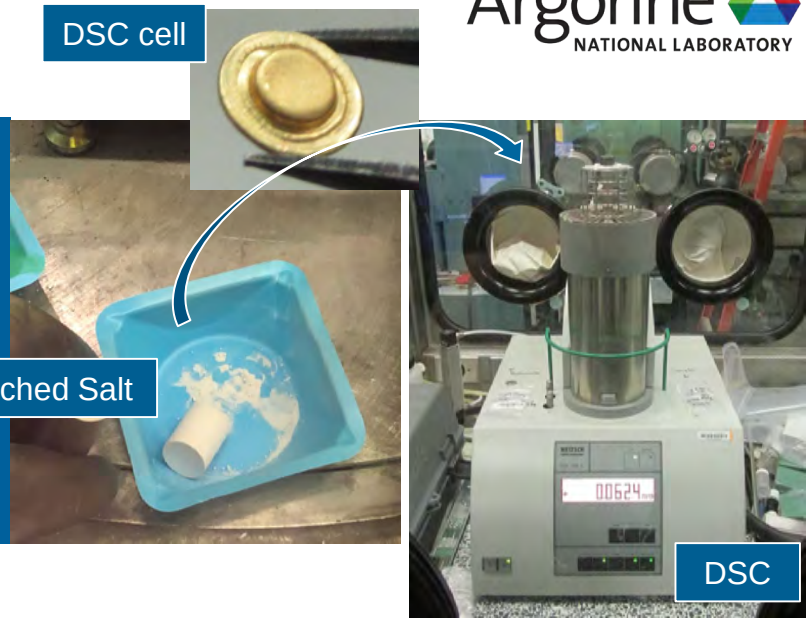
QUALITY ASPECTS OF MOLTEN SALT PROPERTY MEASUREMENTS



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OBJECTIVES

- Identify quality-affecting aspects of property measurements, sensitivities, and measurement controls to achieve NQA-1 data quality
  - Assess precision of measurements
  - Distinguish effects of salt composition and measurement limitations
- Determine property values of reference salts that can be used to compare methods and determine within-lab repeatability, lab-to-lab reproducibility, and bias
  - Develop consensus standard practices and methods through ASTM
  - Establish approved reference material salt (ARM-salt)

QUALITY OF PROPERTY DATA

- Affected by
  - Salt composition
  - Environmental factors
  - Instrumental uncertainties
  - Analytical limitations
  - Calculation method

QUALITY OF PROPERTY DATA

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  - Instrumental uncertainties
  - Analytical limitations
  - Calculation method
- Data quality assured by
  - Reagent purity and controlled batching
  - Controlled & monitored glovebox atmosphere
  - Reliable measurement procedures and device calibrations
  - Reliable reference and standard materials
  - Fundamental understanding

ARGONNE APPROACH

- Salt composition
  - Use batched compositions rather than measured compositions when possible
- Environmental factors
  - Require low and constant oxygen and humidity levels for data acceptance
- Instrumental uncertainties
  - Routine calibration checks of devices and instruments
  - Routine checks of responses with reference materials
  - Control chart calibrations and checks
- Analytical limitations
  - Replicate samples and replicate analyses
  - Reference materials
- Calculation method
  - Identify quality-affecting parameter values subjected to calibration checks
  - Use reference materials and standards for each parameter used for property determination

MEASUREMENT & TEST EQUIPMENT

- Mass
  - Balances calibrated by certified contractor
  - Performance checked daily before use with certified standard weights
  - Use consensus maximum permissible errors
- Dimensions
  - Use calibrated certified calipers, micrometers, depth gauge, bore gauge
  - Devices checked using certified gauge blocks and ring gauges before use
  - Use consensus maximum permissible errors
- Temperature
  - Purchase certified calibrated thermocouples
  - Check periodically using certified dry block
  - Thermocouple in salt-in-furnace used to calibrate furnace set points before use
- Other
  - XRD line standards from NIST
  - Pure metal melting standards for DSC
  - Sapphire heat capacity standard for DSC
  - Pure metal thermal diffusivity standard for LFA
  - Silicone viscosity reference

DENSITOMETER DATA QUALITY

- Calculate molten salt density (ρ) from measured mass difference of Ni bob in air and immersed in molten salt (Δm)

$$\rho = \frac{\Delta m + \frac{\pi D \sigma}{g}}{V_0[1 + \alpha T]^3}$$

D = diameter of hanging wire

σ = surface tension of salt

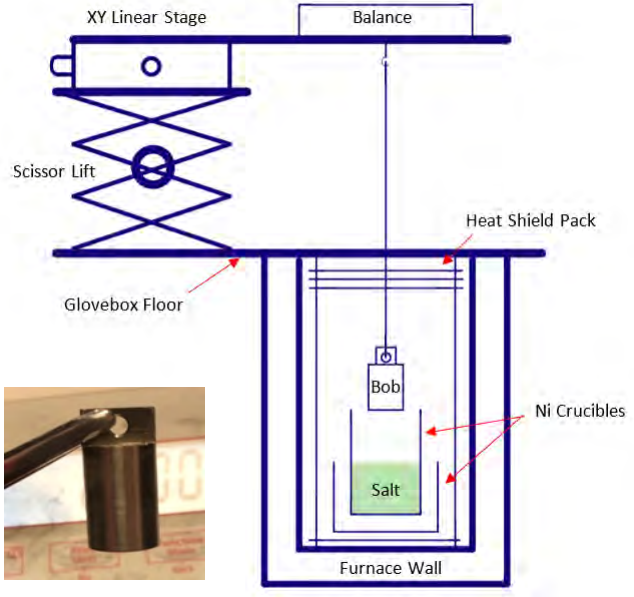
g = gravitational acceleration

V_0 = volume of bob

α = thermal expansion of bob

T = temperature

- Balance for mass (standard weights)
- Calipers for wire diameter (gauge blocks)
- Calibrated thermocouple for molten salt temperature (dry block)
- Ref values for π, g, thermal expansion and density of Ni (to calculate bob volume)
- Determine σ from densities measured with different bobs



DENSITY MEASUREMENT BY ARCHIMEDES METHOD

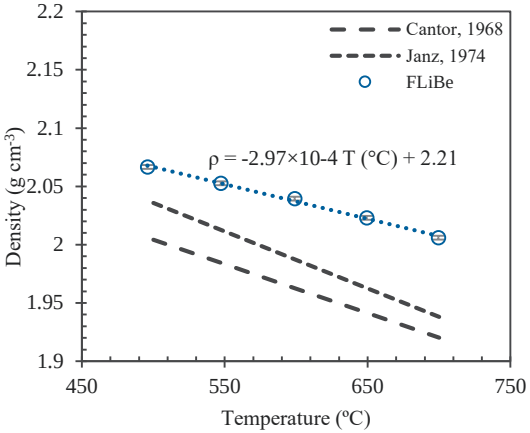
Data quality improvements include:

- Correct for surface tension
  - Depends on T and must be measured
  - Often not considered in the literature
- Checks for preferential volatilization
  - Causes change in salt composition
  - Salt condensing on the suspension wire affects measurement

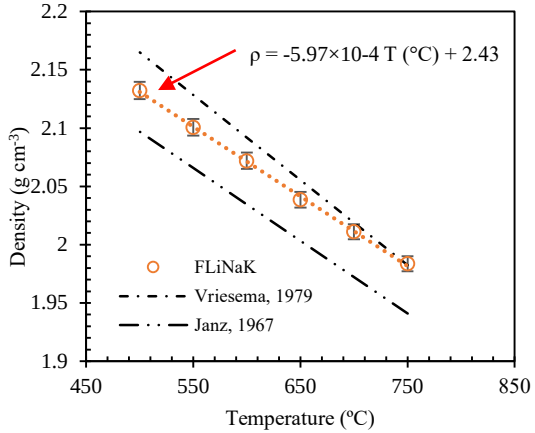
surface tension term

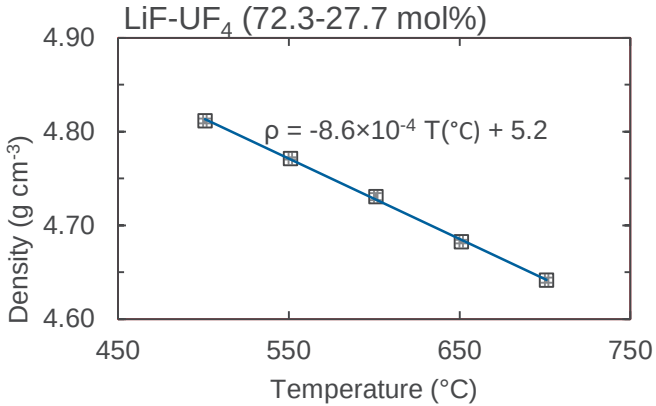
$$\rho = \frac{\Delta m + \frac{\pi D \sigma}{g}}{V_0[1 + \alpha T]^3}$$

FLiBe



FLiNaK

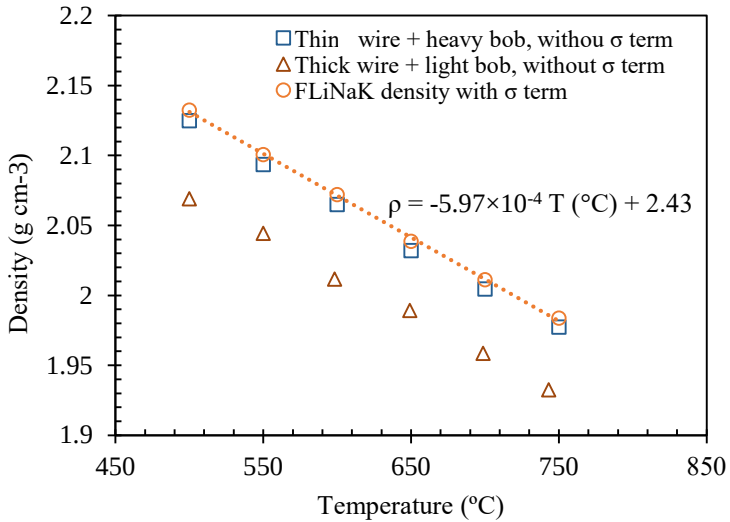




SURFACE TENSION

Calculated from two density measurements

- Surface tension (σ) is calculated from density measurements made at each temperature using two bobs of different mass with support wires of different diameter.



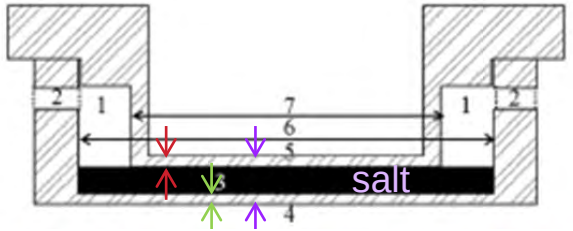
$$\rho = \frac{\Delta m + \frac{\pi D \sigma}{g}}{V_0[1 + \alpha T]^3}$$

Salt, Source	Surface Tension (N/m)
FLiBe, ANL	$\sigma = 1.20\times10^{-4}\,T\,(°C) + 0.329$
FLiBe, Janz [1988]	$\sigma = 1.00\times10^{-3}\,T\,(°C) + 0.365$
FLiNaK, ANL	$\sigma = -1.49\times10^{-4}\,T\,(°C) + 0.385$
FLiNaK, Janz [1988]	$\sigma = -1.01\times10^{-4}\,T\,(°C) + 0.245$

THERMAL DIFFUSIVITY

- Graphite sample holders fabricated to specifications that fix thickness of top and bottom graphite plates that constrain thickness of gap filled with salt
- Cell dimensions measured to verify thickness of salt analyzed

Graphite LFA Cells: closed (top) and open with the lid inverted (bottom left) and the crucible (left).



Schematic diagram of the crucible for measuring thermal diffusivity: 1-space for expansion; 2- holes for gas to escape; 3- molten salt; 4-crucible bottom; 5-lid bottom; 6-inner diameter; 7- inferior diameter.

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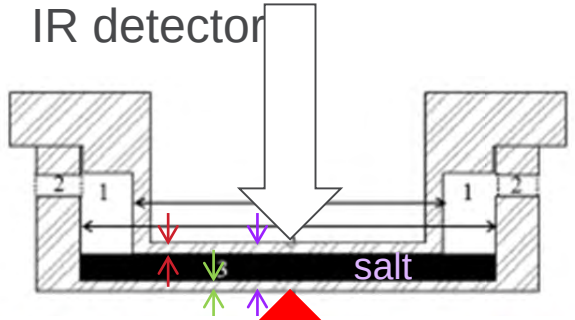


Schematic diagram of th… cible for measuring thermal diffusivity: 1-spa… or expansion; 2- holes for gas to escape; 3- molten …; 4-crucible bottom; 5-lid bottom; 6-inner diameter … inferior diameter.

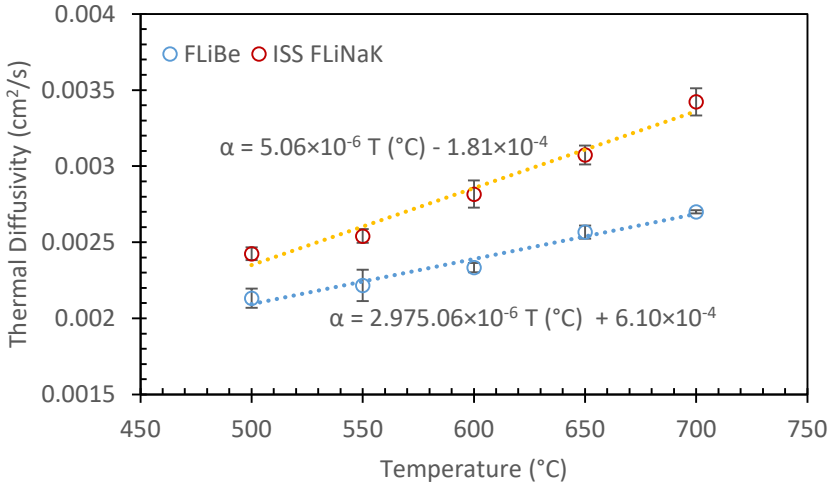
THERMAL DIFFUSIVITY MEASUREMENTS

LFA response is checked regularly with reference materials (Mo, SS, graphite, NaCl).

Molten salt is contained in custom graphite crucibles that provide uniform known thickness of salt.

Replicate measurements to quantify uncertainty
- multiple samples of each salt
- multiple measurements at each temperature

Thermal conductivity calculated from measured thermal diffusivity, heat capacity, and density



VISCOSITY CALCULATION

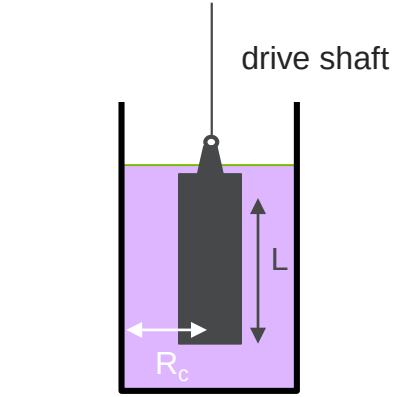
- Viscosity (μ) is the ratio of the shear rate (τ) to the shear stress (γ) produced by an applied torque (M)

$$\mu = \frac{\tau}{\gamma} \qquad \tau = \frac{M}{2\pi R_b^2 L} \qquad \gamma = \frac{2\left(\frac{2\pi}{60}N\right)R_c^2}{\left(R_c^2 - R_b^2\right)}$$

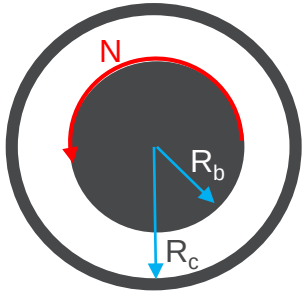
- Torque (M) required to rotate a spindle of know dimensions at a specific rotational velocity (N) used to calculate viscosity (μ) as

$$\mu = \frac{M\left(R_c^2 - R_b^2\right)}{8\pi^2 R_c^2 R_b^2 L\left(\frac{N}{60}\right)}$$

- Torque and rotational velocity not accessible; only viscosity provided at input rotational velocity in rpm



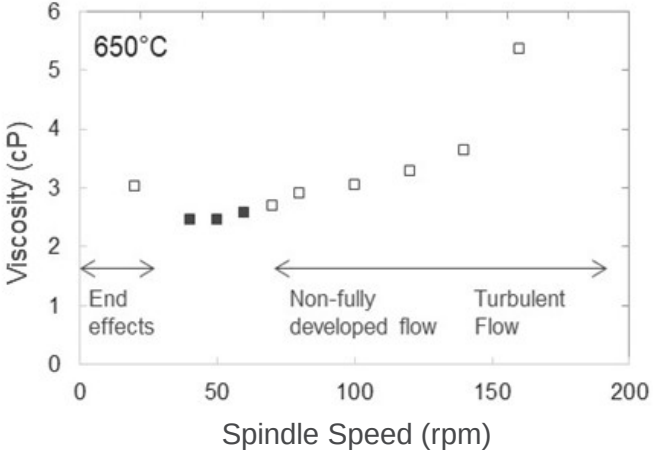
Side view spindle in crucible

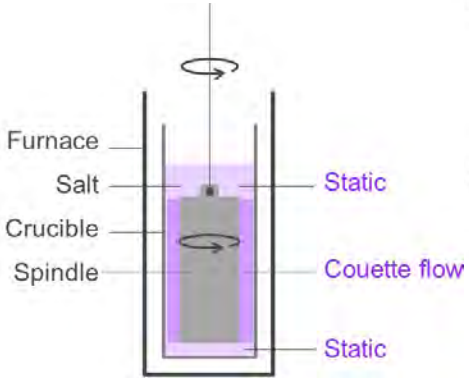


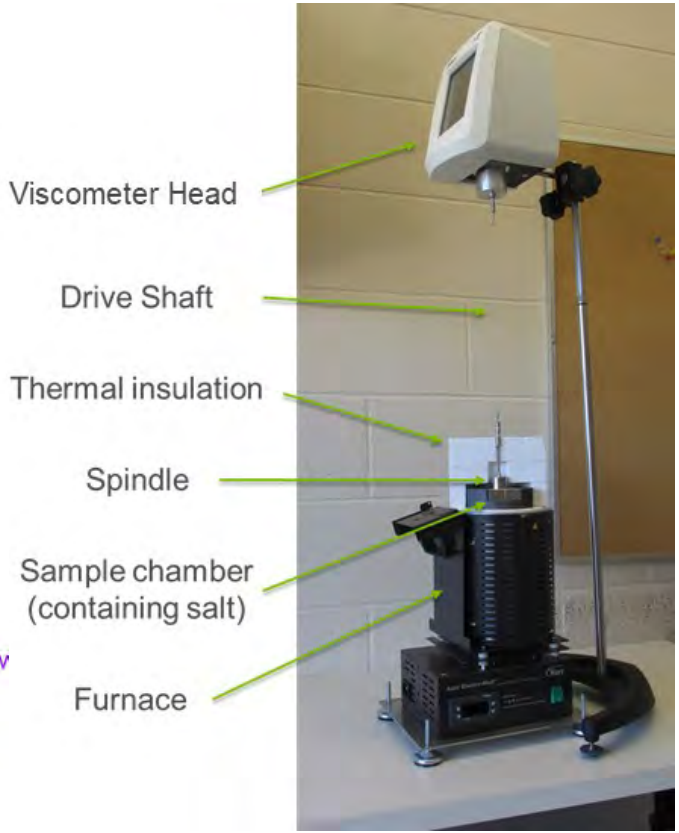
Top view spindle in crucible

VISCOSITY MEASUREMENT

- Commercial viscometer head paired with custom made metallic spindle and inert crucible
- Measurements made at several different rotational velocities to identify values affected by turbulent flow



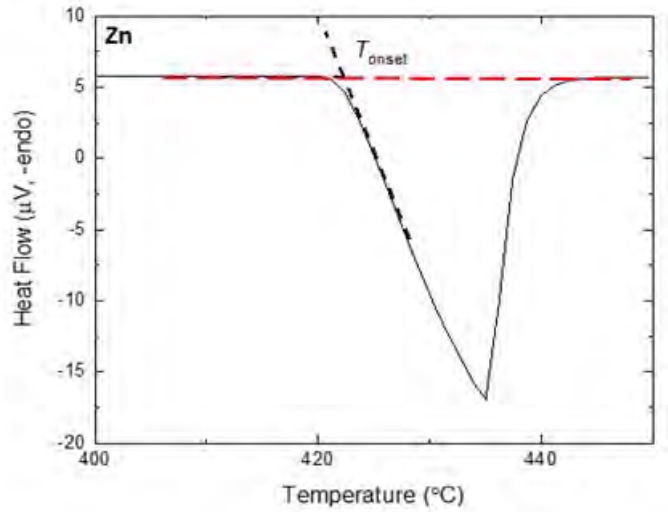




DIFFERENTIAL SCANNING CALORIMETER CALIBRATIONS

- Check balance calibration for measuring crucible, sapphire reference, and sample masses
- Use clock to verify scan rate
- Use pure metals to
  (1) check temperature readout

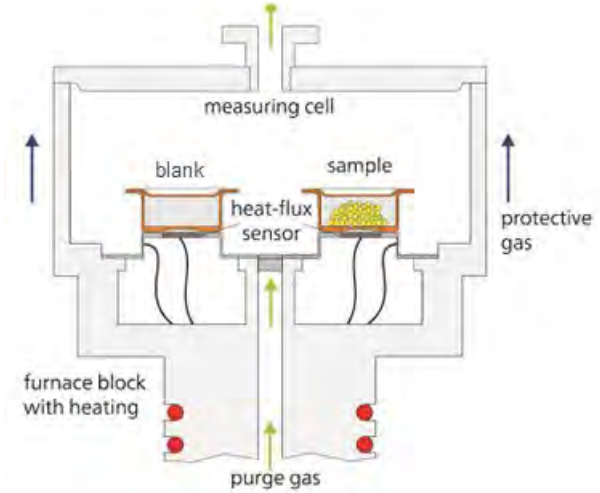
  (2) Check integrated heat flow during scan over fixed range (e.g., 400 to 450 C)



DIFFERENTIAL SCANNING CALORIMETRY (DSC)

gold crucible (empty)

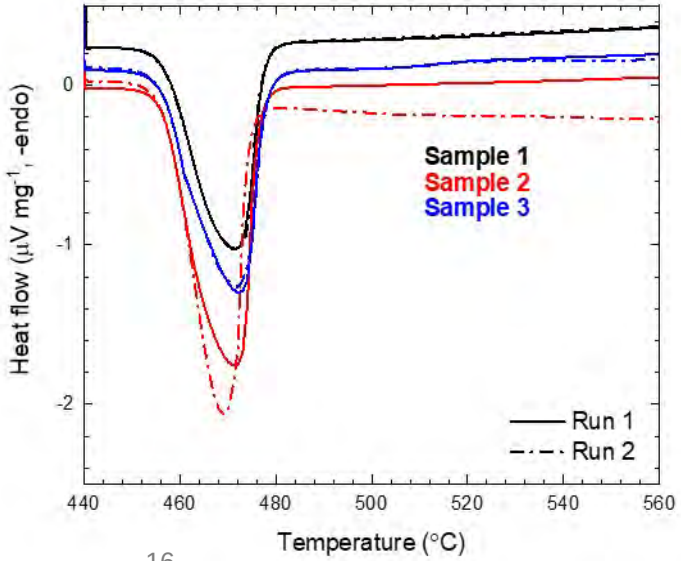
salt (sample)



Ramp temperature at constant rate and measure difference in heat flow through salt sample and empty crucible

Three samples analyzed to check composition homogeneity

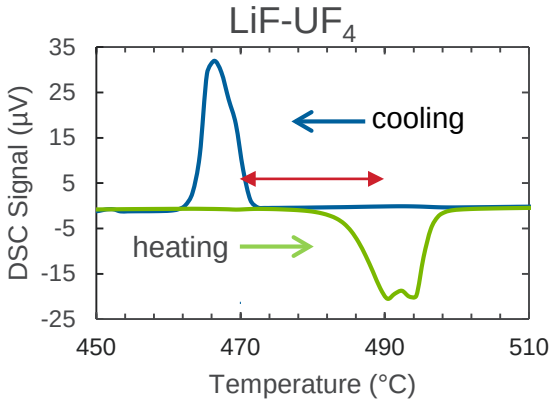
Two analyses run to check system stability



Good stability for Samples 1 and 3, but not Sample 2

THERMAL ANALYSIS

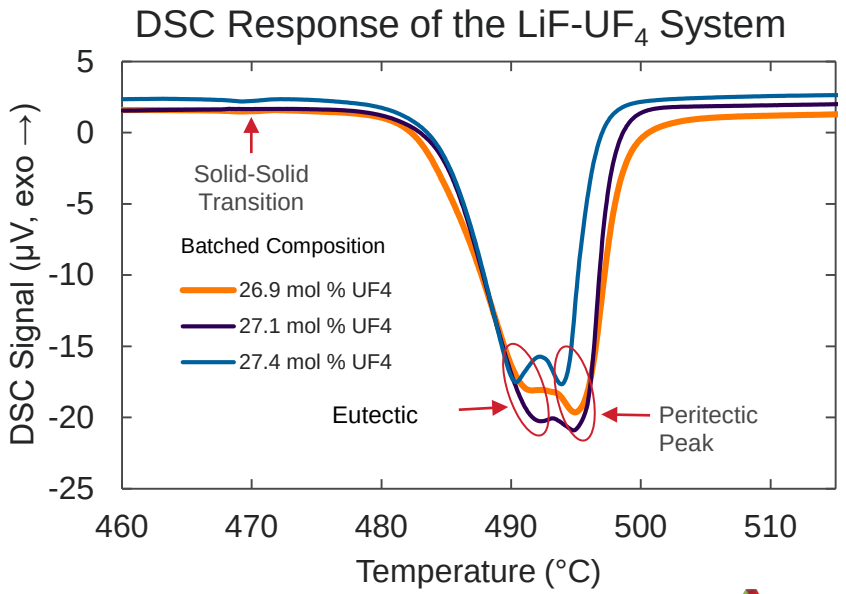
Using a Differential Scanning Calorimeter (DSC)



Significant super cooling can occur, so only use heating data

The DSC response is highly sensitive to small differences in concentration, particularly near eutectic compositions.

Salt mixtures can be batched more accurately than they can be analyzed:
10% analytical uncertainty → 2.7 mol % uncertainty.



HEAT CAPACITY

Using reference salts to optimize method and minimize uncertainty.

Ratio Method:

$$C_p^s = \frac{m_{st}}{m_s}\frac{\Delta\varphi_s}{\Delta\varphi_{st}}C_p^{st} + \frac{m_{cr}^{st} - m_{cr}^{s}}{m_s}C_p^{cr}$$

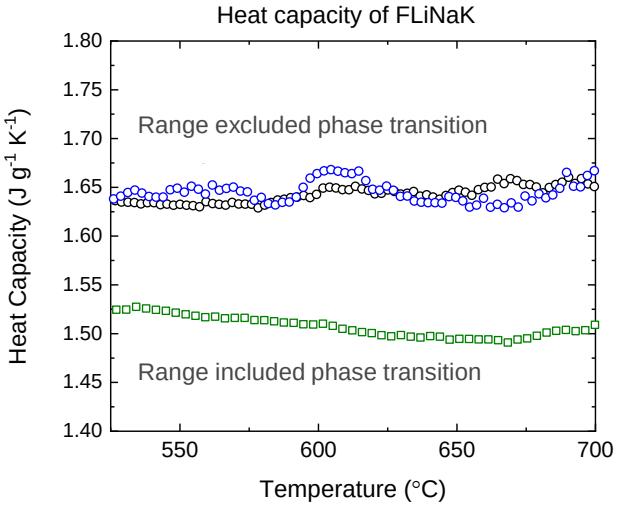
1 0

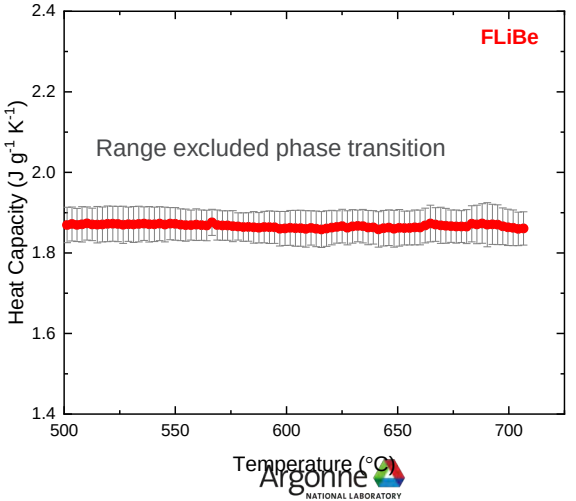
st = sapphire reference with known C_p; *s* = salt; *cr* = gold crucible

Measured C_p is affected by:

- Differences between masses of sample and sapphire
- Differences between masses of crucibles
- Melt transition occurring within the temperature range scanned

Match crucible and sample masses
Exclude phase transition from temp range scanned to measure C_p





SUMMARY

- Quality-affecting aspects of DSC, density, and thermal diffusivity measurements have been identified and are being controlled
- Importance of including surface tension in density measurements demonstrated and simple method implemented
- Precision of measurements being assessed for repeatability (using replicate samples) and reproducibility (through inter-laboratory study)
- Distinguishing effects of salt composition and measurement limitations from analyses made for multiple batches of FLiNaK

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