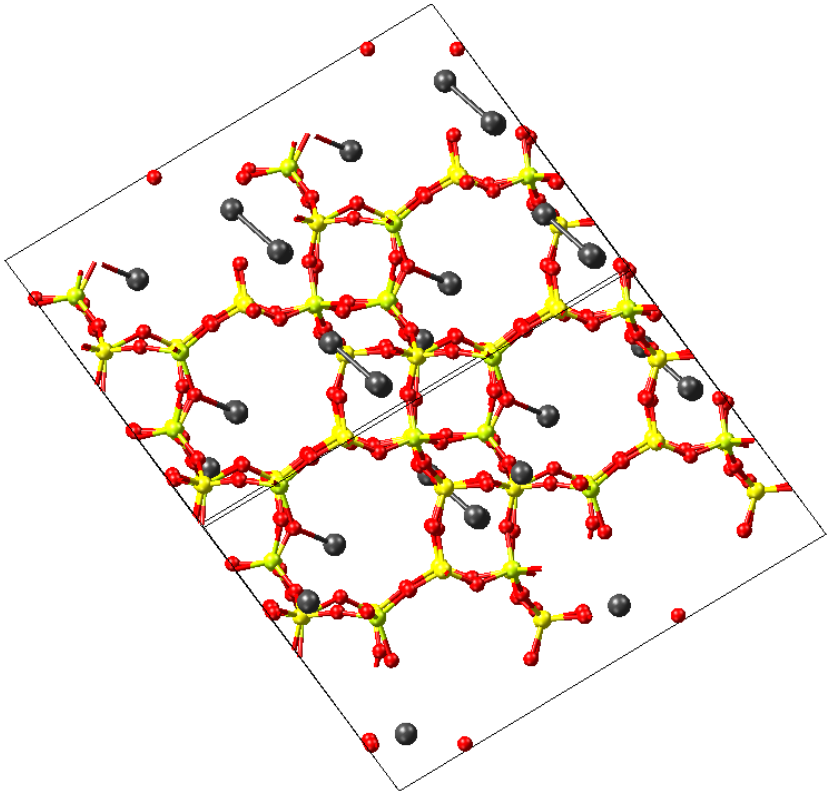
Computational Work: Round 2



Description	Energy (eV)	ΔE (eV)
1 Ag ions		
SIII	-283.778606	0.46
SI	-284.060201	0.18
SIII'	-284.137723	0.10
SII	-284.235418	0
2 Ag ions		
SII-SIII' – Adjacent	-283.760324	0.28
SII-SIII' – Separated	-283.860702	0.19
SII-SII	-284.047073	0
3 Ag ions		
SII-SIII'-SIII' – Separated	-283.617146	0.45
SII-SIII'-SIII' – Adjacent	-283.773661	0.29
SII-SII-SIII'	-284.064328	0

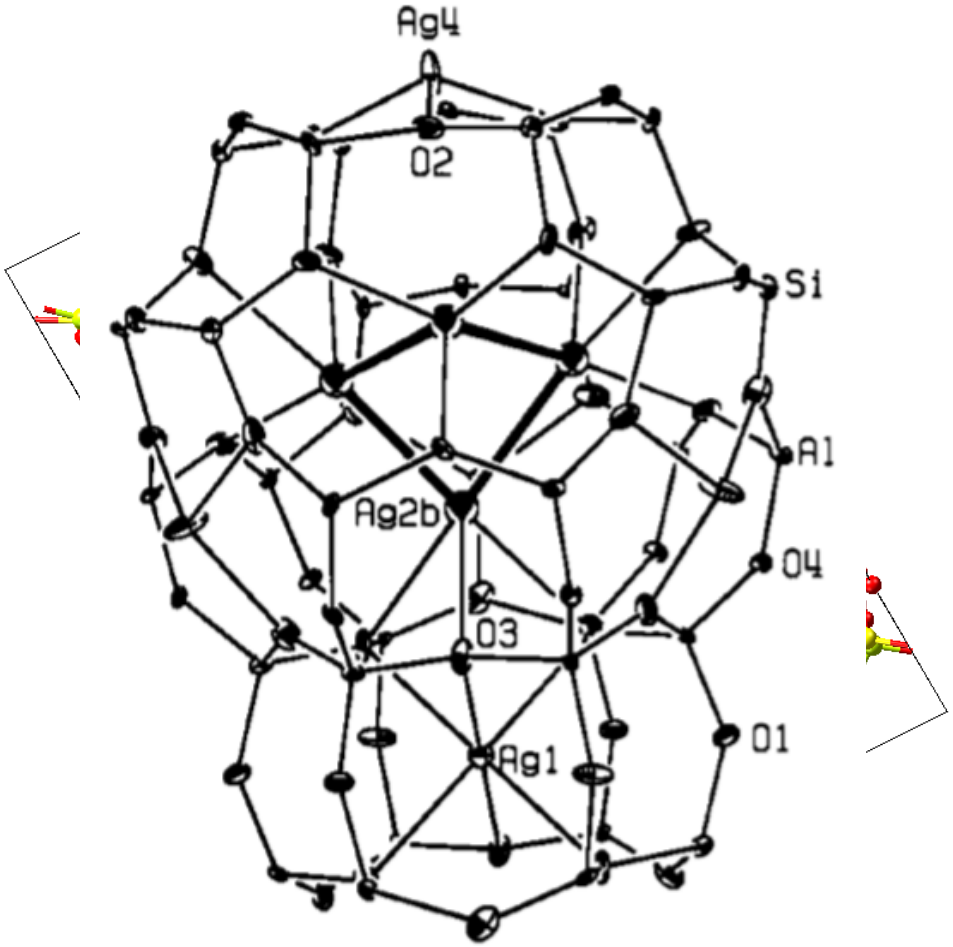
Ag atom additions





Formation of an Ag_3^{2+} trimer

Ag_4^{2+} formation



Is there precedence in the literature?

Future Work

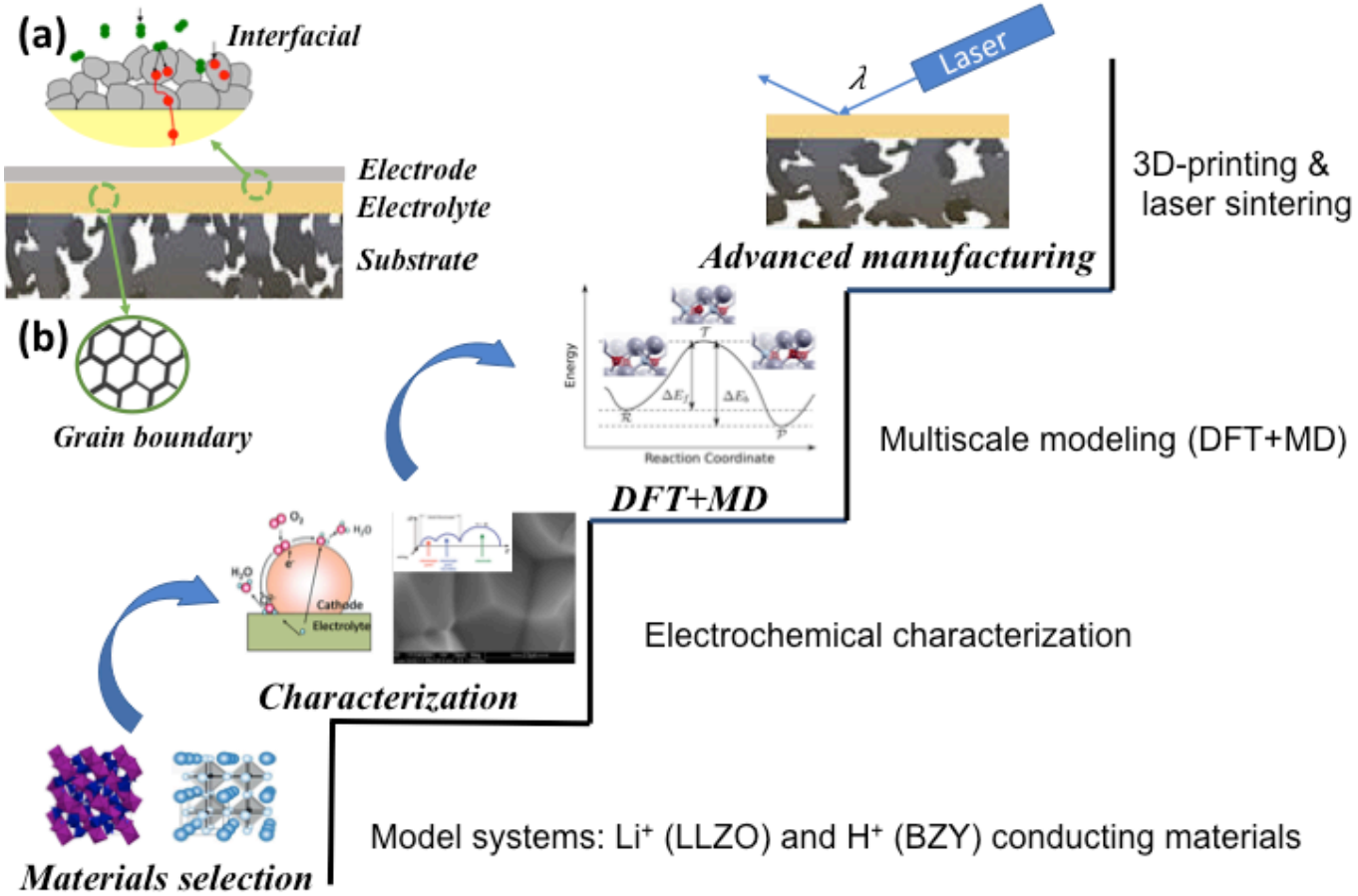
- Ongoing – Currently optimizing an Ag_8^{4+} cluster based on other Ag-zeolites in the literature
- Future studies – Ag NP adsorption on Ag-Chabazite surface, Xe adsorption on optimized structures, others?
- Major breakthrough in Ag cluster formation within the cavity and could explain increased Xe uptake without AgNP formation on surface

This Talk – National and Energy Security (and Science)

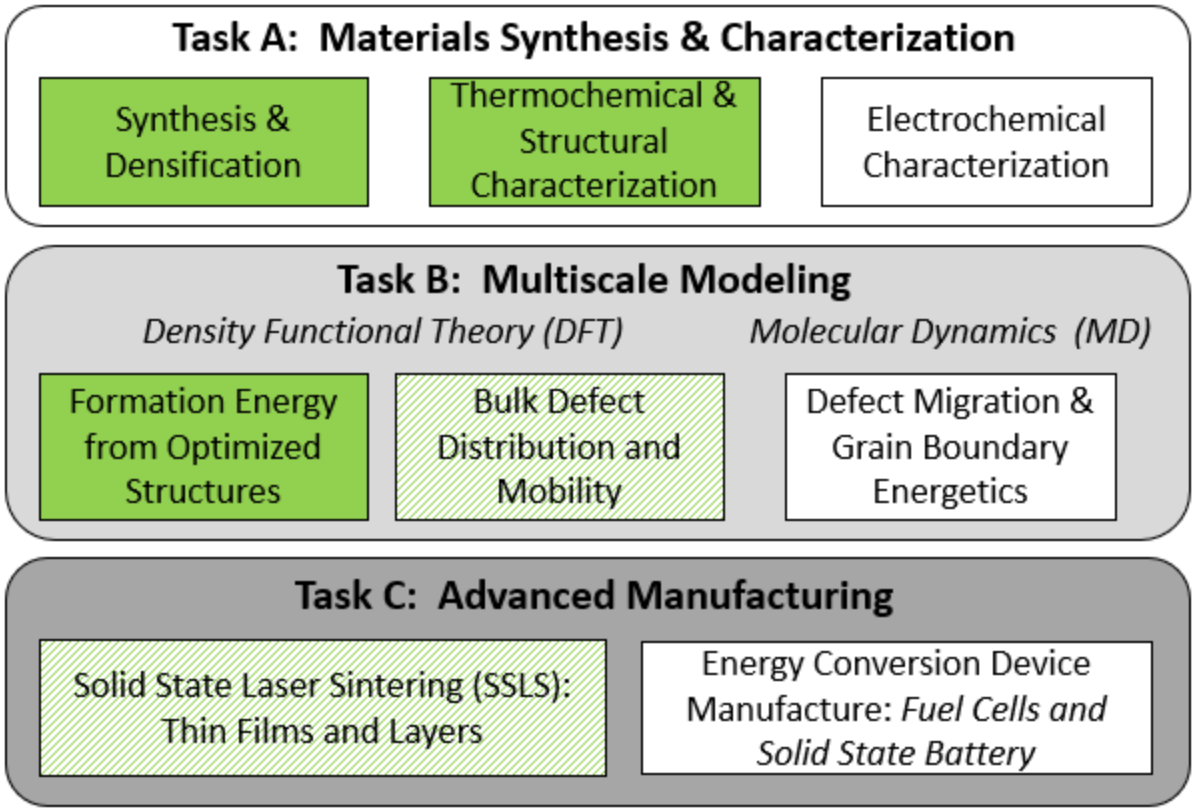
- **Multi-scale Modeling of Plutonium Processing – PreCalc**
  - Calcination Reaction Pathway from $Pu(C_2O_4)_2$ to PuO_2
- **Probing Ag-Zeolite Adsorbents**
  - Silver Cluster Formation in Ag-Chabazite
- **Materials Development of Doped $Li_7La_3Zr_2O_{12}$ (LLZO) Structures**
  - Li-ion mobility in Ga- and Ta-Doped LLZO

Solid State Ionics: Materials Development Research

DEVELOPING **ADVANCED MANUFACTURING TECHNIQUES** FOR DEPOSITION OF THIN FILM ION CONDUCTORS WITH **CONTROLLED MICROSTRUCTURES**



Expt/Theor Methods



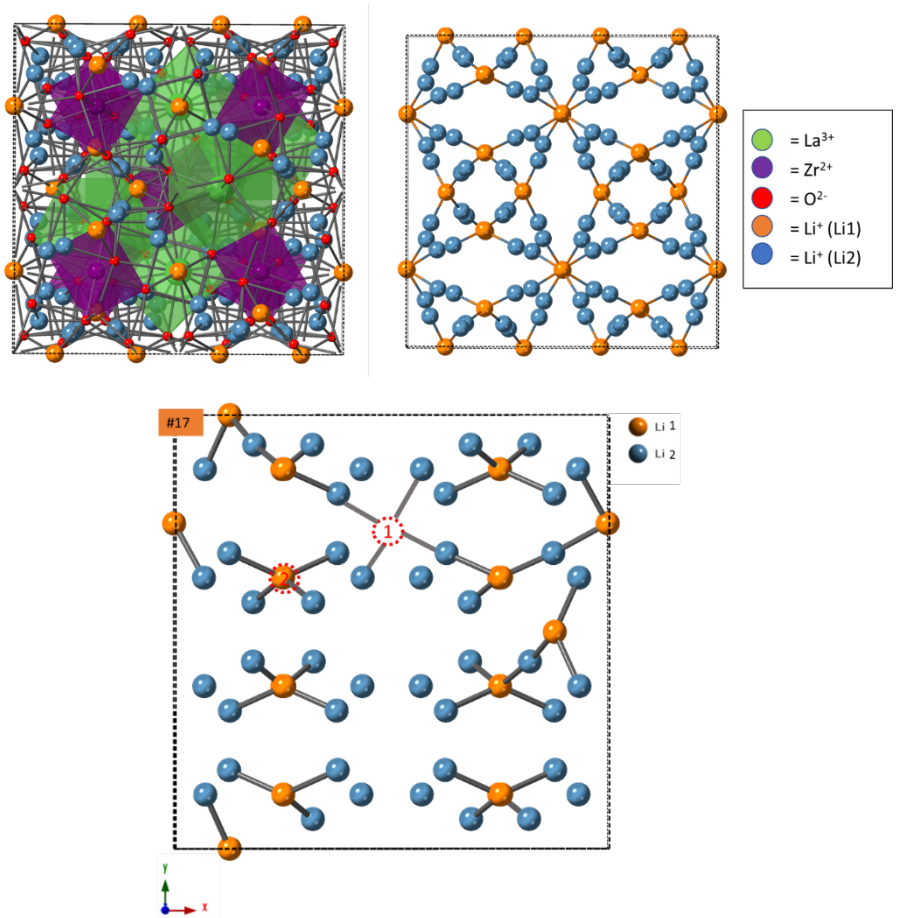
$Li_7La_3Zr_2O_{12}$ – Ga^{3+} and Ta^{5+} Doped Structures

Garnet-type Li-ion conductor:

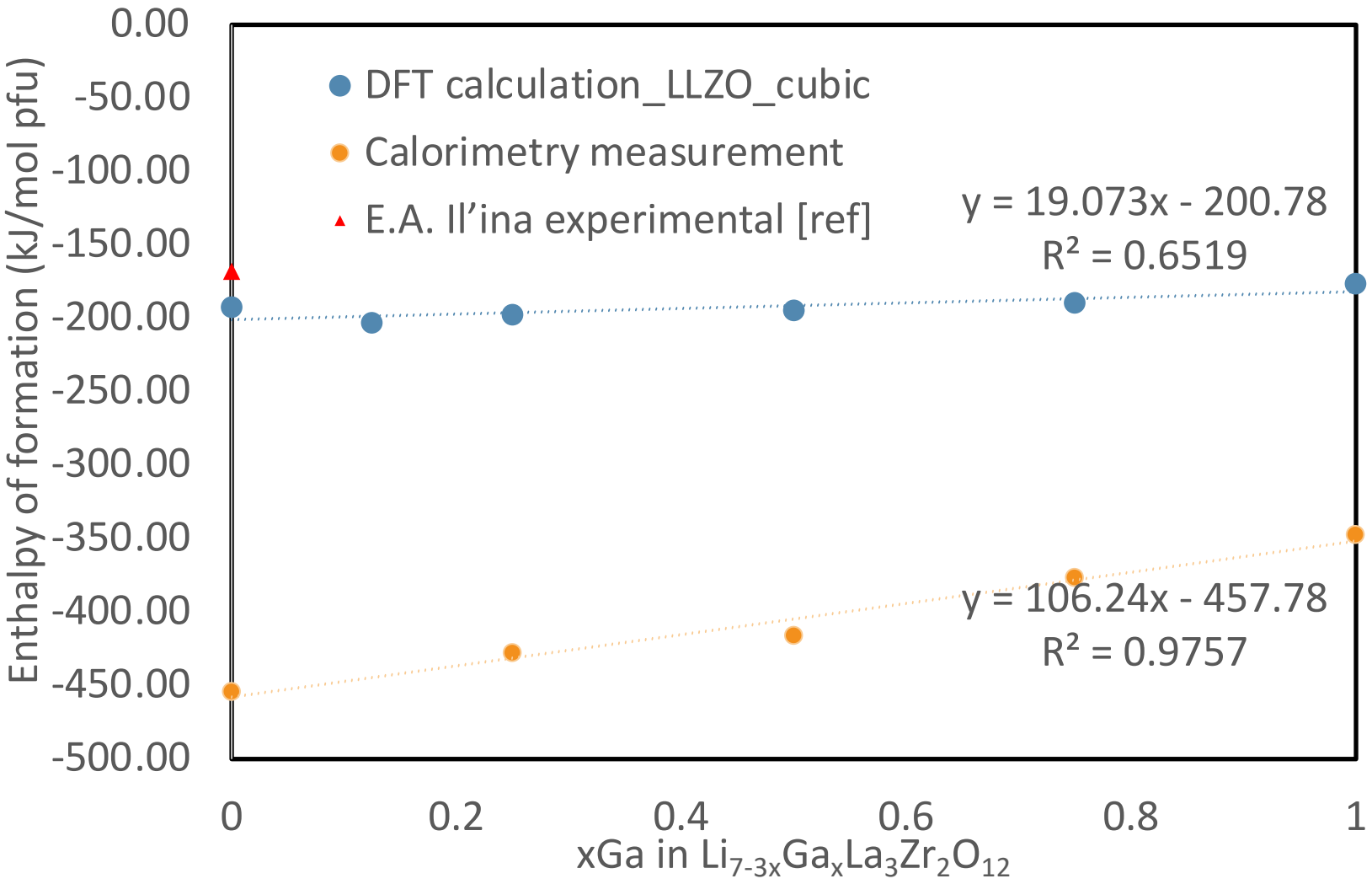
- Bulk ionic conductivity
- Wide E-chem window
- Chemical stability against metallic Li anode

Issues:

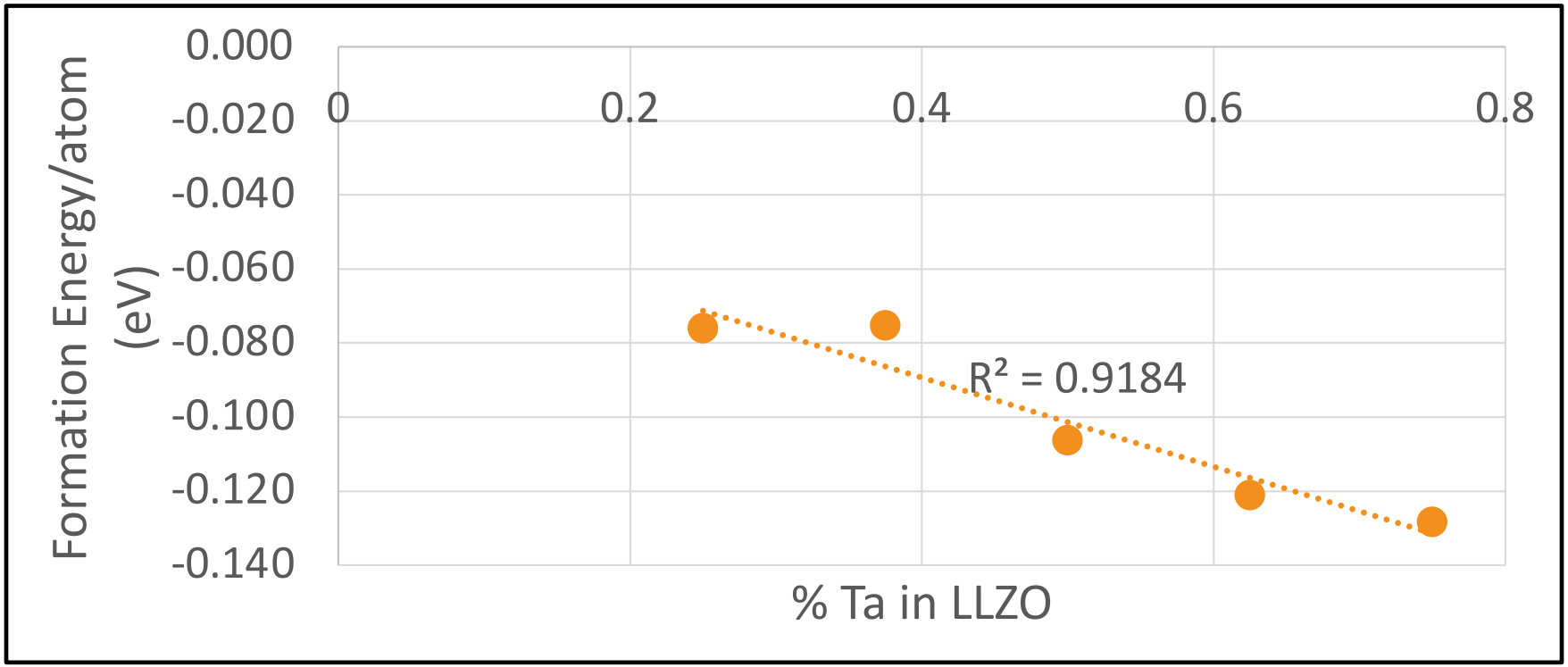
- Nominal Structure – tetragonal *$I4_1/acd$*
- Phase transition ~150˚C to cubic *$Ia\bar{3}d$*
  - Stabilization @ RT using doping strategies
    - Trivalent cation for Li^+
    - Pentavalent cation for Zr^{4+}



Total Energy from DFT vs Calorimetry Data



Formation Energy vs %Ta in Ta-Doped LLZO



Future Work

Task A: Materials Synthesis and Characterization
- M5: Microwave solution combustion synthesis (SCS) of pure cubic phase LLZO
- M6: Electrochemical characterization of bulk and laser sintered LLZO

Task B: Multiscale Modeling
- M4: Bulk defect incorporation and Li+ ion mobility calculations
- M7: Defect migration and grain boundary energetics

Task C: Advanced Manufacturing
- M8: Solid state laser sintering of Ga-doped and Ta-doped LLZO
- M9: Energy conversion device manufacturing

Overall Conclusions

Over the past few years, integration of science into the R&D portfolio is making tremendous impact on our work

- MedeA suite of programs are integral components

Several programs not mentioned:

- Development of adaptive force fields based on ML algorithms for Fe-O phases/surfaces/defects
- Understand the evolution of helium bubbling as a function of temperature near the titanium hydride $TiT_{1.5}$ surface to provide a describe how variation of the orientation can affect helium bubble nucleation, growth and release with respect to various environmental temperatures and He concentration.
- Structure determination of hydrated plutonium-fluoride structures
- Others?

materials design

SRNL

Question and Answer Session

© Materials Design, Inc. 2020

Announcements

Ugm.materialsdesign.com

Professor Richard Catlow FRS

University College London

Dr. Ray Shan

Materials Design

Next Week's Plenary Speaker

October 8th

MedeA Training

October 6th

© Materials Design 2020

Question and Answer Session

Lindsay Roy, Ph.D

Principal Scientist, SRNL

Dr. Taylor Juran

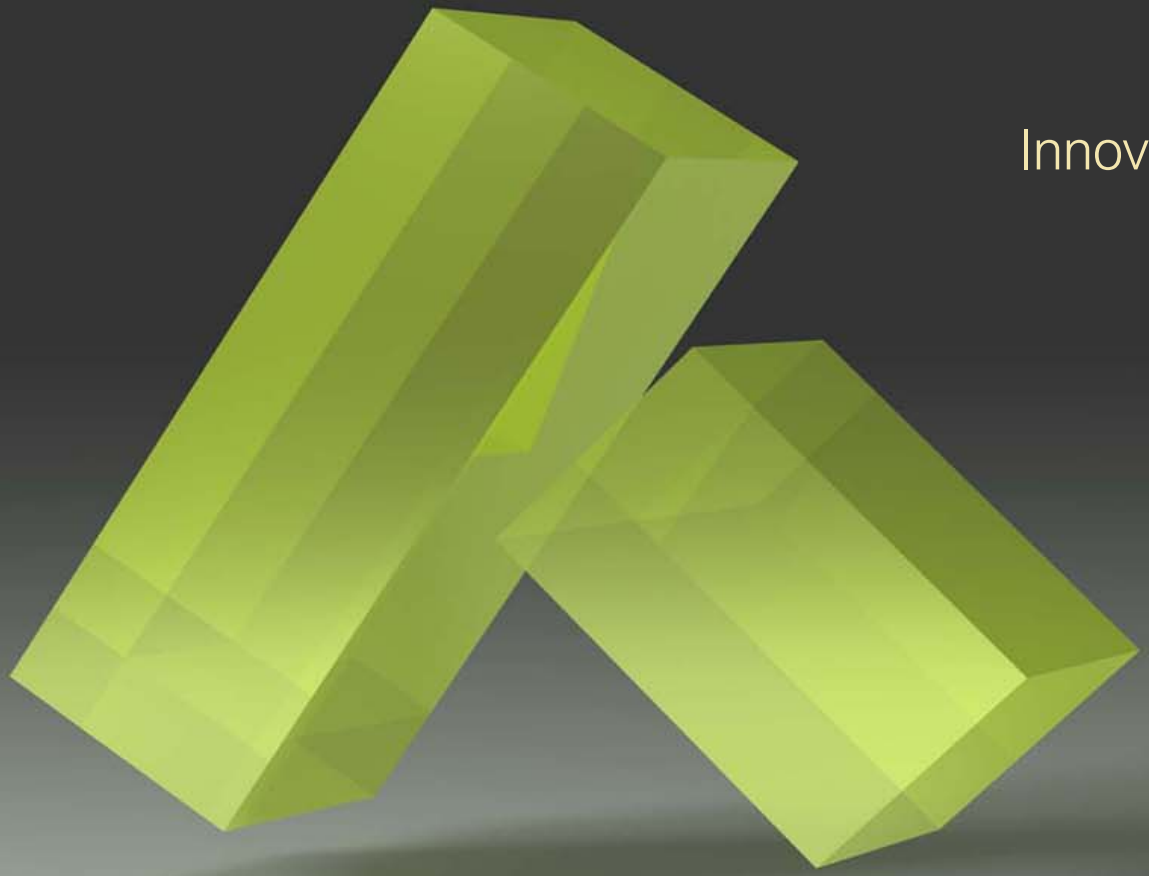
Materials Design Support Scientist

© Materials Design 2020

Questions about the Materials Design UGM Plenary Sessions

Katherine Hollingsworth

khollingsworth@materialsdesign.com



MedeA

Innovation by Simulation