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DSC/DTA for Phase Equilibria and Heat of Transition

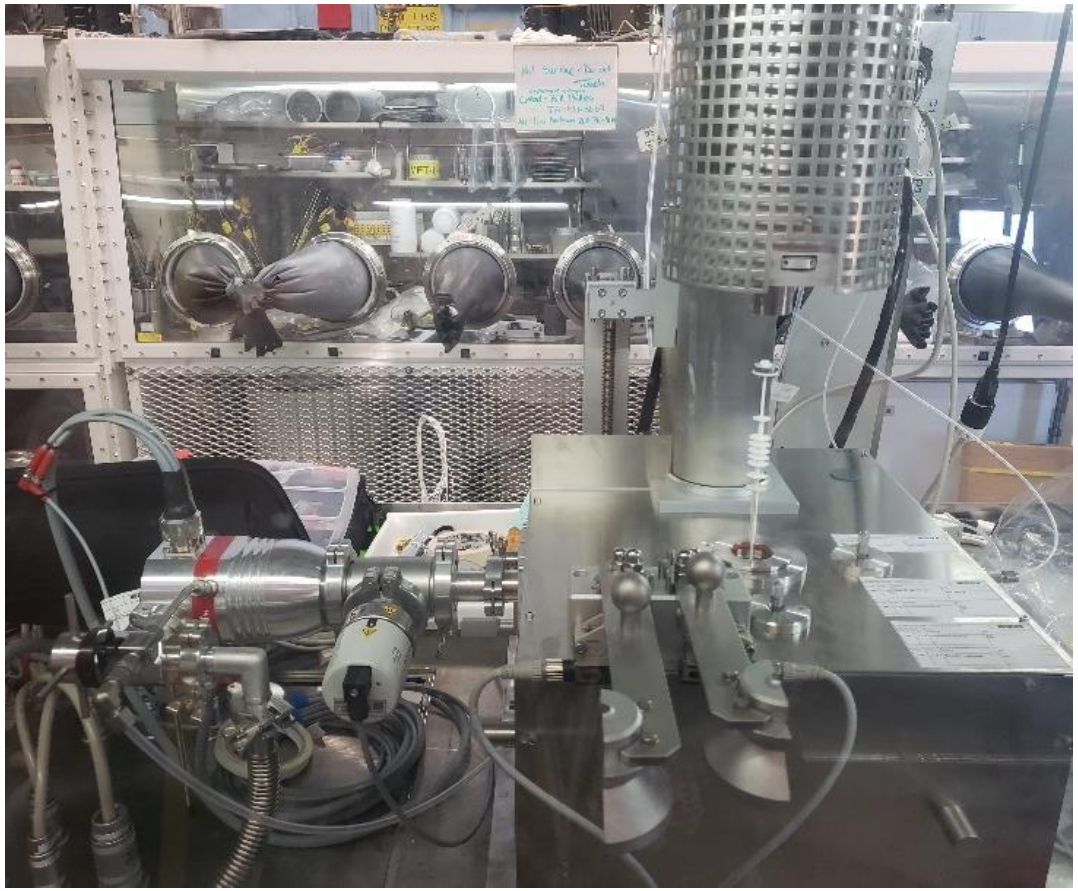
Workshop on Measurement and Analysis of Thermochemical and Thermophysical Properties of Molten Salts – July 2024

INL/MIS-24-79366

Battelle Energy Alliance manages INL for the
U.S. Department of Energy's Office of Nuclear Energy

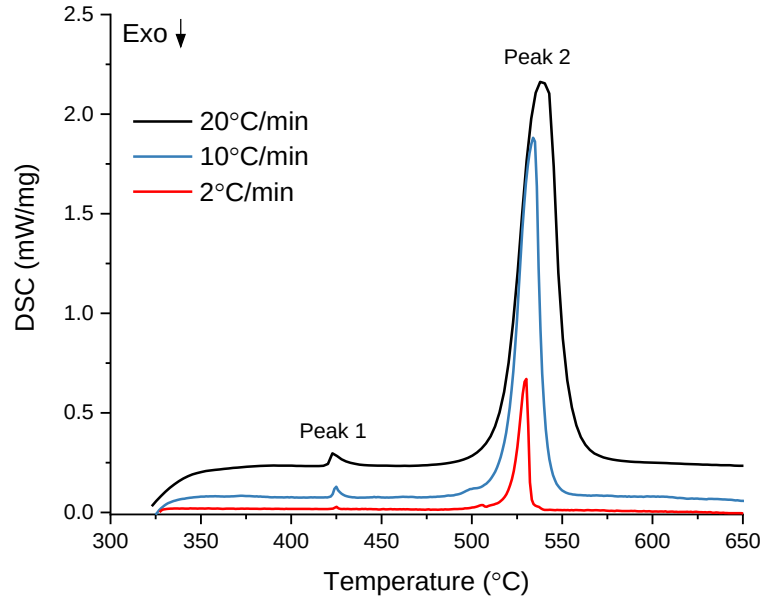
Idaho National Laboratory

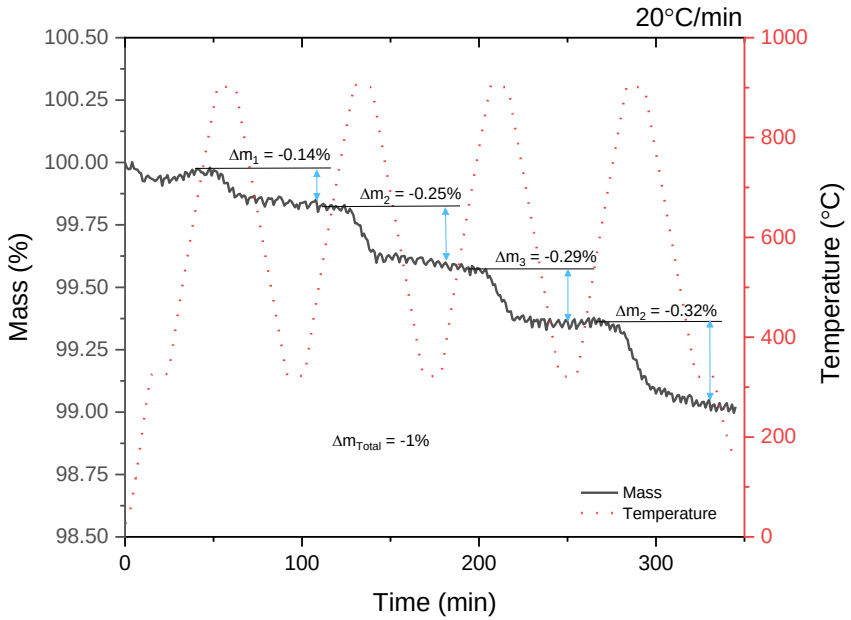
Outline



- Instrumentation
- Calibration
- Standards
- Calibration Check
- Measurements
  - Stability
  - Solidus/Liquidus
  - Enthalpy
- References
- Questions

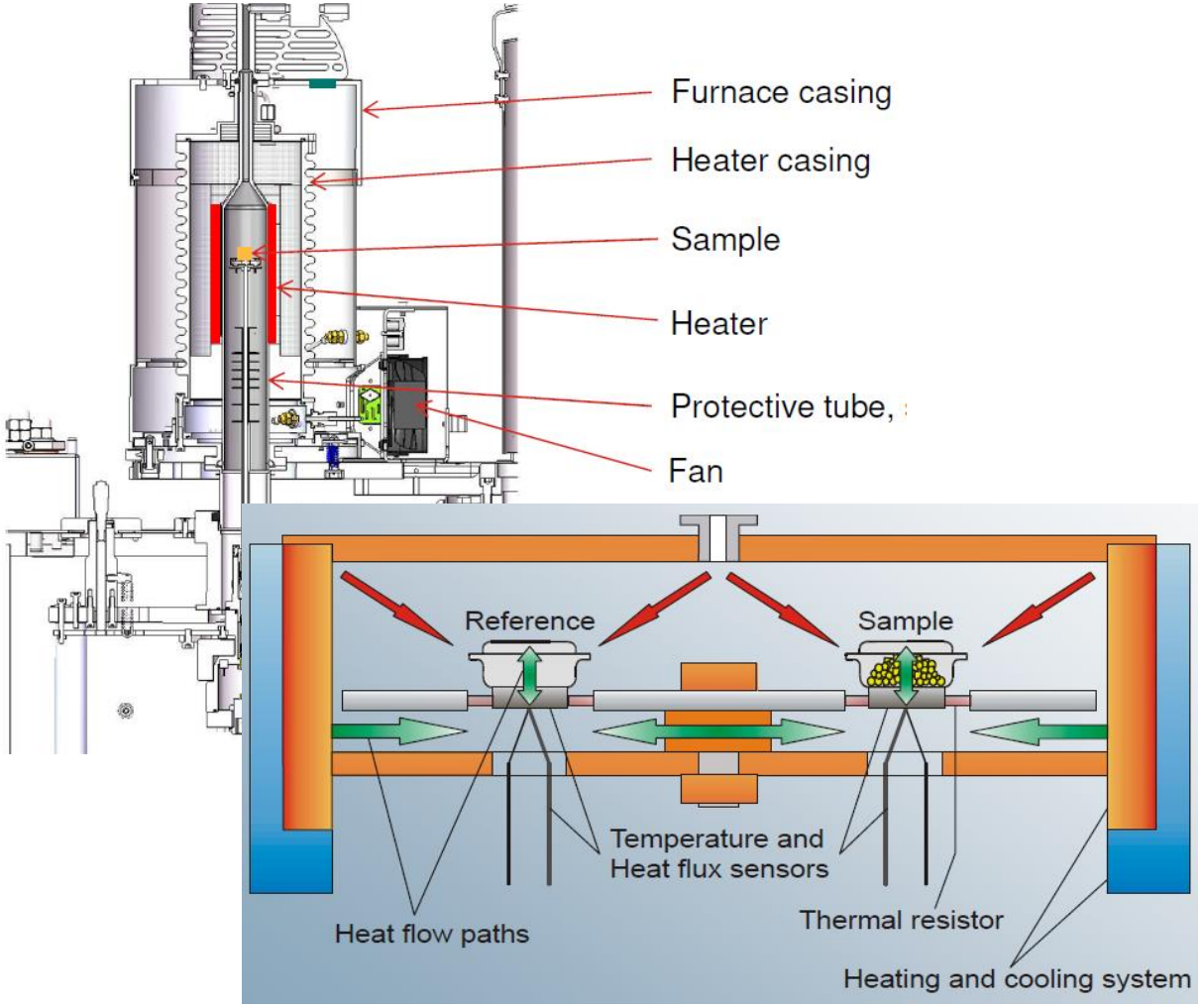
Instrumentation





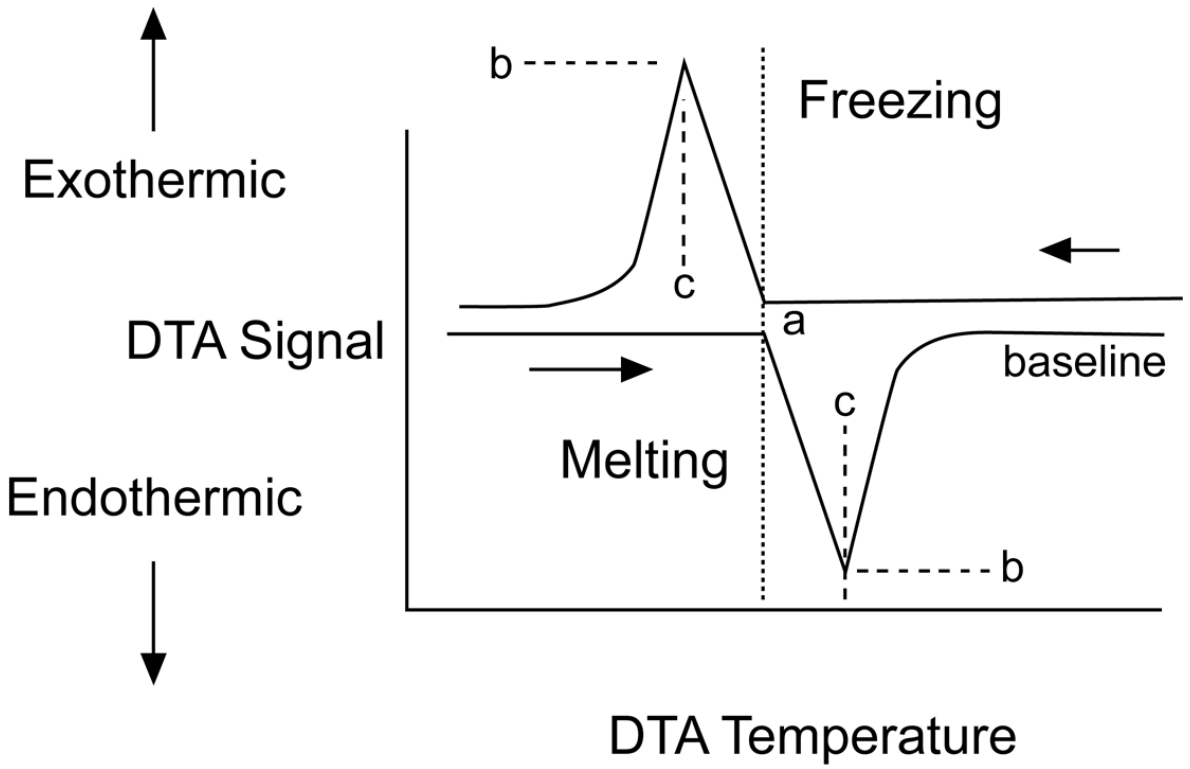
- Differential Scanning Calorimetry (DSC)
  - Technique in which the heat flow difference into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled-temperature program.
- Simultaneous Thermal Analyzer (STA) is a DSC combined with Thermogravimetric Analyzer (TGA)
  - Technique in which the mass of a substance is measured as a function of temperature or time while the substance is subjected to a controlled-temperature program in a specified atmosphere
- STA and DSC can be used to measure enthalpy (heat flow)

Instrumentation



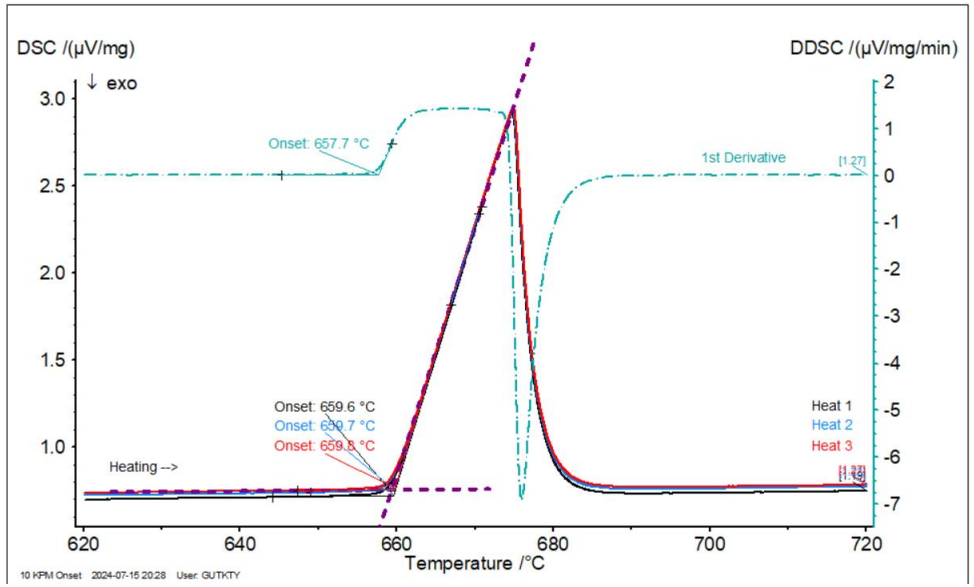
- Measurements are sensitive to the difference between the enthalpy vs. temperature relation of a **sample** and the enthalpy vs. temperature relation of a **reference**
- Sample carrier with two crucibles
  - Sample crucible - contains material being tested
  - Reference crucible (contains reference material, Al_2O_3, nothing, etc.
- Sample carrier chosen for sensitivity, compatibility with crucibles, and desired temperature range
- Many different crucible types
  - Al, Al_2O_3, Ag, BN, C, glassy carbon, Ni, Pt, etc.
  - Sealed, unsealed

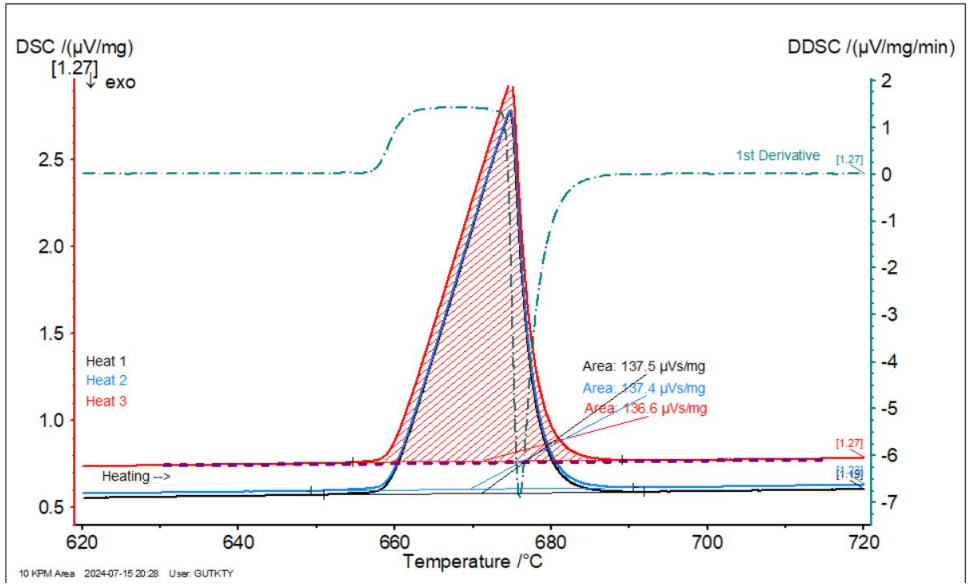
Instrumentation



- Purge Gas is the gas flowing over the sample
  - Glovebox typically Ar is used
  - Benchtop typically Ar or Ar with H_2 (reducing environment to protect crucibles)
  - Typically, 10 – 100 mil/min
- On melting the sample requires an input of heat, on cooling, freezing, releases heat
- Peak shapes have a linear portion up to the maximum deflection from the horizontal followed by an exponential return to the horizontal.

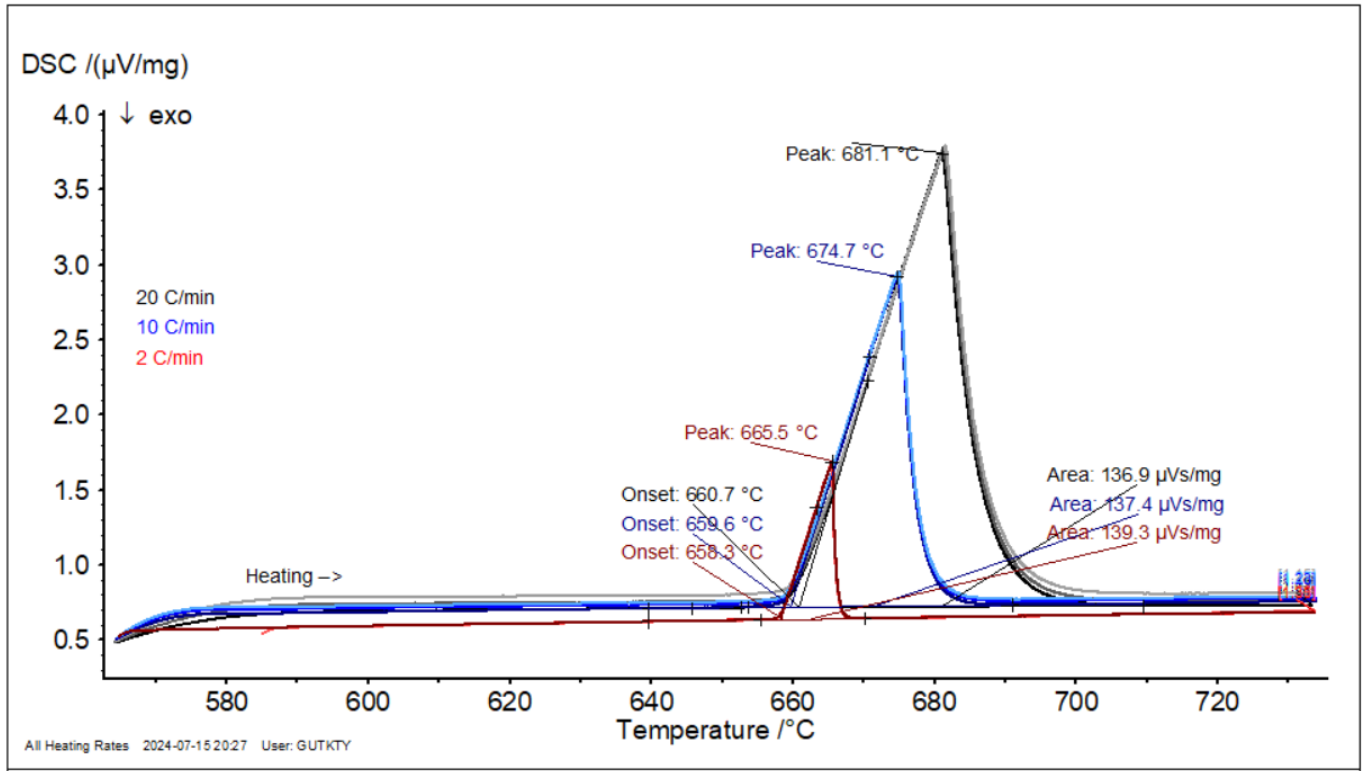
Calibration





- Initial detection of melting or freezing is indicated by the beginning of the linear portion of the peak and is used for temperature calibration. The area of the peak is used for calibration of the heat flow
  - See Al standard examples
- For enthalpy and phase diagram studies several heating rates should be used
- Standards can be run using multiple heating rates in one file
  - Unless there is degradation of the sample or crucible
- Four heating cooling cycles are recommended
  - Data from first heating/cooling cycle is assessed but not used
  - If changes in peaks this suggest degradation of sample/crucible

Calibration

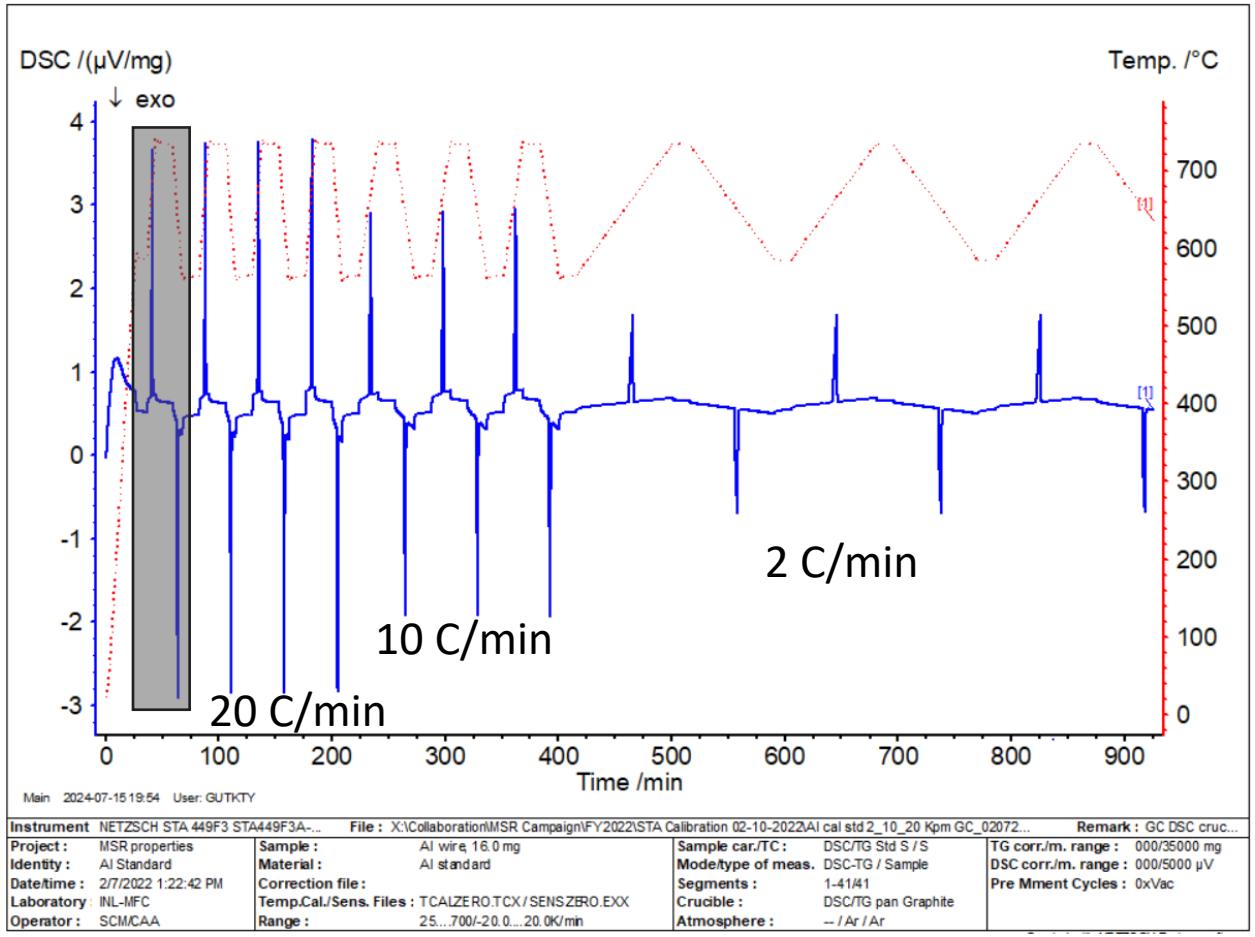


Instrument	NETZSCH STA 449F3 STA449F3A-...	**File :**	X:\Collaboration\MSR Campaign\FY2022\STA Calibration 02-10-2022\Al cal std 2_10_20 Kpm GC_02072...	**Remark :**	GC DSC cruc...
Project :	MSR properties	**Sample :**	Al wire, 16.0 mg	**Mode/type of meas.**	DSC-TG / Sample
Identity :	Al Standard	**Material :**	Al standard	**Segments :**	41
Date/time :	2/7/2022 1:22:42 PM	**Correction file :**		**Crucible :**	DSC/TG pan Graphite
Laboratory :	INL-MFC	**Temp.Cal./ Sens. Files :**	TCALZERO.TCX / SENSZERO.EXX	**Atmosphere :**	-- / Ar / Ar
Operator :	SCM/CAA	**Sample car./TC :**	DSC/TG Std S / S	**TG m. range :**	35000 mg
DSC m. range :	5000 µV				
Pre Mment Cycles	0xVac				

[#] Type	Range	Acq.Rate	STC	P1:–	P2:Ar	PG:Ar	Vac	Corr.	[#] Type	Range	Acq.Rate	STC	P1:–	P2:Ar	PG:Ar	Vac	Corr.
[1.07] Dynamic	530/20.0(K/min)/700	100.00	0	0.0	20.0	50.0	0	---	[1.27] Dynamic	530/10.0(K/min)/700	40.00	0	0.0	20.0	50.0	0	---
[1.11] Dynamic	530/20.0(K/min)/700	100.00	0	0.0	20.0	50.0	0	---	[1.31] Dynamic	530/2.0(K/min)/700	40.00	0	0.0	20.0	50.0	0	---
[1.15] Dynamic	530/20.0(K/min)/700	100.00	0	0.0	20.0	50.0	0	---	[1.35] Dynamic	550/2.0(K/min)/700	40.00	0	0.0	20.0	50.0	0	---
[1.19] Dynamic	530/10.0(K/min)/700	40.00	0	0.0	20.0	50.0	0	---	[1.39] Dynamic	550/2.0(K/min)/700	40.00	0	0.0	20.0	50.0	0	---
[1.23] Dynamic	530/10.0(K/min)/700	40.00	0	0.0	20.0	50.0	0	---									

- Thermal lags between the sample and sample thermocouple must be understood to enable good analysis of data
- Many factors can affect thermal lag
  - Sample Mass
  - Sample Shape
  - Crucible selection
  - Atmosphere
  - Purge gas flow rate
  - Heating/Cooling Rate
- Al Standard
  - 20, 10, 2 °C/min
  - MP = 660.3 C °(Theo.) and Enthalpy = 397.000 J/g (Theo.)
- One must select heating rate, gas flow rate, and temperature range for calibration

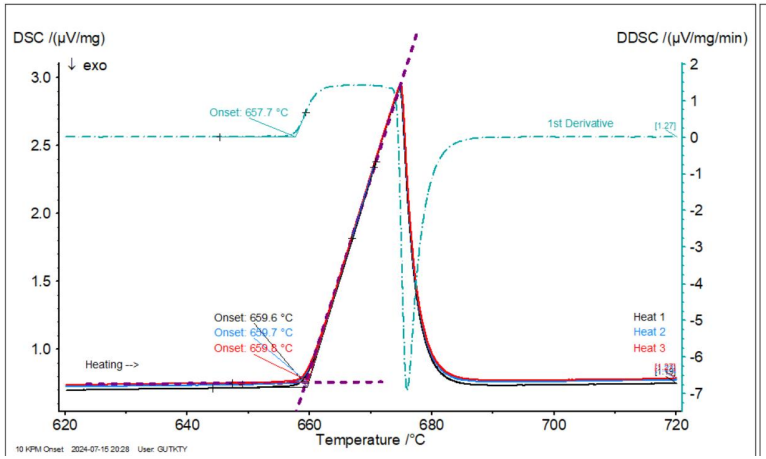
Standards

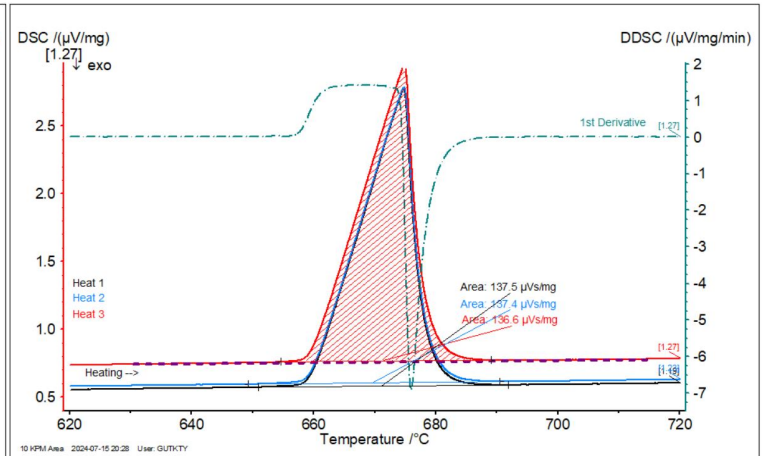


- Calibration standards can be salts and/or metals
  - Salt examples
    - Benzoic Acid (C_6H_5COOH), Rubidium Nitrate ($RbNO_3$), Potassium Perchlorate ($KClO_4$), Cesium Chloride (CsCl), Potassium Chromate (K_2CrO_4)
  - Metal examples
    - In, Sn, Bi, Zn, **Al**, Ag, Au, Ni
- Recommend using 5 – 7 standards for calibration
- Standards chosen based on compatibility with crucible material
  - Vendors have guides to help choose
  - Trail and error!
- Mass
  - Standards recommend 5 - 10mg
  - Toni recommend 10 – 30mg
  - Powders should cover bottom of crucible and metals should use one piece

Calibration

Standard	Avg. Experimental Temperature (°C)	Avg. Area (µV/mW)	Notes
In	155.87	25.85	
Bi	270.7	40.01	
Zn	418.67	60.02	
CsCl	474.6	8.45	
Al	659.67	140.6	Grey ring around the lid hole. Good reproducibility in 2nd,3rd and 4th runs. Slight weight increment.
Ag	959.63	21.49	

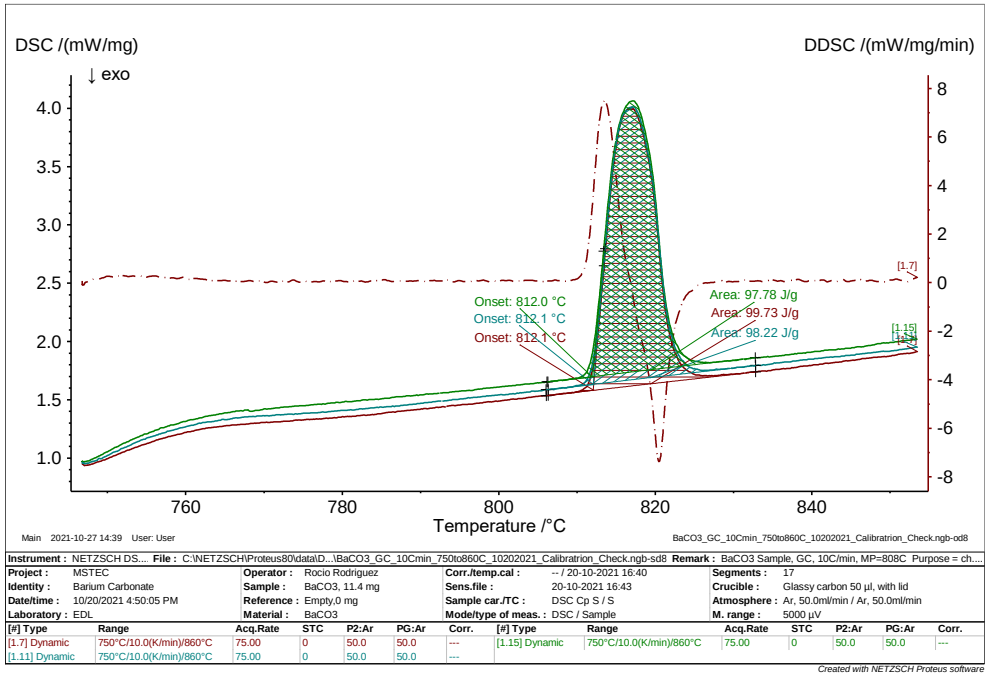




- Temperature and sensitivity calibration curves are created to be applied as correction files during the recording of the sample measurements
- Frequency
  - When? Every time that an experimental condition is changed, i.e., ramping rate, gas type, gas flow, crucible type, sample carrier, etc.
  - Do not be afraid to check calibration or recalibrate frequently

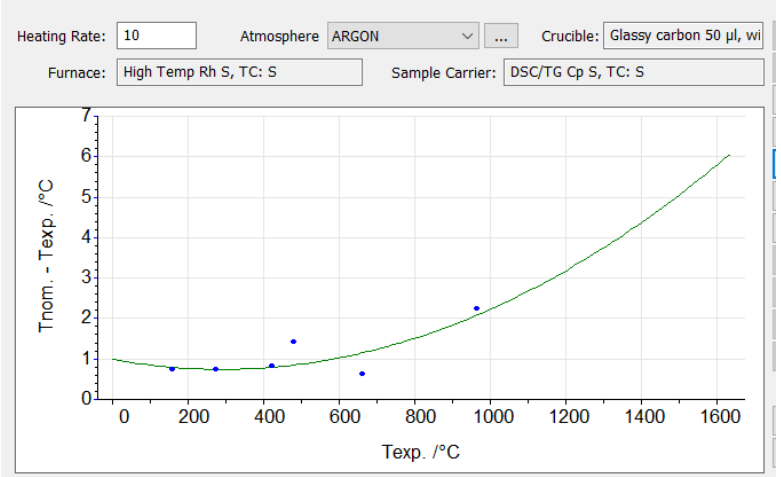
Example with Al, 10 C/min

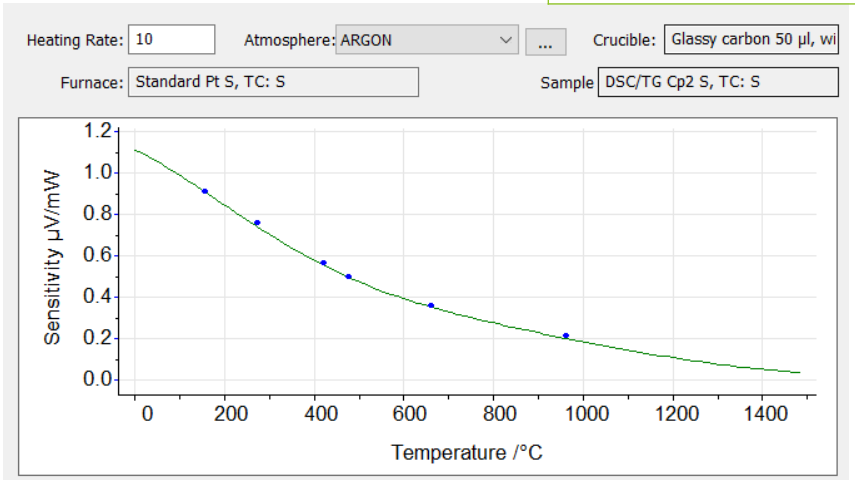
Calibration Check



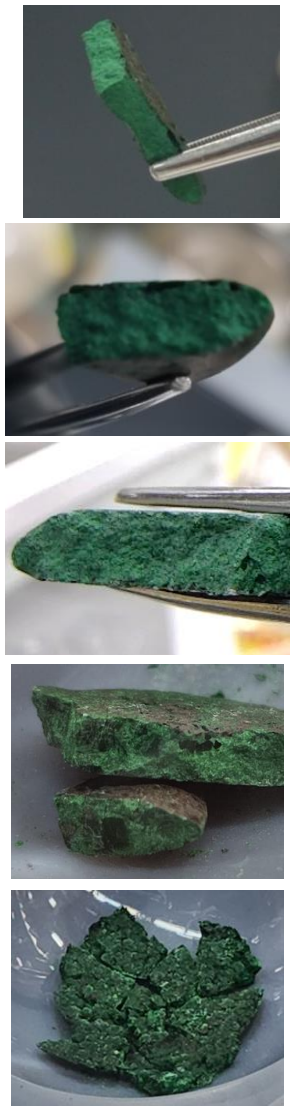
- Setup the calibration files
  - Temperature
  - Sensitivity
- Check/verify your calibration using a standard as a sample
  - $BaCO_3$ example
    - Temperature within 0.5% of theo., report results within +/- 5C
    - Enthalpy within 3.9% of theo.

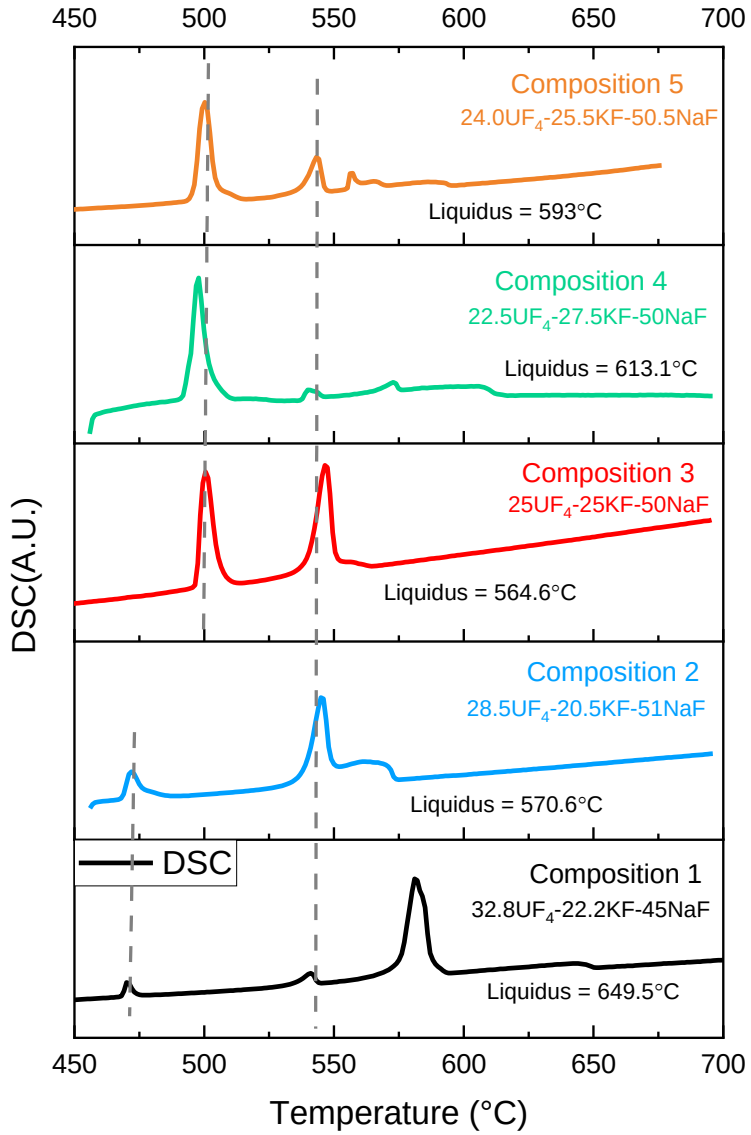
Theoretical MP (°C)	Experimental T. onset (°C)	Theoretical enthalpy (J/g)	Experimental enthalpy (J/g)
808	812.06	94.90	98.58





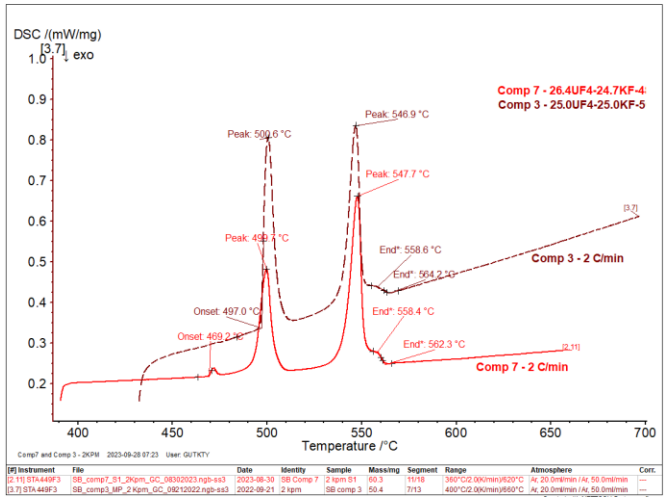
Measurements

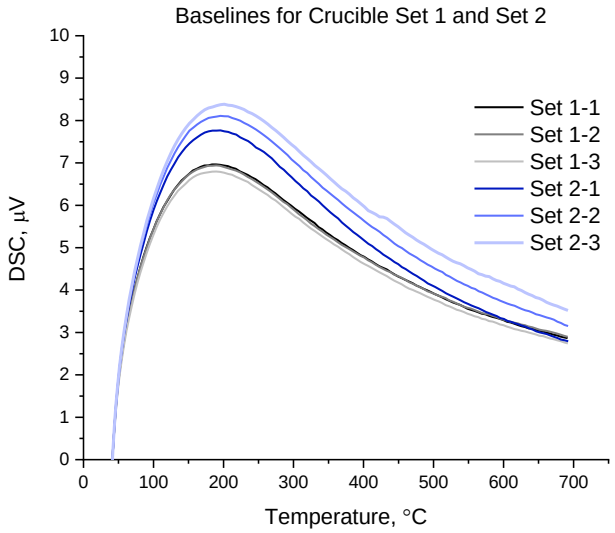




- Once calibrated various measurements can be made
  - Determination of liquidus and solidus temperature
  - Phase diagram research
    - Invariant reaction temperatures (ex. Eutectic, peritectic, etc.)
    - Peak “transition” temperatures
    - Supercooling tendency
    - Sample purity
  - Heat Capacity

Measurements



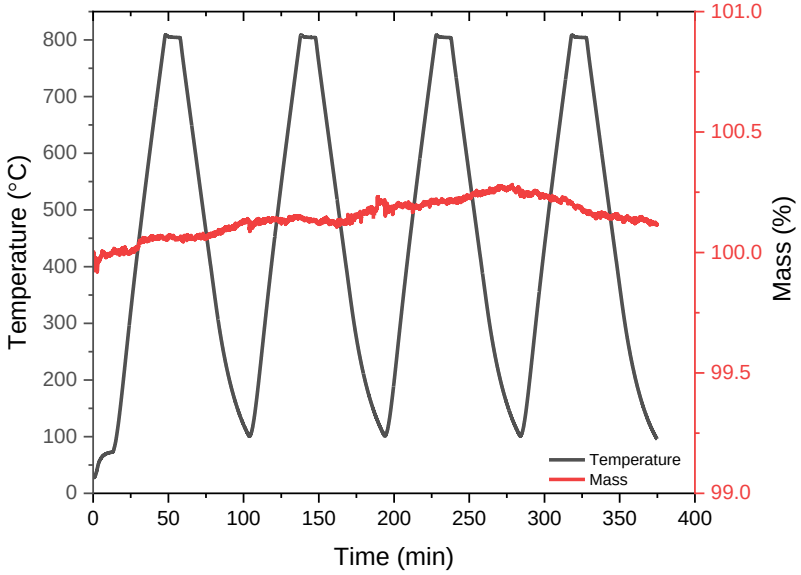


- For enthalpy and phase diagram studies several heating rates should be used
  - New sample for each heating rate
- Crucible orientation is crucial (see pic)
- Baseline correction and four heating cooling cycles are recommended
  - Data from first heating/cooling cycle is assessed but not used
  - Changes in peak suggest degradation of sample/crucible
- Degradation of the crucible can be detected from heat flow measurements
  - Baseline example for crucible degradation
- Sample must be stable (example on next slide)

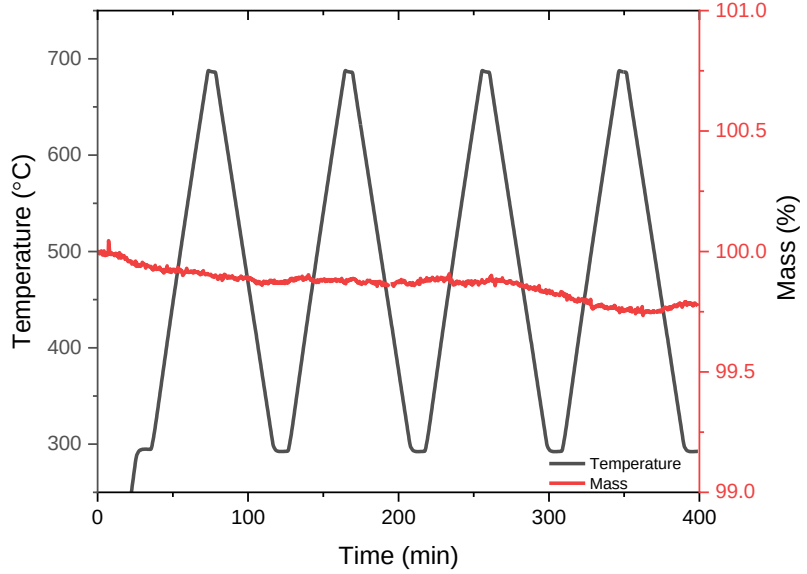
Measurements – $PuCl_3$ Salt

- Salt Stability – 36 mol% $PuCl_3$ in NaCl
- STA in Ar glovebox with UHP Ar purge/protective gas
- Glassy Carbon sample/reference crucible
- Run baseline to remove “buoyancy”
  - Longer runs harder for conditions to remain the same during run
- Less than 0.5 mass % change up to 800 °C

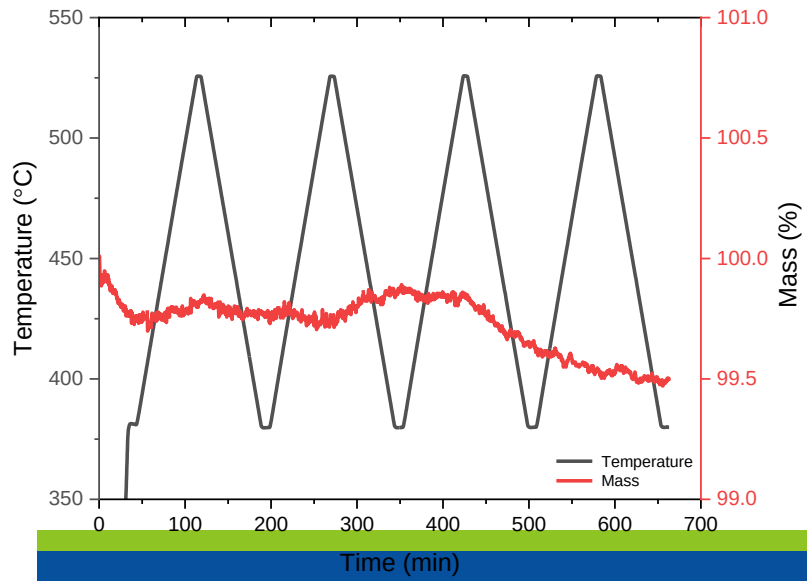
20 kpm



10 kpm

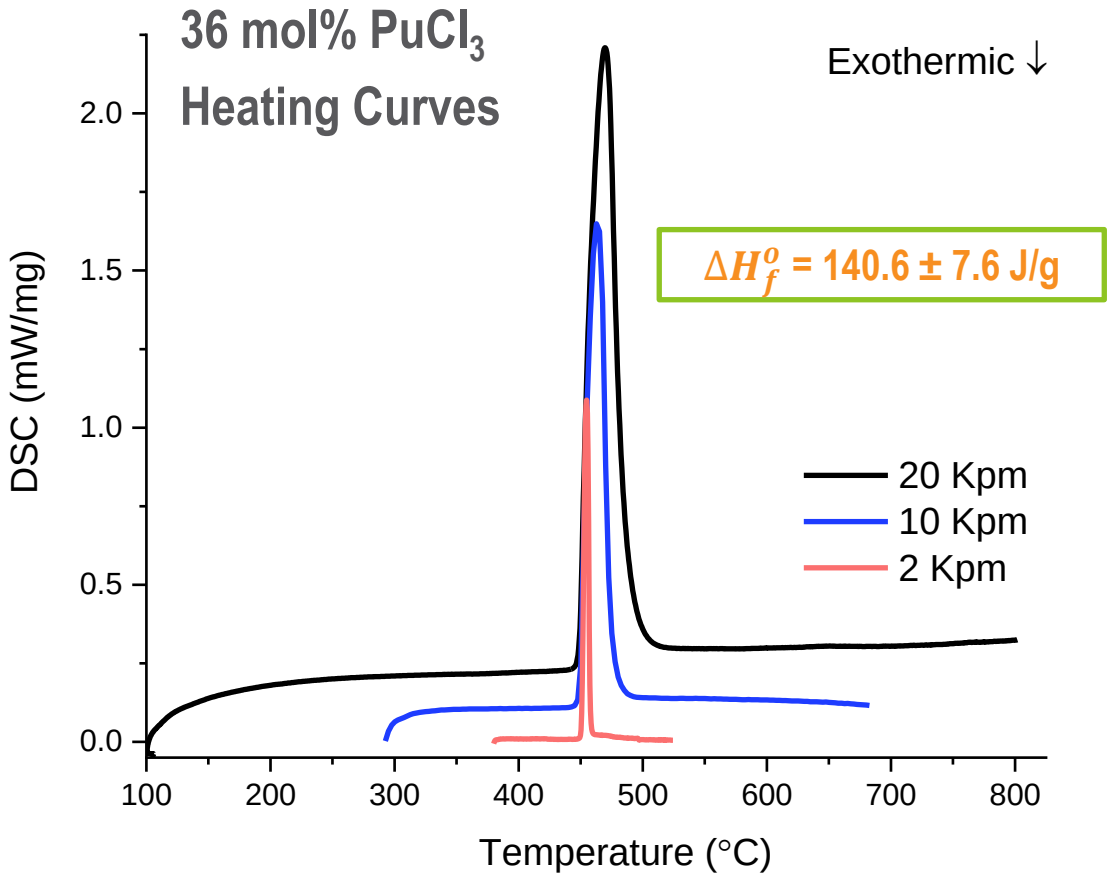


2 kpm

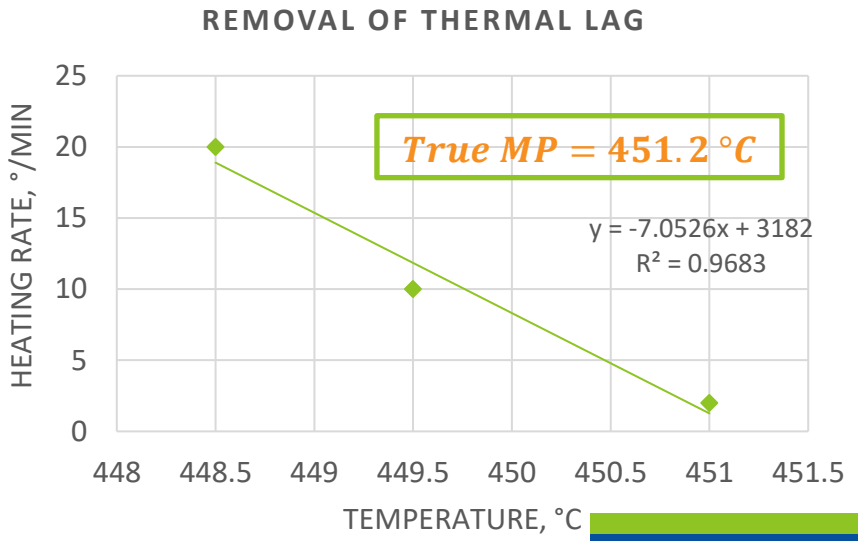


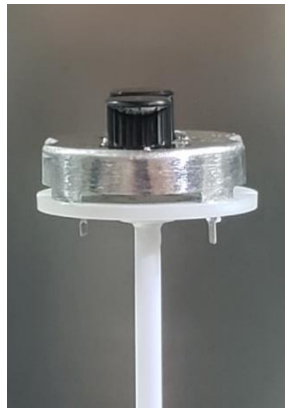
Measurements - $PuCl_3$ Salt

HR	Melt, °C	Peak, °C	Area, J/g
2	451.0	454.6	141.6
10	449.5	463.4	147.7
20	448.5	466.7	132.6
Average	449.7	461.6	140.6
Stdev	1.3	6.2	7.6
RSD, %	0.3	1.4	5.4



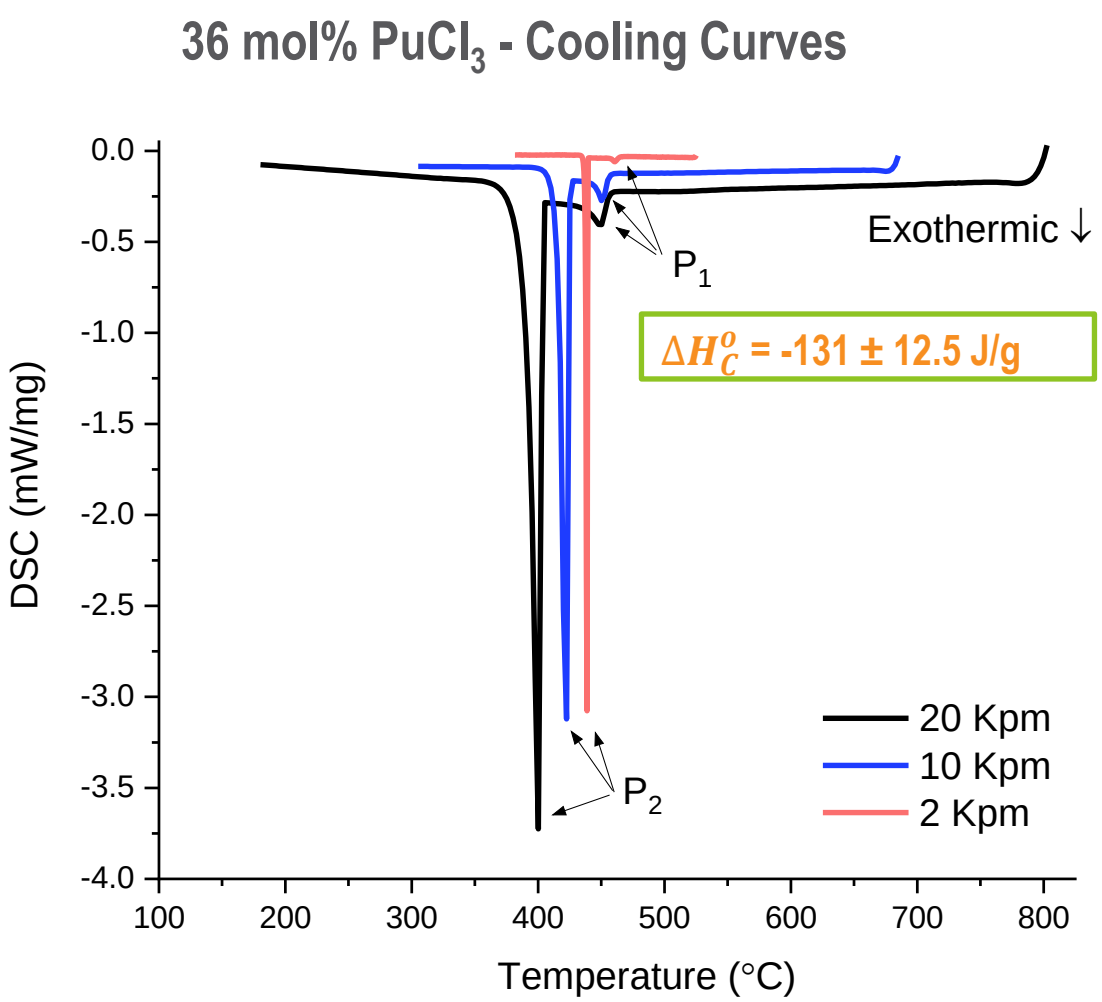
- STA in Ar glovebox
- UHP Ar cover and protective gas
- Calibration of STA with 5 standards
  - Verification of calibration with 2 standards
- Glassy Carbon sample/reference crucible
- Type S thermocouple
- 3 separate samples, one for each heating rate





Measurements - $PuCl_3$ Salt

ΔH_C^o = -131 ± 12.5 J/g

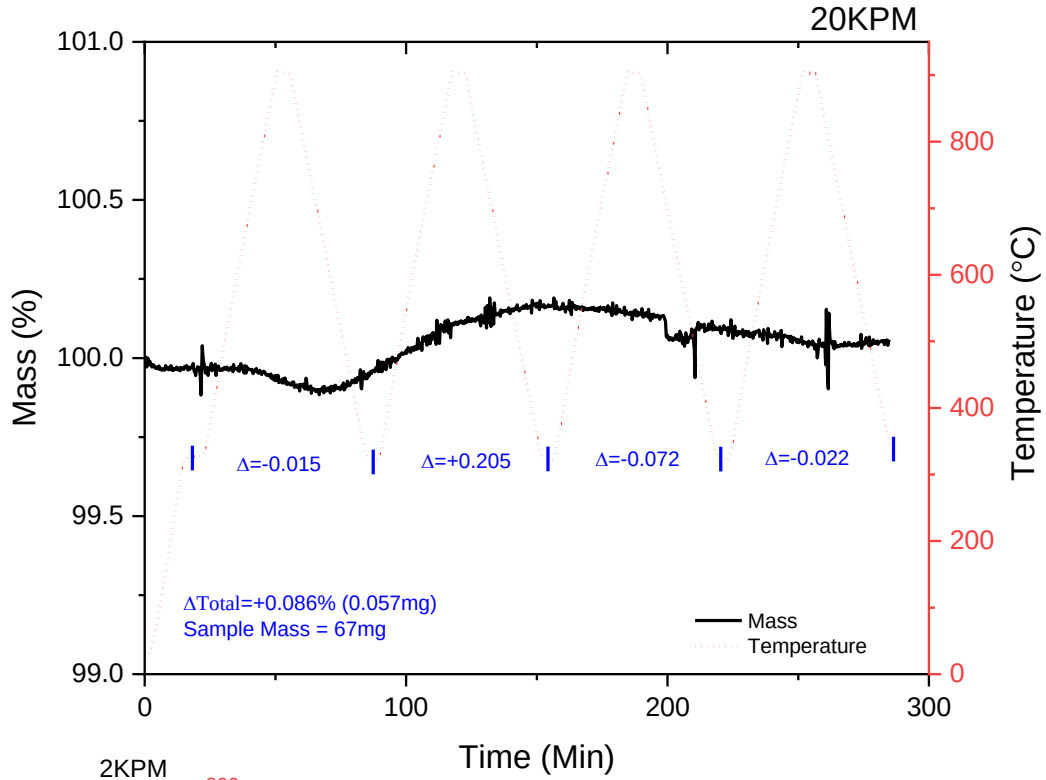


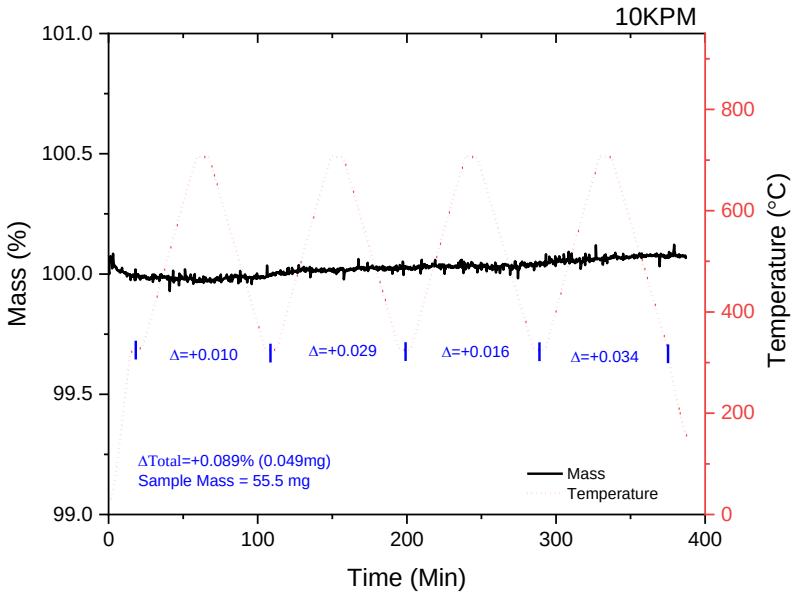
- Appearance of 2 peaks on cooling
- Don't know what peak 1 is
  - Possible Pu allotropic change energy?
  - Slightly off the eutectic composition?
- Higher deviations from cooling curve
- 2nd cooling curve from each cooling rate is shown

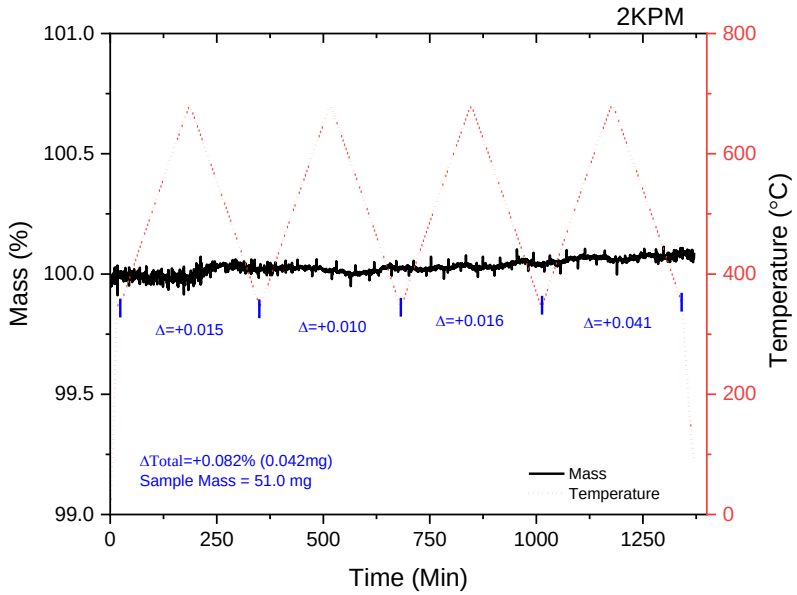
HR	Peak 1 – Onset, °C	Peak 2 – Onset, °C	Peak 2 – Peak, °C	Area, J/g
2	465.3	440.0	438.9	-137.6
10	456.1	415.4	413.4	-139.1
20	456.6	414.2	409.9	-116.7
Average	459.3	423.2	420.7	-131.2
Stdev	5.2	14.6	15.8	12.5
RSD, %	1.1	3.4	3.8	-9.6

Measurements – UF_4–NaF-KF Salt

- 20 KPM – 325 to 900C, 4 cycles
  - +0.086% mass change (0.057mg)
- 10 KPM – 325 to 700C, 4 cycles
  - +0.089% mass change (0.049mg)
- 2 KPM – 325 to 675C, 4 cycles
  - +0.082% mass change (0.042mg)







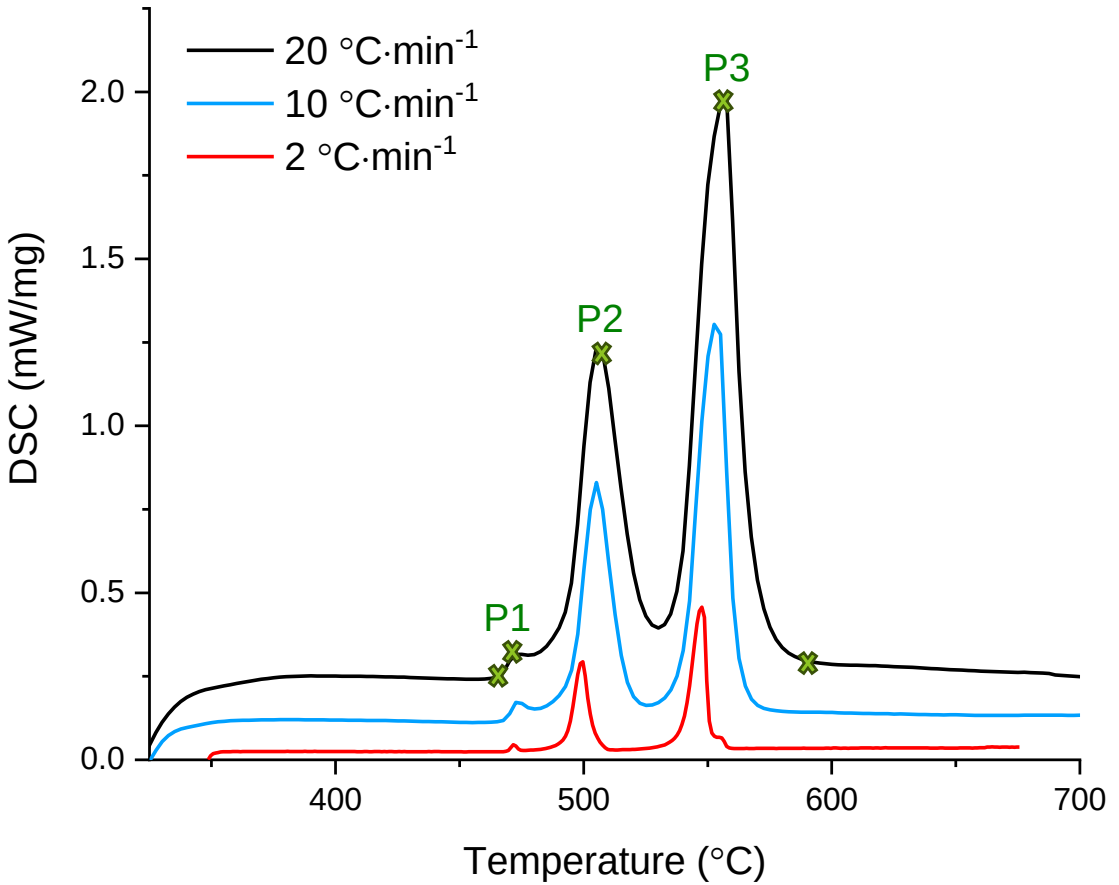
SEABORG

IDAHO NATIONAL LABORATORY

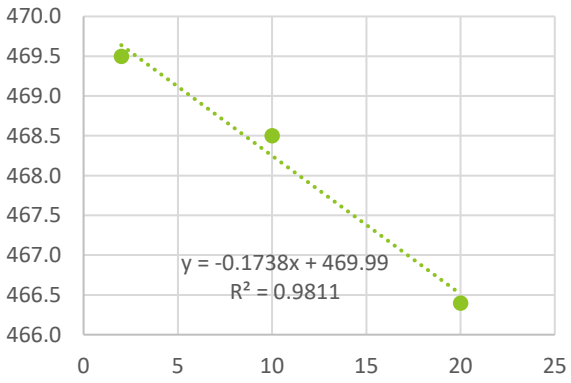
Melting Temp

- Average temperatures reported for each point and HR
- Only second heat curve is shown in figure
  - All are identical
- Data showed thermal effects, can be removed using linear regression

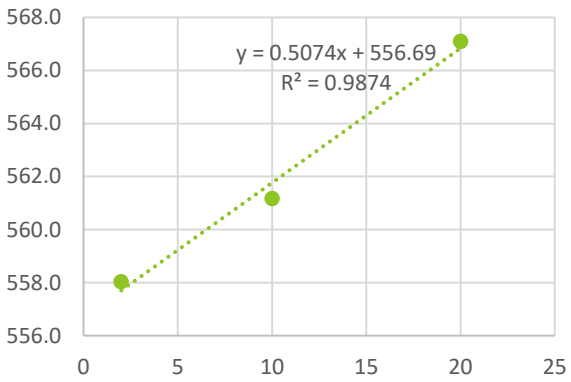
	Onset P1	P1 Max	Onset P2	P2 Max	Onset P3	P3 Max	Endset P3
20	466.4	473.8	492.7	509.8	536.9	556.6	567.1
10	468.5	473.5	494.4	505.2	538.2	553.9	561.2
2	469.5	472.0	493.1	499.4	539.9	547.3	558.0
Regressed	469.7	472.1	493.7	498.7	540.1	547.2	556.7
R2	0.9811	0.8528	0.0911	0.9821	0.9749	0.9146	0.9874



Onset Temp (P1 onset)

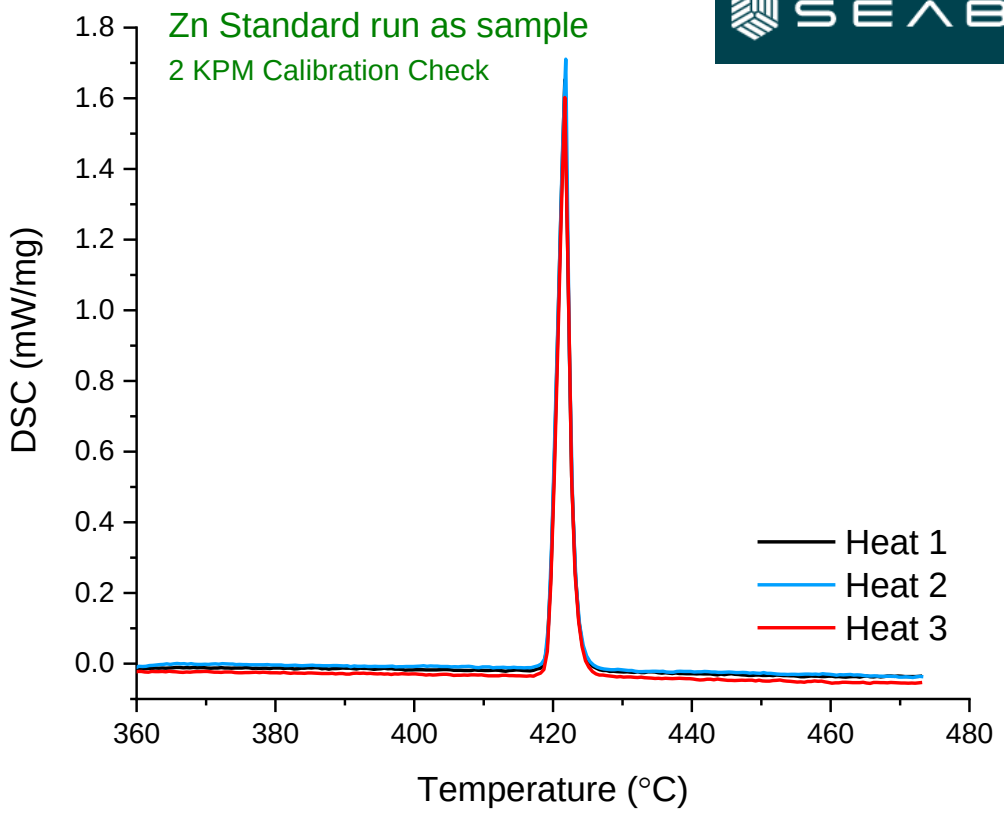


Soludus Temp (P3 endset)



Melting Temp

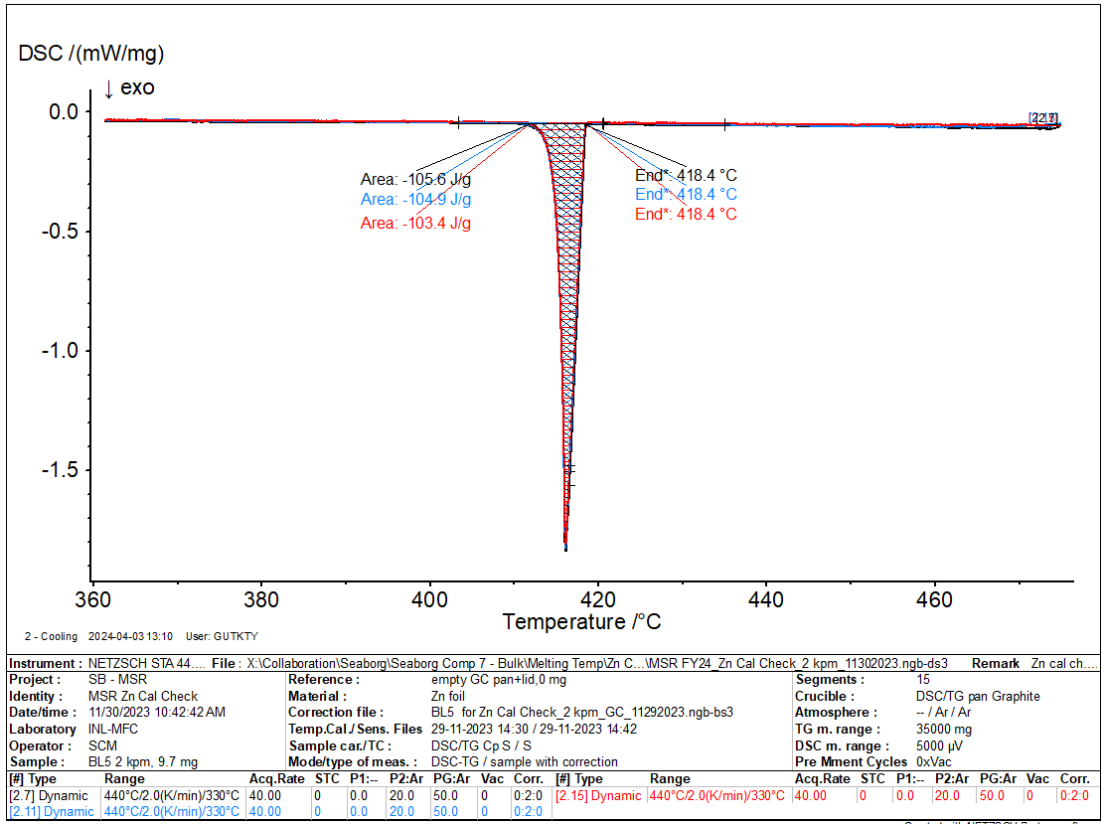
- Calibrated STA
  - Calibrated using In, Bi, Zn, Al, Ag
  - Heating Rate = 20, 10, 2 KPM
  - Glassy-Carbon crucible (w/lids)
  - Purge/Protective Gas = Ar
    - Protective = 50 ml/min
    - Purge = 20 ml/min
  - 4 heating/cooling cycles
    - Eliminate cycle 1
    - Average cycle 2-4 (heating only)
- Generated Heat Flow (area) and Temperature Calibration (onset) Curves
- Validated calibration using Zn as a sample (Theo./Exp.)



Heating Rate	20 KPM	10 KPM	2 KPM	20 KPM	10 KPM	2 KPM
Unit	°C	°C	°C	J/g	J/g	J/g
1	419.9	419.4	419.4	107	106.6	105.8
2	419.8	419.4	419.4	105.8	106.3	106.8
3	419.9	419.4	419.4	105.7	105	105.2
Average	**419.9**	**419.4**	**419.4**	**106.2**	**106.0**	**105.9**
Stdev	0.058	0.000	0.000	0.723	0.850	0.808
RSD, %	0.014	0.000	0.000	0.681	0.803	0.763
	Theo. MP = 419.5 C			Theo. heat Flow = 107.5 J/g		

Zn Calibration Check (cooling)

Heating Rate	20 KPM	10 KPM	2 KPM	20 KPM	10 KPM	2 KPM
Unit	°C	°C	°C	J/g	J/g	J/g
1	414.0	416.1	418.4	-104.6	-104.7	-105.6
2	413.8	416.2	418.4	-103.8	-104.4	-104.9
3	413.8	416.3	418.4	-99.0	-103.3	-103.4
Average	**413.9**	**416.2**	**418.4**	**-102.5**	**-104.1**	**-104.6**
Stdev	0.115	0.100	0.000	3.029	0.737	1.124
RSD, %	0.028	0.024	0.000	-2.956	-0.708	-1.074
	Theo. MP = 419.5 C			Theo. heat Flow = -107.5 J/g		

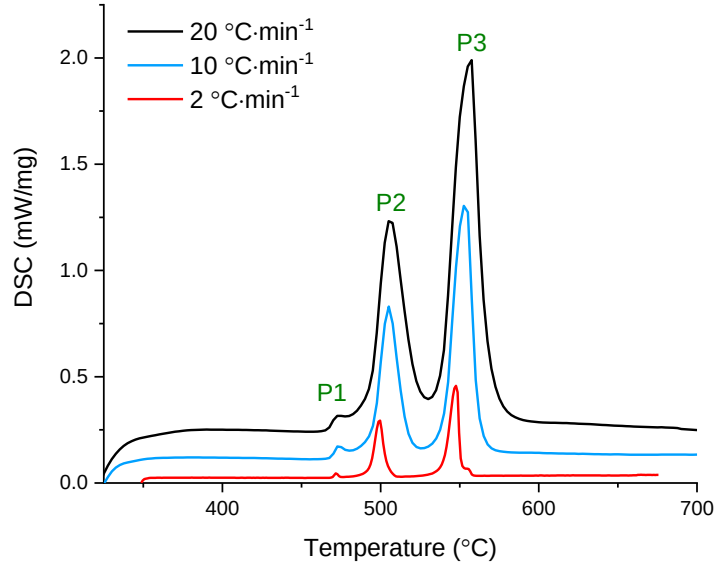


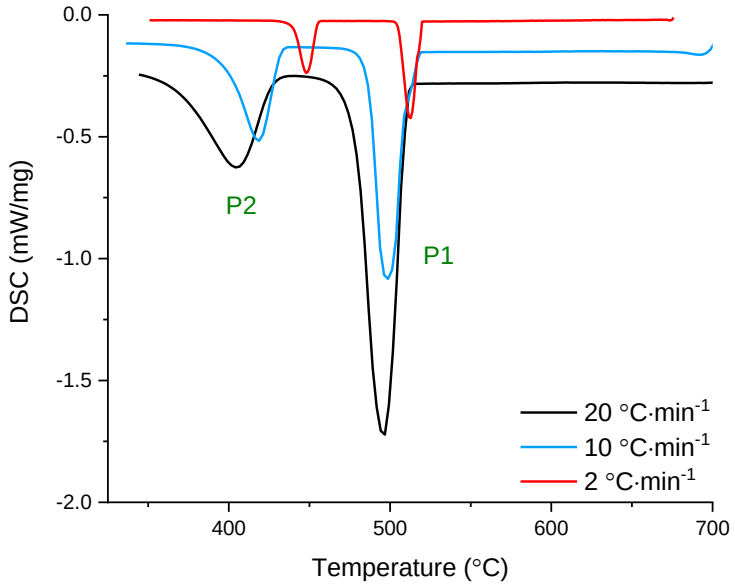
Enthalpy

- Total enthalpy
  - 167.5 ± 2.7 J/g (heating)
  - -147.8 ± 13.3 J/g (cooling)*
- What do peaks mean? (Toni's best guess)
  - Peak 1 = formation of Na_3UF_7
  - Peak 2 = ?
  - Peak 3 = Solid to Liquid transition
- Using 2 KPM heating rate, each peak area could be determined
  - Enthalpy of fusion (only 2 C/min rate)
    - ΔH_f^o = 102.0 J/g
  - Enthalpy of crystallization (all cooling rates)
    - ΔH_C^o = -99.7 ± 2.67 J/g

	Heating				
Heat Rate C/min	Total Peak Area J/g	P1 J/g	P2 J/g	P3 J/g	P1+P2+P3 J/g
20	165.1	nd	nd	nd	0.0
10	170.5	nd	nd	nd	0.0
2	166.9	1.9	60.1	102.0	164.0

	Cooling			
Cool Rate C/min	Total Peak Area J/g	P1 Area J/g	P2 Area J/g	P1+P2 J/g
20	-133.7	-94.9	-42.6	-137.4
10	-149.7	-99.4	-53.5	-152.9
2	-160.1	-99.6	-59.4	-159.0





* Large variation due to min temp for 20 KPM cooling not completing peak

Toni's Closing Remarks

- Take a moment to verify calibrations don't be in a rush
- Talk to your modeling friends
- Data
  - Make sure your sample is stable in measurement range
  - Transition temperatures can be a function of temperature (thermal lag)
  - Can get an idea of sample "purity"
  - Can get enthalpy of fusion/crystallization
  - Don't forget about the cooling curves
    - Peaks have higher resolution
    - But… supercooling
- Literature data can be tricky
  - Heating rate, peak vs onset, etc.
  - State where/how your temperatures/enthalpy are taken
- Crucibles
  - Make a mark
  - Open or closed crucibles?
    - Be consistent
- Setup
  - Check the sample stability
  - Pick a phase, temp range, and heating rate
  - Look at your baselines
  - Heat flow calibration
    - Standards vs sapphire
  - Sample must cover bottom of crucible (40-60mg)
- Easy to get results, difficult to get representative results
- Reach out to your colleagues and ask questions!!!

References

- ASTM E473 - Standard Terminology Relating to Thermal Analysis
- ASTM E1142 - Terminology Relating to Thermophysical Properties
- ASTM E967 - Practice for Temperature Calibration of DSC and DTA
- ASTM E968 - Standard Practice for Heat Flow Calibration of DSC
- ASTM E2253 - Standard Method for Enthalpy Measurement Validation of Differential Scanning Calorimeters
- ASTM E928 - Standard Test Method for Determining Purity by DSC
- ASTM E794 - Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis
- ASTM E793 - Standard Test Method for Enthalpies of Fusion and Crystallization by DSC
- ASTM E1269 - Standard Test Method for Determining Specific Heat Capacity by DSC
- ISO 11357-1 to 11357-8 – Differential Scanning Calorimetry
- DIN 51007 Thermal Analysis – Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) General Principles
- NIST recommended practice guide – DTA and heat flux DSC measurements of alloy melting and freezing

Idaho National Laboratory

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	Temp Range	Heating Rate	Isotherm	Purge/Protective	Step
Initial	25				1
Ramp up	25 - 550	10	-	20/50	2
Isotherm	550	-	5	20/50	3
Ramp up	550– 700	20	-	20/50	4
Isotherm	700	-	5	20/50	5
Ramp down	700 – 550	20	-	20/50	6
Isotherm	550		5	20/50	7
Repeat Steps 4 - 7, three more time (4 heat/cool cycles in total)					
Ramp up	550 – 680	10	-	20/50	8
Isotherm	680	-	5	20/50	9
Ramp down	680 – 560	10	-	20/50	10
Isotherm	560	-	5	20/50	11
Repeat Steps 8 - 11, two more time (3 heat/cool cycles in total)					
Ramp up	560 – 660	2	-	20/50	12
Isotherm	660	-	5	20/50	13
Ramp down	660 – 590	2	-	20/50	14
Isotherm	590	-	5	20/50	15
Repeat Steps 12 - 15, two more time (3 heat/cool cycles in total)					
Ramp down	590 – 25	20		20/50	16