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Fuel Cycle Research and Development

Inorganic Oxide Waste Forms for Iodine Storage

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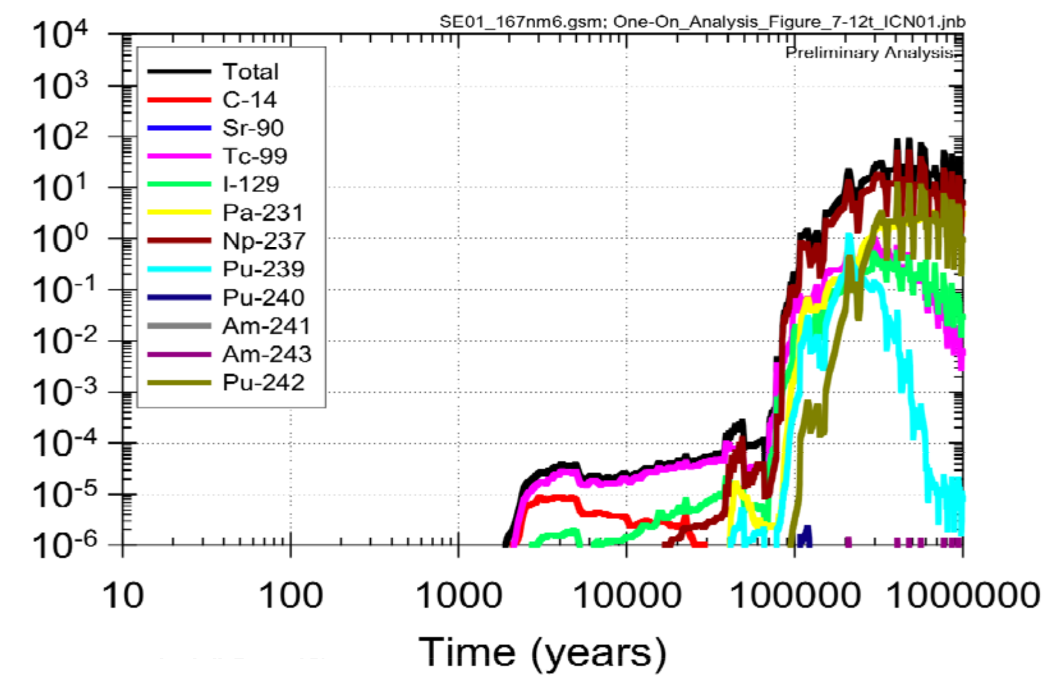
Why Iodine Is Important To Store

Among the various waste steams, volatile gases / long-lived fission products pose unique scientific issues with regards to long term storage. Understanding their interactions with capture and storage materials may ensure a technical basis for predicting stability with time.

2002 SR/FEIS analyses:

1 million year performance studies for Possible *Nuclear Repositories (eg.,* Yucca Mt)

- Np-237 is the largest contributor to dose, followed by other actinides
- Tc-99 (half life 213K yr) & I-129 (half-life 15.7M yr) will dominate peak dose if actinides are removed
- *Iodine-129* tracks with Tc-99, less important than Tc-99 until after 300,000 yr when decay lowers dose from Tc-99.



I-129 is small in concentration but long-lived
Known participant in Human Metabolic Process

On-going SNL I_2 Separations and Waste Form Research

1. Study/Optimize Loading of Iodine into Separations Material and Transition to Waste Form
    - Characterization of Baseline MOR (from ORNL)
    - Characterization of MOR (from INL reactor)
    - Analytical Procedure Development for all MOR Separations Materials

2. Bismuth Oxide Waste Forms – research into durable low temperature encapsulation waste
    - Composition effects (oxide)
    - Weight loading
    - Encapsulation of AgI
    - Durability studies

3. Alternative Waste Forms
    - AgI structure in MOR (correlation of ANL/APS data)
    - Novel Metal-Organic Frameworks for I_2 Separations and Storage
    - Effects of Decay on Waste Form Durability

1. Characterization of ORNL and INL: MOR, Ag-MOR, Ag-I-MOR

Develop a close working relationship between **Iodine Separation** Projects at ORNL and INL, with the **Iodine Waste Form** Projects at SNL

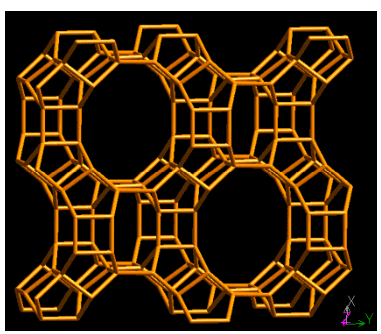
(1) Determined commercially available Mordenite and Ag-Mordenite
Bob Jubin's "Rosetta Stone" of MOR developed

(2) Develop analytical testing method for material from 3 labs including:
Elemental analysis (SEM-EDX, AA/ICP-MS, XRF), Powder X-ray & Thermal Analyses

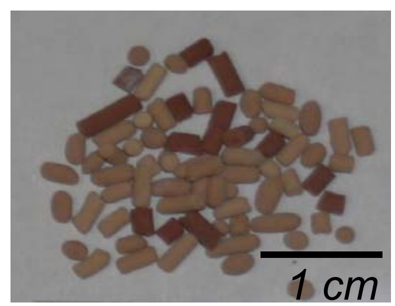
(3) All information has been used to determine baseline material for 3 labs,
and secure reserves for future testing

(4) Next steps include utilizing loaded MOR in waste form development at SNL

MOR structure



Ag-MOR (IONEX)



Voloxidation Off-gas Capture Materials from ORNL

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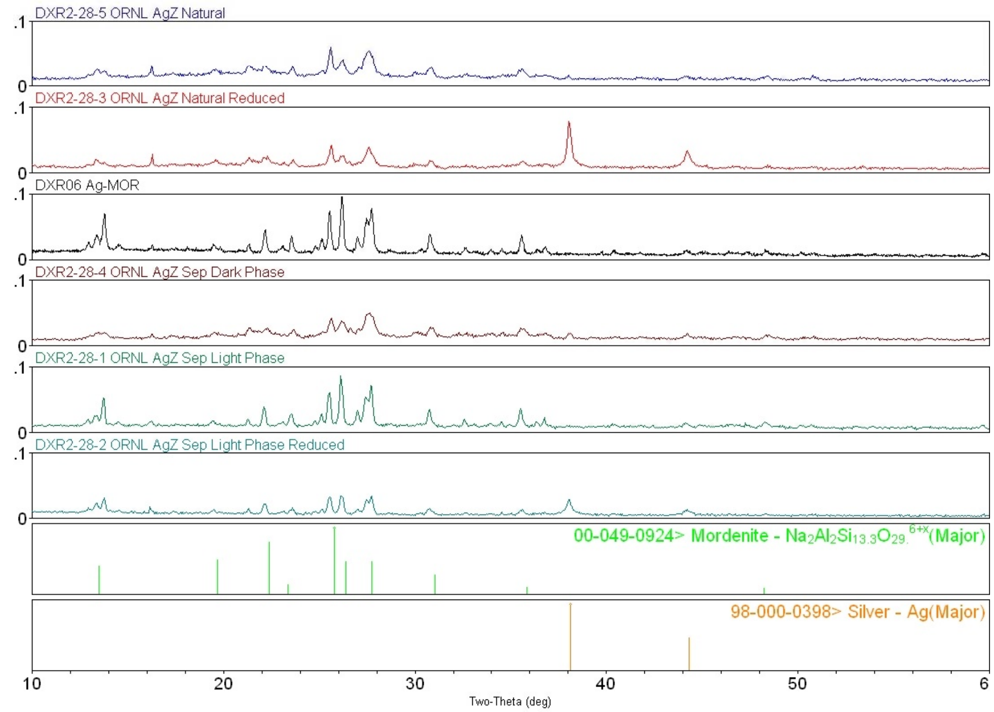
Lab Test of Cycle Separations:
Coupled End to End run (CETE) at ORNL
Closed material balance for volatiles
Investigate release of volatile components during voloxidation –
samples to be sent to SNL



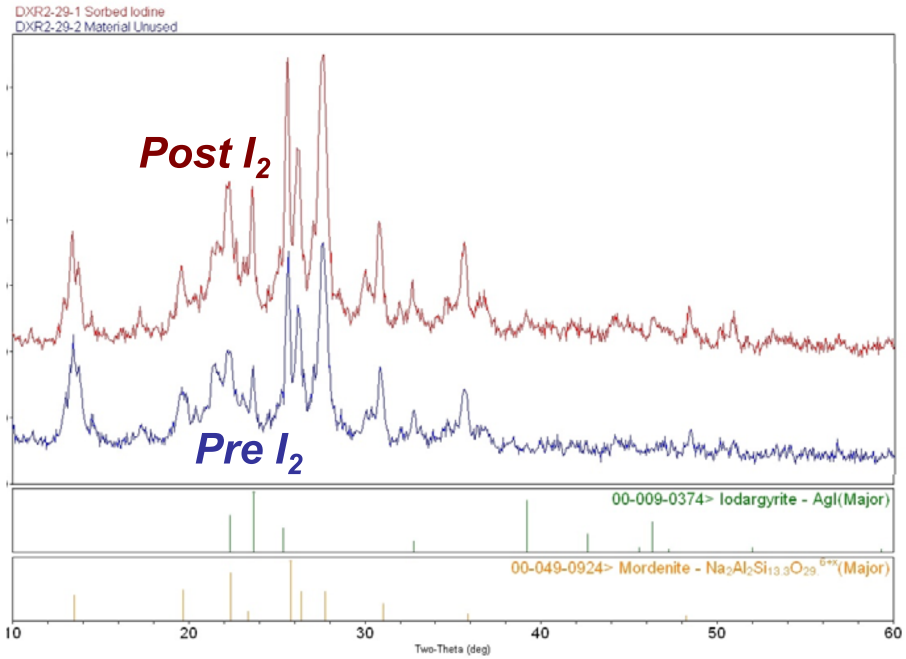
Analysis of "Baseline MOR" contenders:
- Natural Mordenite samples are crystalline
- Larger enough quantities for tri-lab experiments
- Ag°-MOR needs to be "washed" of surface AgI
-Commercial Ag-MOR has mixed crystallinity

SNL 0.122g of ^{129}I (22 µCi; ORNL) for waste form study

Simulated Off-Gas Capture Materials from INL

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)

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Analytic protocols Developed at SNL for Ag-exchanged Mordenite (zeolites):

Analytes of interest: Na, Al, Si, Ag and I

Analytic Tools: ICP-MS, X-ray Fluorescence (XRF) and Atomic Absorption (AA)

ICP-MS Advantages: Good detection limits for all analytes
ICP-MS & AA Disadvantages: Samples must be dissolved in strong acid (HF), and then greatly diluted.

ICP-MS only works well when samples have not been exposed to iodine:
Both AgI and $AgIO_3$ fail to dissolve completely in strong acid;
Elemental iodine vapor escapes during dissolution of samples and is then sorbed by the container.

XRF Analysis performed on powdered samples and method has good sensitivity for Si, I and Ag.
Disadvantages: Poor sensitivity for Na and Al

Conclusions: Analyses for Na and Al require ICP-MS or AA
Si and Ag (if Iodine is absent) may also be done by ICP-MS
XRF can be used to analyze for Si, Ag and I in the same sample.
AA is particularly good for Na, Ag, and other alkali and alkaline earth metals that my enter into experiments

Studies indicate that Ag-MOR exposed to I_2 vapor can sorb Ag:I in 1:1 ratio. Probably forming both Ag_4I_4 clusters in zeolites pores and micron-sized AgI crystals on zeolite surfaces.

Ag°- Natural MOR Chosen as Baseline Material

2. Low Temperature Glass Encapsulants for Iodine

Options for Traditional Iodine Waste Form Research:

leave Iodine in AgI-MOR

remove AgI from MOR and store AgI (sublimation temp ≈550°C)

Historically, glass research with Iodine:

- Low melting glasses of AgI with vanadium and lead oxide
- Low melting AgI/Ag pyro-phosphate glass (500˚C) (MRS. Symp. Proc., 2008,Vol. 1107)
- Encapsulation of AgI-MOR in grout (PNNL).

We have developed a different approach:

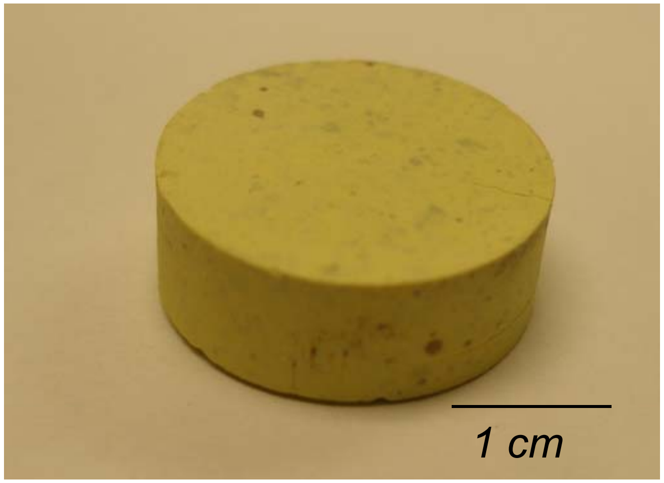
encapsulation with a low temperature sintering bismuth oxide based glass

(Builds on our previous work indicating enhanced solubility of Iodine in Bismuth Oxide phases)

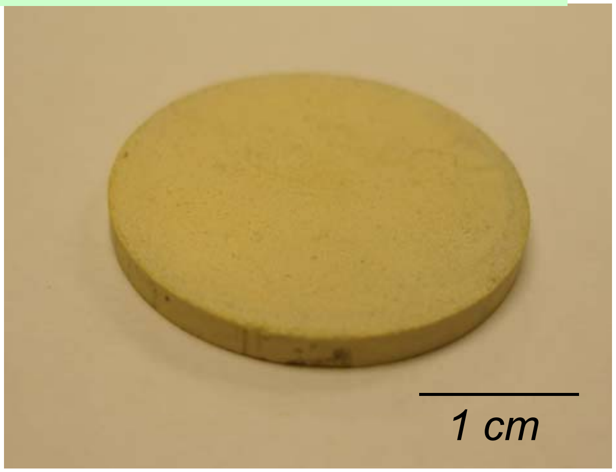
Low Temperature Glass Formation

- Non-radioactive iodine was used.
- 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.

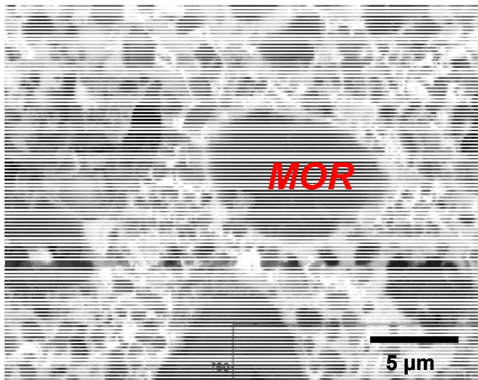


20 wt% AgI- MOR/80 wt% Glass A
500˚C for 1 hr

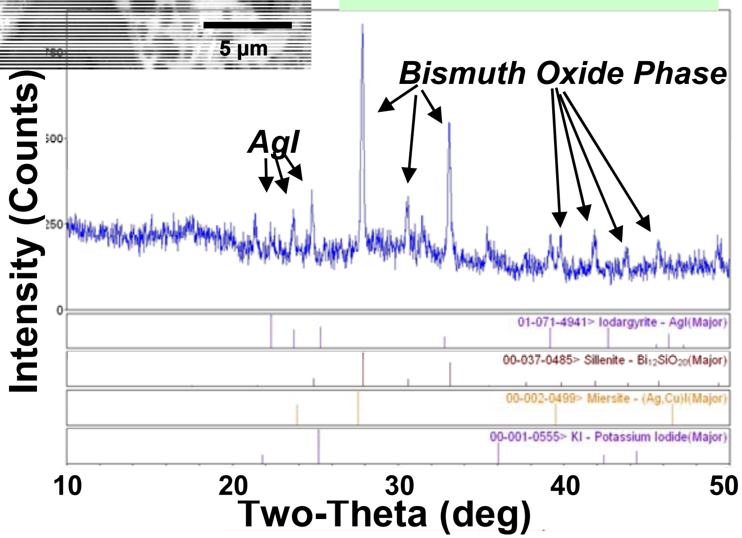


50 wt% AgI/50 wt% Glass A
500˚C for 3 hr

Analysis of Formed Glass Encapsulants

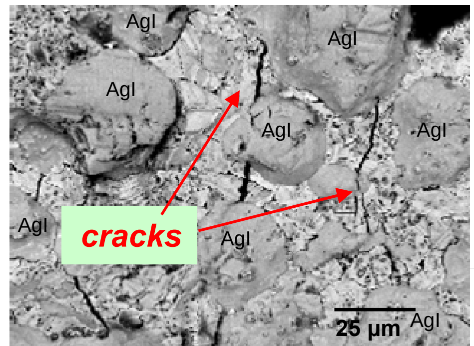


20 wt% AgI- MOR/80 wt% Glass A, 500˚C for 1 hr; dense pellets

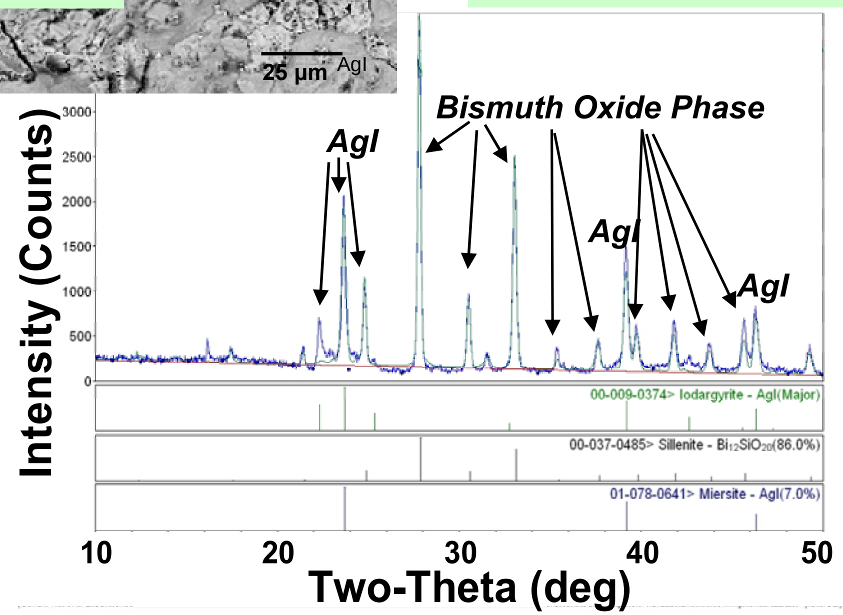


The remnants of MOR particles were no longer crystalline but were surrounded by crystallized Glass A.

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.

Thermal Studies on Glass A Encapsulant loaded with AgI or AgI-MOR

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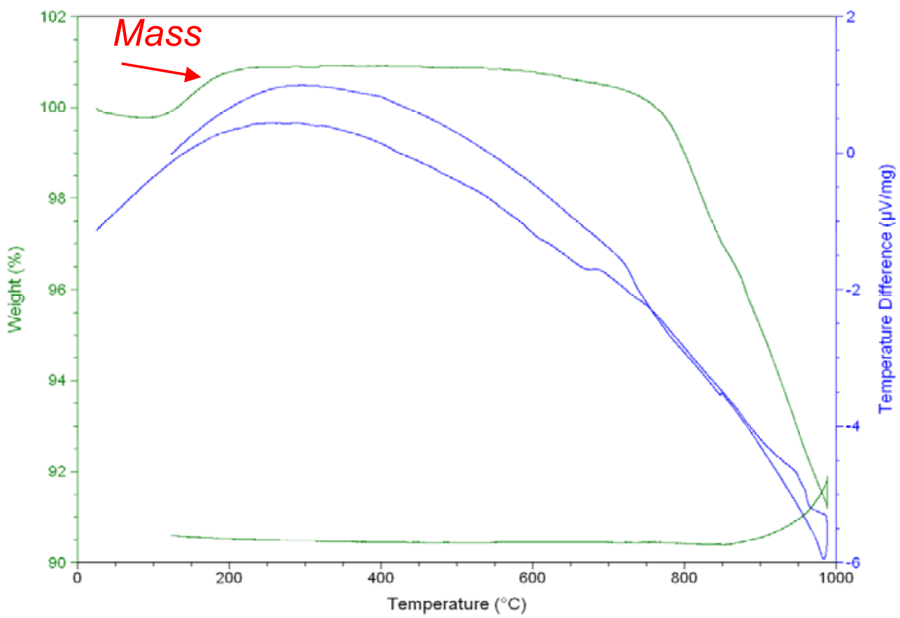
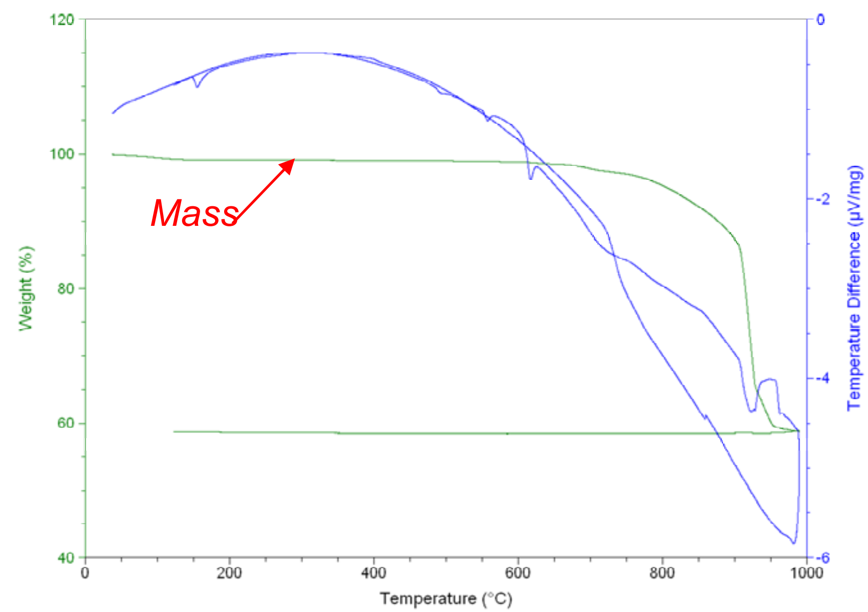
Thermogravimetric analysis of sintered samples indicated stability to > 700˚C.
Next Study: A slightly higher temperature sintering (thus less soluble glass) may result in a better performing glass.



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

On-going studies to determine max weight loadings and durabilities of waste forms

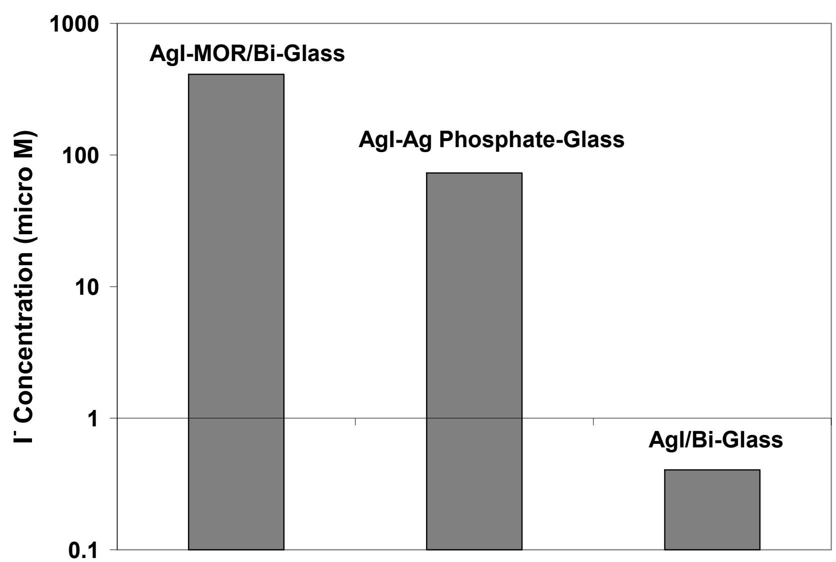
Accelerated Aqueous Leaching Tests-Waste Form Durability.

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

• I^- concentration measured with an I^- -specific electrode.

• High I^- concentration in AgI-MOR/Glass A sample due to loading method at SNL.

• The AgI/Glass A sample had a very low I^- concentration.



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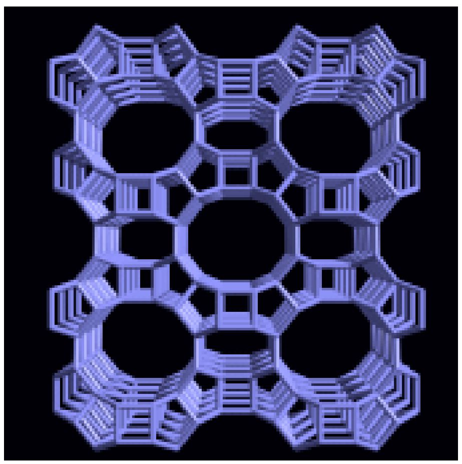
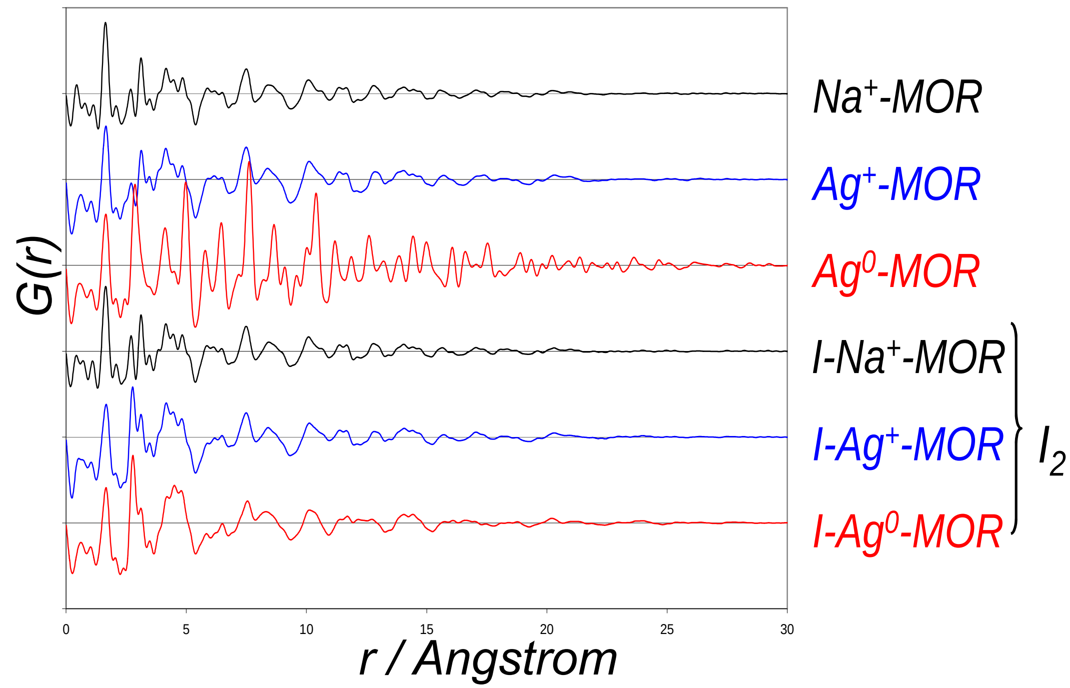
Alternative Waste Forms: Pair Distribution Function Data – ANL/APS

To understand why Ag-MOR "works" at separating Iodine for Waste Forms, we are using Pair Distribution Function studies with ANL

MOR, Mordenite



12 MR, 7.0 x 6.5Å



Peak position ⟷ *Bond length / distance*

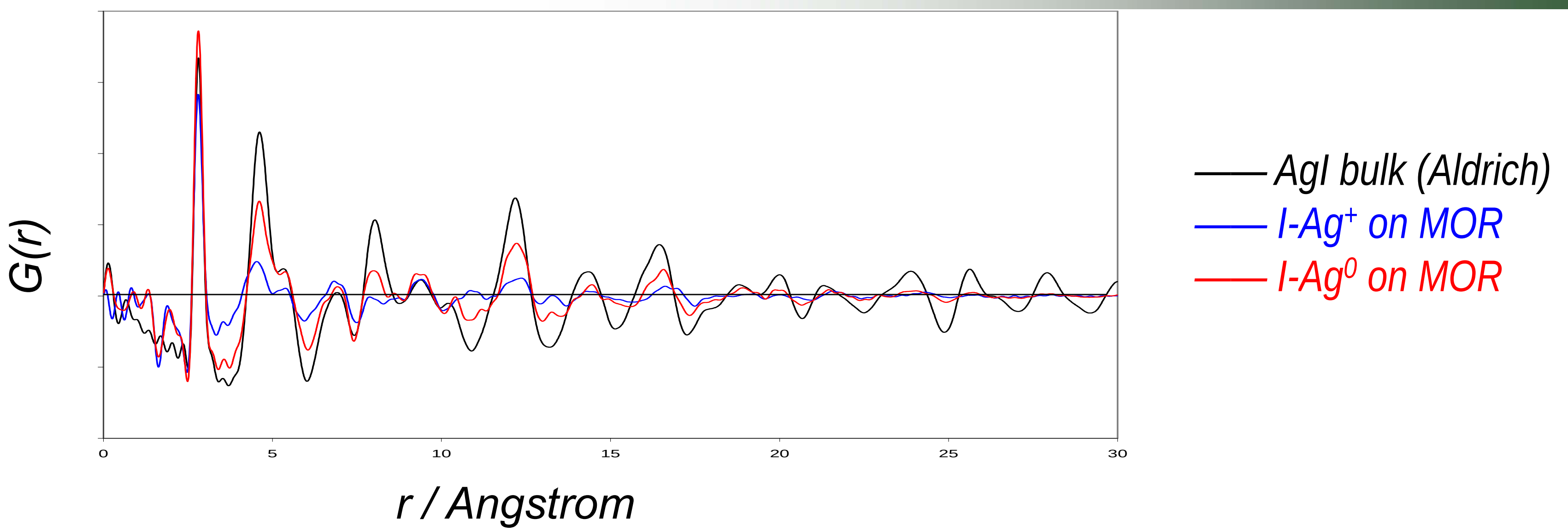
Peak area ⟷ *Coordination #, scattering intensity*

Peak width ⟷ *Disorder, bond angle distribution*

Peak r_{max} ⟷ *Particle size, coherence*

} → ***Structural Modeling***

Iodine Separation by "larger" Ag° Nanoparticles inside Zeolite Pores: Enhanced Trapping for Waste Form



- Ag^0-MOR contains Ag nanoparticles
- Maximum dimension <30 Å
- Likely confined by pore structure

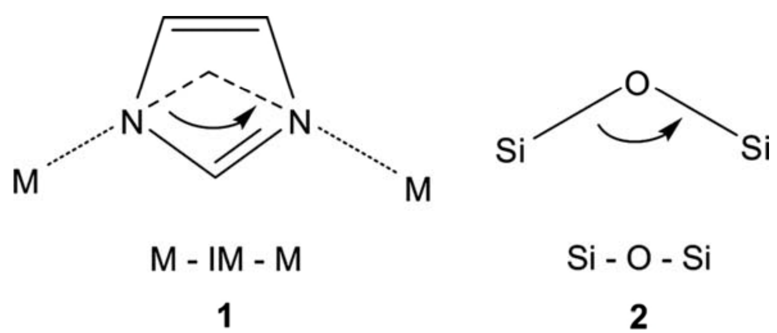
- Both Ag^+-MOR and Ag^0-MOR react with I_2
- Forms nano-scale silver iodide
- Maximum dimension <30 Å
- Ag^+-MOR had smaller, less ordered particles
- Non-spherical morphology – likely confined by pore

Alternative Waste Forms: Metal-Organic-Frameworks (MOFs)

Reason for MOF'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: MOFs



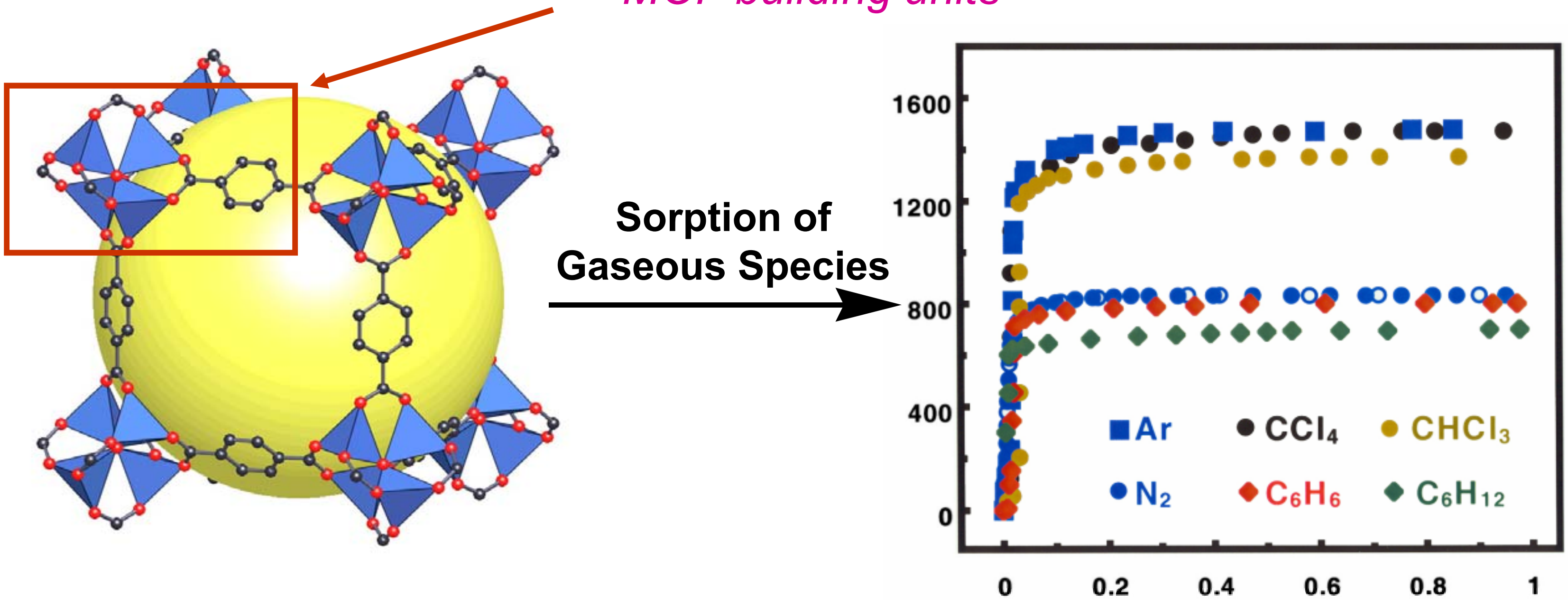
Resulting in ultra high surface areas of ≈1400 m^2/g for ZIF-8

FY09 Alternative Waste Forms : MOFs

- Literature Search
- Sample Prep
- Iodine Loading
- Materials Analysis
- Preparations for FY10
- Final Report

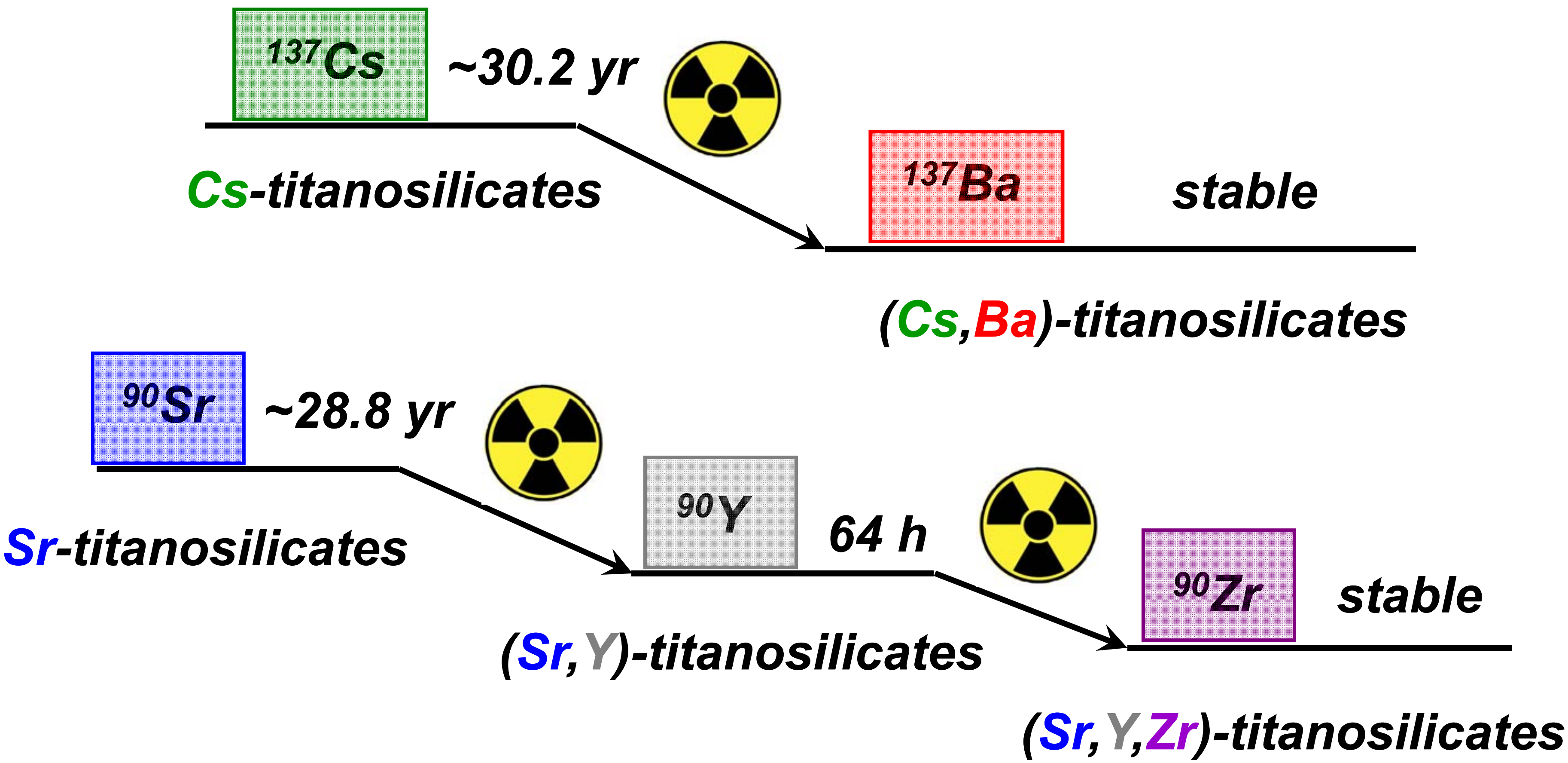
Alternative Waste Forms: Metal-Organic-Frameworks (MOFs)

Extreme Tunability to gas uptake: gas sorption tuned by MOF building units



$Zn_4O(BDC)_3$ IRMOF-1	**I_2 (gaseous)** →	$Zn_4O(I_2BDC)_3 \bullet (I_2)_x$ (Iodinated IRMOF-1)

Alternative Waste Forms: Fission Product Waste Forms Stability w/Decay



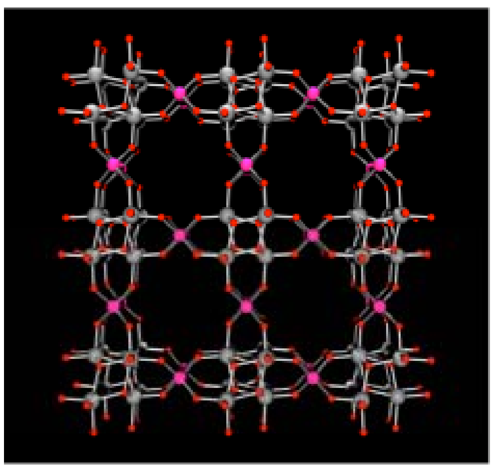
Although the concentration of Y at secular equilibrium is very small

$Sr^{2+} \rightarrow Y^{3+} \rightarrow Zr^{4+}$

How does the structure and its stability respond to these changes?

Synthesis and analysis of Waste Form Composition with Time (Decay)

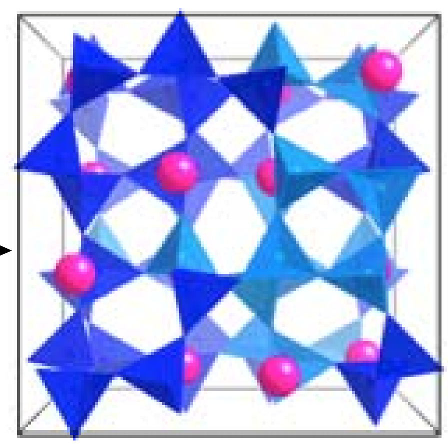
- Ba-substituted $CsTiSi_2O_{6.5}$ (Pollucite Analog) are of interest as durable ceramic waste forms because of their formation from heat treatment of CST Cs-getters.
- Cs,Ba-pollucite samples were prepared by a solid state synthesis.
- Calorimetry, NMR and Neutron Diffraction is in progress to determine stability of waste form with oxidation state change from decay (Cs^+ -> Ba^{2+})



CST: $CsSi_2Ti_4O_{13}$•$4H_2O$

heat

>700℃

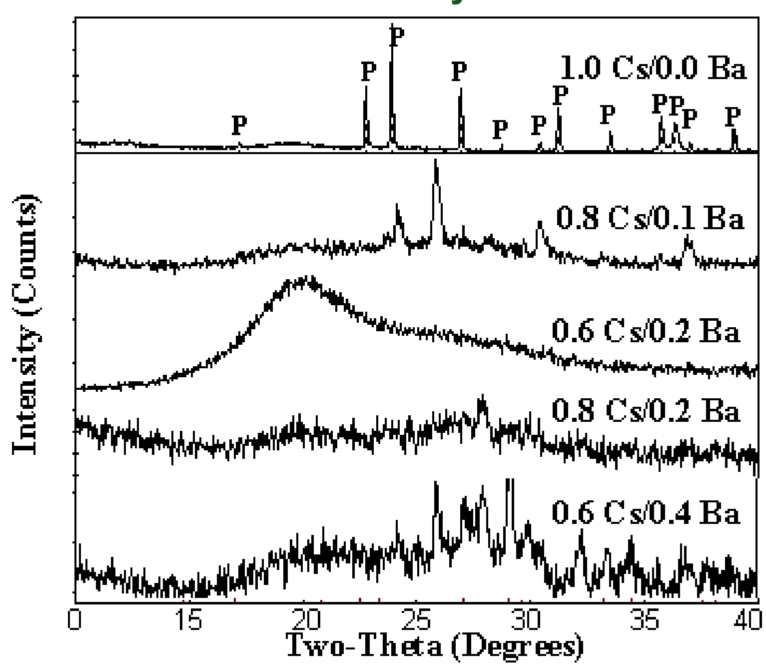


Pollucite: $CsTiSi_2O_{6.5}$

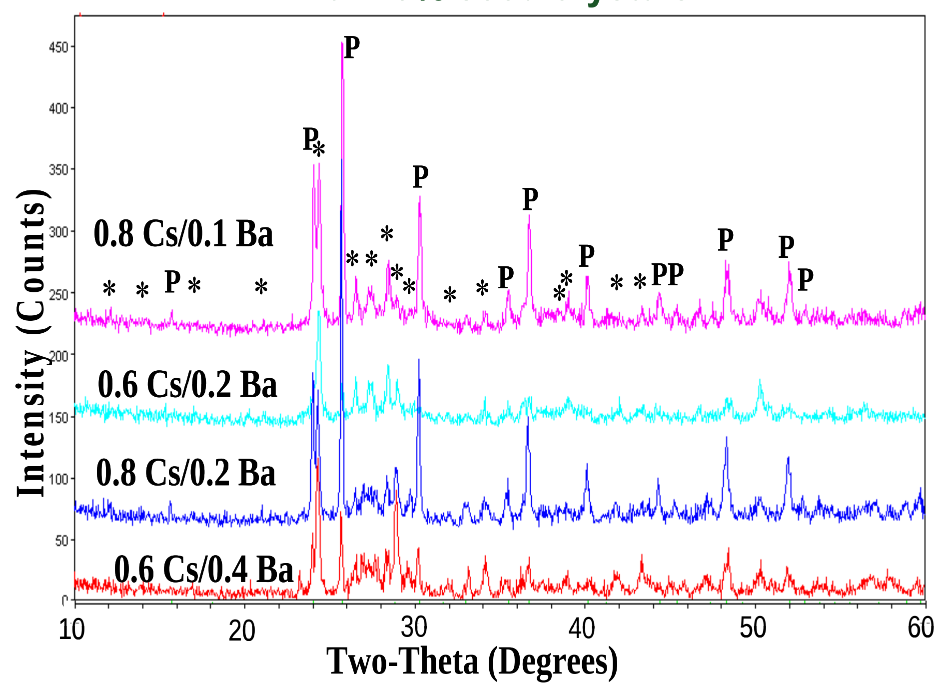
Cs,Ba-Ti-Si-O Pollucite: $Cs_xBa_{(1-x)/2}TiSi_2O_{6.5}$

Ba-substituted $CsTiSi_2O_{6.5}$ with the pollucite structure were synthesized using $CsTiSi_2O_{6.5}$ seed crystals in a wide variety of stoichiometries

no seed crystals



with 10% seed crystals



T. Garino, T.M. Nenoff, T.-J. Park, A. Navrotsky. *J. Am. Ceram. Soc.* **2009**, *92*(9), 2144.

Acknowledgment

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- **Extra Slides**

3. Alternative Waste Forms – PDF of AgI-MOR

To understand why Ag-MOR "works" at separating Iodine for Waste Forms, we are using Pair Distribution Function studies with ANL

*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)**.*

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

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

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

Apply corrections for background, absorption, Compton & multiple scattering