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The Fuel Cycle Research & Development

Iodine Waste Form Development and Technology:
Iodine Capture Focus Area - Materials Characterization

Tina M. Nenoff, James Krumhansl, Terry Garino, Dorina Sava, David Rademacher
Sandia National Laboratories
Albuquerque, NM 87185

Robert Jubin, ORNL
Nick Soelberg, Tony Watson, Jack Law, Daryl Haefner, INL
Karena Chapman, Peter Chupas, ANL

Volatile Fission Gases: Capture and Storage

- Volatile gases/long-lived fission products pose *unique scientific issues* with regards to detection, storage, capture (including ^{129}I, ^{85}Kr, ^{14}C (CO_2), ^{3}H)
- *High Selectivity paired with High Sorption Capacity allows for numerous applications in Nuclear Energy and Security.*
- One example, Iodine: ^{129}I is present in small concentration, however it has a half-life of 1.57 x 10^7 years; ^{131}I is short half life (8 days) but involved with human metabolic processes. *Capture is very important*
- The leading technology:

  Ag-loaded zeolites, which capture the iodine mostly as AgI
- AgI is very insoluble, but it *is not geologically stable* at either the earth's surface or under normal repository conditions
- Additional separations processes/materials and novel *waste forms need to be developed* for both interim storage and permanent disposal in geologic repositories

T.M.Nenoff, tmnenof@sandia.gov

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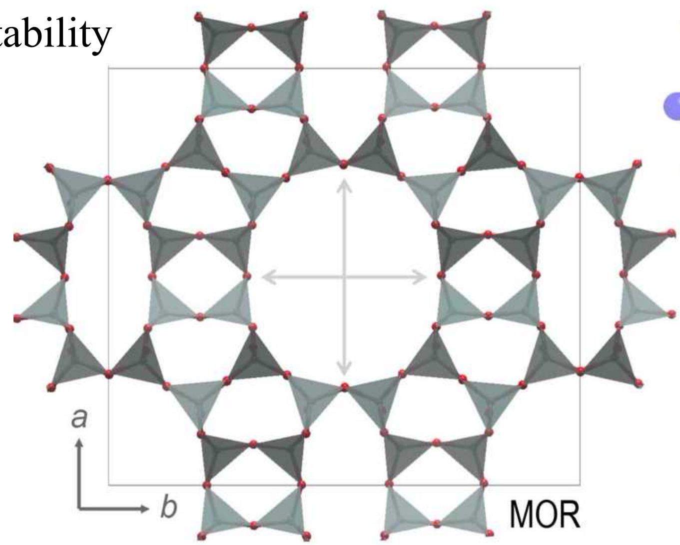
Volatile Gas in Spent Nuclear Fuel Reprocessing: Iodine

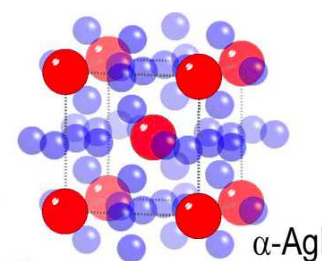
- While I^{129} is only found in small concentrations in nuclear effluent, the effective capture and storage of iodine is critically important to public safety due to its involvement in human metabolic processes and its long half-life (~10^7 years).
- Silver Mordenite (MOR) is a standard iodine-getter, although the iodine binding mechanism remains poorly defined. Presumably an iodide forms within the zeolite's pores
- Understanding **Structure-Property Relationship between Nanoscale and Bulk effects**
  - To optimize capture
  - Impacts processing for long term storage
  - To predict long term stability

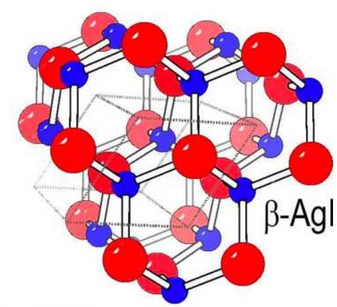
MOR, Mordenite

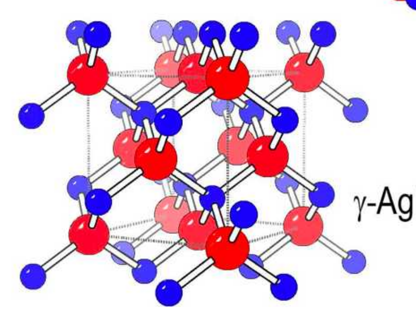
$X_2Al_2Si_{10}O_{24} \cdot 7(H_2O)$

12 MR, 7.0 x 6.5Å









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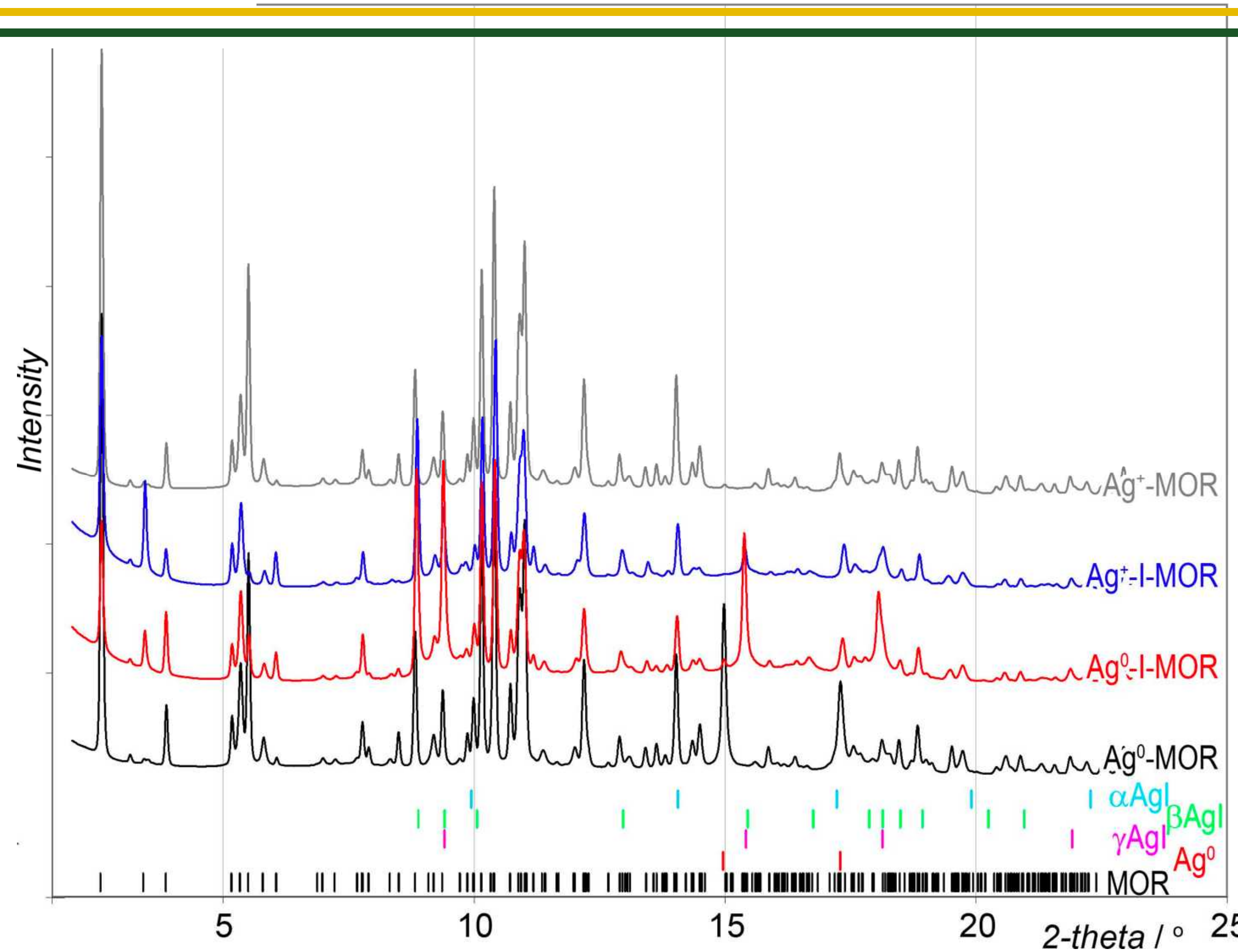
Powder X-ray Diffraction Data



Powder diffraction data for MOR samples,
with expected peak positions for MOR, Ag° and α-AgI, β-AgI and γ-AgI

T.M.Nenoff, tmnenof@sandia.gov

Structure-Property Relationship Study : Nanoscale analysis for Bulk Scale Materials Properties

The Pair Distribution Function (*PDF*): a local structure probe

*The PDF, **G(r)**,* is related to the ***probability*** of finding an atom at a distance ***r*** from a reference atom.
It is the Fourier transform of the total structure factor, ***S(Q)***.

$$\boldsymbol{G(r)} = 4\pi r\, \rho_0[\underbrace{\boldsymbol{g(r)}-1}_{\text{probability}}] = (2/\pi)\int Q[\underbrace{\boldsymbol{S(Q)} - 1}_{\text{structure factor}}]\sin(Qr)\,dQ$$

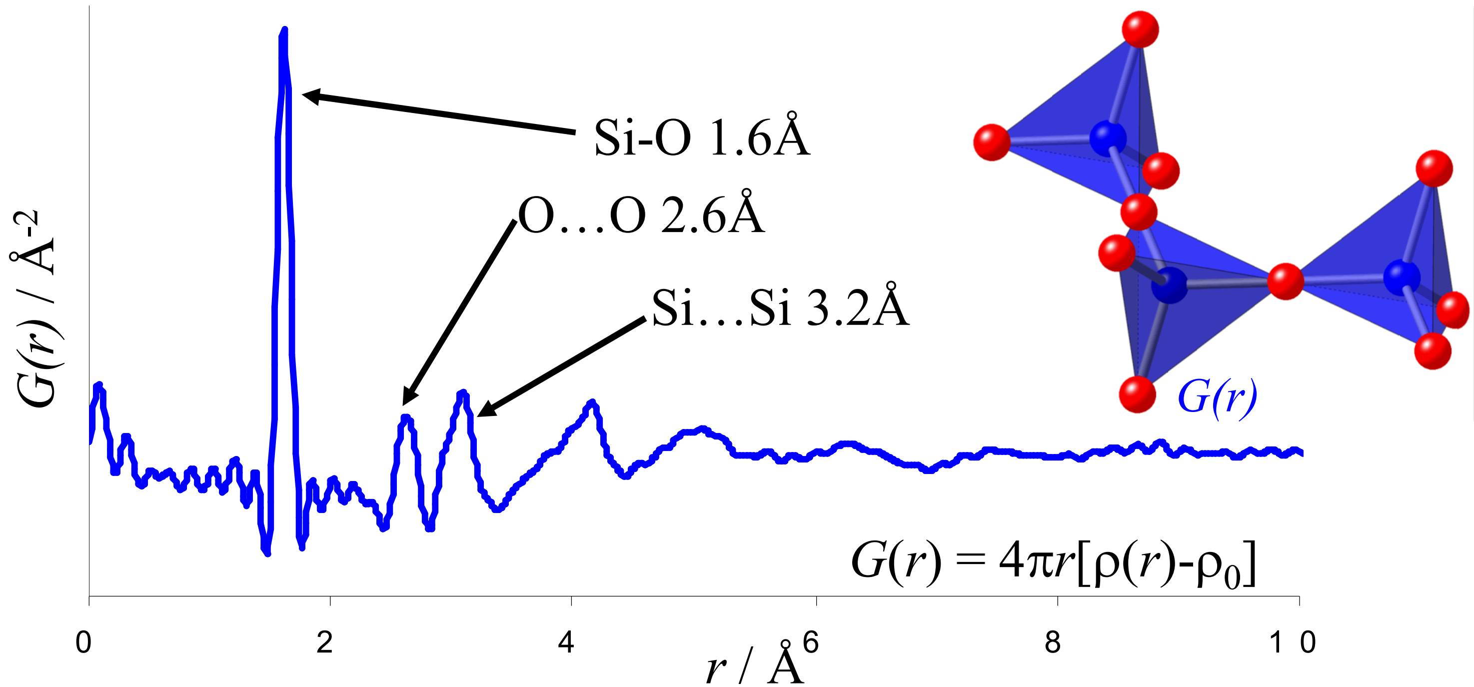
The structure factor, ***S(Q)***, is related to coherent part of the diffraction intensity

$$\boldsymbol{S(Q)} = 1 + [\underbrace{\boldsymbol{I^{coh}(Q)}}_{\text{diffraction intensity (corrected)}} - \sum c_i|f_i(Q)|^2] / |\sum c_i f_i(Q)|^2$$

Apply corrections for background, absorption, Compton & multiple scattering

T.M.Nenoff, tmnenof@sandia.gov

Pair Distribution Function: Short Range Structural Order, eg., Amorphous SiO_2



Peak position ⟺ Bond length / distance

Peak area ⟺ Coordination #, scattering intensity

Peak width ⟺ Disorder, bond angle distribution

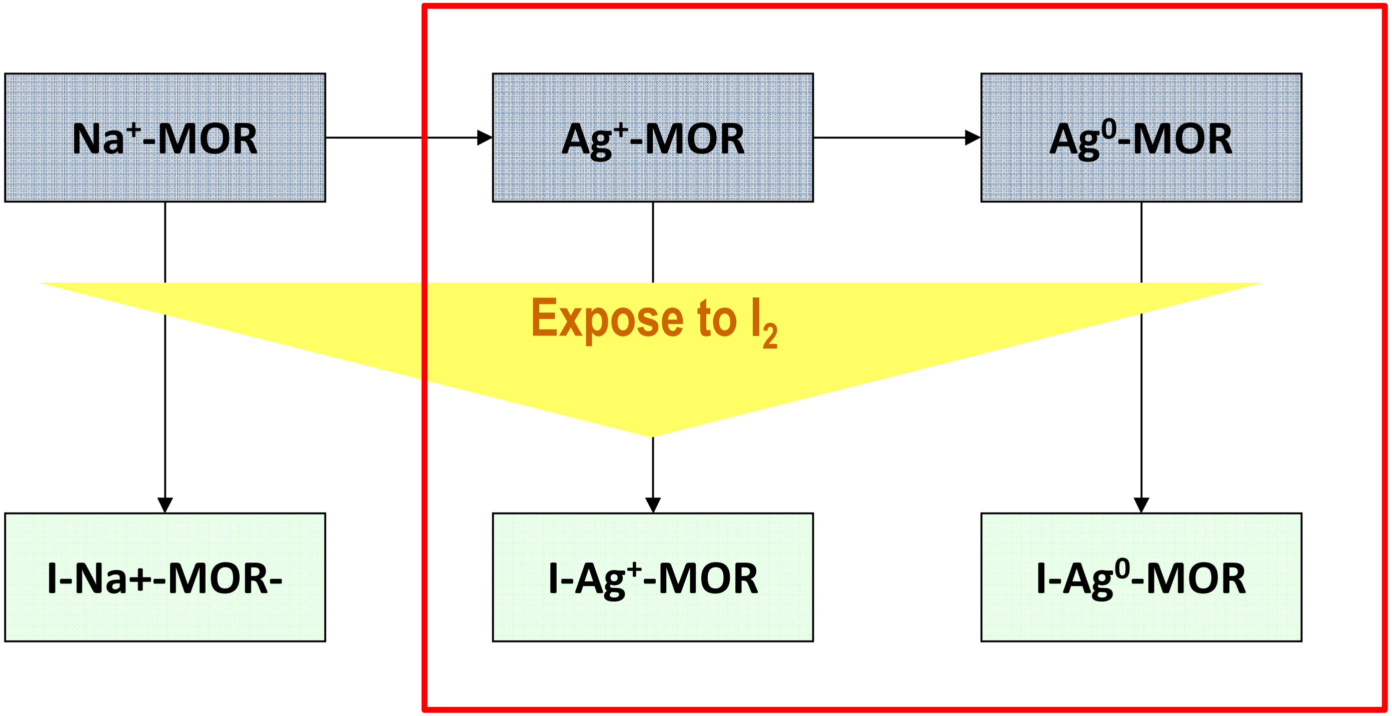
Peak r_{max} ⟺ Particle size, coherence

} → **Structural Modeling**

T.M.Nenoff, tmnenof@sandia.gov

Samples Prepared and Analyzed by *d*-PDF

d-PDF: differential - Pair Distribution Function



Mordenite Zeolite (MOR) Samples from UOP, Corp.: LZM5

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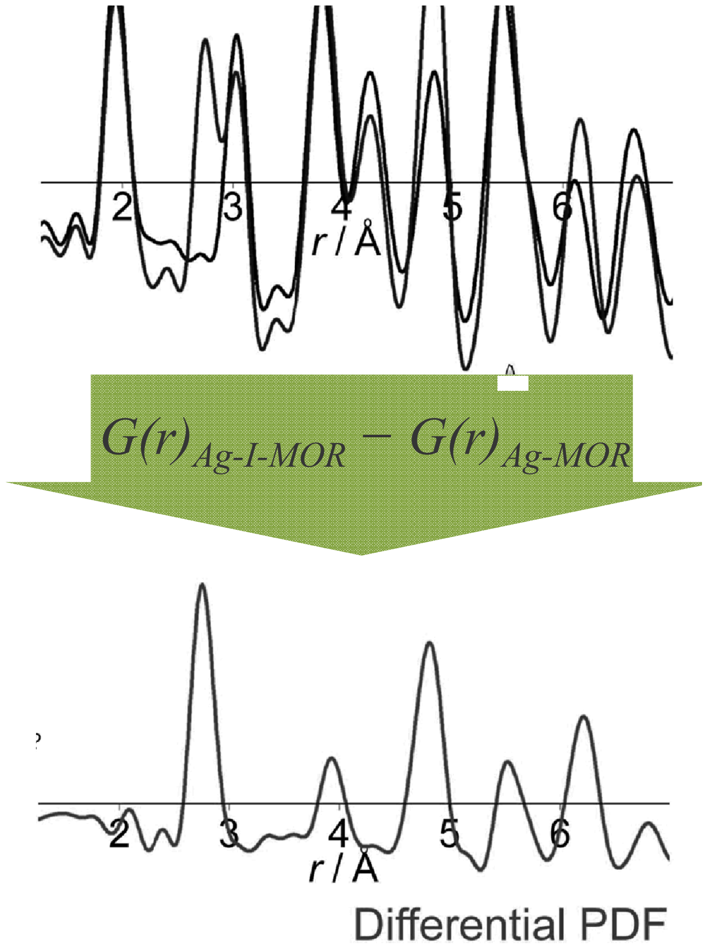
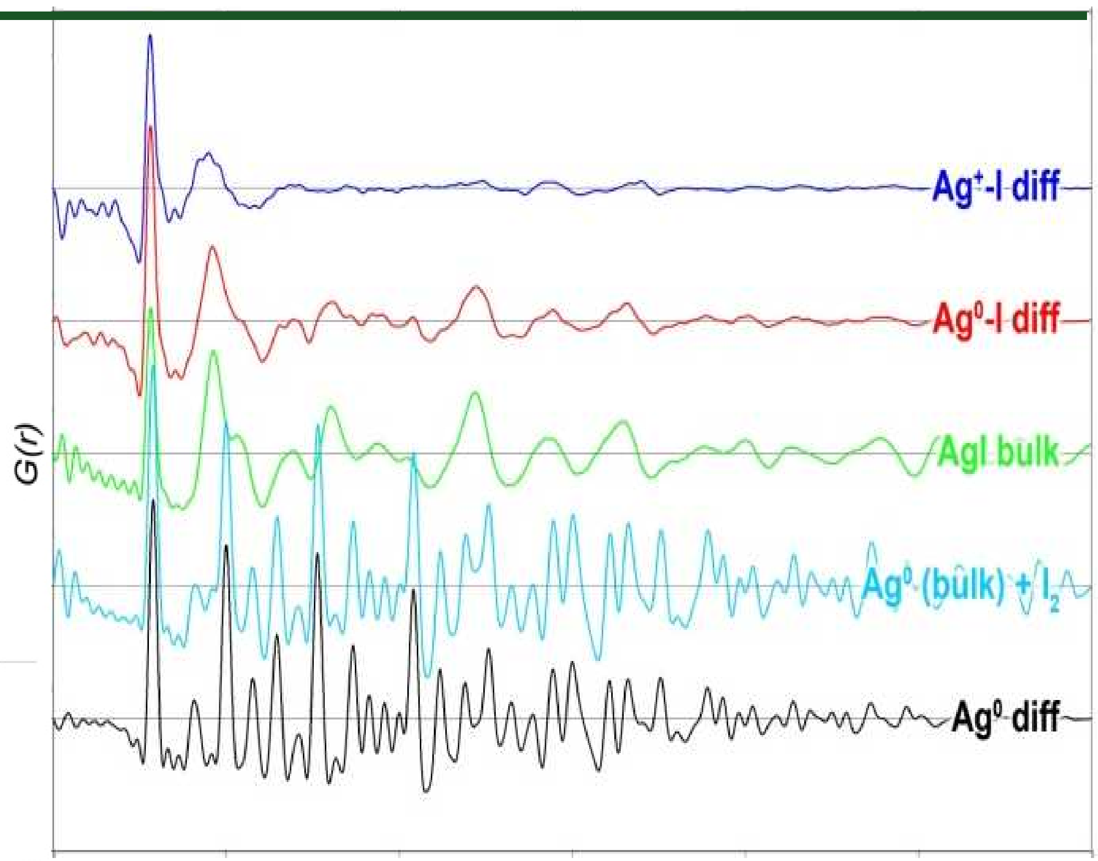
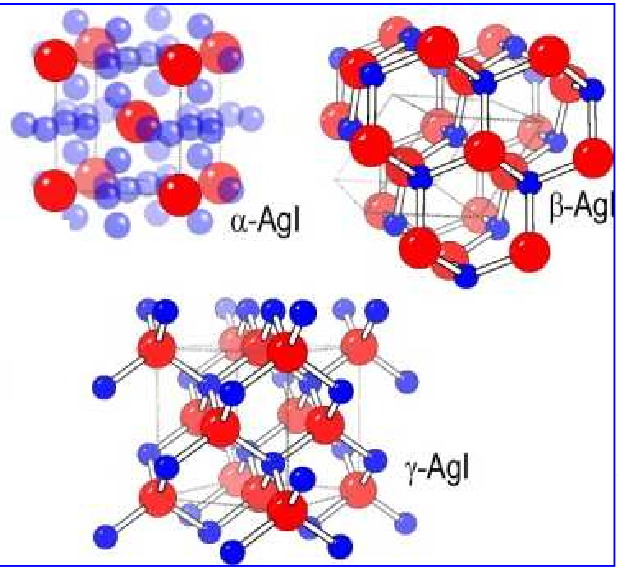
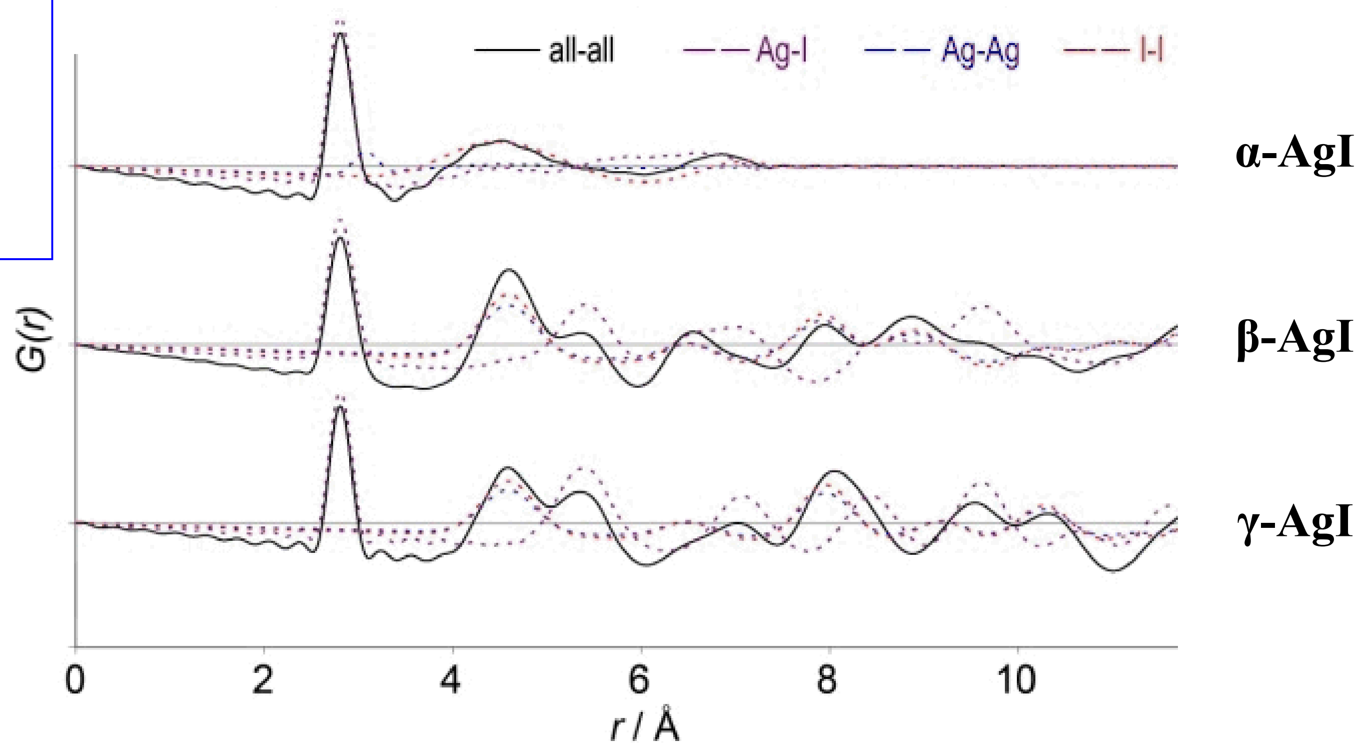
Differential PDFs : Study of Occluded AgI Phases *minus* the MOR Structural Data





Different AgI phases Identified in Ag-I-MOR: model the PDF response for key bonds in various polymorphs of AgI





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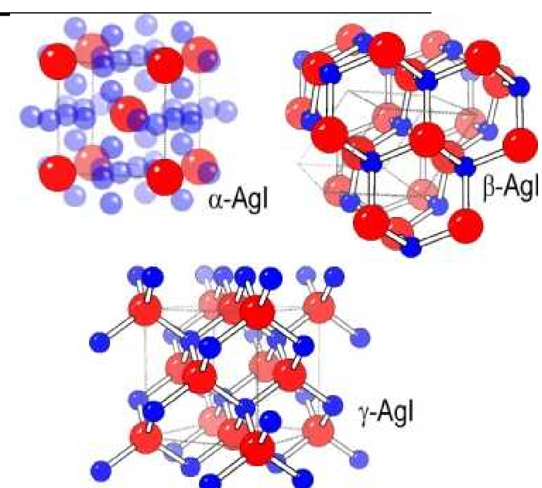
AgI Phases Determined *d*-PDF Analysis per Treatment Processing

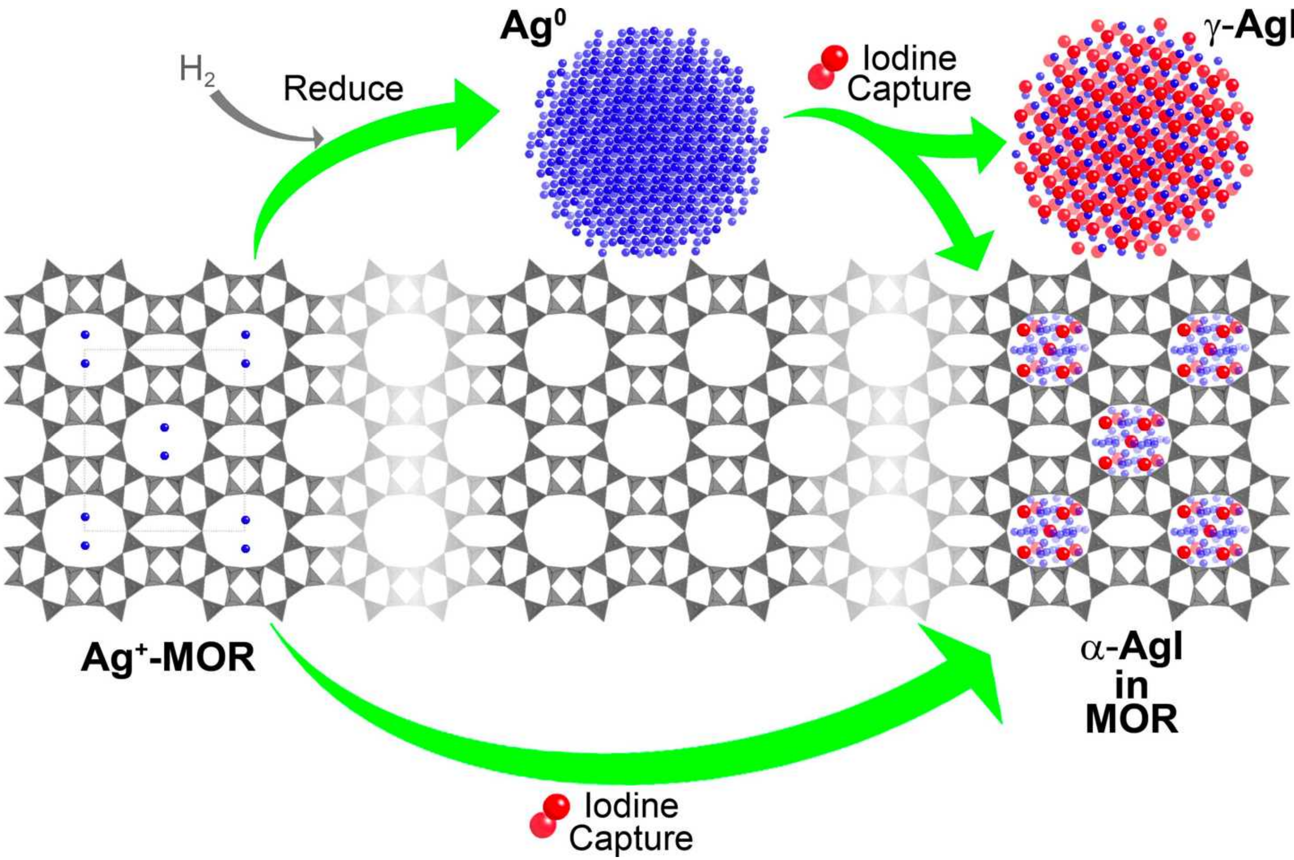
	Form	r-range (Å)	R_{fit}	Phase Composition§			
				Ag^0	α-AgI	β-AgI	γ-AgI
Ag^+-I	on MOR	2-10	27.5%	–	1	–	–
Ag^0-I	on MOR	2-30	18.0%	–	0.6	–	0.4
AgI (Aldrich)	bulk	2-30	13.6%	–	–	0.53	0.47
AgI (Ag^0+I_2)	bulk	2-30	7.97%	0.5	–	–	0.5
Ag^0	on MOR	2-30	9.15%	1	–	–	–

§ Ag^0 (Fm-3m, $a = 4.08$ Å); α-AgI (Im-3m, $a = 5.0$ Å, $r < 7$ Å); β-AgI ($P6_3mc$, $a = 4.6$ Å, $c = 7.8$ Å, wurtzite structure); γ-AgI (F-43m, $a = 6.5$ Å, zinc blende structure).



T.M.Nenoff, tmnenof@sandia.gov

Nanoscale Effects for Bulk Scale Iodine Capture by Silver-Loaded MOR



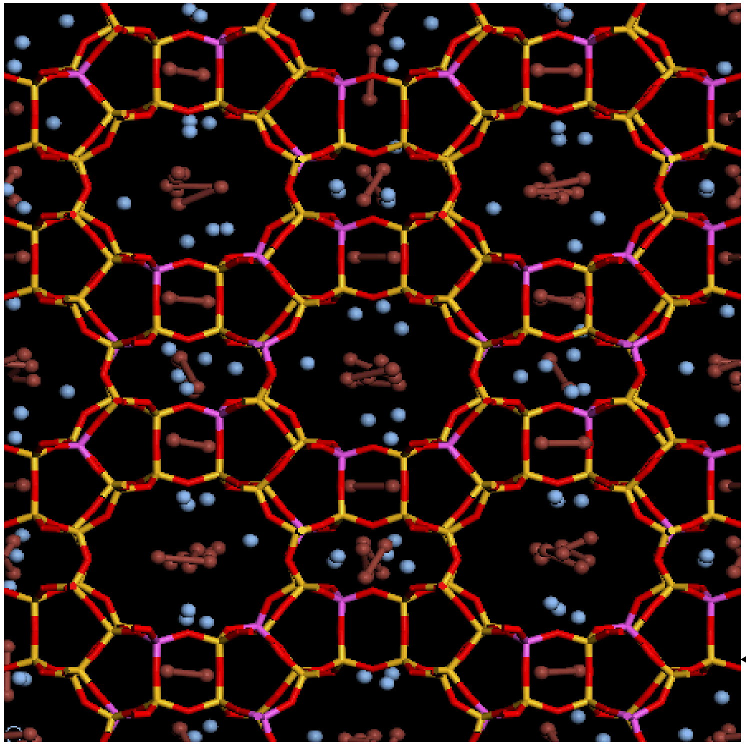
Ag°-MOR + I_2 yields a mixture of γ-AgI bulk surface nanoparticles and sub-nanometer α-AgI.
Ag$^+$-MOR + I_2 produces exclusively sub-nanometer α-AgI ("**perfect fit**", confined in pores)

NEAMS: Molecular Modeling of Volatile Off-Gases in Porous Materials

PIs: Jeffery Greathouse and Paul Crozier (Sandia), collaboration w/Nenoff

Title: Grand Canonical Molecular Dynamics Simulations of Gas Adsorption and Separation

Funding: NEAMS Fundamental Methods and Models (FMM)



- Molecular dynamics (MD) simulation using LAMMPS (http://lammps.sandia.gov)
- Gases: I_2, noble gases
- Sorbents: nanoporous framework materials (zeolites, MOFs, ZIFs)
- Fixed loading simulations: gas mobility and diffusion, adsorption energies
- Grand canonical simulations: adsorption isotherms, adsorption energies

Animation from a 1-ns MD simulation of I_2 (36 wt. %) in Ag-mordenite at 300 K.

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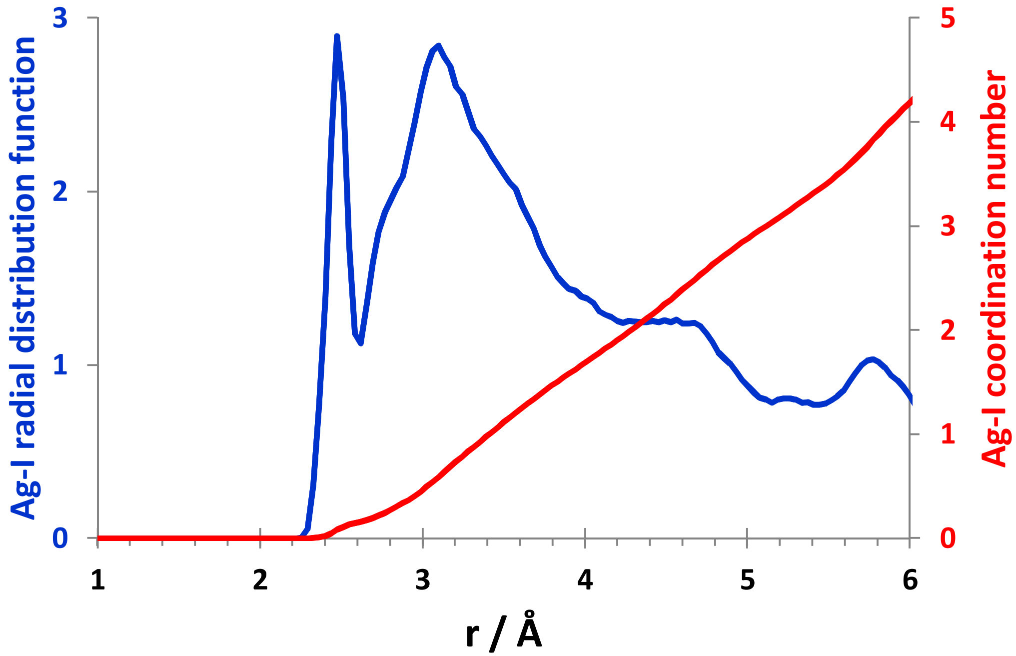
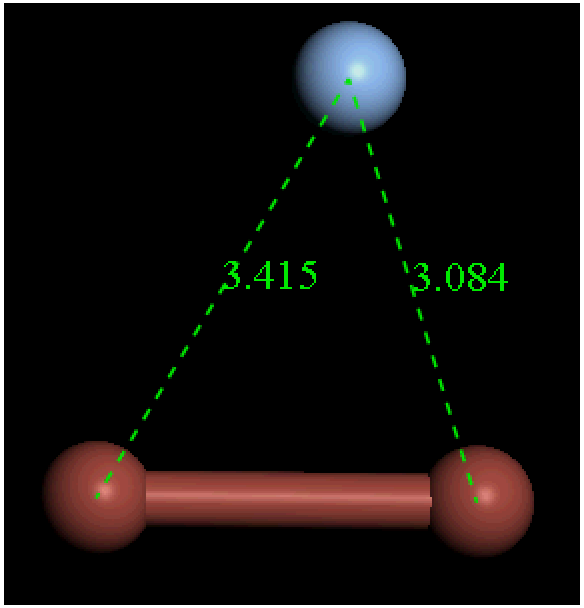
Molecular Dynamics of Ag-I Interactions in Ag-Mordenite





Prominent Ag-I coordination at 3.1 Å with an average of 2 I atoms (1 I_2 molecule) coordinated to each Ag^+ ion.

This closely matches crystallographic data from X-ray (SNL)and Synchrotron (ANL/APS)

Waste Forms: Future Work

Pursue both fundamental and applied research for Iodine and Fission Product Waste Forms.

Science-Based Fundamental Research: We will build upon structure/property relationship studies between waste form, loading levels and durability

- Attractive nature of Bi/I: "how" and "why" waste forms hold I_2, AgI, org-iodides
- Tunability of MOFs for Iodine
- Effects of Decay on waste form durability

Applied Research: we will continue developing compatible inorganic waste form encapsulants for Iodine loaded sequestration materials (including Ag-MOR).

- Focus on Optimized Waste Form (combination of binders and zeolites to form final waste form), such as surface area, binder composition, pellet size
- Testing and durability studies including leach and radiation resistance
- Scale up studies
- Once baseline is achieved: start waste form studies with ^{129}I

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Iodine Waste Form Development and Technology:

Iodine Capture Focus Area - Reduction Mechanism

Tina M. Nenoff, James Krumhansl, Terry Garino, Dorina Sava, David Rademacher

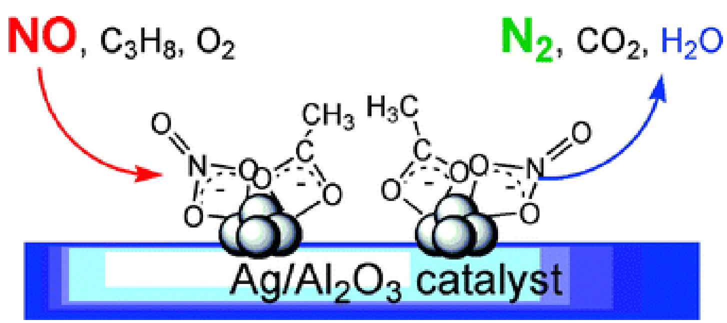
Sandia National Laboratories

Albuquerque, NM 87185

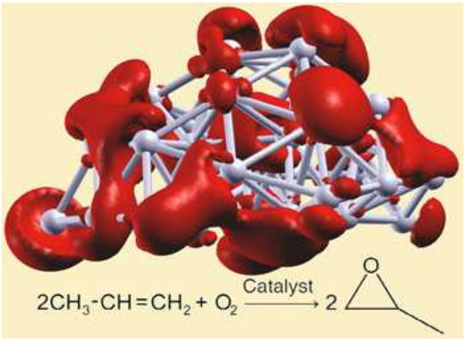
Karena Chapman, Peter Chupas, Haiyan Zhao ANL

The Catalytic Property of Ag Nanoparticles

- Silver Nanoparticles are key to I_2 sorption for Fuel Cycle Applications
- They also shows great promising application as catalytic materials



NO_X reduction



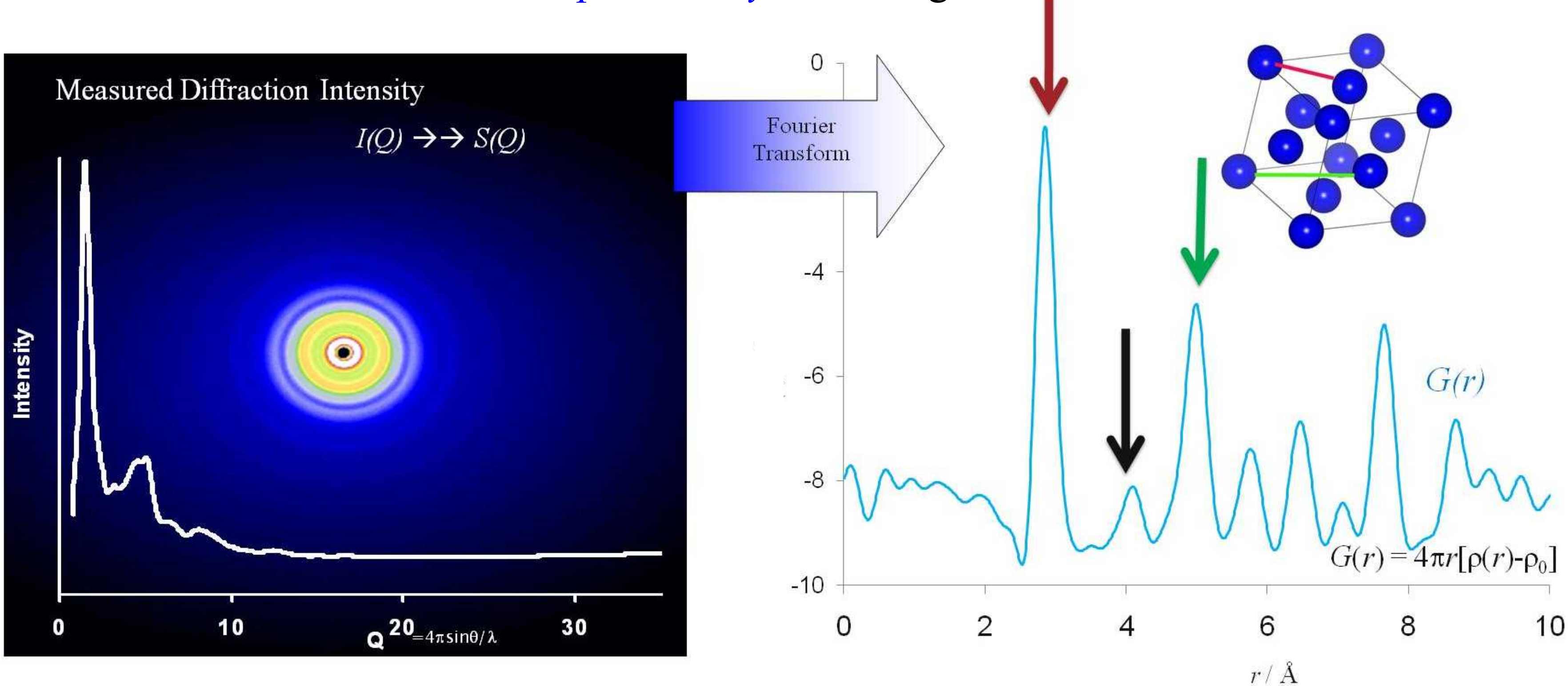
Epoxidation

- Size and shape of nanoparticles is the key to controlling their functional behavior
- Controlled synthesis of catalytic particles highly preferable

T.M.Nenoff, tmnenof@sandia.gov

The Pair Distribution Function (PDF)

Related to the *probability* of finding two atoms at a distance *r*



Peak position ⟷ Bond length / distance

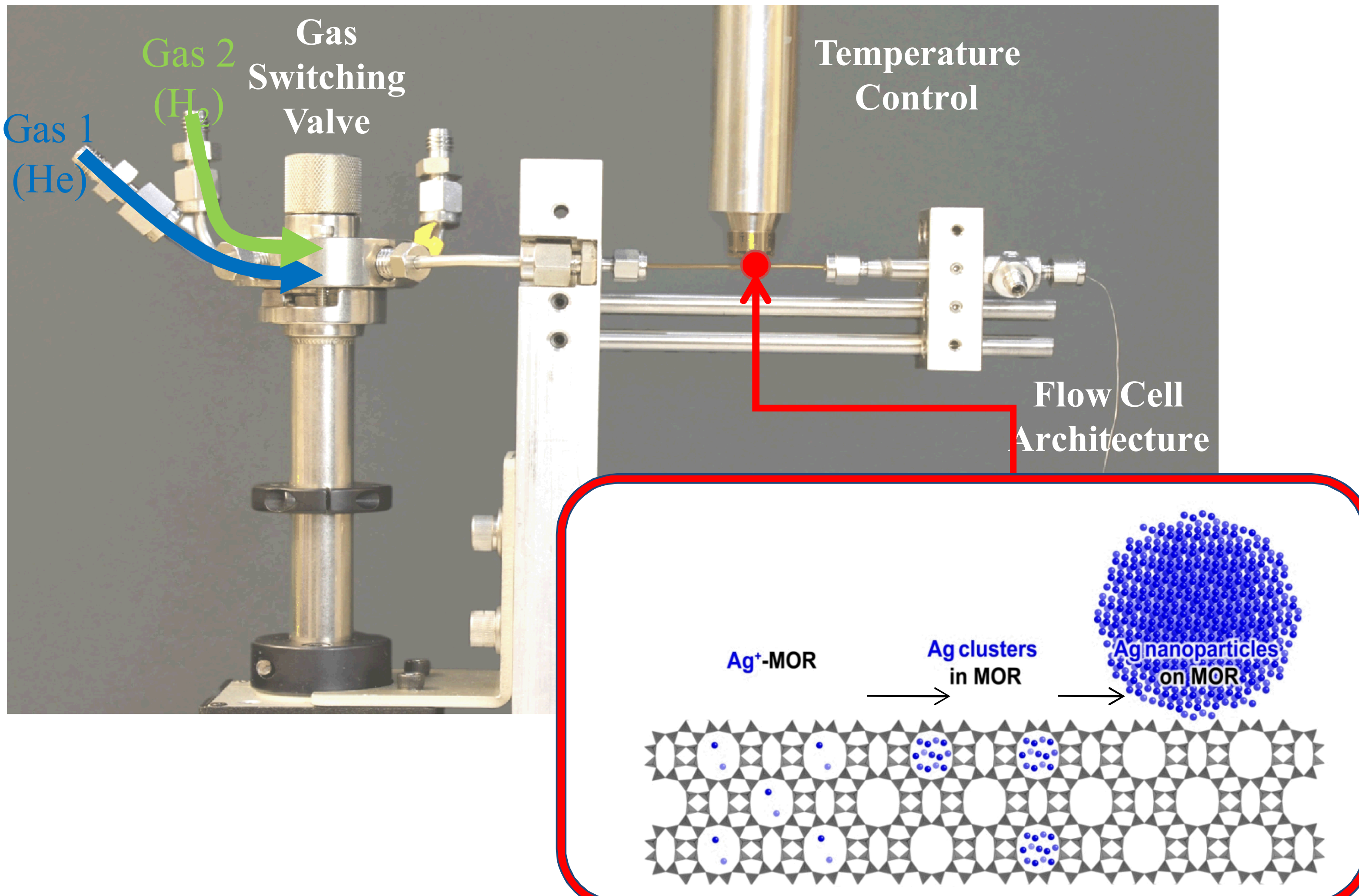
Peak area ⟷ Coordination #, scattering intensity

Peak width ⟷ Disorder

Peak r_{max} ⟷ Particle size, coherence

T.M.Nenoff, tmnenof@sandia.gov

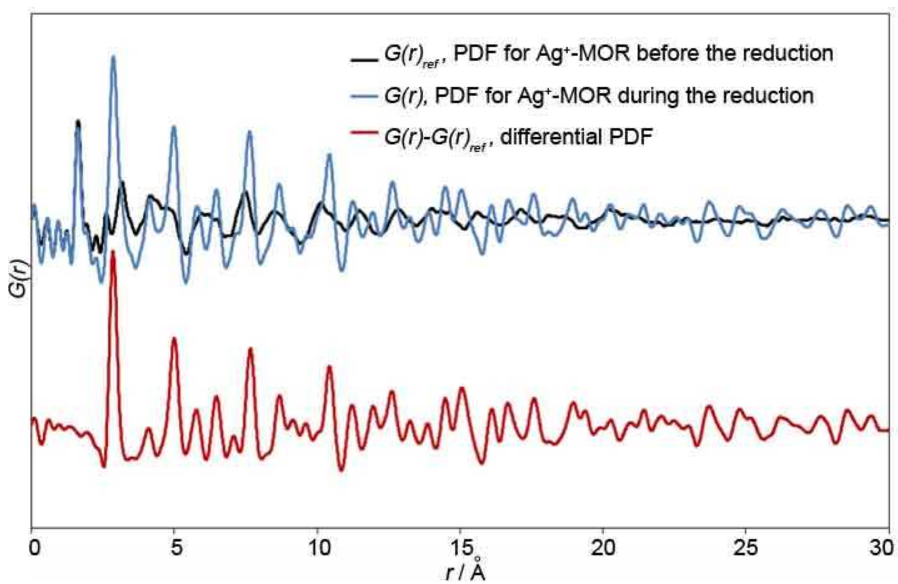
Setup at 11-ID-B for in situ PDF measurements at ANL/APS



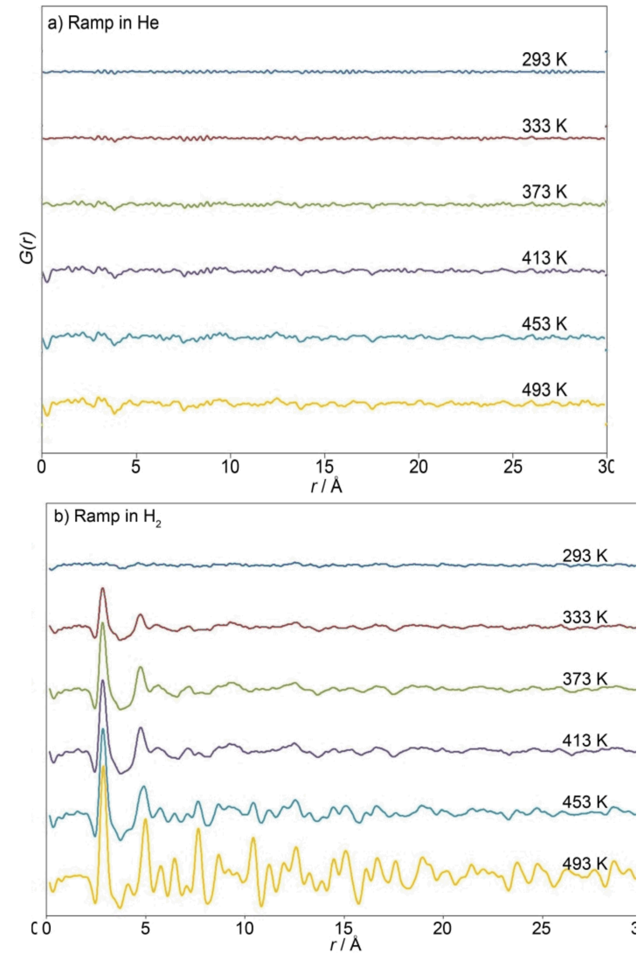
T.M.Nenoff, tmnenof@sandia.gov

Multi-step Mechanism for Silver Particle Growth on a Porous Zeolite

Using Time Resolved PDF



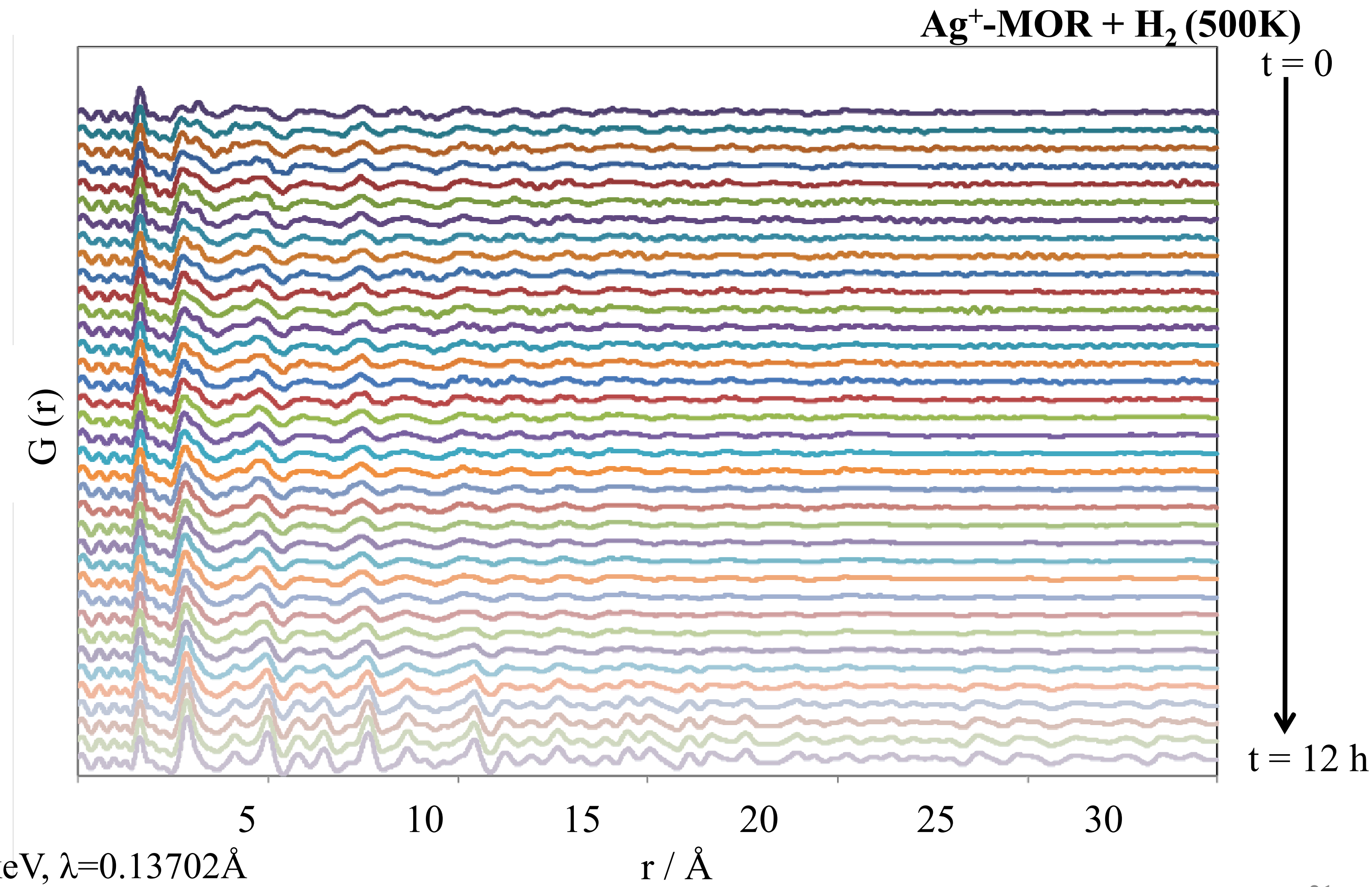
The differential PDF (red) is recovered by direct subtraction of the PDF for unreduced silver MOR (black, $G(r)_{ref}$) from that obtained during / following reduction (blue).



The differential PDFs obtained with heating in inert (a) vs reducing (b) atmospheres.

T.M.Nenoff, tmnenof@sandia.gov

In situ PDF for Ag^{+}-MOR reduction

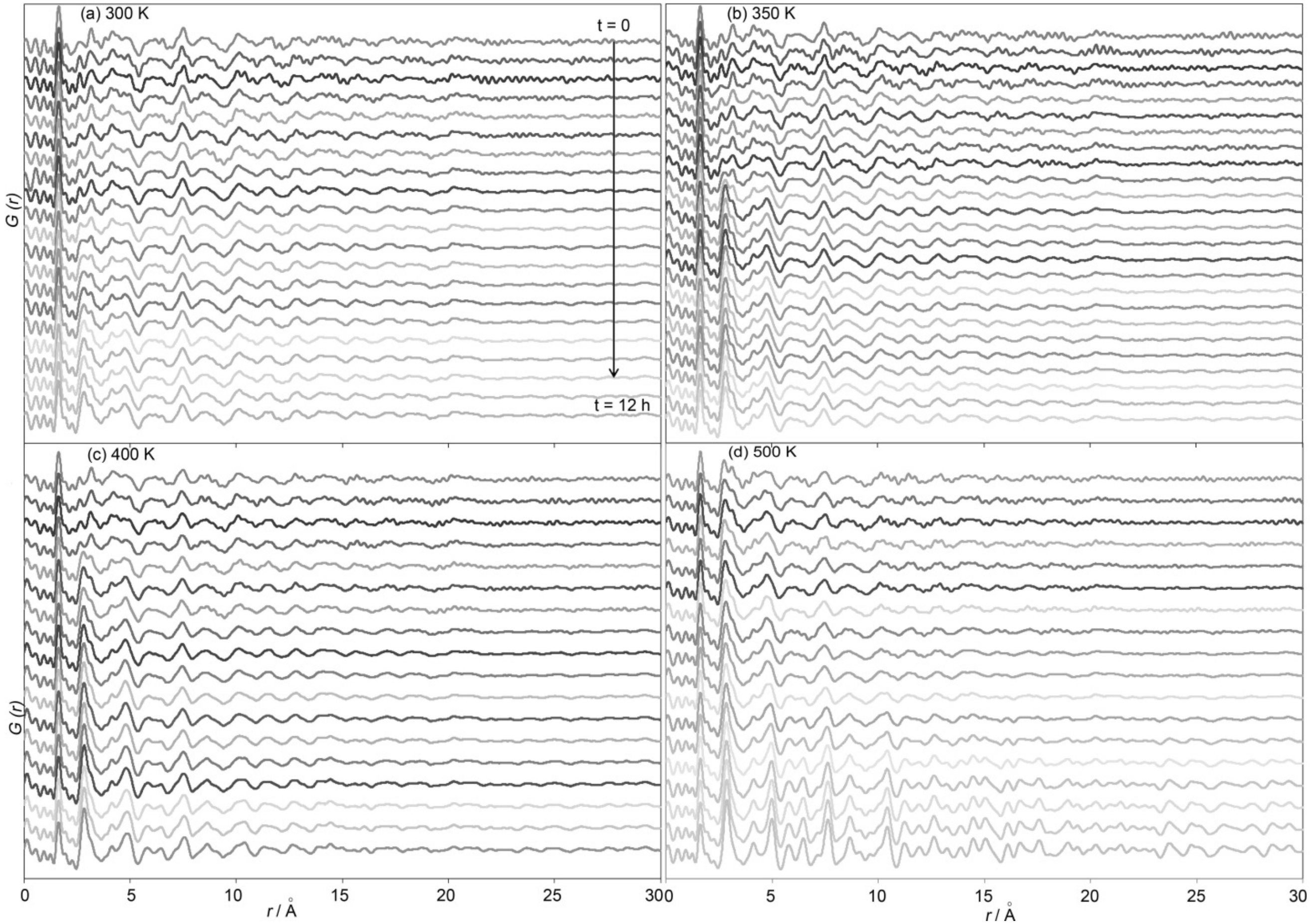


90.48 keV, λ=0.13702Å

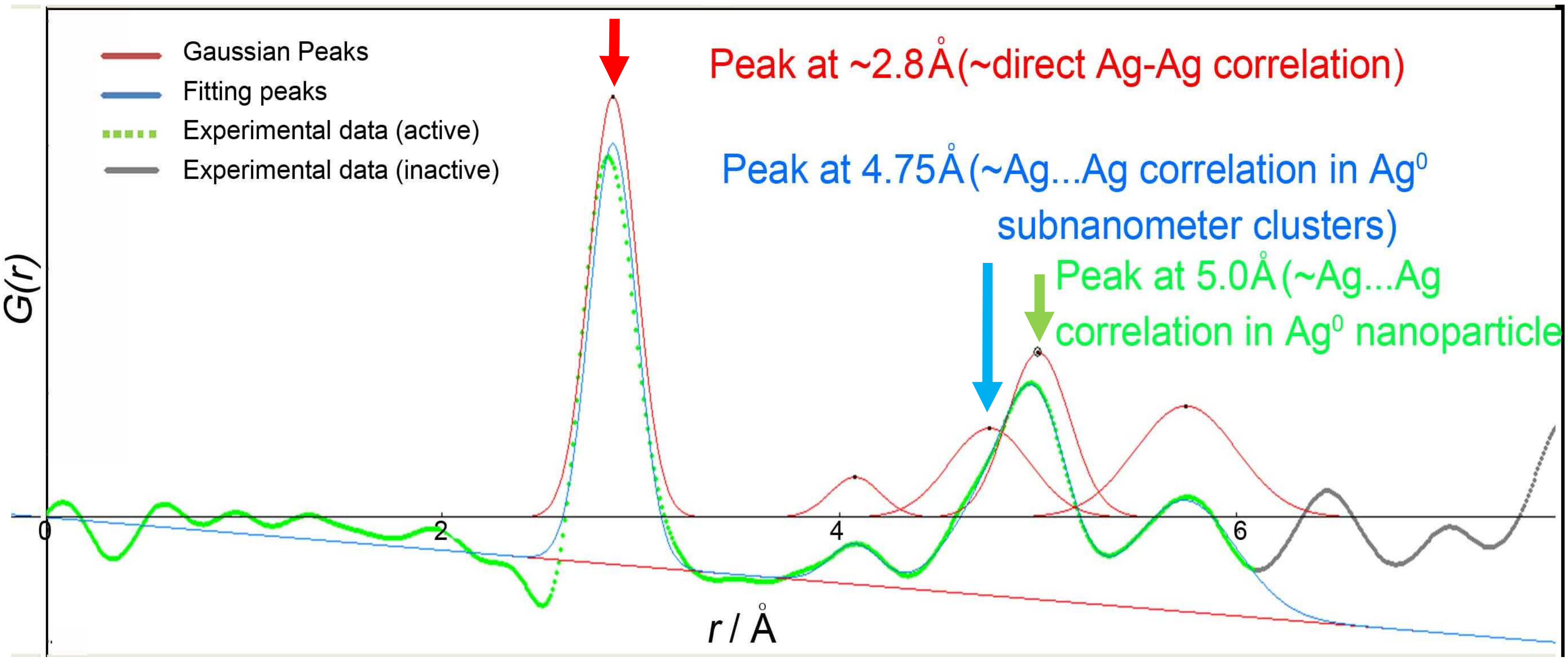
T.M.Nenoff, tmnenof@sandia.gov

Multi-step Mechanism for Silver Particle Growth on a Porous Zeolite

Total PDFs measured during isothermal reduction at 300 K, 350 K, 400 K and 500 K



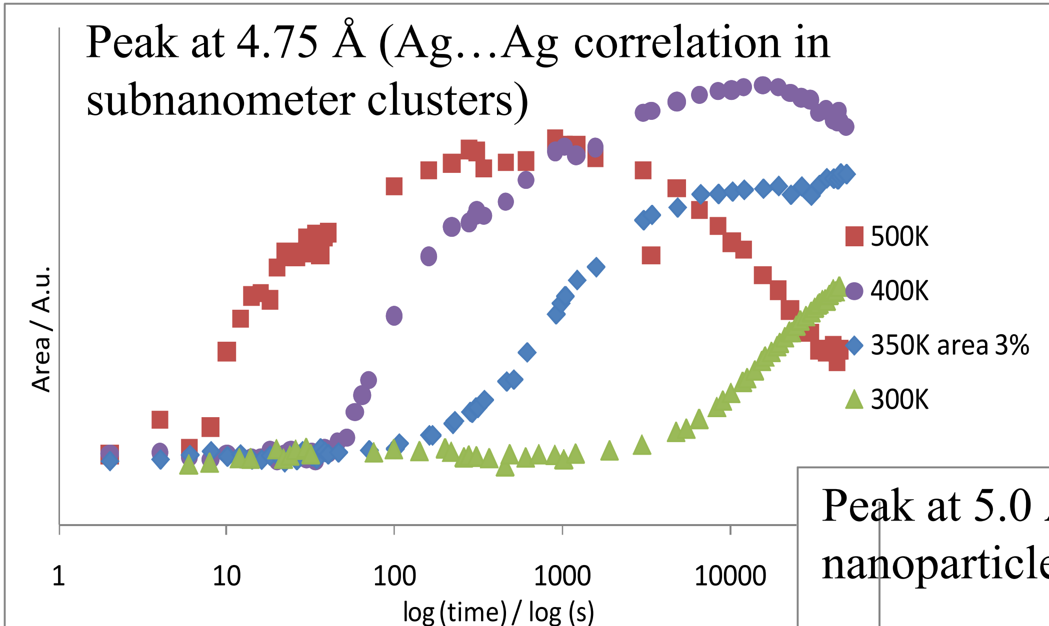
Gaussian Peak Fitting



The intensity of peak around 2.8 Å ⟺ Ag total particle population
The intensity of peak at 4.75 Å ⟺ Ag subnanocluster population
The intensity of peak at 5.0 Å ⟺ Ag nanoparticle population

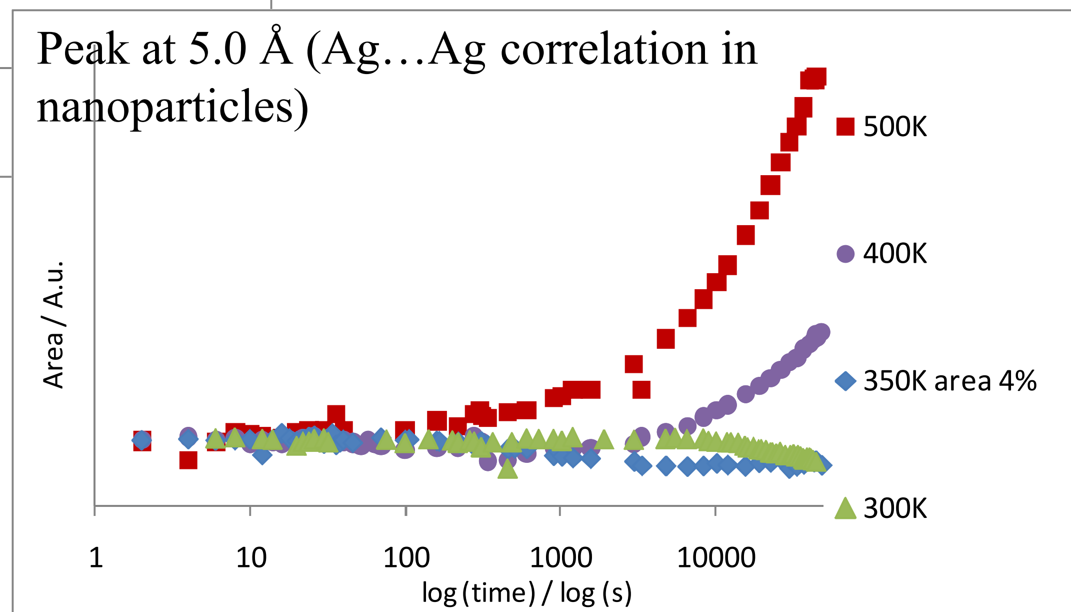
T.M.Nenoff, tmnenof@sandia.gov

Ag Particles Development



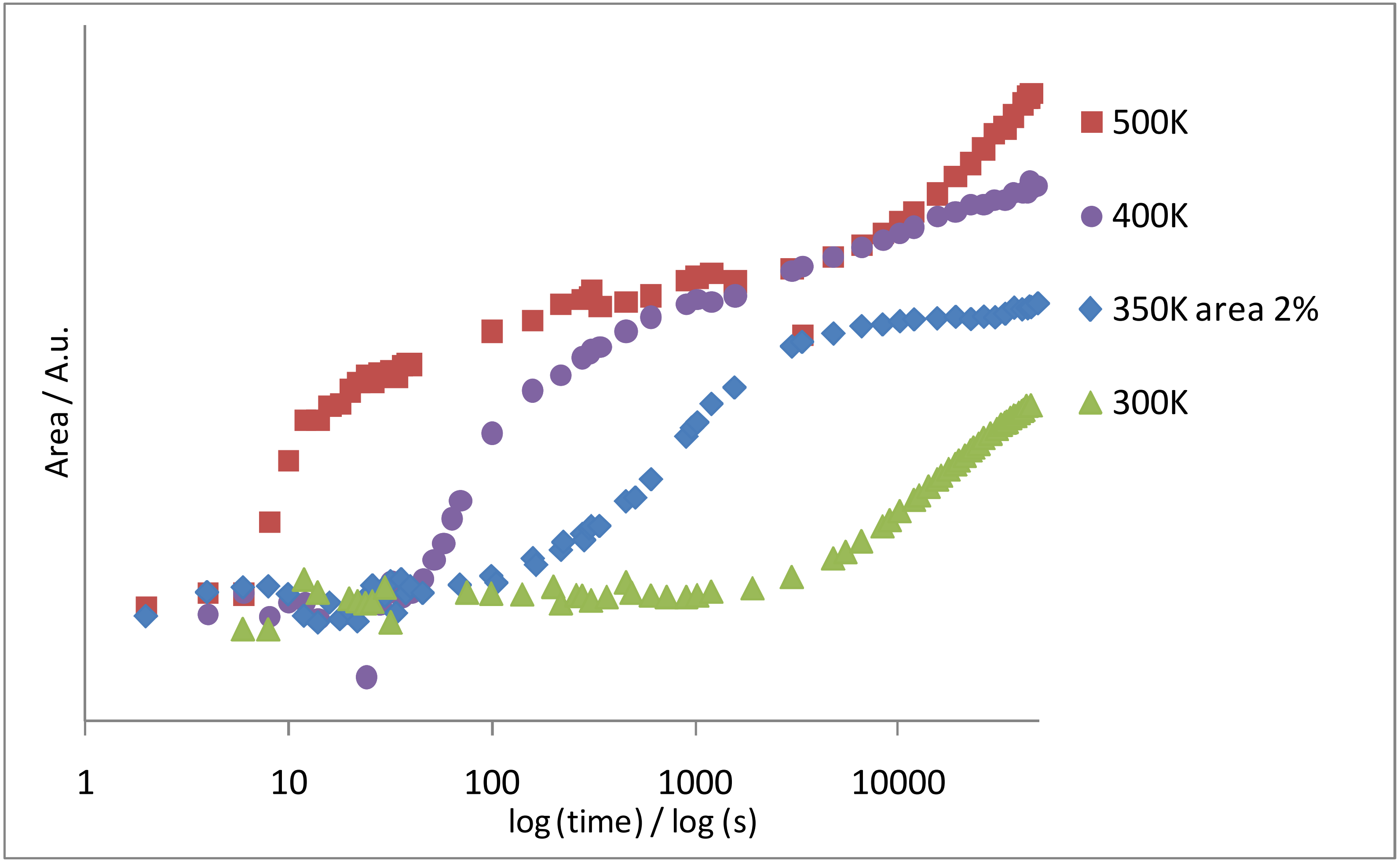
- No big Ag nanoparticles formed at temperature lower than 350 K

- Smaller subnanometer clusters must migrate out of the pore and aggregate into bigger Ag particles



T.M.Nenoff, tmnenof@sandia.gov

Total population of Ag Particle Development



T.M.Nenoff, tmnenof@sandia.gov

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Multi-step Mechanism for Silver Particle Growth on a Porous Zeolite

$$Ag^+(12MR) \xrightarrow{k1a} Ag(12MR)$$
$$Ag^+(8MR) \xrightarrow{k1a} Ag(8MR)$$
Reduction

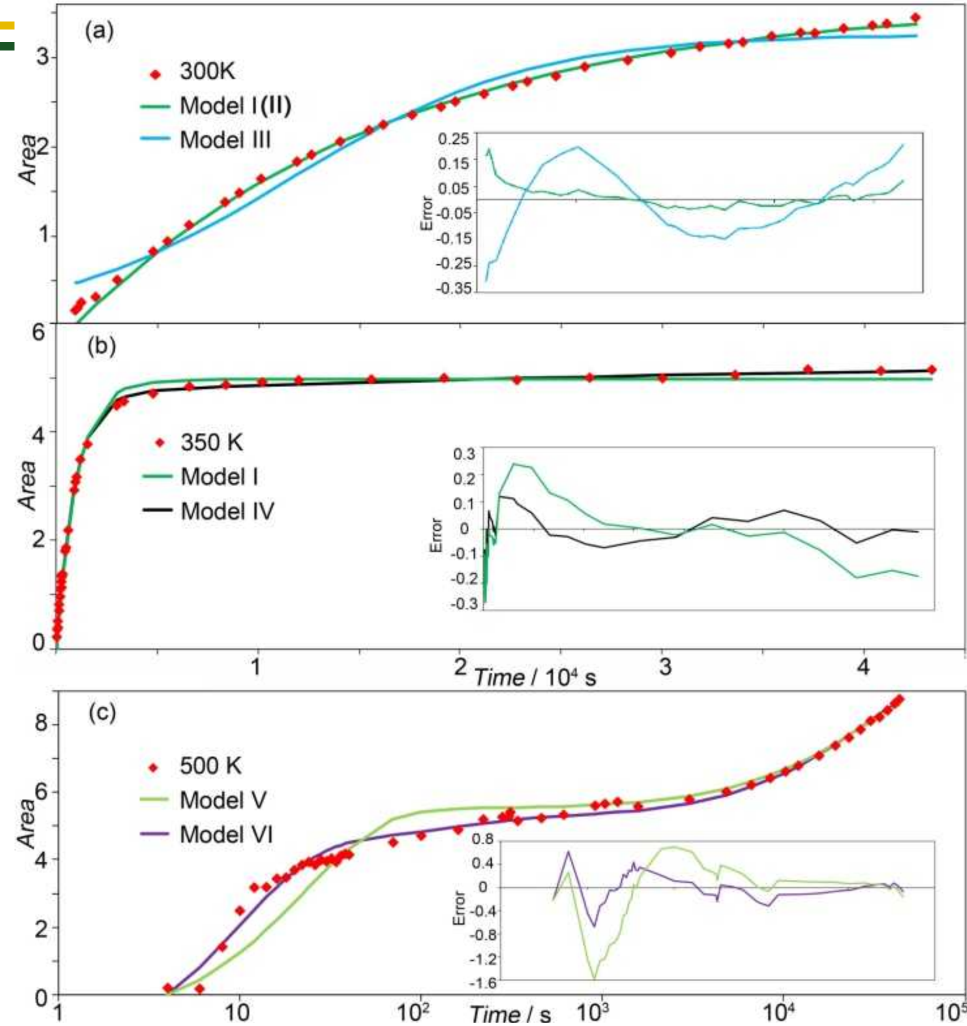
$$Ag_n(\text{inside pore}) \xrightarrow{k_4} Ag_n(\text{outside pore})$$
$$Ag(8MR) \xrightarrow{k_{4a}} Ag(12MR) \xrightarrow{fast} Ag_n(12MR)$$
$$Ag_n(12MR) \xrightarrow{k_{4b}} Ag_n(\text{external surface})$$
Migration and Nucleation

$$2Ag_n(\text{outside pore}) \xrightarrow{k_5} Ag_{2n}$$
Aggregation

Model VI (Mechanism S1 (1a+1b)+(4a+4b))

$$[Ag_n] = \frac{[Ag^+]_{a0}}{n}\frac{k_{1a}}{k_{4a}-k_{1a}}(e^{-k_{1a}t}-e^{-k_{4b}t}) + \frac{[Ag^+]_{b0}}{n}\frac{k_{1b}k_{4a}}{k_{4a}-k_{1b}}\left(\frac{(e^{-k_{1b}t}-e^{-k_{4b}t})}{k_{4b}-k_{1b}} - \frac{(e^{-k_{3a}t}-e^{-k_{4b}t})}{k_{4b}-k_{4a}}\right)$$

$$[Ag_{2n}] = \frac{[Ag^+]_{a0}}{2n}\left(1+\frac{k_{1a}e^{-k_{4b}t}-k_{4b}e^{-k_{1a}t}}{k_{4b}-k_{1a}}\right) + \frac{2[Ag^+]_{b0}}{n(k_{4a}-k_{1b})}(k_{4a}-k_{1b} + \frac{k_{1b}k_{4a}e^{-k_{4b}t}-k_{4a}k_{4b}e^{-k_{1b}t}}{k_{4b}-k_{1b}} - \frac{k_{1b}k_{4a}e^{-k_{4b}t}-k_{1b}k_{4b}e^{-k_{4a}t}}{k_{4b}-k_{3a}})$$

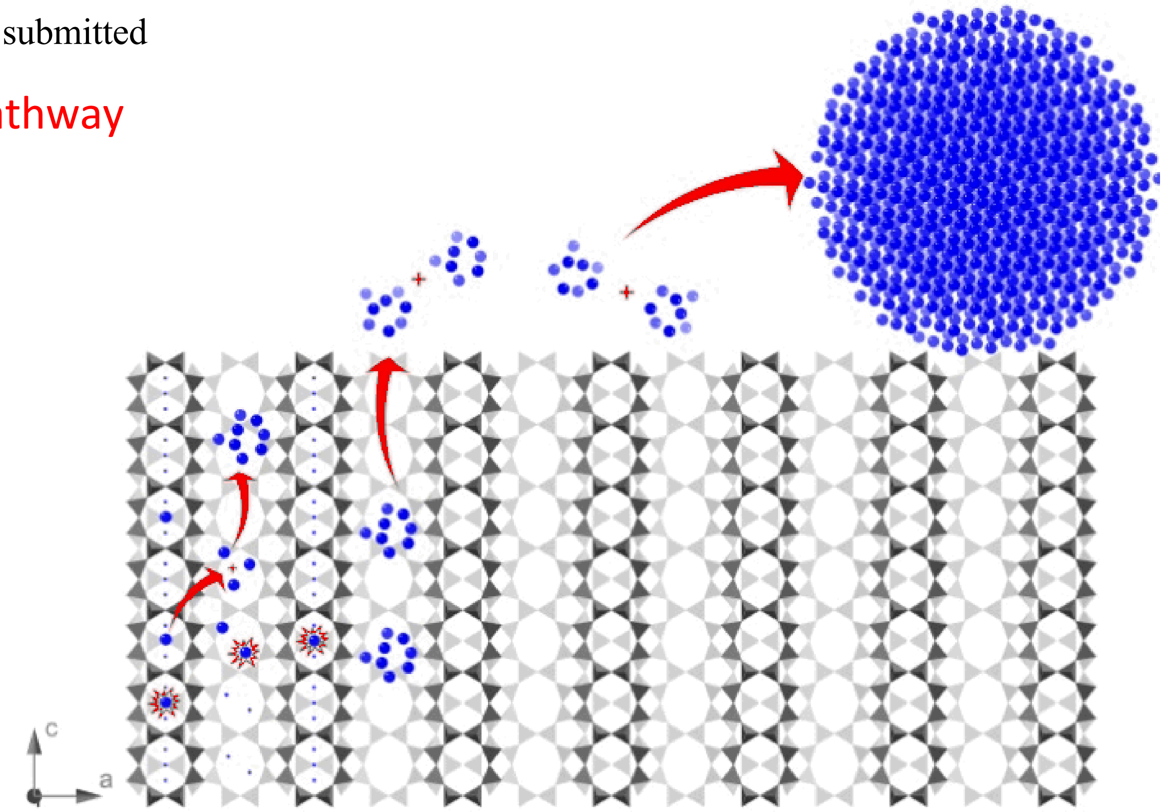


- Comparison of models for cluster formation at (a) 300 K (I/II vs III), (b) 350 K (I vs IV) and 500K (V vs VI).
- Ag^+ reduction (Models I and IV) is rate determining step; reduction rate depends on the cation location (Model IV).

Multi-step Mechanism for Silver Particle Growth on a Porous Zeolite

Angew. Chem., 2011, submitted

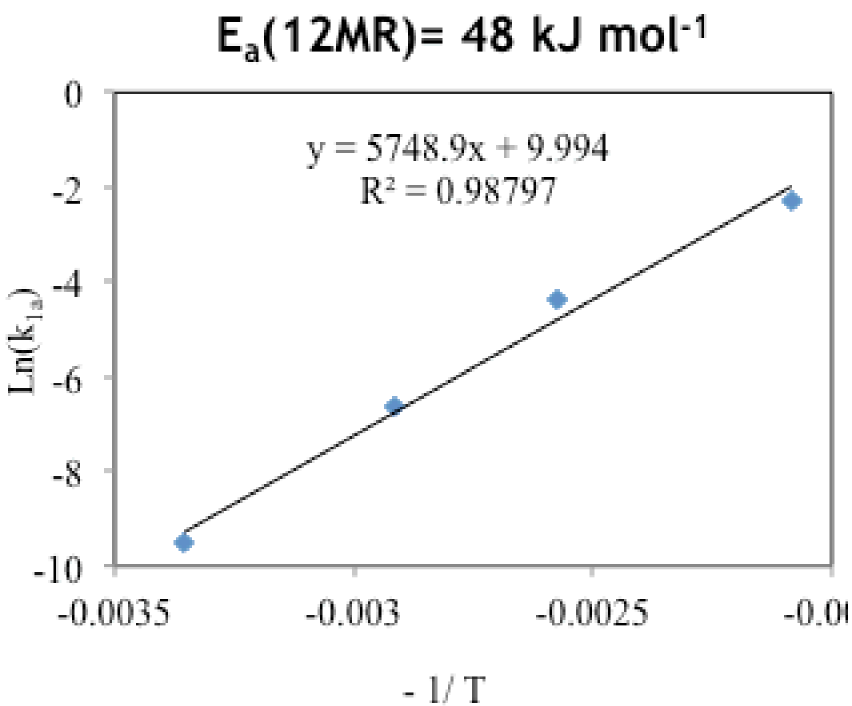
Mechanism Pathway Determined

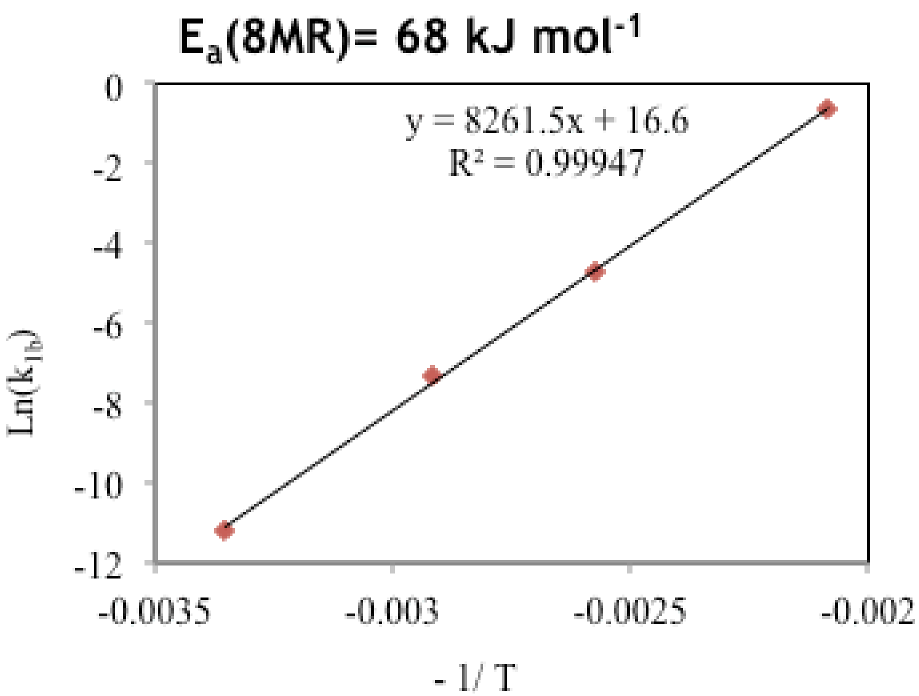


i) Ag^+ reduction in 12 MR and 8MR "Red star"
ii) Ag° migration from 8MR to 12MR
iii) Ag° form clusters within 12 MR channels
iv) Clusters migrate to zeolite surface
v) Clusters aggregate as nanoparticles

Quantitative Kinetic Parameters

With Model Fitting: quantitative kinetic parameters are obtained including: reduction rate constants at different temperature for Ag^+ in 8MR and 12MR

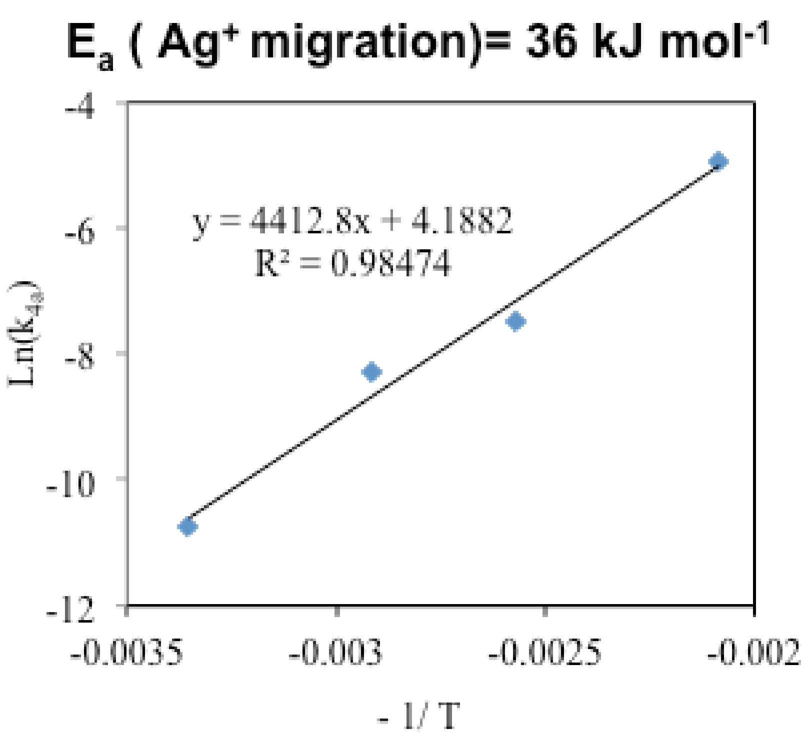


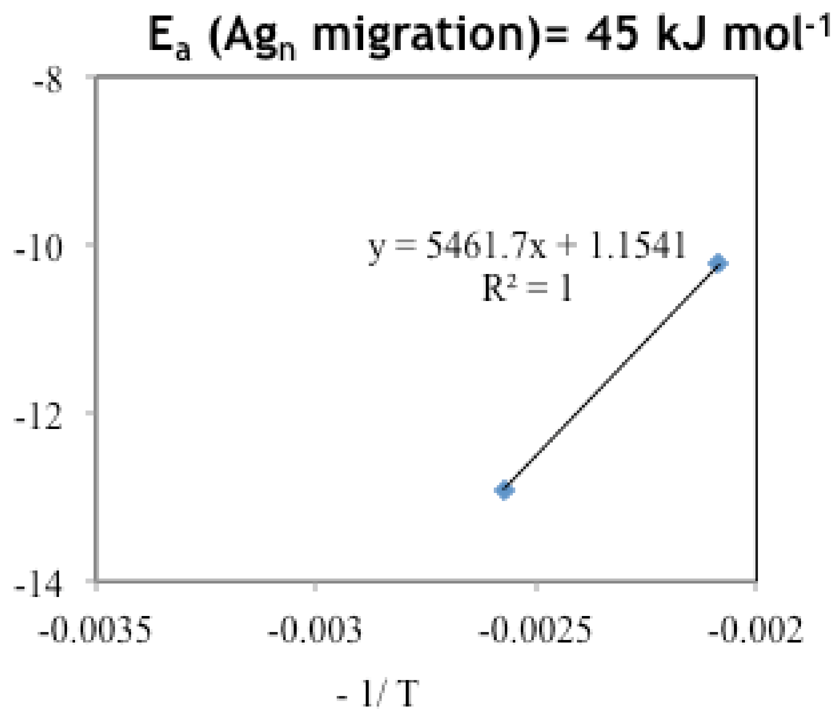


- It is more difficult to reduce Ag^+ at the 8 MR than Ag^+ at the 12 MR
- The activation energy needed for Ag^+ -> Ag° in the 12 MR is comparable to known Ag reduction for Zeolite Y (FAU)

T.M.Nenoff, tmnenof@sandia.gov

Kinetic Parameters From Fitting with Best Fit Model





It is easier for the Ag^+ to migrate from the 8 MR to 12 MR than for Ag_n clusters to migrate from 12 MR to the surface

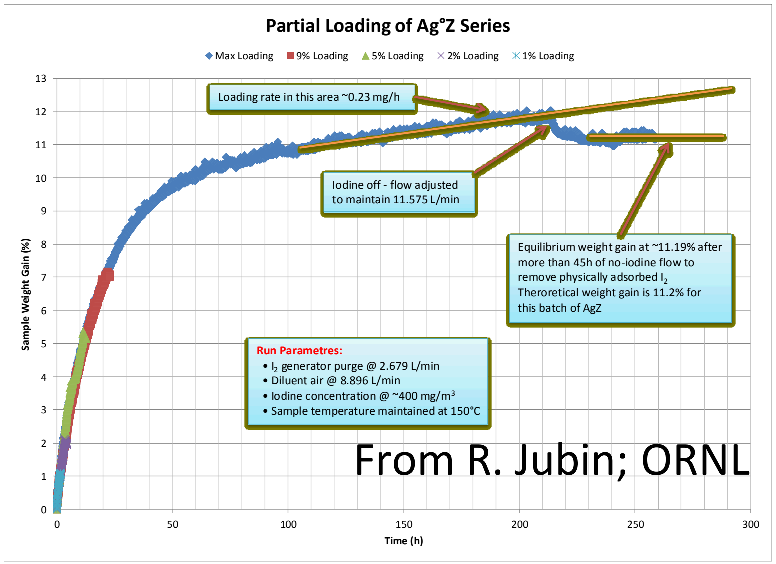
T.M.Nenoff, tmnenof@sandia.gov

Conclusion

- PDF provides quantitative kinetics and mechanism information for nanoparticles formation and growth
- Quantitative kinetics and mechanism were proposed for gas-solid phase reaction in zeolite template
- Silver ions in 12 MR and 8 MR reduced at different rates
- Formation of Ag particles on a porous zeolite occurs via a multi-step process
  - Small (~6-8 atom) initial clusters are presumably confined by the zeolite pores
  - Clusters migrate to zeolite surface and aggregate to form larger nanoparticles at higher temperatures
  - Cluster mobility and larger nanoparticle growth minimized at low temperature

T.M.Nenoff, tmnenof@sandia.gov

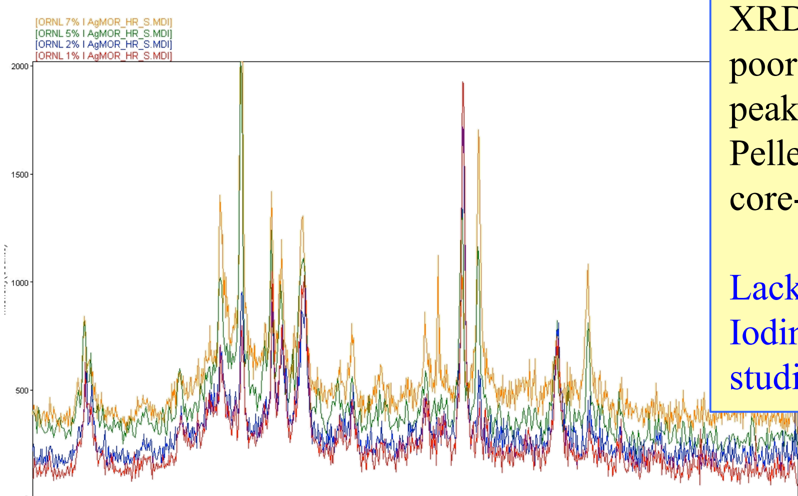
Materials Characterization of Analysis of ORNL Ag°-I-MOR: Samples 1, 2, 5, 7 wt % loadings



Samples for Structural Analysis to locate Iodine in low loading samples

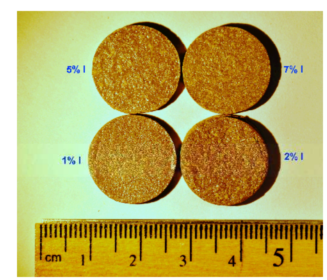
Sample # ORNL Ag-Mordenite %	Wt % I	Moles AgI	Moles Ag metal	Zeolite, note H^+ substituted for initial Ag^+
				Old Al:Si Standards
1% I	1.3	0.10	1.44	$H_{1.54}K_{0.14}Ca_{0.24}Fe_{0.09}Al_{2.10}Si_{9.84}O_{24}.7H_2O$
2% I	2.4	0.19	1.33	$H_{1.52}K_{0.14}Ca_{0.23}Fe_{0.08}Al_{2.10}Si_{9.85}O_{24}.7H_2O$
5% I	6.4	0.52	1.01	$H_{1.53}K_{0.14}Ca_{0.23}Fe_{0.08}Al_{2.09}Si_{9.86}O_{24}.7H_2O$
7% I	9.7	0.79	0.78	$H_{1.57}K_{0.14}Ca_{0.25}Fe_{0.08}Al_{2.09}Si_{9.84}O_{24}.7H_2O$

XRF results for samples:
- Evidence of excess Ag°
- Close agreement with wt loading anticipated by ORNL



XRD of Samples: large background poor crystallinity; MOR, AgI, Ag peaks identified.
Pellet: outer - layer gray/yellow, core- black(unreacted)

Lack of crystallinity no problem for Iodine location study by PDF studies at ANL (on-going)



Homogenous Glasses formed (80 glass/20 Ag-I-MOR/5 Ag)
Pressed, 550°C, 1 hr
PCT studies underway

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The Fuel Cycle Research & Development

Iodine Waste Form Development and Technology:

Iodine Capture Focus Area - Alternate Sorbents – MOFs

Tina M. Nenoff, James Krumhansl, Terry Garino,

Dorina Sava, David Rademacher, Paul Crozier, Jeff Greathouse

Sandia National Laboratories

Albuquerque, NM 87185

Robert Jubin, ORNL

Nick Soelberg, Tony Watson, Jack Law, Daryl Haefner, INL

Karena Chapman, Peter Chupas, ANL

Metal-Organic Frameworks (MOFs): tunable and versatile new generation of porous materials

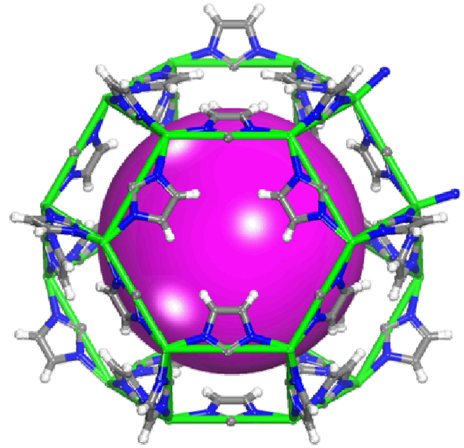
- Alternative materials to Ag-Zeolite for volatile gas sorption
- Highly modular, a large set of materials available and designable
- Highly tunable, amenable for modifications, supporting diverse chemistry
- Mild synthetic protocols
- Recent studies focus on new research topics
- Use characteristics of known MOFs to study gas sorption and selectivity
- Design novel and “tuned” MOFs for specific volatile off-gas sorption

T.M.Nenoff, tmnenof@sandia.gov

Commercially Available MOFs for Volatile Off-Gas Sorption

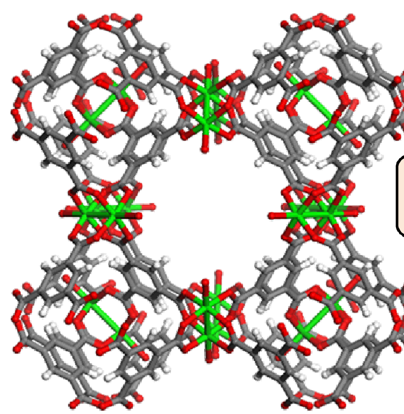
Utilize High Surface Area of MOFs with Selectivity (of Pore Opening or Metal Center)

Basolite Z1200, ZIF-8
Constricted Pore Opening (≈ 3.4Å)
1100 – 1600 m^2/g
Pore Volume = 0.636 cc/g
stable in Air & H_2O



I_2@ZIF-8 ~ 125 wt.% I_2

Basolite C300, HKUST-1
Open Channels, ≈ 1nm in 3D
1500-2100 m^2/g
Exposed Metal Sites of Framework



I_2@HKUST-1 ~ 150 wt.% I_2

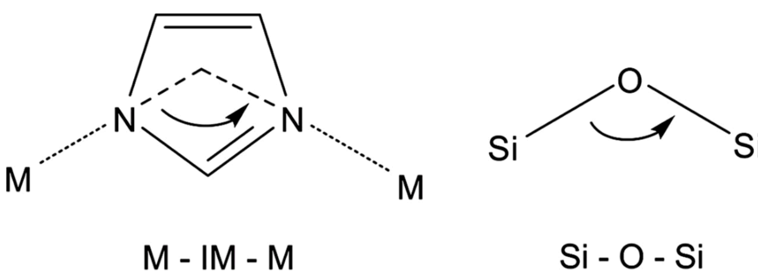
T.M.Nenoff, tmnenof@sandia.gov

Metal-Organic Frameworks (MOFs): tunable and versatile new generation of porous materials

Reason for ZIF's :

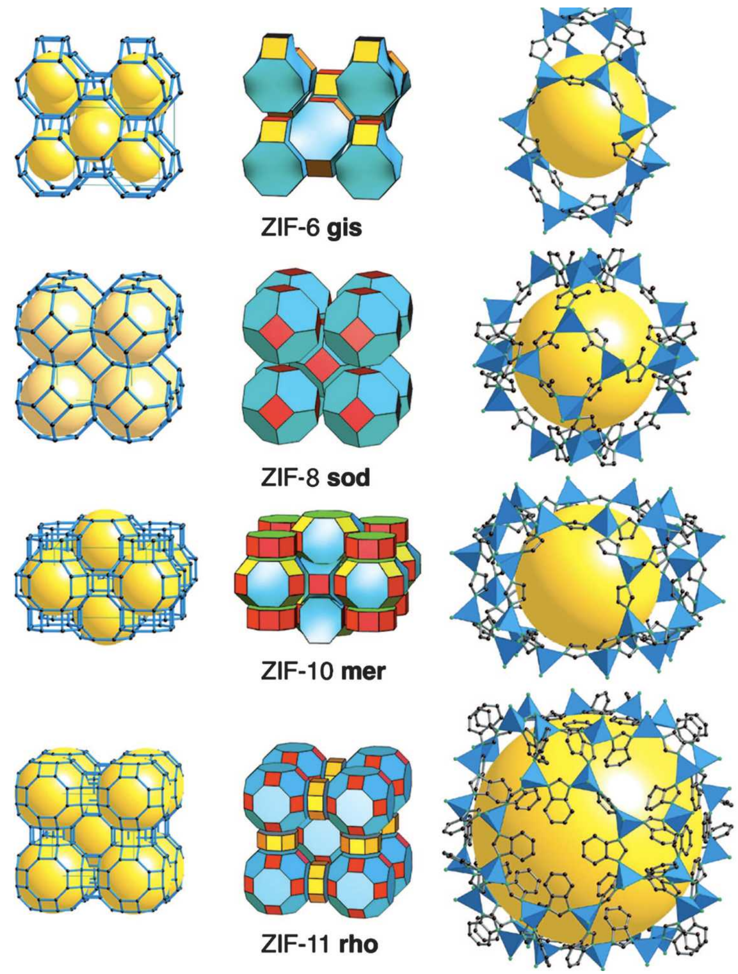
Zeolite Structures (such as MOR) are built from $Si(Al)O_4$ tetrahedra
linked through bridging oxygen atoms;
>150 structures

Possible to build in higher adsorption and selectivity through framework functionalization with metals and organics by replacing
zeolite linkers with transition metals and organics: ZIFs



1 2

Resulting in ultra high surface areas of ≈1600 m^2/g for ZIF-8



Yaghi, et al., Proc. Natl. Acad. Sci. U.S.A. **2006**, *03*, 10186

T.M.Nenoff, tmnenof@sandia.gov

Judicious Selection of "Ideal" MOF Candidate for I_2 sorption

Pre-requisites	ZIF-8
▪ Restrictive pore apertures to impart molecular selectivity for a directional diffusion of iodine (~3.35 Å)	✓ The β-cages, 11.6 Å in diameter, are connected via six-member ring (6 MR) apertures of ~3.4 Å
▪ Large surface area and pore volume	✓ Surface area ZIF-8 = 1,947 m^2 g^{-1} and Pore volume= 0.663 cc g^{-1}
▪ High *chemical*, *thermal*, and *moisture* stability	✓ Chemically stable in boiling solvents (including water), and thermally stable up to 550°C

Park, K. S.et.al *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103,* 10186.

T.M.Nenoff, tmnenof@sandia.gov

Challenges: Structural Characterization of Adsorbed Guest Species within Porous Hosts

- Considerable effort has been devoted to *understanding guest binding within porous systems*
- The high symmetry of the ZIF-8 poses *challenges in locating guests*, which often can be crystallographically disordered
- Complete understanding of guest binding can only be obtained by *combining insights from local and long-range structural probes, and molecular simulations:*
  Synchrotron Crystallographic Data and Structural Analysis
  Pair Distribution Function Analysis (short and long range crystallinity of I_2…Framework interactions
  Molecular Modeling and Simulation : maximum gas molecule loading per cage, inter/intra-cage mobility of I_2

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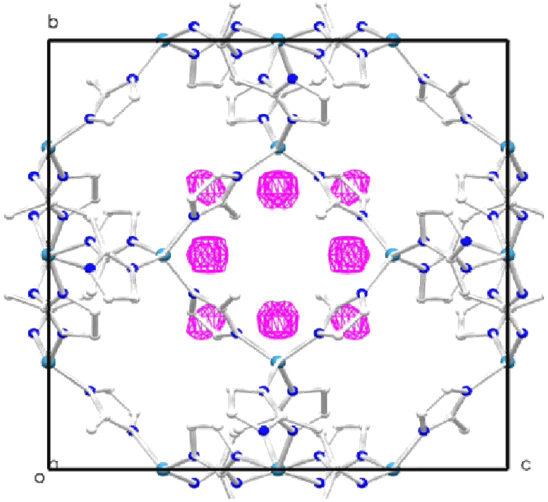
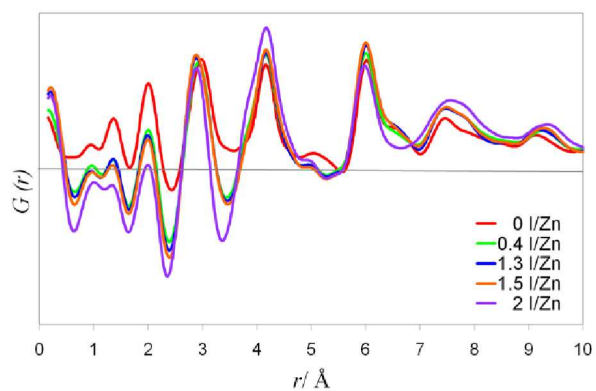
Integration of Experiment and Modeling to Identify Preferred Binding Sites for I_2 in ZIF-8

Complementary local and long-range structural probes

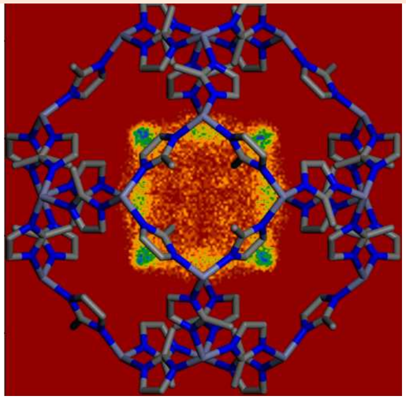


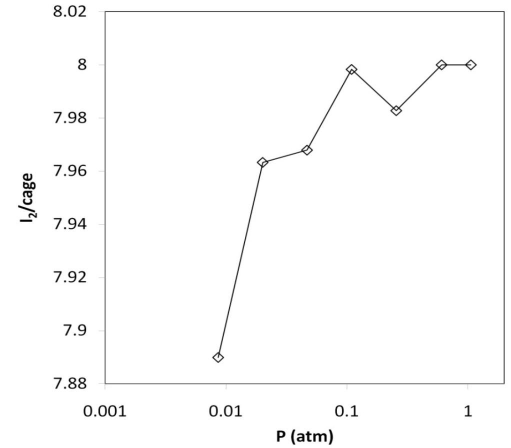
Difference-Fourier analysis map



Pair Distribution Function analysis

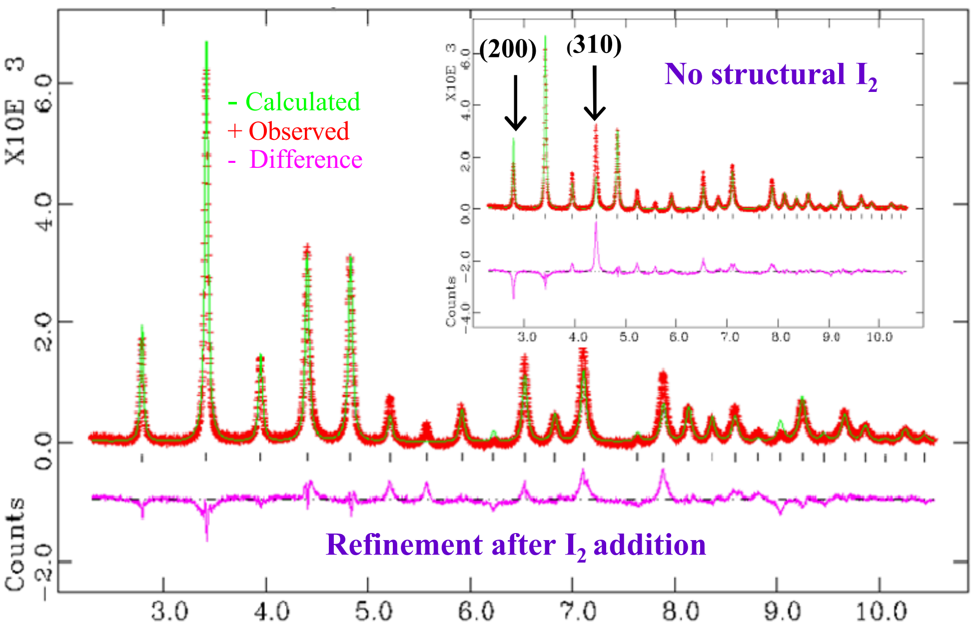
Molecular modeling: MD and GCMC





T.M.Nenoff, tmnenof@sandia.gov

High-Resolution Synchrotron-based XRD

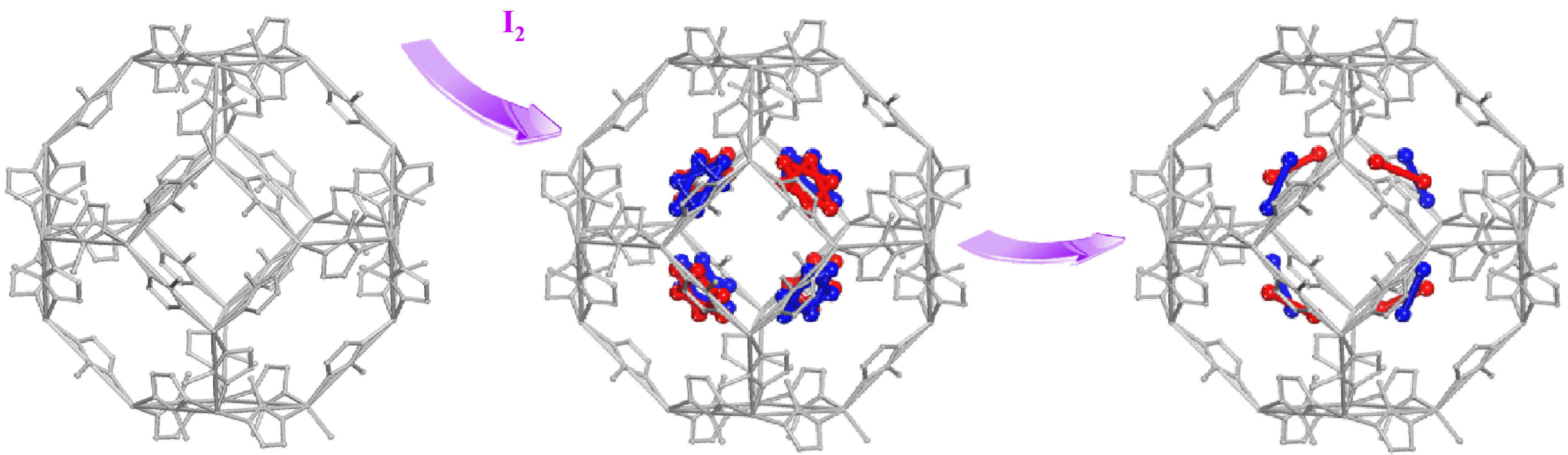


Calculated, observed and difference spectrum of 0.4 I/Zn (30wt%) loading of I_2@ZIF-8 after I_2 inclusion in structure refinement by Rietveld analysis (inset: before I_2 inclusion).

- Sample crystallinity is maintained up to ~1.3 I/Zn (70wt%) loadings
- Bragg reflections broaden significantly > 1.3 I/Zn
- difficult to distinguish from the pronounced diffuse features in the "background"
- MOF lattice contracts to accommodate increased I_2 loadings

T.M.Nenoff, tmnenof@sandia.gov

Determination of I_2 Binding Locations inside ZIF-8 Pore



Activated β-cage

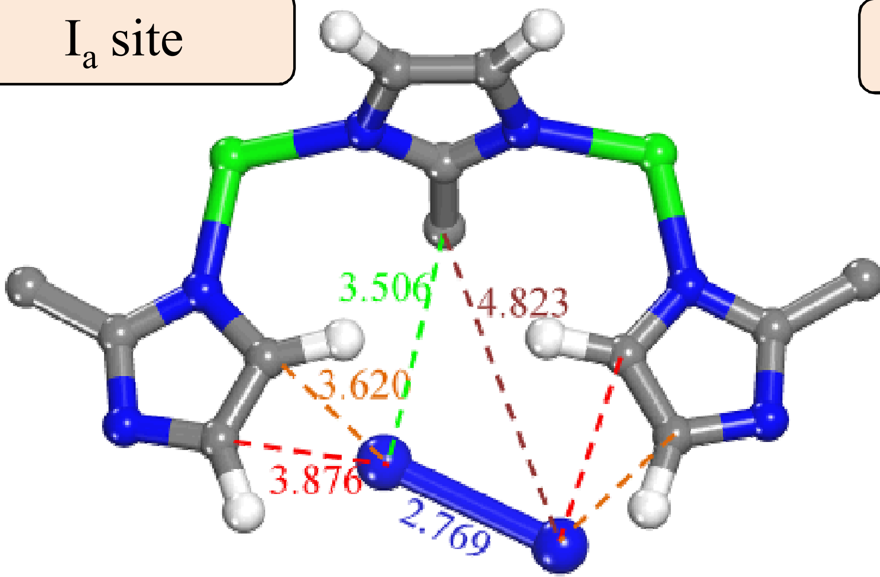
Dynamically disordered I_2 molecules

Refined I_2 sites: I_a (blue) and I_b (red)

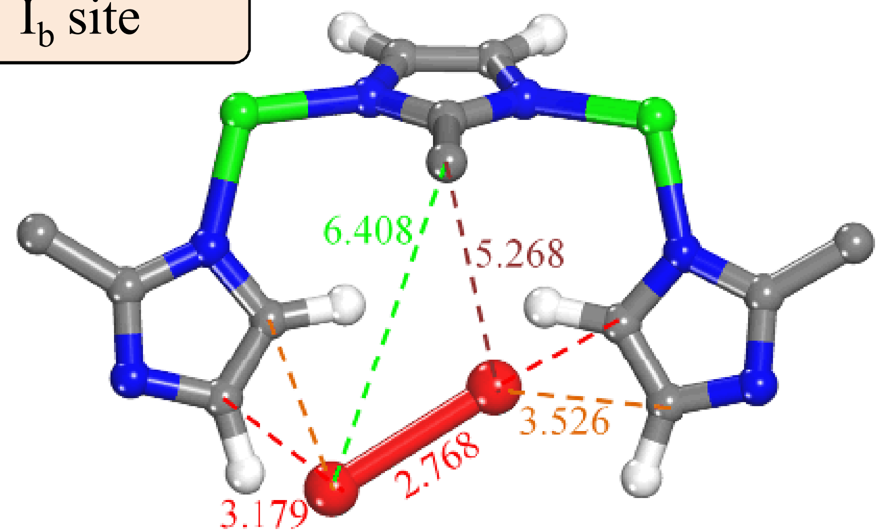
T.M.Nenoff, tmnenof@sandia.gov

Two distinct I_2 binding sites Indentified in ZIF-8 for I_2 sorption

I_a site



I_b site



I_2 site occupancy and I_2···MeIM close contacts in I_2@ZIF-8

I_2 site	Site occupancy		Contacts with MeIM	
	0.4 I/Zn	1.3 I/ Zn	C (CH_3)	C(H=CH)
I_a	0.28	0.88	3.506 Å; 4.823 Å	3.620 Å; 3.876 Å
I_b	0.14	0.38	5.268 Å; 6.408 Å	3.179 Å; 3.526 Å

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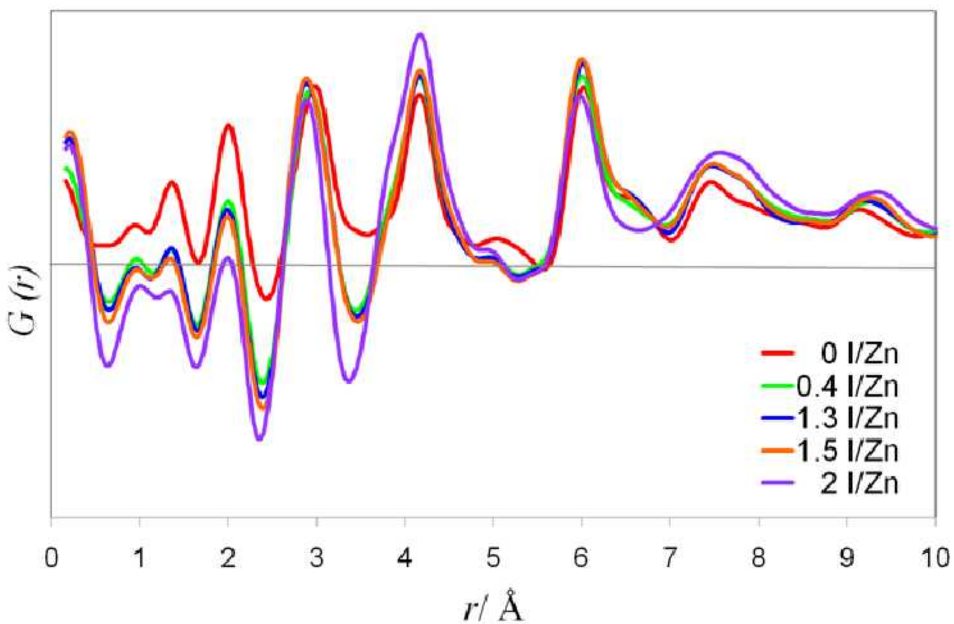
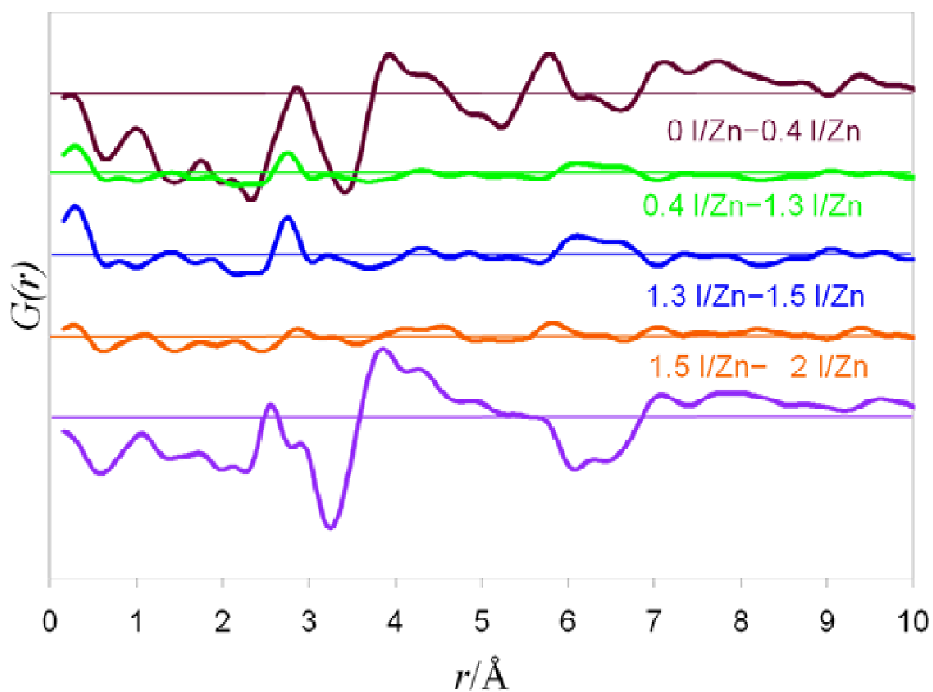
Pair Distribution Function Analysis: Local Structure Probe



short-range order and framework connectivity are maintained at all loading levels

- The PDF method- a weighted histogram of the atomic distances, independent of sample crystallinity
- Below ~6 Å, the *MOF cage features are retained in the PDF at all* I_2 *loading levels*
- The persistence of the peak at ~6 Å, corresponding to the Zn-(MeIM)-Zn′ distance
- >1.3 I/Zn (70wt) lose long range structural information though individual cages maintain crystalline integrity

Differential Pair Distribution Function Analysis (d-PDF)



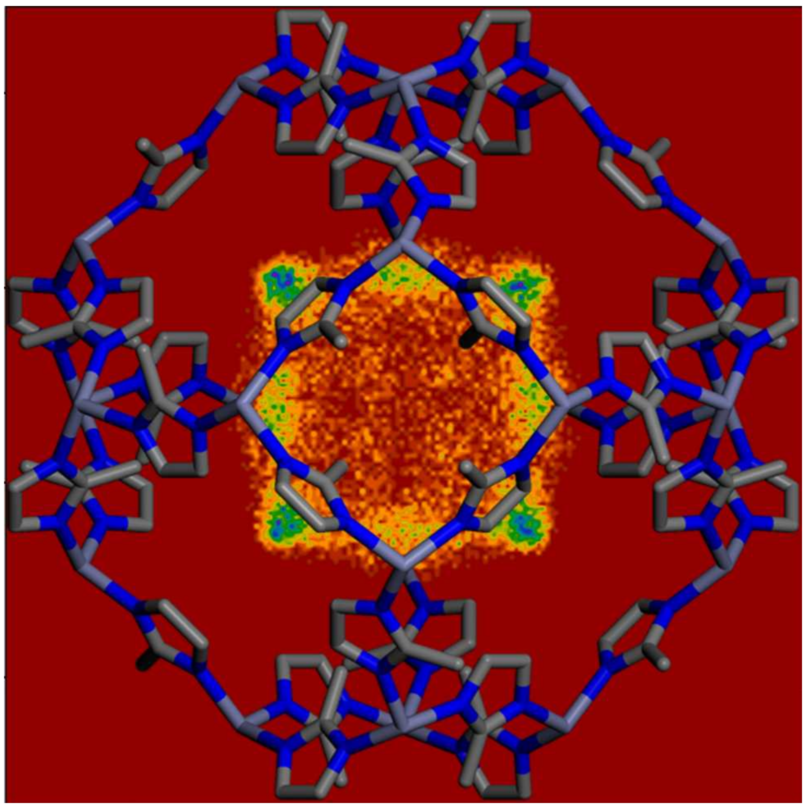
- Differential analysis applied to isolate I_2 guest molecules contributions
- Incremental I_2 loading up to 1.3 I/Zn (70wt%) peaks at 2.75 Å, 3.23 Å, 4.29 Å, 4.91 Å, 5.46 Å, 6.01 Å, and 6.61 Å
- I_2 loading >1.3 I/Zn: changes observed to MOF cage structure
  - new peaks 2.56 Å, 2.94 Å, and 3.79 Å
  - intensity changes for peaks 4.29 Å. 4.91 Å, and 3.23 Å

At loadings above 1.3 I/Zn (70 wt%), rearrangement of I_2 molecules required inside cage

T.M.Nenoff, tmnenof@sandia.gov

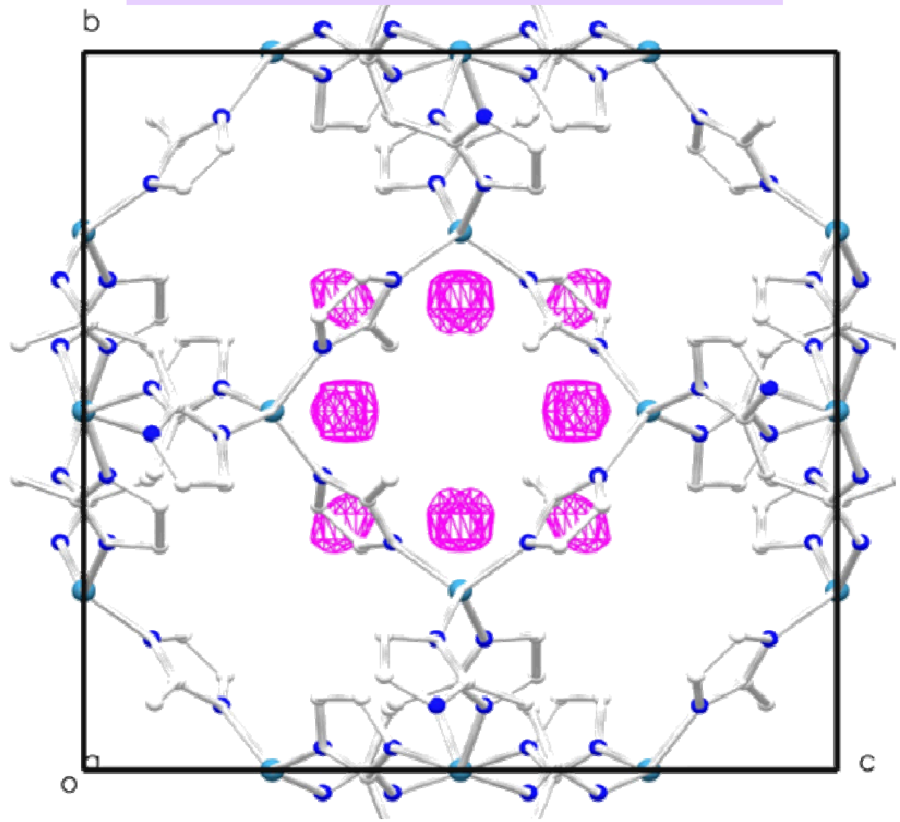
MD Simulations Closely Match Modeling Predictions of I_2 Electron Density

MD Simulation Analysis



2 I/Zn (~6 I_2 per cage)

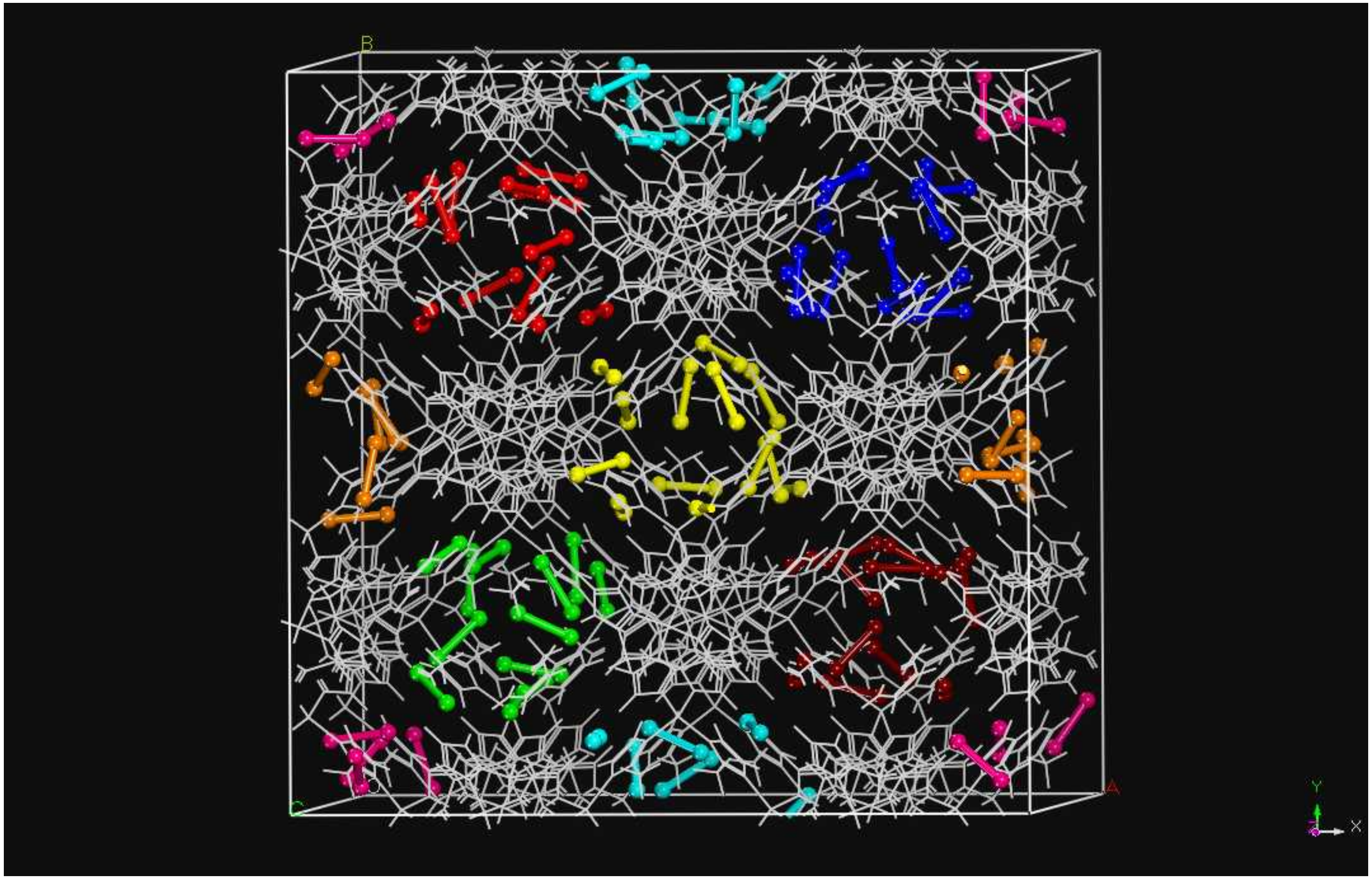
Crystallographic Data:
Difference-Fourier analysis map



1.8 I/Zn (~5.4 I_2 per cage)

T.M.Nenoff, tmnenof@sandia.gov

Dynamics of I_2 Within Cages: No Predicted Mobility of Gas Molecules In/Out of Individual Cages



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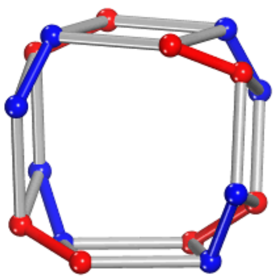
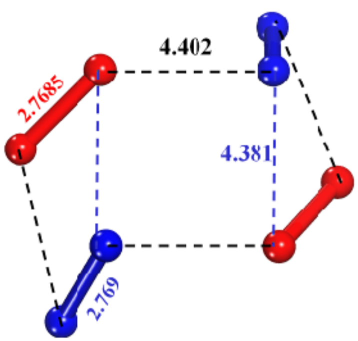
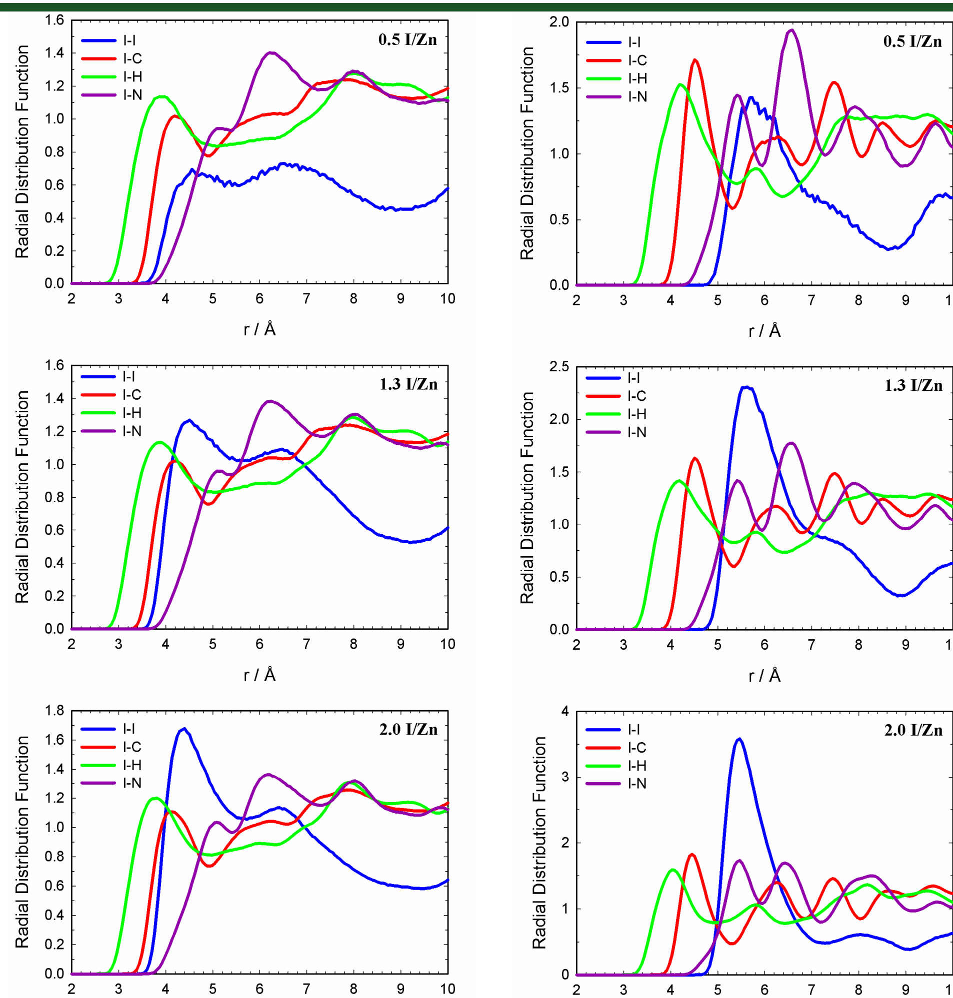
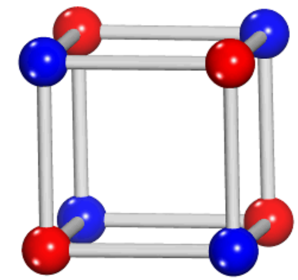
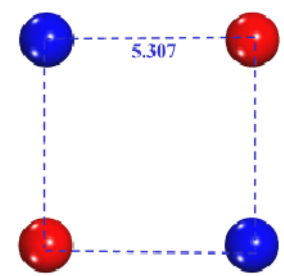
Experimental−Modeling Agreement Radial Distribution Functions (RDFs) for Diatomic and United-Atom Models









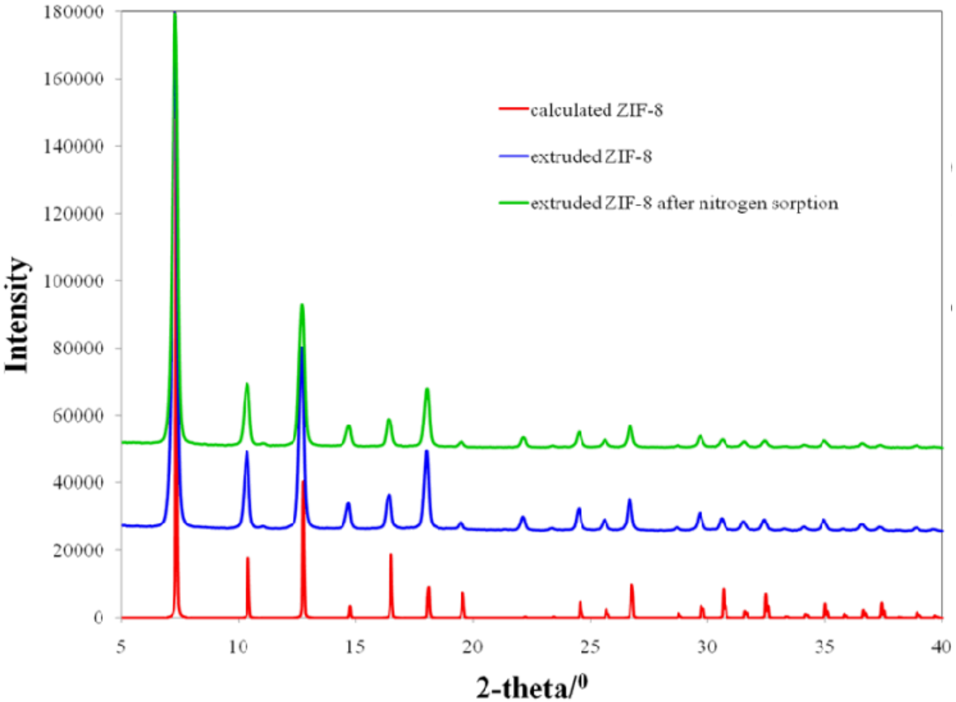


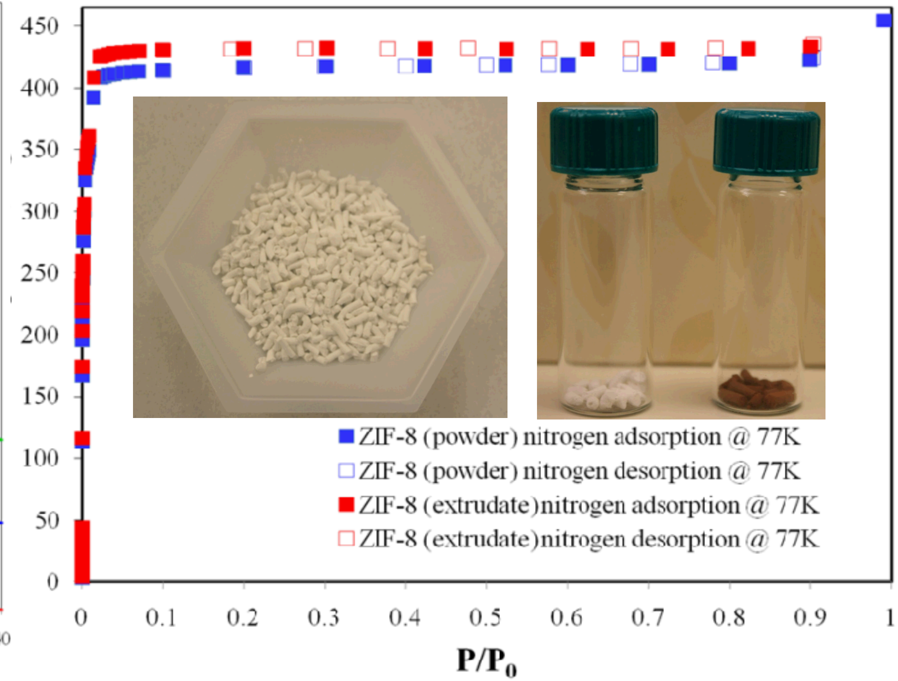
Good agreement between crystallography, PDF and modeling regarding nearest neighbors distances

T.M.Nenoff, tmnenof@sandia

Sample Pelletizing / Characterization for Industrial Applications

US Patent submitted, 2011; SD# 11971





Regularly sized pellets
Maintained surface area of MOF
1850-1900 m^2/g
3.5 grams prepared

JACS, 2011, submitted

Irradiations stability testing of SNL Waste Forms at Sandia Gamma Irradiation Facility (GIF)

Dose rates:

-long-term exposure/low dose:

0.1 Rads/sec, with an overall dose of 2.59×10^5 Rads (2218Gy)

-short-term exposure/high dose:

800 Rads/sec, 1×10^6 Rads (10,000 Gy)

Samples tested include:

EG 2922 Glass (550°C), 87.5Glass/12.5SiO_2

80Glass/20AgI-MOR/10Ag

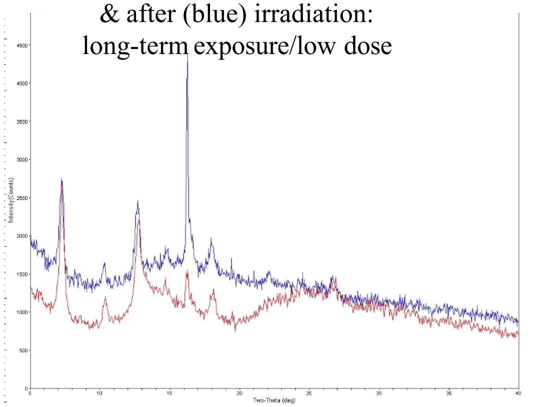
ZIF-8 (MOF), ZIF-8/I_2

HKUST-1(MOF), HKUST-1/I_2, Glass/HKUST-1/I_2

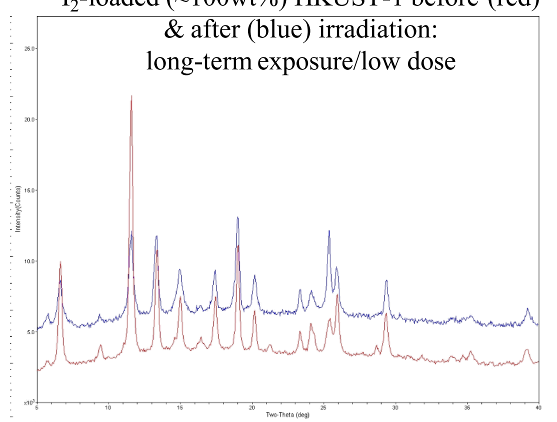
Bi-I-O

Examples of MOF irradiation studies:

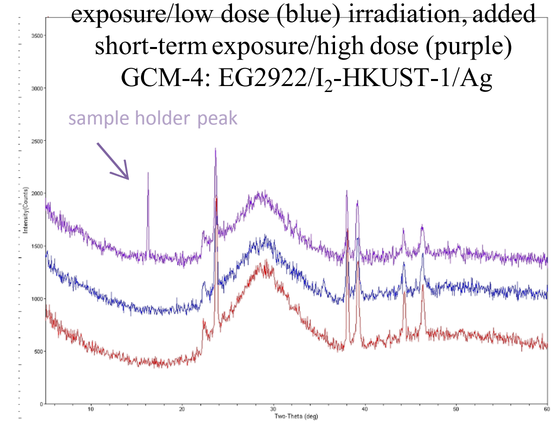
90 wt.% I_2-loaded ZIF-8 before (red) & after (blue) irradiation: long-term exposure/low dose



I_2-loaded (≈100wt%) HKUST-1 before (red) & after (blue) irradiation: long-term exposure/low dose



GCM-4 before (red) & after long-term exposure/low dose (blue) irradiation, added short-term exposure/high dose (purple) GCM-4: EG2922/I_2-HKUST-1/Ag



No structural changes as seen by XRD or in PCT responses of any samples. This radiological characterization is a good approximation of an adequately shielded long-term disposal environment.*

*R. H. Jones, Radiation Effects; A Compilation of Special Topic Reports, prepared for the Waste Package Materials Performance Peer Review submitted to U.S. DOE and Bechtel SAIC Company, 18-1 (2002).

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Nuclear Energy

Future studies for enhanced Structure/Property Relationship studies for Iodine Capture

MOF development:

(1) new ligands for newly designed MOFs
(2) structure-property relationships to optimizing competitive gas sorption
(3) Engineered extrudates (no binders) for process studies at ORNL and INL

single crystal MOF-I_2 diffraction for structural studies
Optimization of glass compositions and weight loading for waste forms

- Complex Iodine stream interactions with MOR, MOF and resulting WF

- Use of ORNL mordenite / MOF loaded samples in structural studies and WF development
  - Partial Iodine loading on Ag°-MOR
  - Partial loading of Ag on Na-MOR
  - Partial loading of Iodine on Ag-Na-MOR
  - Iodine loaded MOFs (by ORNL) structure and WF development

- Incorporation of NEAMS MD and GCMC modeling and simulation of gas sorption and competitive sorption of complex streams

T.M.Nenoff, tmnenof@sandia.gov

The Fuel Cycle Research & Development

Iodine Waste Form Development and Technology:
Iodine Waste Forms – Glass for Ag-Zeolites

Tina M. Nenoff, James Krumhansl, Terry Garino, Dorina Sava, David Rademacher
Sandia National Laboratories
Albuquerque, NM 87185

Waste Forms by Design: Encapsulation in Low Temperature Sintering Glasses

- For Iodine Storage: utilized chemistry of glasses and sorption materials to durably store the iodine during decay.
- Known iodine getters include Ag, Ag-Zeolite. Temperature dependence of AgI (mp = 558˚C) dictates temperature processing limit of waste form
- Volatile Gas Sorption by Zeolites and MOFs: still need a waste form to incorporate the oxide getter material, gas (eg., iodine), and additional components into matrix with no adverse environmental effects
- *Addition of Ag metal to composition to capture any gas liberated during waste form processing (in-situ formation of AgI)*
- Targeted waste form:

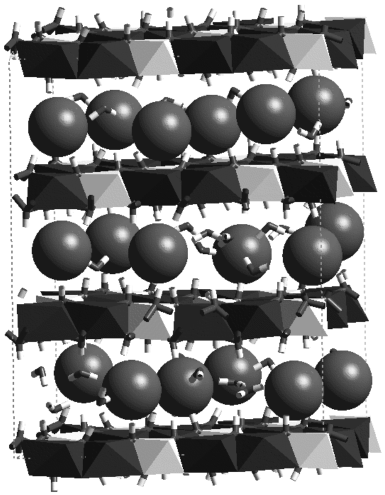
✓ compact and monolithic

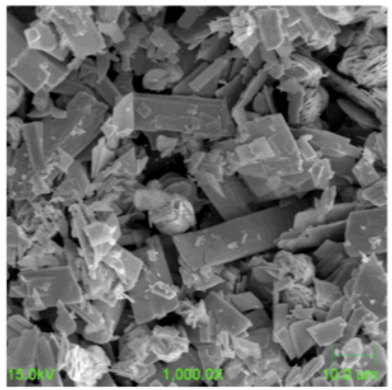
✓ mechanically, thermally, and chemically stable

✓ able to sustain compatibility with various repository conditions

Examples of SNL Developed Waste Forms for Iodine Storage

Iodine from solution: Bi-I-O Hydrotalcites

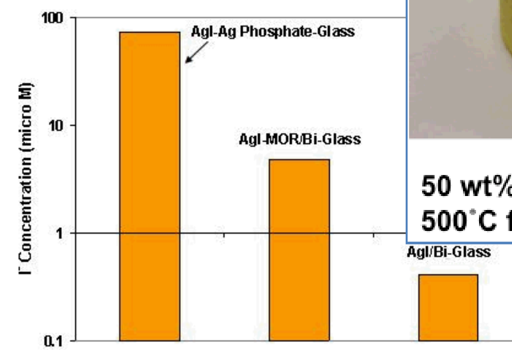




Applied Geochem, 2011, 26, 57.; US Patent filed 2010

AgI off-gas, Ag-I-MOR Low temperature glasses

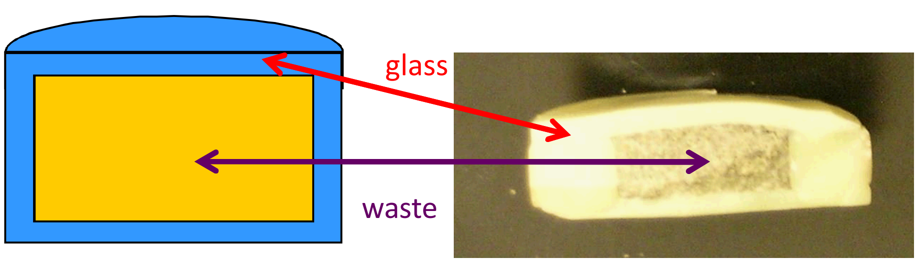
50 wt% AgI/50 wt% Glass 500˚C for 3 hr



Leach tests
90°C, 7d, DI H_2O

Ceram. Trans. ***2010****, 224*, 305; *US Patent file 2010*

Core-Shell Glass Waste Forms



Shell: 100% Glass; Core: Glass : AgI-MOR (250 to 600 µm) : Ag
J. Amer. Ceram. Soc. **2011**; DOI: 10.1111/j.1551-2916.2011.04542.x

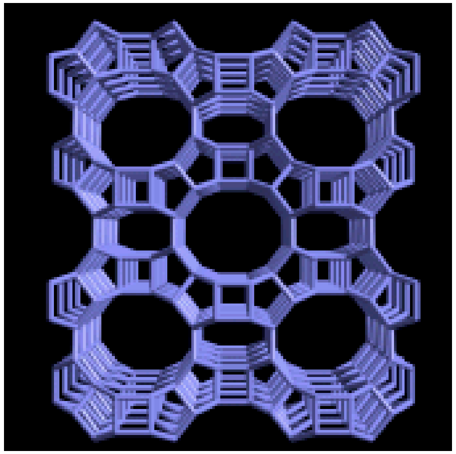
Ag-I-MOFs + Low temp glasses

Ind. Eng. Chem. Res, **2011**, in press, DOI: 10.1021/ie200248g

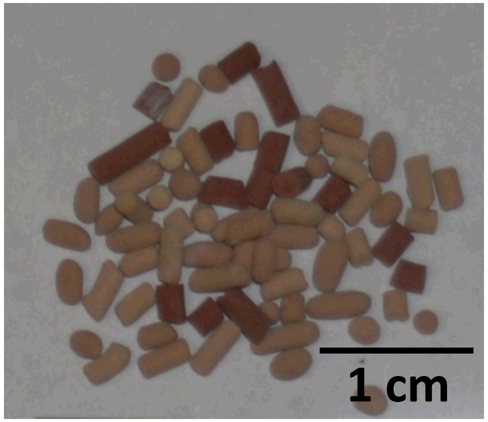
T.M.Nenoff, tmnenof@sandia.gov

The DOE baseline I_2 Capture Material is Ag-Mordenite

- ^{129}I is present in the off-gas streams.
- It is separated by passing the vapor through a bed of silver-zeolite.
- Silver-Mordenite (Ag-MOR) is the leading candidate: $Ag_2Al_2Si_{10}O_{24}\cdot 7(H_2O)$.
- Silver Iodide is formed by reaction of the I_2 vapor with Ag.



12 MR, 7.0 x 6.5Å



IONEX Ag-MOR

T.M.Nenoff, tmnenof@sandia.gov

Bi-Zn-oxide Based Low Temperature Sintering Glasses

Bismuth known affinity for Iodine (Applied Geochem, 2011, 26, 57)

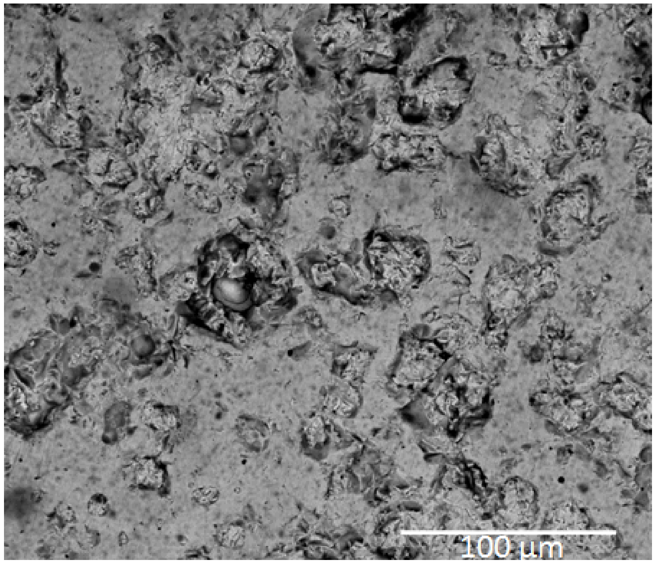
50 wt% AgI/50 wt% Glass
500˚C for 3 hr

Glass characteristics (Ferro Corp.)	**EG2998 (c)**	**EG2922 (a)**
Composition	Bi-Zn-B	Bi-Zn-Si
Firing temperature	500°C	525°C–550°C
Crystallinity	Crystallizing	Vitreous - Amorphous
Density	5.65 g cc^{-1}	5.8 g cc^{-1}

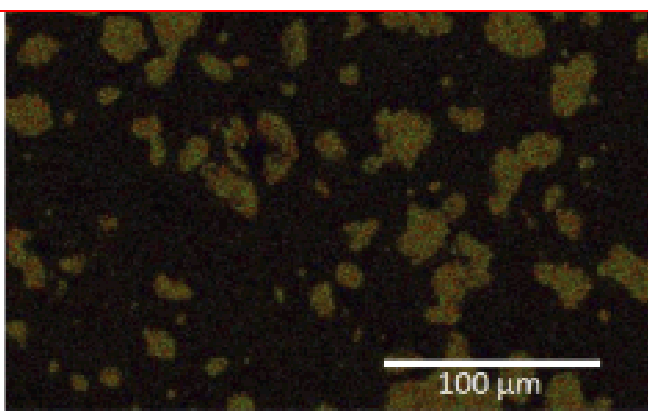
Glass	ZnO		Bi_2O_3		Al_2O_3		B_2O_3		SiO_2	
	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %
EG 2922	14.2	7.8	20.2	63.4	57.8	23.4	7.8	5.4		
EG 2998	49.7	26.9	18.9	58.6					31.3	14.5

T.M.Nenoff, tmnenof@sandia.gov

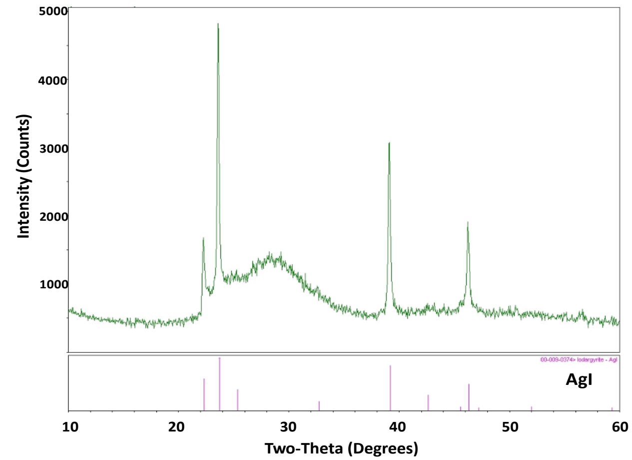
Durable Glass Composite Material (GCM) Waste Form of Sintered Glass-AgI



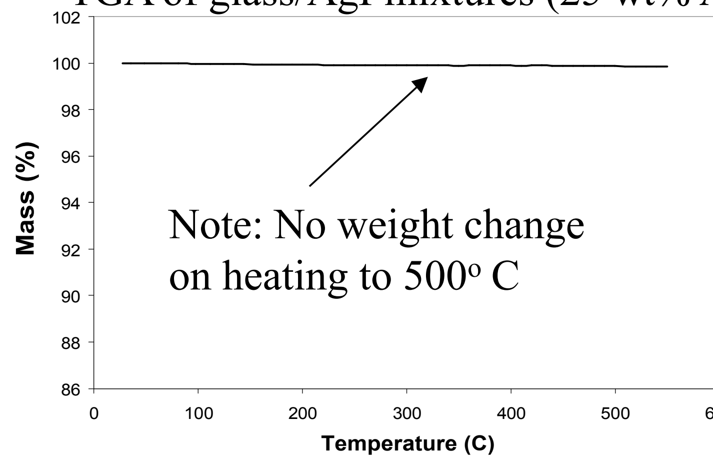
SEM-EDS of high density Glass/AgI mixtures sintered at 550°C (EG2922)



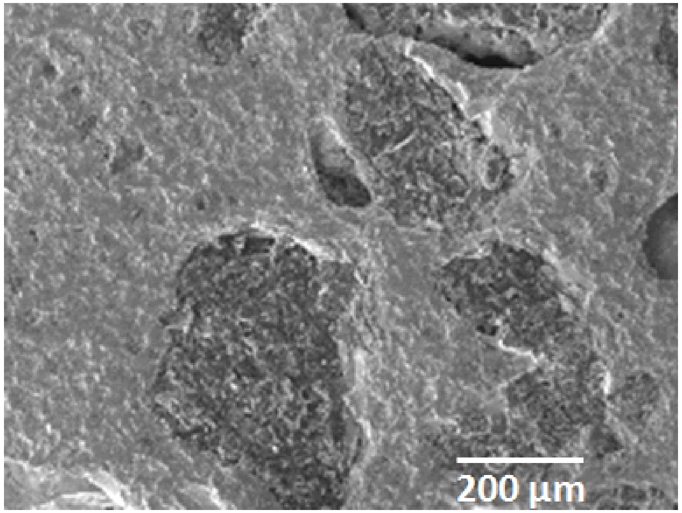
Glass matrix remains amorphous and AgI is encased in glass



TGA of glass/AgI mixtures (25 wt% AgI)



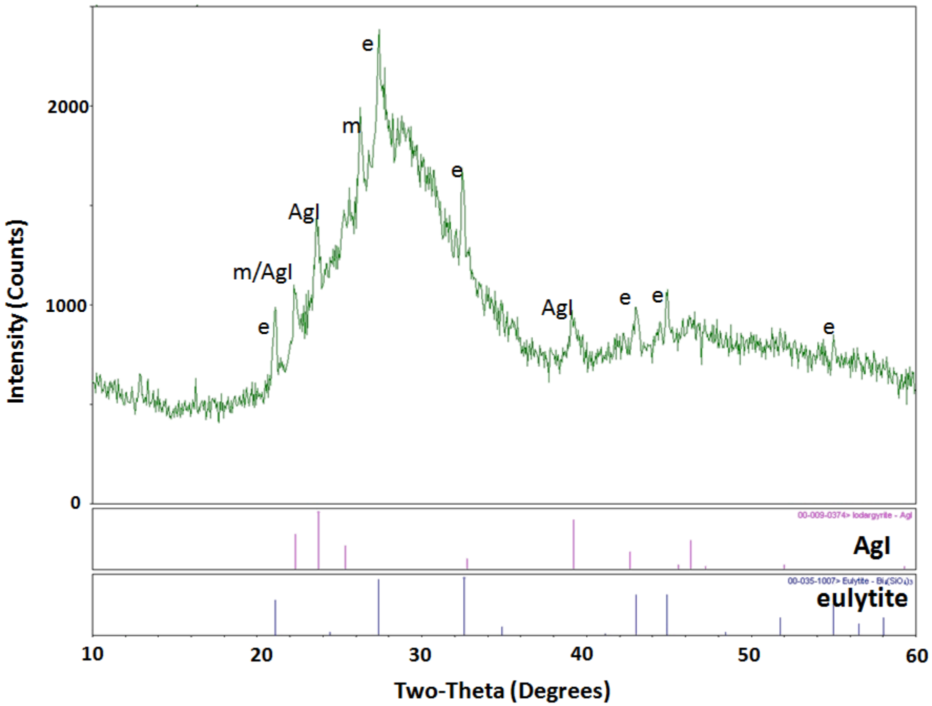
Durable Glass Composite Material (GCM) Waste Form of Sintered Glass-AgI-Mordenite



Glass/AgI-MOR/Ag pellet sintered to high density at 550°C (EG2922) (80:20:5 by mass).

AgI-MOR particles size 100-250µm

Crystallized Phases During Sintering:
AgI, MOR, Eulytite



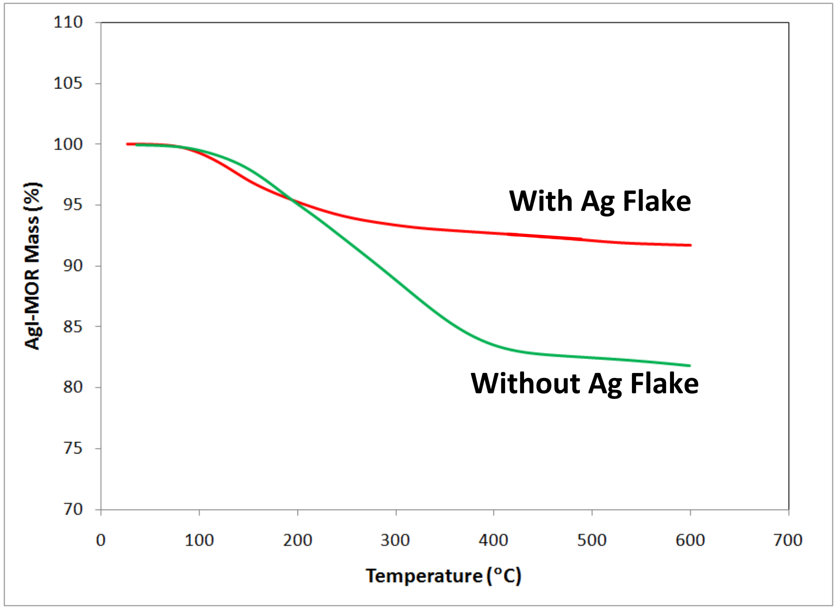
Eulytite: $Bi_4(SiO_4)_3$

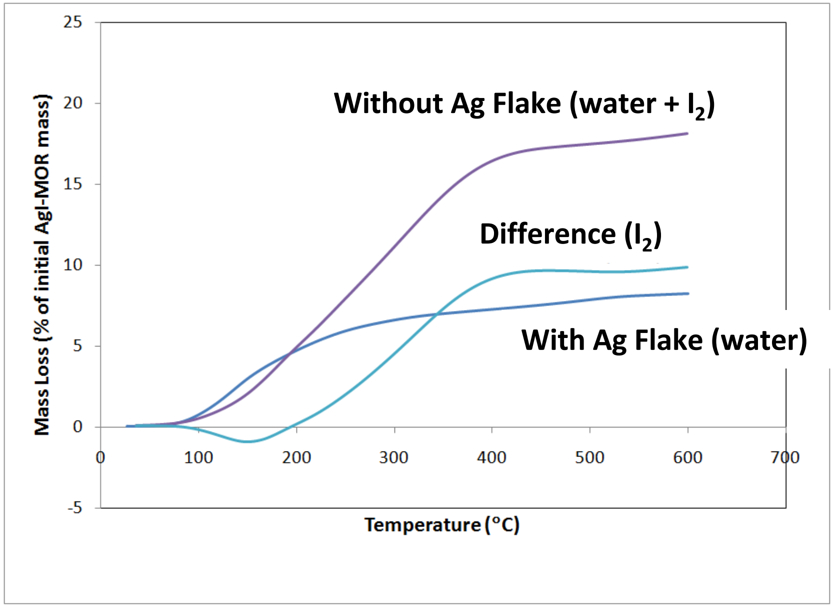
T.M.Nenoff, tmnenof@sandia.gov

Step 3: Eliminate I_2 vapor loss on sintering by adding excess Ag

Unlike Glass/AgI-Glass mixes, Glass/AgI-Mordenite may lose I_2 during heating.

Addition of Ag flake to any composite containing I_2 induces AgI formation; No Iodine loss





T.M.Nenoff, tmnenof@sandia.gov

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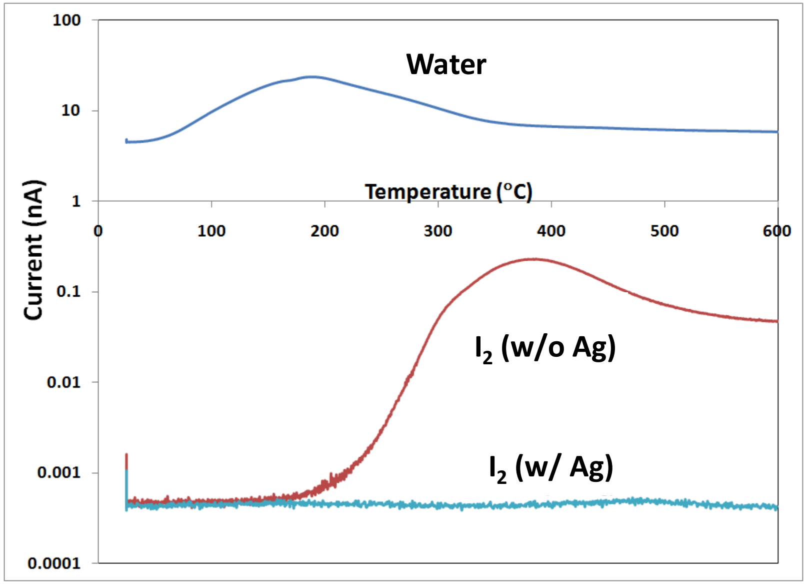
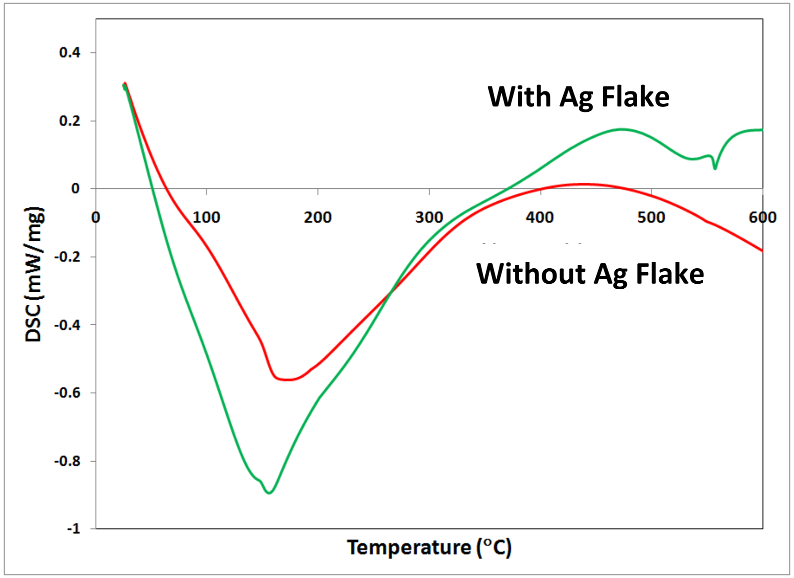
Confirmation of Iodine retention by Ag flake addition

TGA/MS monitoring of Iodine retention by Ag flake



AgI presence confirmed in Ag flake mixture with AgI melting at 558°C



T.M.Nenoff, tmnenof@sandia.gov

Short term aqueous leaching tests showed the GCM have good durability

- PCT (Product Consistency Test, ASTM Designation: C 1285 – 02) test was done on crushed material: 90˚C for 1 week.
- Samples run: base glass, glass/AgI and glass/AgI-MOR
- ICP/MS analysis on the leachant showed low levels of dissolved species.

PCT Leachant ICP/MS Results (ppm)

Composition	B	Na	Si	K	Zn	Ag	I	Bi
BiSi-Glass	0.6	3.4	1.9	1.4	0.6	0.0	0.02	0.08
BiSi-Glass (75wt%)/AgI (25 wt%)	0.7	1.5	1.9	0.8	1.2	0.0	2.3	0.02
BiSi-Glass (80wt%)/AgI-MOR(20wt%)/Ag(+5wt%)	8.6	6.5	5.6	0.4	0.05	7.7	0.3	2.2

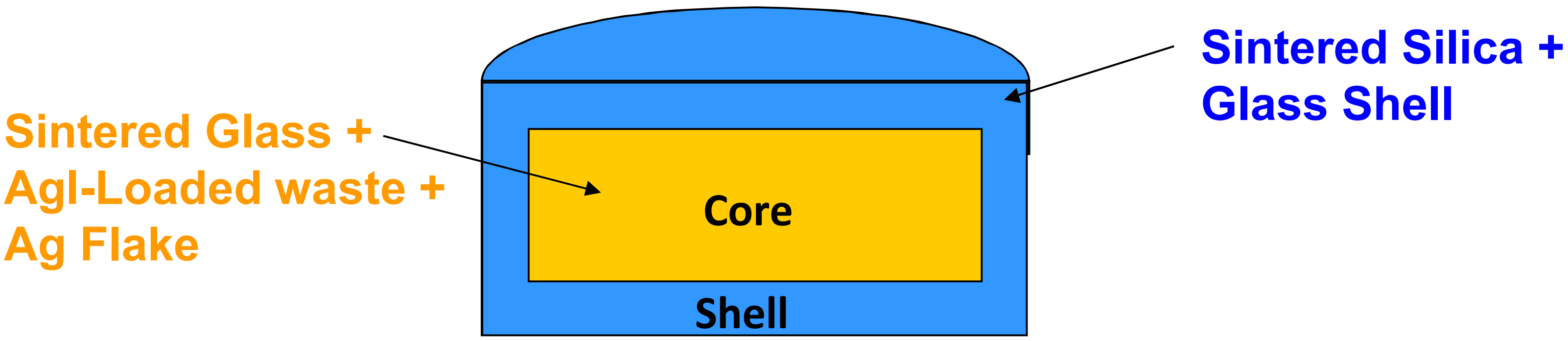
T.M.Nenoff, tmnenof@sandia.gov

Core/Shell Waste Form was developed to further improve long term iodine retention

The core contains the iodine and is encased in a shell of glass.

The glass shell protects the core from contact with the environment.

Such a structure was fabricated using simple processing techniques.



Cross-sectional view

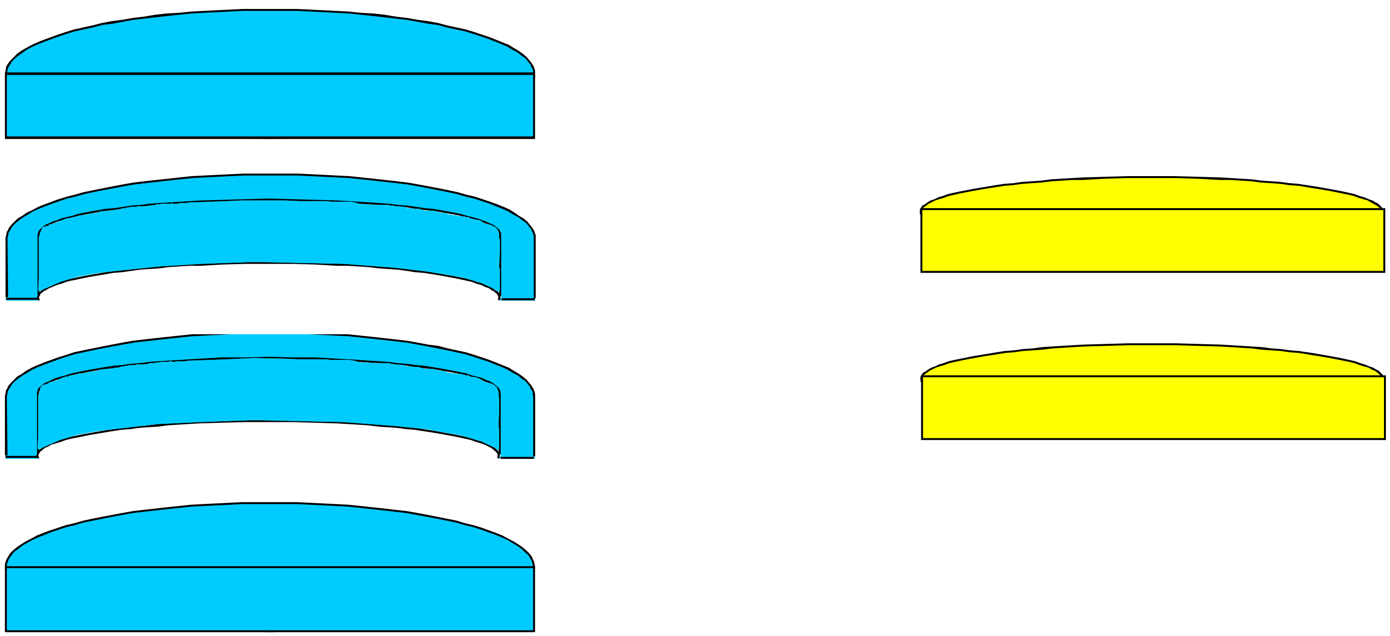
JACerS, 2011, in press; DOI: 10.1111/j.1551-2916.2011.04542.x.

T.M.Nenoff, tmnenof@sandia.gov

Core/Shell Fabrication:
Individual pieces are formed

Shell Parts: Glass Only

Core: Glass w/ AgI or AgI-MOR

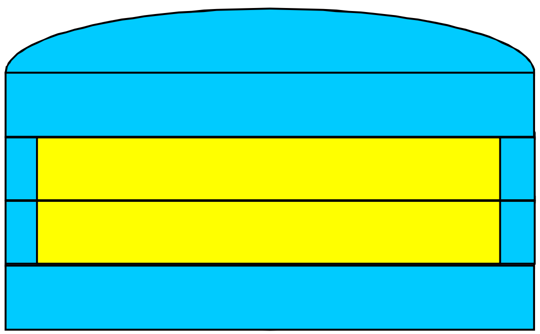


Parts can be made by dry pressing, filter or slip casting or centrifugation.

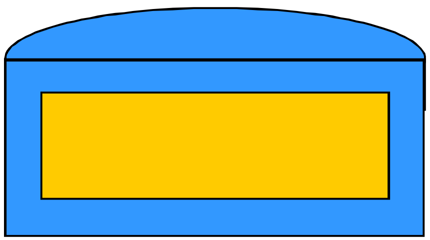
T.M.Nenoff, tmnenof@sandia.gov

Next, parts are assembled and the package is sintered

Step 2. Assembly



Step 3. Sintering

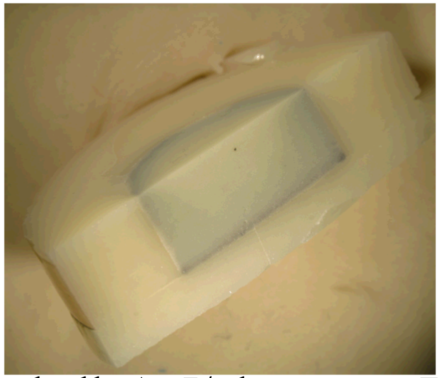


During sintering, the parts merge to form a monolith. The glass shell protects the iodine-containing core from the environment.

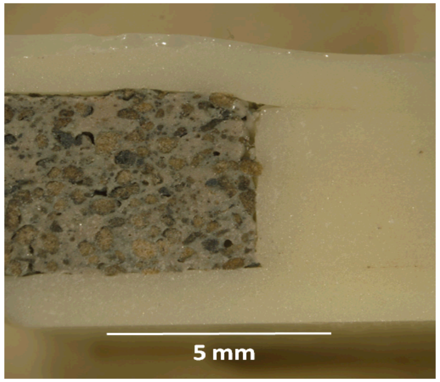
T.M.Nenoff, tmnenof@sandia.gov

Result: A "Universal" Low Temperature Glass Encapsulation Method

Sintering conditions : heat at 10°C/min for the AgI/glass, or at 2° for the AgI-MOR/glass/Ag, in air to 550°C for 1 hr

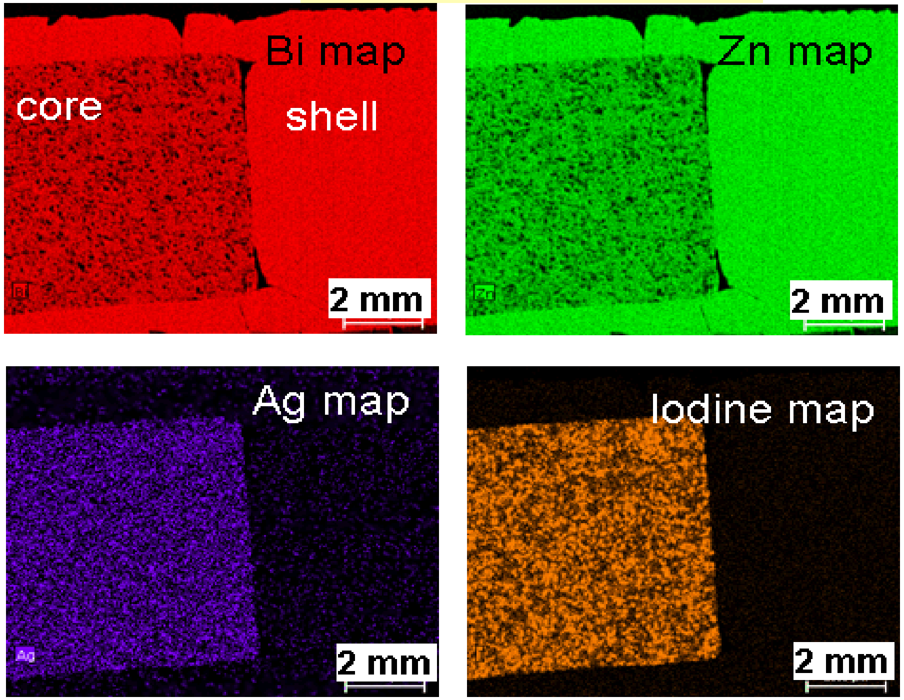


Glass shell, AgI/glass core 75/25



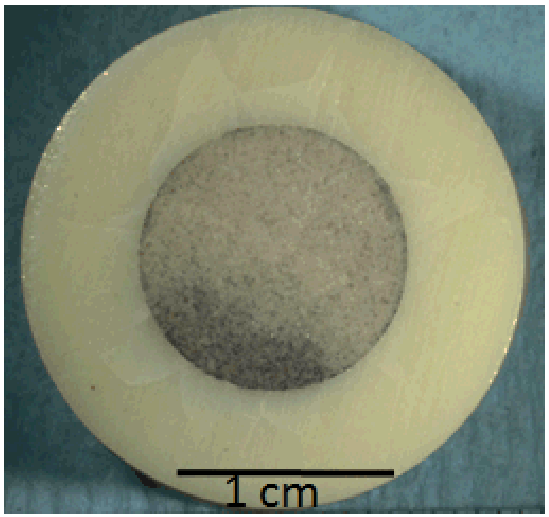
Glass shell,
AgI-MOR/Ag/Glass core 80/20/5

Iodine is Contained

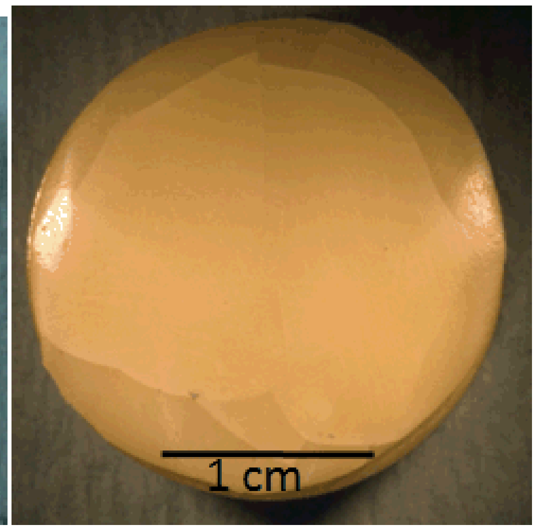


Micro XRF Analysis

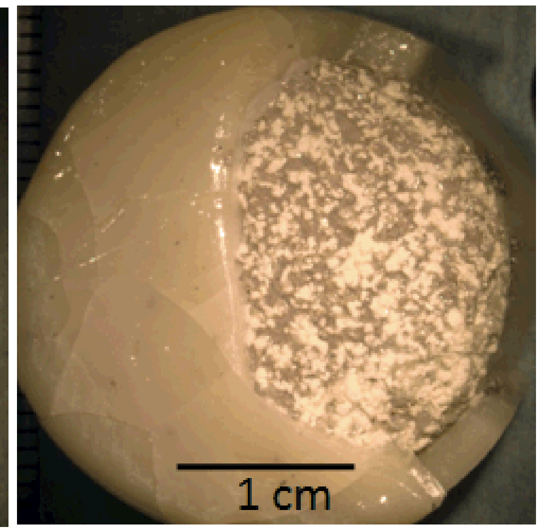
Rare Occasions: Core/Shell Waste Forms Crack in Processing



Radial Cracking



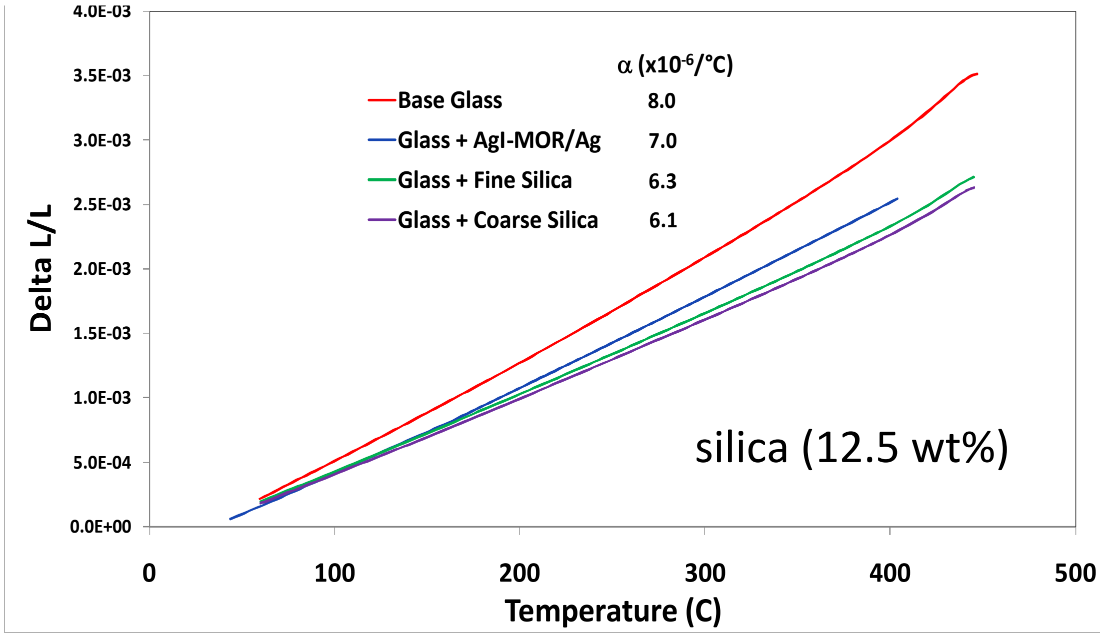
Circumferential Cracking

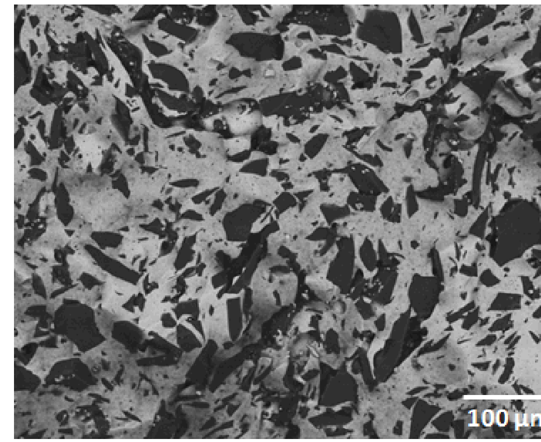


Larger Size= More Cracks

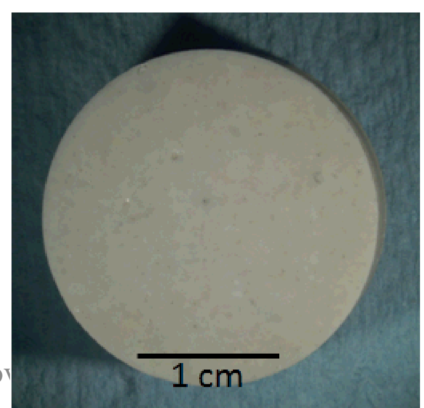
The cracks are caused by tensile stresses in the shell due to thermal expansion mismatch between the core and shell.

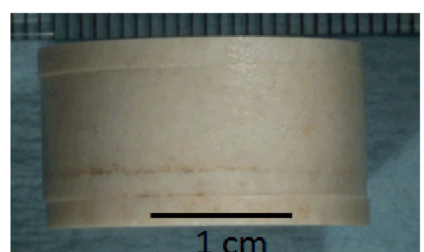
Phase Expansion Optimization was achieved by adding silica to the shell





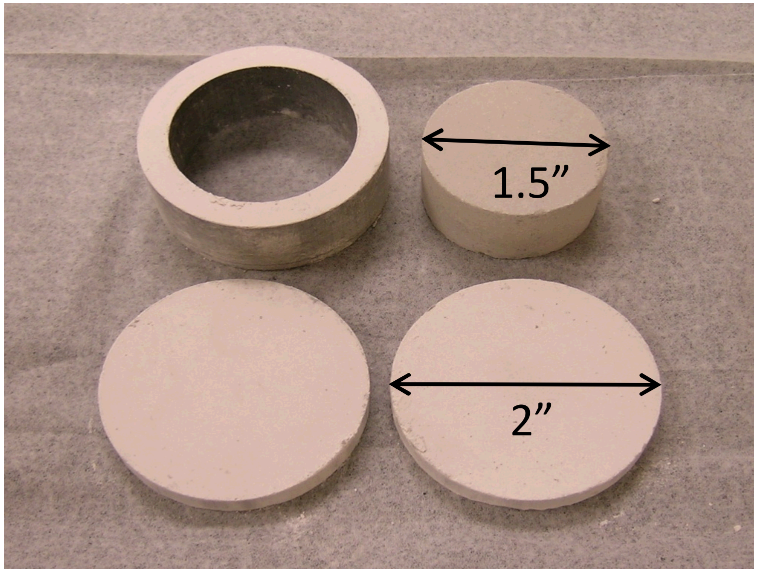
SEM image of silica glass composites (15 wt% silica) with < 50 µm silica particles

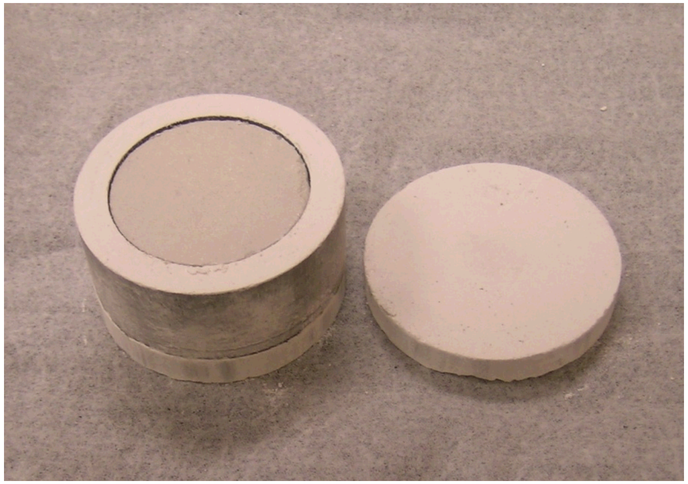




In Waste Form: 12.5wt% Silica in glass shell

Core/Shell Waste Form Scale Up For Larger Samples: Dies Designed and Fabricated





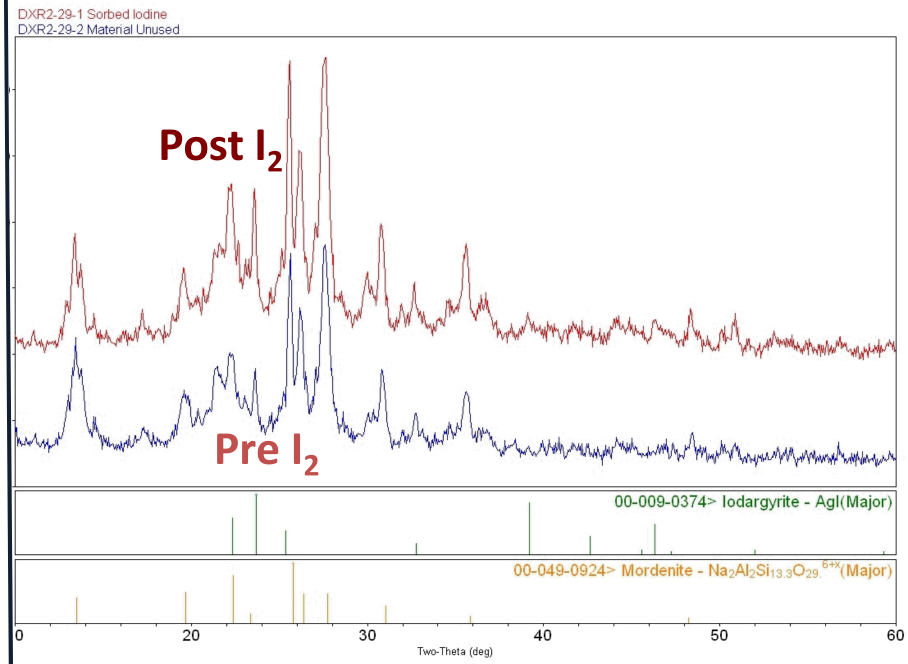
Increased Waste Form Size Produced:
≈ 8 gram core sample, 9x area, 2x thickness = 18x volume increase
AgI-MOR 10wt% w/Ag flake, pressed pellets of new enlarged core-shell samples
Silica added to glass for expansion matching

T.M.Nenoff, tmnenof@sandia.gov

INL Simulated Off-Gas Capture Materials received for WF development work at SNL

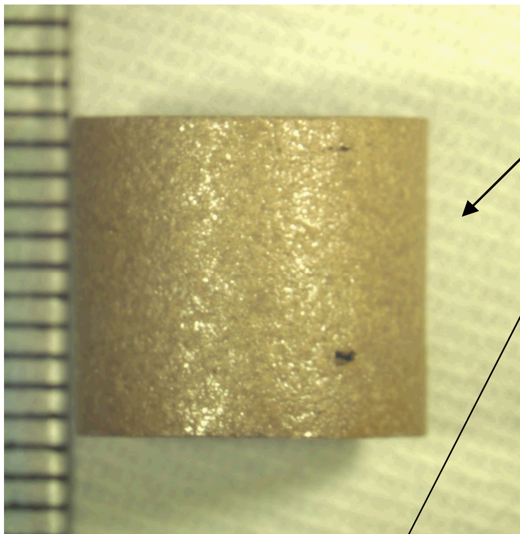
Courtesy of D. Haefner, INL

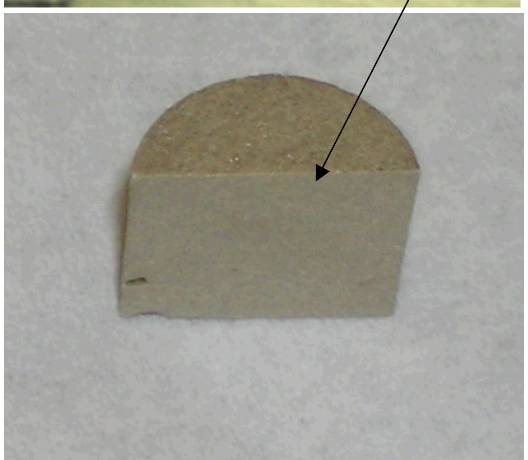
INL simulated dissolver off-gas setup



Pre- and Post- I_2 exposure,
- no indication of MOR framework changes,
- no isolated AgI post I_2 exposure, and
- probable AgI incorporation in MOR pores
(as seen by changes in relative peak intensities)

Fabricate and test GCM Waste Form made with INL AgI-MOR

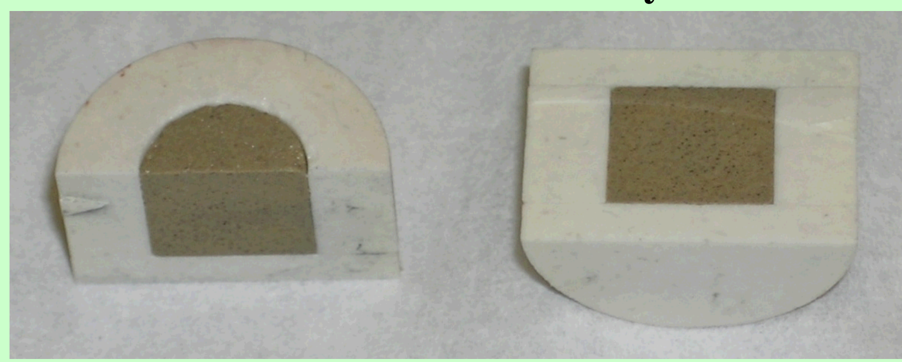




A. Homogenous GCM Waste Form Successfully Fabricated:

<u>GCM Waste Form Composition:</u>
80 parts BiSiZn 550°C sintering glass
20 parts INL AgI-MOR
5 parts Ag flake

B. Core/Shell Waste Form Successfully Fabricated



<u>Shell Composition</u>:
80wt% BiSiZn Glass
20wt% Amorphous Silica

C. PCT testing revealed no detectable iodine releases

T.M.Nenoff, tmnenof@sandia.gov

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The Fuel Cycle Research & Development

Iodine Waste Form Development and Technology:
Iodine Waste Forms – Glass for I_2-MOFs

Tina M. Nenoff, James Krumhansl, Terry Garino, Dorina Sava, David Rademacher

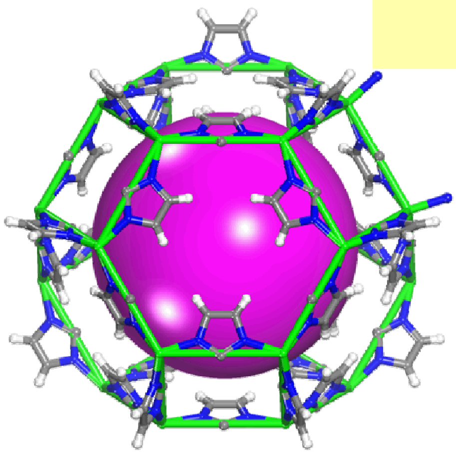
Sandia National Laboratories

Albuquerque, NM 87185

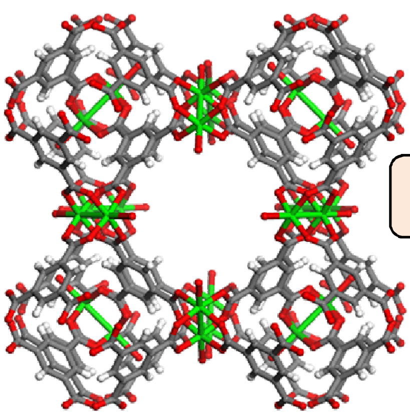
Invited Article, special issue: Nuclear Energy
Ind. Eng. Chem. Res., **2011**, DOI: 10.1021/ie200248g

Glass Composite Materials (GCM) Waste Forms

Utilize High Surface Area of MOFs with Selectivity (of Pore Opening or Metal Center)



I_2@ZIF-8 ~ 125 wt.% I_2 +
- EG 2998, Ag → 500 C, 1hr → GCM-1 (c)
- EG 2922, Ag → 525 C, 1hr → GCM-2 (a)

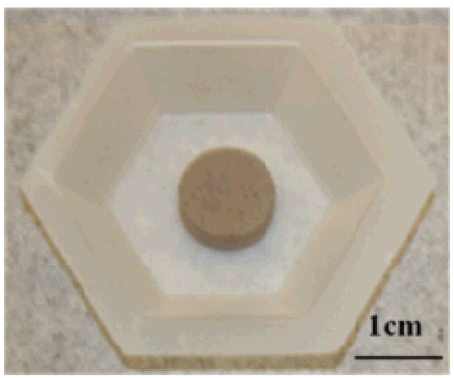


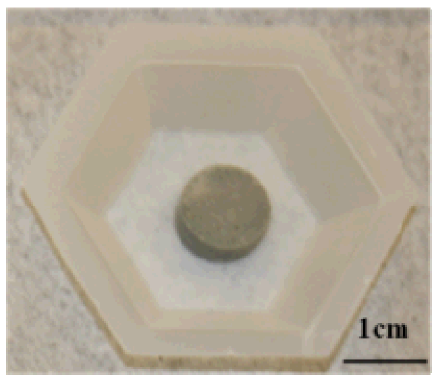
I_2@HKUST-1 ~ 150 wt.% I_2 +
- EG 2998, Ag → 500 C, 1hr → GCM-3 (c)
- EG 2922, Ag → 525 C, 1hr → GCM-4 (a)

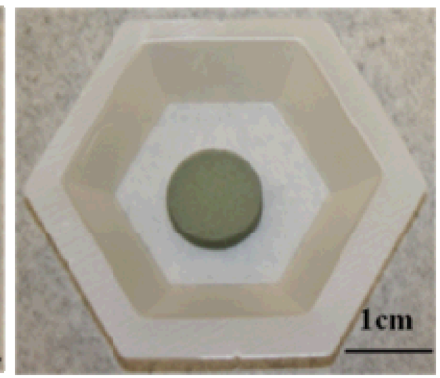
80 wt.% glass, 10 wt. % I_2@MOF, 10 wt% Ag

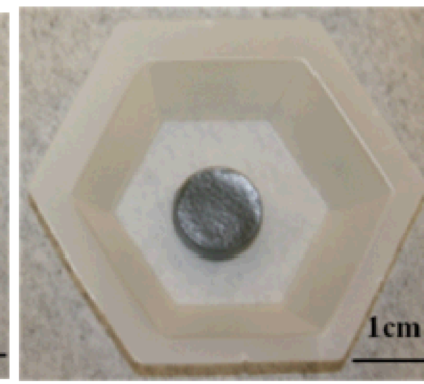
Glass Composite Materials (GCM) Waste Forms – Pressed Pellets

- The powders were homogeneously mixed in a mortar and pestle
- Bulk samples of approximately 2.5 g and 1.2 cm in diameter were pelleted in a binder-free process, by applying a uniaxial mechanical pressure of 70MPa in a steel die









GCM-1 Crystalline

GCM-2 Amorphous

ZIF-8

GCM-3 Crystalline

GCM-4 Amorphous

HKUST-1

T.M.Nenoff, tmnenof@sandia.gov

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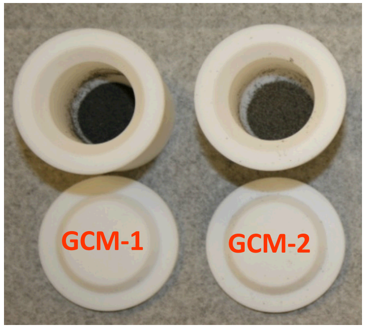
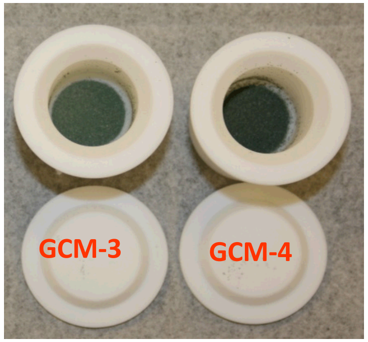
Product Consistency Test (PCT): Leach Durability Results

Standard PCT* test conditions:

1 g of GCM (particle size = 150 -250 µm) in 10mL of DI water at 90°C, 7 days

	GCM-1	GCM-2	GCM-3	GCM-4
B	113	3.1	109	0.5
Na	441	2.1	546	1.8
Si	2.2	2.2	0.8	1.1
K	1	3.6	1.3	2.7
Zn	0	0.05	0	0.5
Ag	0.02	0	0.02	0.2
I	97	0.2	0	0
Bi	0.09	0.01	0.05	0.17

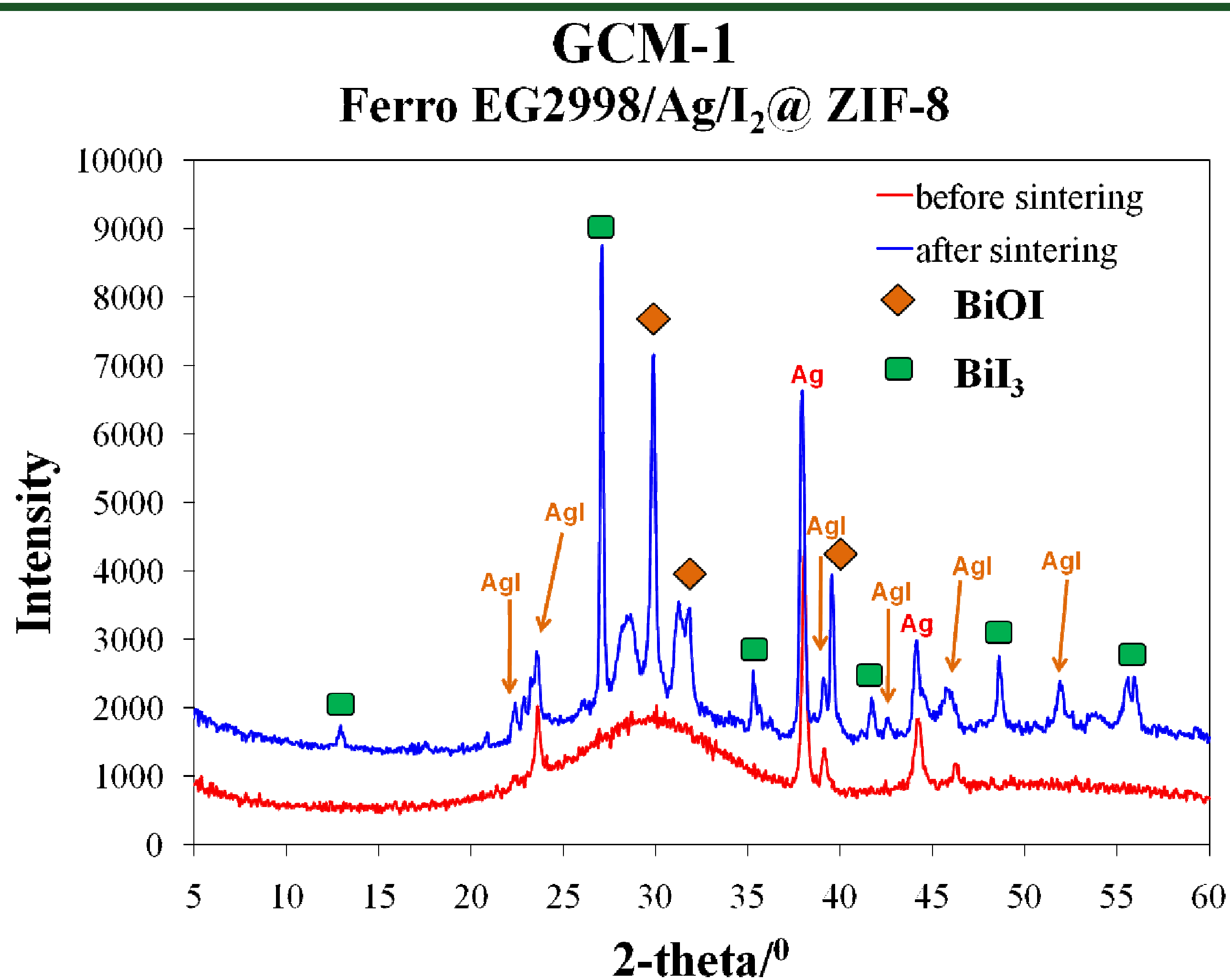




*ASTM Test Designation: C 1285 – 02, ASTM Int., West Conshohocken, PA, 2008

T.M.Nenoff, tmnenof@sandia.gov

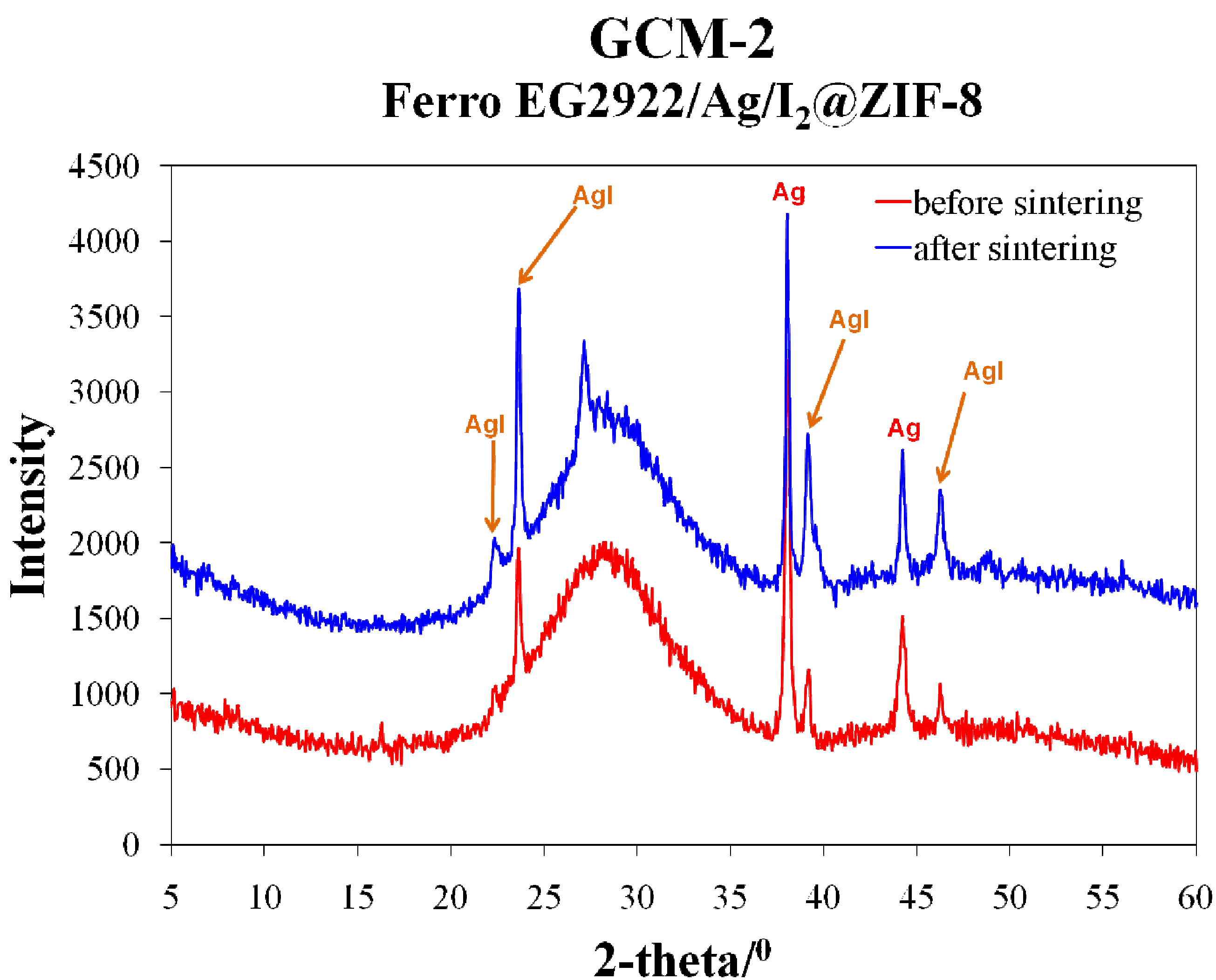
Powder X-ray Diffraction Pattern for GCM-1 Before and After Thermal Treatment (500°C)



BiI_3 is phase is soluble in warm water (90°C); decreasing the durability of waste form.

T.M.Nenoff, tmnenof@sandia.gov

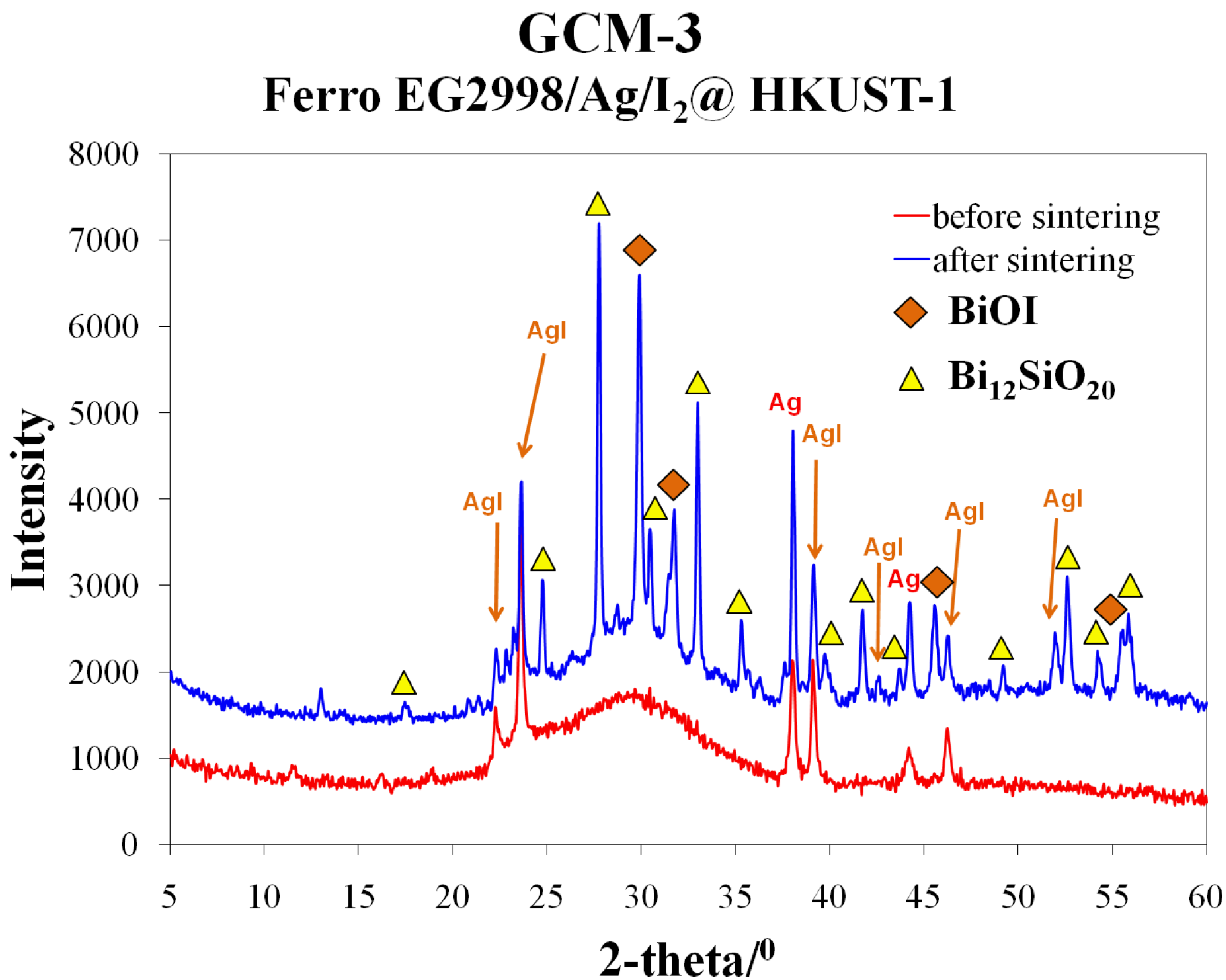
Powder X-ray Diffraction Pattern for GCM-2 Before and After Thermal Treatment (525°C)



No soluble iodine phases at 90°C

T.M.Nenoff, tmnenof@sandia.gov

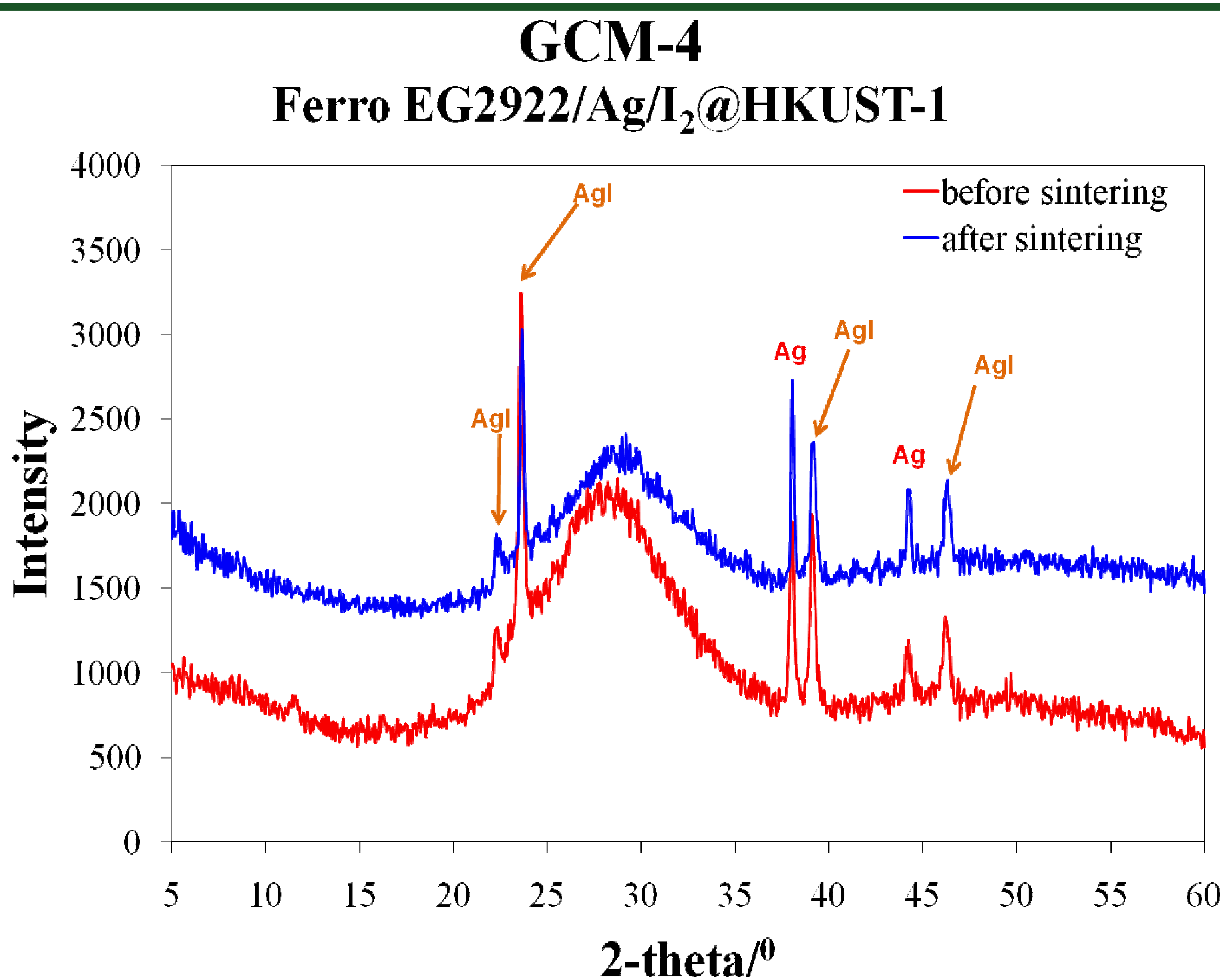
Powder X-ray Diffraction Pattern for GCM-3 Before and After Thermal Treatment (500°C)



No soluble iodine phases at 90°C

T.M.Nenoff, tmnenof@sandia.gov

Powder X-ray Diffraction Pattern for GCM-4 Before and After Thermal Treatment (525°C)



No soluble iodine phases at 90°C

T.M.Nenoff, tmnenof@sandia.gov

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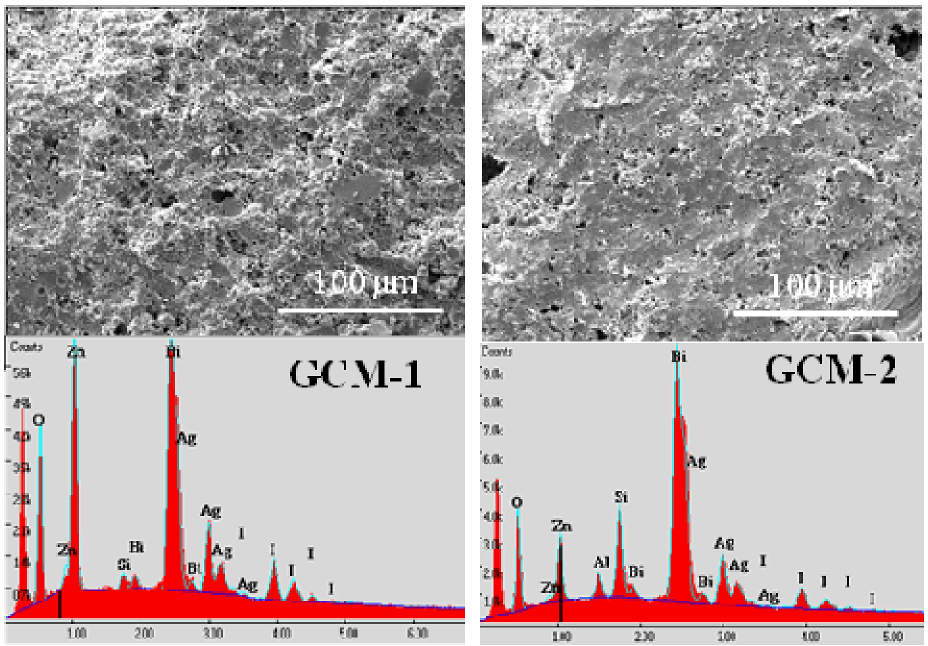
SEM-EDS Spectra of the Sintered GCM pellets (EDS at Full Field of View)

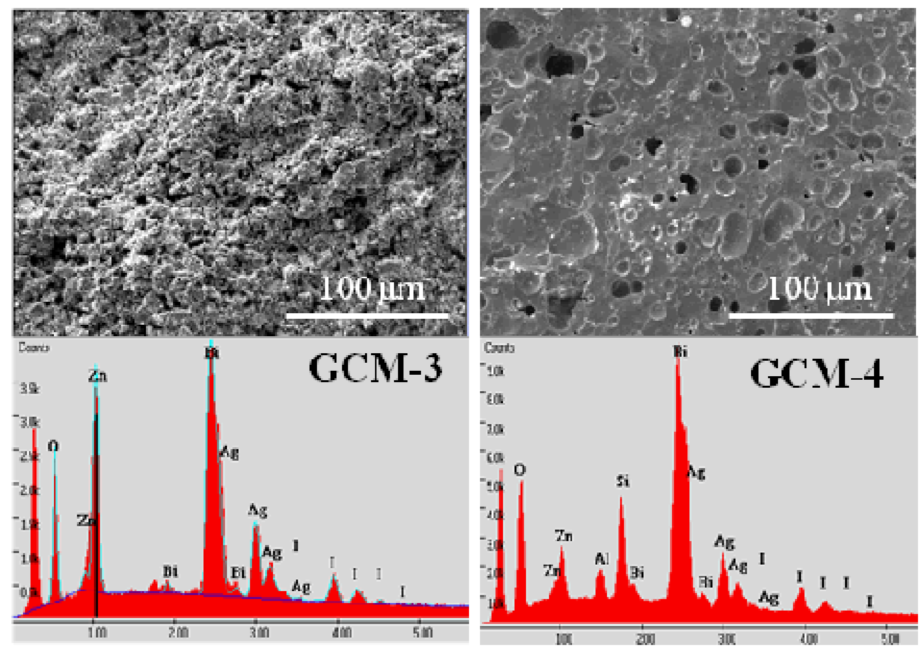


Crystalline Amorphous

ZIF-8

HKUST-1

Crystalline Amorphous



T.M.Nenoff, tmnenof@sandia.gov

Summary and Future Directions

Novel Glass-Composite-Materials (GCM) have been developed and characterized for long-term storage (for 1st time using MOFs as getter materials)

Improved low temperature glass composition

- slightly higher sintering temperature allowed for enhanced glass durability
- excellent processing ability in homogenous and core-shell waste forms
- high durability (PCT testing)
- high iodine retention in both MOF and MOR

Enhanced iodine retention in waste form production by addition of Ag powder; escaping iodine is captured to AgI

Enhanced glass durability with SiO_2 addition; matched thermal expansion

GCMs reveal excellent thermal and chemical stability; *no iodine is lost during processing or after undergoing leach durability studies*

Ongoing studies:

- Optimization of composition of GCMs
- Waste Form Studies for Getters used in Mixed Iodine Streams
- Comprehensive studies of GCMs under irradiating conditions

T.M.Nenoff, tmnenof@sandia.gov

Recent Project Publications

1. Chapman, K; Chupas, P.; Nenoff, T.M. "Radioactive Iodine Capture in Silver-Loaded Zeolites Through Nanoscale Silver Iodide Formation" *JACS*, **2010**, 132 (26), 8897–8899.

2. Krumhansl, J.L.; Nenoff, T. M. "Hydrotalcite-like Layered Bismuth-Iodine-Oxides as Waste Forms" *Applied Geochemistry*, **2011**, *26(1),* 57-64.

3. Garino T.J.; Nenoff, T.M.; Krumhansl, J.L.; Rademacher, D.X. "Development of Waste Forms for Radioactive Iodine", *Ceram. Trans.* **224,** 305-314.

4. Park, T-J.; Nenoff, T.M.; Garino, T.J.; Navrotsky, A. "The Effect of Vacancy and Ba-Substitution on the Stability of the $CsTiSi_2O_{6.5}$ Pollucite" *J. Amer. Ceram. Soc.* **2011**, in press; DOI: 10.1111/j.1551-2916.2011.04521.x.

5. Garino, T.J.; Nenoff, T.M. "Low-Temperature Sintering Bi-Si-Zn Oxide Glasses For Use in Either Glass Composite Materials or Core/Shell ^{129}I Waste Forms" *J. Amer. Ceram. Soc.* **2011**, in press; DOI: 10.1111/j.1551-2916.2011.04542.x.

6. Sava, D.F.; Garino, T.J.; Nenoff, T.M. "Iodine Confinement into Metal-Organic Frameworks (MOFs): Low Temperature Sintering Glasses to form Novel Glass Composite Material (GCM) Alternative Waste Forms", *Ind. Eng .Chem. Res*, **2011**in press**,** DOI: 10.1021/ie200248g. (Invited Paper)

7. Sava, D.F.; Chapman, K.; Chupas, P.; Rodriguez, M.; Nenoff, T.M. "Structure-Property Relationship of MOFs and Volatile Off-Gases", *JACS*, **2011,** submitted.

8. Zhao, H.; Chapman, K.; Chupas,P.; Nenoff,T.M. "Time-Resolved PDF Studies of Ag° Nanoparticles in Mordenite Zeolite", *Angew. Chem.*, **2011**, submitted.