Molten Salt Reactor
PROGRAM

Update on Fluid Inclusion Characterization, Thermophysical Property Measurements, and U-Salt Synthesis at PNNL

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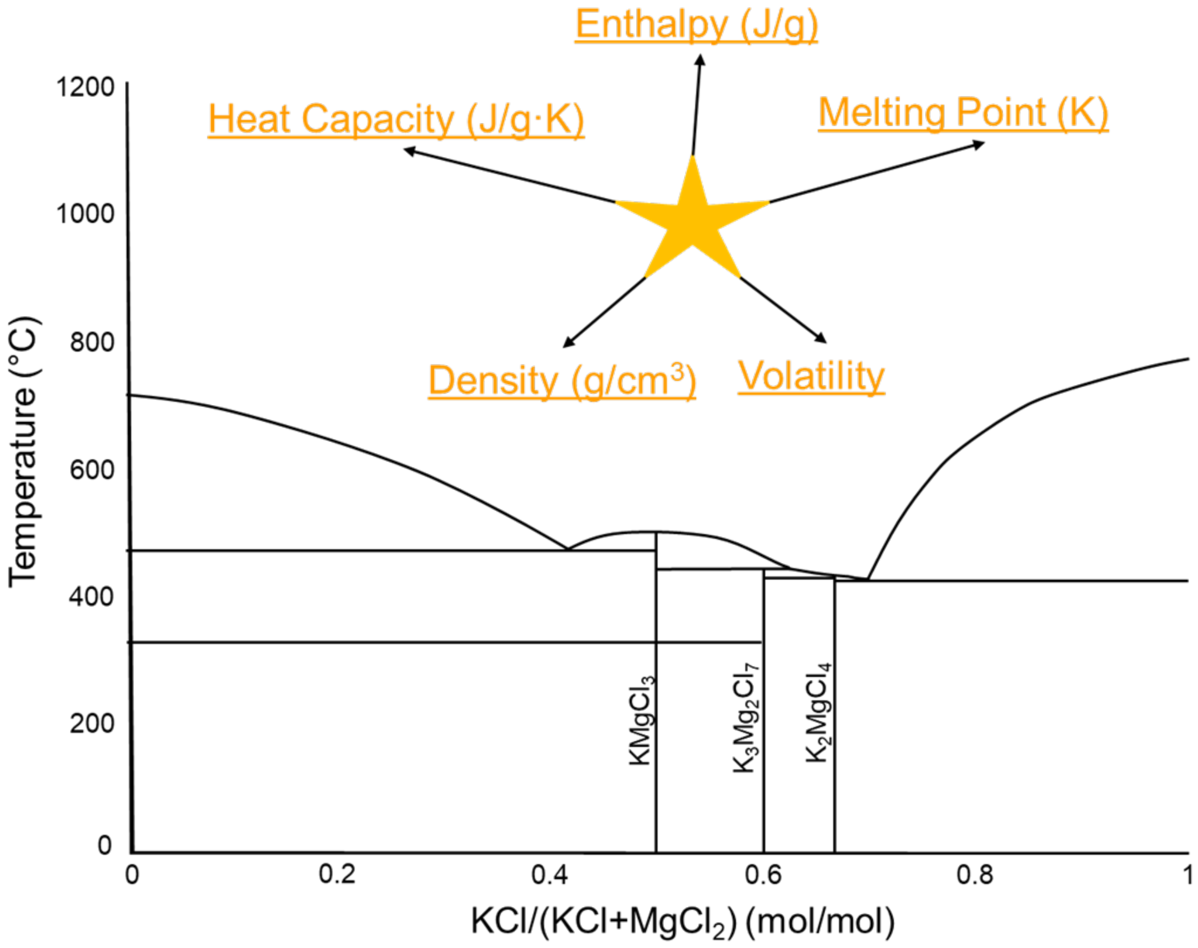
Argonne National Laboratory · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · Los Alamos National Laboratory · Oak Ridge National Laboratory · Pacific Northwest National Laboratory · Sandia National Laboratories · U.S. Department of Energy Office of Nuclear Energy

Introduction

- Leverage PNNL expertise to perform thermophysical property measurements
  - ➢ Heat Capacity via Drop Calorimetry
  - ➢ Volatility via condensed phase cold trap
- Achievements to date:
  1. Improvement of sample preparation methodology for thermophysical property data
  2. Volatility method development
  3. Extensive work on $MgCl_2$ binary systems- KCl, LiCl, $AlCl_3$
  4. **Salt fluid inclusion characterization**
  5. **Density by thermomechanical analysis**
  6. **Phase mapping via TGA-DTA**

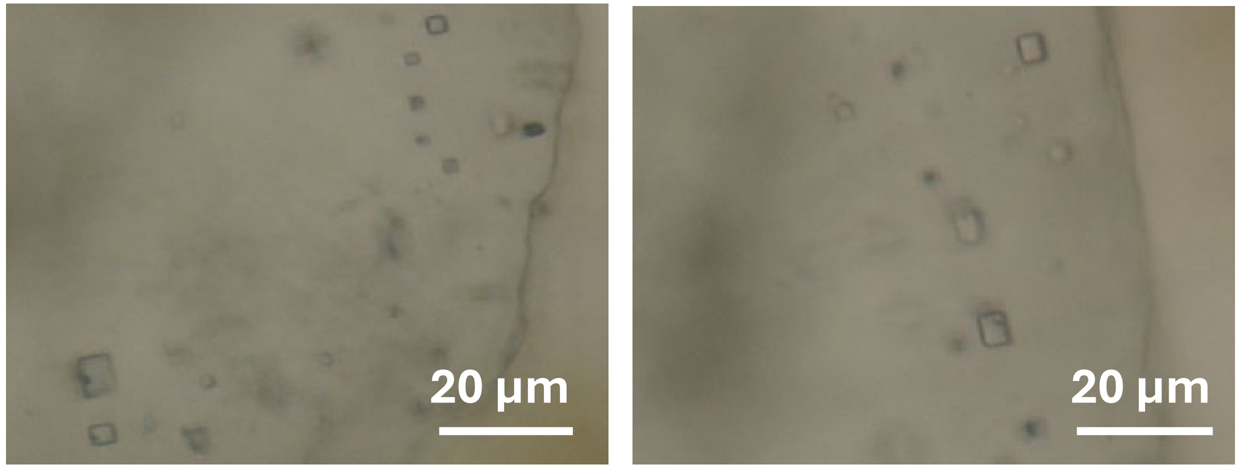


FY25 Summary

Formation of Fluid Inclusions

- Skeletal growth of crystals
  - Lack of nutrients at crystal center relative to edges
  - Undercooling
- Constitutional supersaturation
- Rapid crystal growth
- Favorable wetting characteristics

American Elements KCl 99.999% pure



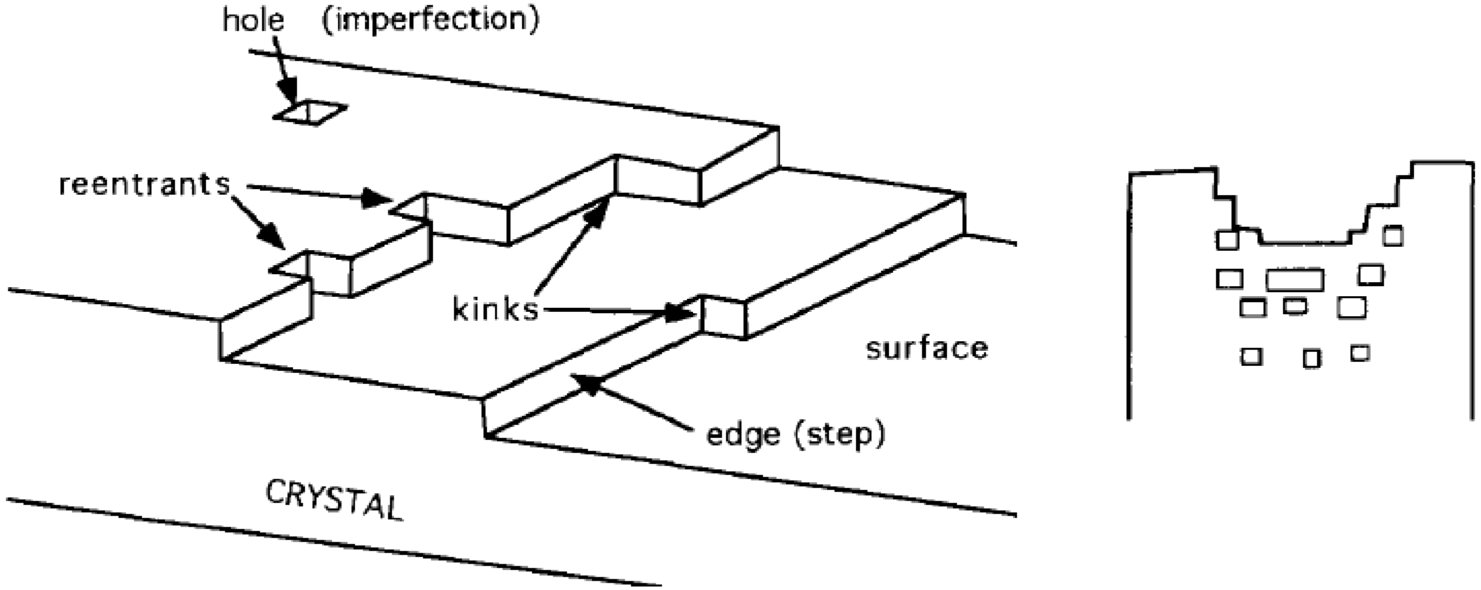
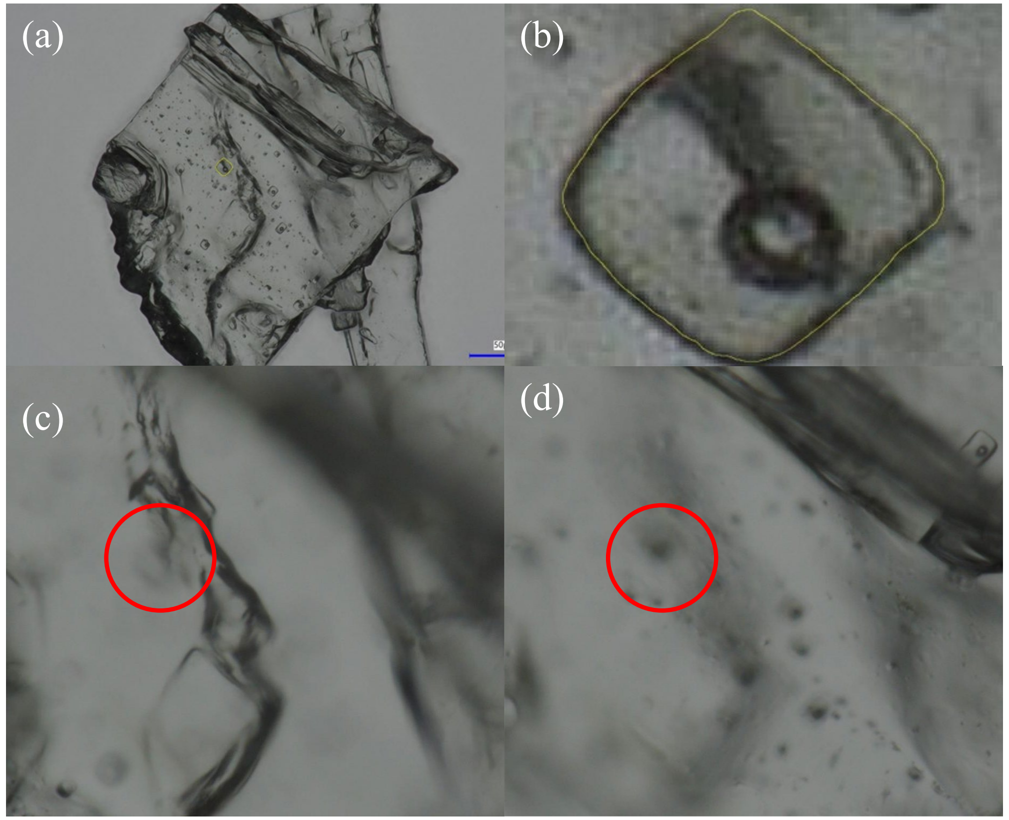
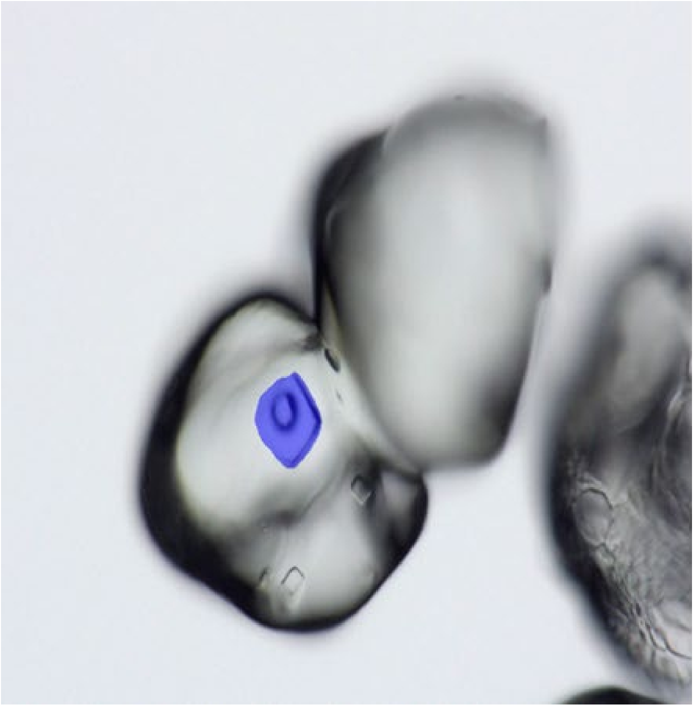


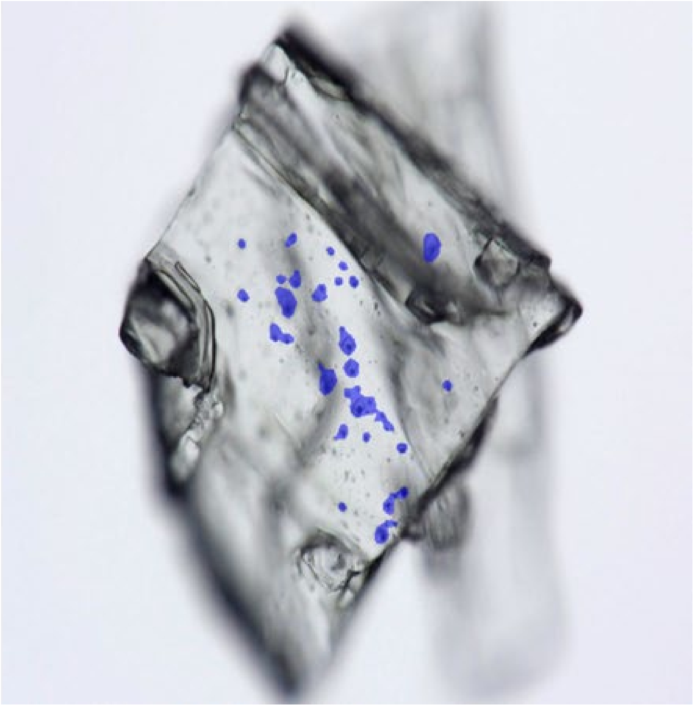
Figure from Goldstein and Reynolds (1994)

Estimation of fluid inclusion volume



- Transmitted light optical microscopy and analysis using ImageJ
- ML-model developed to segment two-phase fluid inclusions
- Grain-to-grain volume highly variable, ranging from 0.02 - 1.79 volume %
- Manual vs automated results generally agree





Salt	ML Model Volume (μm^3)	Total Volume Fraction (%)	Hand Segmented Volume (μm^3)	Total Volume Fraction (%)
NaCl-1 Grain 1	67164.9	0.65	177111.9	1.71
NaCl-1 Grain 2	9736.7	1.79	6006.4	1.10
NaCl-2 Grain 1	13928.3	0.05	N/A	N/A
NaCl-2 Grain 2	6762.6	0.02	N/A	N/A
NaCl-2 Grain 3	9911.7	0.02	N/A	N/A
KCl-1 Grain 1	1735.3	0.11	N/A	N/A
KCl-1 Grain 2	35188.9	1.00	61431.5	1.70
KCl-1 Grain 3	14022.9	0.13	53382.4	0.50
KCl-2 Grain 1	29164.8	0.09	N/A	N/A
KCl-2 Grain 2	4826.8	0.04	N/A	N/A
KCl-2 Grain 3	5149.1	0.11	N/A	N/A

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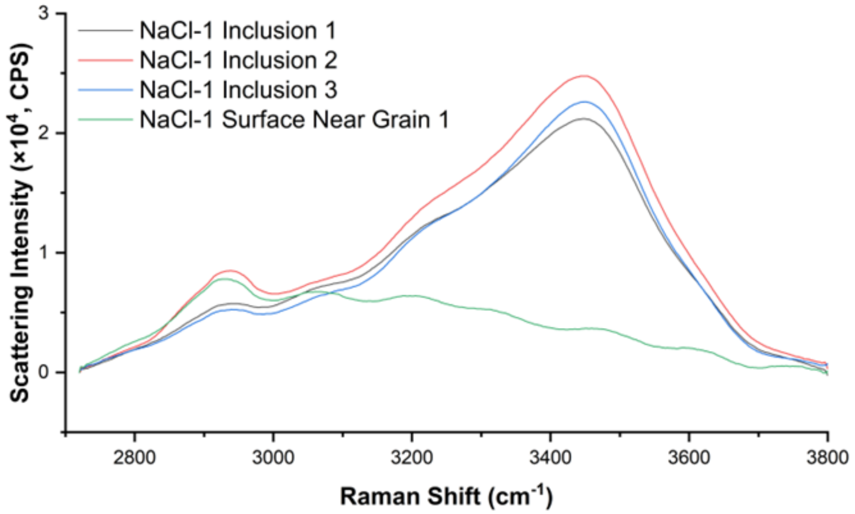
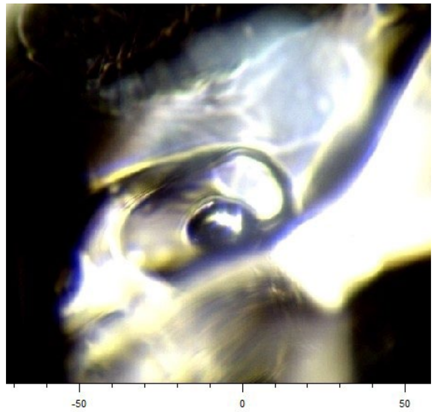
Fluid inclusion chemistry

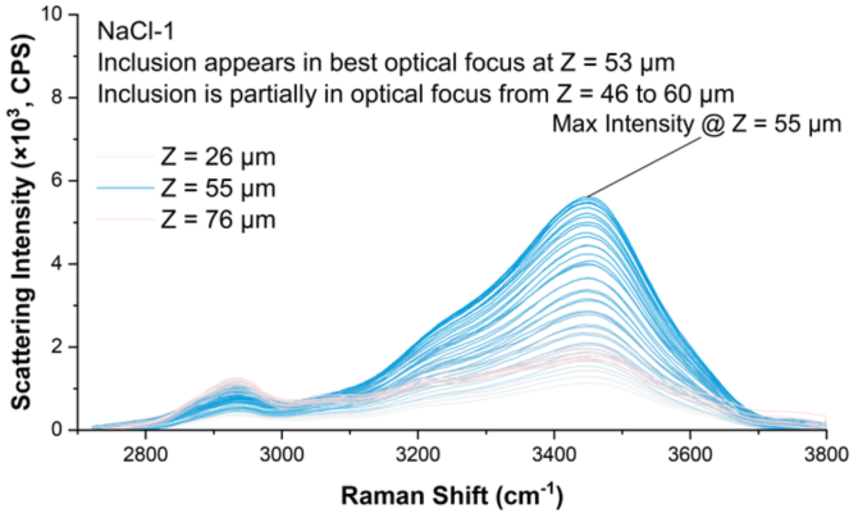
- It was assumed most commercial salts are precipitated from an aqueous solution; however, some may be derived from ionic solutions
- Two-phase inclusions analyzed by micro-Raman spectroscopy
  - In situ
  - Non-destructive

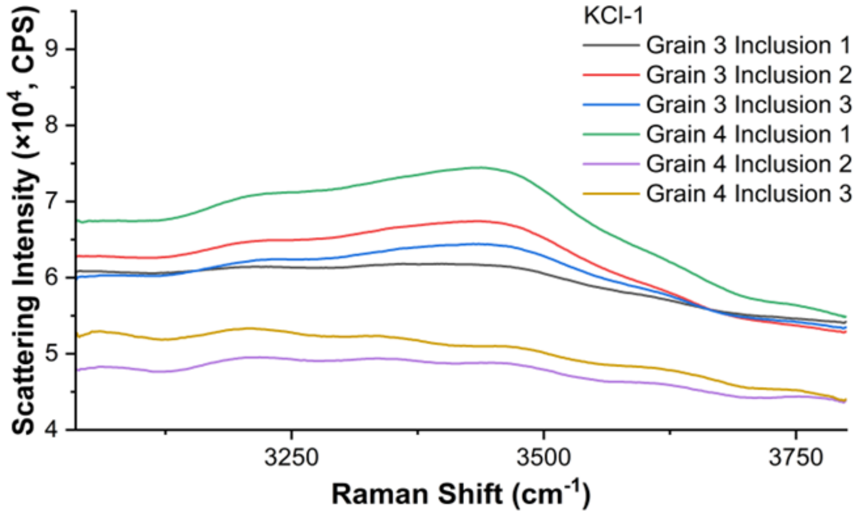
Fluid inclusion chemistry

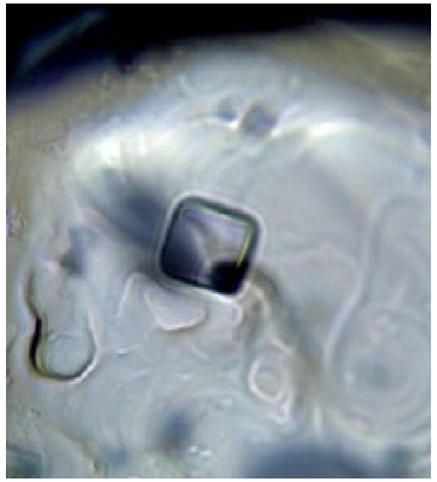
- Three to five inclusions investigated from NaCl and KCl
- Measurements taken at center (z-axis) of inclusion
- Depth profiles from surface to base

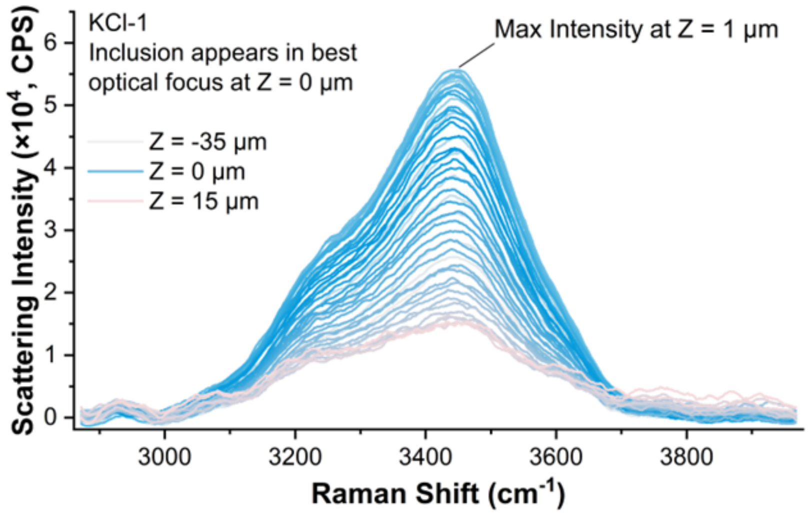




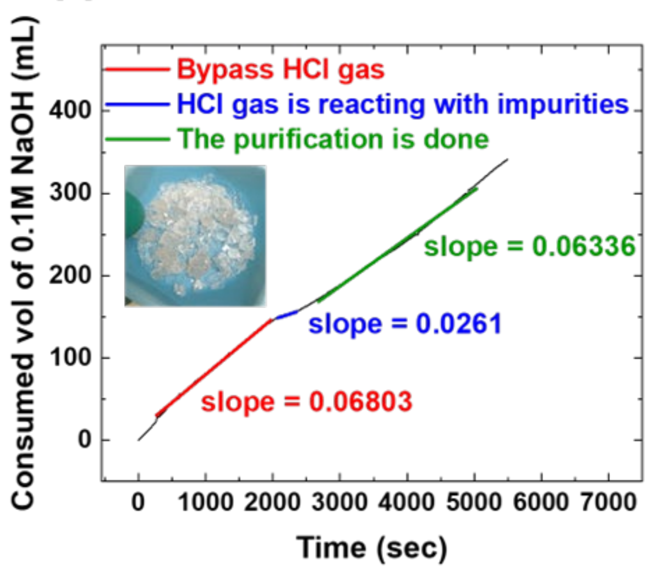


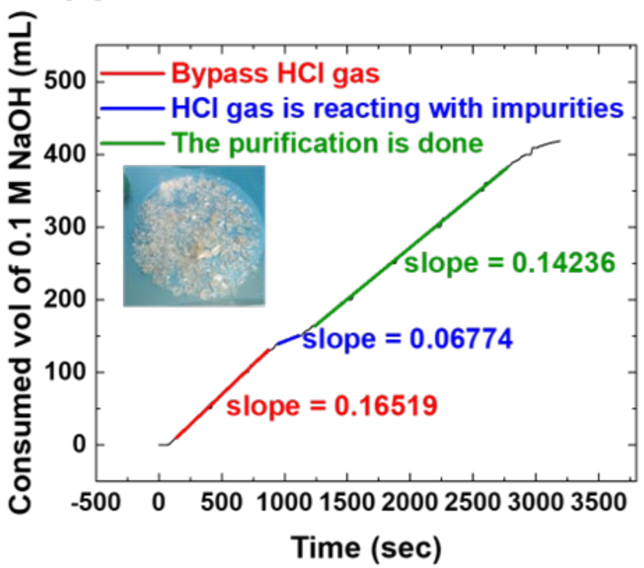


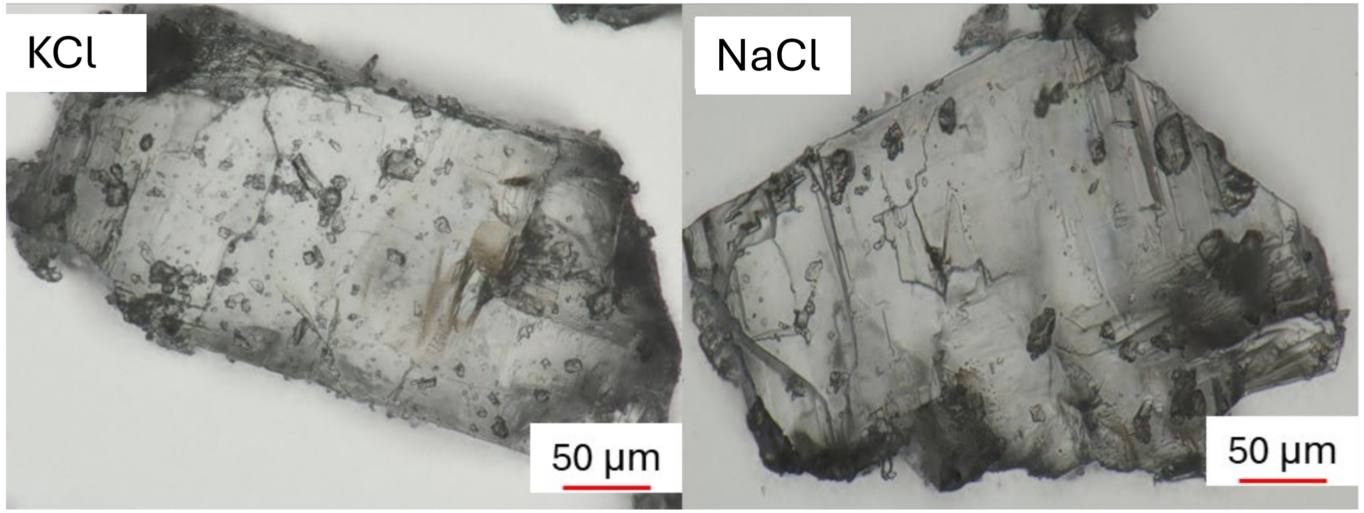




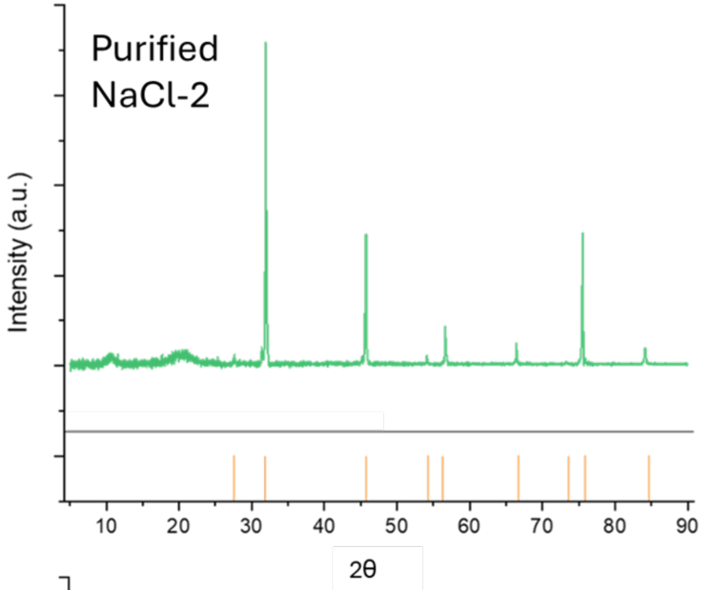
Effects of fluid inclusions on melting point

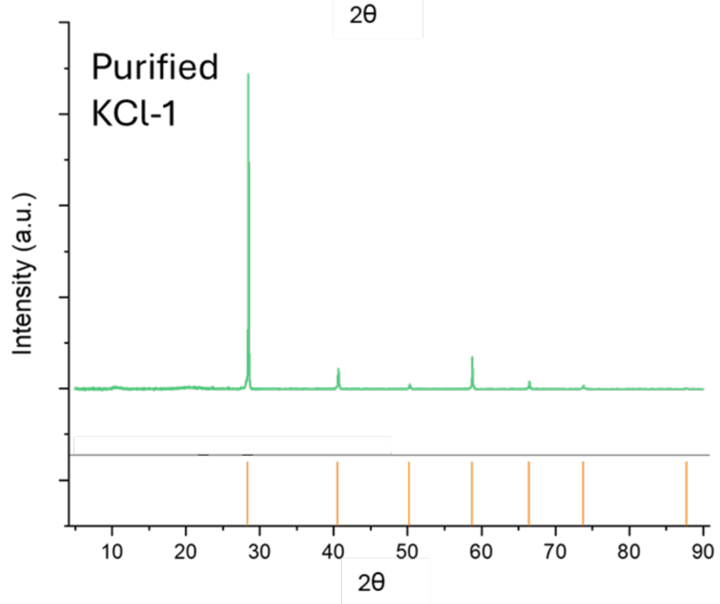




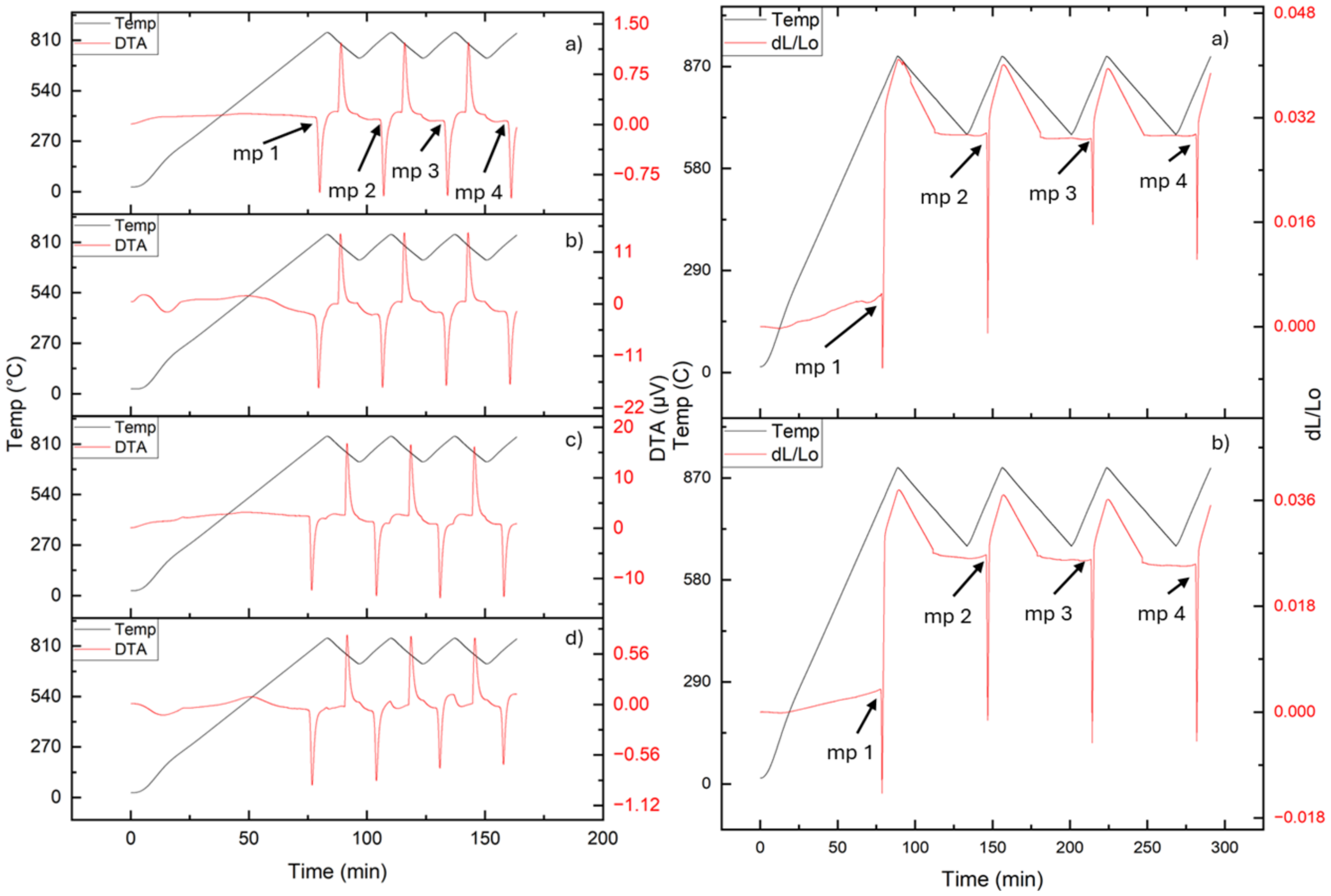


- Subsamples of NaCl and KCl used for fluid inclusion analysis were purified by hydrochlorination
- Phase purity confirmed by inert-XRD
- Transmitted light optical microscopy confirms no fluid inclusions are present in the purified salt





Effects of fluid inclusions on melting point



- Melting point measured by differential thermal analysis and thermomechanical analysis
- Unpurified-purified pairs evaluated for both NaCl and KCl
- Hypothesis- first melt temperature will be lower than subsequent melt temperatures due to fluid inclusions
- DTA shows little to no change in melting temperature
- TMA shows depression of NaCl melting temperature by ~5.5 degrees C (but this may only be an artifact of being the first melt from pressed powder)

Salt	First Melt Temperature (°C)	Average Temperature of Subsequent Melts (°C)	Cited Melting Point (°C)
NaCl-1 As Received	807.1; 798.7	807.2; 804.0	800.9 ± 2.1[1]
NaCl-2 As Received	806.9;	807.1;	
NaCl-2 Purified	803.6; 797.6	803.7; 803.1	
KCl-1 As Received	775.1; N/A	775.5; N/A	775.1 ± 2.1[1]
KCl-1 Purified	775.7; N/A	774; N/A	

FY25 Thermophysical Property Method Development and Results

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Development of Thermomechanical Analysis for density measurements

Motivation:

- Commercially available instrumentation
- Reduced sample size
- Hazard mitigation

Mass Correction:

Total annular volume is unknown

Initial mass

higher density

Total mass ~ constant

Not high enough to fully explain volume drift

Volume Corrections:

Blank correction

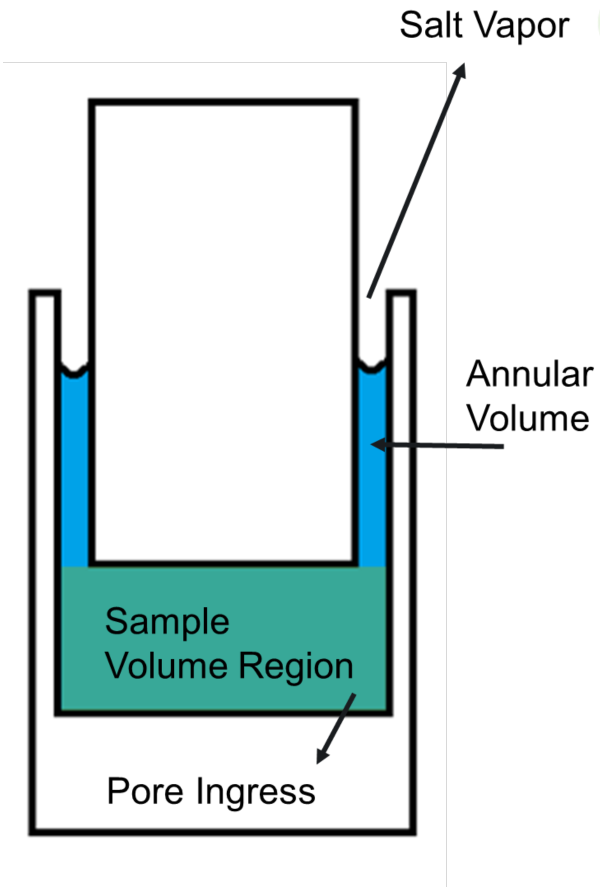
Instrument expansion

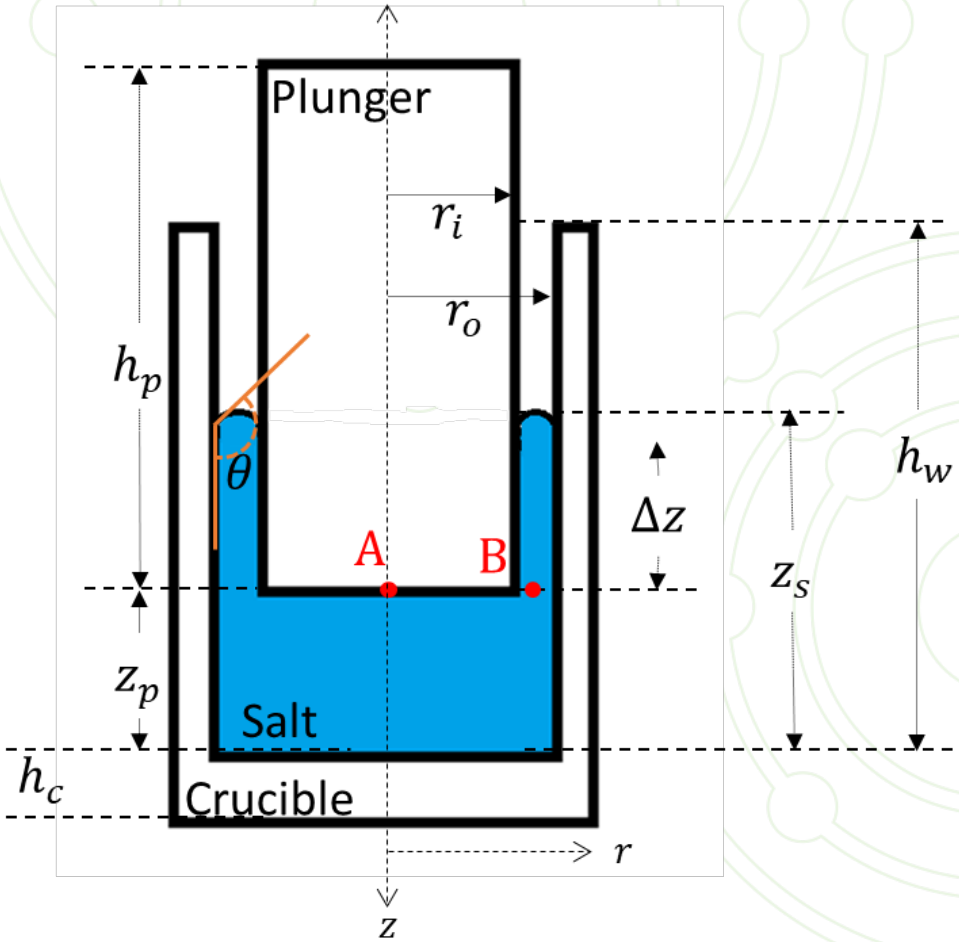
Liquid Transition and Flow

Crucible expansion

Radial expansion

Axial Expansion





$$V_s(T) = V_s(T_0)\left[1 + 2\alpha_r \Delta T + \frac{\Delta h(T) - \alpha_h \Delta T\left[h_{c_0} + h_{p_0}\right]}{h_0 - h_{c_0} - h_{p_0}}\right]$$

Crucible Design Criteria for Annular Leaks

Annular Leak Prevention:

- Buoyancy
- Instrument Force
- Surface Tension/Contact Angle (ST/CA)

Surface Tension/Contact Angle :

- **ONLY** force that does not increase the fluid level in the annulus (Δz) when contact angle is non-wetting (>90°)

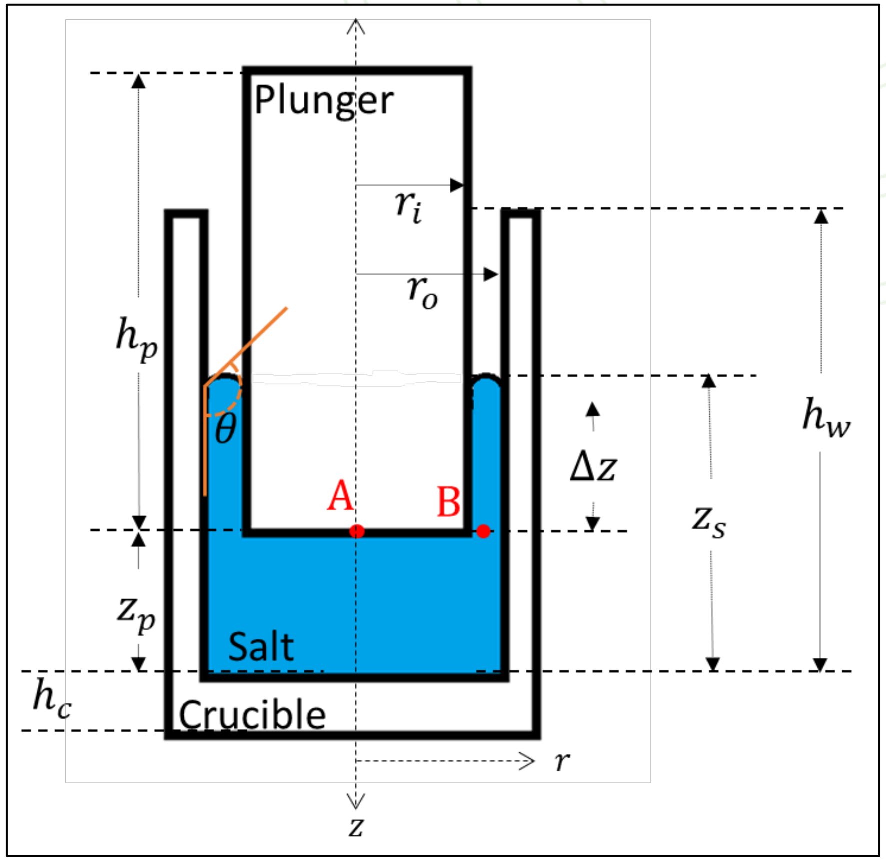
$$\Delta z = \underbrace{\frac{\rho_p h_p}{\rho_s \kappa^2}}_{\text{Buoyancy}} + \underbrace{\frac{F_n}{\rho_s g \pi r_o^2}}_{\text{Instrument Force}} + \underbrace{\frac{2\sigma \cos(\theta)}{\Delta r \rho_s g \kappa}}_{\text{ST/CA}}$$

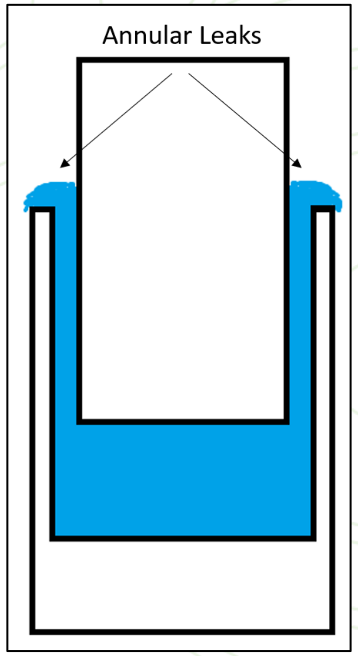
where

$$\kappa = \frac{r_o}{r_i} \; and \; \Delta r = (r_o - r_i)$$

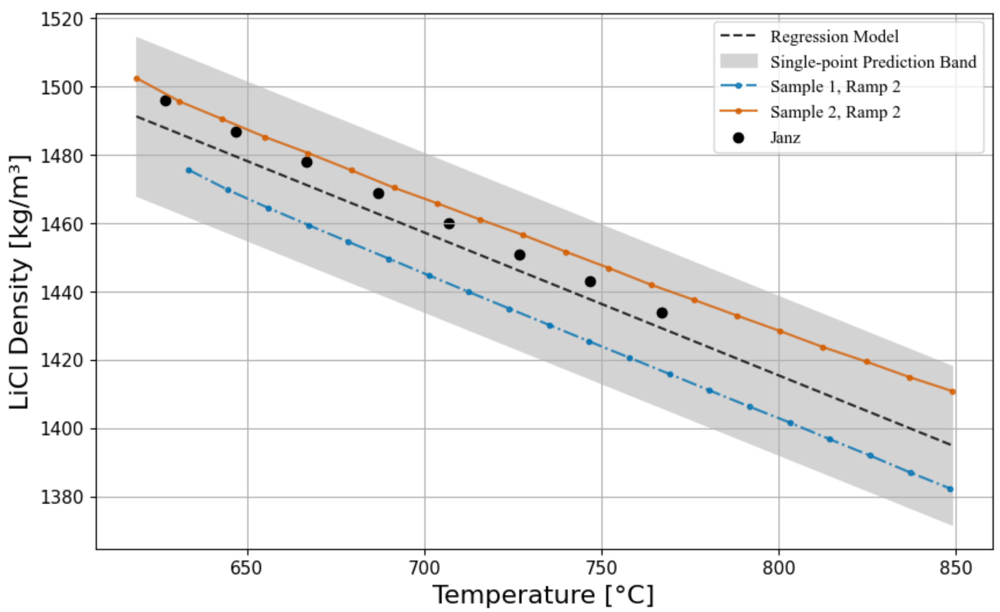
- For a known sample volume, the level in the anulus is known:

$$z_s = \frac{V_{salt}}{\pi r_o^2} + \Delta z \left(\frac{1}{\kappa^2} - 2 \right)$$





Density Results



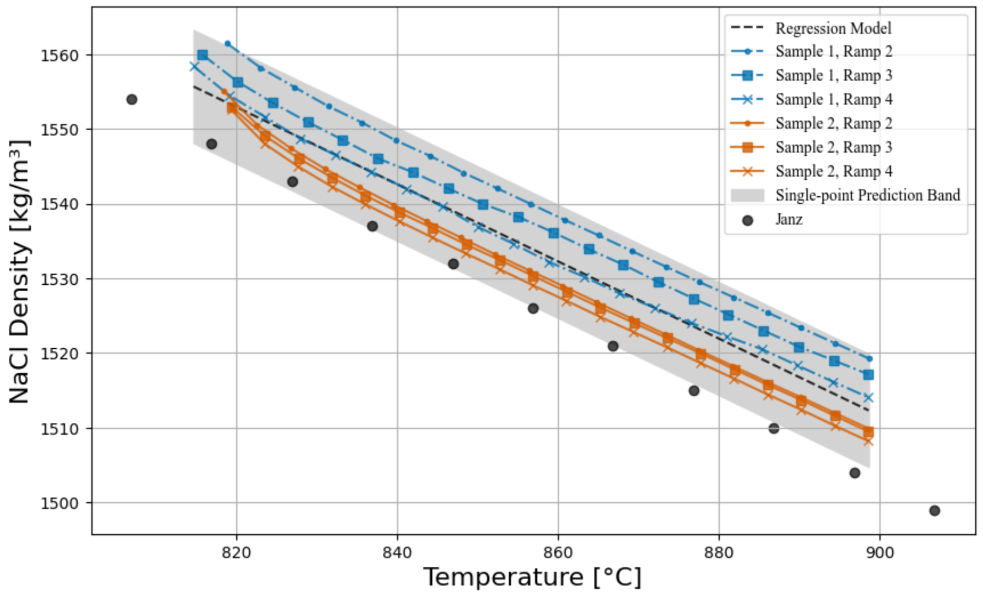
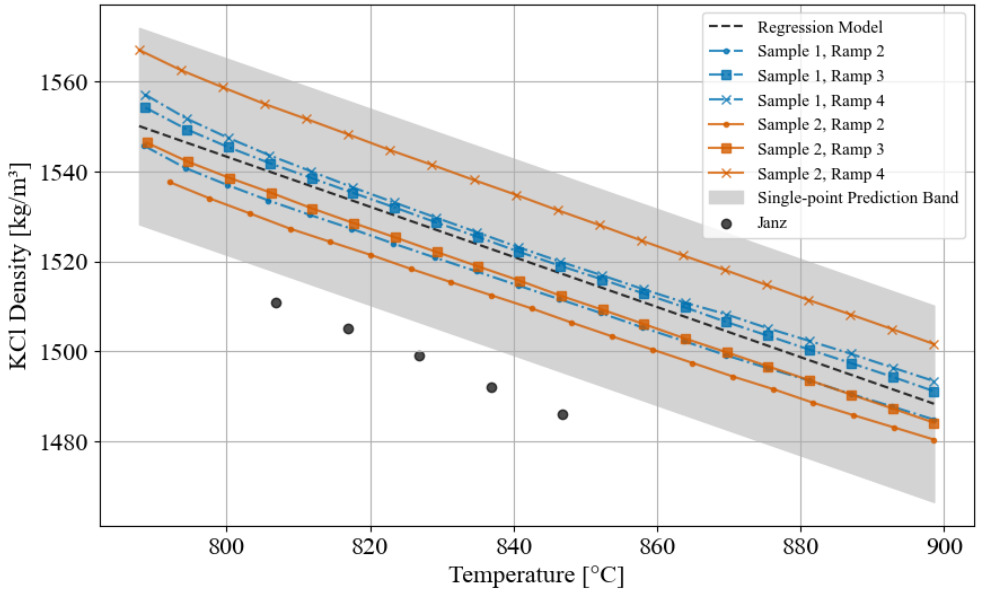


Table 4.2: Volumetric expansion coefficient data compared to those values calculated from the recommended data in Janz et al. [1].

Salt	This Work $\beta/[\mathrm{K}^{-1}] \cdot 1\times10^4$	Janz $\beta/[\mathrm{K}^{-1}] \cdot 1\times10^4$	Relative Error
LiCl	2.75 ± 0.29	3.02	-8.9%
NaCl	3.47 ± 0.11	3.66	-5.3%
KCl	3.66 ± 0.12	4.17	-12.3%



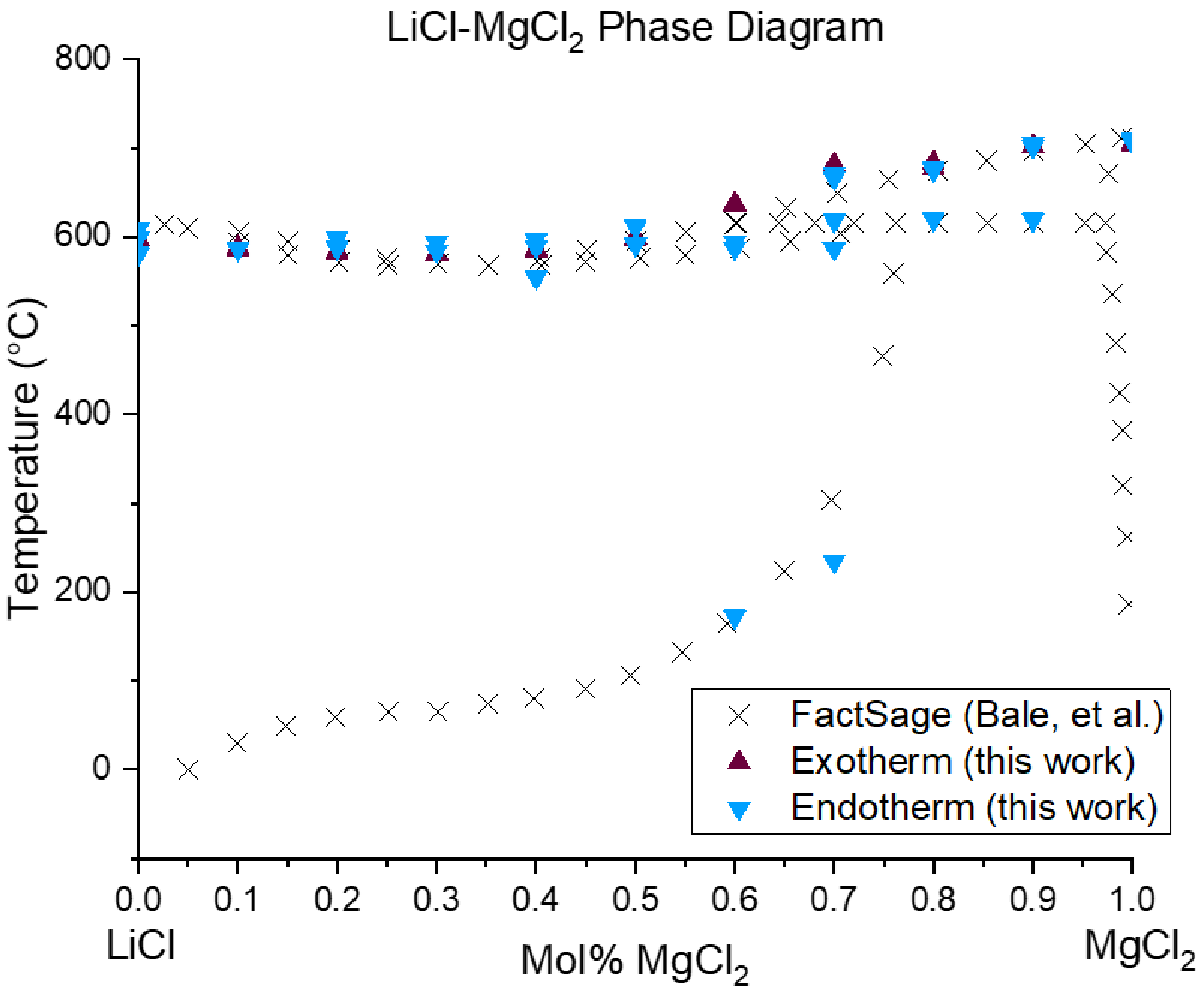
Density and Melting Point Results

Table 4.1: Linear regression, best fit model for TMA data collected as part of this study, for density of each molten salt has the parameters in this table using equation, $\rho\left[\frac{kg}{m^3}\right] = m \cdot T[°C] + b$. Average mass loss rate based on mass correction slope.

Salt	$m/\left[\frac{kg}{m^3 \cdot °C}\right]$	$b/\left[\frac{kg}{m^3}\right]$	Average mass loss rate, $\left[\frac{\mathrm{mg}}{\mathrm{min}}\right]$	Melting Point, $[°C]$
LiCl	-0.4186 ± 0.0054	1770.3 ± 4.0	-0.066	610.1 ± 8.5
NaCl	-0.5162 ± 0.0038	1976.1 ± 3.2	-0.013	803.9 ± 2.6
KCl	-0.5570 ± 0.0086	1988.9 ± 7.3	-0.022	777.3 ± 1.6

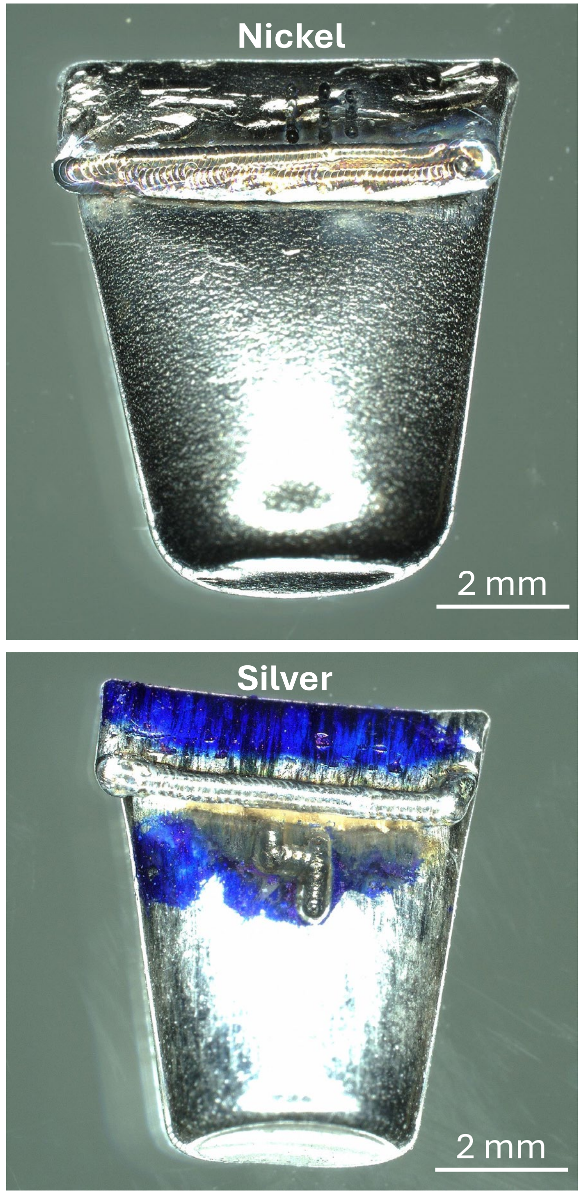
Phase Mapping of LiCl-$MgCl_2$ Binary

- Samples increased by 10 mol% $MgCl_2$
- Endothermic curves corresponds to solidus lines of the phase diagram
- Exothermic curves correspond with liquidous lines of the phase diagram.
- Measurements from the TGA-DTA correspond with the modeled phase diagram.
- Low temperature (<150°C) were not collected due to instrument limitations



Bale, C. W., E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, A. E. Gheribi, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, and M. A. Van Ende. 2016. "FactSage thermochemical software and databases, 2010–2016." *Calphad* 54: 35-53. https://doi.org/10.1016/j.calphad.2016.05.002.

New Capability- Inert Laser Welder



- Inert glovebox equipped with ytterbium fiber laser (Model: YLR-300/3000-QCW by IPG photonics)
  - Allows max peak power of 3000 W in quasi continuous wave mode

- Laser welder used to seal sample crucibles for drop calorimetry

FY26 Thermophysical Property Preliminary Results

PNNL-SA-222192

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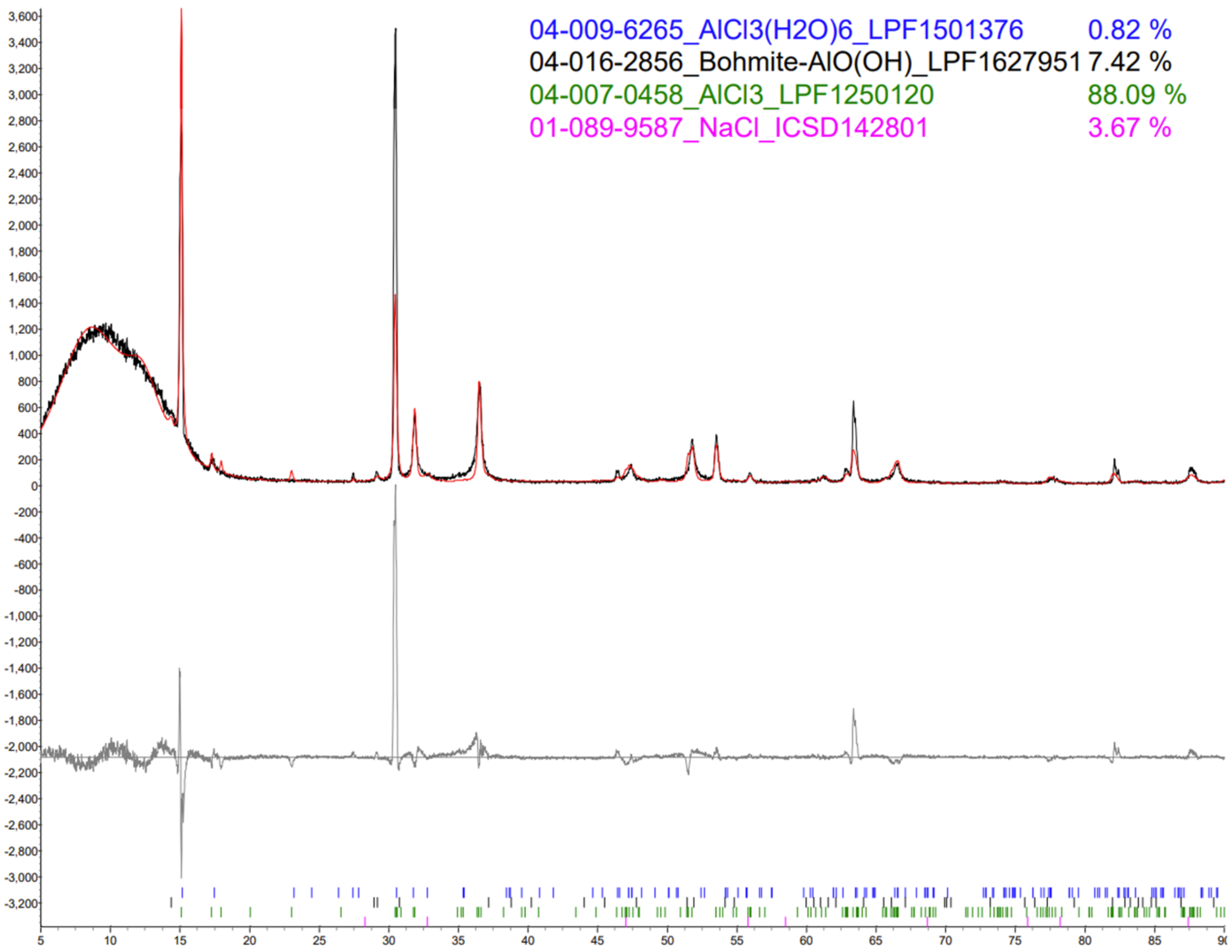
Source Aluminum (III) Chloride

- Purchased as ultra-dry, anhydrous
- X-ray Diffraction Scan Parameters:
  - 5-90 2/theta
  - 0.02 step
  - 1 dpm
  - RWP (error): 25%
  - Standard head (no rotation)
  - Dome holder
- Impurities assumed to be from synthesis process.



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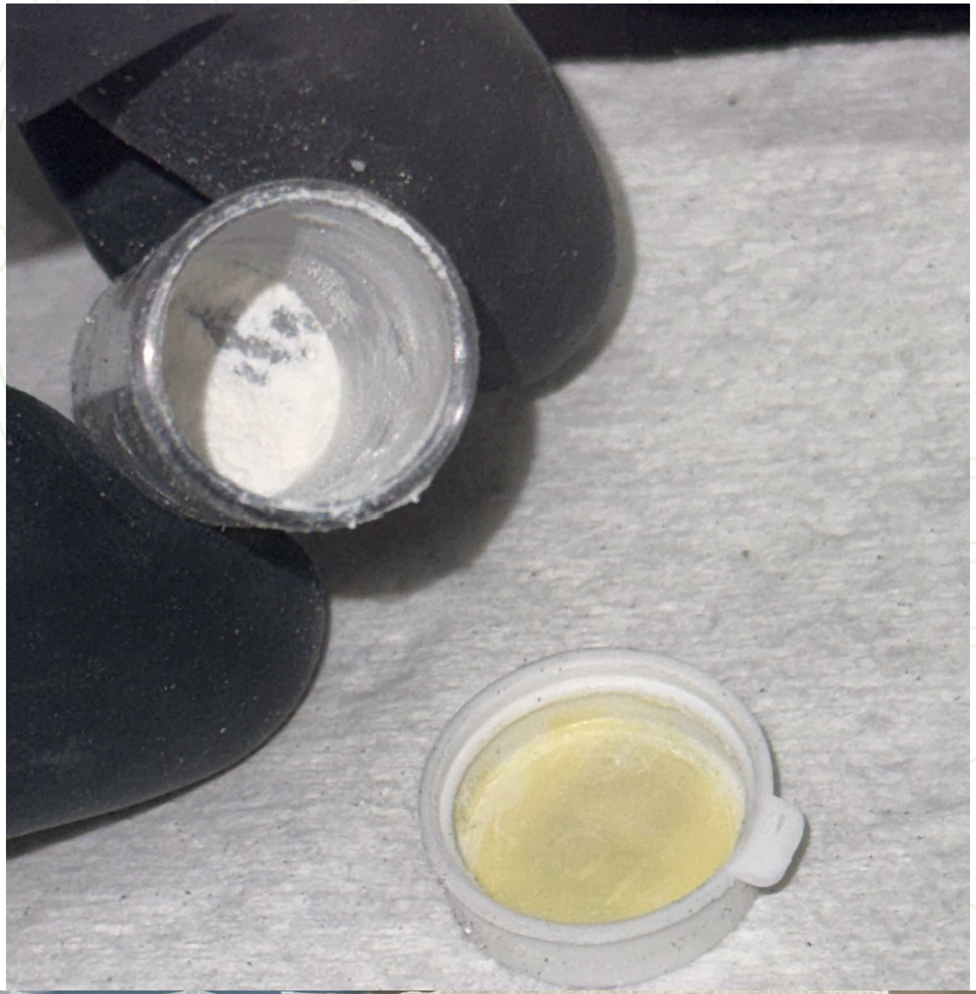
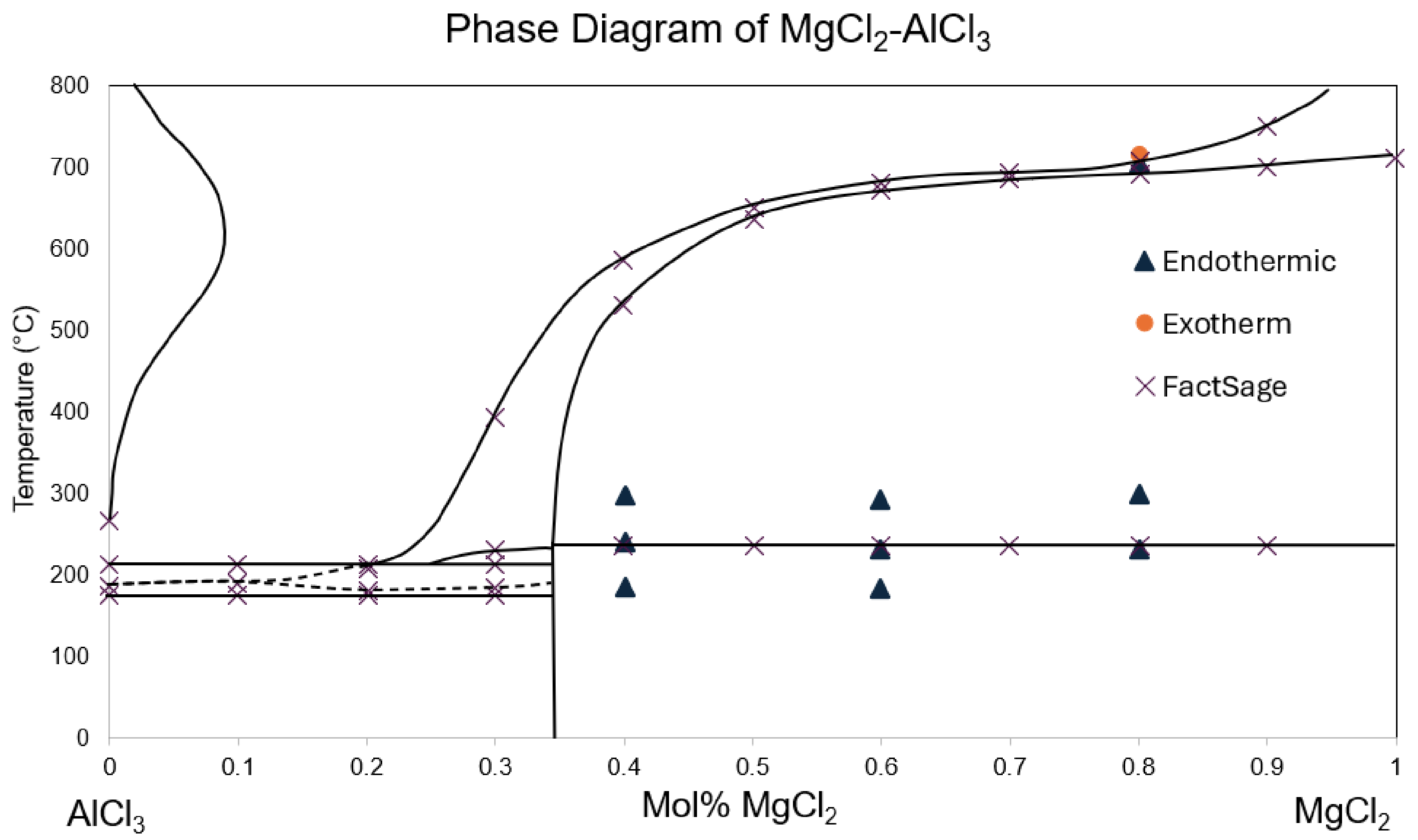
$AlCl_3$-$MgCl_2$ - Batching

- $AlCl_3$ and $MgCl_2$ compositions batched by mol%, increasing the $AlCl_3$ by 10%
- 9 samples total
- Massed in triplicate before mixing
- Mixed using miniature ball mill and ZrO_2 beads
- Mixing media and tubes were cleaned, rinsed with ethanol, and degassed in glovebox for 24 hours
- The discoloration is likely from vapor release of the unstable $AlCl_3$



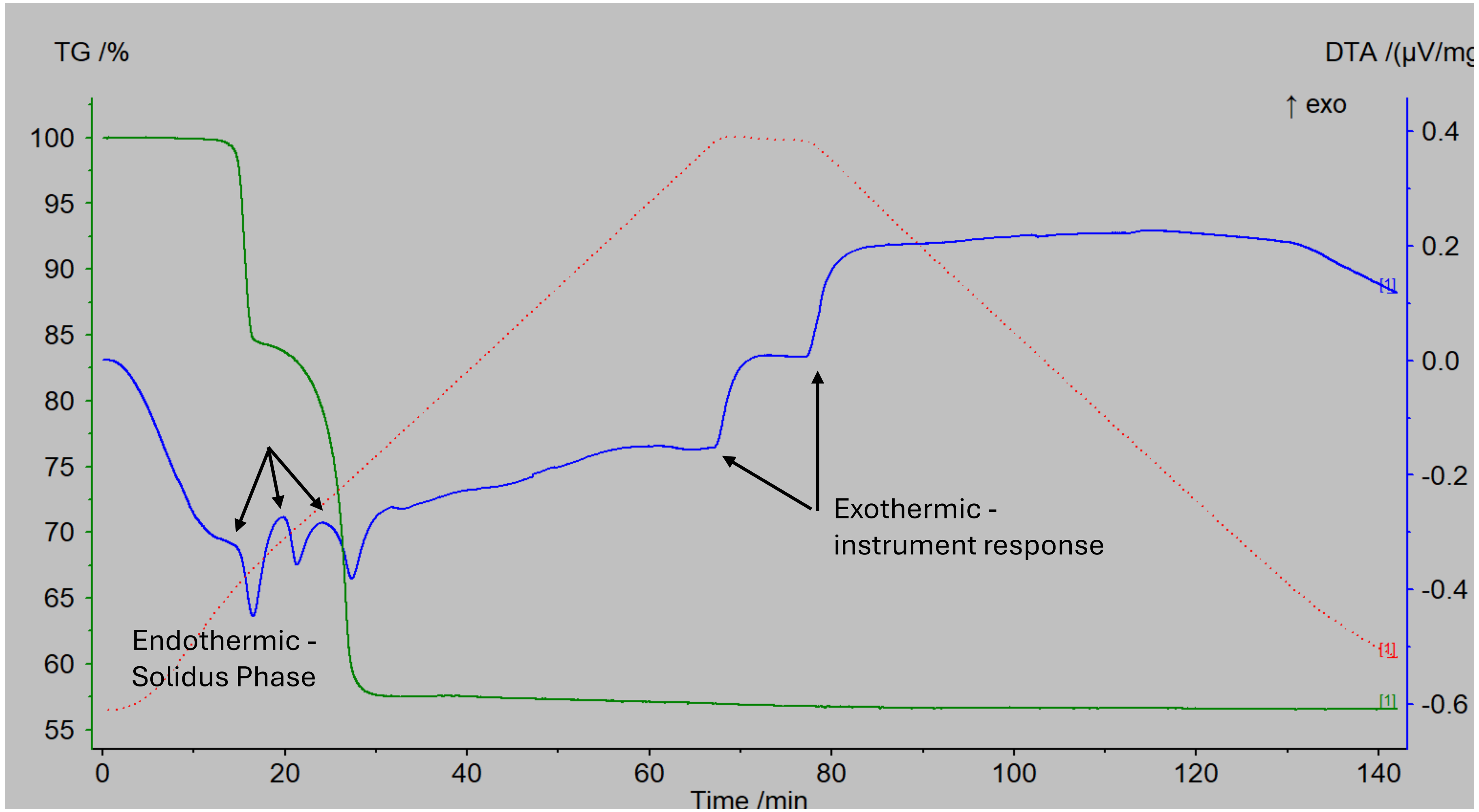
$AlCl_3$-$MgCl_2$ Phase Map – Preliminary Results

- Sample was prepared in inert atmosphere (N_2)
  - Loaded in nickel crucible
  - Crimped and folded
- NETZSCH STA449 with TGA/DTA stage
  - Temperature calibration conducted with standards (In, Sn, Zn, Al, and Ag) loaded in Ni crucibles.
  - Background correction conducted prior to each sample.
  - 10 °C/min heating rate to target temperature (50 °C above melting point)
  - 10-minute isothermal hold at target temperature
  - 10 °C/min cooling rate to 50 °C
  - 50 mL/min argon flow and 20 mL/min protective flow



$AlCl_3$-$MgCl_2$ - Discussion

- Material is highly reactive, corrosive, and volatile
- 50-80% mass loss during temperature profile
- Ni crucibles did not indicate corrosion damage or leaks
- Mass loss prevented phase change detection upon cooling

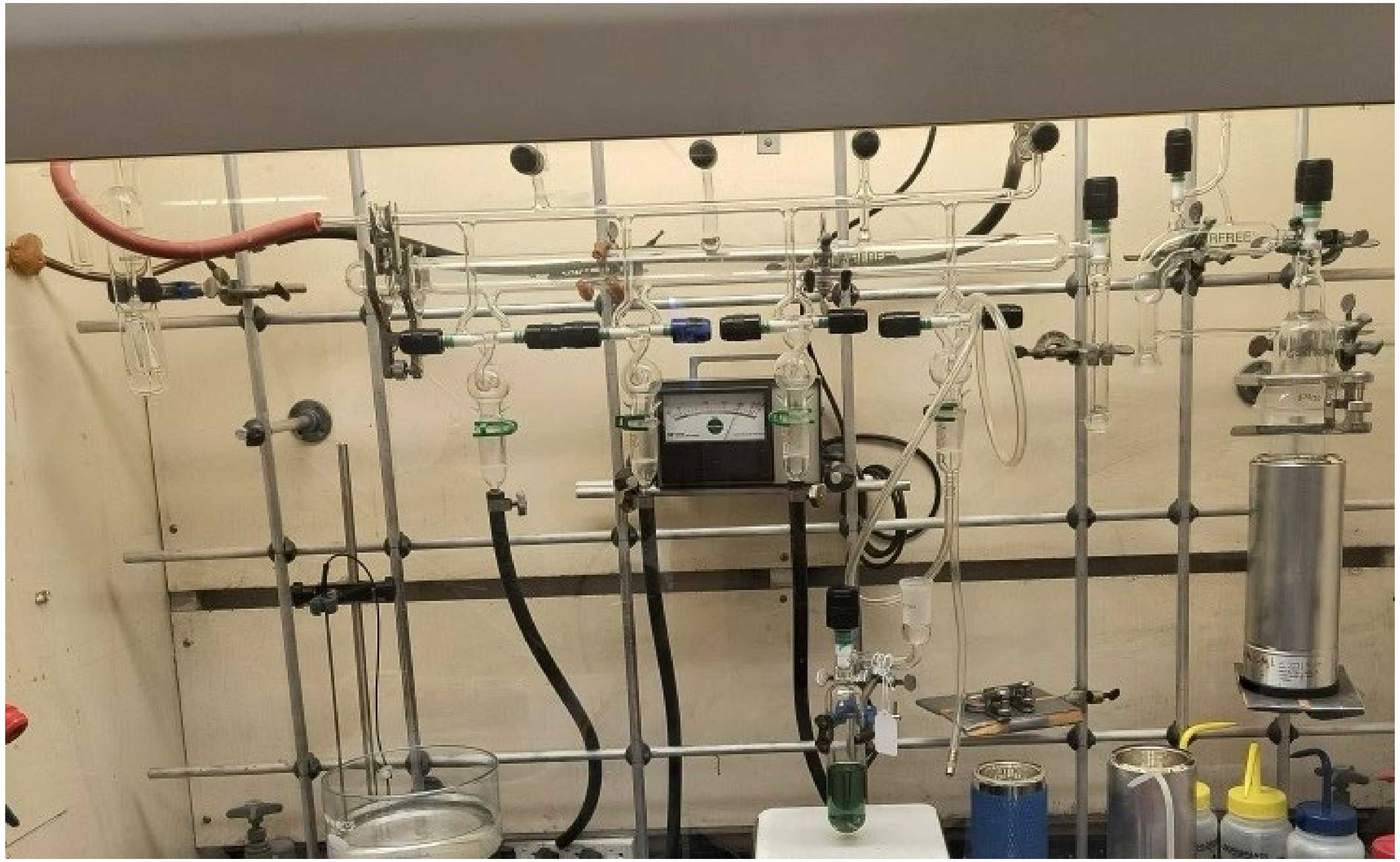


40 mol% $AlCl_3$ and 60 mol% $MgCl_2$

FY26- Synthesis Progress

Schlenk Line

- Inert gas/vacuum manifold
- Allows for reactions and manipulation of air- and water-sensitive materials and solutions
- Waiting on procurements and gas-line modifications before assembly of components



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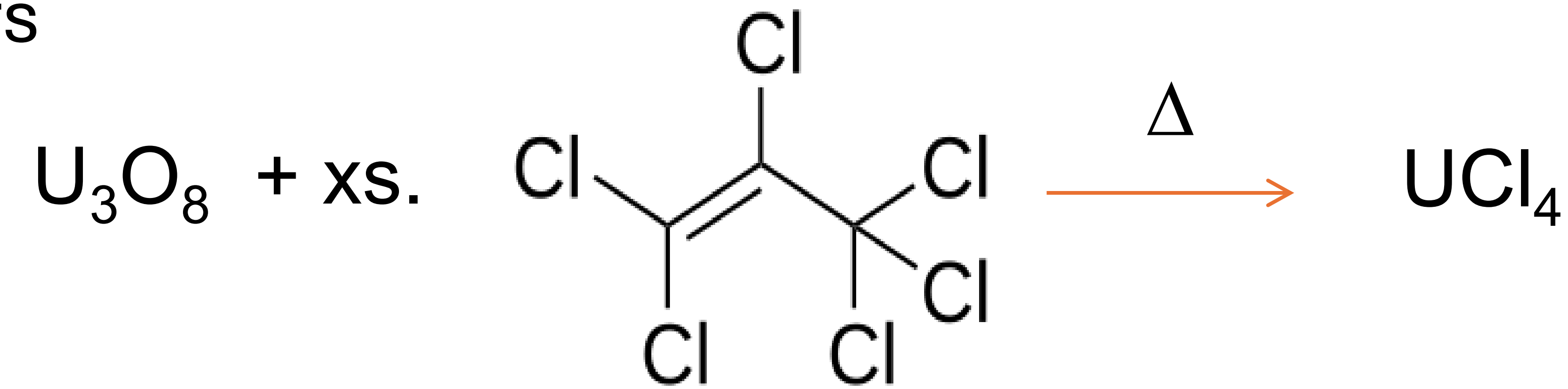
Conversion of U_3O_8 to Anhydrous UCl_4

- Reflux of U_3O_8 in excess hexachloropropene at ca. 180 °C
- Controlled, radical-initiated reaction
- Subsequent workup using dry dichloromethane solvent under inert atmosphere to remove polymerized byproducts and residual hexachloropropene
- Typical reaction time 12-24 hours



Kiplinger, et al. *Organometallics*, **2002**, 21, *26*, 5978−5982. 10.1021/om0206610.

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Conversion of U Metal Turnings to Anhydrous UI_3

- Clean U metal turnings with nitric acid to remove oxide layer
- Suspend the cleaned U metal in dry diethyl ether with dissolved iodine
- Catalytic amounts of GaI_3 and sonication are used to speed up the U metal oxidation and mitigate decomposition
- Typical reaction time 2-5 days at room temperature

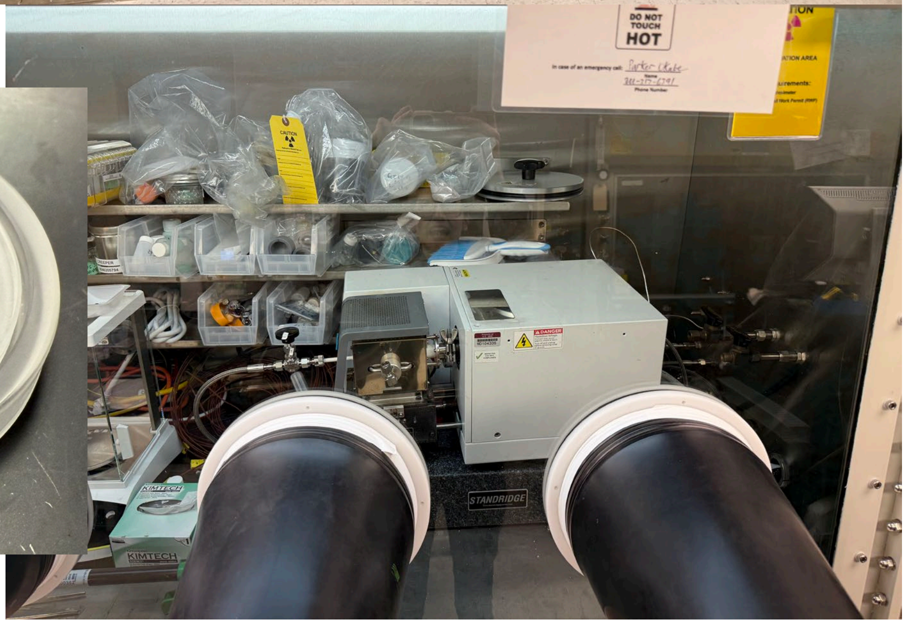
$$2U_{(s)} + 3I_2 \xrightarrow[\text{Et}_2\text{O, RT}]{\text{cat. GaI}_3} 2UI_3$$

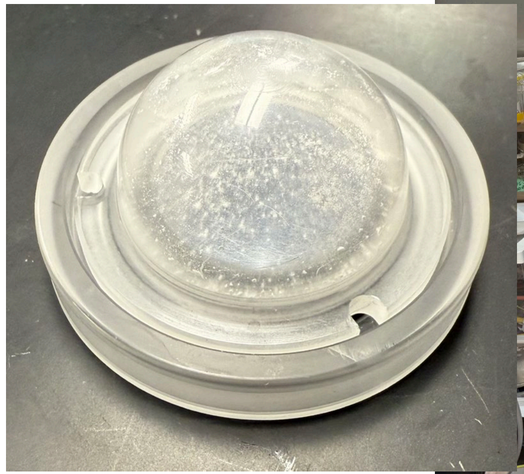
Arnold et al. *Inorganic Chemistry,* **2008**, 47, *19*, 8577-8579. 10.1021/ic801138e

Boncella et al. *Organometallics*, **2024**, 43, *3*, 284-298. 10.1021/acs.organomet.3c00458

Future Work

- Inert atmosphere working chamber with TGA/DTA commissioned and operational
- Establish Schlenk line and begin UI_3 and UCl_4 synthesis
- Determine density, heat capacity, and volatility of $AlCl_3$-$MgCl_2$
- Complete phase mapping of $AlCl_3$-$MgCl_2$
- Determine density and heat capacity UCl_4-$MgCl_2$,UF_3, and UI_3





Thank you!

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