SAND2013-8043C

U.S. DEPARTMENT OF ENERGY | Nuclear Energy

The Fuel Cycle Research & Development

OPTIMIZATION OF SINTERED AgI-MORDENITE COMPOSITES FOR ^{129}I STORAGE

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Global 2013

Salt Lake City, Utah

October 3rd, 2013

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

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Outline

1. Background
   - Spent fuel reprocessing: I-129 separation
   - Ag-Mordenite (Ag-MOR)
   - Low temperature sintered glass compoosites

2. Minimizing Loss of Iodine During Heating
   - Loss of Adsorbed I_2: Ag Additions
   - Evaporation of AgI

3. Sintering: Temperature and Loading Effects

4. Crystallization of the Glass Phase

5. PCT and MCC-1 Testing

6. Conclusion

Volatile ^{129}I, from spent fuel must be captured and stored safely.

- Increased worldwide energy demands, balanced with the need to reduce greenhouse gas emissions have fueled research in clean, safe, and responsible nuclear energy.

- Appropriate nuclear waste management: a main concern for safety associated with nuclear energy.

- ^{129}I is a long-lived isotope (half-life of 1.57×10^7 years), requiring reliable storage while it decays.

- Once in the environment, iodine can be very mobile.

- The tendency of iodine to concentrate in the thyroid make ^{129}I exposure a health concern.

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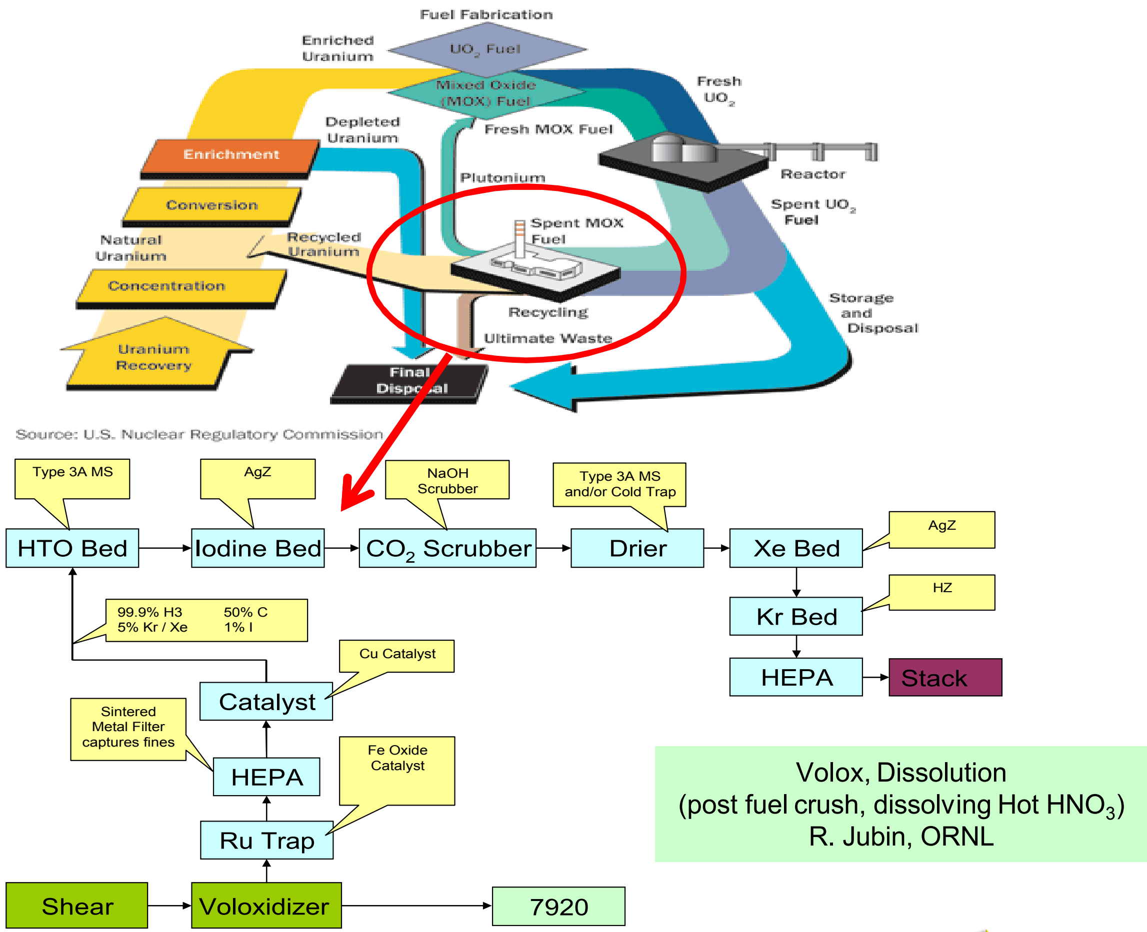
DOE Nuclear Fuel Reprocessing: Volatile radionuclides like $^{129}I_2$ will be separated and then safely stored.



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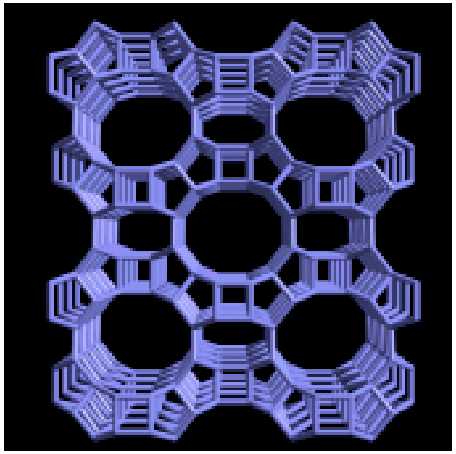
The DOE baseline I_2 capture material is Ag-Mordenite

- ^{129}I is present in low concentration (0.66% per ^{235}U fission) 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

As - Received *Ag-Exchanged* *I_2 Vapor Ag-MOR*

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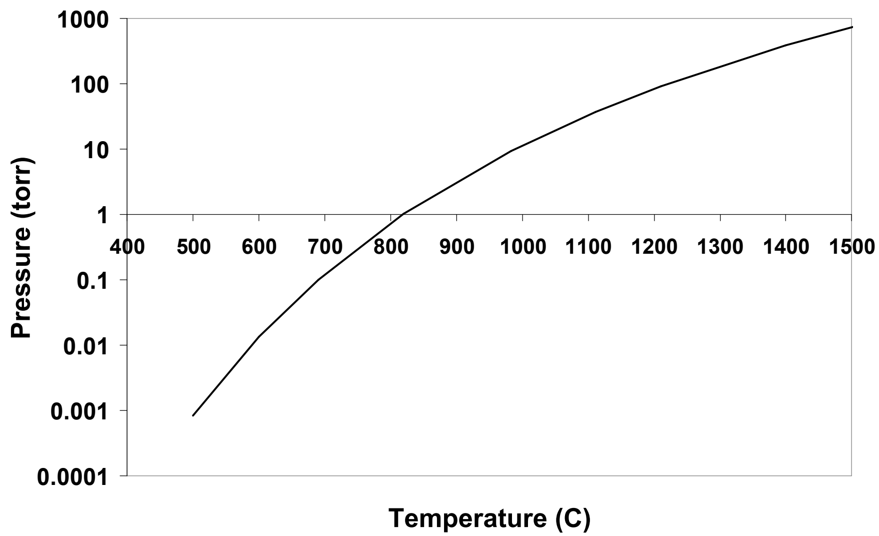
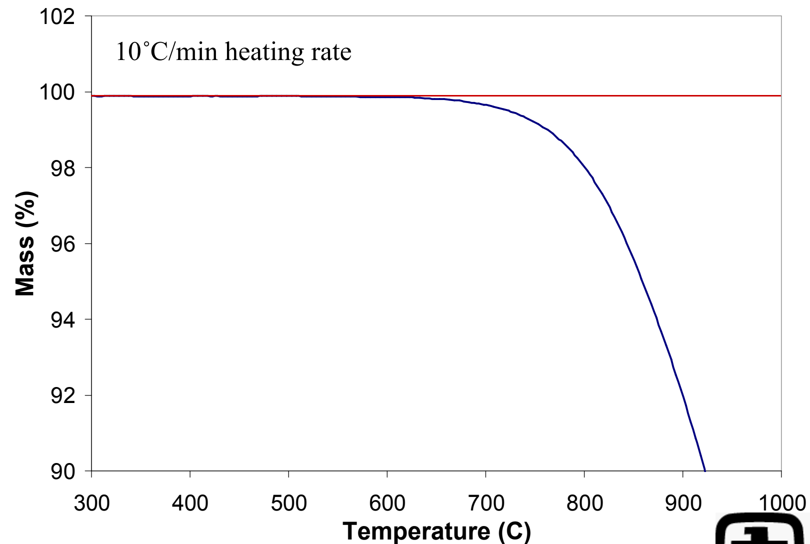
AgI has low solubility but a relatively high vapor pressure.

- The solubility in water at 20˚C is 3×10^{-6}g/L or 1.3×10^{-8} mol/L.
- It undergoes a β to α phase change at 147˚C and it melts at 558˚C.
- It has a vapor pressure of 10 mT at 600˚C.
- These limit the thermal processing temperature.

Vapor Pressure of AgI with Temperature



TGA of AgI During Heating



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Low-sintering temperature glasses for ^{129}I waste encapsulation.

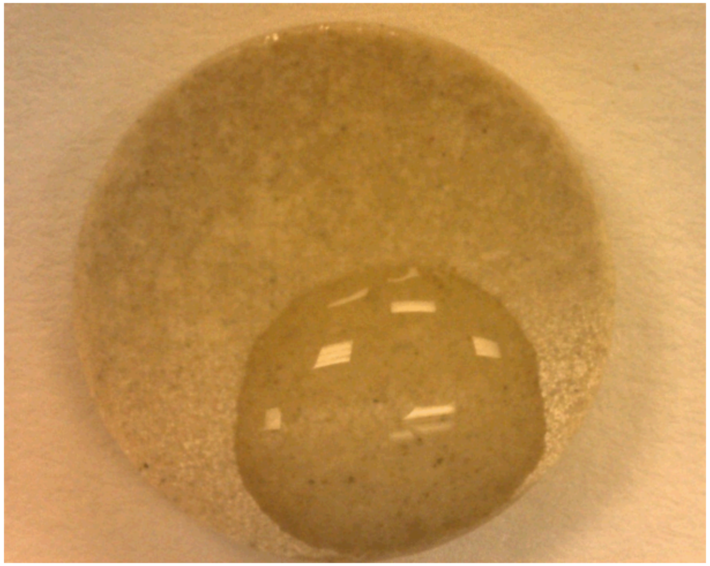
- Lower temperature compared to melting is possible since glass powder is densified by sintering. No HIPping is required.
- A composite is formed with a dense matrix surrounding I-containing phase.
- Initial studies indicated that a commercially available Bi-Si-Zn-Al oxide glass worked the best.
- Flexible matrix: Both AgI/glass and AgI-MOR/glass compositions were fabricated.

Property	Value
Composition	Bi-Si-Zn-Al oxide
Sintering Schedule	550°C for 1 hr
CTE	7.8×10^{-6}/°C
Density	5.8 g/cm^3

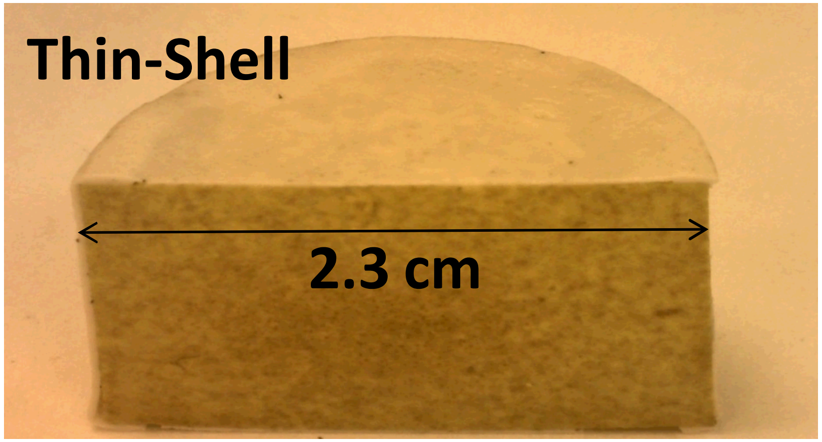
"Low-Temperature Sintering Bi–Si–Zn-Oxide Glasses for Use in Either Glass Composite Materials or Core/Shell ^{129}I Waste Forms," T. J. Garino, T. M. Nenoff, J. L. Krumhansl, and D. X. Rademacher, J. Am. Ceram. Soc., Pub. Online April 20, 2011.

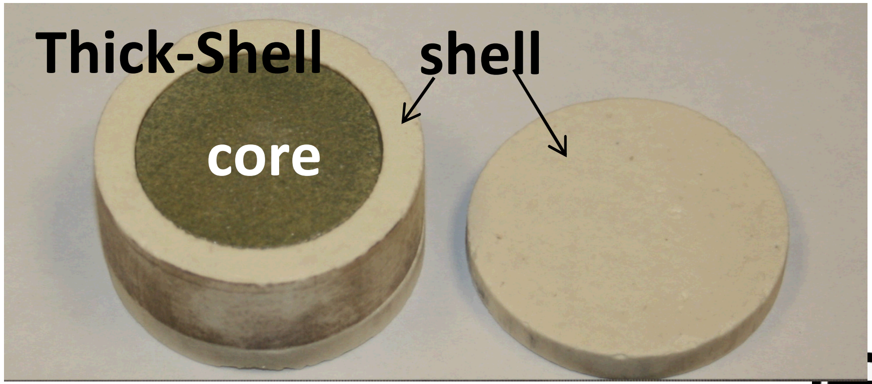
AgI-MOR composite waste forms from pressed and sintered powder.

Baseline: 20 wt% fully I_2 loaded AgI-MOR with 5 wt% Ag added and sintered at 550°C for 1 hr.



Core-Shell: AgI-MOR/glass core with SiO2/glass shell.





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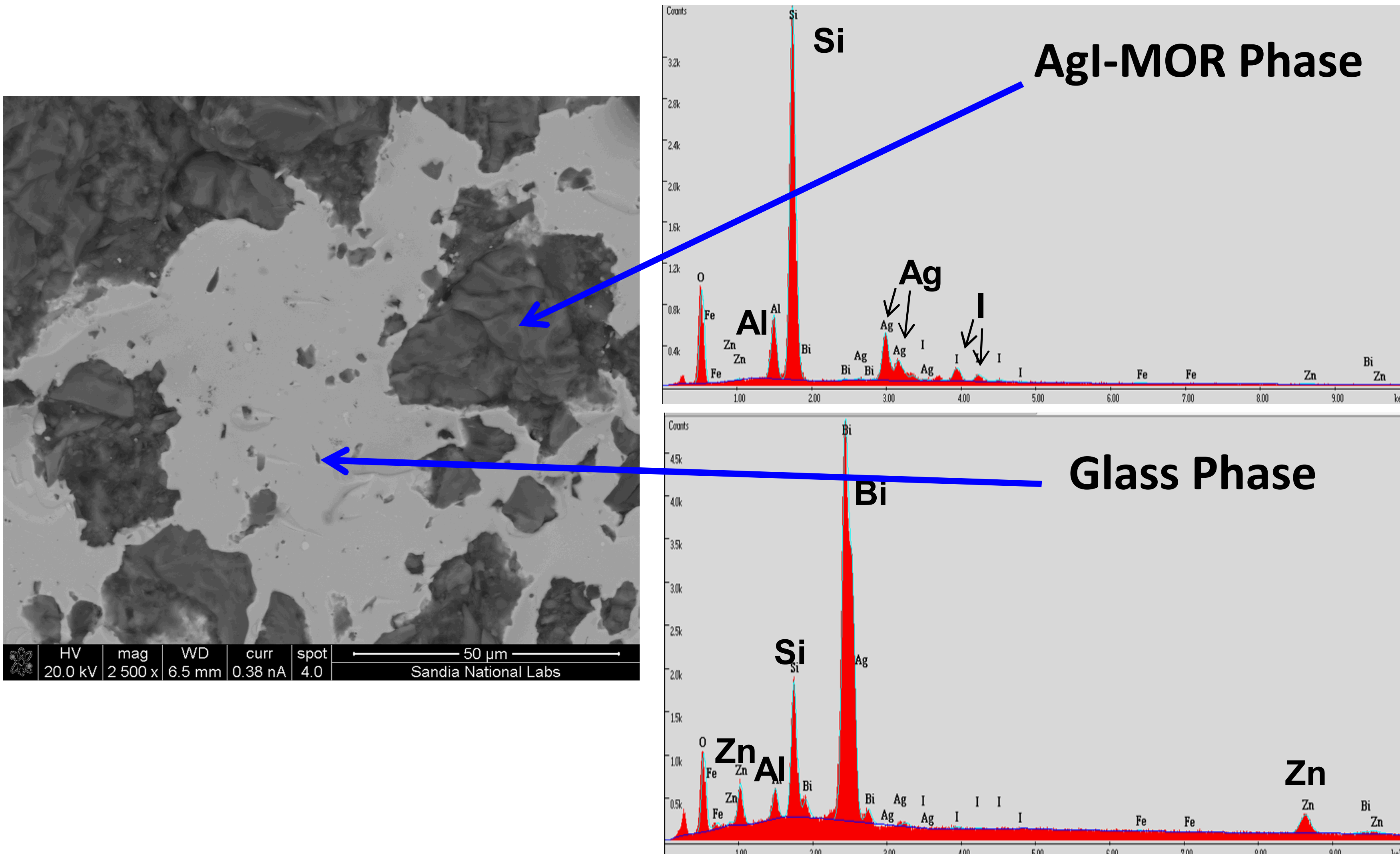
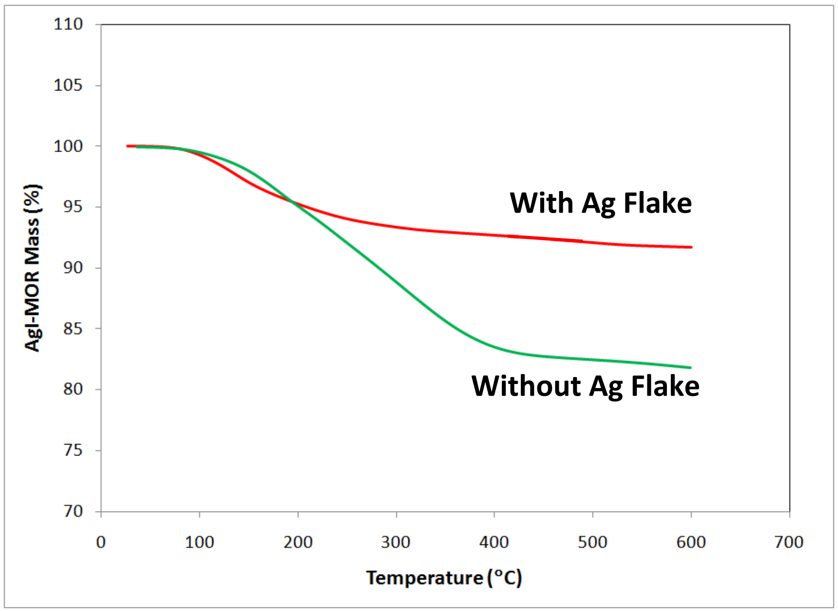
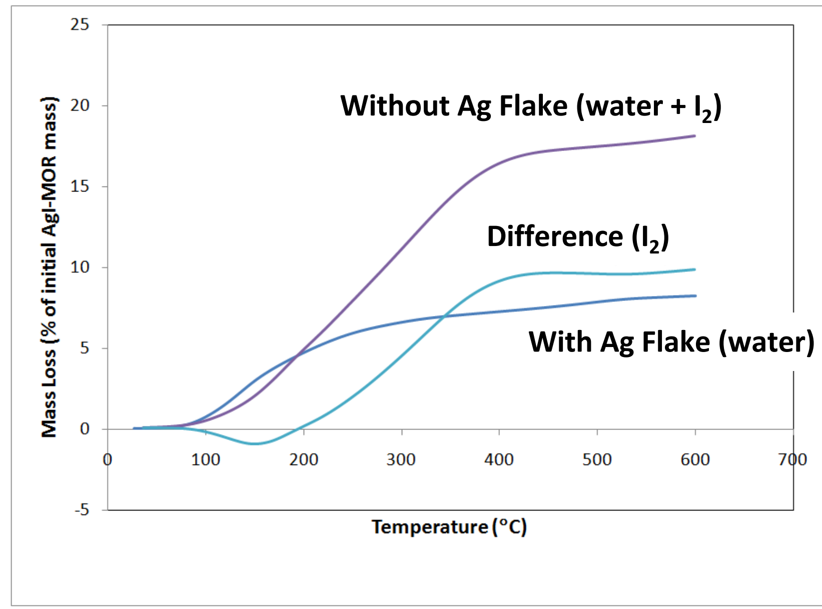
Microstructure: AgI-MOR isolated by dense glass matrix.



I_2 vapor treated Ag-MOR can lose I_2 during heating.

When silver flake is added to the AgI-MOR, any I_2 released reacts with the Ag.





Fully loaded AgI-MOR was used (~23 wt% Iodine)

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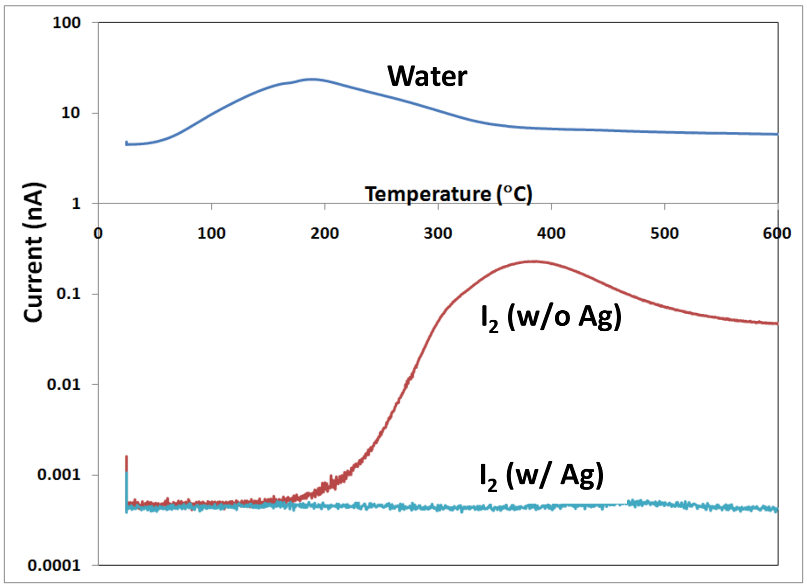
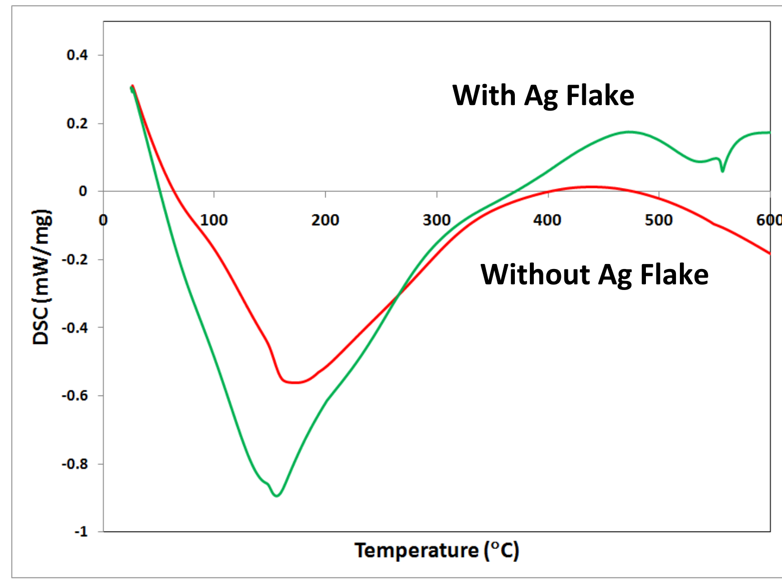
I_2 loss is confirmed by MS of TGA off-gas and by DSC.

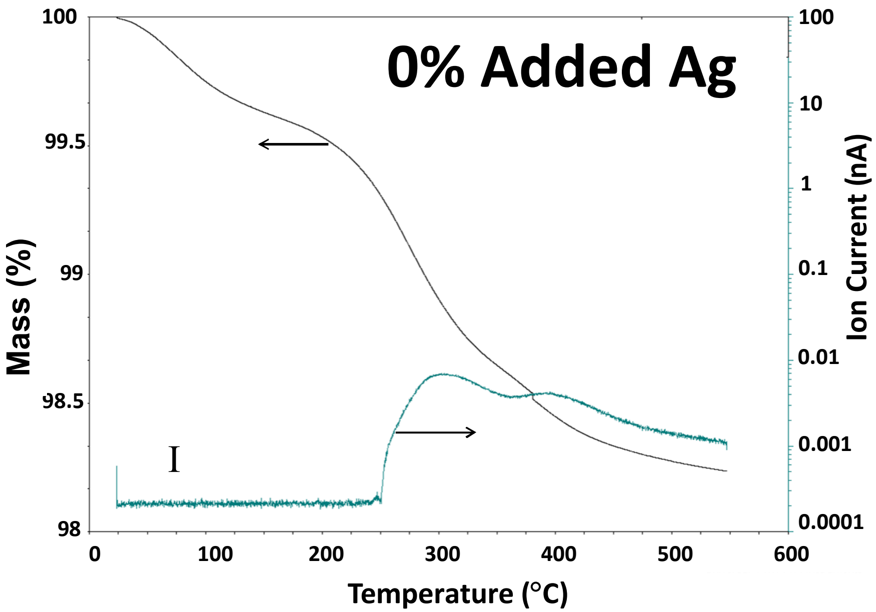
Mass Spec of off-gas indicates absence of I_2 when Ag is added.

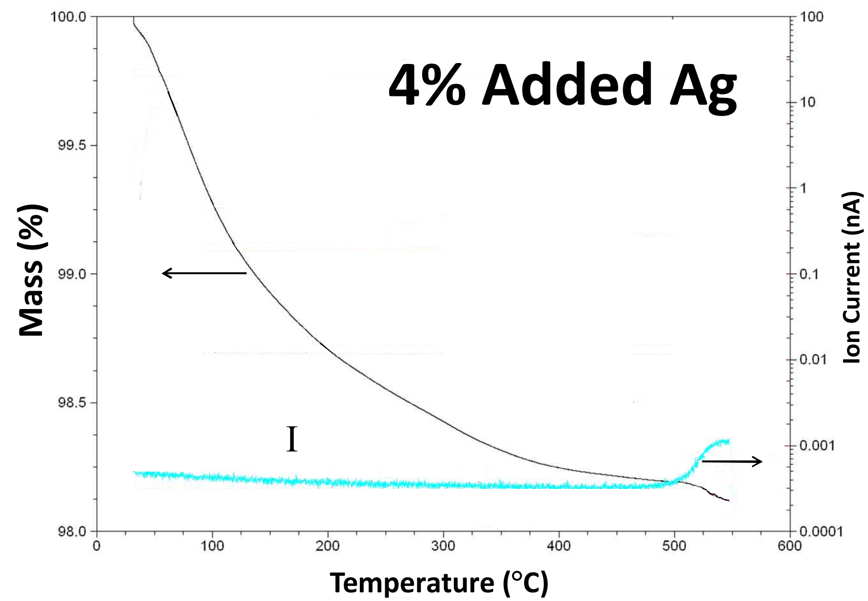


DSC shows AgI melting at 558°C when Ag is added.

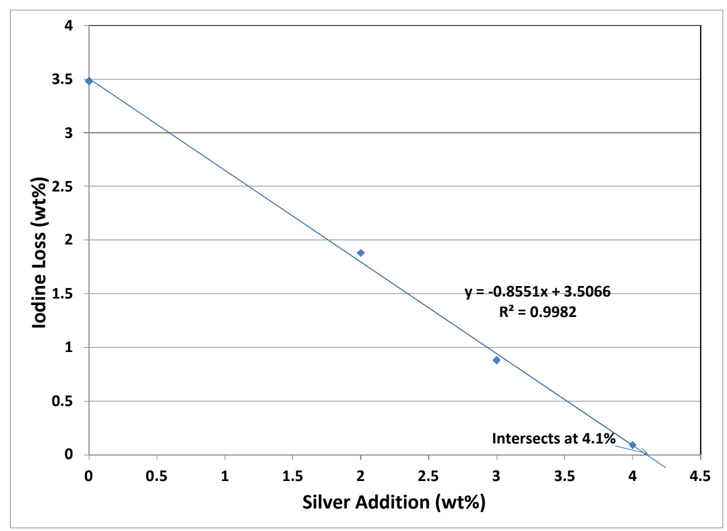


A study was performed to determine the minimum amount of Ag needed.





4.1 wt% of Ag must be added to fully loaded 20 wt% AgI-MOR/80 wt% glass to prevent I_2 loss (0.205 g Ag per gram of AgI-MOR.



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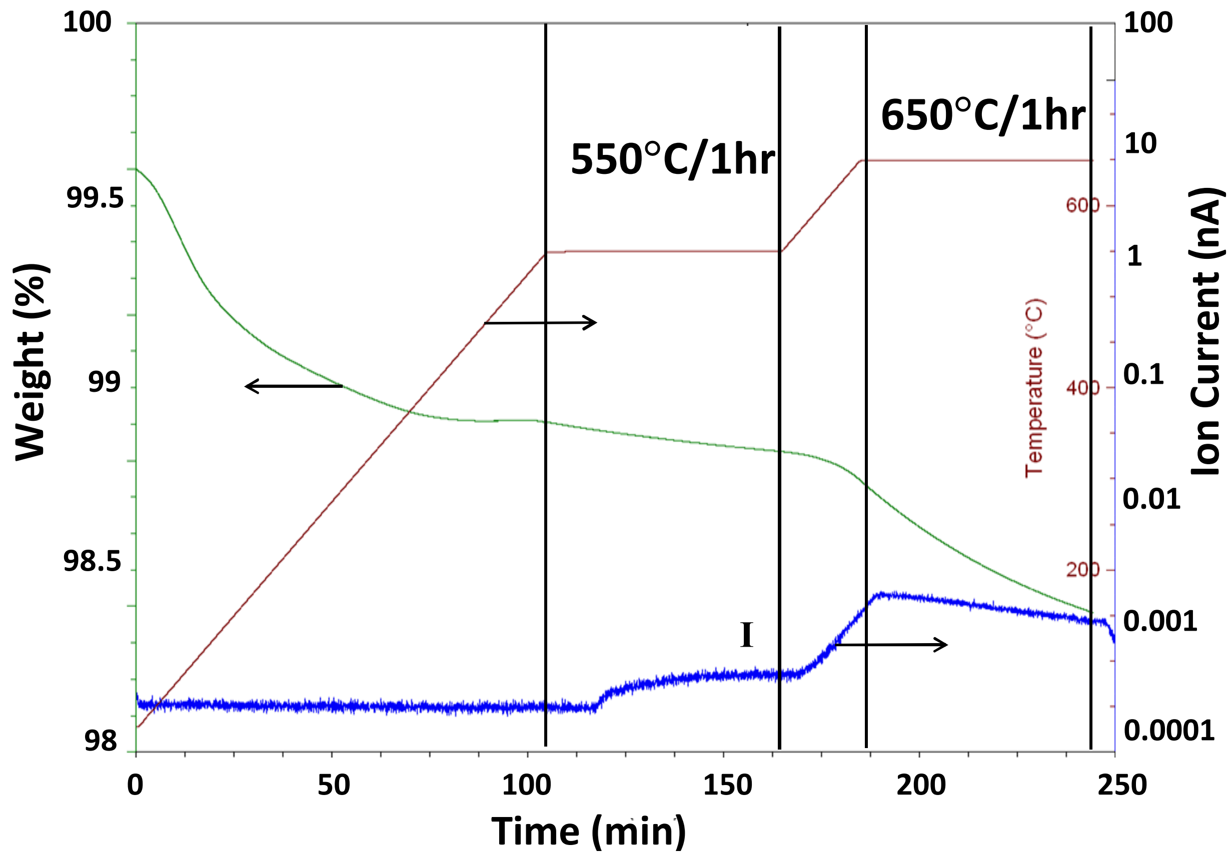
Rate of AgI loss is 5 times higher at 650°C than at 550°C.

Iodine loss rates:

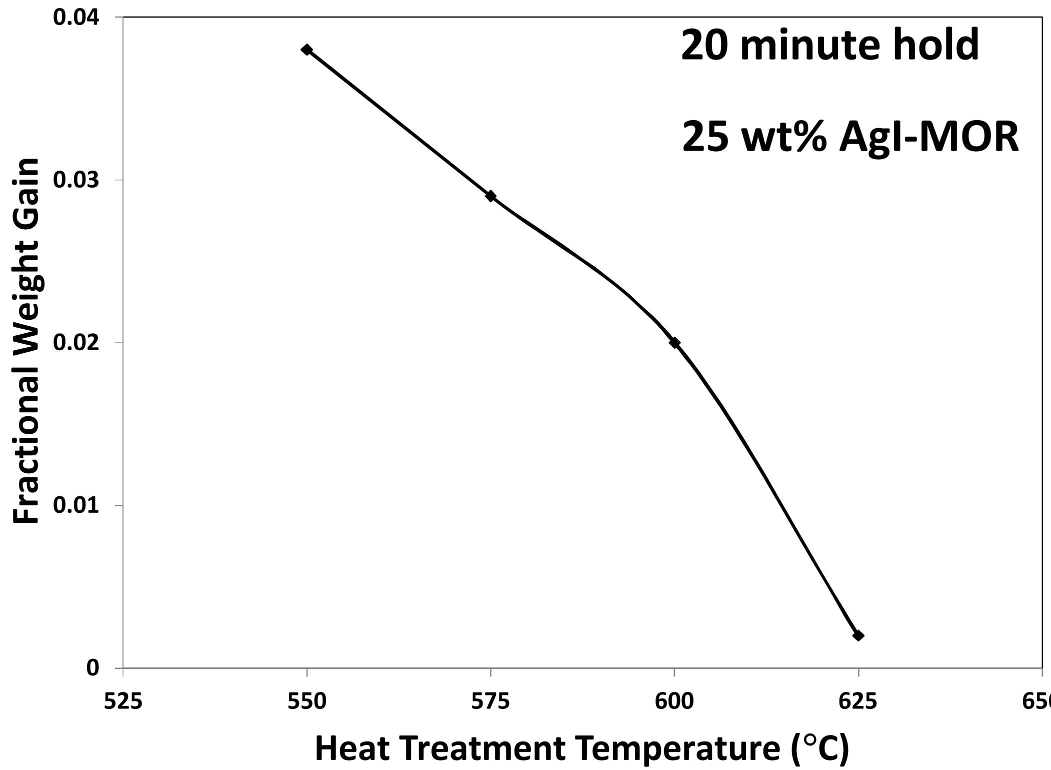
550°C: 4.9×10^{-4} g I/cm²/hr

650°C: 2.4×10^{-3} g I/cm²/hr



A higher loading level can be attained with no open porosity by sintering at higher temperature.

Mass Gain of Sintered Samples After Soaking in Water

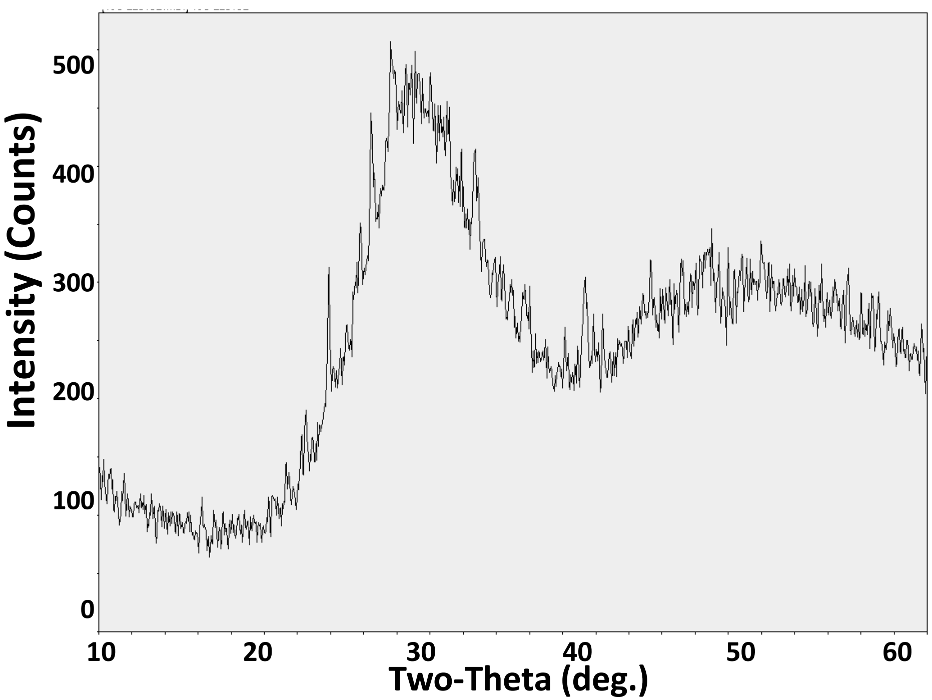


- Sintering at 625°C for 20 minutes produces a composite with no open porosity.
- Higher rate of AgI loss partly offset by shorter time at temperature.

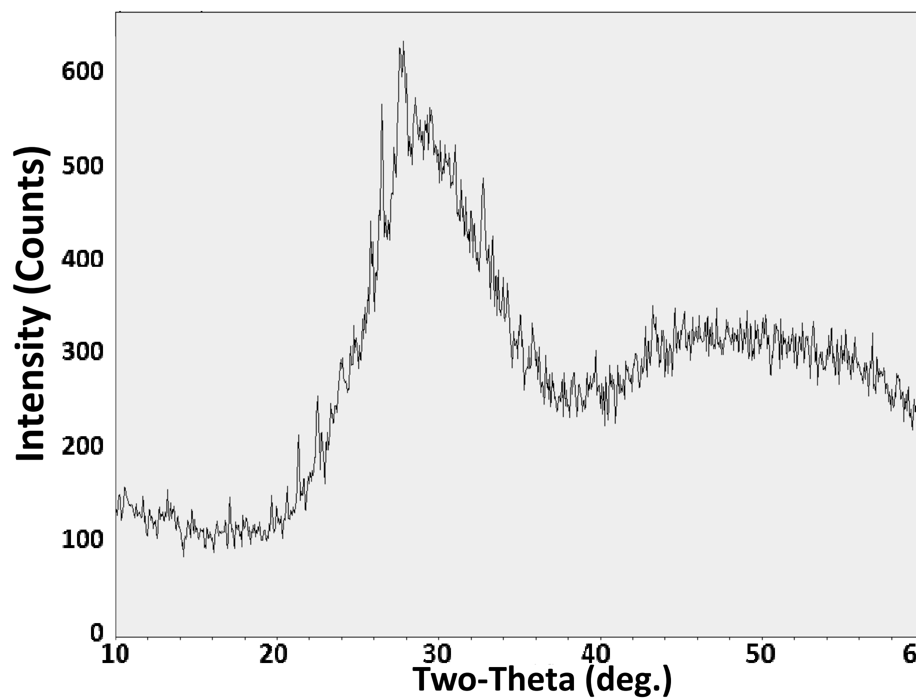
After 550°C for 18 min the glass is still amorphous .

20 wt% AgI-MOR: 80 wt% EG2922 with 5 wt% Ag

-150 µm AgI-MOR



-45 µm AgI-MOR



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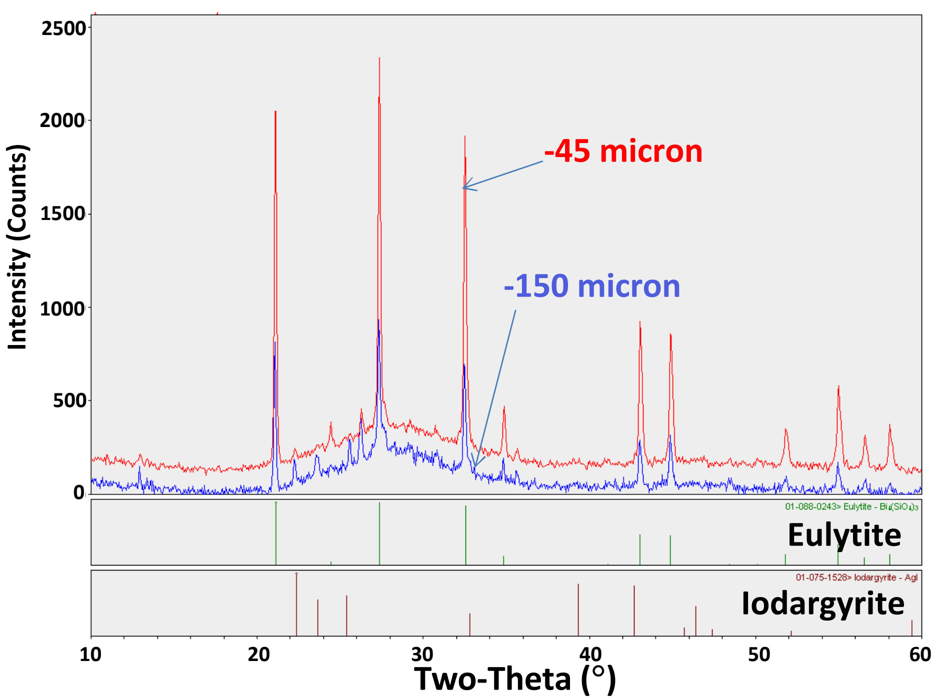
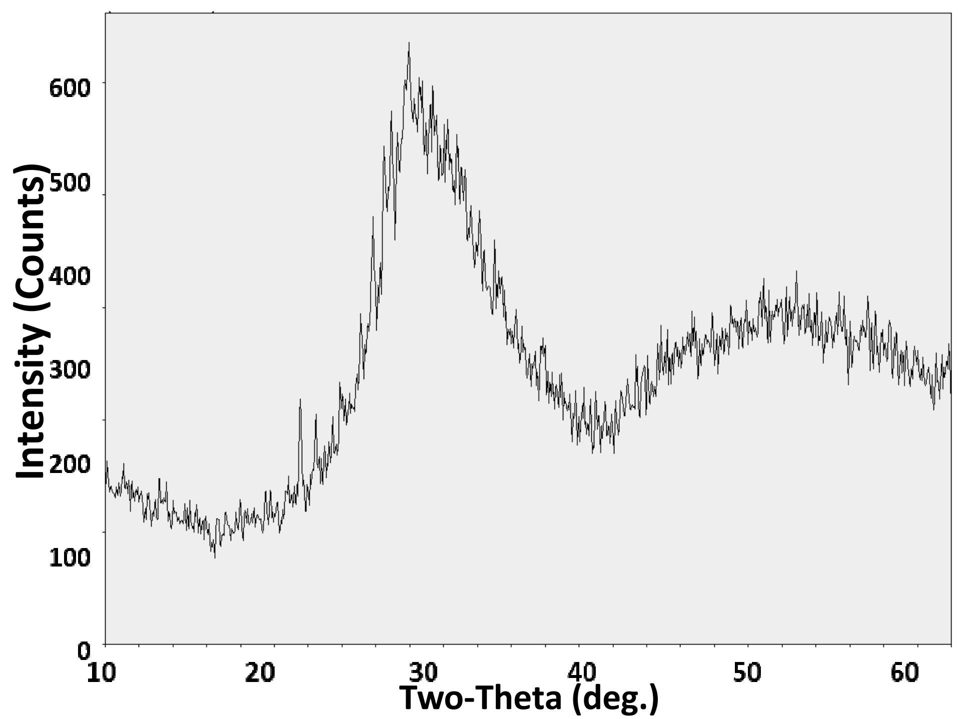
After 1 hour at 550°C, degree of crystallization depends on AgI-MOR size and on the presence of iodine.

More crystallization occurs for finer AgI-MOR particle size.



Sample with Ag-MOR (not reacted with I_2) does not crystallize.

15 wt% Ag-MOR (-45 μm) : 85 wt% EG2922



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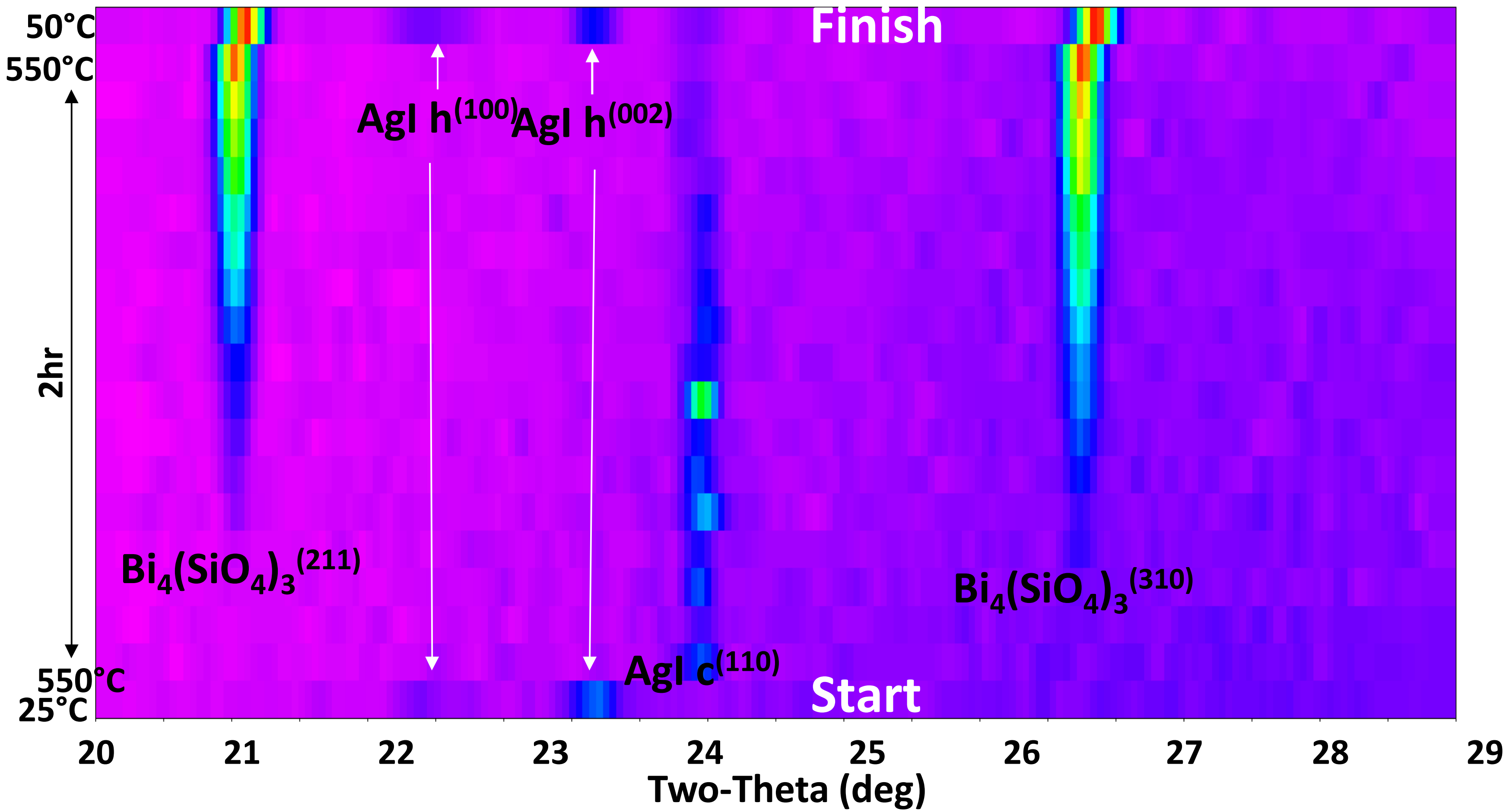
In situ XRD showed the eulytite crystallization starts after ~30 min at 550°C.

20w% AgI 80w% EG2922: heated to 550°C and held for ~2hr



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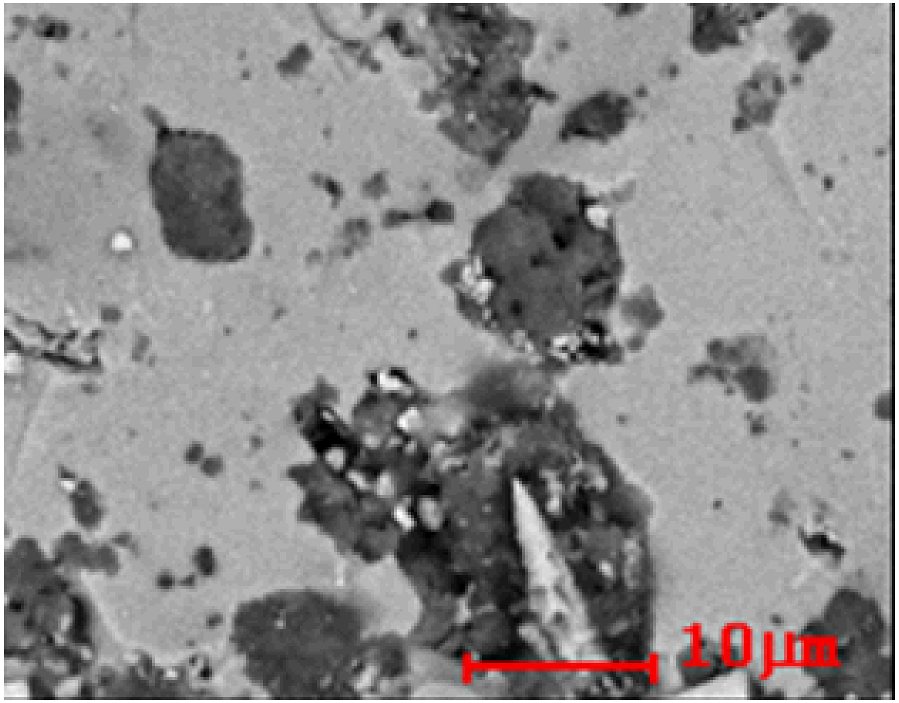
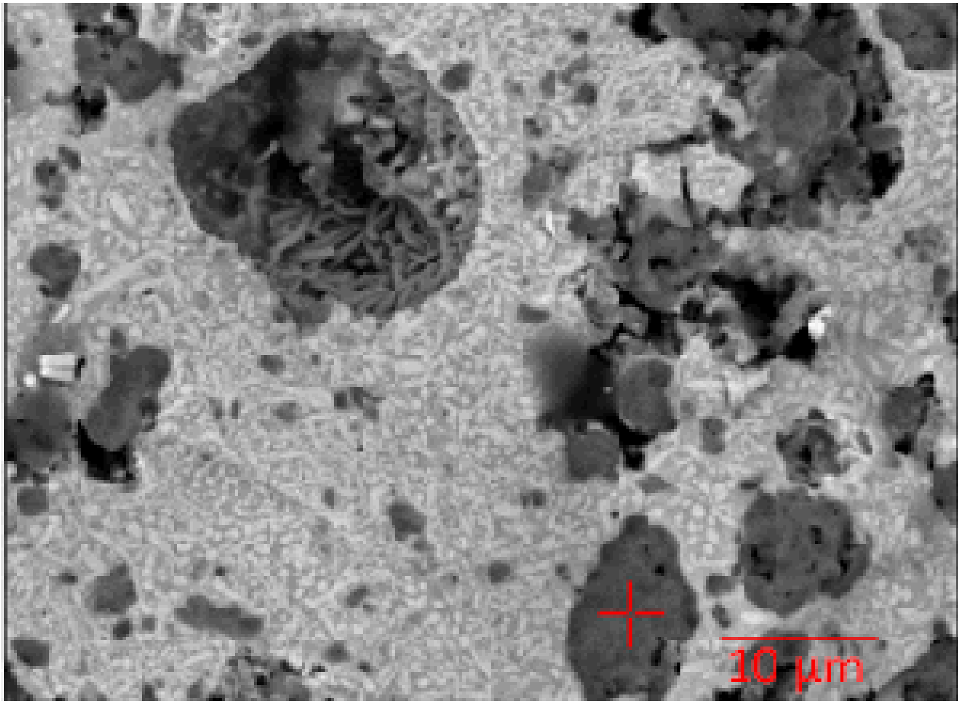
The eulytite crystals are acicular and uniformly distributed in the glass phase.

550°C for 20 min



575°C for 1 hr



15 wt% AgI-MOR samples

PCT and MCC-1 leach tests were performed on both amorphous and crystallized samples.

PCT (Product Consistency Test): Granules in DI water for 7 days at 90°C.

Leachate Analysis Results (ppm)

	Si	Bi	Zn	Al	I
Amorphous	20.3	0.021	14.6	0.234	0.002
Crystallized	18.4	0.064	98.7	0.494	0.001

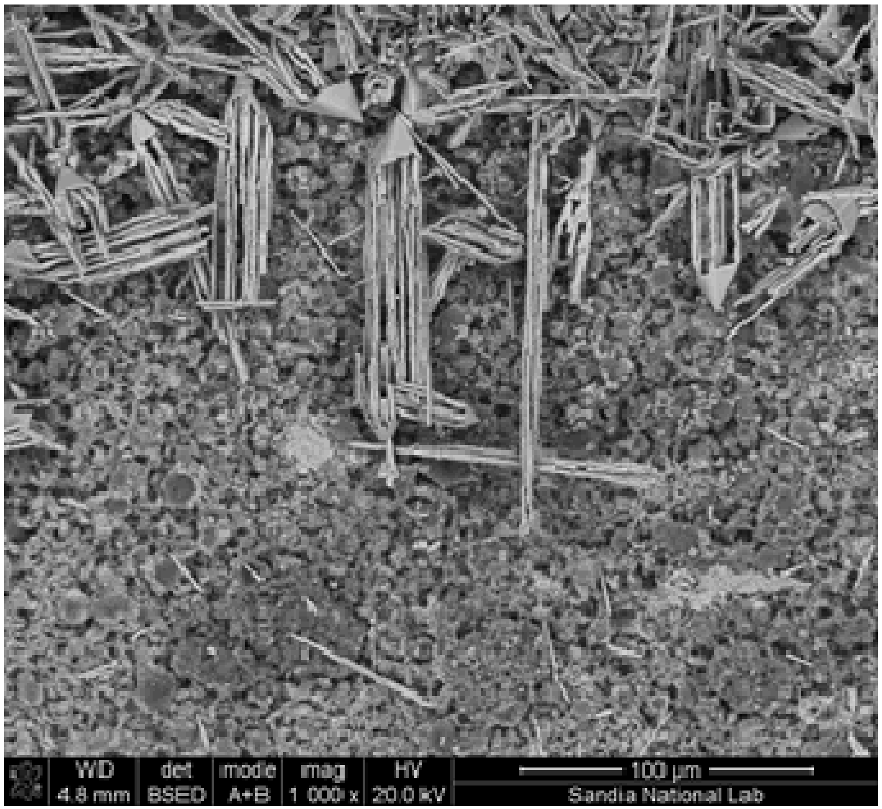
MCC-1 (Static Leach Test): Monoliths in DI water for 7 days at 90°C.

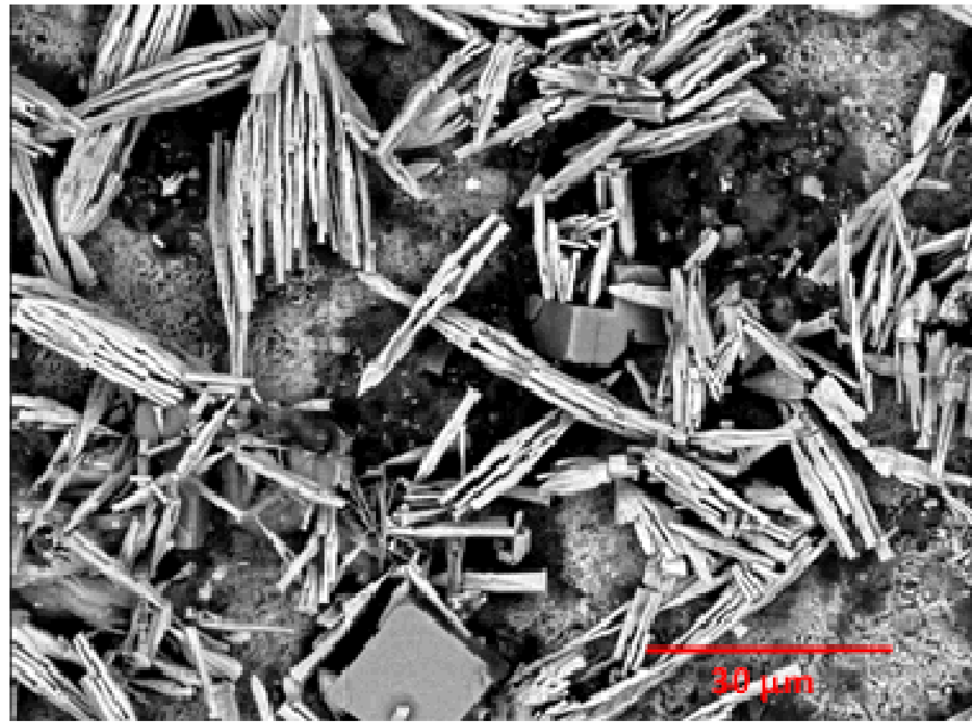
Leachate Analysis Results (ppm)

	Si	Bi	Zn	Al	I
Amorphous	38.3	0.10	75.2	6.0	0.0007
Crystallized	20.1	0.017	84.0	1.2	0.007

- **Very low iodine levels in all leachates.**
- **Higher Zn concentration in leachate from crystallized sample.**

Both MCC-1 samples had Bi_2O_3 crystals of their surfaces.





Conclusions

1. For fully I_2 loaded Ag-MOR, 0.205 g Ag per gram of AgI-MOR is needed to react with adsorbed I_2.
2. The specific rate of iodine loss at 550°C from a sintered glass composite with 20 wt% fully loaded AgI-MOR is 4.9×10^{-4} g $I/cm^2/hr$ and the rate is about 5 times higher at 650°C.
3. A loading of 25 wt% of fully loaded AgI-MOR can be achieved while maintaining no open porosity by sintering at 625°C for 20 min.
4. Crystallization of eulytite in the glass phase can occur at 550 and above in AgI-MOR loaded composites and extent depends on particle size and loading of AgI-MOR.
5. PCT and MCC-1 testing of sintered composites indicates low iodine release and only slight differences between amorphous and crystallized glass matrices.

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