

Additional Physical Property Measurements and Assessment of Salt Compositions Proposed for the Intermediate Heat Transfer Loop

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1. Abstract

A study of salt properties was focused in areas not previously investigated. Ten new compositions were prepared for study of the relatively unexplored LiF-KF-ZrF₄ and LiF-KF-AlF₃ salt systems. Differential scanning calorimetry was conducted on the LiF-KF-ZrF₄ salt compositions to determine the thermal properties of the salts (i.e., phase transition temperatures and heat capacities). A measure of the reactivity (with air/moisture) and volatility of these compositions was also obtained. Room temperature density of the salts was also measured by gas-pycnometry for the purpose of estimation of the volume change upon melting of the salts. LiF-KF and LiF-NaF-KF eutectic mixtures were used as standards for all thermal and volumetric measurements. Results from these studies will be used to augment or revise previous tables of physical properties and derived physical property metrics.

2. Introduction and Motivation

Previous reports for the DOE/NE Generation IV Nuclear Energy Systems Program have summarized, analyzed, and provided a synthesis of the current state of knowledge about the properties of high-temperature salt systems [1,2]. In the course of these studies it became apparent that a few important salt systems have not been investigated, and that additional work is merited on these systems.

The LiF-KF-ZrF₄ system is one of the few fluoride-salt ternary mixtures for which almost no phase diagram information exists. Measurement of the thermal properties of this system is also necessary, as nearly all of the heat capacity measurements on ZrF₄-salts were conducted in the 1950s and 1960s on rather primitive instruments. Thus, the calorimetric study of this ZrF₄-salt system accomplishes two goals simultaneously.

The LiF-KF-AlF₃ eutectic salt (~ 6-48-46 mol%, ~ 490°C liquidus) is an attractive salt because the raw materials necessary for its synthesis are relatively inexpensive. However the phase-diagram information for this eutectic is incomplete, and the thermal properties of this eutectic mixture have not been defined. Therefore it was decided that a calorimetric study was needed to define the phase diagram in the neighborhood of the reported eutectic composition, and to measure key thermal properties of the eutectic composition.

It is now possible to measure the density of room temperature salts accurately with modern gas-pycnometers. Previous measurements with liquid pycnometers often yielded results substantially different than those obtained from X-ray-diffraction (XRD) studies. This is likely due to effects associated with open-porosity that is not penetrated by liquids, thus registering a lower liquid-pycnometer density than that measured by XRD. Gas-pycnometers readily penetrate all open porosity, and are expected to give a more useful result. The room temperature densities measured for both reference and sample salts were also used for a projection of the change in volume that occurs during the melting process. The volume change upon melting is needed for the design of salt handling equipment and for operation of high temperature salt systems.

3. Experimental Methods

Salt Preparation

Samples of LiF-NaF-KF eutectic salt (“FLiNaK”) that were already present at Oak Ridge National Laboratory (ORNL) were used in this study. The LiF-KF, KF-AlF₃ and ZrF₄-salts were obtained through Electrochemical Systems Inc. (ESI) of Oak Ridge, Tennessee. Both the FLiNaK and LiF-KF eutectic salts were prepared according to procedures developed and refined at ORNL [3]. The FLiNaK, LiF-KF, and KF-AlF₃ salts were each purified by hydro-fluorination of commercially obtained raw salts. The hydro-fluorination is done to remove the anion and metal impurities. Total anion and cation impurities are typically less than 100 ppm (each) for the hydrofluorination preparations. The ZrF₄ salt was purified by multi-stage sublimation until coherent, white, crystals were obtained. Figures 1 and 2 show the physical appearance of the purified materials to be white coherent crystals, with no trace of discoloration from metallic impurities.

Different compositions of salt were made by mixing different masses of the purified salts of each constituent inside a glassy carbon cylinder. The salts were then melted in a small furnace, mixed, and cooled. The salt was then removed from the bottom of the glassy carbon cylinder. The masses of the constituents and the resulting composition of the mixed salt are listed in Table 1. All of this work was done in an inert-atmosphere glovebox.

Table 1. Nominal and measured ZrF₄ compositions for ternary salt samples

Nominal ZrF ₄ concentration in sample (mol%)	LiF-KF mass (g)	ZrF ₄ mass (g)	[ZrF ₄] (mol %)
25% ZrF ₄	0.8832	1.1711	24.99 ± 0.01
30% ZrF ₄	0.6832	1.1734	30.14 ± 0.01
35% ZrF ₄	0.6603	1.4123	34.96 ± 0.02
40% ZrF ₄	0.5594	1.4928	40.14 ± 0.03
45% ZrF ₄	0.4730	1.5301	44.84 ± 0.04
50% ZrF ₄	0.4028	1.5923	49.83 ± 0.05



Fig. 1. Salt samples and hermetic capsule-press in glovebox (left), 30 mol% ZrF₄ sample (right).

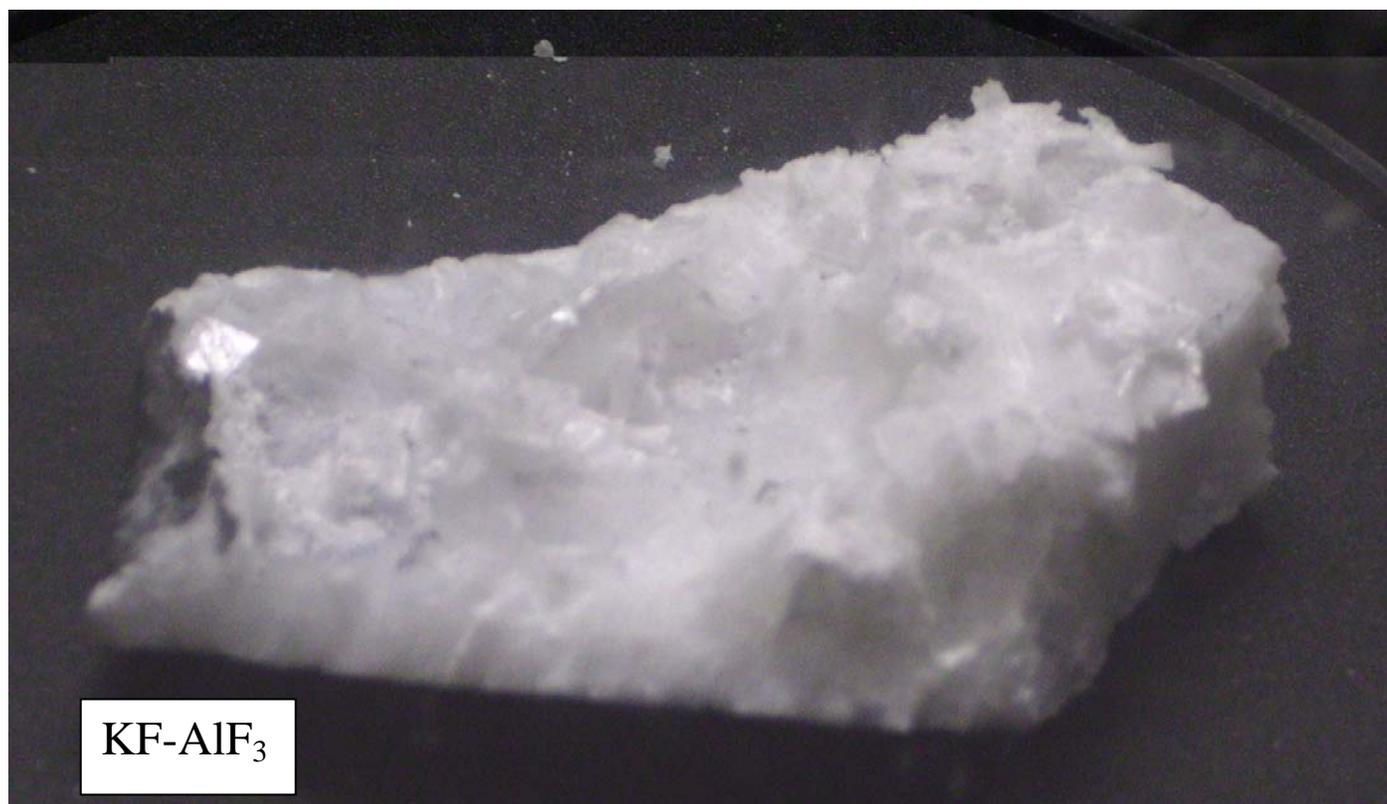
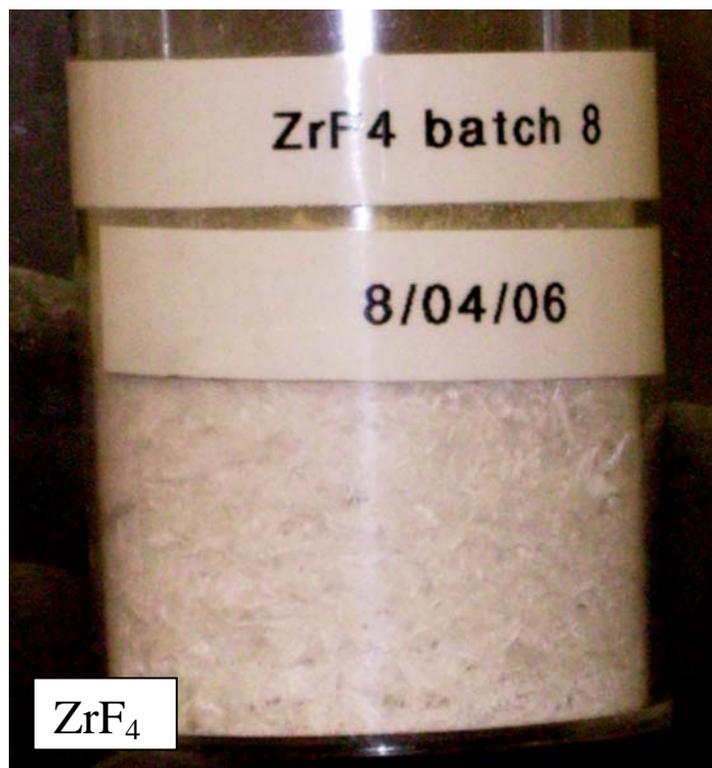


Fig. 2. Purified salt stocks prepared for this investigation.

Density Measurements

The gas pycnometer shown in Fig. 3 (Quanta-Chrome Ultra-Pycnometer 1000) was used to measure the room-temperature density of FLiNaK, LiF-KF, and the ZrF₄-ternary-salts listed in Table 1. Prior to salt measurements a careful calibration of the volumetric standards (metal spheres shown in Fig. 1) was conducted in order to account for temperature effects. The pycnometer was turned on and left running overnight to allow the system to thermally equilibrate. The following morning the system was calibrated using one of the small calibration spheres, $V = 7.0699 \text{ cm}^3$, using the small sample holder and small cell with the lid. The samples were then placed in the cell and allowed to sit for thirty minutes before the density run was started. This time allowed the salt and the cell to reach thermal equilibrium.

Twenty density measurements on each sample were taken in succession and averaged to obtain the density of the salt. The temperature of the pycnometer did vary slightly over the course of the day, most likely due to the change in the ambient conditions. The value of the temperature during the last of the twenty-run set was recorded. Density measurements were performed prior to the calorimetry measurements and were made shortly after the samples were prepared. The pycnometer was located inside of a pressure-controlled inert-atmosphere glovebox. Variations of the pressure in the glovebox can cause a variation in the measured density, therefore other activities in the glovebox were suspended while the density measurements were conducted.



Fig. 3. Gas pycnometer in inert-gas glovebox (left), benchtop DSC instrument (right).

Calorimetry Measurements

The Differential Scanning Calorimeter (DSC), model TA Q-10, shown in Fig. 3 was used to determine phase transition temperatures, heats of fusion, and heat capacities for FLiNaK, LiF-KF, and the ZrF₄-salt mixtures. Two types of DSC sample cells were used. In the first series of tests, graphite capsules were used for both reference and sample measurements. The graphite capsules were then placed on top of a gold lid that was inverted to protect the DSC sensor, in the event that the graphite capsule cracked (which did occur a few times). In a second series of tests on the ZrF₄-salts, hermetically-sealed gold capsules were used as the

sample holder and reference. Each sample holder (graphite or gold) requires only a very small fraction (~ 20 mg) of the ~2-gram lot of sample.

Fluoride salts are hygroscopic and readily absorb moisture from air. For the graphite sample cells (which do not establish a gas-tight seal) the following procedure was developed. Each salt sample was weighed in the inert-atmosphere box and then placed in a sealed glass jar (with associated lid) and left in the glovebox antechamber (also filled with inert gas) until the capsules were ready to be loaded. The glass jar containing the salt was then removed from the antechamber and taken to the DSC. At the DSC, the jar was opened and the salt was placed in the graphite capsule, the lid placed on, and the sensor chamber closed. As recommended by the manufacturer, an ultra-high purity nitrogen sweep of 50 ml/min was used to maintain an inert environment in the DSC chamber. There was evidently still some oxygen and water in the DSC chamber; as was apparent due to the mild-oxidation of copper and graphite capsules. The total time that the salt was exposed to the air outside of the DSC chamber was less than 1 minute.

The empty graphite capsules were baked out in the DSC up to 700°C until the signal was repeatable. The baseline for the capsules was then measured using a ramp rate of 10°C per minute. Cell calibration for temperature and heat of fusion was obtained by standardization measurements with a Zn-metal sample. The Zn-sample was removed and the salt was placed in the capsule and scanned in the heating mode of 10°C per minute. The nitrogen purge flow rate was maintained at 50 ml/min throughout all calibrations and measurements.

The FLiNaK, LiF-KF, and 25mol%-ZrF₄-salt were scanned only in the heating mode and allowed to cool as fast as possible. The cooling rate of the capsules for the rest of the tests were controlled. The rest of the curves were heated at rates of 5°C or 10°C per minute and cooled at rates of 5, 10, 15, 20, and (or) 30°C per minute. The maximum temperature for the DSC runs was limited to 650°C and 600°C for the 45% and the 50% runs, respectively. Fig. 4 shows the view of the capsule after the DSC was opened.

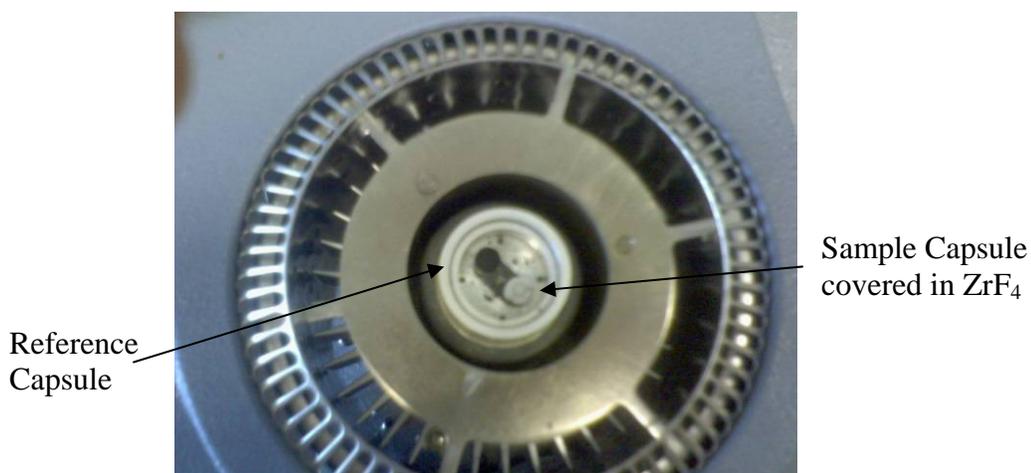


Fig. 4. The sample capsule for the 45% ZrF₄ salt was covered with ZrF₄ that had re-crystallized onto the surface of the capsule.

In a second series of measurements, the hermetic gold-capsule sample holders were sealed inside of the inert glovebox, and thereafter handled without need for isolation from the ambient atmosphere. DSC scans (at 20°C/minute) and heat capacity determinations were made for the second series of DSC measurements using hermetic-gold sample holders. A standard sapphire calibration was used according to ASTM method E1269-05 [4] in order to determine the heat capacity.

4. Results and Discussion

Room Temperature Salt Density

Understanding of volumetric properties of mixtures is based upon the reference condition of each constituent contributing its pure-component-volume to the mixture. This idealized salt mixture exhibits a molar volume that is the mole-fraction-weighted sum of individual constituents, and an excess volume is defined by difference:

$$\Delta V^E = V_{mix} - \sum x_i \cdot V_i \quad (1)$$

ΔV^E = molar excess volume (cc/mol)
 V_{mix} = measured mixture volume (cc/mol)
 V_i = molar volume of constituent i (cc/mol)

Conversion between density and molar volumes is defined by:

$$\rho = \text{mass density} = M / V \text{ (g/cc)}$$

$$\rho_{mix} = \sum x_i \cdot M_i / V_{mix}$$

M = formula weight (g/mol)
 x_i = mole fraction of constituent i

The density predicted for an ideal mixture with zero excess volume of mixing is:

$$\rho_{mix}^0 = \sum x_i \cdot M_i / \sum x_i \cdot V_i \quad (2)$$

Table 2 contains the density results obtained in this investigation, the literature values for each salt constituent [5], and the deviation from the density predicted from Equation 2. Because eutectic mixtures are known to be mixtures of pure component phases [6], rather than solid solutions or new compounds, the close agreement (within ~1%) for experiment and prediction for the alkali fluoride eutectics is expected, and provides confidence that the experimental method used provides reasonably accurate results.

Table 2. Comparison of measured density and ideal mixture predictions

Salt	Formula weight (g/mol)	Composition (mol %)	ρ measured density (g/cc)	ρ_{mix}^0 predicted density ^a (g/cc)	$(\rho - \rho_{\text{mix}}^0) / \rho_{\text{mix}}^0$ ($\Delta\%$)
<i>single compounds</i>					
LiF	25.94	100	2.635		
NaF	41.99	100	2.558		
KF	58.1	100	2.48		
ZrF ₄	167.21	100	4.43		
<i>alkali fluoride eutectics</i>					
LiF-KF	42.0	50-50	2.56	2.526	1.35
LiF-NaF-KF	41.3	46-5-11.5-42	2.56	2.533	1.08
<i>ZrF₄ + LiF-KF eutectic</i>					
sample ID		(mol% ZrF ₄)			
1	73.3	25	3.01	3.346	-10.0
2	79.6	30	3.14	3.465	-9.4
3	85.9	35	3.24	3.573	-9.3
4	92.1	40	3.65	3.672	-0.60
5	98.4	45	3.89	3.763	3.4
5 (repeated)	98.4	45	3.81	3.763	1.2
6	104.6	50	3.78	3.847	-1.8

^aPredicted densities correct values in the July 2006 LS-VHTR Progress Report: ORNL/GEN/LTR-06-02.

No such close correspondence between measurement and prediction is expected for the LiF-KF-ZrF₄ salts. Detailed study of closely related phase diagrams [7,8] leads us to expect diverse binary and ternary coordination compounds to be formed in the LiF-KF-ZrF₄ system. The trend of density behavior is depicted in Fig. 5, and shows that while the density is proportional to the ZrF₄ content at low ZrF₄ concentrations, it does not conform to the predictions based upon an assumption of zero excess volume. The density at higher ZrF₄ concentrations conforms more closely to the predictions of Equation 2, but this does not necessarily correspond to a condition associated with the presence of LiF, KF, and ZrF₄ as solid phases. One of the few studies of this ternary system [9] showed that the surface tension changes in molten LiF-KF-ZrF₄ reflect a very diverse and complex equilibrium between various coordination complexes. We expect this solution behavior to be reflected in the solid phase as a diverse combination of coordination compounds. The apparent correspondence with the Equation 2 predictions at higher ZrF₄ concentration is a coincidence.

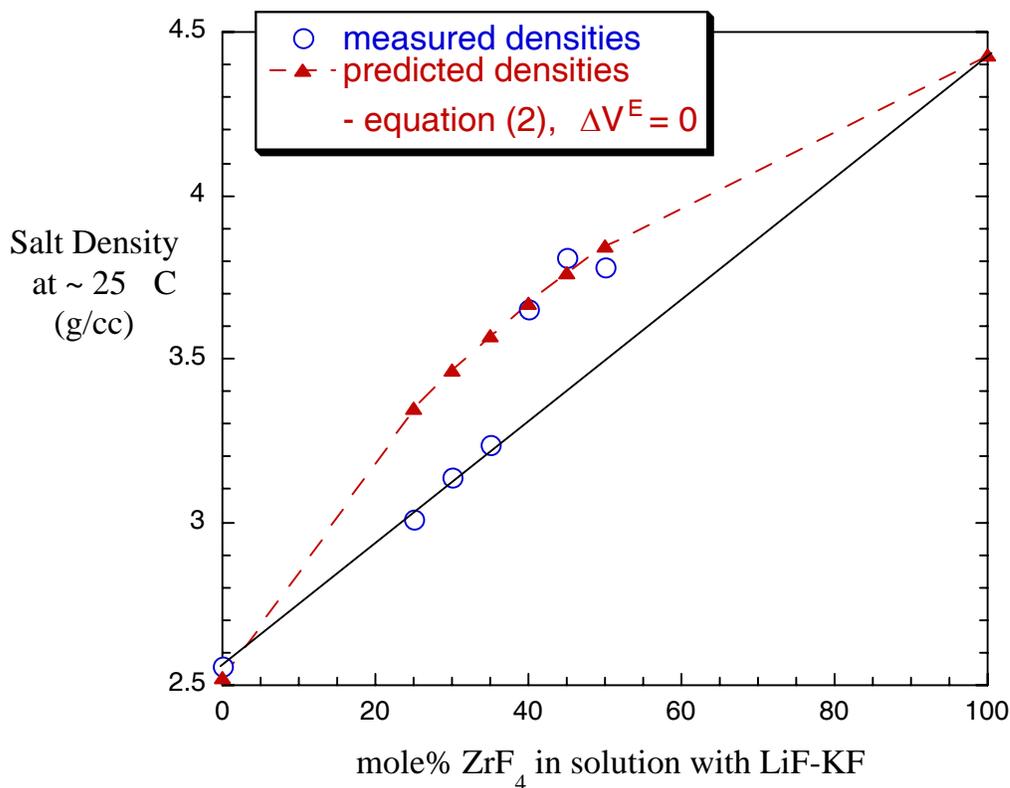


Fig. 5. Comparison of measured and predicted salt density at $\sim 25^{\circ}\text{C}$.

Volume Change upon Melting

Accurate values for salt volumetric properties for a wide range of conditions exist for many simple salt compounds, and for some more complex salt mixtures. This information can be used to make accurate estimates of the volume change that occurs during melting for a wide range of salt mixtures. The value for the solid density of alkali halide compounds can be used to make an accurate prediction of the solid density of a eutectic mixture of alkali halides using Equation 2.

Less information is available for more complex salts systems. In general, information exists on the density of multicomponent coordination compounds at room temperature, but not on the density near the melting point, and only occasionally is the density of the molten salt at the melting point available. For other systems that do not exhibit congruent melting points, the situation is more complicated because these systems usually do not exhibit a simple transition between the solid and liquid state. Instead, a large number of volume changes can occur during many different phase transition events (solid-solid and solid-liquid). This is the situation that exists in the ternary LiF-KF-ZrF₄ system, and many other salts of practical interest.

Tables 3 and 4 contain estimates of the density and volume changes that occur during melting for a variety of salts. The eutectic salts represent a variety of the salts that are being considered as candidate coolants for the heat transfer loop. Because it is not possible to make accurate melt-transition estimates for a number of the more complex salt systems listed in Tables 3 and 4, the volume change between room temperature salt and molten liquid is also included for comparison purposes.

Note that the volume change associated with melting of pure alkali halides (~ 25%) is much higher than that associated with eutectic mixtures of these compounds (~8%). The eutectic salts formed by mixing alkali halides with alkaline earth halides exhibits a very wide variety of behavior. The $2\text{LiF}\cdot\text{BeF}_2$ eutectic exhibits an extremely small volume change upon melting (< 2%), but the $\text{NaCl}\cdot\text{MgCl}_2$ eutectic exhibits one of the largest volume changes, ~18% [10]. The small volume change associated with $2\text{LiF}\cdot\text{BeF}_2$ is very unusual, and is not expected to be found in other salts [11,12]. Although these trends are interesting, there appears to be no substitute for obtaining good experimental information in order to make accurate predictions of the volume change upon melting.

The last column in Tables 3 and 4 contain the volume change experienced during the transition from room temperature to the molten state. It is apparent that the lower ZrF_4 content salts exhibit lower volume changes over this transition. It is likely that they also exhibit lower volume change during melting. This factor, along with the expense, volatility, and reactivity of high- ZrF_4 content salts recommends that we consider salts with the lowest possible ZrF_4 content.

Table 3. Estimated salt density change for melting, $\Delta\rho_m / \rho_s$

Salt	Formula weight (g/mol)	Melting point (m.p.) (°C)	ρ^0 20°C density (g/cc)	ρ_s solid density at m.p. (g/cc)	ρ_l liquid density at m.p. (g/cc)	$\Delta\rho_m / \rho_s$ = $(\rho_l - \rho_s) / \rho_s$ (%)	$\Delta\rho / \rho^0$ = $(\rho_l - \rho^0) / \rho^0$ (%)
<i>Single component salts</i>							
LiF	25.9	848	2.635	2.342	1.81	-22.7	-31.3
NaF	42.0	988	2.558	2.482	1.948	-21.5	-23.8
KF	58.1	856	2.48	2.239	1.91	-14.7	-23.0
LiCl	42.4	610	2.068	1.896	1.502	-20.8	-27.4
NaCl	58.4	801	2.165	1.945	1.556	-20.0	-28.1
KCl	74.6	771	1.984	1.791	1.527	-14.7	-23.0
<i>Eutectics</i>							
LiF-NaF-KF	41.3	454	2.561	2.315	2.152	-7.0	-16.0
LiF-KF	42.0	492	2.558	2.291	2.125	-7.2	-16.9
LiCl-KCl	55.5	355	2.034	1.853	1.691	-8.8	-16.9
2LiF-BeF ₂	33.0	460	2.168		2.056	< -2	-5.2
NaCl-MgCl ₂	73.7	445				~ (-18)	
<i>Congruently melting compounds</i>							
7NaF•6ZrF ₄	108.5	525	4.11		3.243		-21.1
KF•ZrF ₄	112.7	475	3.86		3.115		-19.3
2LiF•ZrF ₄	73.1	596	3.646		2.968		-18.6
<i>LiF-KF-ZrF₄ Salts (this study) - multiple S/L and S/S phase transitions</i>							
(mol % ZrF ₄)							
25	73.3	515	3.01		2.616		-13.1
30	79.6	~ 470	3.14		2.705		-13.9
35	85.9	424	3.24		2.793		-13.8
40	92.1	~ 420	3.65		2.882		-21.1
45	98.4	416	3.89		2.968		-23.7
50	104.6	~ 450	3.81		3.054		-19.9

Table 4. Estimated salt volume change for melting ($\Delta V_m / V_s$)

Salt	Formula weight (g/mol)	Melting point (m.p.) (°C)	V^0	V_s	V_l	$\Delta V_m / V_s$	$\Delta V / V^0$
			20°C volume (cc/mol)	solid volume at m.p. (cc/mol)	liquid volume at m.p. (cc/mol)	{ $(V_l - V_s) / V_s$ } (%)	{ $(V^0 - V_l) / V^0$ } (%)
<i>Single component salts</i>							
LiF	25.9	848	9.84	11.08	14.33	29.4	45.6
NaF	42.0	988	16.42	16.92	21.56	27.4	31.3
KF	58.1	856	23.43	25.95	30.42	17.2	29.8
LiCl	42.4	610	20.5	22.36	28.22	26.2	37.7
NaCl	58.4	801	26.99	30.05	37.56	25	39.1
KCl	74.6	771	37.58	41.63	48.83	17.3	29.9
<i>Eutectics</i>							
LiF-NaF-KF	41.3	454	16.13	17.84	19.19	7.6	19.0
LiF-KF	42.0	492	16.43	18.35	19.77	7.8	20.3
LiCl-KCl	55.5	355	27.29	29.94	32.82	9.6	20.3
2LiF-BeF ₂	33.0	460	15.22		16.05	< 2	5.5
NaCl-MgCl ₂	73.7	445				18.0	
<i>Congruently melting compounds</i>							
7NaF-6ZrF ₄	108.5	525	26.39		33.44		26.7
KF-ZrF ₄	112.7	475	29.18		36.16		23.9
2LiF-ZrF ₄	73.1	596	20.05		24.63		22.8
<i>LiF-KF-ZrF₄ Salts (this study) - multiple S/L and S/S phase transitions</i>							
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25	73.3	515	3.01		2.616		13.1
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40	92.1	~ 420	3.65		2.882		21.1
45	98.4	416	3.89		2.968		23.7
50	104.6	~ 450	3.81		3.054		19.9

Calorimetry Measurement

Measurements were first conducted for LiF-NaF-KF (or FLiNaK) and LiF-KF alkali-fluoride eutectic salts, and for all ZrF₄ using the graphite sample holders. The results for the alkali-fluoride eutectic salts corresponded closely to literature values and also were very repeatable. The results for the ZrF₄ salts were not repeatable for concentrations of ZrF₄ > 35%, and in all cases showed evidence of some denaturing of the sample with time for all concentrations. As the ZrF₄ content of the salt increases both its volatility and reactivity increase, and therefore the observed denaturing trend was expected. Ternary salts with [ZrF₄] = 25, 35, and 45 mol% were repeated using the hermetic gold-sample holders. For the very first DSC trial with these new samples the results were almost identical with those of the graphite samples holders. This correspondence between separate ~20 mg salt samples from the same salt lot confirms that the ternary salt was reasonably homogeneous with respect to spatial distribution of phases.

With additional study of these systems it became apparent that the assignment of the liquidus temperature should be related to the tangent at the mid-height of the leading edge of the final peak feature during the heating cycle. There are many sub-liquidus phase transitions in the ZrF₄-salts, and it is difficult to separate the overlap between closely spaced features at low values of heat flow. Cooling curves show the liquidus point with less ambiguity as a sharp leading edge. The relevant calorimetric scans are contained in an appendix at the end of this report.

Table 5 contains the assignment of liquidus temperatures and heats of fusion for the samples that were measured. Because of the complicated nature of the multiple phase transitions that occur in ZrF₄ systems, only heats of fusion for FLiNaK and LiF-KF salts are reported. The measured values of liquidus temperature and heat of fusion for FLiNaK and LiF-KF eutectics are quite close to the values reported in the literature [13]. A few (ZrF₄ = 30, 40, 50 mol %) of the DSC scans made during the first series of experiments with the graphite sample holder were not well resolved, therefore no liquidus temperature is reported. Figure 6 summarizes our current understanding of the liquidus temperatures associated with the closely related pseudo-binary representations of the ternary LiF-KF(eutectic) + ZrF₄ and quaternary LiF-NaF-KF + ZrF₄ (eutectic) salts.

Heat capacity measurements were performed during the second series of measurements using hermetic capsules and an in-house sapphire standard. The results are preliminary and more analysis is needed, but it appears that the heat capacities of these new ZrF₄ salts are close to those measured in the 1950s – in the range of 0.25–3 cal/g•°C. Additional heat capacity measurements are being conducted to confirm these results, and to validate the experiments by making measurements on salt standards and using a manufacturer-supplied sapphire standard.

Table 5. Phase transition temperatures and heats of fusion identified in DSC experiments

Salt	Liquidus series 1 tests (graphite sample holder, 10°C/min)	Liquidus series 2 tests (gold-sample holder, 20°C/min)	Literature liquidus Temperature	Measured heat of fusion (cal/g)	Literature heat of fusion (cal/g)
LiF-KF	487.6°C		492°C	377	389
LiF-NaF-KF	457.6°C		454°C	387	397
LiF-KF- 25%ZrF ₄	525°C	515°C			
LiF-KF-35%ZrF ₄	431°C	424°C			
LiF-KF- 45%ZrF ₄		416°C			

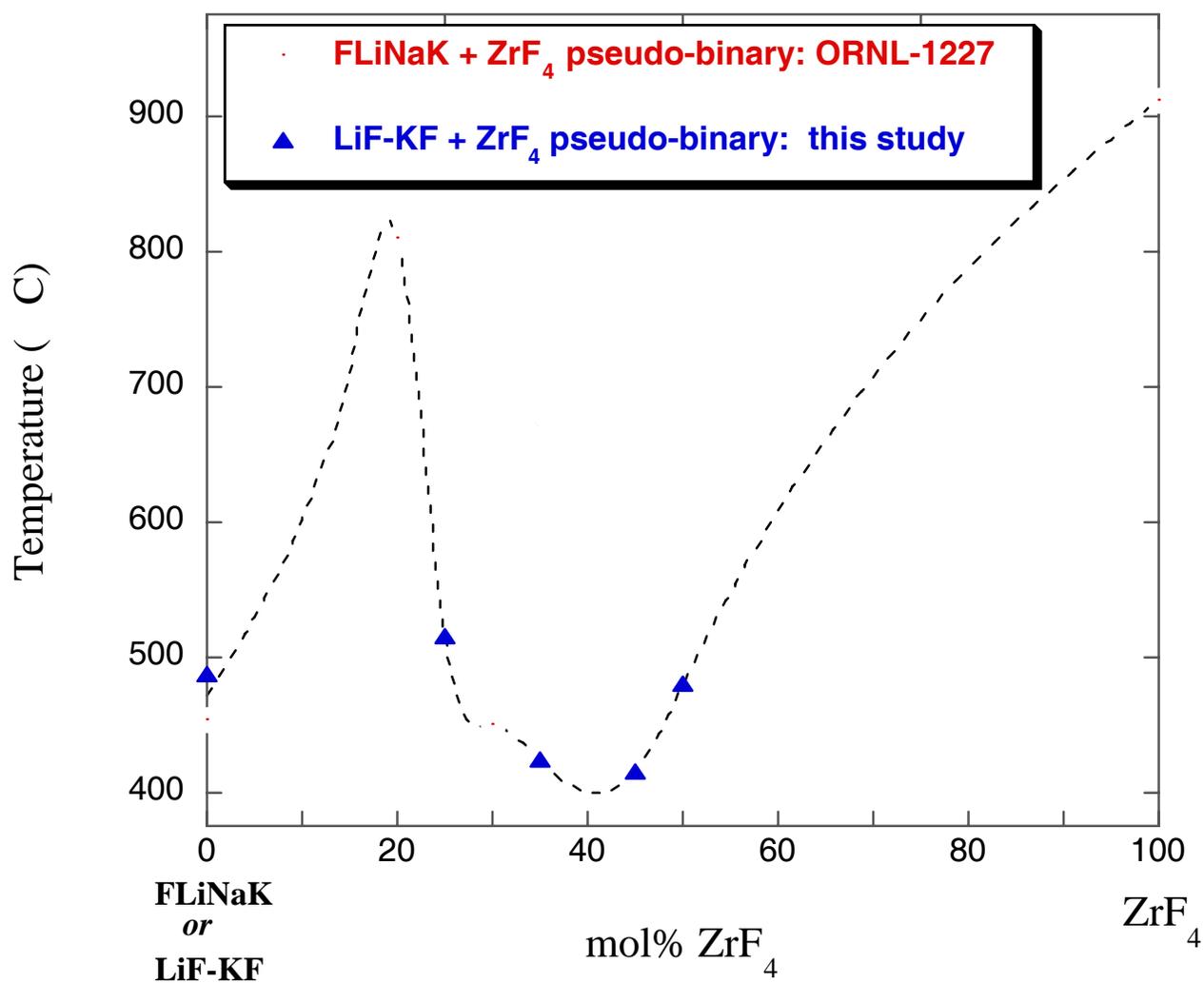


Fig. 6. Pseudo-binary representation of liquidus temperatures for {alkali-fluoride eutectic + ZrF₄} salt solutions.

5. Conclusions and Recommendations

1. Compositions with usefully low melting points ($< 450^{\circ}\text{C}$) were identified in the LiF-KF-ZrF₄ ternary system using differential scanning calorimetry. Compositions with ZrF₄ < 35 mol % appear to offer the best tradeoff of good heat transfer properties, low volatility, lower cost, and potentially a lower volume change upon during phase transitions near the liquidus temperature. Further investigation of this ternary system could identify compositions with even lower melting points.
2. Additional measurements of solid salt densities by gas pycnometry can aid in the assessment of phase change volume changes for congruently melting coordination compounds. These compounds constitute a simple and useful model system for this purpose because complications associated with multiple phase changes below the liquidus point are avoided.
3. Differential scanning calorimetry studies on the LiF-KF-ZrF₄ ternary are in basic agreement with measurements made fifty years ago using ice-bath calorimeters. ZrF₄ salts possess heat capacities about 1/3 that of water, and are a decreasing function of ZrF₄ content.
4. Future studies should include the investigation of the LiF-KF-AlF₃ salt that was prepared in this investigation. Suspension of FY07 funding for the salt assessment task has meant that these measurements were postponed because of the need to provide for orderly maintenance of the laboratory.
5. The volume change during melting for useful eutectic salts spans a wide range; from a low value of $\sim 1\%$ for Li₂BeF₄, to nearly 20% for NaMgCl₃. The low value associated with Li₂BeF₄ is a unique feature associated with a very unusual solid-state structure. A typical value for volume change is about 8%, and is the approximate value measured for three alkali-halide eutectic salts.

6. Acknowledgment

All of the gas pycnometry measurements and the first phase of the calorimetry measurements were conducted by James Ambrosek (Nuclear Engineering Ph.D. candidate from the University of Wisconsin) during his 2006 summer session at ORNL. James' diligence and careful attention to experimental detail is greatly appreciated, and this study would not have been successful without his dedication. Dr. L. M. Toth (Harbach Engineering) and Dr. G. D. Del Cul (ORNL) helped prepare the laboratory, provided technical guidance for the early phase of this work, and completed the final phase of the experimental work. These contributions were essential for launching this study and bringing it to a successful conclusion. The staff at Electrochemical Systems Inc. (ESI) of Oak Ridge provided expert preparation of a number of novel high-purity salt compositions, and offered assistance during the interpretation of experiments. This study could not have been conducted without the contributions of ESI and Harbach Engineering staff.

7. References

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8. Appendix: Calorimeter Scans

Series 1 = Experiments conducted with graphite sample holder, 10°C/min scan rate

Series 2 = Experiments conducted with hermetic gold sample holder, 20°C/min scan rate

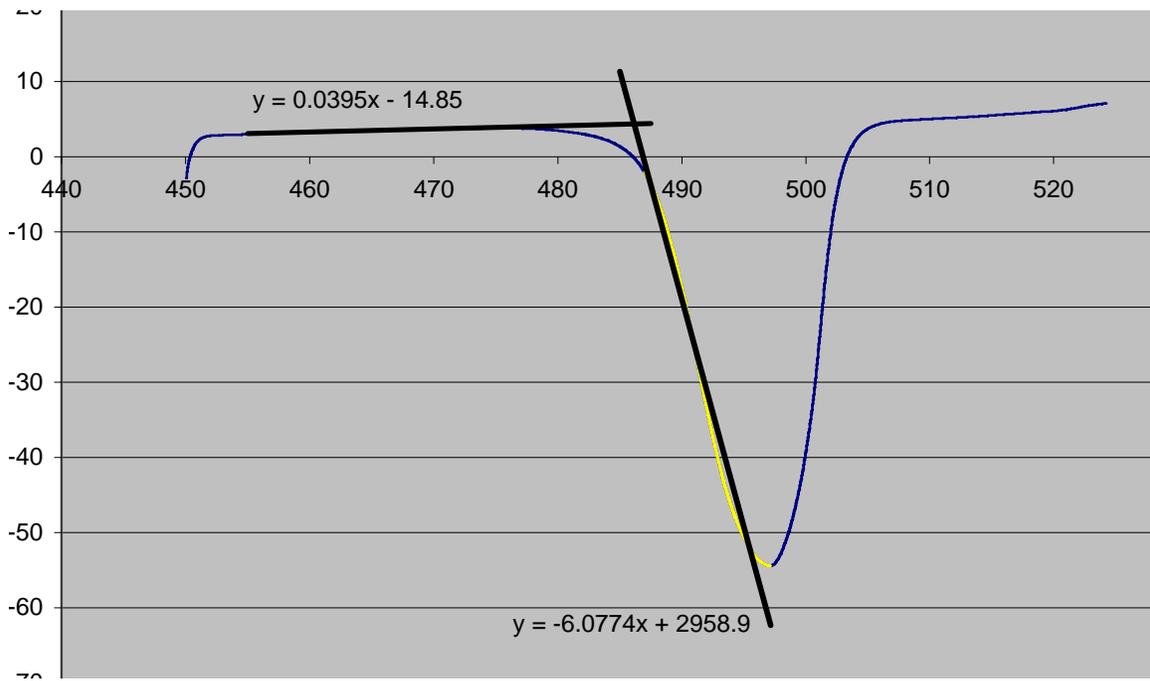


Fig. A1. Series1 DSC scan of LiF-KF eutectic salt: 488°C Liquidus.

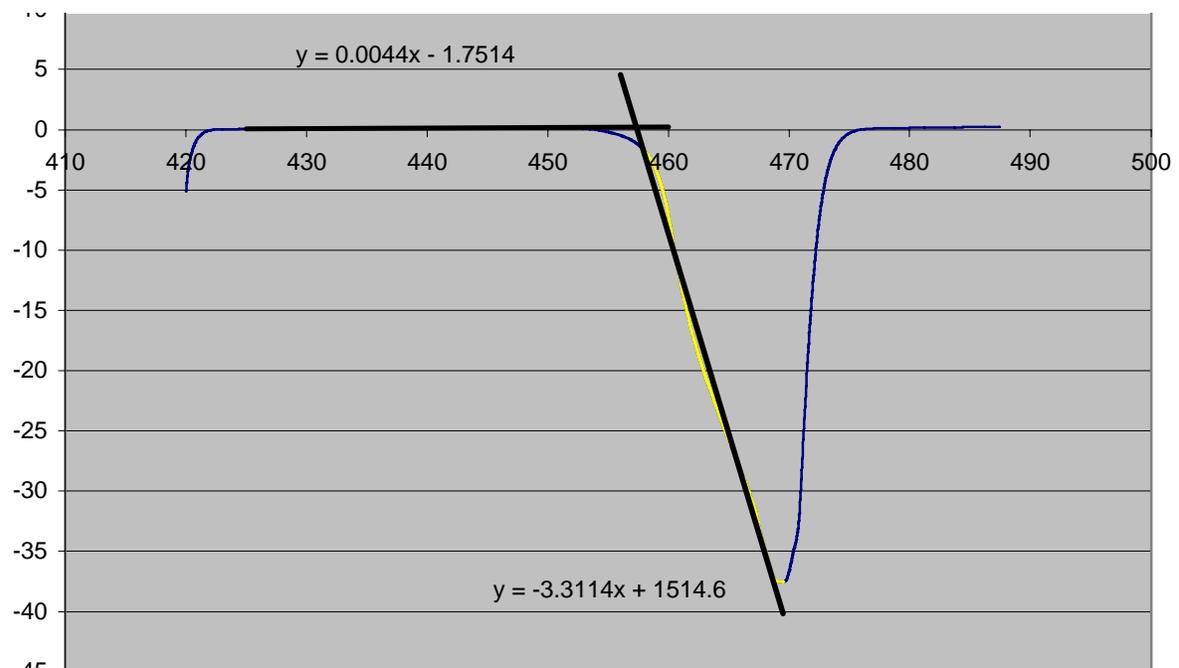


Fig. A2. Series 1 DSC scan of LiF-NaF-KF eutectic salt: ~ 458°C Liquidus.

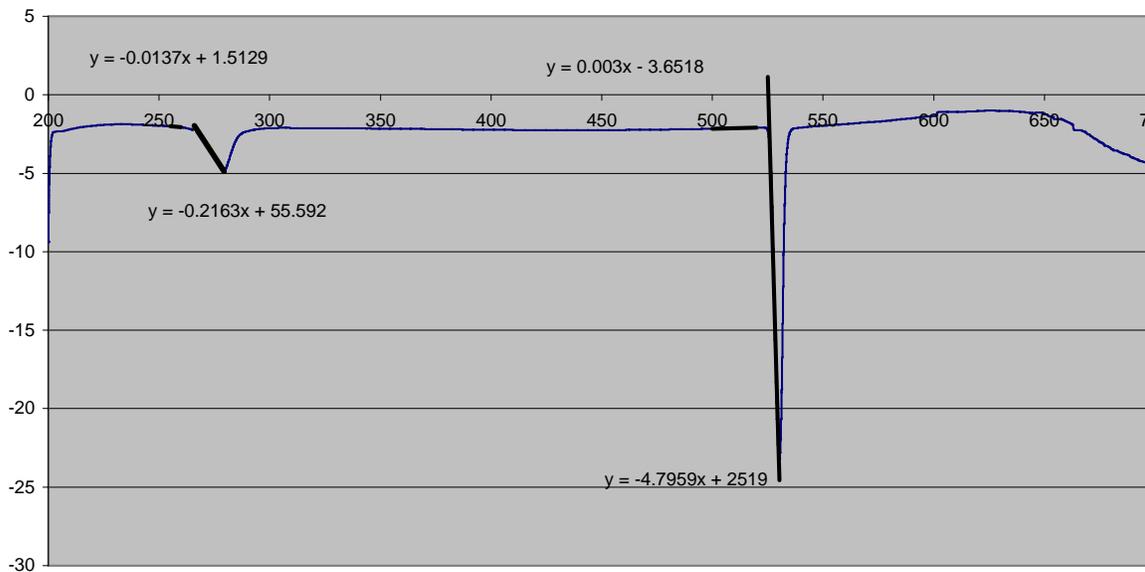


Fig. A3. Series 1 DSC scan of LiF-KF-25 mol % ZrF₄: 525°C Liquidus assignment.

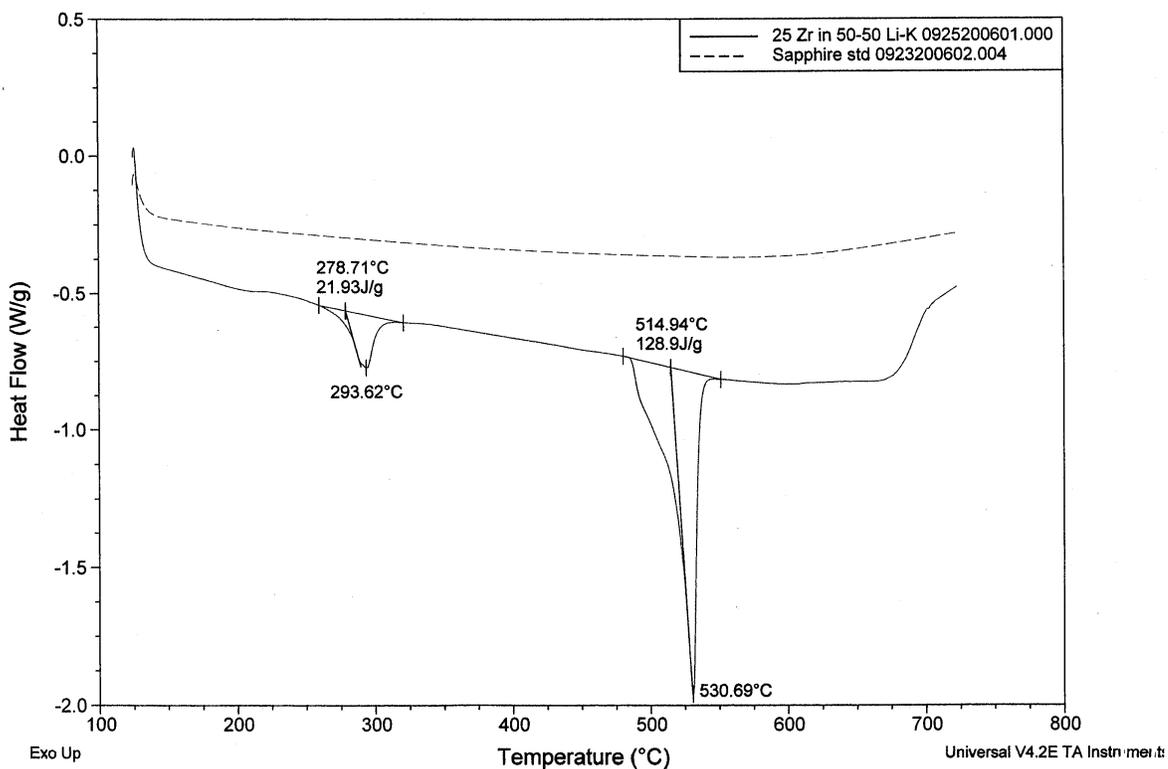


Fig. A4. Series 2 DSC scan of LiF-KF-25 mol % ZrF₄: 515°C Liquidus assignment.

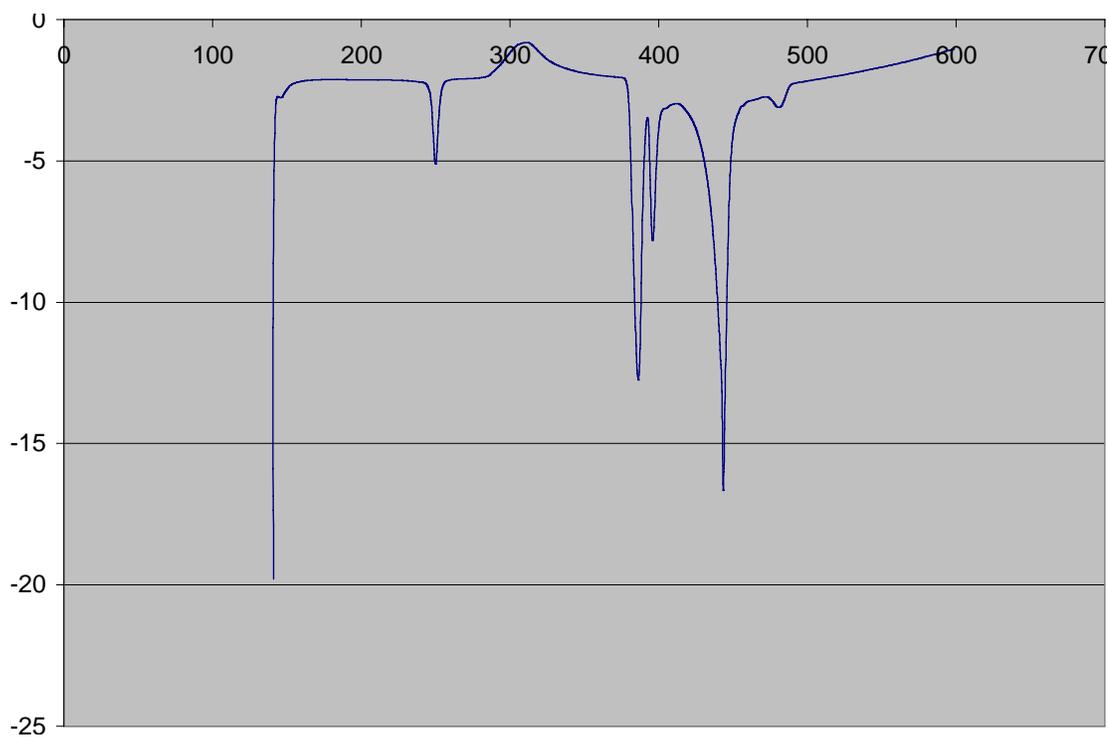


Fig. A5. Series 1 DSC scan of LiF-KF-35 mol % ZrF₄: 525°C Liquidus assignment.

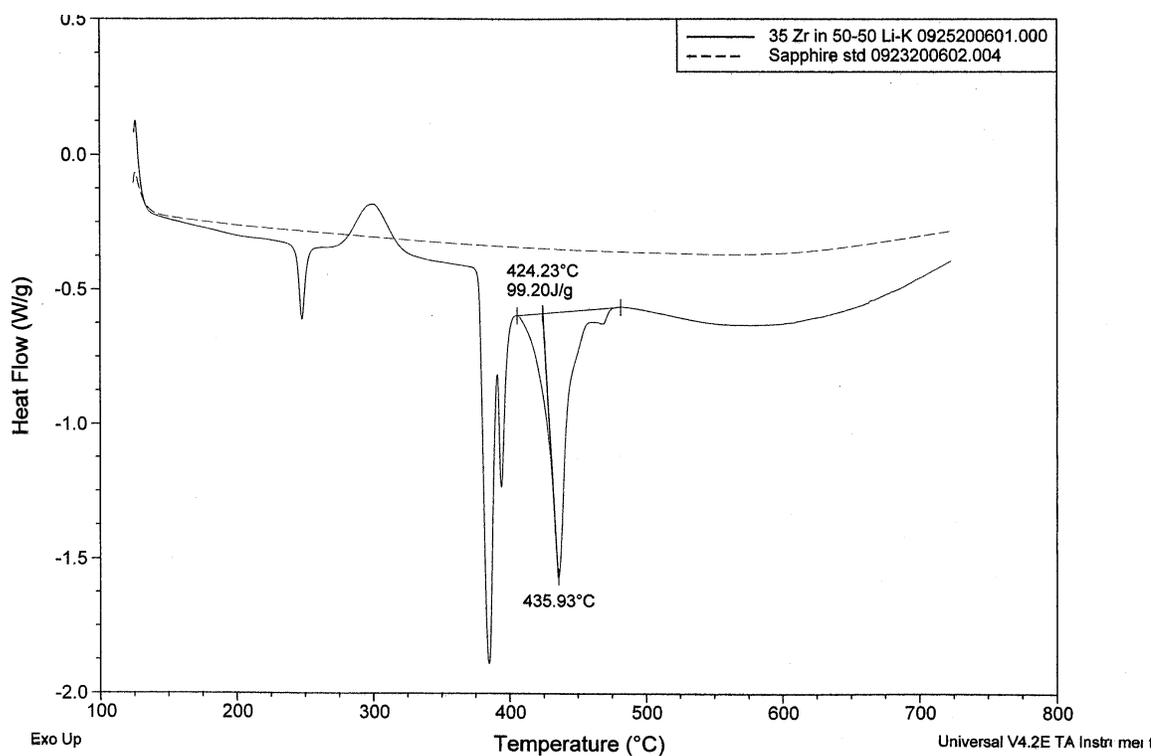


Fig. A6. Series 2 DSC scan of LiF-KF-35 mol % ZrF₄: 424°C Liquidus assignment.

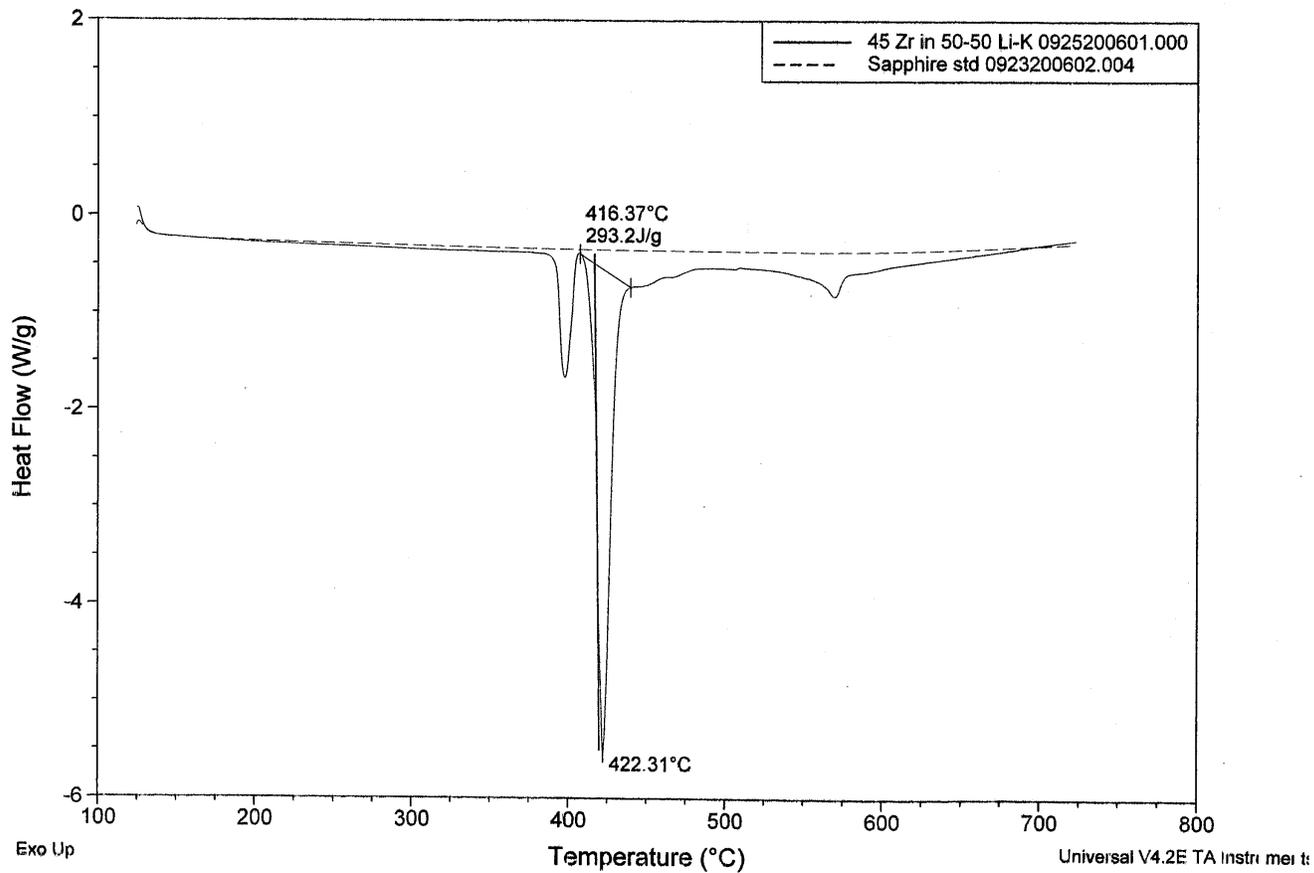


Fig. A7. Series 2 DSC scan of LiF-KF-45 mol % ZrF₄: 416°C Liquidus assignment.