SAND2011-0671 C
SAND2011-0671C

# Novel Materials Involved in Radiological Environments

Tina M. Nenoff
Sandia National Laboratories
Albuquerque, NM 87185 USA
www.sandia.gov/nenoff

India
February 2010

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



Sandia National Laboratories

# Team Members

**Nanoparticle LDRDs:**

Synthesis: Summer Ferreira, Zhenyuan (Mark) Zhang, Donald Hanson

TEM: Jianyu Huang, Paula Provencio

NP Sintering/ Heated Stage TEM: David Robinson, Benjamin Jacobs

Modeling: Kevin Leung, Veena Tikare

**Separations and Waste Forms for Radioactive Fission and Volatile Gas Products:**

Synthesis: Dorina Sava, Terry Garino, Jim Krumhansl

Neutron Diffraction: Hongwu Xu (LANL)

Synchrotron/PDF: Karena Chapman, Peter Chupas (ANL)

Calorimetry: Tae-Jin Park, Alexandra Navrotsky (UCDavis)

MAS NMR: Robert Maxwell, Harris Mason (LLNL)

Modeling: Weilin Jiang (PNNL)

# Nenoff Group Research Programs

Sponsors: SNL; LDRD

*** Room Temp Nanoparticles**

Radiolysis & interfacial studies of
Surface modification; NP sintering

DOE/NE-FCRD; NERI

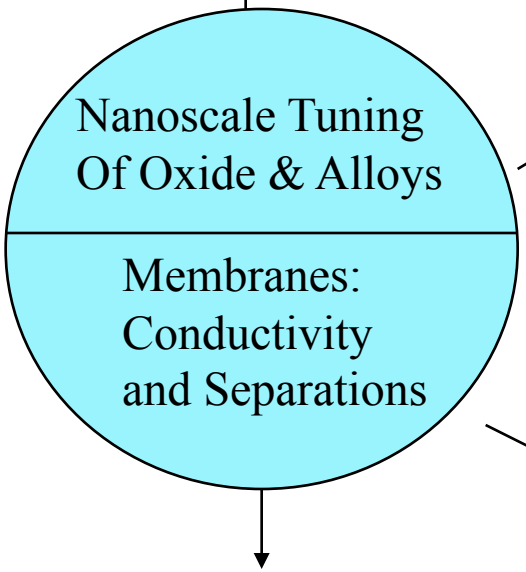
**Durability of Ceramic Waste Forms- Decay**

Material synthesis,
structure/property,
application, testing
UCDavis; PNNL

DOE/NE-FCRD

*** Iodine Gas Storage**

Separations and Waste Form
Ceramics & glasses,
MOFs - novel getters




Sponsor: DOE/NE-FCRD

**Nanofiber Ceramics Membranes**

Tunable nanoporous fiber
Ceramic membranes for
Volatile gas sorption

Sponsors: DOE/ITP

**$H_2$ Production from $H_2S$ & Low Value Streams**

Modified zeolite membranes,
Separations and Autothermal
Reforming
ExxonMobil, Praxair, UCin.

Sponsors: LDRD; DOE/$H_2$

**$H_2$ Purification From Biofuel & Reforming Streams**

Membranes (Modified Zeolites & Alloys)
Pure & mixed gases, variable temp/pressure

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# Accessibility to Novel Alloy Meta-Stable Phase Spaces

Use of Radiolysis to access new phase spaces of metals, binaries, alloys
experimentation at Room Temperature
room temp NP formation + sintering: fewer defects, wider composition range alloys

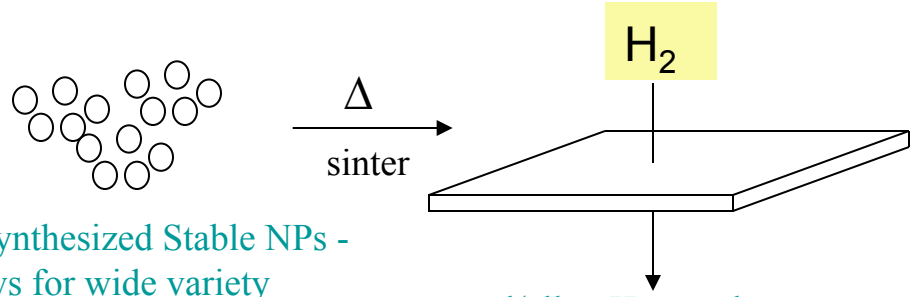
Radiolysis of aqueous solutions by γ-radiation:
production of oxidizing (OH°) and reducing ($e^-$ and H°) agents

By varying the dose rate, we vary the chemistry of nanoparticle growth in solution
Room temperature reactions & Universal Method

**Variety of high energy sources** to produce water radicals for NP chemistry.
Radiolysis is a room temperature method
to produce kinetically favorable, metastable alloy nanoparticles.

Sintered Materials for: $H_2$ membranes, gas turbine microengines, lightweight aircraft, etc.

***• State of the Art: Pd and Pd-alloys for durable $H_2$ dissociative membranes operate at high temperatures and are CO and Sulfur Tolerant***

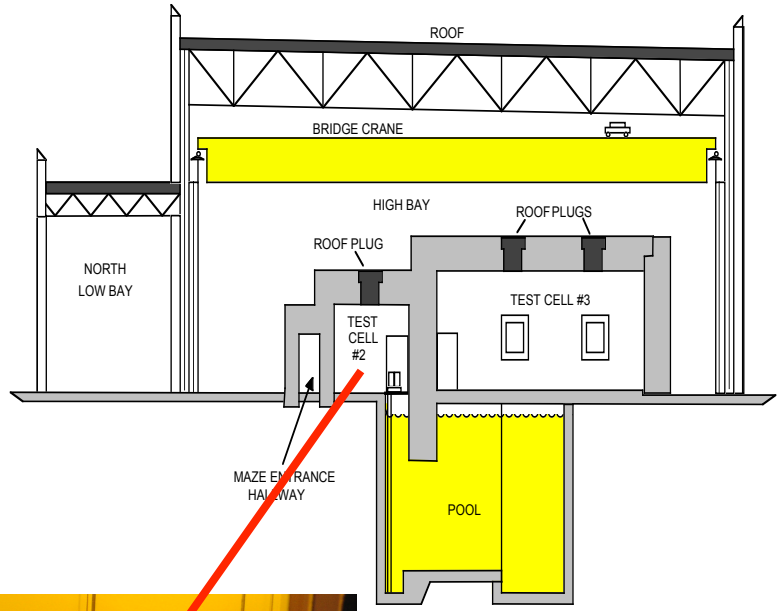


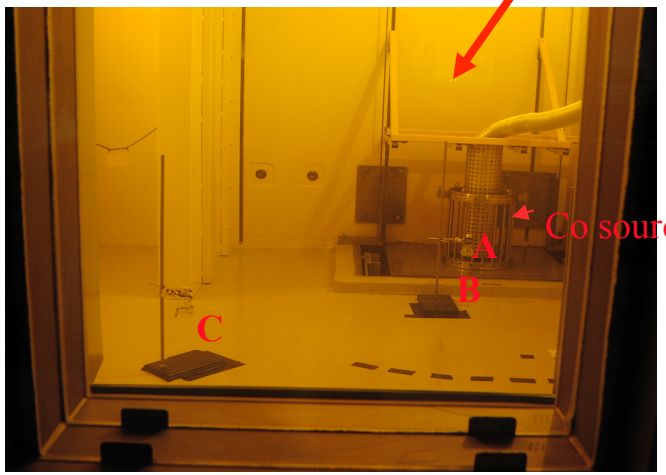

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# Room Temp Radiolysis : Common sources include UV-vis, gamma, X-ray

Sandia Gamma Irradiation Facility (GIF) is a
$^{60}$Co source : 1.345 x $10^5$ Ci, ≈ 300K rad/hr.



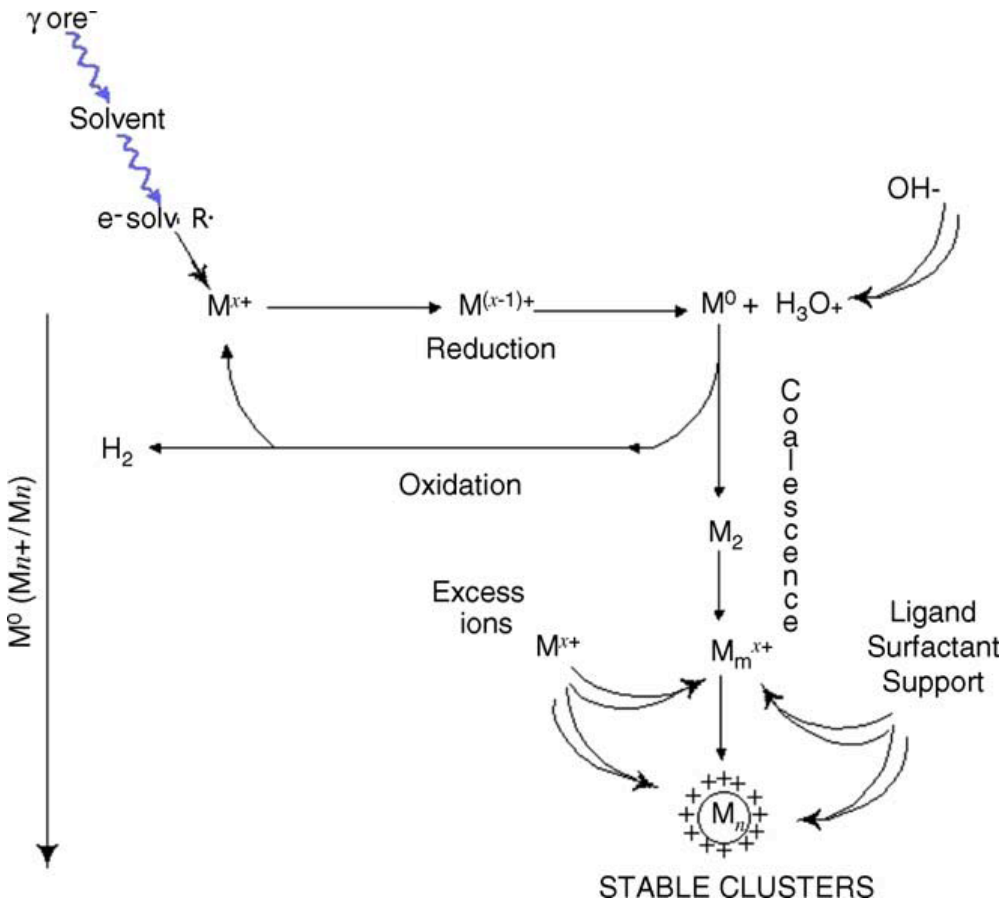




Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# Radiolysis for Nanoparticle Formation

**Metal Ion Reduction by Ionizing Radiation:**
**Dose Rate dictates [$e^-$] in reaction solution thereby affecting the chemistry of the NP formation**




Belloni, *Catalysis Today*, **2006**,*113*,141

**Tina M. Nenoff; tmnenof@sandia.gov**

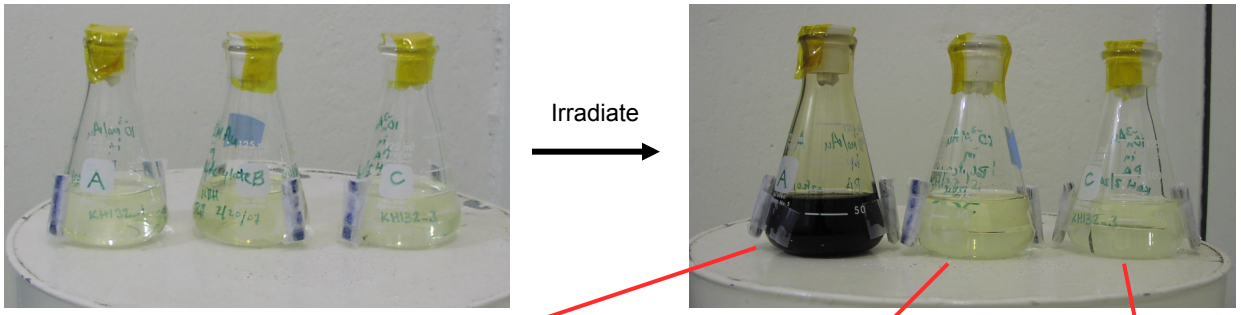
Sandia National Laboratories

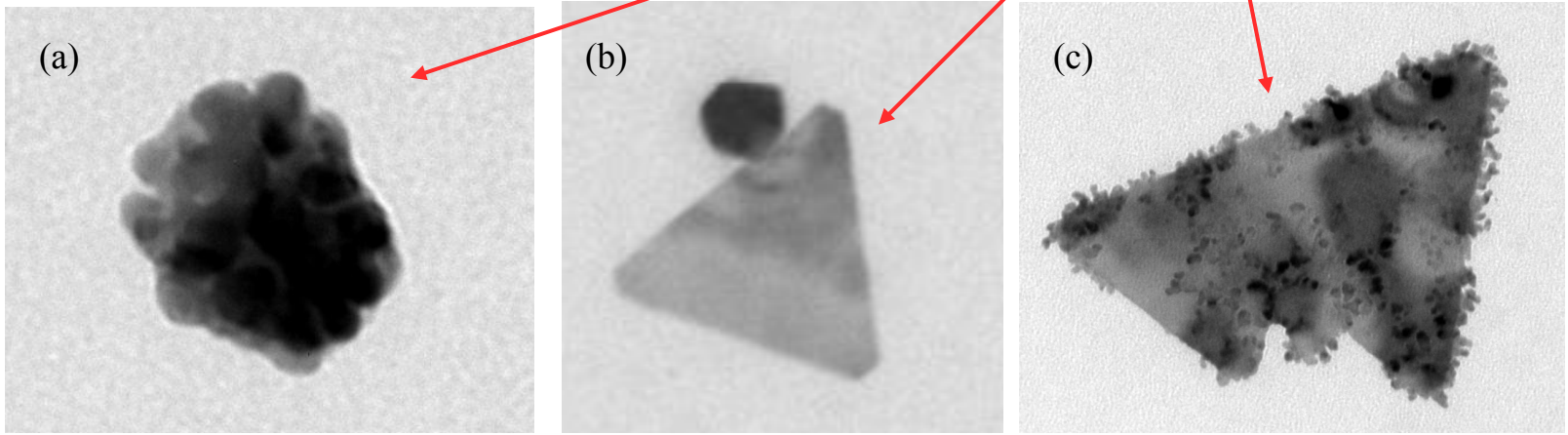
# Gold Nanoparticles: Morphology Determined by Low Dose Rate

*MRS Symp Proc. Volume 1043E, 2008.*

Reaction Conditions: 25ml solutions in 100ml vials
$HAuCl_4 \cdot 3H_2O$ (1000ppm Au in dilute HNO), poly(vinyl alcohol) (PVA, MW of 88000), DI $H_2O$
Purged solution with $N_2$, sealed and stored in dark
Exposed solutions to γ-irradiation; allowed to age and crystals to grow

(a) 770, (b) 72.3, (c) 7.07 rads/sec for 3 min dose (≈$10^3$ rad)



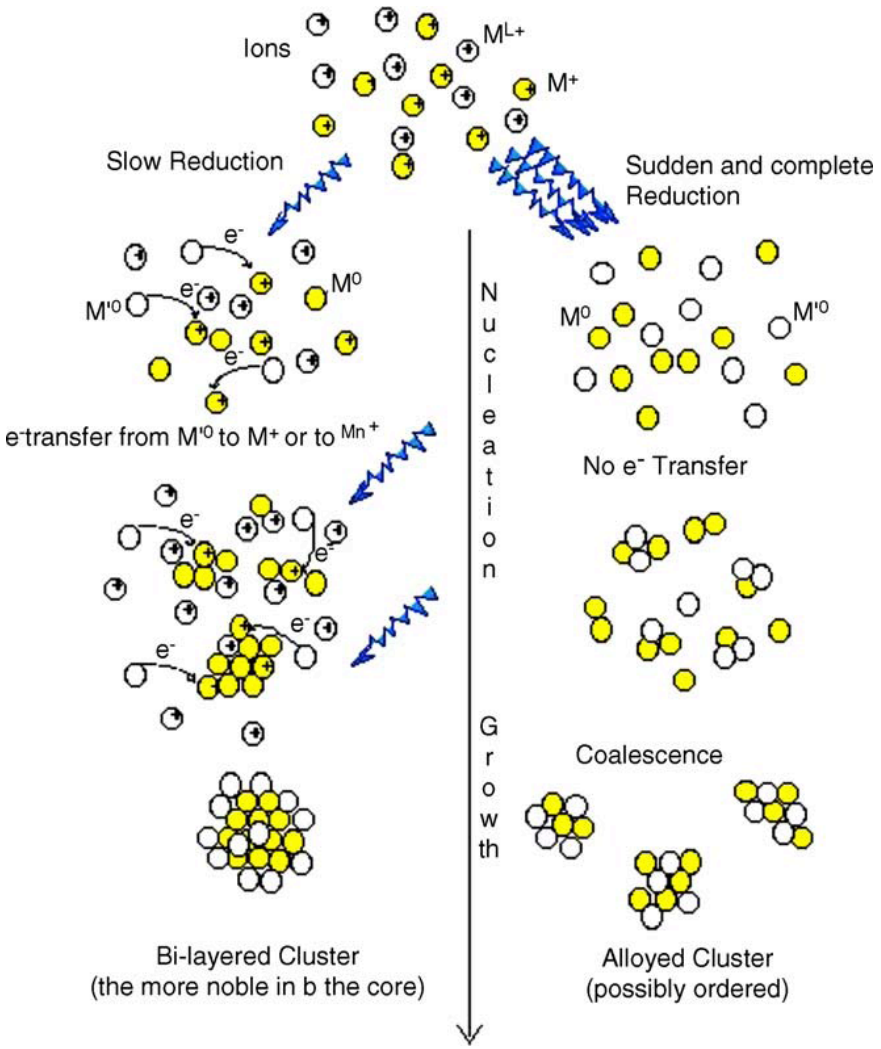




Tina M. Nenoff; tmnenof@sandia.gov

All **Gold Nanoparticle Clusters or single crystals** shown ≈ 30 nm in size

Sandia National Laboratories

# Methodology to Access Ni-based Alloy Phase Spaces




Belloni, *Catalysis Today*, **2006**,*113*,141

Alloys: Possibility to access different phase space than with traditional melting

Using high radiation dose and High dose rate, we will pursue nanoparticle alloy(s) formation

Dose ≈ $10^5$ rad
Dose Rate ≈ 75 rad/sec

**Tina M. Nenoff; tmnenof@sandia.gov**

Sandia National Laboratories

# Experimental Methods: Nanoparticle (NP) Synthesis & Analysis

## Experimental NP Synthesis:

Into 25ml solutions in 100ml vials add dilute metal salt solutions, alcohol (MeOH), organic polymer (PVA) and DI $H_2O$.

Purged solution with $N_2$, sealed and stored in dark

Exposed solutions to γ-irradiation; allowed to age and crystals to grow

## NP Analysis:

(1) UV-vis: Varian Cary 300 Scan UV-visible Spectrophotometer

(2) Transmission Electron Microscopy (TEM): JEOL 1200EX (120 kV) bright-field,

(3) High Resolution TEM and scanning TEM: FEI Tecnai G(2) F30 S-Twin (300 kV) TEM at Sandia's Center for Integrated Nanotechnologies (SNL CINT)

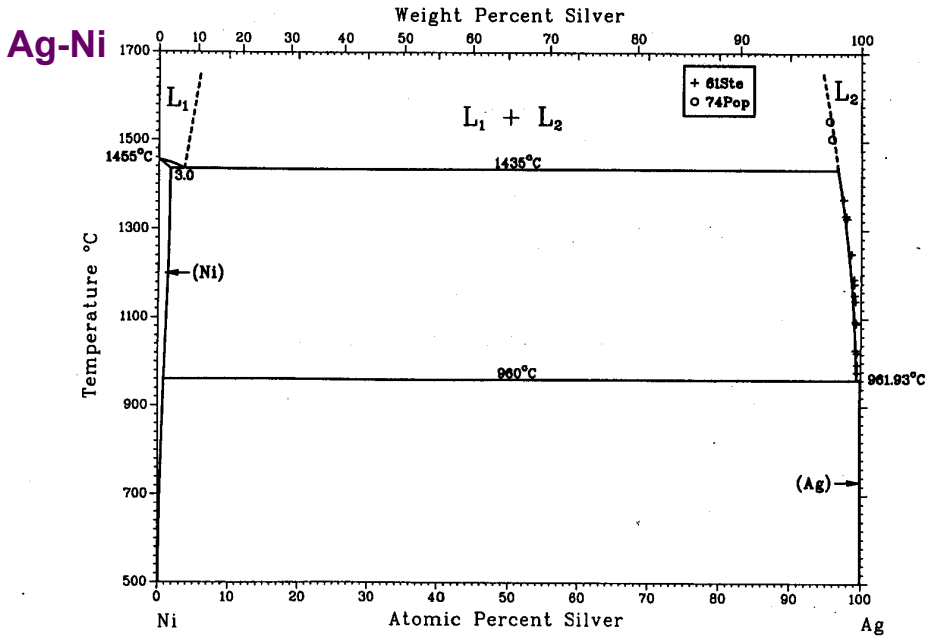
- 0.14 nm resolution in high-angle annular dark-field (HAADF) mode
- equipped with energy-dispersive X-ray (EDX) & electron energy-loss spectrometer (EELS)

(4) Aberration-corrected VG HB501 STEM and the TEAM microscope at the National Center for Electron Microscopy (NCEM), Lawrence Berkeley National Laboratory.

Tina M. Nenoff; tmnenof@sandia.gov

# Ag-Ni Alloy Particle Formation – Kinetically Driven Access to New Phases

Thermodynamic Phase Diagram




T. B. Massalski, *ASM International*, 2nd Ed., **1990**

High Dose Radiolysis: RT Kinetic Phase Growth

## Particle Formation via radiolysis (γ-irradiation)

$$\dot{O}H(\dot{H}) + e_{aq}^- + CH_3OH \longrightarrow e_{aq}^-/\ \dot{C}H_2OH + H_2O(H_2)$$

$$e_{aq}^-/\ \dot{C}H_2OH + Ag^+(Ni^{2+}) \longrightarrow Ag^0(Ni^0) + \dot{C}H_2OH$$

## Particle Growth

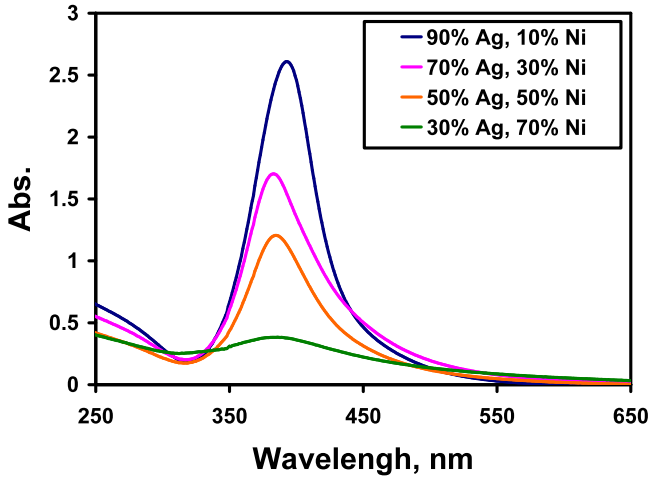
$$x\dot{C}H_2OH + (AgNi)_n \longrightarrow (AgNi)_n^{x-} + xCH_2O + xH^+$$

Tina M. Nenoff; tmnenof@sandia.gov

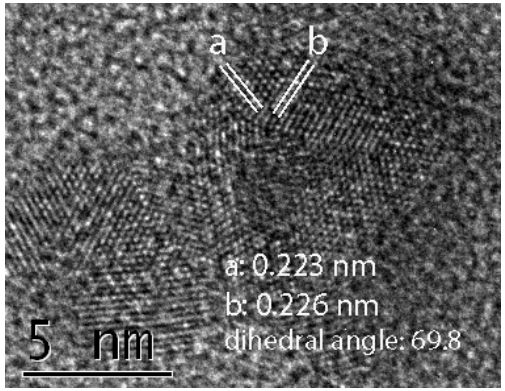
Sandia National Laboratories

# Ag-Ni Alloy NPs – Characterization

$AgClO_4$ and $NiSO_4$ are used to synthesize Ag-Ni particles by radiolysis (high dose rate, 300 rad/s).




Ag plasmon band dampens from $Ag_{0.9}$-$Ni_{0.1}$ to $Ag_{0.3}$-$Ni_{0.7}$




Lattice spacing of 50% Ag and 50% Ni may be present.
Theory: 0.220 nm

Different stoichiometries of $Ag^+$ and $Ni^{2+}$ used to prepare Ag-Ni alloy NPs

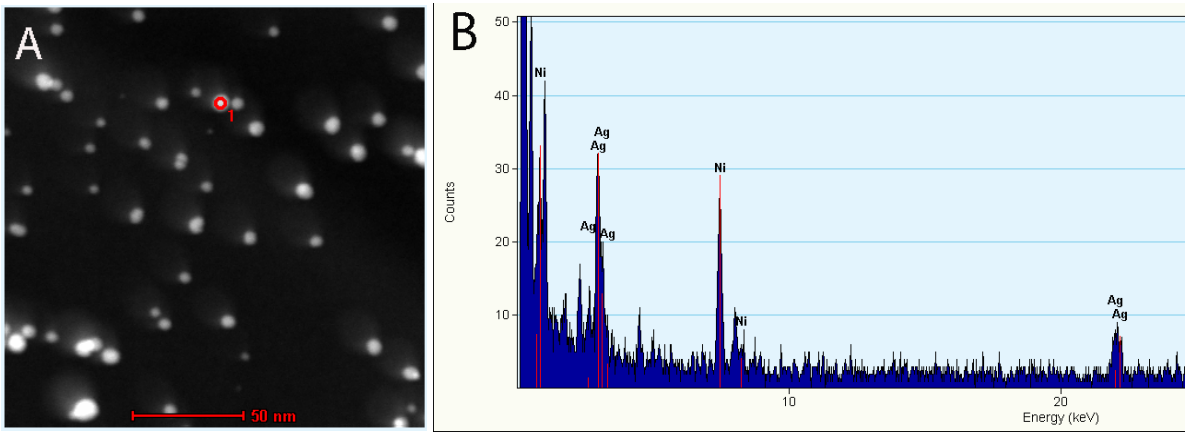
| | Ag | $Ag_{0.9}$-$Ni_{0.1}$ | $Ag_{0.7}$-$Ni_{0.3}$ | $Ag_{0.5}$-$Ni_{0.5}$ | $Ag_{0.3}$-$Ni_{0.7}$ | Ni |
|---|---|---|---|---|---|---|
| $[Ag^+]$, × $10^{-4}$ M | 2 | 1.8 | 1.4 | 1 | 0.6 | 0 |
| $[Ni^{2+}]$, × $10^{-4}$ M | 0 | 0.2 | 0.6 | 1 | 1.4 | 2 |
| $[Ag^+] + [Ni^{2+}]$, × $10^{-4}$ M | 2 | 2 | 2 | 2 | 2 | 2 |
| $[Ag^+]$:$[Ni^{2+}]$ | pure Ag NPs | 9:1 | 7:3 | 5:5 | 3:7 | pure Ni NPs |

Tina M. Nenoff; tmnenof@sandia.gov

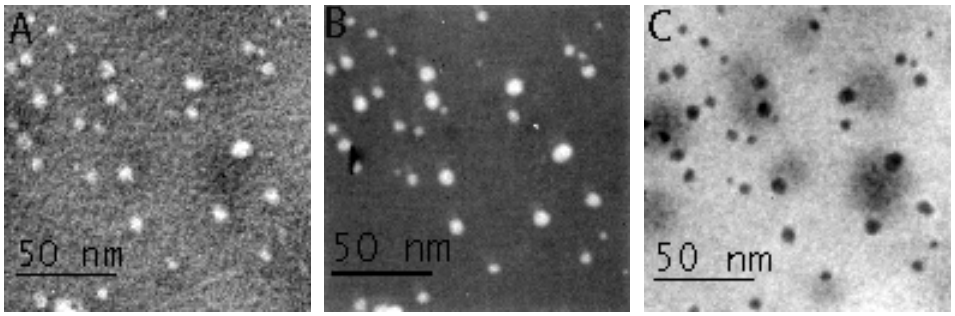
Sandia National Laboratories

# Ag-Ni Alloy NPs: Alloy Characterization

HAADF-STEM and single particle EDX images $Ag_{0.5}$-$Ni_{0.5}$ NPs




$Ag_{0.5}$-$Ni_{0.5}$ NPs




Ag map Ni map carbon map

*JPCC, 2010, 114,* 14309; *JPCC*, 2009, *113*, 1155; US Patent Tech Advance, 2008: SD10767

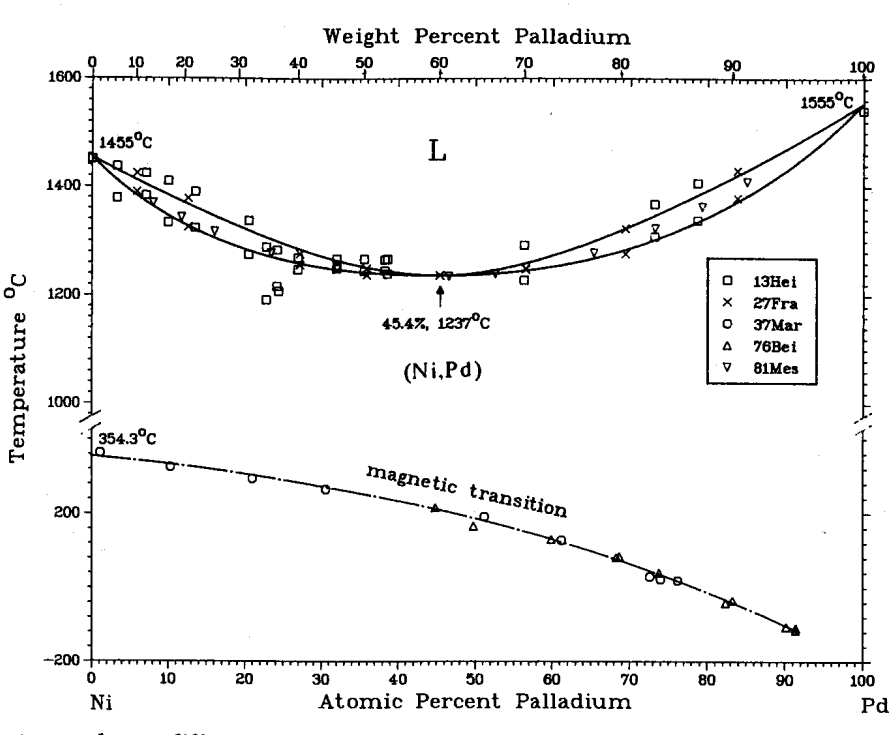
**Tina M. Nenoff; tmnenof@sandia.gov**

Sandia National Laboratories

# PdNi Alloy Nanoparticles

**Pd/Ni**

## PdNi NPs: 50% Ni, 50% Pd



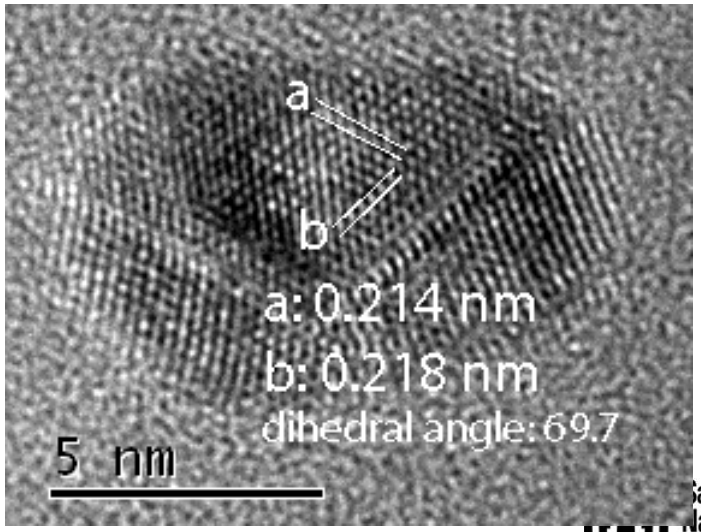

T. B. Massalski, *ASM International*, 2nd Ed., **1990**

- HRTEM (CINT): (twinned crystal)

Ni (111) = 0.203 nm, Pd (111) = 0.225 nm

Pd-Ni alloy based on 50% Ni = 0.214 nm

- STEM & EDX: Single particle data indicates homogenous composition of Pd & Ni; confirmed by EELS maps

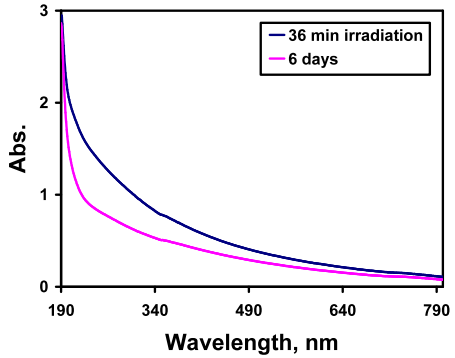


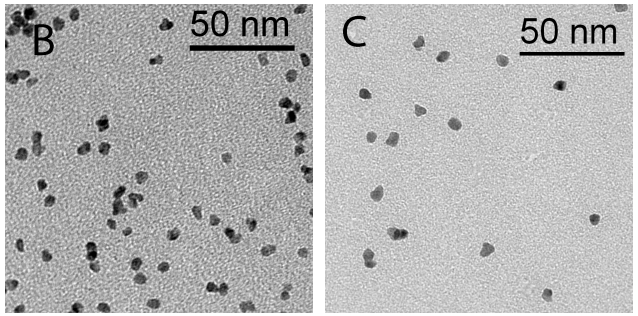

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

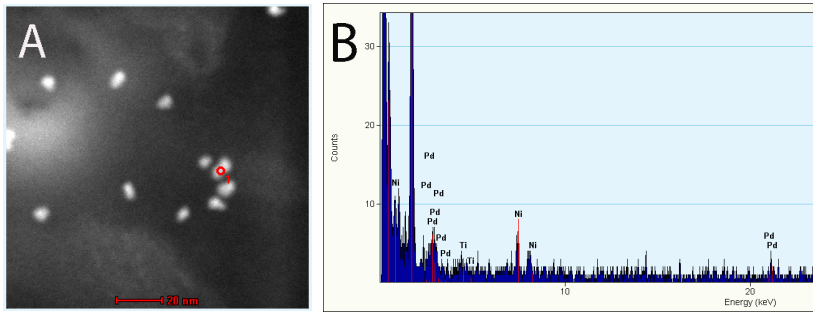
# Characterization of Pd-Ni Alloy NPs

$Pd(NH_3)_4Cl_2$ and $NiSO_4$ are used to synthesize $Pd_{0.5}$-$Ni_{0.5}$ particles by radiolysis (high dose rate, 300 rad/s)

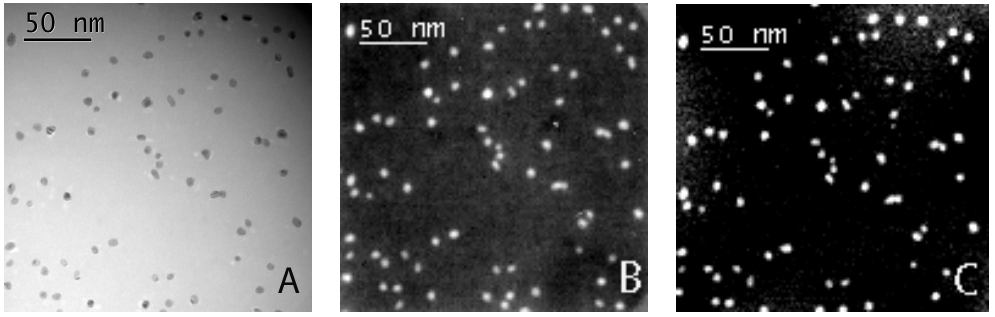



as-synthesized upon 6 days aging




HAADF-STEM and single particle EDX images




zero loss image Ni map Pd map

EFTEM maps

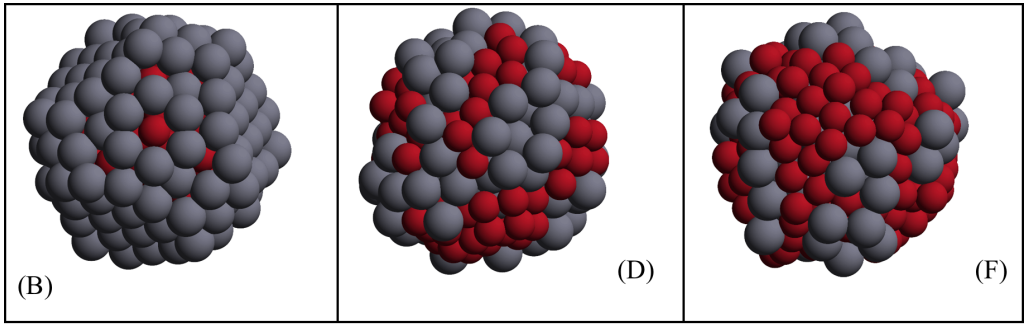
Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# Kinetically Driven Alloy Phase Formations – Confirmed with 1st Principles Modeling

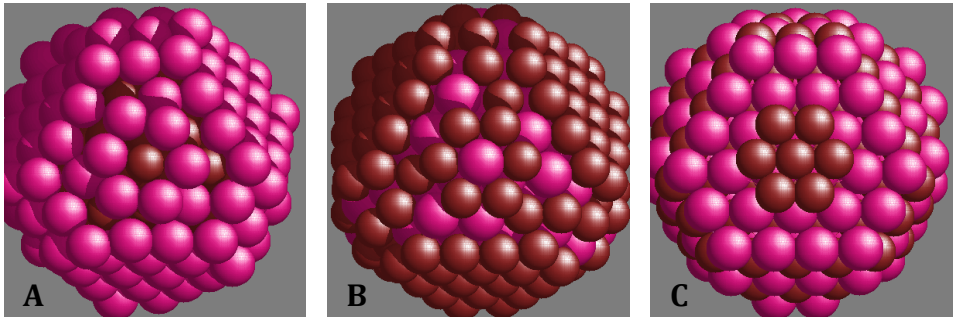
DFT Modeling using the VASP Code; FCC simulation using 240 atoms/NP

Optimized $Ni_{core}$-$Ag_{shell}$, alloy, $Ag_{core}$-$Ni_{shell}$




Potential Energy = 0eV, 43.7eV 57.2eV

Optimized $Ni_{core}$-$Pd_{shell}$, alloy, layered Ni-Pd




Potential Energy = 0eV, 16.6eV 16.7eV

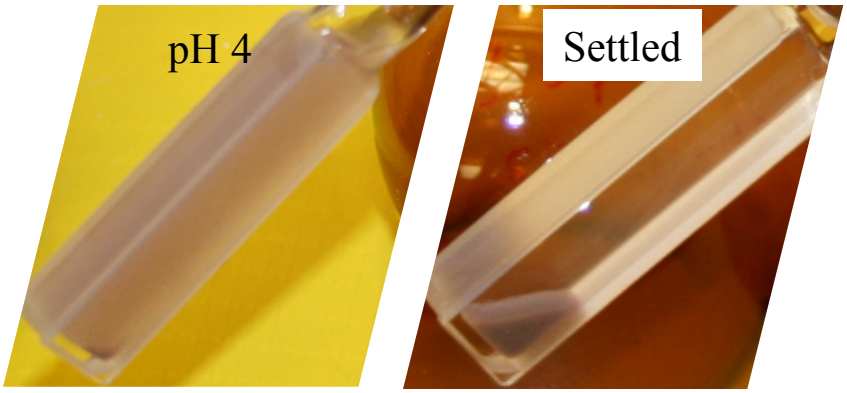
Tina M. Nenoff; tmnenof@sandia.gov

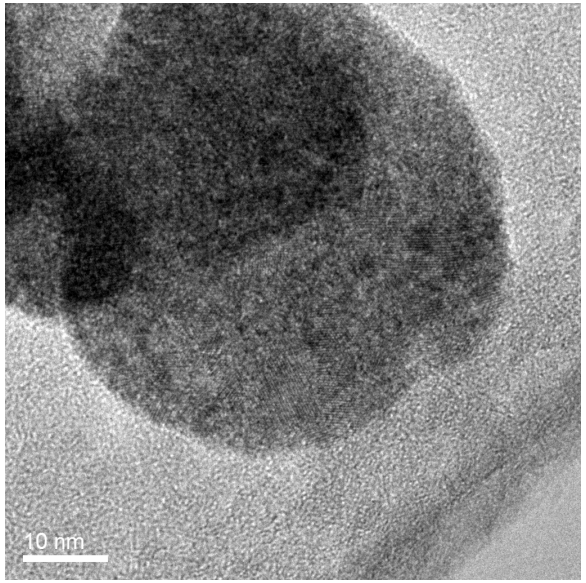
Sandia National Laboratories

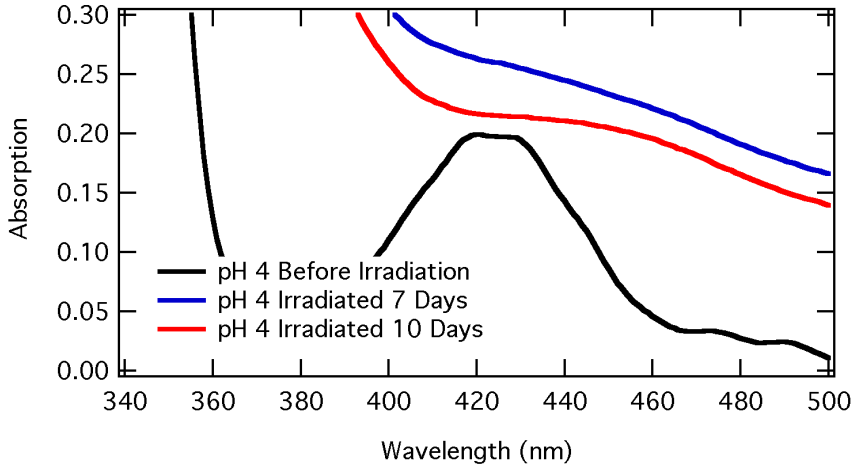
# Nuclear Fuel Surrogate Nanoparticles

- Radiolytic formation of actinide nanoparticles
- Novel approach for nuclear fuels synthesis
- NPs are formed at RT, reduced sintering temps
- Reducing defect formations in bulk metals
- Normal sintering of bulk at 1500-1700°C

Experimental:
Uranyl nitrate in aq. solution,
10% alcohol (IPA), deaerated
Irradiated: 5 rad/sec 7-10 days




Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# NP Sintering to High Densities

Sintering of NPs to high densities (>85%) also cannot be achieved using traditional sintering methods. Low temperature bulk processing is enabled by NP sintering.

The melting points of nanoparticles are greatly reduced as compared to bulk materials; sintering occurs at about two-thirds of suppressed melting temperatures, since the surfaces of nanoparticles have melting points that are lower than those of their cores.*

This work is performed on a heated-stage TEM to reveal sintering temperatures and mechanisms:

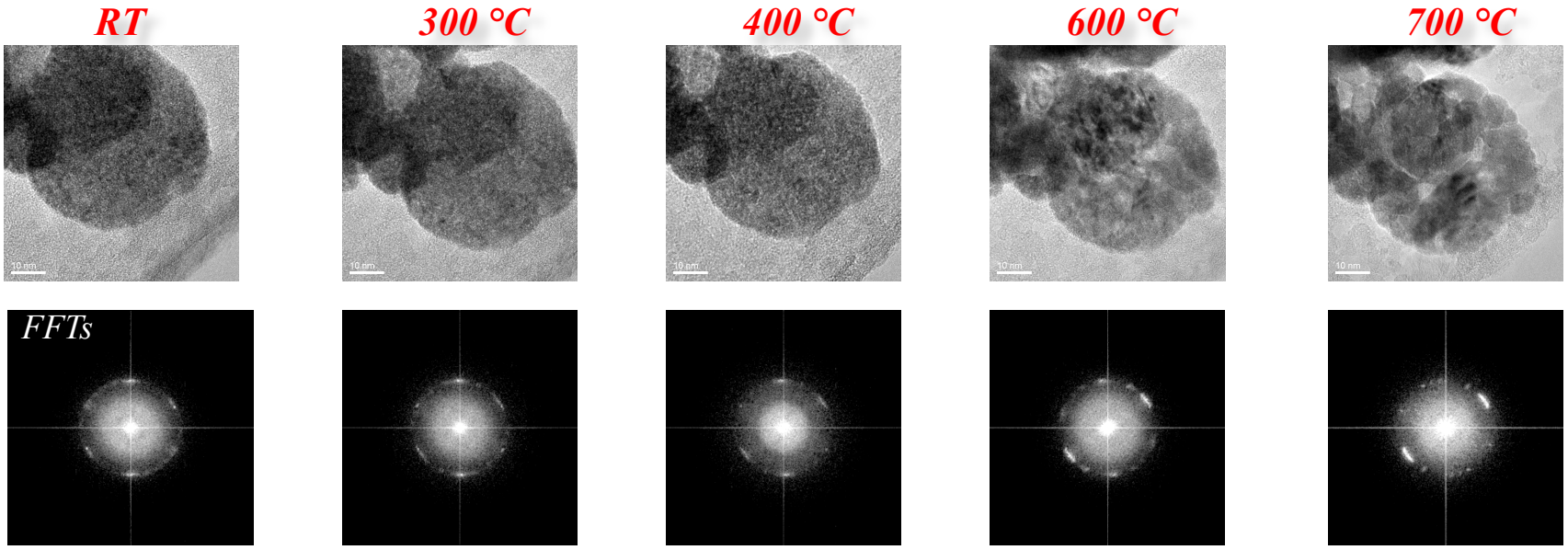
JEOL 2010F field emission electron microscope;
bright field imaging mode at 200kV
Gatan model 652 heating stage (range 25 – 800°C)

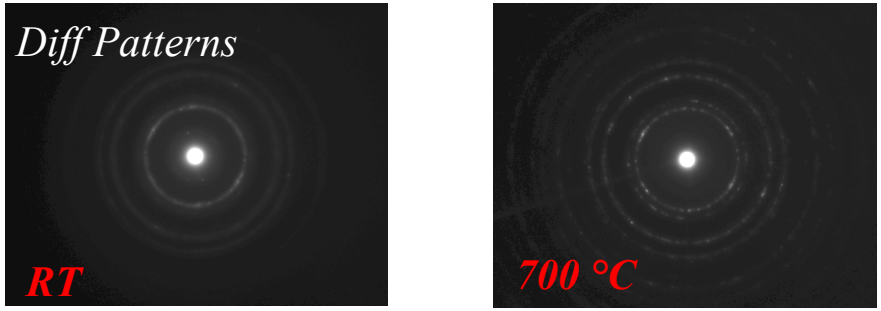
* *Nanostructured Mat.* 1999, *12*, 987; *Robinson, etal., SAND*2009-0218P

Tina M. Nenoff; tmnenof@sandia.gov

# Lowered Temperature for Sintering of d-$UO_2$ NPs:
## Dramatic decrease in sintering temp (< 600°C)

d-$UO_2$ NPs, Protochips Aduro holder, small scale ripening from RT-700°C




Diffraction Data in Angstroms

| RT | 700° C | Lit. Values $UO_2$ 41-1422 | Lit. Values $UO_2$ 36-89 |
|---|---|---|---|
| 6.51 | | | |
| 3.23 | 3.15 | 3.15 | 3.15 |
| 2.78 | 2.72 | 2.73 | 2.70 |
| 1.97 | 1.93 | 1.93 | 1.94 |
| 1.69 | 1.64 | | |
| | 1.58 | | |
| | 1.35 | | |
| | 1.24 | | |

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# NPs via Radiolysis Conclusion

- Room Temperature Radiolysis allows for access to new phase spaces (kinetically driven reactions)
- High dose rate, alloyed Ag-Ni & Pd-Ni NPs are formed. Rate overrides electrochemical or thermodynamic process, and competes with possible intermetallic electron transfer.
- No DeAlloying of NPs observed under heating in vacuum
- Low dose rate, but long irradiation time is needed for nanoparticle growth uranyl oxide NPs
- Sintering of alloy NPs of various compositions continues, from ≈ 5nm NPs to large / mesoscale bulk formation

New/On-going : Use of Radiolysis to produce Nuclear Fuel Surrogate Nanoparticles (NPs)

- Low Temp synthesis leads to no volatility of fuel components (eg. Am)
- Production of NPs for sintering (fewer defects than high temp melting procedures)
- Control of NP size and shape
- High reproducibility of product as pure/homogenous NP phases
- Inexpensive method to make research quantities of fuel surrogates for advanced materials studies and use in DOE/NE reactor concepts
- Combined effort for Structure/Property Relationships & Optimization: synthesis, characterization, modeling, irradiation & thermodynamics

Tina M. Nenoff; tmnenof@sandia.gov

# Separations and Storage Needs in Nuclear

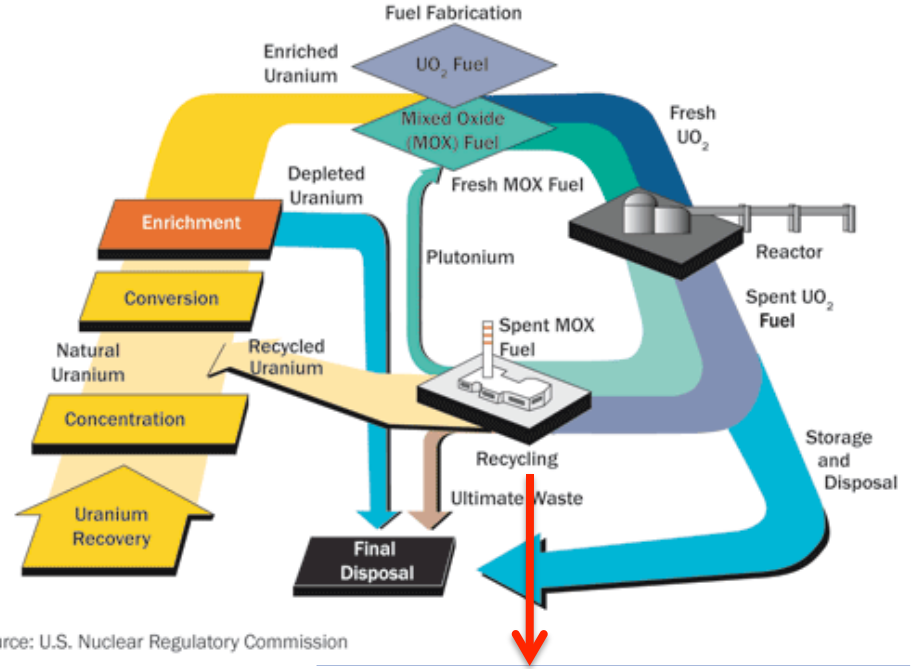
## I. Nuclear Waste Legacy

| | |
|---|---|
| Spent nuclear fuel (commercial) | 61,800 tHM<br>39,800 MCi |
| Spent nuclear fuel (weapons programs) | 2500 tHM |
| High-level waste (reprocessing) | 380,000 $m^3$<br>2400 MCi |
| Buried waste (low-level waste) | 6.2 x $10^6$ $m^3$<br>50 MCi |
| Excess nuclear materials: | |
| Highly enriched uranium | 174 t |
| Plutonium | |
| • weapons capable | 38.2 t |
| • not weapons usable without processing | 14.3 t |
| Depleted uranium as $UF_6$ | 700,000 t |
| $^{137}Cs$ and $^{90}Sr$ separated from high-level waste in capsules as CsCl and $SrF_2$ | 90 GCi |
| Uranium mine and mill tailings | 438 x $10^6$ $m^3$<br>3000 MCi |
| Contaminated soil | 30 to 80 x $10^6$ $m^3$ |
| Contaminated water | 1800 to 4700 x $10^6$ $m^3$ |

t = metric tonnes; tHM = metric tonnes of heavy metal; MCi = megaCuries

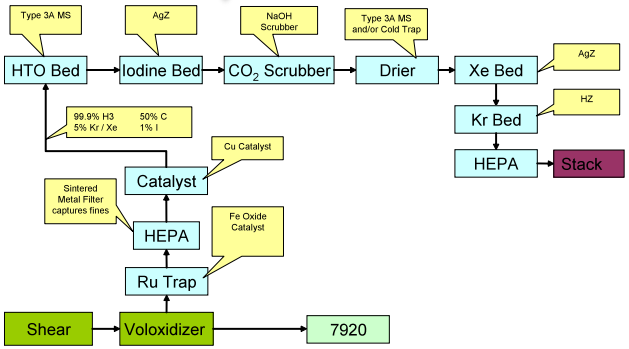
*Elements, Dec 2006*

## II. Nuclear Fuel Reprocessing




Source: U.S. Nuclear Regulatory Commission

Volox, Dissolution (post fuel crush, dissolving Hot $HNO_3$)
R. Jubin, ORNL




**Tina M. Nenoff; tmnenof@sandia.gov**

Sandia National Laboratories

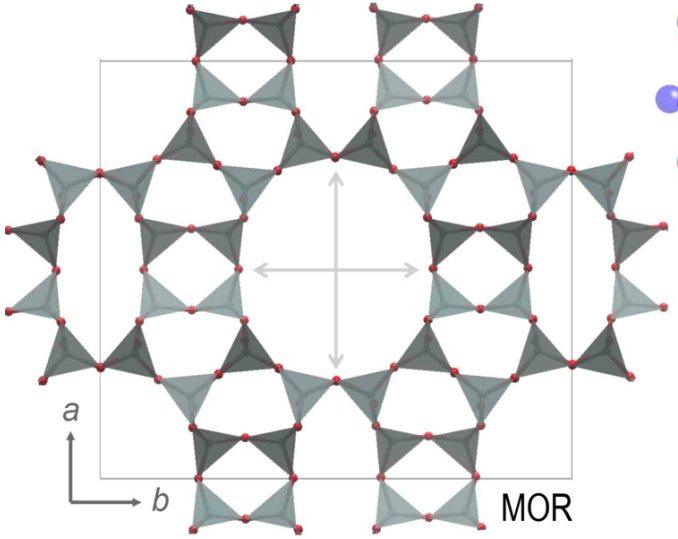
# Iodine in Spent Nuclear Fuel Reprocessing

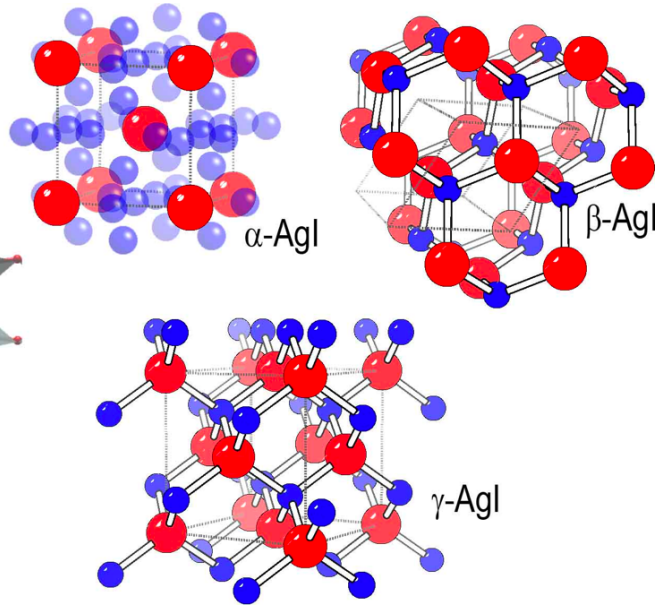
- While $I^{129}$ is only found in small concentrations in nuclear effluent, the effective capture and storage of iodine is critically important to public safety due to its involvement in human metabolic processes and its long half-life (~$10^7$ years).
- Silver Mordenite (MOR) is a standard iodine-getter,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

MOR, Mordenite

$X_2Al_2Si_{10}O_{24}$•$7(H_2O)$

12 MR, 7.0 x 6.5Å




Tina M. Nenoff; tmnenof@sandia.gov

# The Pair Distribution Function: 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)****.*

$$\boldsymbol{G(r)} = 4\pi r\,\rho_0[\boldsymbol{g(r)}-1] = (2/\pi)\int Q[\boldsymbol{S(Q)} - 1]\sin(Qr)\mathrm{d}Q$$

probability — structure factor

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

$$\boldsymbol{S(Q)} = 1 + [\boldsymbol{I^{coh}(Q)} - \sum c_i|f_i(Q)|^2]/\,|\sum c_i f_i(Q)|^2$$

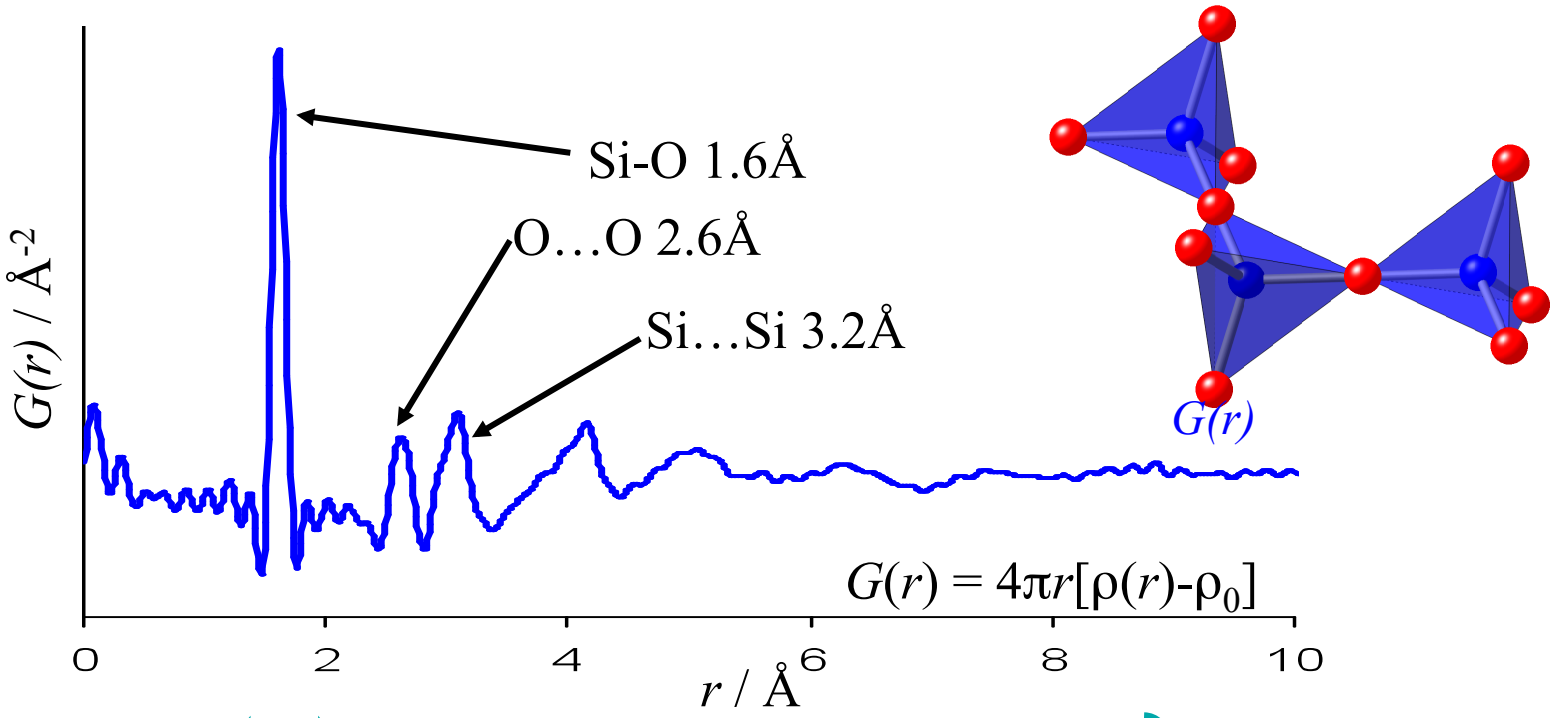
diffraction intensity (corrected)

Apply corrections for background, absorption, Compton & multiple scattering

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# A 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

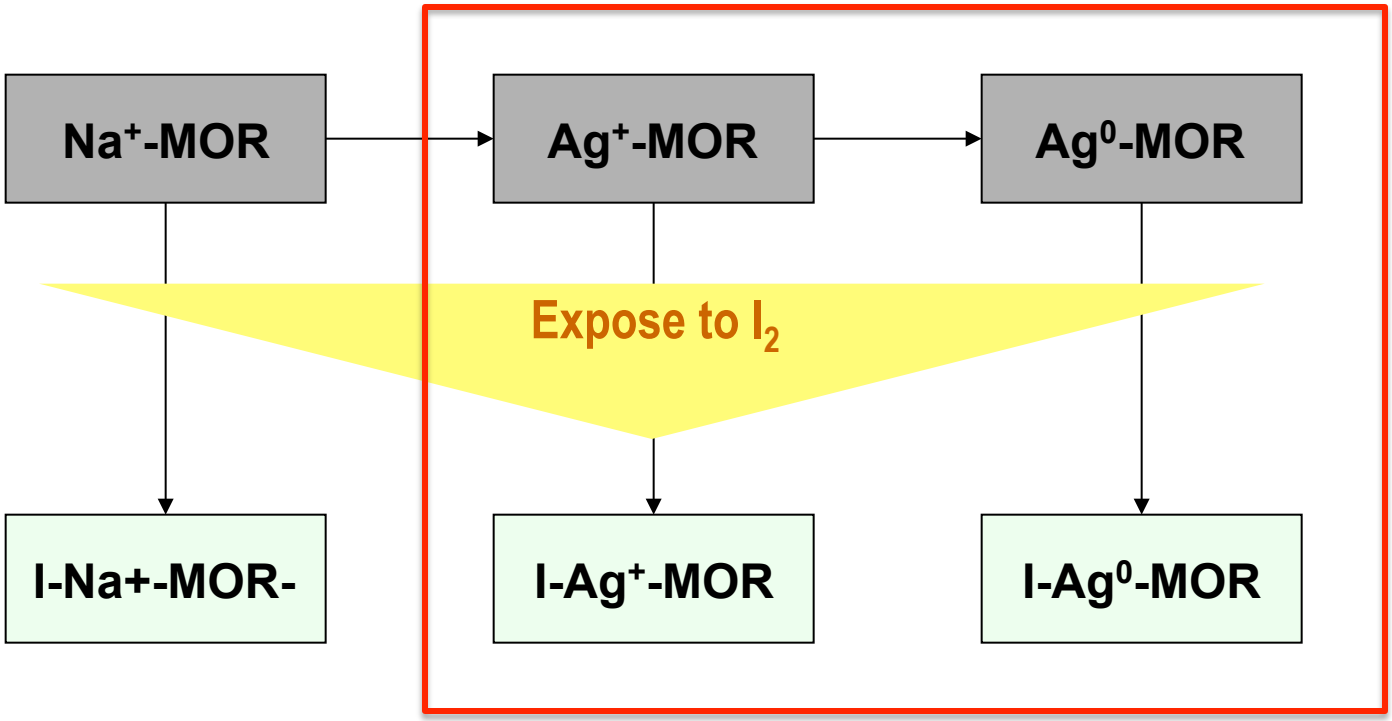
→ **Structural Modeling**

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# Samples Prepared and Analyzed by *d*-PDF

d-PDF: differential Pair Distribution Function

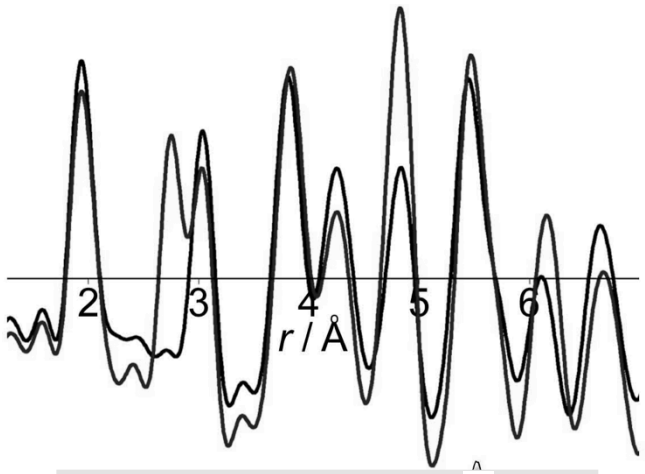



MOR Samples from UOP: LZM5

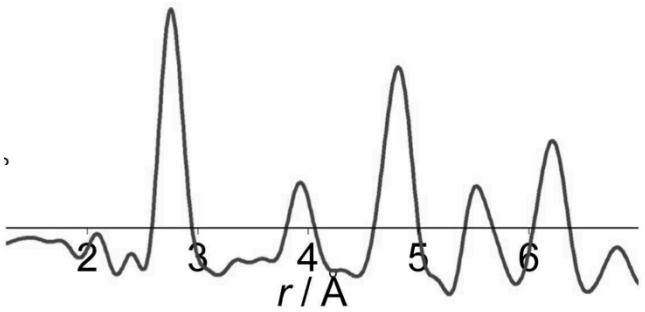
Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

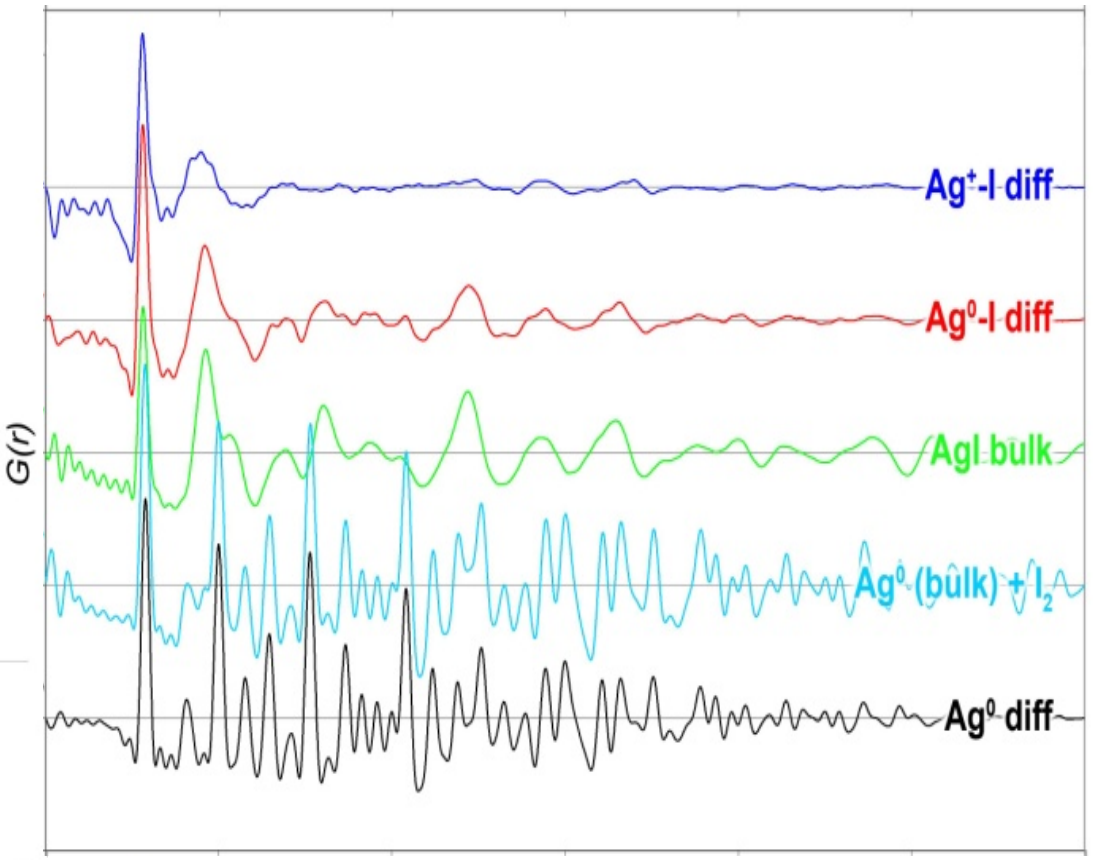
# Differential PDFs : Study of occluded AgI phases minus the MOR structural data




$$G(r)_{Ag\text{-}I\text{-}MOR} - G(r)_{Ag\text{-}MOR}$$




Differential PDF




Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

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

| | Form | *r*-range (Å) | $R_{fit}$ | Phase Composition[§] | | | |
|---|---|---|---|---|---|---|---|
| | | | | $Ag^0$ | $\alpha$-AgI | $\beta$-AgI | $\gamma$-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 | – | – | – |

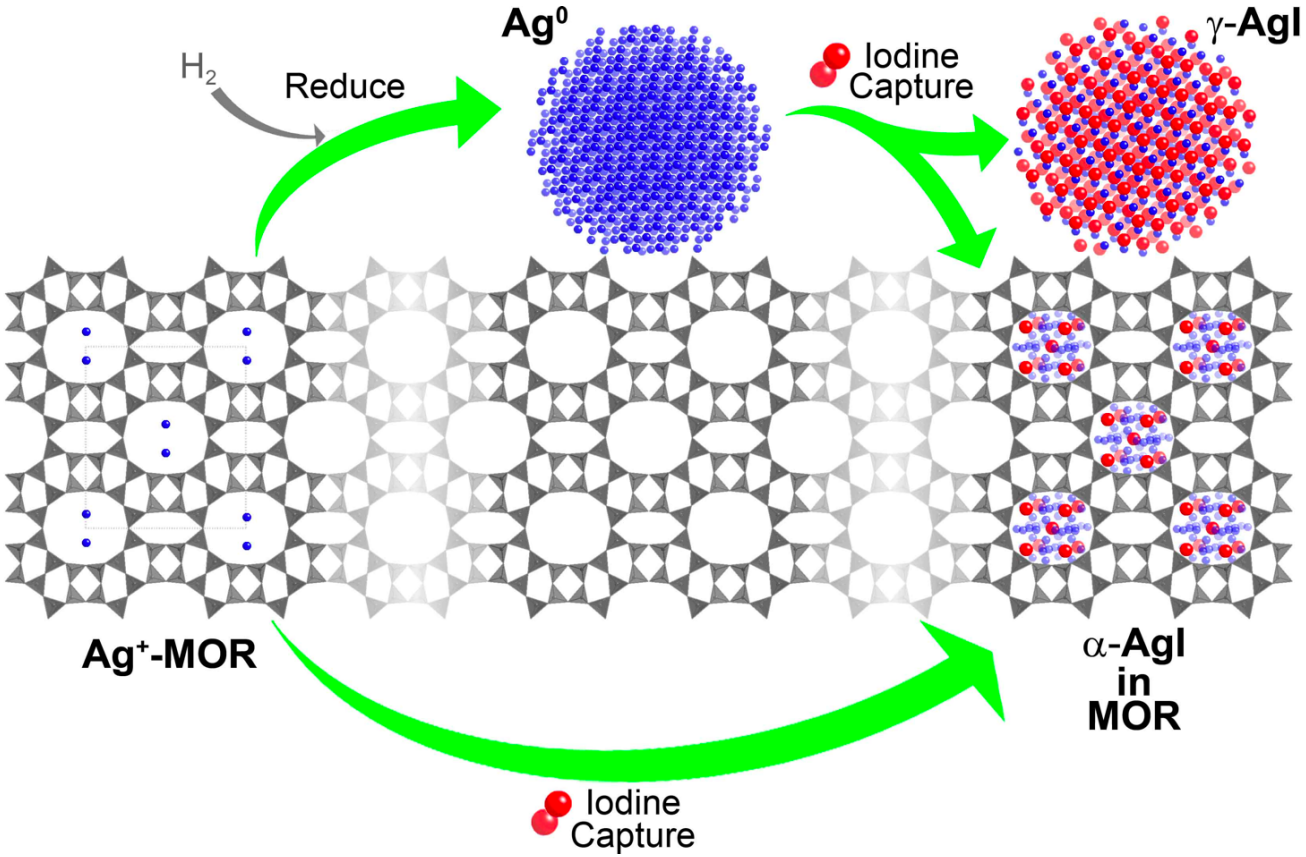
[§] $Ag^0$ (*Fm*-3*m*, $a = 4.08$ Å); $\alpha$-AgI (*Im*-3*m*, $a = 5.0$ Å, $r < 7$ Å); $\beta$-AgI ($P6_3mc$, $a = 4.6$ Å, $c = 7.8$ Å, wurtzite structure); $\gamma$-AgI (*F*-43*m*, $a = 6.5$ Å, zinc blende structure).

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# A Molecular Scale Illustration of Iodine Capture by Silver-Loaded MOR

*JACS, 2010, 132 (26), 8897*



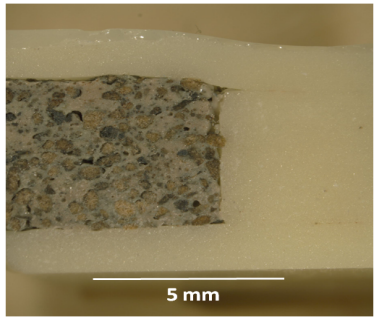

Ag°-MOR + $I_2$ yields a mixture of γ-AgI bulk surface nanoparticles and sub-nanometer α-AgI.
$Ag^+$-MOR + $I_2$ produces exclusively sub-nanometer α-AgI ("**perfect fit**", confined in pores)

Tina M. Nenoff; tmnenof@sandia.gov

# Durable Waste Forms: Incorporation of Ag-I-Zeolite

## EXAMPLES Include:

Homogenous Glass Waste Form
Contains: 50 wt% AgI/50 wt% BiZnB
500˚C for 3 hr
(Garino, et. al., Ceramic Transactions, **2010**, 224, in press)




Core-Shell Waste Form:
Glass shell (BiZnSi)
AgI-MOR/Ag/Glass core 80/20/5
(Garino, et. al., JACerS, 2010, submitted)

Room Temperature Silicogeopolymer
Waste Form containing
AgI-Zeolite particles
(Nenoff, etal., GNEP-WAST-PMO-MI-DV-2008-000149 )

**High Success Probability** by
Leveraging DOE/NE-SWG
Iodine program successes

1-step Separations & Waste Form
- No secondary waste
- Phase compatible
- Temperature compatible

Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# 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 $^{129}I$

Tina M. Nenoff; tmnenof@sandia.gov

# Acknowledgement

This work was supported in part by the Laboratory Directed Research and Development (LDRD) program of Sandia National Laboratories.

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

This project is partially funded under the US DOE/NE-FCR&D Separations and Waste Form Campaign.

Work performed at Argonne and use of the Advanced Photon Source were supported by the U.S. DOE, Office of Science, BES, under Contract No. DEAC02-06CH11357.

Tina M. Nenoff; tmnenof@sandia.gov

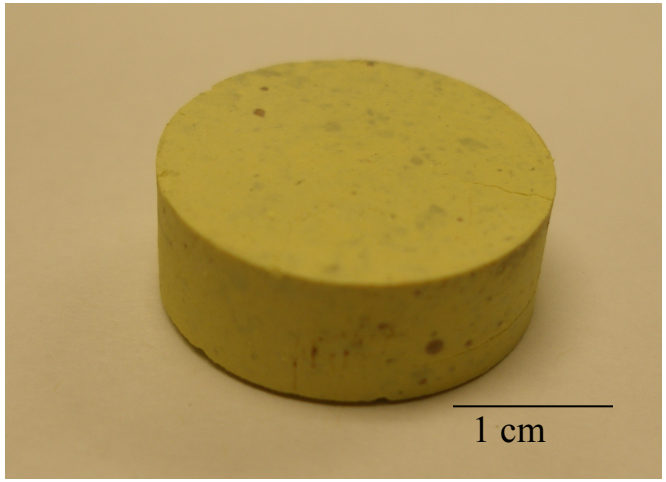
Sandia National Laboratories

# Low Temperature Glass Formation with either AgI or AgI-Mordenite Zeolite

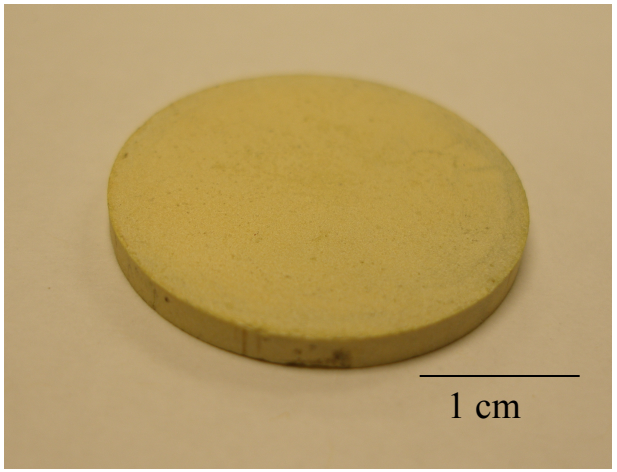
Nenoff, et.al, 2 US Patents Submitted, 2009 & 2010.

- Non-radioactive iodine was used.
- Initial Materials Studies; NON-OPTIMIZED FORMULATIONS
- AgI-MOR was ground to -400 mesh (<37 μm)
- AgI powder or ground AgI-MOR powder was mixed with Glass A powder
- Pellets (3.2 cm in diameter) were pressed without binder
- Pellets were heated in air at 5˚C/min to 500˚C for 1 to 3 hr

After heating to 500°C, the pellets were dense and crack-free.




*20 wt% AgI- MOR/80 wt% Glass A*
*500˚C for 1 hr*

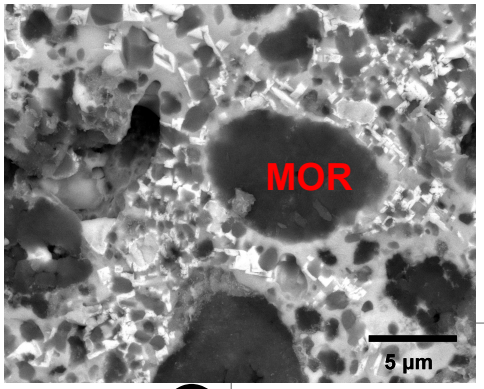



*50 wt% AgI/50 wt% Glass A*
*500˚C for 3 hr*

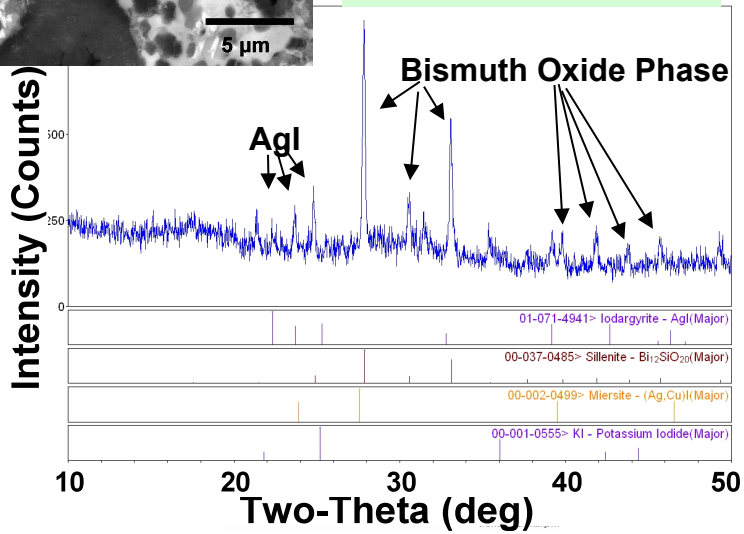
Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# Analysis of Formed Glass Encapsulants

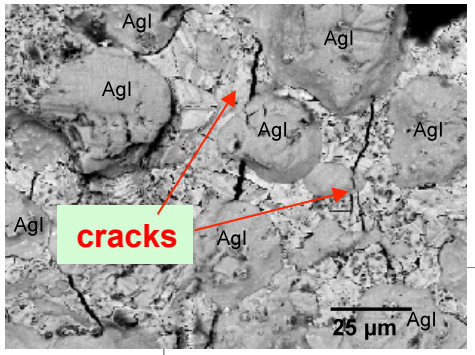



20 wt% AgI- MOR/80 wt% Glass A, 500˚C for 1 hr; dense pellets

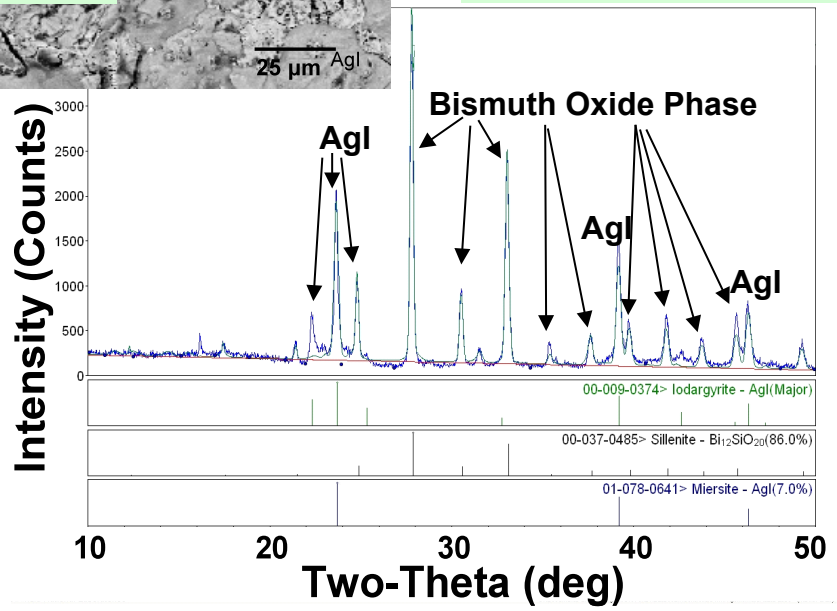



The remnants of MOR particles were no longer crystalline but were surrounded by crystallized Glass A.

The AgI was not located only in the MOR regions.




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




The AgI particles are surrounded by a crystalline matrix

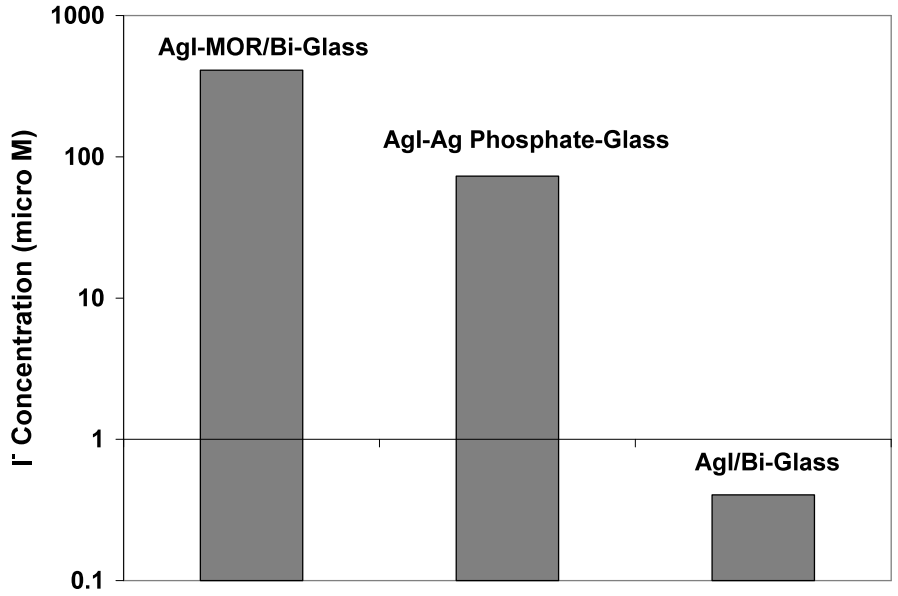
Cracks in the Glass - phase are most likely due to mismatch is thermal expansion coefficients.

No cracks propagating through the glass.

# Analytical Studies on Glass Encapsulant plus AgI or AgI-MOR

Thermogravimetric analysis of sintered samples indicated stability to > 700˚C.
On-going studies to determine max weight loadings and durabilities of waste forms

PCT (Product Consistency Test, ASTM Designation: C 1285 – 02)
Test performed on crushed material: 90˚C for 1 week.



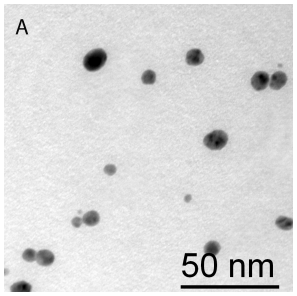

Particle size studies needed! Enhanced solubility of MOR in glass for optimized chemical and physical encapsulation in waste form.

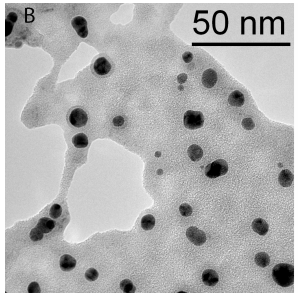
Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories

# Ag-Ni Alloy NPs – TEM Images

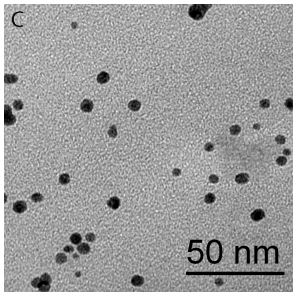
pure Ag
8.5 nm

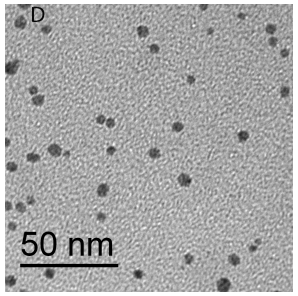



$Ag_{0.9}$-$Ni_{0.1}$
7.4 nm

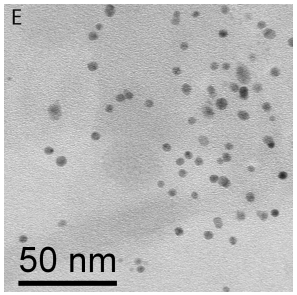
$Ag_{0.7}$-$Ni_{0.3}$
5.7 nm

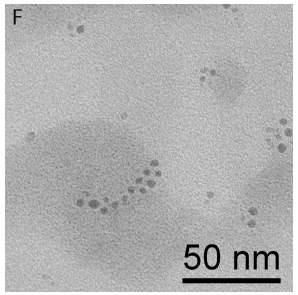



$Ag_{0.5}$-$Ni_{0.5}$
5.4 nm

$Ag_{0.3}$-$Ni_{0.7}$
4.0 nm



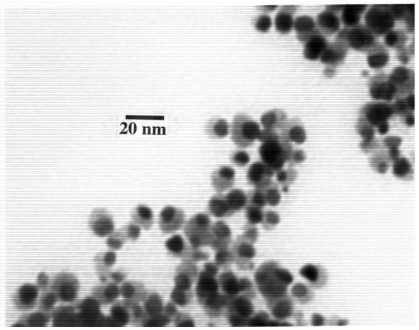




pure Ni
3.4 nm

The size of Ag-Ni NPs is decreased with higher Ni ratio

Particle size in diameter and size distribution of Ag, Ag-Ni, and Ni NPs

| | Ag | $Ag_{0.9}$-$Ni_{0.1}$ | $Ag_{0.7}$-$Ni_{0.3}$ | $Ag_{0.5}$-$Ni_{0.5}$ | $Ag_{0.3}$-$Ni_{0.7}$ | Ni |
|---|---|---|---|---|---|---|
| size in diameter, nm | 8.5 | 7.4 | 5.7 | 5.4 | 4.0 | 3.4 |
| size distribution | 24% | 24% | 20% | 15% | 18% | 19% |




Pt core-Ag shell NPs.

*(Zhang, Meisel, Univ. Notre Dame, unpublished)*

**Tina M. Nenoff; tmnenof@sandia.gov**

Sandia National Laboratories

# *d*-PDF Sample Preparations for (Silver/ Iodine) - Mordenite Studies

Experimental Section:

Starting material: sodium MOR (LZM-5Na, UOP Corporation)
$Ag^{+}$-MOR: Na-MOR ion exchanged with $AgNO_3$
Ag°-MOR: reduced under $H_2$ (3%, 150°C, 24hrs)
$I_2$ loading: 95°C, 12 hrs
Bulk AgI: purchased from Sigma-Aldrich

Data Analysis Section:

- Powder X-ray Diffraction analysis: APS beamline 1-BM ($\lambda = 0.61518$Å)
- PDF analysis: ANL/APS beamline 11-ID-B
  high energy X-rays ($\lambda = 0.1370$Å) used in combination with a large amorphous-silicon-based area detector
  collected data to high values of momentum transfer ($Q_{max} \approx 19$ Å$^{-1}$)
- *d*-PDFs direct subtraction of PDF measured for $Ag^{+}$-MOR from the reduced and $I_2$-treated systems
- Fitting of the data and calculation of partial pair contributions within $PDF_{fit}$ and $PDF_{gui}$

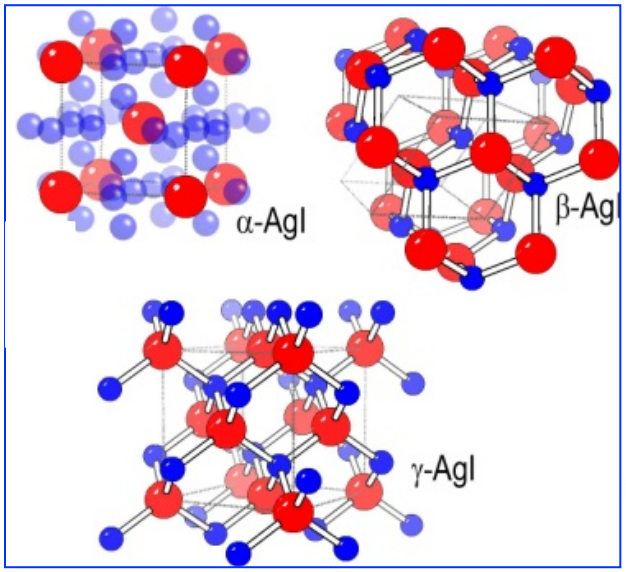
Tina M. Nenoff; tmnenof@sandia.gov

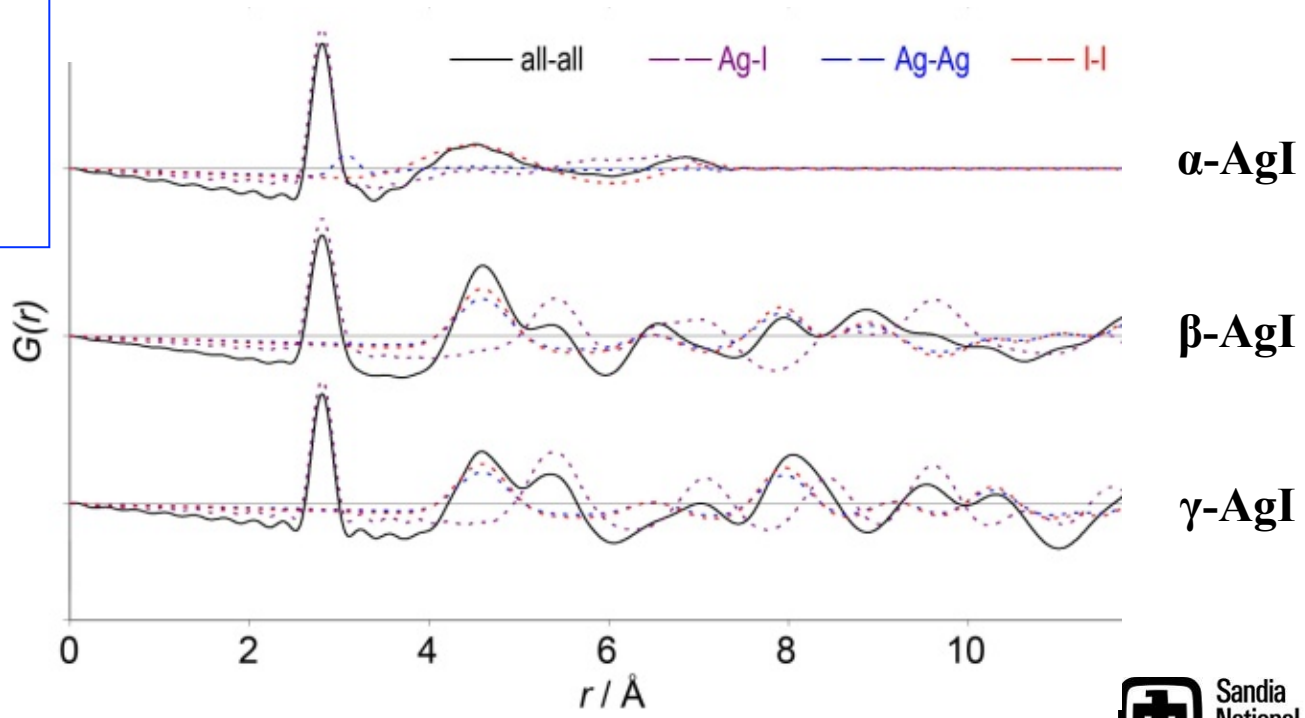


Sandia National Laboratories

# Different AgI phases Identified in Ag-I-MOR:

## Dependent Upon Synthesis Procedure




Tina M. Nenoff; tmnenof@sandia.gov

Sandia National Laboratories