Molten Salt Reactor Campaign FY24 Report

Thermophysical Properties of Uranium-Bearing Molten Salts

Hannah K. Patenaude

S. Scott Parker

Marisa J. Monreal

Oct 2024

Los Alamos
NATIONAL LABORATORY

Prepared for: U.S. Department of Energy/National Nuclear Security Administration, Los Alamos MSR campaign

Prepared by: Hannah K. Patenaude, Postdoctoral Research Associate
Inorganic, Isotope, and Actinide Chemistry (C-IIAC)

Derivative Classifier Review	
Reviewed and determined to be UNCLASSIFIED. This review does not constitute clearance for public release.	
Derivative Classifier Name and Position/Title: Josh White, Scientist MST-8	Date: 16 Dec 2024

Los Alamos NATIONAL LABORATORY

Contents

Figures

Tables

1 Introduction

The mission of the U.S. Department of Energy – Nuclear Energy (DOE-NE) Molten Salt Reactor (MSR) Campaign is to develop the technological foundations to enable MSRs for safe and economical operations while maintaining a high level of proliferation resistance. The DOE-NE MSR Campaign serves as the hub for efficiently and effectively addressing, in partnership with other stakeholders, the technology challenges for MSRs to enter the commercial market. The MSR Campaign supports experimental and computational efforts to characterize molten salt systems relevant to reactor operation, safety, and maintenance, including, but not limited to, thermophysical properties measurements of actinide (An)-bearing salts. The inherent challenges of measurements in high temperature, corrosive molten salt environments require meticulous preparation for carefully planned experiments to provide reliable data that can support MSR design, computational models, and licensing.

Understanding fundamental thermodynamic properties such as the enthalpy of fusion (ΔH_{fus}), heat capacity (C_p), and phase transitions of An-bearing molten salts is of utmost importance to the MSR community. Experimental data are used to validate and improve advanced models powered by resources like the Molten Salt Thermal Properties Database (MSTDB).[1] This report includes the experimental progress made during FY24 at Los Alamos National Laboratory (LANL), for which differential scanning calorimetry (DSC) was the primary technique for characterizing uranium-containing chloride and fluoride salts for the MSR Campaign. First, preliminary results of successful pathways for novel approaches to the synthesis of UF_4 are discussed, in preparation for C_p measurements of pure UF_4 in FY25. Then, the C_p of the binary UCl_3-NaCl eutectic is described. Finally, initial efforts and planned work to map out phase boundaries of the UCl_3-NaCl-$MgCl_2$ ternary system, whose phase transitions are primarily—if not exclusively—reported via calculations,[2,3] is discussed for two compositions. Each of these accomplishments are foundational to continued exploration of An chloride and fluoride salt properties, and will ultimately expand the available information needed by the MSR community.

2 Novel UF_4 Synthesis Pathways

Procuring UF_4 is nontrivial and ad hoc synthesis is typically more practical. Common techniques include the use of fluorine gas (F_2(g)) or hydrogen fluoride gas (HF(g)), which have specific processing requirements and cannot be utilized with the current infrastructure. Therefore, novel approaches have been considered and tested in order to produce quantities of UF_4 suitable for DSC studies, which typically require < 100 mg per sample.

Multiple pathways have been successful in synthesizing > 98% pure UF_4, taking inspiration from actinide fluoride literature.[4–6] This work uses inorganic uranium compounds that can be readily made from metallic or oxide forms of uranium. The product purity was confirmed by powder X-ray diffractometry and C, H, N, halide combustion elemental analysis. The procedures are being refined and will be finalized in the next fiscal year in preparation of thermophysical properties measurements of UF_4, as is discussed in the following sections. The reagents used are commercially available and the synthesis is scalable to > 1 g. All required equipment is off-the-shelf. Therefore, we anticipate that the ease of these preparations compared to traditional hydrofluorination methods will make pure uranium fluorides more synthetically accessible to the MSR community.

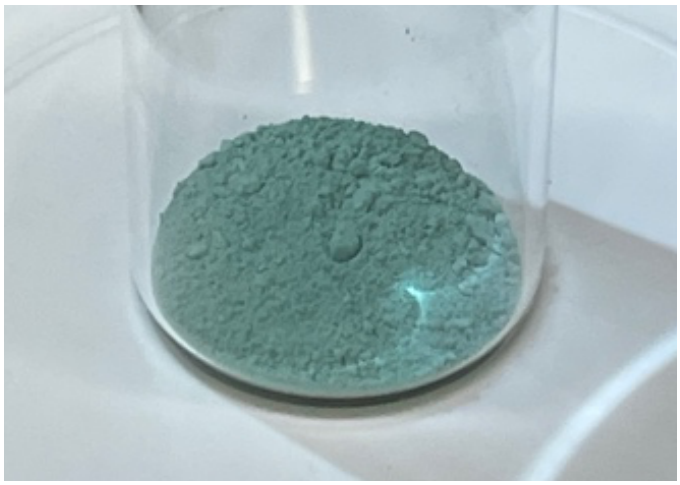

Figure 2-1. UF_4 synthesized using non-hydrofluorination processes.

As described in greater detail in Section 3, the pure UF_4 will also be cast using the graphite mold system and subsequent polishing to pursue solid-phase heat capacity measurements which are vastly under-represented in the literature.

3 Comprehensive Approach to UCl_3-NaCl Heat Capacity

The degree to which molten salts absorb and store heat is an important property to consider when using them as a primary coolant or fuel-bearing medium. The challenges associated with molten salt measurements and complexity of multicomponent systems make sensitive techniques like DSC nontrivial and result in significant gaps in literature. There are preliminary reports of experimentally and computationally determined liquid C_p for certain mixtures of interest to the MSR community (e.g., UCl_3-NaCl).[7–9] The ASTM E1269[10] guide recommends using the ratio method when measuring C_p with DSC where a standard, like sapphire, is measured first and used for the final calculation against the sample data. This process is difficult to adapt for liquid salt systems due to the elevated vapor pressure of the liquid phase, salt interaction with the sample crucible, and essential differences between measurement on liquid samples against solid reference materials. A goal of this work is to consider a comprehensive approach to measurement of the C_p of solid and liquid salts by combining direct and indirect measurements.

The temperature dependence of C_p across solid, liquid, and gas phases exhibits discontinuities at the phase transition temperatures. When considering integral heat capacity, these discontinuities are measured as the enthalpy associated with the respective phase transition. The total energy (Q) measured using DSC from room temperature to well past the melting point (T_m) can be described using the relationship illustrated in Figure 3-1 as the sum of the total energy retained in the solid phase ($M*C_{p,\,solid}$) for the solid phase, the enthalpy associated with melting (ΔH_{fus}), and the total energy retained in the liquid phase ($M*C_{p,liquid}$). $C_{p,solid}$ can be reliably determined as a function of temperature using the ratio method and a polished cast of the salt sample matching the geometry of the reference (sapphire). Ideally, standards should be chosen so that the reference and sample volumes are similar. ΔH_{fus} is determined from cyclic melt point measurements. Following a blank baseline, a measurement of the total energy retained by the sample across a wide temperature range from room temperature to well above the melting point allows calculation of the integral heat capacity in the liquid phase.

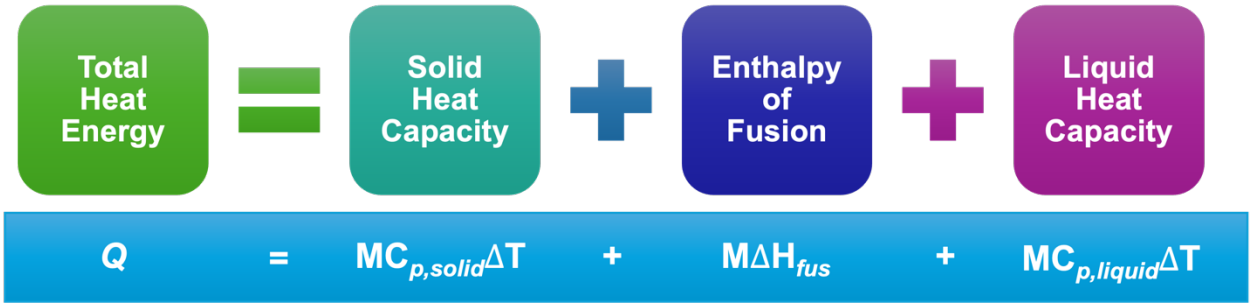

Figure 3-1. Relationship describing the total heat energy as a sum of the heat capacity of the solid phase as a function temperature, enthalpy of fusion, and the liquid heat capacity as a function temperature.

There are no reported data from experimental or computational work for $C_{p,solid}$ of any UCl_3-NaCl compositions. This work provides novel information characterizing both solid and liquid heat capacity, which is of practical value for salt management when adding or removing salt for high temperature applications. The initial measurements to determine $C_{p,solid}$ and ΔH_{fus} are discussed below, especially in the context of derivation of integral $C_{p,liquid}$, which can be compared to ratio-method or computationally-derived data available in the literature.

3.1 Materials and Methods

A Netzsch 404 F1 Pegasus High-Temperature Differential Scanning Calorimeter (Rh/Pt furnace) was calibrated following the methods described in ASTM Standard E1269-11.[10] The temperature calibration followed practice E967[11] and the sensitivity calibration followed practice E968 (five-point standard calibration).[11,12] Platinum crucibles with lids were selected for heat capacity measurements in order to maximize measurement sensitivity. High purity (>99.9%) benzoic acid, $KClO_4$, CsCl, Li_2SO_4, and $BaCO_3$ (Netzsch) standards were selected so that the phase transition temperatures of the standards span the temperature range of interest, and because the glass transitions of these materials do not result in reaction with the crucible material.* The CrNi steel calibrations were performed with Ag, $BaCO_3$, CsCl, Pb, In, and Sn (Netzsch) with CrNi steel crucibles (Netzsch) sealed with Ni (>99.9%) foil using 3 N-m of torque under Ar(*g*) in an inert atmosphere glovebox. This two-crucible strategy was employed in order to (1) produce more sensitive heat capacity measurements on the solid phase materials, and (2) minimize any potential oxidation or evaporation of material during cyclic melting with the hermetically sealed steel crucibles. Following the ratio method for determination of solid heat capacity,[10] a high purity sapphire disc (6 mm diameter, 1 mm height) was used as a reference for calculations of solid C_p. Ultra high-purity (UHP) Ar(*g*) was supplied as the purge, protective, and sheath gases during all measurements. The NaCl (Fisher Scientific, 99.0%) was dried in a VAC NextGen Glovebox (< 1 ppm O_2, < 1 ppm H_2O) vacuum oven antechamber.

3.2 Melt Point Measurements of the NaCl-UCl_3 Eutectic

Measurement of the melt point of eutectic mixtures serves to confirm congruent melting (i.e. the composition is correct), and integrating the heat flow signal through the melt event allows calculation of the enthalpy of fusion (ΔH_{fus}). The sample was heated at ramp rate of 20 °C/min for one cycle followed by three heating cycles at 5 °C/min. Average values of the extrapolated onset and peak temperatures were

*Benzoic acid is particularly volatile with a very low melting point temperature (122 °C) and is used as the reference phase transition such that the material does not interact with the Pt crucible.

determined using the three slow heating cycles. The phase transition ($s \rightarrow l$) for the UCl_3-NaCl eutectic is shown in Figure 3-2, from which the melt onset (523.5 ºC), peak melt (530 ºC), and ΔH_{fus} (144.2 J/g) are determined. These values align closely with what has been experimentally determined and reported in literature.[3,7,13]

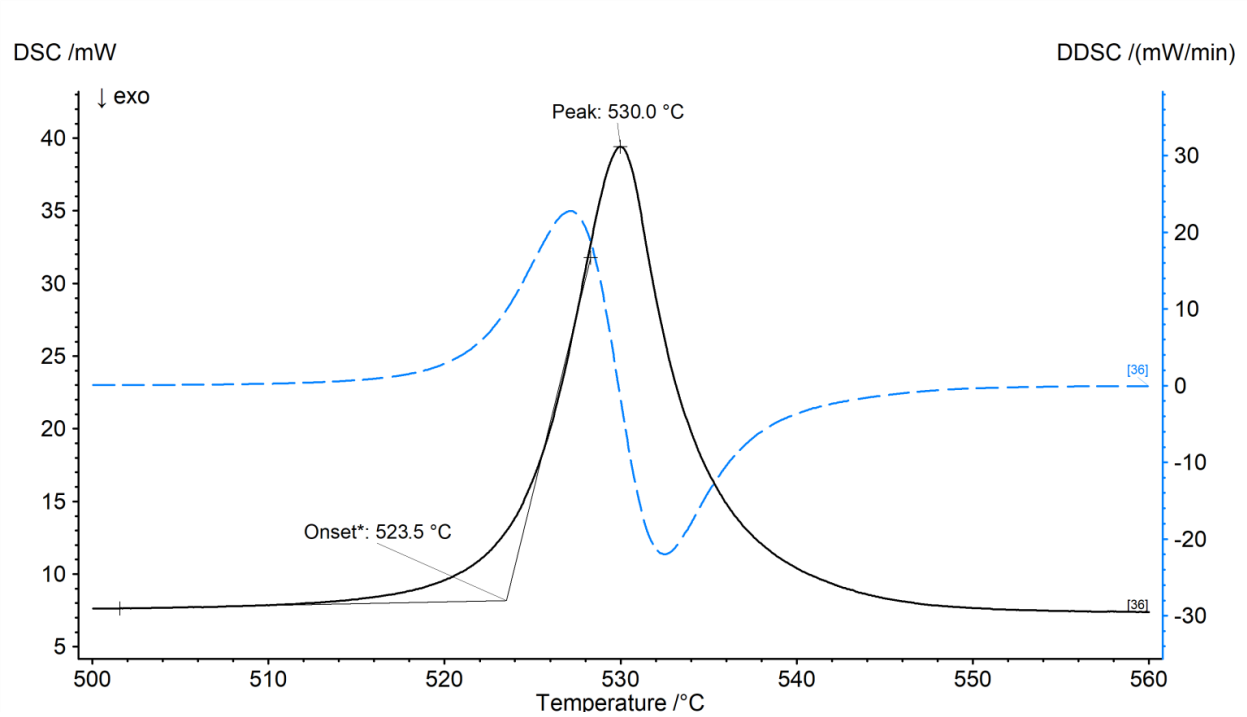

Figure 3-2. DSC thermogram of UCl_3-NaCl melting process (black line). The first derivative is plotted as the blue dashed line.

3.3 Heat Capacity

3.3.1 *Salt Casting*

The sample was cast in a graphite mold created in-house to produce pellets that fit easily into the Pt crucibles, to optimize the surface contact and accuracy of heat transfer measured by the DSC sample carrier and mimic the geometry of the sapphire standard. A sample of the eutectic composition of UCl_3-NaCl (34-66 mol%)[14] in an in-house fabricated graphite mold was held at 700 ºC for 30 minutes in an MTI KSL1100 muffle furnace in an inert atmosphere glovebox. Each casted salt pellet was sanded to a height where it fit in the crucible without making contact with the lid. The bottom surface of the sample in contact with the base of the crucible was polished to a mirror finish. The graphite mold and polished salt cast are shown in Figure 3-3.

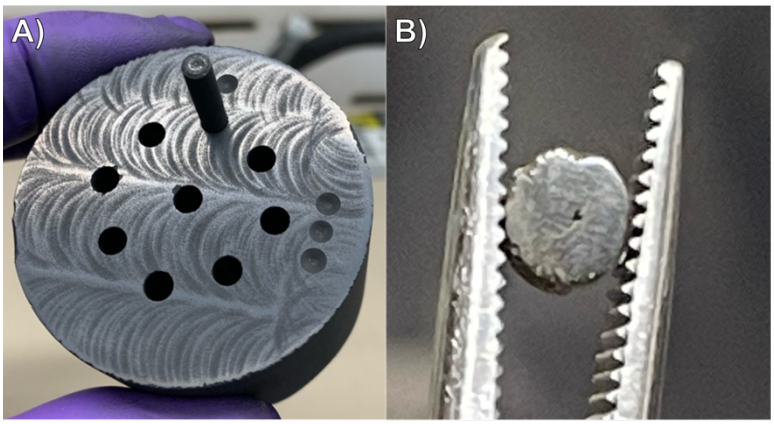

Figure 3-3. In-house fabricated graphite mold (A) and UCl_3-NaCl cast (B) for solid-phase C_p measurements.

3.3.2 *Solid-Phase Heat Capacity*

A baseline measurement of empty reference and sample crucibles was taken from 30 ºC to ~50 ºC below the melt point of the sample. A sapphire standard was heated over the same temperature range, followed by the cast salt which was measured in triplicate. A final baseline measurement was repeated to ensure no changes to the crucible occurred throughout the runs with the standard or sample. The series of measurements were taken in quick succession in order to minimize the impact of baseline drift.

The measured solid $C_p(T)$ for UCl_3-NaCl is illustrated in Figure 3-4 and the average value across 150-400 ºC is 0.45 ±0.01 J/(mol·K). To the best of our knowledge, the UCl_3-NaCl eutectic $C_{p,solid}$ is not reported in the literature. Published reports of $C_p(T)$ for the eutectic system target temperature ranges at and above the melt point, in which case the heat capacity is slightly higher (0.60 J/(g·K)).[7,8] This increase in heat capacity on melting is common in chloride salts mixtures, and the apparent difference correlates with ΔH_{fus}. For the present study, ΔH_{fus} = 144.2 J/g was determined during the melt point measurement (see *Section 3.2*). Thus, average heat capacity of the liquid phase across ΔT (from T_1 to T_2 where T_1 is the completion of the melt and is the final temperature) is:

$$\overline{C_{p(l)}} = \frac{Q - m\int_{30}^{523} C_{p(s)}(T)dT - \Delta H_{fusion}}{m\Delta T} = 0.6\,J/g\cdot K$$

$\Delta T = T_2 - T_1$ where T_1 is the completion of the melt and T_2 is the final temperature. This value of heat capacity for the liquid phase aligns with what has been reported experimentally (0.60 J/(g·K))[7,8] and for calculations using MSTDB-TC data (0.63 J/(g·K)).[9]

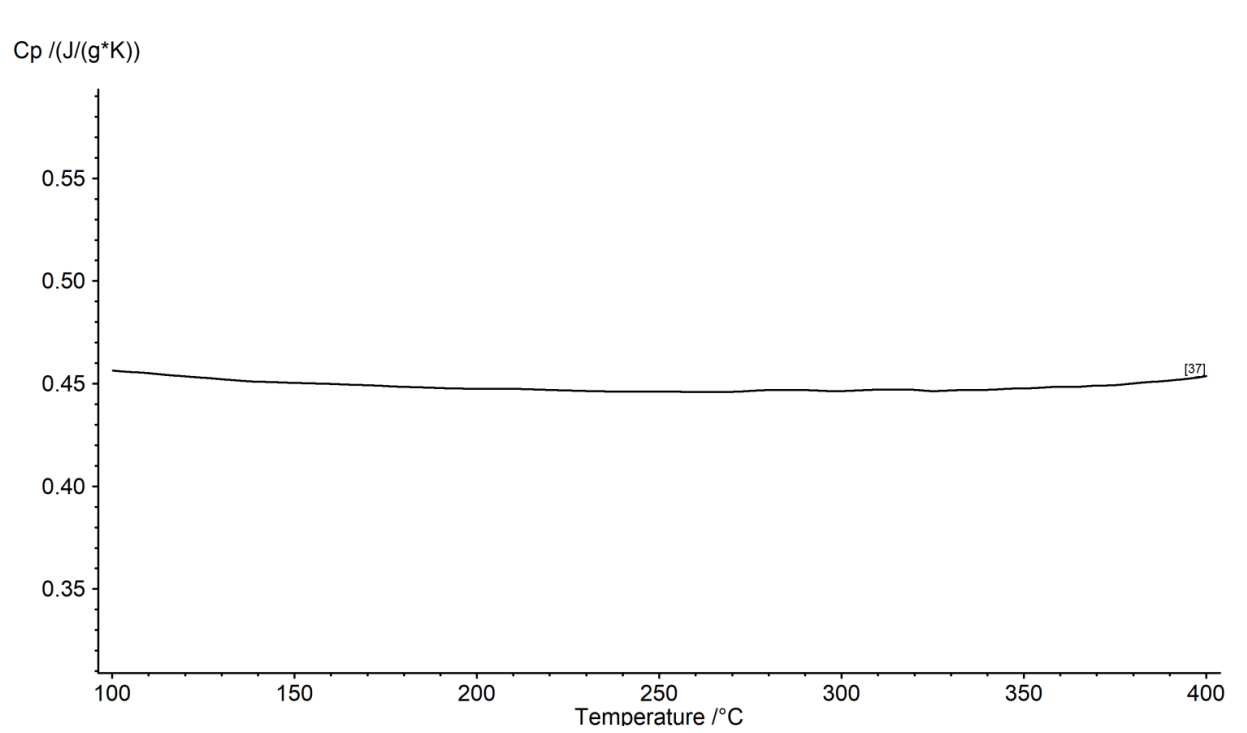

Figure 3-4. Solid-phase C_p of UCl_3-NaCl from 150 to 400 °C.

4 Phase Transitions of the UCl_3-NaCl-$MgCl_2$ System

The ternary UCl_3-NaCl-$MgCl_2$ system is also of interest to the MSR community, however, limited experimental results exist in the published literature concerning the phase transitions in this mixture. The primary source of information describing the liquidous nature of this ternary was calculated by Beneš and Konings in 2008.[15] Studies have been published describing the three pseudo-binaries (UCl_3-NaCl, UCl_3-$MgCl_2$, and NaCl-$MgCl_2$) comprising the ternary using experimental data,[16–18] but none can be found for the ternary. In this work, the anticipated eutectic composition (UCl_3-NaCl-$MgCl_2$, 11.6-63.3-25.1 mol%) and an off-eutectic composition (UCl_3-NaCl-$MgCl_2$, 5.7-68.4-25.9 mol%) were measured using DSC to verify T_m and report values for ΔH_{fus}.

4.1 Materials

The Netzsch DSC 404 F1 Pegasus was calibrated for temperature and sensitivity using a six-point standard set comprising Ag, $BaCO_3$, CsCl, Pb, In, and Sn (Netzsch) with CrNi steel crucibles (Netzsch) sealed with Ni foil using 3 N-m of torque under Ar(*g*) in an inert glovebox. The NaCl (Fisher Scientific, 99.0%) and $MgCl_2$ (Beantown Chemical, 99%) were dried in the vacuum oven antechamber.

4.2 Ternary Phase Transitions

The melt point of the eutectic composition of UCl_3-NaCl-$MgCl_2$ (11.6-63.3-25.1 mol%) has been reported as 446 °C[15] and other thermodynamic assessments of the ternary have only been described using non-experimental techniques.[2,3,15] The results of this work will help to further develop the UCl_3-NaCl-$MgCl_2$ phase diagram by measuring phase transitions near the eutectic composition (Table 4-1). Approximate liquidous temperatures for each composition have been calculated using data from Beneš and Konings (see Fig. 2, Ref. 15).

Table 4-1. Compositions studied of the UCl_3-NaCl-$MgCl_2$ ternary system.

Composition	UCl_3 (mol%)	NaCl (mol%)	$MgCl_2$ (mol%)	Estimated liquidous (°C)
A	11.6	63.3	25.1	446[15]
B	5.7	68.4	25.9	ca. 520[15]

The samples were heated at ramp rate of 20 °C/min for one cycle followed by three heating cycles at 5 °C/min. Average values of the onset and peak temperatures were determined using the three slow heating rates. The phase transitions observed compositions A (blue) and B (black) are illustrated in Figure 4-1.

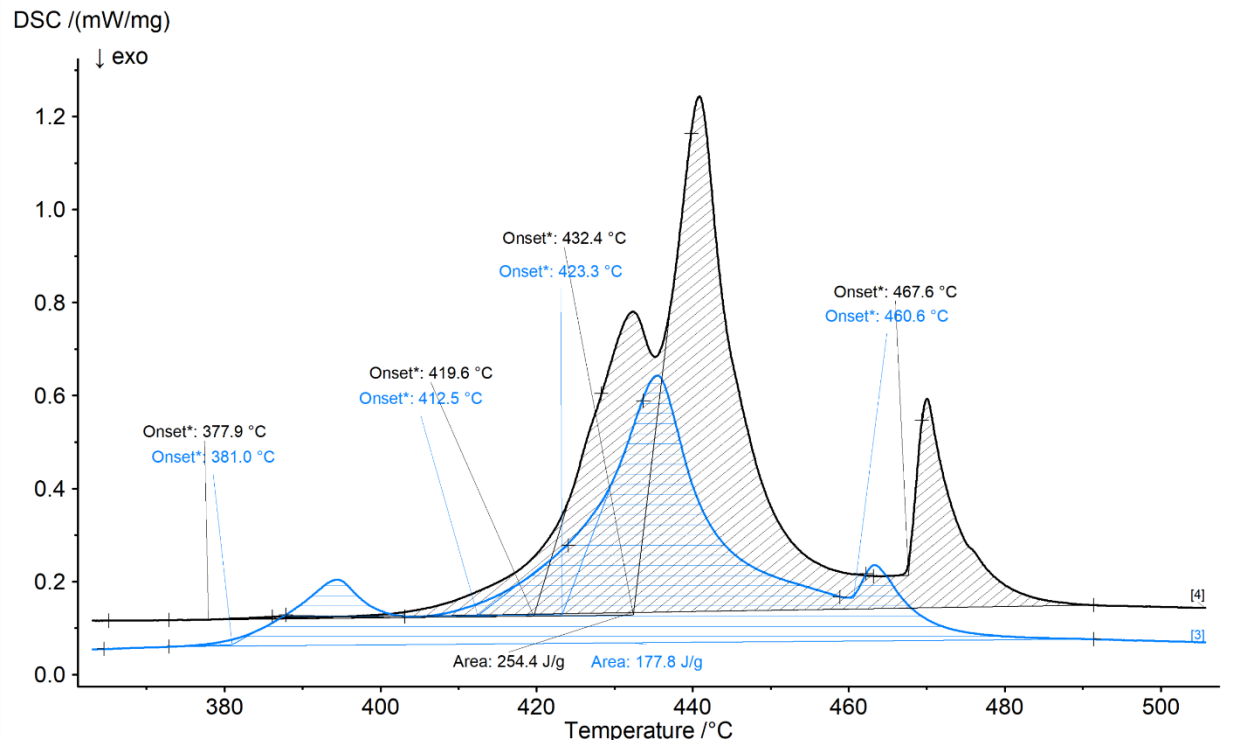

Figure 4-1. Differential scanning calorimetry curves of two compositions of UCl_3-NaCl-$MgCl_2$.

Both compositions exhibited a complicated peak structure during the melting process. This finding suggests that the actual eutectic composition for this system is quite different than the current theoretical estimate. Preliminary analysis of the approximate peak onset temperatures and total ΔH_{trans} are shown on Figure 4-1. In both measurements, the majority of the melt occurs around 440 °C, which aligns with the computational value for the eutectic at 446 °C. Given the wide peak separation spanning over a 100 °C range, a more comprehensive set of measurements encompassing a range of compositions are required. Although the differences between the two compositions is far less significant than what was expected based on the calculations reported in the literature, there are notable changes indicating that the increased NaCl concentration (63.3 to 68.4 mol%) and decreased UCl_3 concentration (11.6 to 5.7 mol%) are important to consider. Shifting the NaCl-$MgCl_2$ pseudo-binary phase diagram from 71.6-28.4 mol% to 72.5-27.5 mol% would likely constitute a very minor change to the overall ternary system. The NaCl-rich region of the pseudo-binary phase diagram gives only a minor melting point increase.[16] In the case of the UCl_3-$MgCl_2$ system, a shift from 31.5-68.5 mol% to 18.0-82.0 mol% would take the pair from close to their eutectic

composition (32.5-67.5 mol%, 673 ºC) to a slight increase in homogenous liquid temperature region following the decreasing UCl_3 concentration.[2] This change is likely less significant for the overall ternary compared to the NaCl system considering the melting point of pure $MgCl_2$ melting point is only 718 ºC.[17] Finally, experimental and computational reports of the pseudo-binary UCl_3-NaCl phase diagram generally agree and indicate that a composition shift from 15.4-84.6 mol% to 7.7-92.3 mol% would result in a steep melting point increase to over 700 ºC as the UCl_3 concentrations drops below 10 mol%.[18] This change is likely the most significant contribution to the temperature shift of the primary phase transition process represented by the second peak.

Given the discrepancy between what is observed experimentally and reported through calculations, there is a need to further investigate the UCl_3-NaCl-$MgCl_2$ ternary. Additional compositions with varying amounts of each end component will be evaluated both for phase transitions and eventual C_p following the methodology outlined for the UCl_3-NaCl eutectic previously. While the total ΔH_{fus} for the three-peak systems increases with increasing molar concentration of UCl_3, the global minimum in ΔH_{fus} is not yet known.

5 Conclusions

The work performed at LANL in FY24 to support the MSR Campaign has laid the groundwork to fill the gaps pertaining to experimental studies of UF_4, the eutectic composition of UCl_3-NaCl, and the UCl_3-NaCl-$MgCl_2$ ternary. The novel approaches taken to synthesizing actinide halide salts both produces high-quality species for DSC (and other) measurements and expands access to such materials at other institutions where corrosive gases are challenging to use. In some cases, the organic synthesis routes may propose alternative pathways that could be practical for industrial-scale applications. Future pursuits will include Pu chloride and fluoride species as the LANL Plutonium Science (PluS) Laboratory nears completion and prepares for small-scale plutonium operations in FY25.

The heat capacity of these systems is critically important to operation but is especially challenging to measure accurately and precisely. However, the systematic, careful approaches taken for the data presented herein, and planned for future experiments, produce highly valuable results. Adaptations to further improve the current infrastructure includes determining pathways for constructing hermetically sealed crucibles that can be used to maintain inert environments and extend to liquid-phase C_p studies of An-bearing molten salts.

Further investigations of phase transitions within the ternary system will validate or improve the current models that have been published or determined using the MSTDB. Additionally, a more detailed analysis is required to better understand the complex processes involved in phase transitions of ternary systems.

6 Acknowledgements

The authors would like to acknowledge support from the Chemistry and Sigma Divisions at the Los Alamos National Laboratory. This work was funded by the US Department of Energy's Office of Nuclear Energy Molten Salt Reactor (MSR) Campaign.

7 References

(1) Besmann, T. M.; Schorne-Pinto, J. Developing Practical Models of Complex Salts for Molten Salt Reactors. *Thermo 2021, Vol. 1, Pages 168-178* 2021, *1* (2), 168–178. https://doi.org/10.3390/THERMO1020012.

(2) Yingling, J. A.; Aziziha, M.; Schorne-Pinto, J.; Palma, J. P. S.; Ard, J. C.; Booth, R. E.; Dixon, C. M.; Besmann, T. M. Thermodynamic Assessment of CrCl2 with NaCl-KCl-MgCl2-UCl3-UCl4 for Molten Chloride Reactor Corrosion Modeling. *ACS Appl Energy Mater* 2023, *6* (11), 5868–5882. https://doi.org/10.1021/ACSAEM.3C00306/ASSET/IMAGES/LARGE/AE3C00306_0024.JPEG.

(3) Yingling, J. A.; Schorne-Pinto, J.; Aziziha, M.; Ard, J. C.; Mofrad, A. M.; Christian, M. S.; Dixon, C. M.; Besmann, T. M. Thermodynamic Measurements and Assessments for LiCl-NaCl-KCl-UCl3 Systems. *J Chem Thermodyn* 2023, *179*, 106974. https://doi.org/10.1016/J.JCT.2022.106974.

(4) Mayhew, P. A.; Boyle, L. D. The Fluorination of Uranium and Zirconium Oxides with Xenon Difluoride Initiated by the Addition of Water. *J Fluor Chem* 1998, *87* (1), 97–99. https://doi.org/10.1016/S0022-1139(97)00126-7.

(5) Brechovskich, M. N.; Popov, A. I.; Fedorov, V. A.; Kiselev, Y. M. The Reaction of Fluoroxidizers with Rare Earth Elements, Zirconium and Hafnium Oxides. *Mater Res Bull* 1988, *23* (10), 1417–1421. https://doi.org/10.1016/0025-5408(88)90266-8.

(6) Kagan, B. D.; Lichtscheidl, A. G.; Erickson, K. A.; Monreal, M. J.; Scott, B. L.; Nelson, A. T.; Kiplinger, J. L. Front Cover: Synthesis of Actinide Fluoride Complexes Using Trimethyltin Fluoride as a Mild and Selective Fluorinating Reagent (Eur. J. Inorg. Chem. 11/2018). *Eur J Inorg Chem* 2018, *2018* (11), 1244–1244. https://doi.org/10.1002/EJIC.201800115.

(7) Rose, M. A.; Gardner, L. D.; Lichtenstein, T. T.; Thomas, S. A.; Wu, E. *Property Measurements of NaCl-UCl3 and NaCl-KCl-UCl3 Molten Salts*; 2023. https://doi.org/https://doi.org/10.2172/1985295.

(8) Rose, M. A.; Gardner, L. D.; Lichtenstein, T. T. Property Measurements of NaCl-UCl3 and LiF-NaF-KF Molten Salts Doped with Surrogate Fission Products. 2023. https://doi.org/10.2172/2007391.

(9) Thomas, S.; Jackson, J. *MSR Salt Spill Accident Testing Using Eutectic NaCl-UCl3*; 2022. https://doi.org/10.2172/1889274 (accessed 2024-12-04).

(10) Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry. ASTM International: West Conshohocken, PA April 1, 2018. https://doi.org/10.1520/E1269-11R18.

(11) Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers. ASTM International: West Conshohocken, PA March 15, 2018. https://doi.org/10.1520/E0967-18.

(12) Practice for Heat Flow Calibration of Differential Scanning Calorimeters. ASTM International: West Conshohocken, PA March 10, 2002. https://doi.org/10.1520/E0968-02.

(13) Parker, S. S.; Long, A.; Lhermitte, C.; Vogel, S.; Monreal, M.; Jackson, J. M. Thermophysical Properties of Liquid Chlorides from 600 to 1600 K: Melt Point, Enthalpy of Fusion, and Volumetric Expansion. *J Mol Liq* 2022, *346*, 118147. https://doi.org/10.1016/J.MOLLIQ.2021.118147.

(14) Parker, S. S.; Long, A.; Lhermitte, C.; Vogel, S.; Monreal, M.; Jackson, J. M. Thermophysical Properties of Liquid Chlorides from 600 to 1600 K: Melt Point, Enthalpy of Fusion, and Volumetric Expansion. *J Mol Liq* 2022, *346*, 118147. https://doi.org/10.1016/J.MOLLIQ.2021.118147.

(15) Beneš, O.; Konings, R. J. M. Thermodynamic Evaluation of the NaCl–MgCl2–UCl3–PuCl3 System. *Journal of Nuclear Materials* 2008, *375* (2), 202–208. https://doi.org/10.1016/J.JNUCMAT.2008.01.007.

(16) Chartrand, P.; Pelton, A. D. Thermodynamic Evaluation and Optimization of the LiCl-NaCl-KCl-RbCl-CsCl-MgCl2-CaCl2 System Using the Modified Quasi-Chemical Model. *Metall Mater Trans A Phys Metall Mater Sci* 2001, *32* (6), 1361–1383. https://doi.org/10.1007/S11661-001-0227-2.
(17) Desyatnik, V. N.; Izmodenov, Y. A.; Mel'nikov, Y. T.; Nichkov, I. F.; Raspopin, S. P. Fusibility Diagrams of Systems Based on Magnesium and Uranium Chlorides. *Soviet Atomic Energy* 1969, *26* (6), 634–635. https://doi.org/10.1007/BF01218787/METRICS.
(18) Sooby, E. S.; Nelson, A. T.; White, J. T.; McIntyre, P. M. Measurements of the Liquidus Surface and Solidus Transitions of the NaCl–UCl3 and NaCl–UCl3–CeCl3 Phase Diagrams. *Journal of Nuclear Materials* 2015, *466*, 280–285. https://doi.org/10.1016/J.JNUCMAT.2015.07.050.