Molten Salt Reactor PROGRAM

Generation of Molten Salt Thermochemical Properties at USC

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Accomplishments

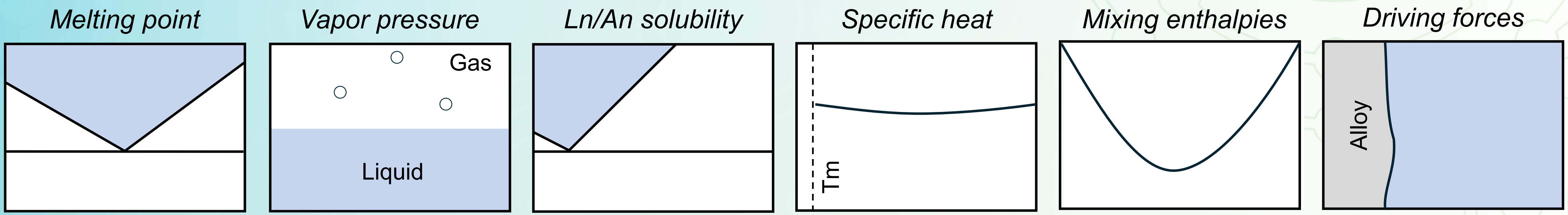
- **MSD-TC Version 4.1 released on March 2026** with expanded documentation.
- **Papers:**
  - Thermodynamic Assessment of the Na, K, Cs | Cl, I Reciprocal Salt for Chloride-Fueled MSR Accident Analysis (accepted), *Nuclear Science and Engineering*
  - Thermodynamic assessment of SmF_3 with LiF, NaF, and KF (FLiNaK) for Molten Salt Reactors (accepted), *ACS Omega*
  - Thermodynamic properties of $ZrCl_4$ with LiCl, NaCl, KCl, CsCl, $MgCl_2$, and UCl_3 for molten salt reactor applications, *Journal of Molecular Liquids*, 437, part C, 128578
  - Thermophysical Properties of NaCl-UCl_3-$PuCl_3$ Molten Salts: A Combined Computational and Experimental Study, *ACS Applied Energy Materials*, 8(10), 6482-6491
  - Papers under review: **4**
- **Conference Presentations:** IAEA workshop: 2; ACS Fall: 5; NuFuel: 1; Mines: 2; ACS Spring: 1; TMS: 3

Collaborations

- Tony Birri and team (ORNL): Workshops, database management and road map development
- Matt Christian (SNL): Database content evolution and mass accountancy challenges
- Joanna McFarlane and team (ORNL): Complex gas behavior
- Jacob Yingling and Robin Roper (INL): U-Cl heat capacity studies
- Toni Karlsson and team (INL): Study of transuranics' phase equilibria
- Mel Rose (ANL): Road map development
- Slava Bryantsev (ORNL): Computation predictions of BeF_2 behavior
- Molten Salts in Extreme Environments (MSEE): For sharing salts

Molten Salt Database –Thermochemical

- Self-consistent thermodynamic database
- Some relevant properties that can be calculated for complex systems



- Predicting behavior requires accurate Gibbs energy functions
  - Exhaustive literature review
  - Critical evaluation of experimental data
  - Use of first principles calculations and correlations to predict properties
- **Measurements are made to address knowledge gaps and validate historical thermochemical data**

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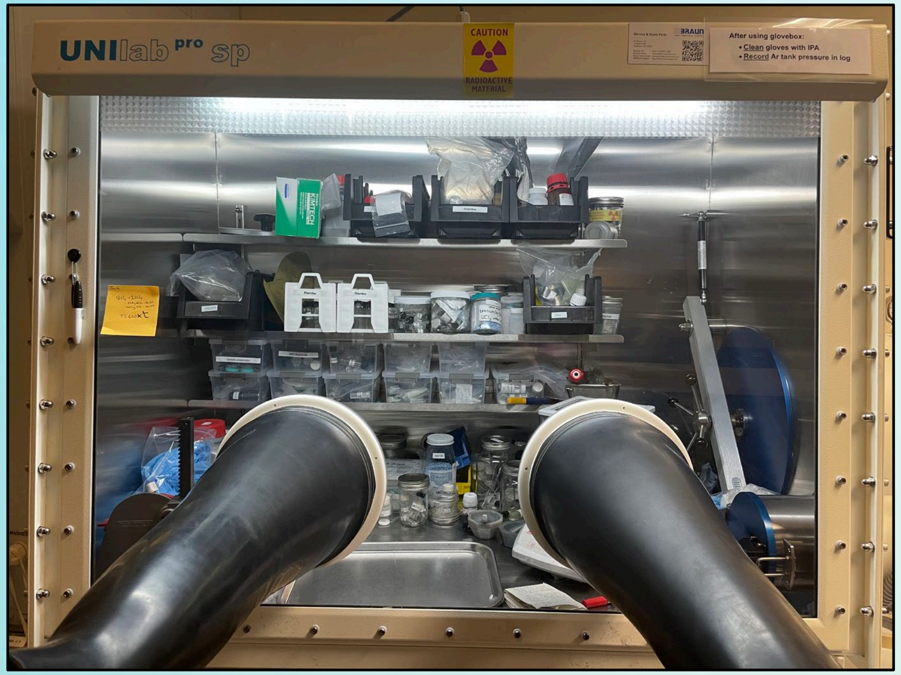
Salt Purity Characterization and Purification

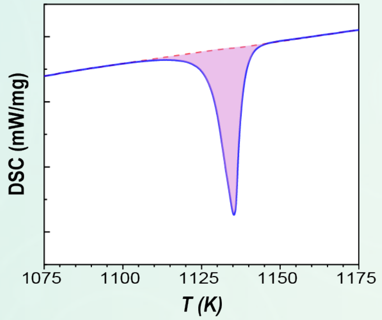
Salts

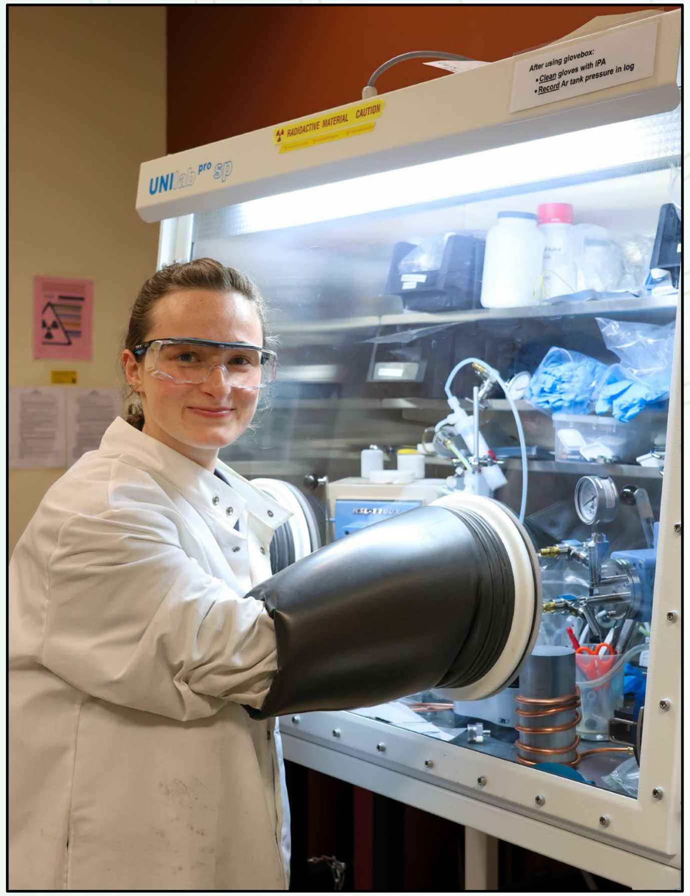


Argon glovebox#1, H_2O < 3 ppm, O_2 < 0.1 ppm
> 50 salts (chlorides, fluorides and iodides)

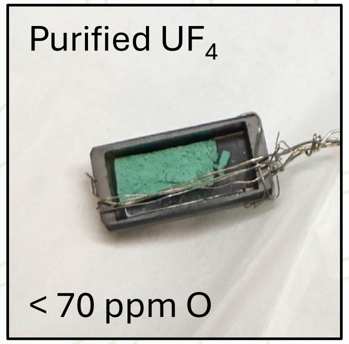
Contaminated salt

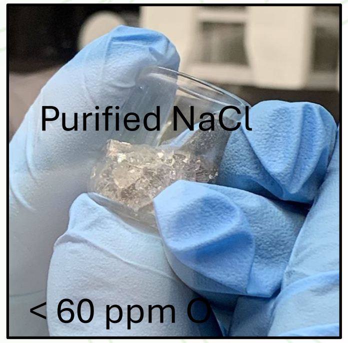
Melting point

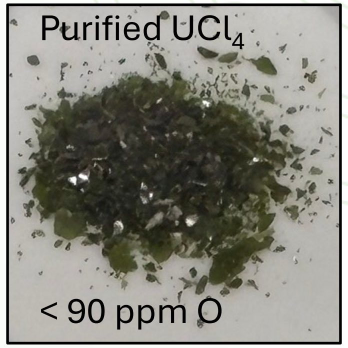




Argon glovebox#2, H_2O < 0.1 ppm, O_2 < 0.1 ppm
Two furnaces to dry/purify and synthesize salts

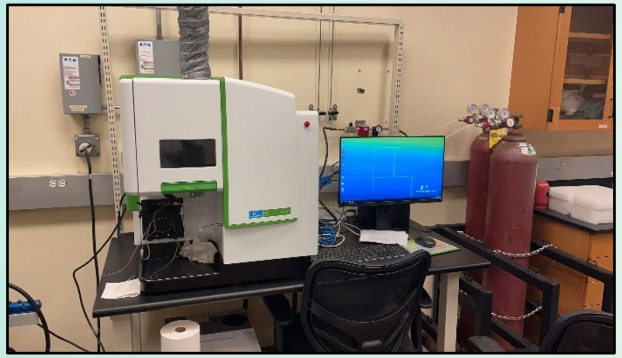




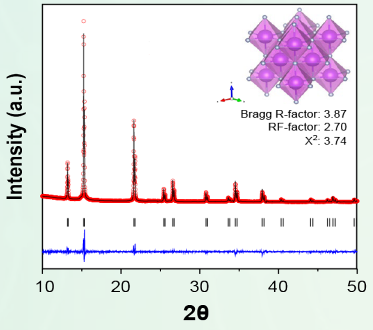


O and H analysis

Chemical analysis by ICP-OES



Phase purity by XRD



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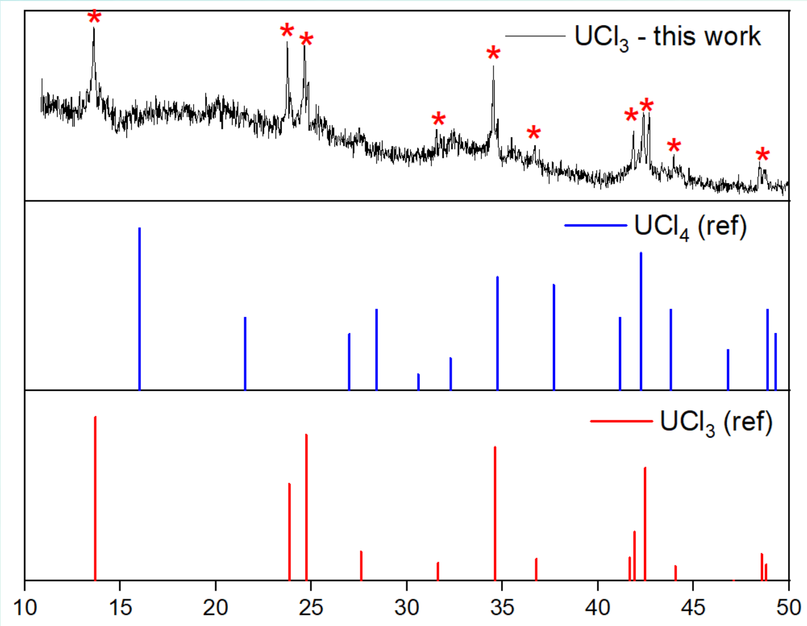
Synthesis of UCl_3

Obtaining ultra-dry UCl_4 starting material

Before purification	Identified impurities	After purification
450 ppm oxygen	$UOCl_2$ and UO_2	87 ppm oxygen
1924 ppm oxygen		242 ppm oxygen

Preliminary results on synthetizing UCl_3

UCl_3 salt



XRD UCl_3 pattern

Synthesis of CrF_2

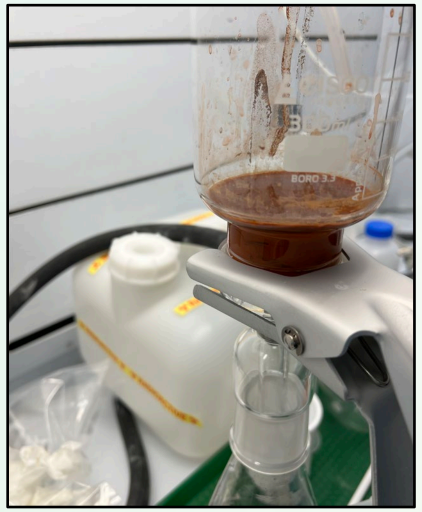
No commercial source is sufficiently pure for thermochemical studies.

Synthesis steps:

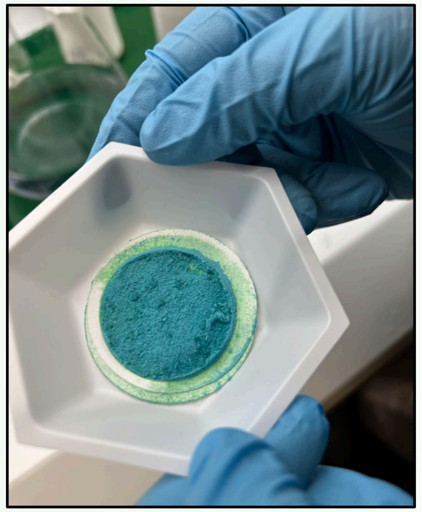
$2Cr(s) + 4COOCH_3(aq) \rightarrow \boldsymbol{Cr_2(O_2CCCH_3)_2(s)}$

$Cr_2(O_2CCCH_3)_2(H_2O)_{2(aq)} + 3NH_4F \cdot HF(aq) \rightarrow \boldsymbol{2NH_4CrF_3(s)} + \ldots$

$2NH_4CrF_3(s) \rightarrow \boldsymbol{CrF_2(s)} + NH_3(g) + HF(g)$



Anhydrous chromium tetraacetate



Ammonium chromium trifluoride

Chromium difluoride

Solid State Reactions for Phase Equilibria Studies

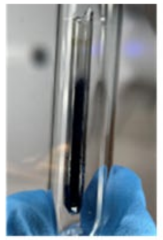
Formation of intermediary phases in salt systems are often poorly understood.

Adapted crucibles for salts

Quartz 5ml or flame tubes | Vitreous Carbon 0.9ml & 5ml | Ni boats 1.5ml

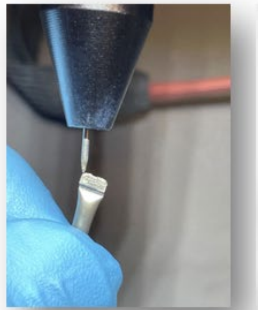
- Volatile chlorides:

Flame sealing



For quenching

- Volatile fluorides

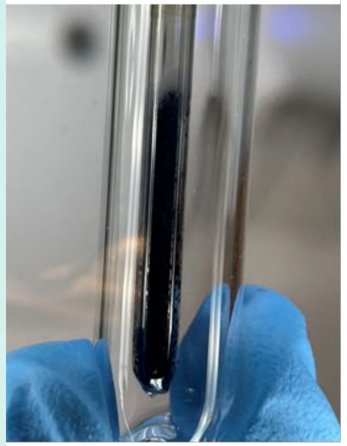


TIG welding

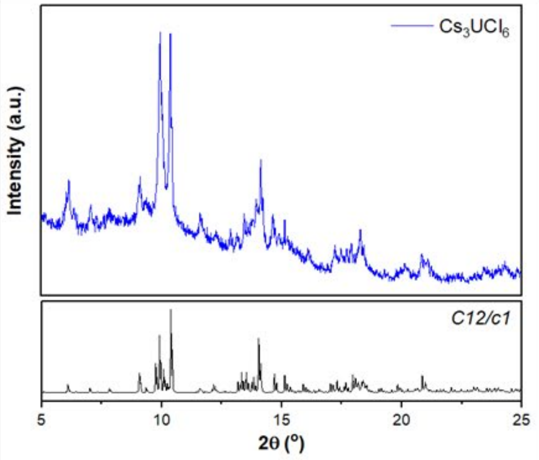
Laser welding

Synthesis using furnaces inside/outside gloveboxes

Cs_3UCl_6

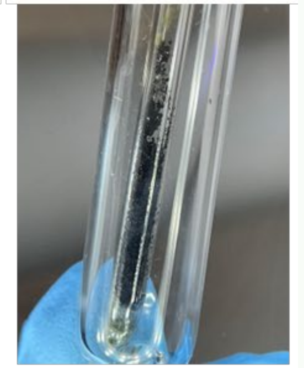


No standard/low precision PXRD pattern



CsU_2Cl_9

CsU_2Cl_7



Synthesis → Characterization → Thermochemical measurements → Modeling

Results suggest that working directly with uranium, rather than surrogates, will be more representative of MSR conditions!

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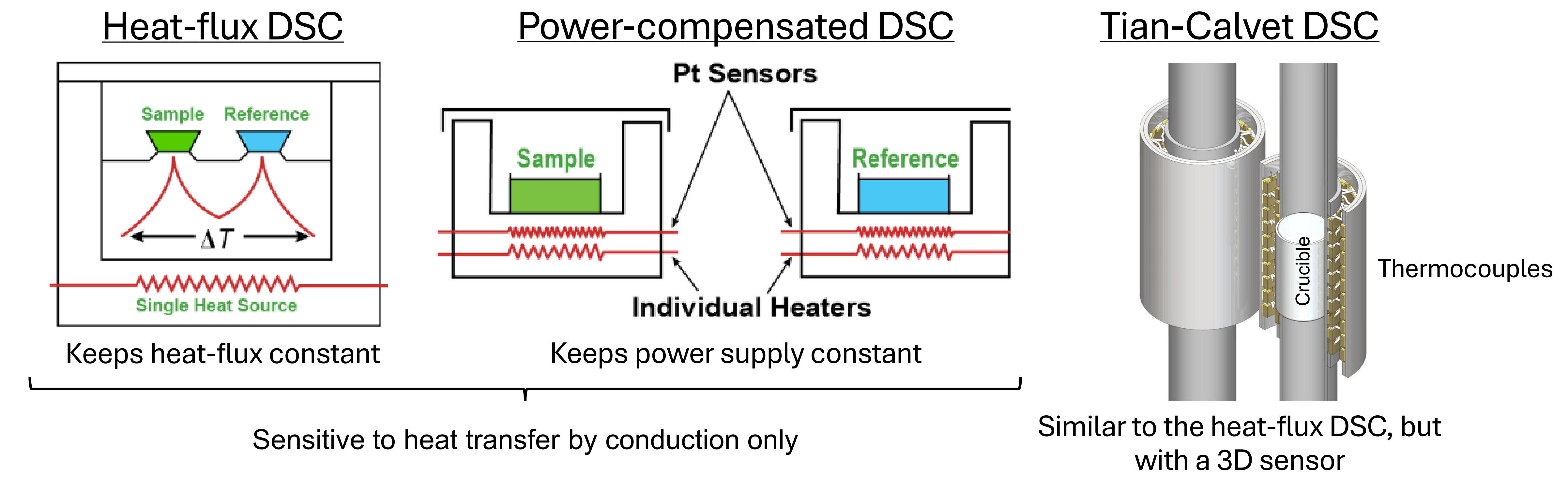
Measuring Thermal Properties of Salts

DSC classification by measurement principle:



At USC: Heat-flux DSC (2) and Tian-Calvet DSC (1)

“Handbook of Differential Scanning Calorimetry – Techniques, Instrumentation, Inorganic, Organic and Pharmaceutical Substances”, edited by J. D. Menczel & J. Grebowicz, Elsevier (2023)

K. Parwani (2018) - Thermal Analysis of Cobalt Chloride using DSC

https://setaramsolutions.com/

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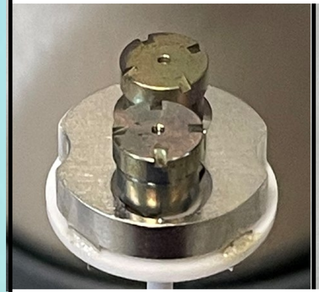
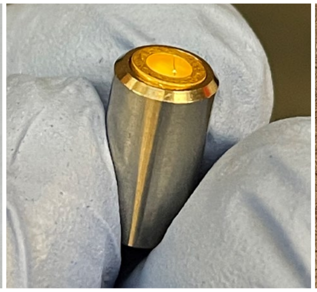
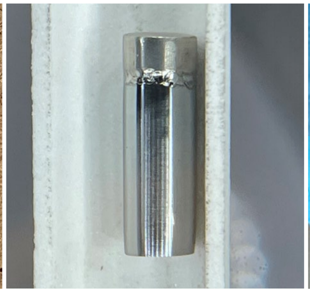
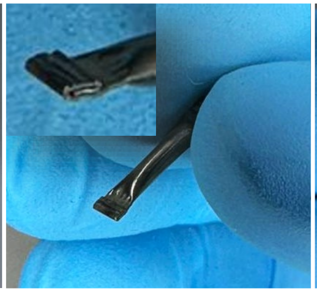
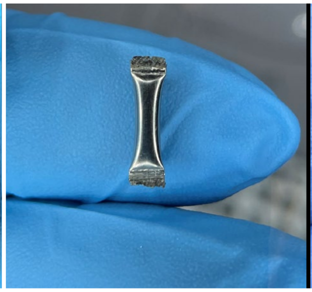
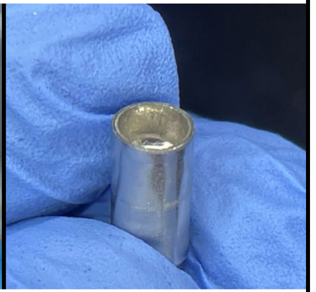
Containing Oxygen/Moisture Sensitive Samples for Measurements Outside of a Glovebox

Developed and tested a series of crucibles*

2020 → **2025/26**

	100 µl SS w Ni liner	27µl SS w Ni liner	130µl SS w Au liner	Sealed quartz	31.5 µl TZM	44 µl Ni folded	44 µl Ni welded	100 µl Ni
								
Source	Netzsch + UOIT	Netzsch + USC	Setaram + USC	USC	USC	USC	USC	USC
Mass	**~1480 mg**	**~ 875 mg**	**~2240 mg**	**~450 mg**	**~2435 mg**	**180 mg**	**110 mg**	**~320 mg**
Max. sample mass	10-50 mg	10-20 mg	50-80 mg	>100 mg	30-50 mg	30-50 mg	30-60 mg	Up to 200 mg
Symmetry	**Good**	**Good**	**Good**	**Poor**	**Poor**	**Poor/Good**	**Poor/Good**	**Better**
Leak resistant	Yes	Yes	Yes	Yes	No	No	Yes	Yes
Fluorides	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
Chlorides	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Heat capacity	**Poor**	**Poor**	**Good**	**Bad**	**Bad**	**Good**	**Good**	**Best**
Calorimeter	HF-DSC	HF-DSC	Calvet only	Calvet only	All DSCs	Calvet & drop	Calvet & drop	Calvet & drop

* MSD-TC (internal work)

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Melting Point and Enthalpy of Fusion Determinations

Using HF-DSCs and SS crucibles with Ni liners

It needs rigorous quality check of the liners to identify

- Defects
- Weight variation
- Nonuniform thickness

It allows high input of samples to determine phase transitions and initial insight about sample purity.

Sodium fluoride

DSC 404 F3 Pegasus® – Netzsch

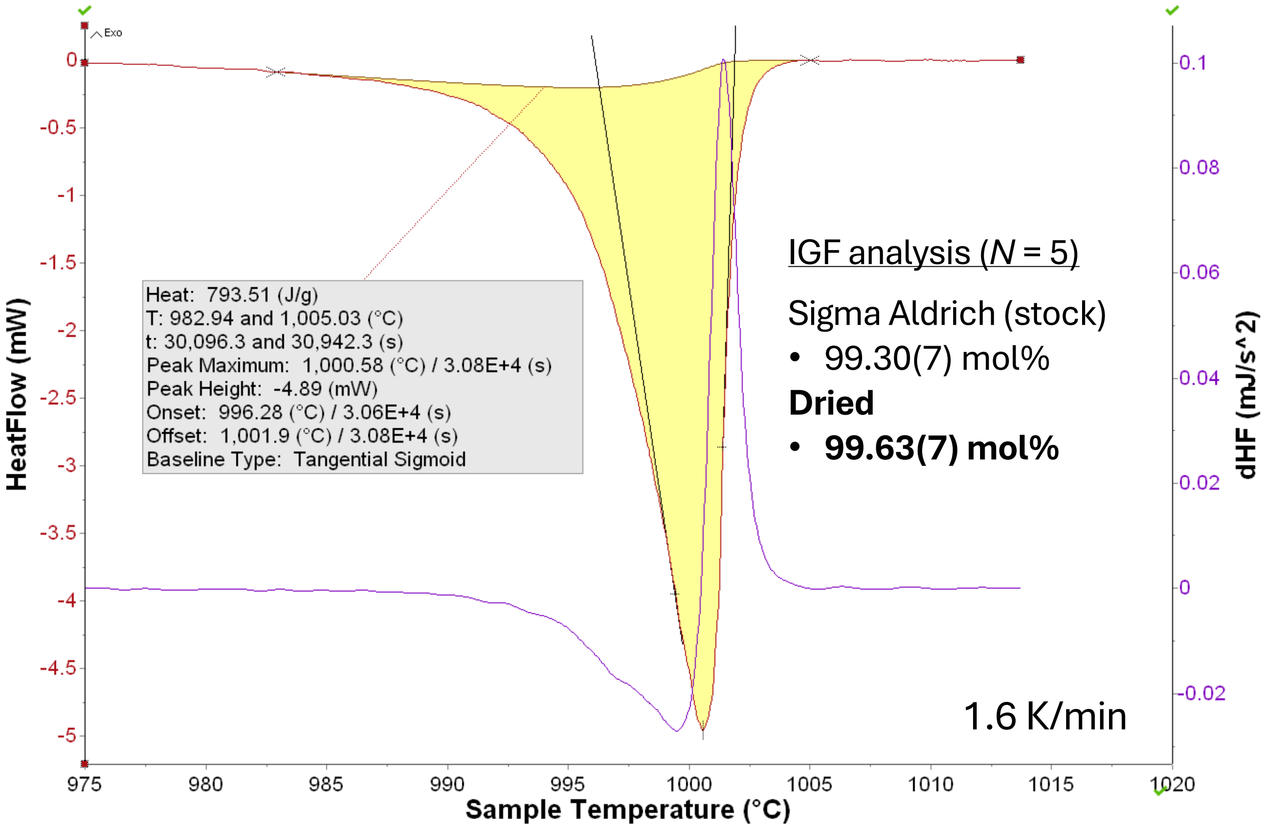
Sensor Type S (DSC404F1A72)

Crucibles: 100 µl SS w Ni liner

Calibrated with purified NaCl and Ag

Melting point

- Measured = 995.4 ± 2 °C
- Reference = 995.9 ± 1 °C



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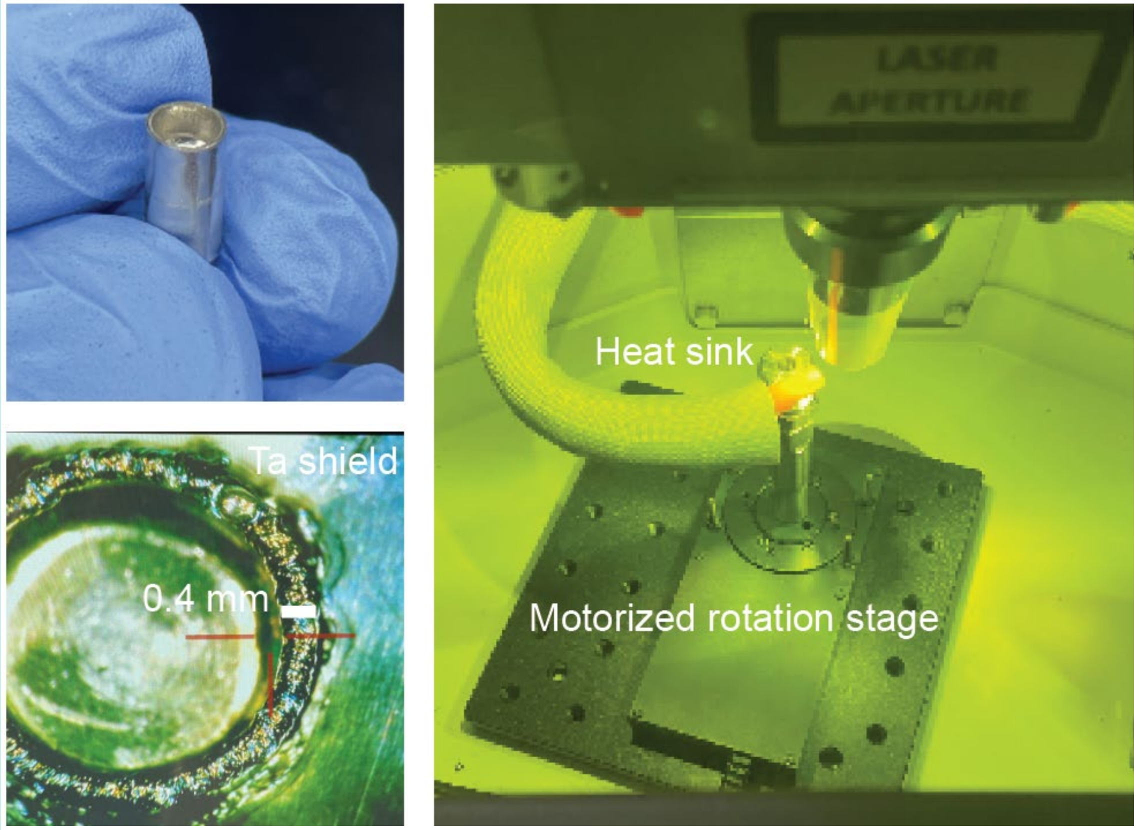
Improving Melting Point and Enthalpy of Fusion Determinations of Salts Using Custom-Made Crucibles

- Samples well-characterized by XRD and Inet Gas Fusion (O & H contaminants)
- Developed salt encapsulation and laser welding capabilities to improve sample:crucible weight ratio

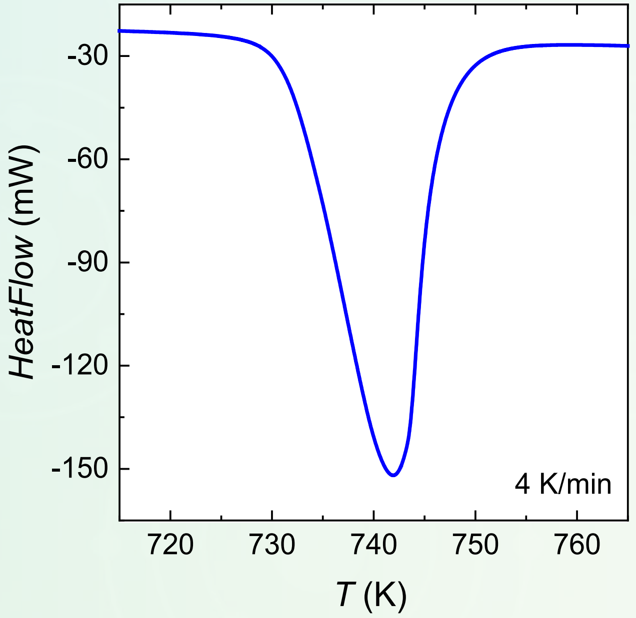


Calvet – Setaram

Sensor Type S, 240 thermocouples

Crucible: Nickel

FLiNaK (<120 ppm O, *N* = 13)



Melting point& Enthalpy of fusion

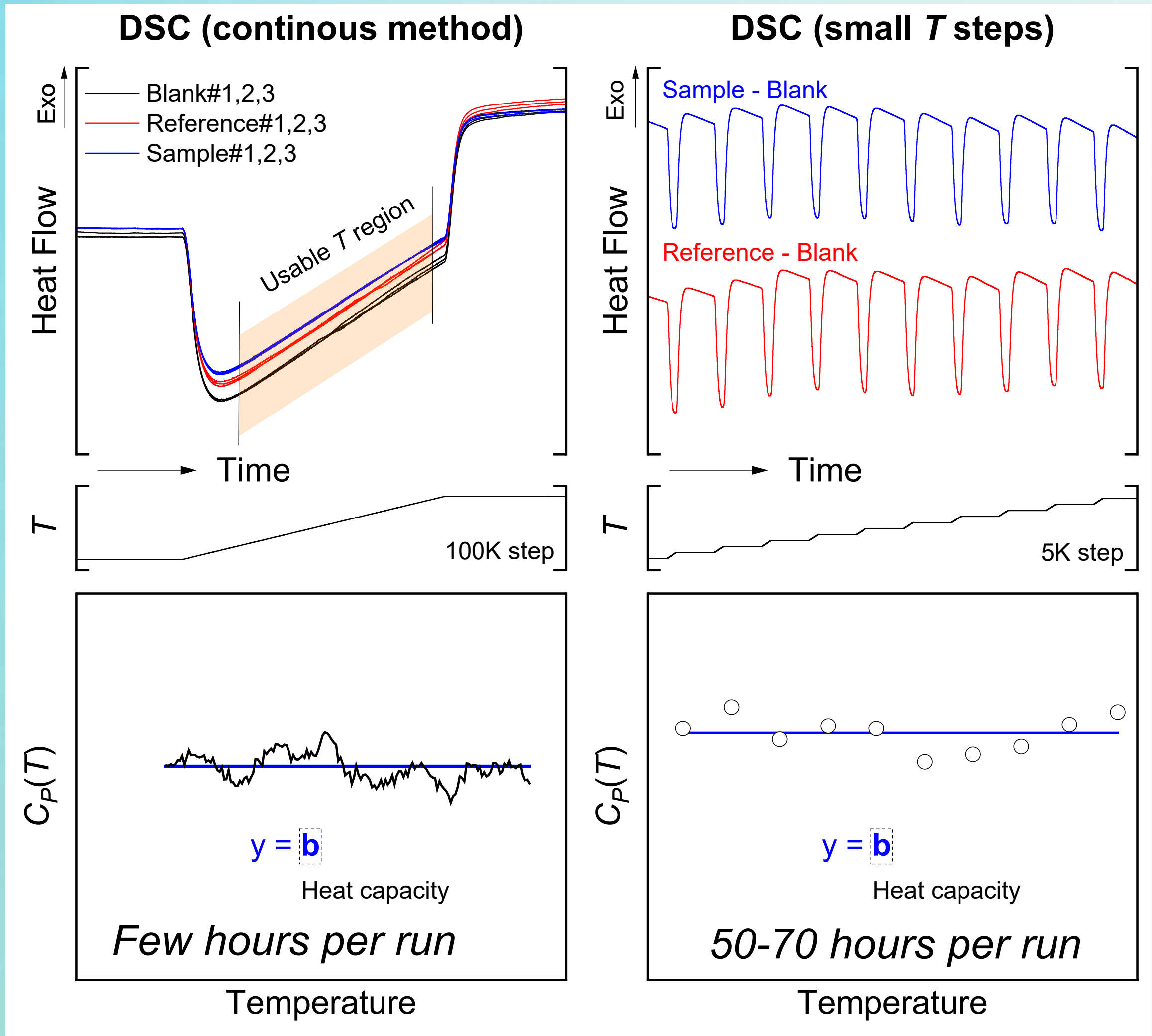
Rate	Cycle 2	Cycle 3	Cycle 4	Cycle 5
K.min^{-1}	K	K	K	K
4	731.9	731.8	732.1	732.0
K.min^{-1}	J.mol^{-1}	J.mol^{-1}	J.mol^{-1}	J.mol^{-1}
4	16,565	16,641	16,704	16,633

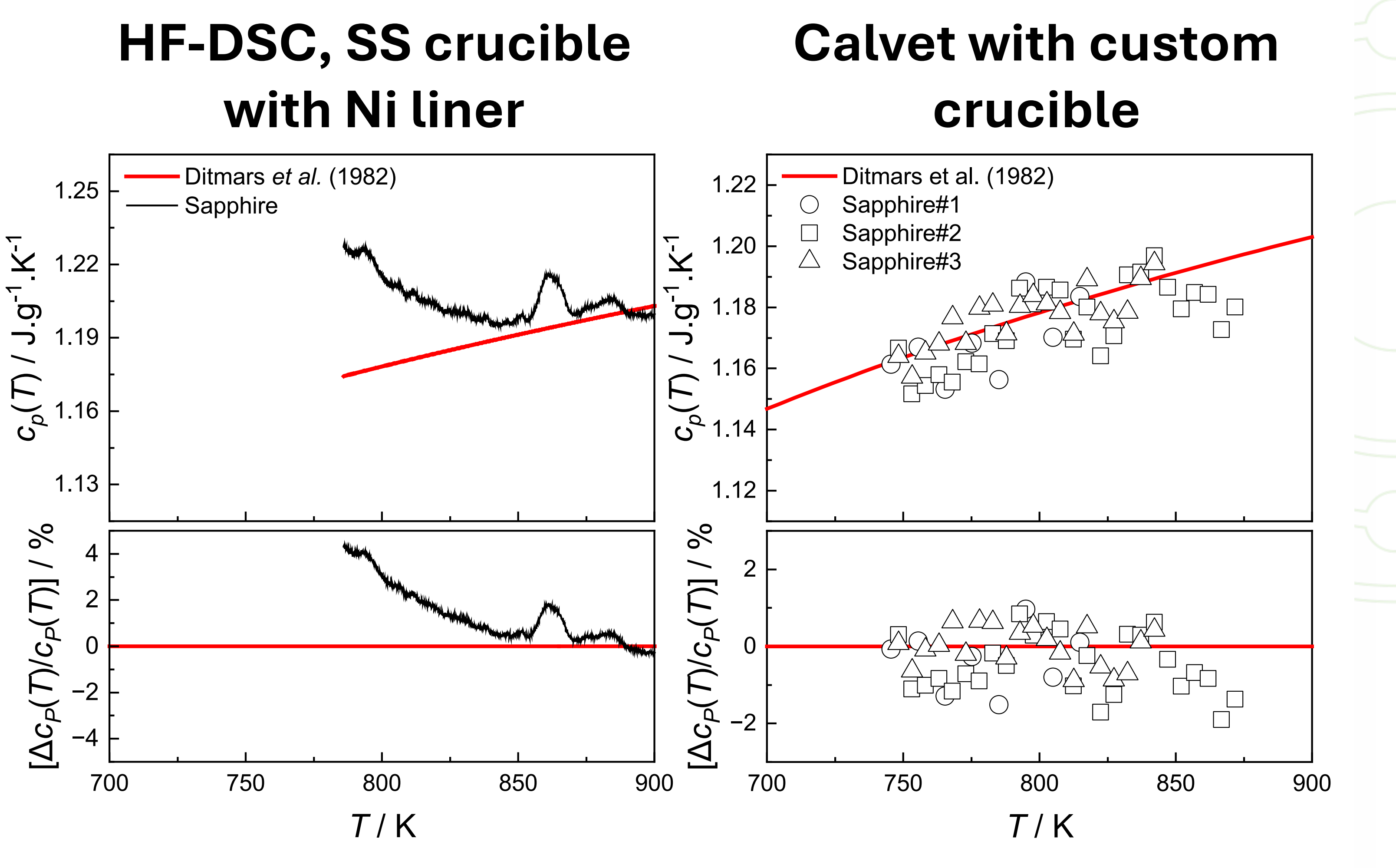
Average	2*SD
K	K
732.0	**0.2**
J.mol^{-1}	J.mol^{-1}
16,636	**90**

Schorne-Pinto *et al.* (under review) High-Accuracy Method for Measuring the Specific Heat of Molten Salts: Application to the FLiNaK and NaCl-$MgCl_2$ Eutectics

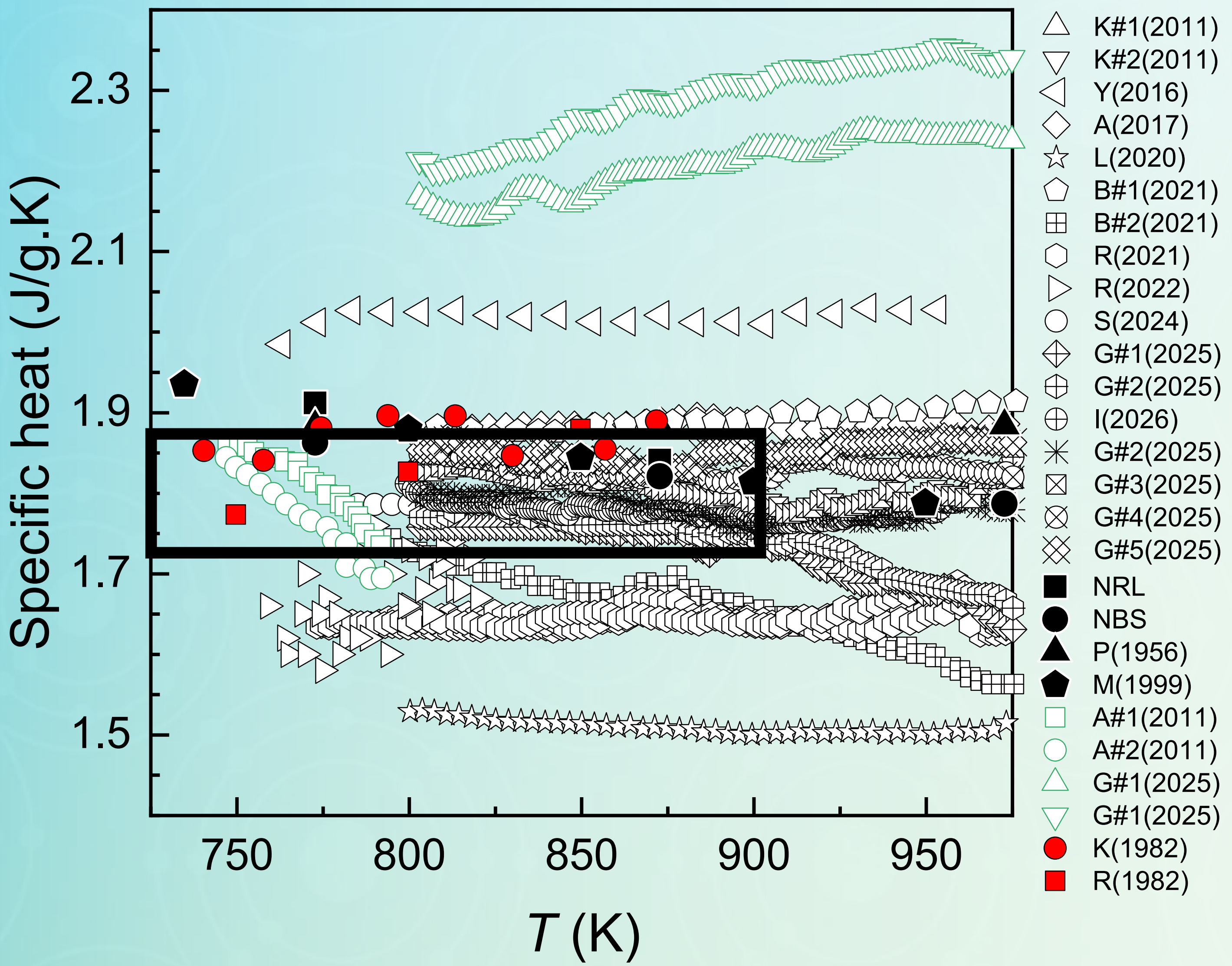
Measuring Highly Accurate c_P of Salts with a Calvet Instrument and Custom-Made Crucibles

Comparing different methods used to determine c_P

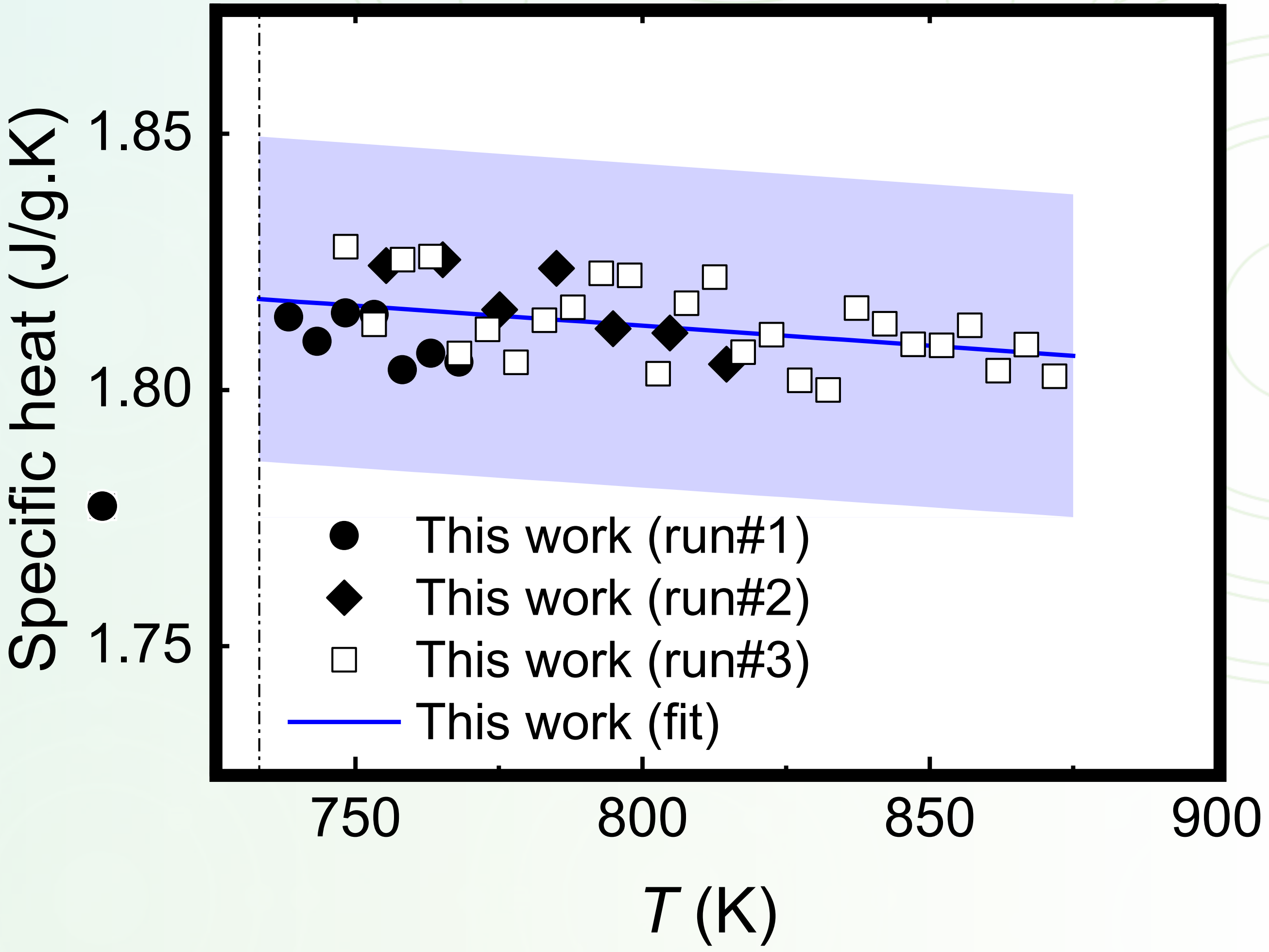




Superior Heat Capacity Determination: Example of Molten FLiNaK



Our measurements



Schorne-Pinto *et al.* (under review) High-Accuracy Method for Measuring the Specific Heat of Molten Salts: Application to the FLiNaK and NaCl-$MgCl_2$ Eutectics

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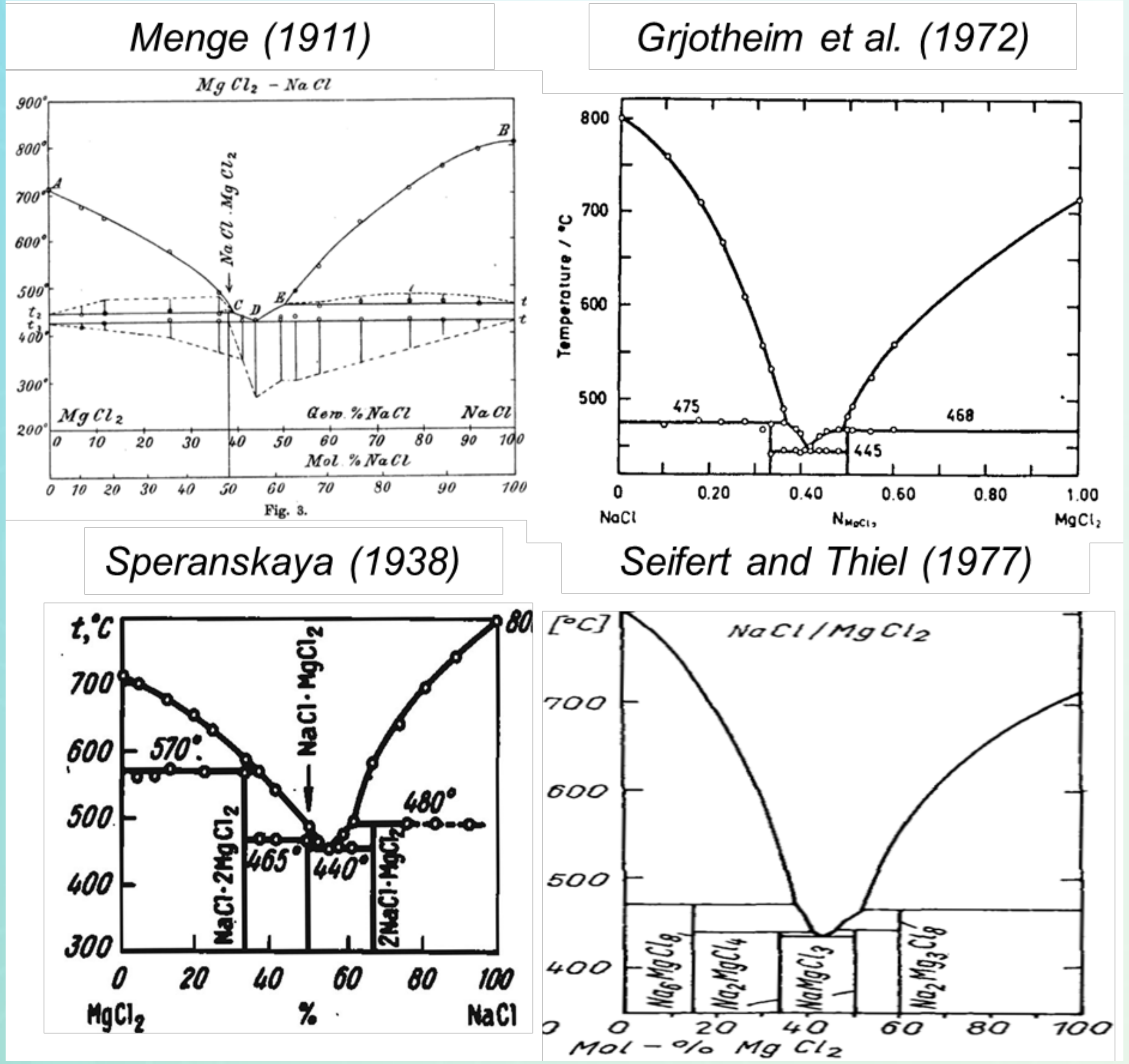
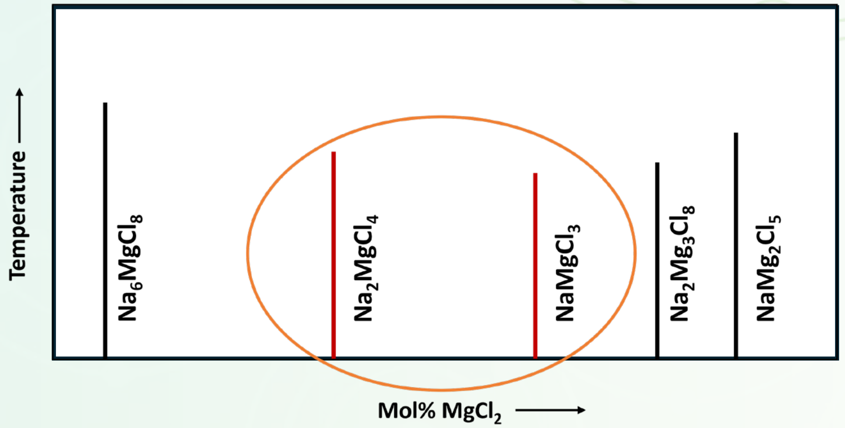
Elucidating the Thermodynamics and Phase Equilibria of the NaCl–$MgCl_2$ System

- Contradictory information in the literature



<u>Five intermediate phases</u> have been reported so far in the system by various investigators.

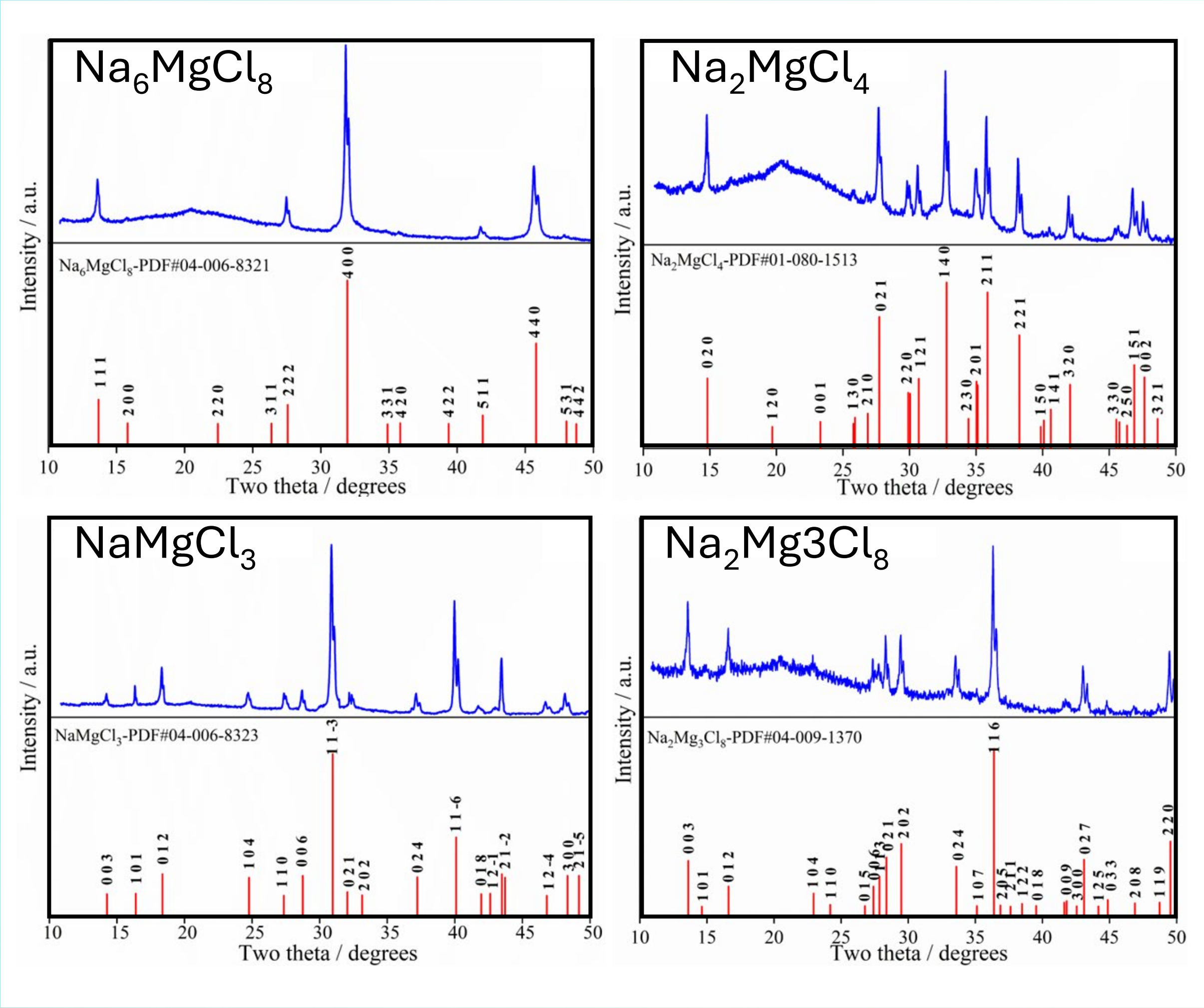


Our effort:

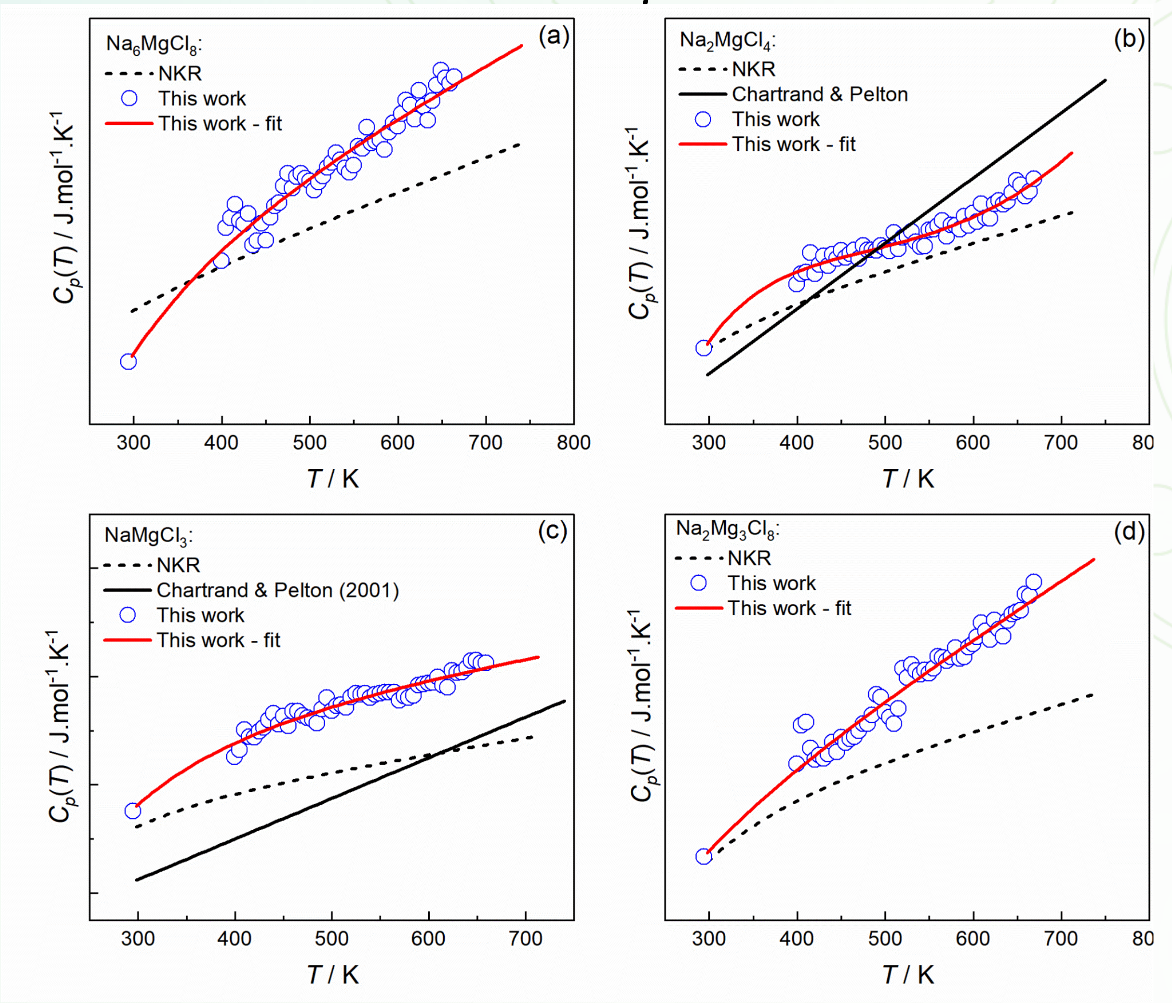
- Confirming the existence of reported intermediate phases by their synthesis.
- Establishing their thermal stability by DSC and HT-XRD.
- Determining the thermochemical properties of the intermediate phases.

First-Time Measurement of the C_p of the Four Intermediate Phases of the NaCl-$MgCl_2$ system

- Four phases proved to be stable



- First time direct C_p measurements



Manissery *et al.* (under review) Elucidating the Thermodynamics and Phase Equilibria of the NaCl–$MgCl_2$ System

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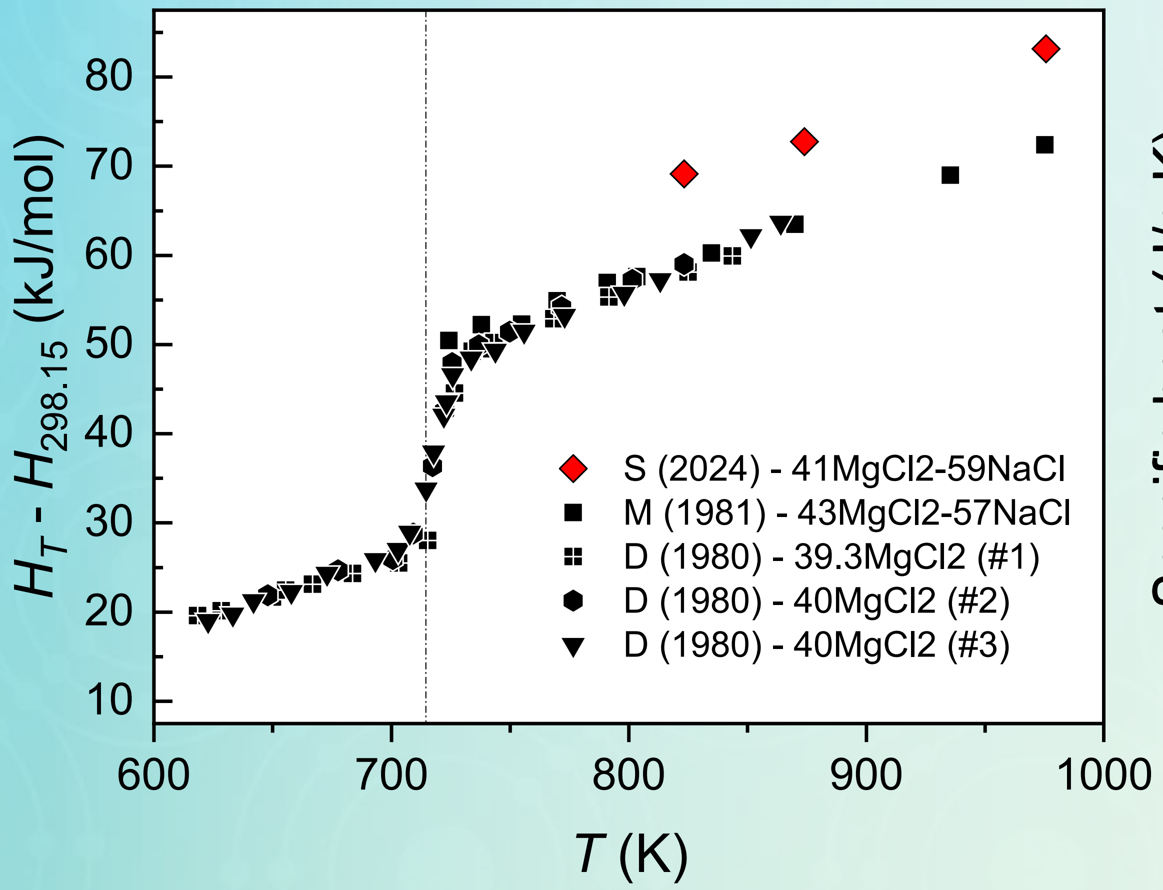
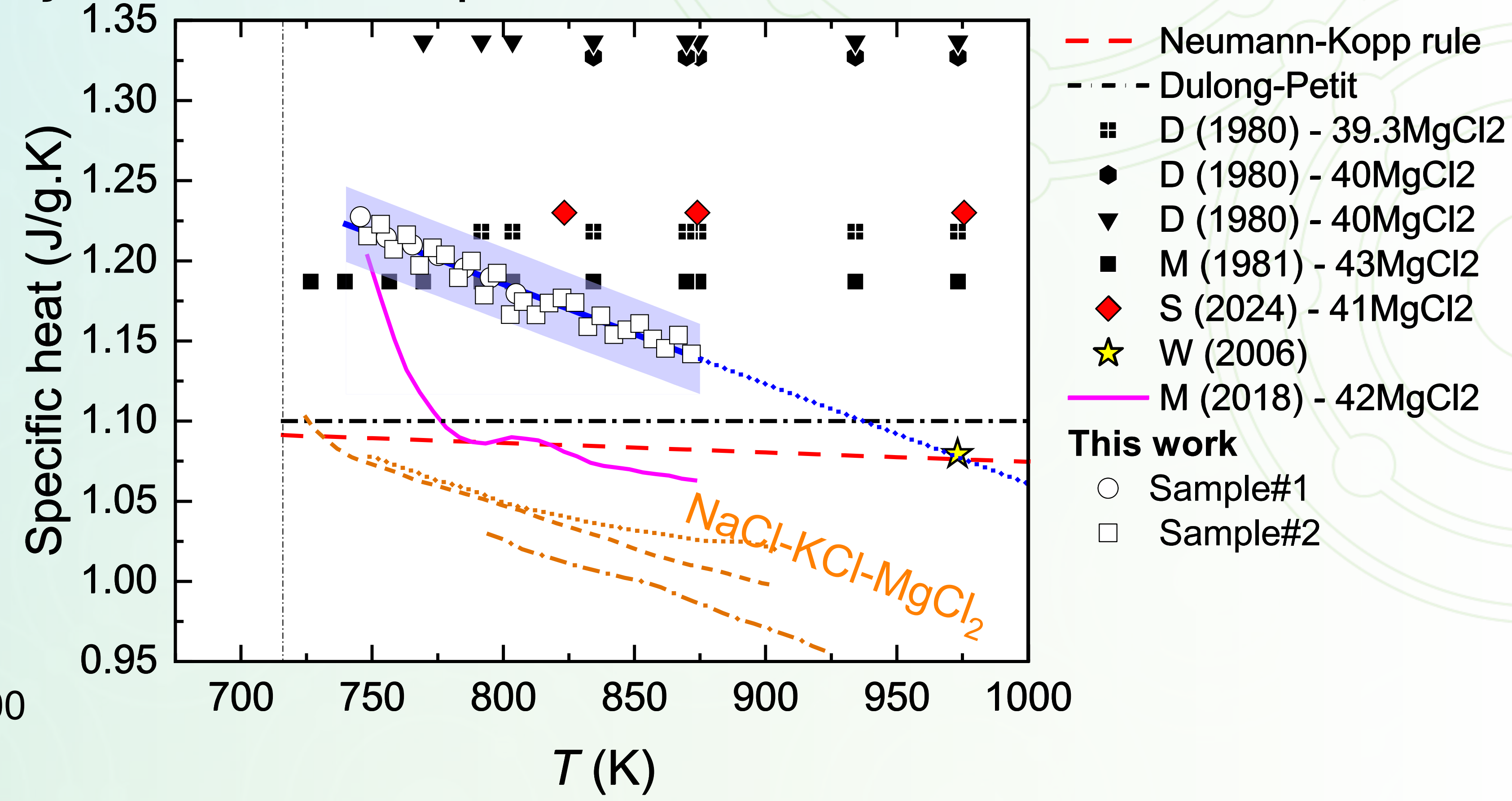
Disclosing the c_p Behavior of 58NaCl-42MgCl$_2$ Eutectic Using State-of-the-Art Calorimetry

Enthalpy increment is contradictory



Specific heat

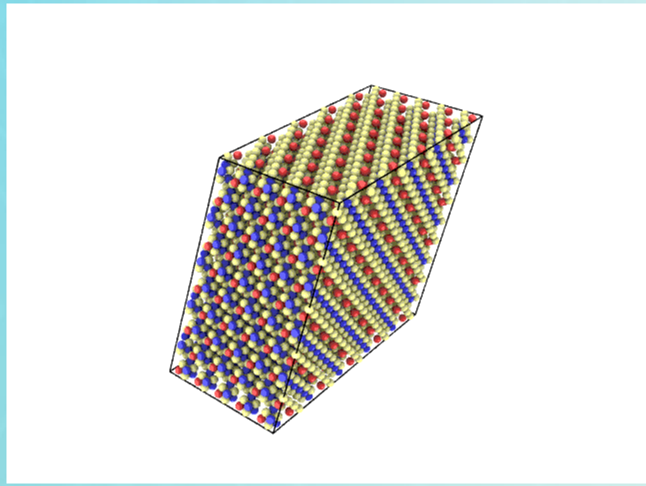


The protocol is highly accurate, and it is being used to generate reference data for MSD-TC/TP

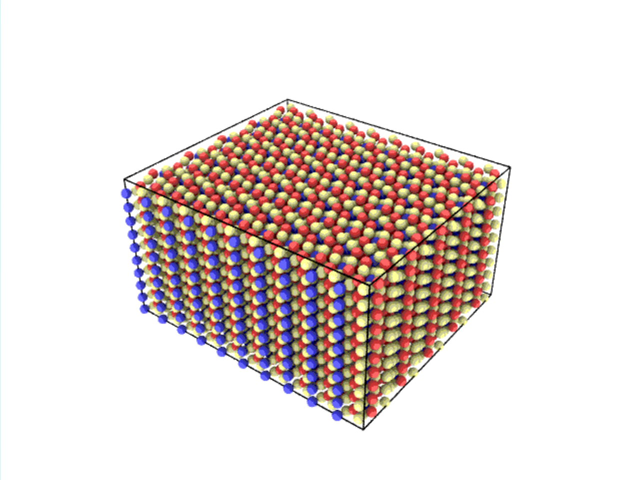
Schorne-Pinto *et al.* (under review) High-Accuracy Method for Measuring the Specific Heat of Molten Salts: Application to the FLiNaK and NaCl-MgCl$_2$ Eutectics

Filling The Gaps: Atomistic Simulations with Experimental Reference at USC

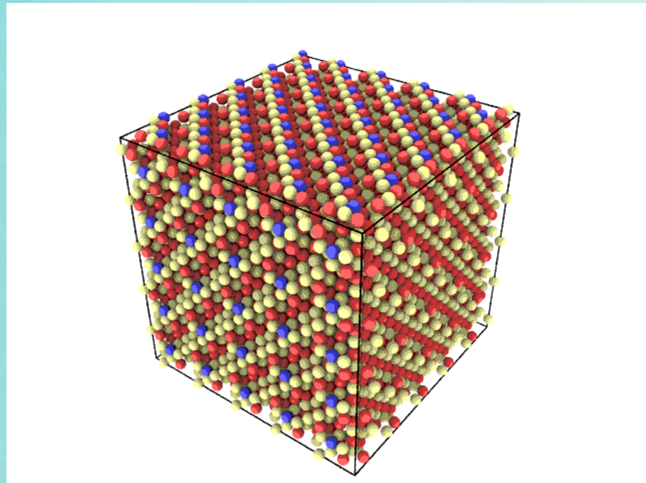
$Na_2Mg_3Cl_8$



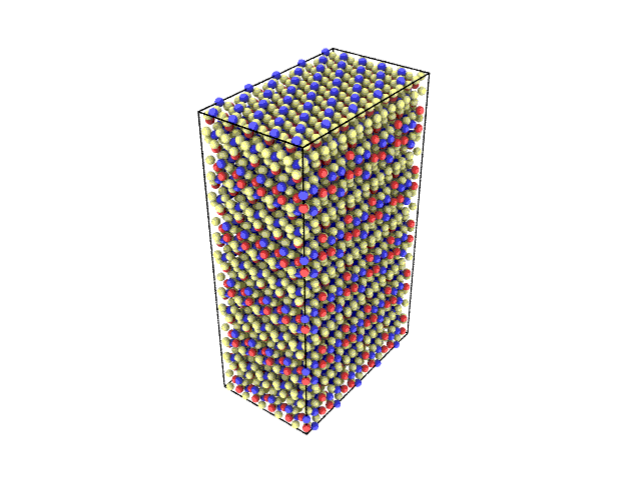
Na_2MgCl_4



Na_6MgCl_8



$NaMgCl_3$



Simulations at 850 K

Machine Learning-accelerated Molecular Dynamics (ML-MD) simulations provide atomistic-scale interpretation of the anomalous temperature dependence of the specific heat. Examples:

- Anharmonic in solids.
- Resolving contributions from short-range order evolution and coordination changes.

It is a key tool to assist interpretation of experimental data.

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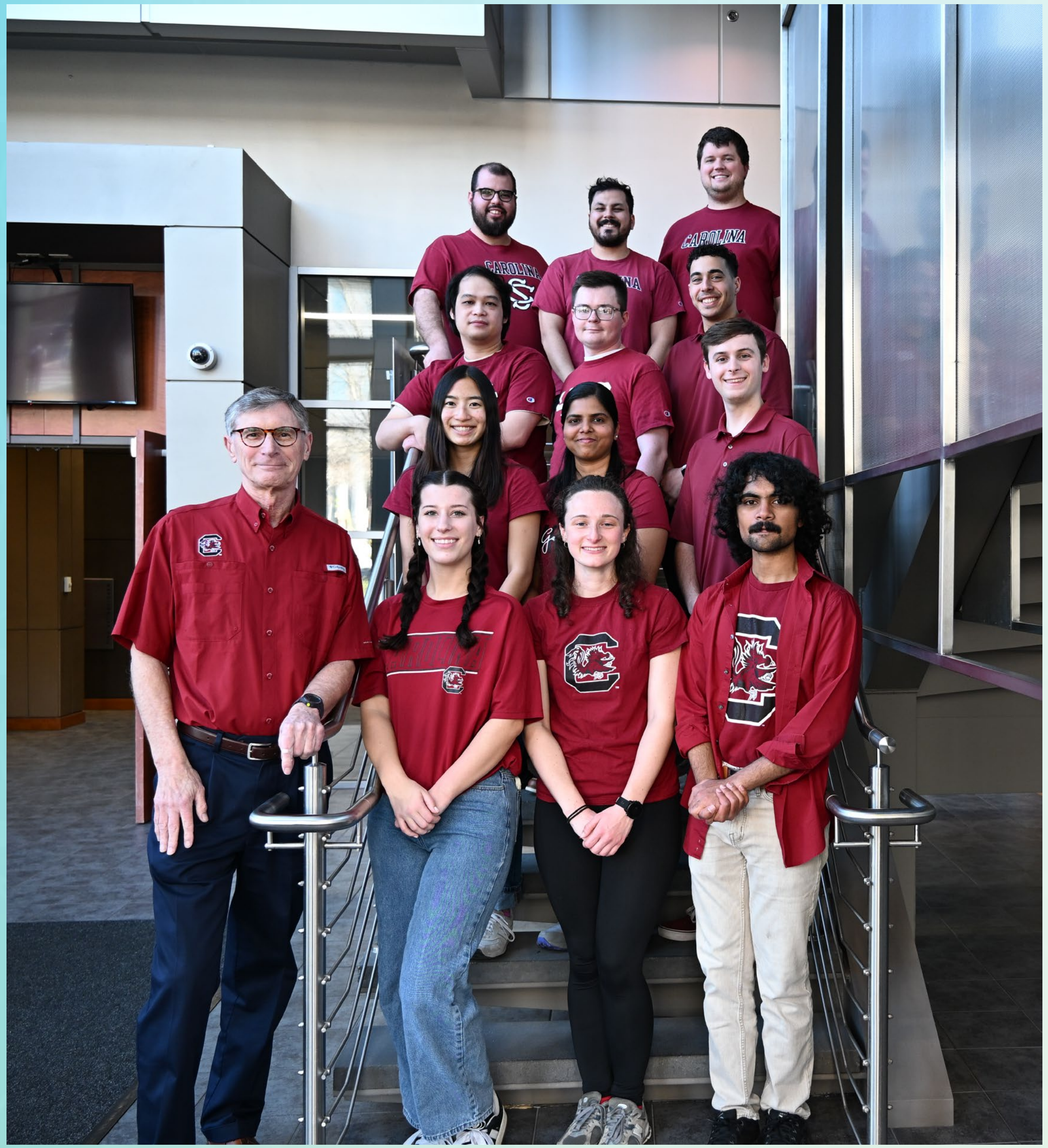
Conclusions

- Extensive experimental work was performed to purify and synthesize salts to reduce any bias that contamination may have.
- Thermochemical measurements are made to address knowledge gaps and validate historical thermochemical data.
- A custom laser-welded hermetic nickel crucible was developed specially to improve enthalpy of fusion and heat capacity of salts.
- It is considered an improvement over the current methods, obtaining heat capacity for molten salts and solid phases with uncertainty below 2%.
- The protocol is readily transferable to other molten salts, including actinide-bearing fuels, providing reference data and enabling future systematic investigation of oxygen contamination effects on molten salt thermochemical properties.

USC General Atomics Center Group



Support for related activities provided by

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Nuclear Energy Advanced Modeling and Simulation

NEUP Nuclear Energy University Program
U.S. Department of Energy

Laboratory Directed Research & Development
INL Idaho National Laboratory

Thank you

Juliano Schorne-Pinto

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