ESTABLISHING A LAB SCALE PRODUCTION FOR LITHIUM, BERYLLIUM, AND THORIUM FLUORIDE SALTS

A Thesis

by

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ABSTRACT

The work performed for this project demonstrated a method for producing purified LiF-BeF_2-ThF_4 salts using ammonium-bifluoride (NH_4F_2) as an alternative to pure anhydrous hydrofluoric acid (HF) gas. The objective was to produce purified material for use in molten salt experimental systems that are being developed at Texas A&M University's Fuel Cycles and Materials Laboratory. Small salt samples (~6g) were generated and analyzed to evaluate the efficacy of the process. The purification process comprised: 1) preparing and mixing source materials, 2) melting the components at 600°C in a controlled atmosphere glovebox to facilitate the purification reaction, and 3) post-test evaluation and analyses. Salt samples were prepared with a base composition of 72LiF-$8BeF_2$-$20ThF_4$; this was the target composition for a subcritical molten salt experiment. This method was used to produce 35g of salt without ammonium-bifluoride purification and 50g of salt with purification. The products from these small-scale tests appeared satisfactory and the methods were scaled up in a large vacuum furnace to produce more than 60kg of purified salt. While the small-scale process produced satisfactory results, it was observed that the larger scale purification process was unsuccessful. Therefore ammonium-bifluoride was rejected for future process development.

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NOMENCLATURE

ACU	Abilene Cristian University
ARE	Aircraft Reactor Experiment
BeF_2	Beryllium Fluoride
FCML	Fuel Cycle’s and Materials Laboratory
FLiBe	LiF-BeF_2 (66-33mol%)
HEPA	High Efficiency Particulate Air filter
HF	Hydrofluoric Acid
LiF	Lithium Fluoride
MSBR	Molten Salt Breeder Reactor
MSRE	Molten Salt Reactor Experiment
NESC	Nuclear Engineering and Science Center
NEXT	Nuclear Energy eXperimental Testing
NH_4HF_2	Ammonium-bifluoride
NPT	National Pipe Tapered
NRIC	National Reactor Innovation Center
RTV	Room Temperature Vulcanizing
ThESA	Thorium Engineering Science Assembly
ThF_4	Thorium Tetrafluoride
ThO_2	Thorium Dioxide
UF_4	Uranium Tetrafluoride
WPPF	Whole Powder Pattern Fitting

XRD	X-Ray Diffraction

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1. INTRODUCTION

1.1. Motivations

There has been a resurgence of interest in recent years to design and implement molten salt reactor technologies. Benefits of molten salt reactors include their high operating temperature, low pressure, and inherent safety features [1]. Many designs have the fuel salt dissolved inside the working fluid salt allowing for inline fission product filtering and chemistry control of the fuel. Fuel-containing salts have been studied previously in the Aircraft Reactor Experiment (ARE) and the Molten Salt Reactor Experiment (MSRE). Future reactors, like those in Table 1, look to use novel salt forms for their next-generation reactor designs. Novel fuel compositions must undergo rigorous qualification before use in full-scale reactor designs including operations in subcritical assemblies. The present work describes the methodology developed at the Texas A&M Fuel Cycles and Materials Laboratory (FCML) for producing these a novel fluoride-based thorium-containing salt. This process takes advantage of the laboratories capability to work with both radioactive materials and beryllium powders.

Table 1. Proposed molten salt reactors adapted from NRIC Gap Assessment. [2]

Company Name	**Reactor Name**	**Salt Description**
Alpha Technology Research	ATRC	Fluoride based, LEU, Th
Copenhagen Atomics	CAWB	Fluoride based, Th, Pu
Core-Power	m-MSR	Chloride based, HALEU
Elysium Industries	MCSFR	Chloride based, Flexible Fuel
Flibe Energy	LFTR	Fluoride based, Th, U^{233}
Micronuclear LLC	MSNB	Fluoride based
Moltex Energy	SSR	Chloride based, Pu
Natura Resources	MSRR	Fluoride based, U
Rolls-Royce	CFNR	
Seaborg Technologies	CMSR	NaOH, U [3]
TerraPower	MCFR, MCRE	Chloride based
Terrestial Energy	IMSR	Fluoride based, LEU
ThorCon Power	ThorCon	$NaF-BeF_2-ThF_4-UF_4-ZrF_4$, LEU [4]

1.2. Objectives

The Thorium Engineering Science Assembly (ThESA) in the FCML was designed to show the feasibility of thorium-based fast neutron fission. The assembly would be a fast neutron source driven subcritical assembly. A vessel three feet in diameter and one and a half feet tall was to be filled with ~300 L of molten salt at 600℃ to mimic operating temperatures of proposed molten salt reactors.

As part of the ThESA program, a process to produce the requisite thorium salt using solid Ammonium Bi-Fluoride (NH_4HF_2) was considered [5]. The process was designed to produce small 10-g. samples and be scaled up to produce large kilogram sized samples. The vessel would require over 1000-kg of salt to operate, not accounting for excess salt needed to flush the vessel. FCML would produce the salt before being transferred to the NESC for use in the vessel. These salts would need to be measured and melted to fuse the components together before loading into the assembly. The salt was to be a mixture of lithium fluoride, beryllium fluoride, and thorium fluoride to capitalize on the abilities and experience of the FCML. Salt contamination of oxygen would have to be minimized and controlled during processing and movement of the salts.

2. BACKGROUND

2.1. Salt Selection

Salts have long been proposed as fuel carriers for nuclear reactors. Salt looking to be used as a fuel carrier must have good neutronic properties, low melting point, low vapor pressure, chemical and radiation stability, low corrosivity of structural materials, good viscosity, and ideally the ability to remove fission products easily [6].

Chloride and fluoride salts have both been investigated for use in fueled reactor configurations. Fluoride salts have substantially more experimental data than chlorides for reactor operations having been used previously for both the ARE and MSRE which provided a wealth of data on fluoride salts for current research. It was for this reason that fluoride salts were chosen for the ThESA project. A major barrier in the use of chloride salts is the long-term study of chloride salt facing core components for fears of corrosion and electrochemical changes [7].

These reactor designs formed the basis of study for the ThESA project. The first use of molten salt with dissolved fuel was the ARE in 1955. It used a ternary sodium-zirconium-uranium fluoride (3.09 NaF - 40.73 ZrF_4- 6.18 UF_4 mol%) salt at 815℃ to produce 2.5 MW_{th} power [8]. The salt wetted components were made from Inconel, a nickel-based alloy. Fueled salt was also used for the MSRE in 1965. It was a 7.4 MW_{th} reactor fueled by (65 Li^7F -29.1 BeF_4 -5 ZrF_4-0.9 UF_4 mol%) salt operating at a temperature of 650℃ [9]. The reactor operated for five years providing much of the knowledge we have today on operating molten salt reactors and fueled salt production methods. The lithium was enriched from the naturally dominant Li^6 due to its high thermal absorption cross section. Salts were purified of metallics, sulfides, and oxides by hydrogen and hydrofluoric gas sparging, discussed further in Section 2.2. Relevant observations from the MSRE included a strong need on proper chemistry control of the salt using during processing and operations. The Molten Salt Breeder Reactor (MSBR) was proposed to build on the knowledge from the MSRE. It would be the first to use ThF_4 and UF_4 dissolved in LiF-BeF_2 as a fuel breeding the thorium into fissile U^{233} [10]. It was never built but the ideas of thorium-based fission continue on.

For the ThESA project a LiF and BeF_2 salt base was chosen for its melting point at the expected thorium loading, as well as organizational knowledge of (66 LiF – 33 BeF_2 mol%) (FLiBe). Based on phase interpolation of the ternary phase diagram in Grimes, W.R. a salt composition of LiF-BeF_2-ThF_4 (72-8-20 mol%) was chosen for the project to melt at the projected 600℃ operating temperature of the assembly [11]. The pool type nature of the assembly did not require corrosion controls, like the addition of ZrF_4. The thorium tetrafluoride loading of 20 mole percent was chosen for two main reasons. When adding actinides to LiF, there is a solubility limit near 20 mole percent; concentrations above this could increase exceed the liquidus above 600℃. The 600℃ operating temperature was chosen to mimic possible molten salt reactor operating temperatures. The loading amount was also chosen for economic reasons, as the total amount of thorium tetrafluoride needed to fill the assembly quickly became difficult to source. This loading was enough to see some subcritical multiplication in the fast spectrum according to simulations.

2.2. Salt Purification

Oxide impurities present in the assembly will react with thorium forming insoluble precipitates, disproportionately effecting thorium fluoride concentration in the assembly. This oxidation will potentially create free fluorine's in the system, increasing the corrosivity of the salt [12]. Sulfides will attack nickel in vessel walls, while metallic fluorides upset the electrochemical balance, leading to increased corrosion.

When preparing the molten salt reactor experiment (MSRE) salts, a gaseous hydrofluoric acid system was used to purify and remove the oxygen and moisture from the salts which required an expensive and large safety system. Ammonium-bifluoride removes the oxide impurities, but in solid state chemistry [5]. This allows us to process salt using ammonium-bifluoride without the need for large HF gas safety systems. The removal of oxide impurities from our salt samples is done as part of the salt fusing process. At room temperature, oxidized ThO_2 will begin forming complexes with the ammonium-bifluoride, shown in Equation 1, 2 and 3. A slight increase in temperature will increase the rate at which the ThO_2 is fluorinated to the complex form. When the temperature is raised to above 400℃ the waste byproducts are removed with the cover gas leaving the now fluorinated ThF_4, shown in Equation 4 . The equations below are adopted from Wani, et. al. [13]

Equation 1

$$ThO_2 + 4NH_4HF_2 \rightarrow [NH_4]_4ThF_8 \cdot 2H_2O$$

Equation 2

$$[NH_4]_4ThF_8 \cdot 2H_2O \rightarrow [NH_4]_2ThF_6 \cdot 2H_2O + 2NH_4F$$

Equation 3

$$[NH_4]_2ThF_6 \cdot 2H_2O \ \rightarrow \ ThF_4 \cdot 2H_2O + 2NH_4F$$

Equation 4

$$ThF_4 \cdot 2H_2O \ \rightarrow_{HT} \ ThF_4 + \ 2H_2O$$

This ammonium-bifluoride method lacks evidence that it removes other impurities that could be harmful to the final assembly, like sulfides and metallics, and it is unlikely to do so. These are usually removed during hydrogen and hydrofluoric gas sparging [14].

3. EXPERIMENTAL PROCEDURE

Salt samples were prepared inside an inert atmosphere MBRAUN Labmaster^{Pro} SP glovebox with attached vacuum furnace as shown in Figure 1. The atmosphere was ultra-high purity helium kept at –1.0 mbar. The inert atmosphere was required to limit the exposure of the hygroscopic salts to oxygen and water while matching the conditions of the proposed subcritical assembly. If a leak were to occur, the beryllium fluoride would be contained inside the glovebox without contaminating the lab work area. The helium gas would also be used for assumed backfilling transfer containers to the assembly.

Figure 1. MBRAUN glovebox housing the salt experiments.

Samples of less than 10 grams, classified as groups 1 and 2, were weighed on a Mettler Toledo MS304TB/00 scale. They were then heated and melted inside a sealed cylindrical 50.8-mm alumina tube furnace from McDaniels Ceramics, shown in Figure 2. The furnace was oriented horizontally so that samples in a 20-ml nickel crucible from VWR could be inserted into the furnace using a nickel guide. A lid was constructed from alloy 620, featuring two 6.35-mm NPT taps and another 3.175-mm NPT tap. These larger ports were fitted with Inconel 620 Hy-Lok tube fittings for cover gas control. The small port was used with a 3.175-mm Type-K thermocouple with Inconel sheath from Nanmac. The lid had five heat shields made from 1.5875-mm Inconel pressed into place, and used a custom Viton gasket to seal, shown in Figure 3. Heat was provided by a Watlow VC404AOGA 120-volt, 101.6-mm ceramic tube furnace. Temperature was managed by a Thermal Solutions of Texas TSOT-13 thermocouple temperature controller. Temperatures of the salt crucible were read and recorded by an external Omega HH306A thermocouple reader. These readings were reported as salt temperatures. As the process is followed, possible contaminants from the decomposition of ammonium-bifluoride would flow out of the furnace by an argon cover gas. The cover gas then exited out of the glovebox and passed through a HEPA beryllium filtering system.

Figure 2. In-glovebox alumina tube furnace with Mettler-Toledo scale on the side.

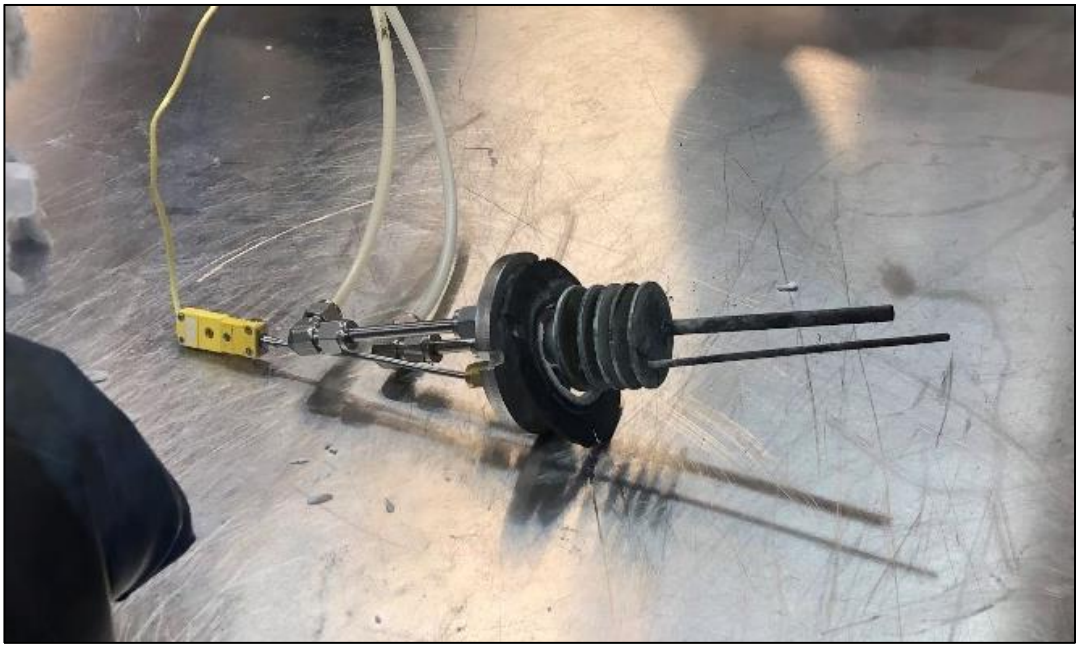

Figure 3. Tube Furnace lid with heat shield and thermocouple protrusions.

The fluoride salts were purchased from Materion for this project. ThF_4 was sourced as a slightly powdered stock material. The LiF was received as a powder. Powdered BeF_2 was originally sourced from stock used in a different project. For larger samples, an amorphous glass stock of BeF_2 was used.

3.1. Small samples prepared without Ammonium-BiFluoride

Samples in the 6.08±0.02 g range were made using LiF, BeF_2 and ThF_4 salts from Materion. Salt components were weighed using hexagonal weigh boats inside the glovebox then combined in the small nickel crucible and mixed using a stainless-steel spatula. The crucible was then placed inside the alumina tube furnace using a nickel crucible holder. The Inconel lid with thermal shield, seen in Figure 3, was sealed at three points with wingnuts over the Viton rubber gasket. A cover gas of ultra-high purity argon was opened to flow into the furnace with a line pressure of 100 kPa. The furnace controller was then turned on and the temperature program set, shown in Figure 4. The temperature was set to 600℃ over an hour to enable salt melting and mixing. After dwelling for 30 minutes at the set temperature, the furnace was turned off and the sample was allowed to cool down naturally. The sample was then removed and crushed in an agate mortar and pestle till it was easy to transfer into glass vials. This process was repeated for eight experiments to determine the processing temperatures and times. Information on each experiment’s components can be found in Table 2.

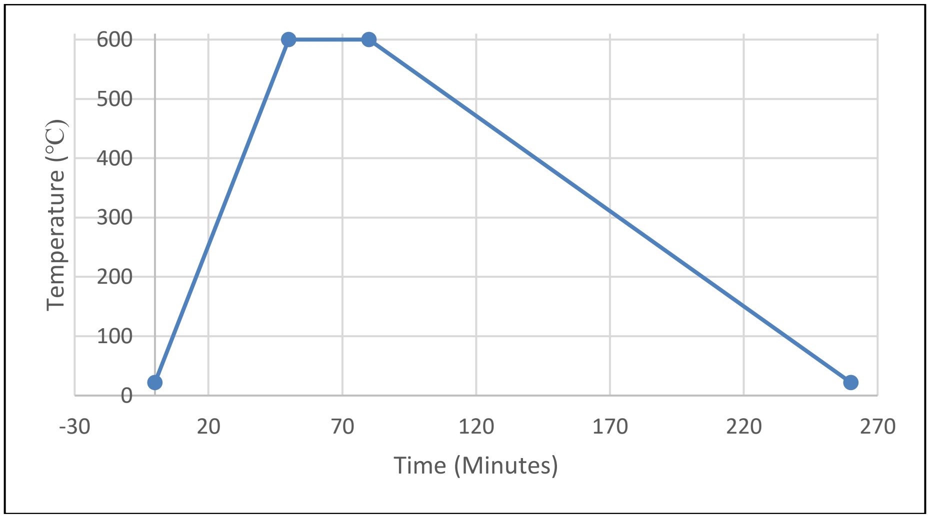

Figure 4. Heating Profile for samples without ammonium-bifluoride.

Table 2. Group 1 salt components used in production of experimental salts. (g.)

Material	**Exp 1**	**Exp 2**	**Exp 3**	**Exp 4**	**Exp 5**	**Exp 7**	**Manufacturer Number**
LiF	0.9312	1.1924	1.3404	1.3388	1.3387	1.3349	#409052
BeF_2	0.8709	0.4819	0.2658	0.2645	0.2648	0.2687	#8518507061
ThF_4	4.1996	4.3259	4.4017	4.4064	4.4139	4.377	#101418722A

Experiment 1 was assembled using the process described above with minor adjustments. A novel LiF-BeF_2-ThF_4 (52.75-27.25-20 mol%) salt mixture was heated to 615℃ for 30 minutes with an argon cover gas set to 103kPa. The sample was removed after cooling overnight without ultra-high purity argon cover gas flowing. Upon visual examination, evidence of melting was not observed after the first heating cycle and the salt was reheated to 650℃ for 30 minutes. After cooling to room temperature, three grams of the produced salt were sampled for use in another experiment outside of the glovebox and the rest of the melted sample was stored in a glass vial inside the glovebox.

Experiment 2 was performed using the technique described above with a few minor adjustments. A LiF-BeF_2-ThF_4 (65.5-14.5-20 mol%) salt mixture was heated to 600℃ for 32 minutes under 103 kPa of an argon cover gas. The sample was removed after allowing to cool overnight with cover gas flowing. The melted sample was stored in a glass vial inside the glovebox.

Experiment 3 was performed following the now-standard technique described above. This was a novel LiF-BeF_2-ThF_4 (72-8-20 mol%) salt mixture. The salt mixture was prepared and heated without incident. The salt sample was removed after cooling overnight with ultra-high purity argon cover gas flowing. One gram of salt was sampled for experiments outside of the glovebox and the rest was stored in a glass vial inside the glovebox.

Experiment 4 was produced following the generalized production technique described above. A mixture of LiF-BeF_2-ThF_4 (72-8-20 mol%) salt was prepared and heated without incident. The salt sample was cooled for three hours with ultra-high purity argon cover gas. The sample was removed from the crucible and stored inside a plastic petri dish because of bubbles observed frozen in the salt. Later it was crushed and stored in a glass vial inside the glovebox.

Experiment 5 followed the same technique described above. The sample was ground, mixed, and heated to 600℃. When the sample was removed after cooling it did not look to have fully melted, shown in Figure 5. The sample was reheated the following day to 700℃ for 1 hour. Melting was observed so the sample was crushed and stored in a glass vial inside the glovebox.

Figure 5. Experiment 5 sample before being reheated.

Experiment 6 began like the previous samples, however during the weighing of beryllium fluoride some was spilt. The correct proportions could not be verified for the salt. It was allowed to continue and melt but data generated was deemed unreliable and discarded.

Experiment 7 was performed using the technique described above with minor adjustments. It was heated to 600℃ and held for 30 minutes, then the sample was removed after cooling naturally for 5 hours without a cover gas. It was crushed and stored in a glass vial inside the glovebox.

3.2. Small Samples prepared with Ammonium-BiFluoride

Samples in the 6.08±0.02-gram range were made using LiF, BeF_2, ThF_4 salts and NH_4HF_2 from Materion. Salt components and NH_4HF_2 purifier were weighed inside the glovebox and then combined in the small nickel crucible and mixed using a stainless-steel spatula. Similar to previous samples, they were melted in the alumina tube furnace.

The furnace controller was set to a two-step temperature program, shown in Figure 6. The temperature was first raised to 120℃ for 1 hour which allowed the oxide impurities to react with NH_4HF_2 then raised to 700℃ to melt the salt mixture. After dwelling for 30 minutes at the set temperature, the furnace and cover gas was turned off and the sample was allowed to come to room temperature. Samples were crushed and stored inside the glovebox. This process was repeated for eight experiments to dial in the processing temperatures and times. Table 3 contains information on the initial salt component measurements for group 2.

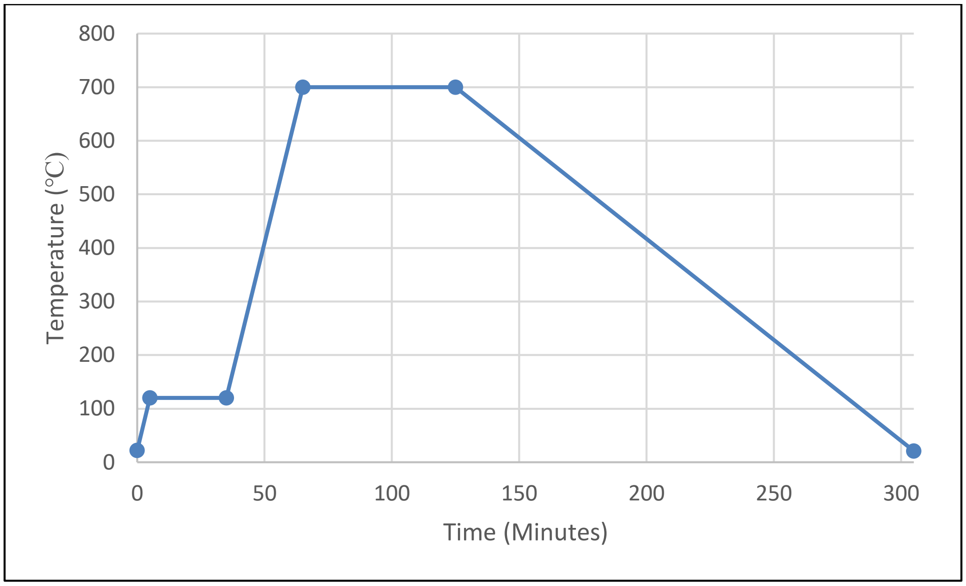

Figure 6. Heating Profile for group 2 samples with ammonium-bifluoride.

Table 3. Salt components for purified experiments.

Material	**Exp 8**	**Exp 9**	**Exp 11**	**Exp 12**	**Exp 13**	**Exp 14**	**Exp 15**	**Exp 16**	**Manufacturer Number**
LiF	1.3365	1.3349	1.3349	1.3330	1.3382	1.3370	1.3393	1.7786	#409052
BeF_2	0.2644	0.2687	0.2631	0.2629	0.2668	0.2649	0.2626	0.3571	#8518507061
ThF_4	4.4011	4.3770	4.4073	4.4065	4.4047	4.4070	4.4026	5.8696	#101418722A
NH_4-F_2	0.2063	0.1334	0.2064	0.1997	0.1997	0.2062	0.2083	0.2079	MKCJ9868

Experiment 8 salt was produced following the standard technique described above. Ammonia-Bifluoride was added and the oxide conversion heating step was followed. A LiF-BeF_2-ThF_4 (72-8-20 mol%) salt with NH_4HF_2 was weighed and transferred to the crucible then heated from room temperature to 120°C for 1 hour and 1 minute for oxide conversion with an argon cover gas set to 100kPa. Afterwards the temperature was raised to 610°C for 30 minutes. The sample was removed after allowing to cool for 2 hours and fifteen minutes without a cover gas.

Experiments 9 and 11 were produced following the technique described above. The sample was removed after allowing to cool overnight without a cover gas and crushed and stored in a glass vial.

Experiment 12 was performed using the technique described above with adjustments to the temperature. It was heated to 120°C and held at that temperature for 1 hour for oxide conversion then raised to 610°C for 30 minutes to melt after the temperature controller malfunctioned and undershot the set temperature. The sample was removed after allowing to cool overnight without a cover gas.

Experiment 13 was produced following the technique described above with adjustments to the temperature. It was heated to 130°C and held at that temperature for 1 hour then raised to 700°C for 30 minutes. The sample was removed after allowing to cool overnight without a cover gas.

Experiment 14 was using the technique described above with adjustments to the temperature. It was heated to 120°C and held for 32 minutes for oxide conversion. The temperature was then raised to 700°C for 1 hour. The sample was removed after allowing to cool overnight without a cover gas.

Experiment 15 followed the same procedure as experiment 14. It was heated to 150°C and held at that temperature for 30 minutes for oxide conversion. The temperature was then raised to 700°C for 1 hour. 1.5 grams were sampled for X-Ray Diffraction (XRD) analysis.

Experiment 16 was performed using the technique above with adjustments to time and temperature protocols. An 8-gram salt mixture of LiF-BeF_2-ThF_4 (72-8-20 mol%) was weighed and transferred to the crucible. It was heated to 150°C and held e for a 30 minutes oxide conversion. The temperature was then raised to 700°C for 31 minutes to melt. The sample was removed after allowing to cool overnight without a cover gas.

3.3. Large Samples Prepared in the Vacuum Furnace

3.3.1. Beryllium Fluoride Preparation

The beryllium fluoride ordered for the large samples from Materion was delivered in solid black glass-like crystals, seen in Figure 7 and Figure 8. This phase was better for maintaining purity during transport than powders. This amorphous BeF_2 as extremely difficult to break and reduce to powder by hand inside the glovebox. The beryllium was transformed into a beta-phase, shown in the phase diagram from Smith et. al, by baking in a steel pan in the vacuum furnace for 5 hours at 500°C [15]. This made the beryllium very brittle and easily broken by a masonry hammer and chisel before addition into the novel salt mixture seen in Figure 9.

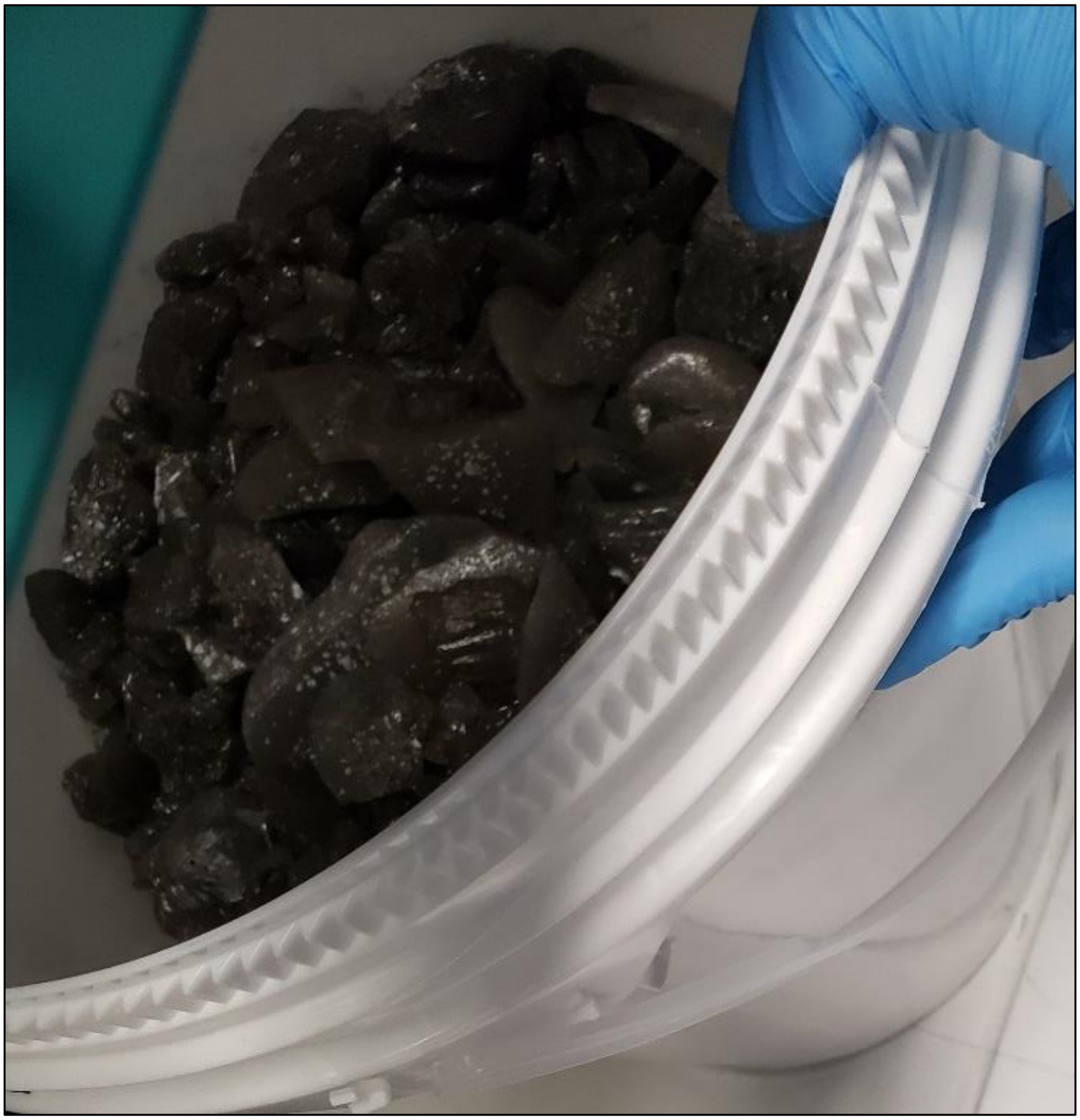

Figure 7. Beryllium Fluoride as received from Materion.

Figure 8. Glassy BeF_2 as received from Materion.

Figure 9. BeF_2 after being phase transformed and broken inside the glovebox.

3.3.2. Ammonium-Bifluoride Purification

The purification equipment assembled for large samples is shown in Figure 10; it effectively consisted of a modified full pan and lid. The lid had two bulkhead fittings punched through the top to connect to a cover gas and outlet system. It was sealed around the edge with fluoropolymer gasket and any gaps were filled with RTV silicone. Heat was provided for the reaction by a 30.48x20.48cm hot plate. The temperature was measured by a type-K thermocouple set onto the steel lid. Off gas chemistry control could be managed by a Jupiter Scientific Callisto 40L filled with Silane Hydride to remove possible HF, NH_4, or aerosolized salt components before being released into a beryllium rated hood and HEPA filter.

Figure 10. The purification system on top of the hot plate.

3.3.3. Equipment

Large samples were melted inside the MB-VOH-600 furnace, shown in Figure 11. attached to the MBRAUN Labmaster^{Pro} glovebox. The furnace could heat to 600℃ while holding a vacuum of up to $5x10^{-2}$ mBar. Salt was loaded in a large nickel crucible or a 1/9th stainless steel pan or three full-sized pans. The large nickel crucible was 1L in size and was purchased from VWR. The 1/9th pan and full pans were purchased from a local restaurant supply store. The pans were made from Stainless Steel 304 18/8 24 gauge. The 1/9th pan was 17.78cm long by 10.80cm wide and 10.16cm deep with a volume of 1.05L. The full-size pan was 52.71cm long by 32.39cm wide and 15.24cm deep with a volume of 19.87L. The pans were cleaned with Gojotm soap and scrubbed with 100% acetone to remove surface oils. The pans were individually heat treated inside the vacuum furnace at 400°C for 4hrs. A scrubbing FLiBe salt of 2.4 kg was melted in the bottom of the pans for 4 hours at 600°C, shown in Figure 12. This waste salt was to remove leachable steel components from the pans. This saturated waste salt was then stored in the 5.5-gallon bucket inside the glovebox with the other large salts.

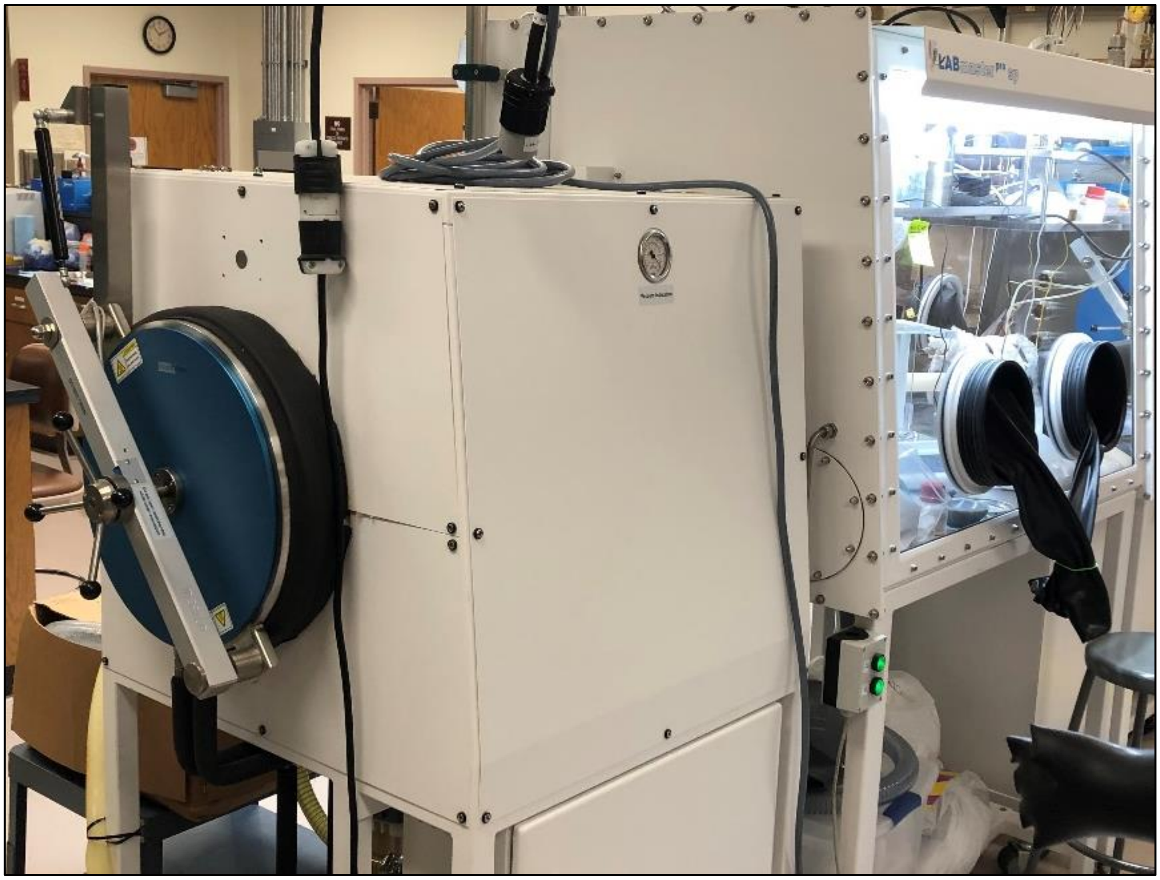

Figure 11. The BRAUN MB-VOH-600 attached vacuum furnace.

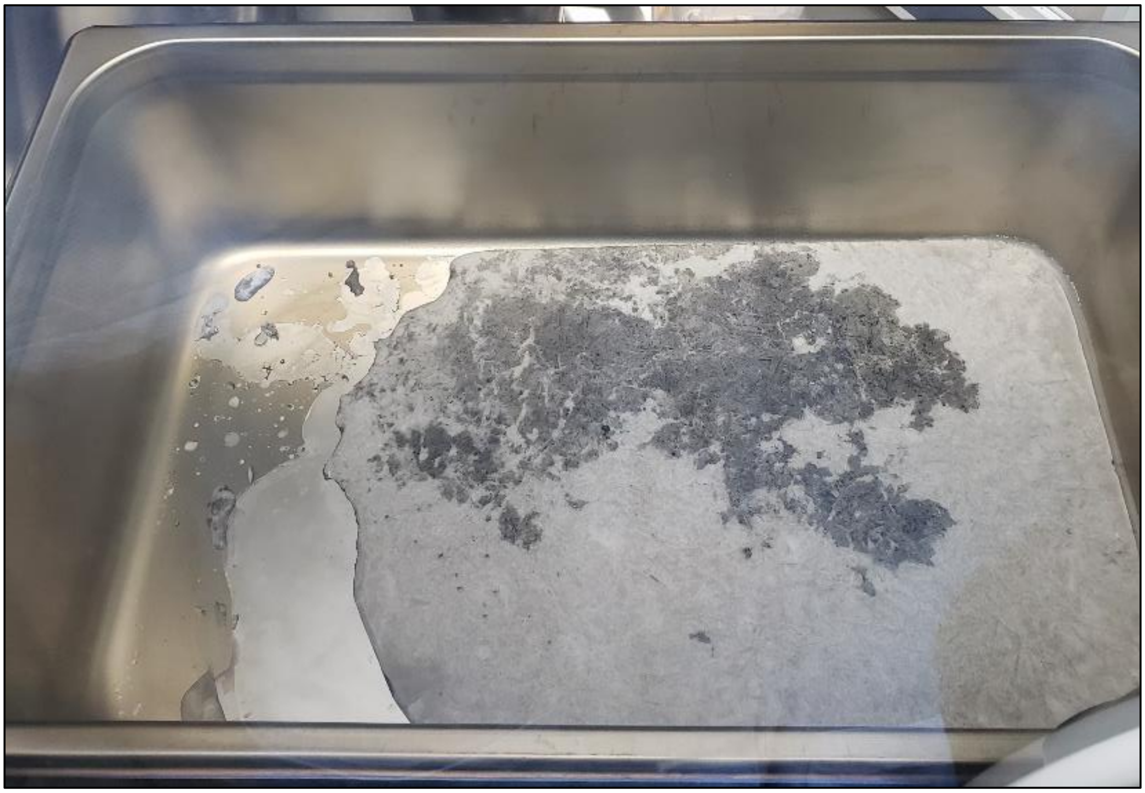

Figure 12. A full-size pan after it has been heat treated with the scrubbing salt inside.

Salts were weighed and mixed inside a stainless-steel bowl. After melting, they were crushed by masonry hammer and chisel inside the stainless-steel bowl. They were then stored inside a 5.5-gallon bucket inside the glovebox.

3.3.4. Experiments

The first large sample was made in the vacuum furnace inside the 1L nickel crucible. 1.4kg of (72-8-20mol%) LiF-BeF_2-ThF_4 was weighed into the crucible and placed into the vacuum furnace tray. The NH_4HF_2 purifier was not used. The sample was heated to 500°C for 3 hours then allowed to cool over night until the furnace returned to ambient temperature. The salt was then removed and no melting was observed. The salt was crushed by hand and mixed again then heated again to 500°C. After cooling and inspection melting was not observed. It was reheated without mixing to 550°C. It was cooled and inspected where incomplete melting or sintering was observed. It was reheated to 600°C for a period of 4 hours and full melting was observed.

The next large sample of 1kg of novel (72-8-20mol%) LiF-BeF2-ThF4 salt was made using a 1/9th pan. The glassy amorphous BeF2 was used without being transformed and broken. The NH_4HF_2 purifier was not used. It was heated in the vacuum furnace for 2 hours at 600°C and left to cool overnight.

Large salt sample batches were produced using the full-size pans. Salt components were weighed inside the stainless-steel bowl with a (72-8-20mol%) LiF-BeF_2-ThF_4 ratio and transferred into the purification system pan. Purifier at a ratio of 0.2 g/kg was added in powdered form to the salt inside the purification pan. It was sealed with C-clamps and a cover gas of Helium was applied. The hot-plate was turned to high, and temperature was monitored with a type-K thermocouple on the lid of the vessel. The salt was held at high for 6 hours while the ammonia-bifluoride reacted with the salt. The purified salt was then transferred to one of the heat-treated pans for melting. It was brought up to 600℃ stepwise in 100℃ increments for off-gassing control from any leftover purifier then left to cool overnight and removed. It was broken up into large chunks by masonry hammer and chisel and stored inside the 5-gallon bucket inside the glovebox. This technique was reproduced to make another 67-kg which was then stored with the first batch inside the glovebox.

4. RESULTS

4.1. Small samples prepared without Ammonium-BiFluoride

Small samples prepared without purifier were helpful in determining the melting point of our salt. The list of experiments can be seen in Table 4. The salt mixture was modified for experiment 3 into the LiF-BeF_2-ThF_4 (72-8-20 mol%) composition to ensure melting at the 600°C operating temperature.

Table 4. Group 1 experimental results.

Material	**Exp 1**	**Exp 2**	**Exp 3**	**Exp 4**	**Exp 5**	**Exp 7**	**Manufacturer Number**
LiF (g)	0.9312	1.1924	1.3404	1.3388	1.3387	1.3349	#409052
BeF_2 (g)	0.8709	0.4819	0.2658	0.2645	0.2648	0.2687	#8518507061
ThF_4 (g)	4.1996	4.3259	4.4017	4.4064	4.4139	4.377	#101418722A
Recorded Temperature (°C)	615	606	594	610	598	597	
Dwell Time (Min.)	31	32	30	30	31	30	

Experiment 1 produced a LiF-BeF_2-ThF_4(52.75-27.22-20.03 mol%) mixture that failed to melt at 600°C and was required to be reheated to 650°C. We used this information to change to composition of our salts.

Experiment 2 produced a salt with a composition of LiF-BeF2-ThF4 (65.42-14.59-19.99 mol%). The salt melted when heated to 600℃. It was of a light pink color. This salt was much tougher to grind to powder with a mortar and pestle compared to the experiment 1 salt. The melting point was still too high, around 575℃, for the designed operating temperature of the assembly so changes were again made to the composition of the salts.

Experiment 3, shown in Figure 13, produced a salt with a final composition of LiF-BeF_2-ThF_4(72-8-20 mol%). It was sampled for analysis however none was performed. Large grain crystal growth can be observed on its surface.

Figure 13. Experiment 3 inside the nickel crucible after being melted.

A fully fused experiment 4 can be seen in Figure 14. Nucleation can be found along the bottom of the sample. The pink color was not evenly distributed in the sample and was concentrated on the bottom.

Figure 14. Experiment 4 after being removed from the crucible.

The half-melted image of experiment 5 can be seen in Figure 15. After the sample was reheated it was observed to fully melt into a puck like the other samples. A leak in the cover gas system was noticed and repaired during the processing of this sample.

Figure 15. Experiment 5 before being re-melted at 700°C.

Experiment 6 data was not usable because of a mismeasurement while measuring components. Experiment 7 successfully melted without comment.

4.2. Small samples prepared with Ammonium-BiFluoride

The solid purifier was used to remove any possible remaining oxidation from the component salts before they were melted into a composite salt. This had the overall effect of making the salts easier to break and having less discoloration throughout the salt.

Experiment 8 was the first salt produced with a purifier. It appeared to be black along the bottom layer and white throughout the salt. This coloration can be seen in experiment 9 and 11, shown in Figure 16 and Figure 17.

Figure 16. Crushed salts from experiment 9.

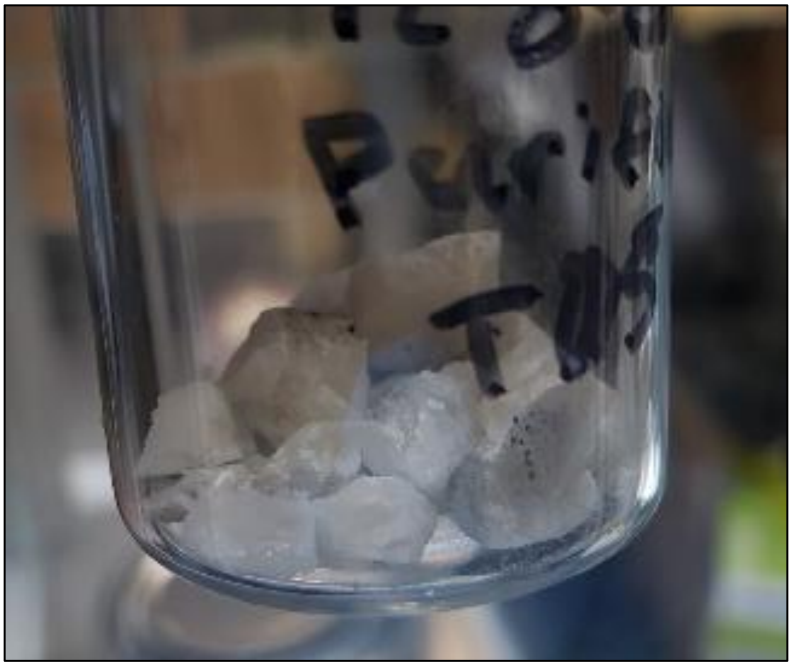

Figure 17. Crushed salts from Experiment 11.

When the salt from Experiment 13 was ground in the mortar and pestle it shattered into a powder which can be seen on the bottom the vial in Figure 18.

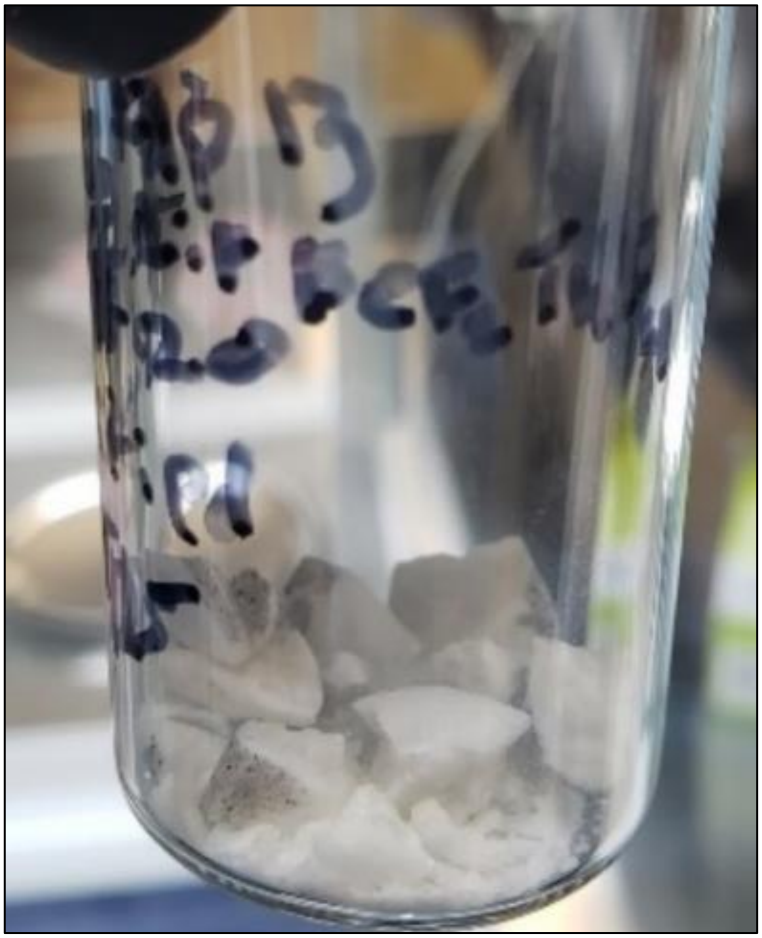

Figure 18. Crushed salts from Experiment 13.

Experiment 14, shown in Figure 19, spent less time in the oxide conversion and more time melting at a higher temperature and was easier to break than Experiment 13.

Figure 19. Crushed salts from Experiment 14.

Experiment 15 was left in rough pieces, shown in Figure 20. There was a lack of blackened discoloration in the salt.

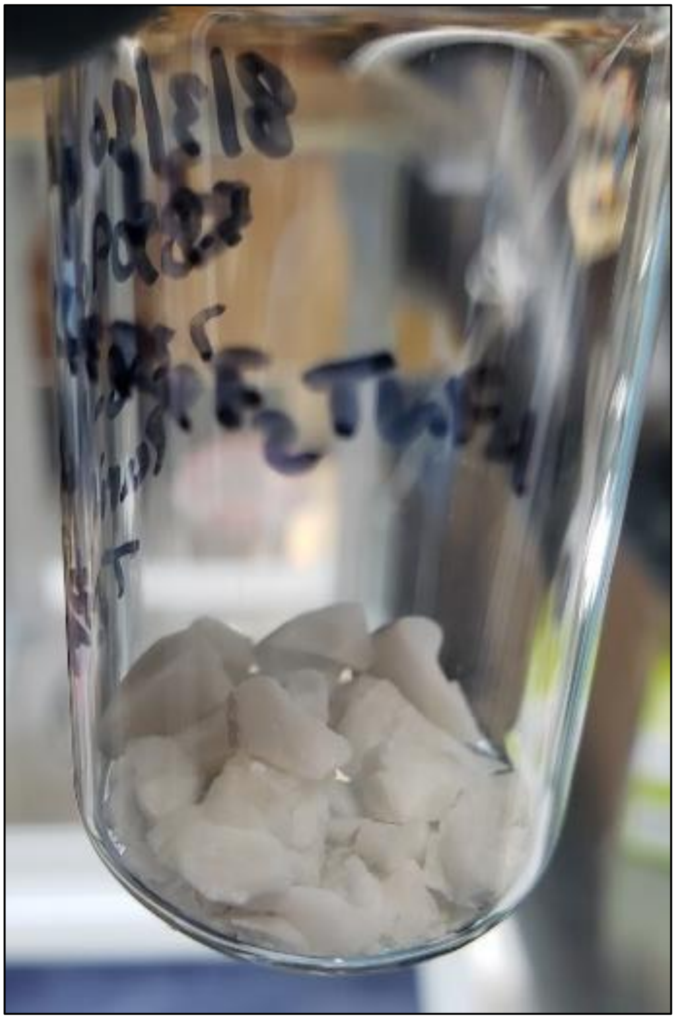

Figure 20. Crushed salts from Experiment 15.

Experiment 16 standardized the time the salt was both purified and melted to 30 minutes each while producing the maximum amount of salt for the small nickel crucible at 8 grams. Figure 21 shows the salt after it was ground fine in the agate mortar and pestle for XRD analysis.

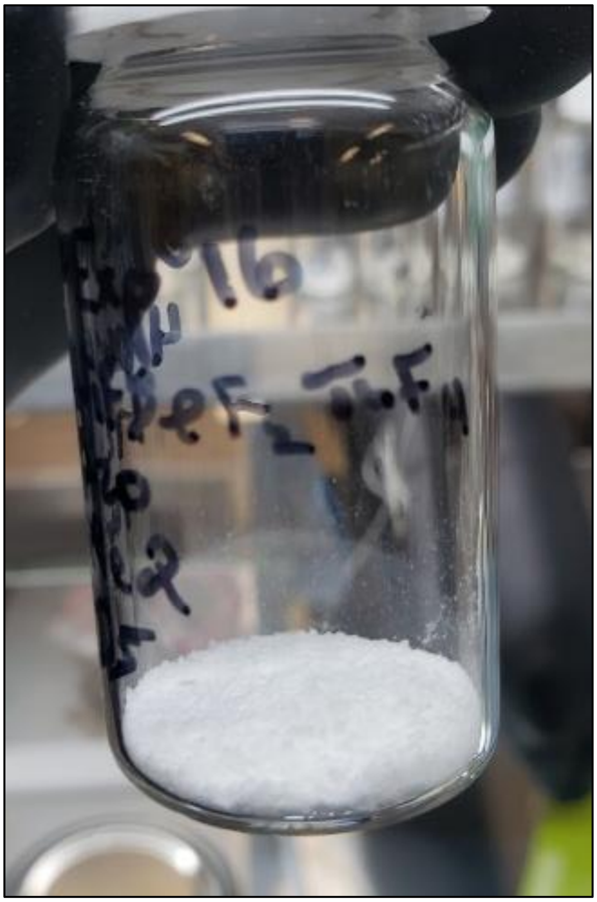

Figure 21. Experiment 16 after being ground fine for XRD analysis.

A comparison of the different salt coloration can be seen in Figure 22. Experiment 8 has a stark color contrast to the previous un-purified samples. Its bright white color is not repeated until experiment 14. The bright coloring of experiments 14, 15, and 16 are indicative of advances in purification technique.

Figure 22. Salt samples lined up for pictures inside the glovebox.

A sample of experiment 15 was prepared for XRD analysis because it was the last sample produced using the nickel crucible and purifier. 1.547g of the experiment 15 were retrieved and ground into a fine powder, resampled and loaded into the inert atmosphere sample holder. The holder was transferred out of the MBRAUN glovebox and into the Rigaku Benchtop 3000 XRD. Settings are shown in Table 5. Results from XRD analysis can be seen in Figure 23 and Table 6.

Table 5. XRD scan settings for the Experiment 15 sample.

Name	Value
X-ray generator	40 kV, 15mA
Scan Speed	1.00°/min.
Step Width	.005°
Range	10~80°

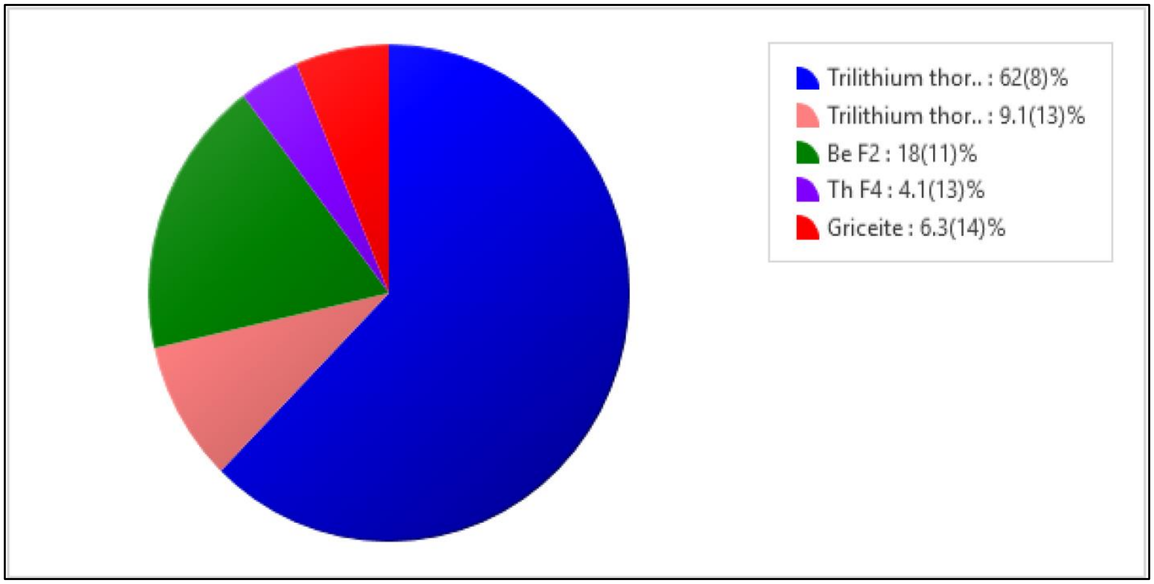

Figure 23. XRD Whole Powder Pattern Fitting (WPPF) results of Experiment 15 sample.

Table 6. XRD WPPF results from Experiment 15.

Salt	Mass %	Mol %
LiF	6.25	34.01
BeF_2	9.07	27.21
ThF_4	84.68	38.78

Table 7. Summary of small samples made with purifier.

Material	**Exp 8**	**Exp 9**	**Exp 11**	**Exp 12**	**Exp 13**	**Exp 14**	**Exp 15**	**Exp 16**	**Manufacturer Number**
LiF (g)	1.3365	1.3349	1.3349	1.3330	1.3382	1.3370	1.3393	1.7786	#409052
BeF_2 (g)	0.2644	0.2687	0.2631	0.2629	0.2668	0.2649	0.2626	0.3571	#8518507061
ThF_4 (g)	4.4011	4.3770	4.4073	4.4065	4.4047	4.4070	4.4026	5.8696	#101418722A
NH_4-F_2 (g)	0.2063	0.1334	0.2064	0.1997	0.1997	0.2062	0.2083	0.2079	MKCJ9868
Oxide Conversion Temperature (℃)	123	123	121	120	129	120	149	149	
Oxide Conversion Time (Min.)	61	64	60	61	66	32	30	30	
Melt Temperature (℃)	608	616	601	602	701	701	701	701	
Melt Time (Min.)	34	30	31	30	30	60	60	31	

4.3. Large Salt Samples Prepared in the Vacuum Furnace

Large samples varied in the amount produced. The first small batch was produced in a large nickel crucible. Melting was attempted repeatedly on the large crucible sample. The final temperature that melting was observed was at 600℃. This is less than ideal for the experimental setup due to the maximum temperature of the furnace being 600℃. The large crucible sample is pictured below in Figure 24.

Figure 24. Salt sample produced in the large nickel crucible.

Samples prepared in the 1/9th pan with glassy BeF_2 were observed to be melted at 600℃. The salt had a black speckling throughout. It was difficult to break by masonry hammer and chisel. The pan underwent a dark discoloration afterwards, appearing black, visible in Figure 25.

Figure 25. Salt produced in the small untreated 1/9th pan.

Samples produced in the full pan with heat-treated BeF_2 were of mixed color. The salt had a black layer on the top and bottom and was difficult to break by masonry hammer and chisel inside the glovebox, seen in Figure 26. After the third melting procedure, while the salt was being removed a hole was punctured in the pan. 67-kg. of salts produced and ground this way can be seen in Figure 27 stored in a five-gallon bucket inside the glovebox.

Figure 26. Salt in pans being broken up by masonry hammer and chisel.

Figure 27. The five-gallon bucket full of thorium salt.

A sample from group 3 was chosen for XRD analysis because it was produced using the stainless-steel pans and purifier. Less than 7-g. of salt from the group 3 experiments was retrieved and ground into a fine powder, resampled and loaded into the inert atmosphere sample holder. The holder was transferred out of the MBRAUN glovebox and into the Rigaku Benchtop 3000 XRD. Results from the XRD analysis can be found in Figure 28 and Table 8. Table 9 shows the expected mass fraction of each component.

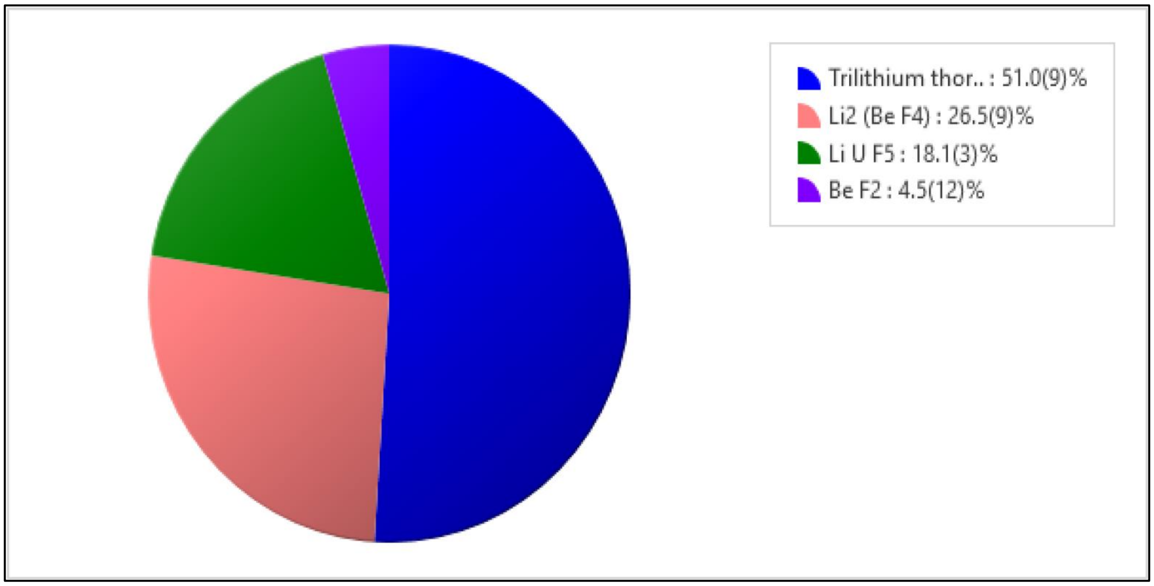

Figure 28. XRD WPPF results of salts produced in the large pan.

Table 8. XRD WPPF results of the large pan salt.

Salt	Mass %	Mol %
LiF	6.73	36.03
BeF_2	8.77	25.89
ThF_4	84.50	38.08

Table 9. As designed salt composition.

Salt	Mass %	Mol %
LiF	22.22	72.00
BeF_2	4.47	8.00
ThF_4	73.30	20.00

5. DISCUSSION

Small samples prepared without ammonium-bifluoride helped identify the correct composition to use for the assembly as well as provide a shake down for the equipment and methods we were planning to use. As a result of these tests it was decided that a cover gas was not necessary during cooling as it did not shorten the cooling time to a needed degree. The tube furnace worked well, keeping the temperature profile and limiting heat exposure to the rest of the glovebox.

Salt produced using ammonium-bifluoride were oddly discolored. This discoloration varied between the different batches and experiments. Unpurified salts were an observable pinkish or salmon color. Purified salts had dark grey color with black streaks throughout. This black streaking became even more prevalent in the salts made in the larger pans. It is assumed this discoloration is a function of possible contamination of the salt. The ammonium-bifluoride decomposition also proved difficult. It would consistently clog the off-gas lines as it solidified on its way out of the glove box. The lines had to be over pressurized to remove the blockage. This problem increased when large samples were prepared. It could be fixed or mitigated in the future by adding a bubbler or other purifier closer to the furnace off gas location.

Producing large volumes of salt using this method proved to be beyond the capabilities of the current system. The solid mixing chemistry of the NH_4HF_2 and the large sample size did not provide enough surface area for reaction. It is estimated that most of the purifier decomposed during the melt step. This is evidenced by the difficulties in maintaining a low pressure inside the vacuum furnace. Another practical limitation of the process was the amount of NH_4HF_2 used for each batch and difficulties procuring large amounts in high purity.

The brittleness of the salt was a major problem in the processing of salt for possible transfer out of the glovebox. All the crushing was done by hand. Some attempts were made to grind the chunks of salt using a rock tumbler, but it did not lead to any significant reduction in size of the salt chunks. A large mortar and pestle used for the smaller samples, but the samples in the pans were impractical to powder. Eventually the pan broke as the salt was removed, perhaps because of the leeching of stainless-steel components, like chromium, into the salt.

For future use of this methodology, efforts must be made to effectively scale the system up. Besides size, the limiting factor was the grinding and powdering process. The salt was hard to grind by hand or accessible mechanical means. A milling system that could be modified to work in the glovebox space is the first choice. A better off gas chemistry system would also be necessary to prevent the clogging of gas lines. The powdered components could also be mixed better by using a co-milling process or the like. This would enhance the effectiveness of the ammonium bi-fluoride.

6. SUMMARY

A method for producing lab scale quantities of salt was demonstrated at the Fuel Cycles and Materials Laboratory. Using a small alumina tube furnace purified LiF-BeF_2-ThF_4 salts of 6g in mass were generated and analyzed. 35g. of unpurified salts were initially generated as a show of proof for the system design. 50g. of purified salts were then produced to identify issues with the use of ammonium-biflouride. These purified samples were visibly brighter and cleaner than the unpurified samples. The decomposition of the purifier was a concern at this scale, as it would create blockages in the off gas lines. Larger production of salts was attempted inside a vacuum furnace. Troubles were identified with the use of ammonium-bifluoride in larger quantities. Large salt samples were unwieldy and difficult to handle inside the glovebox. Around 67kg of salt was produced using the large sample process. Future work will continue to scale these production techniques to supply experimental salts for other thermophysical analyses. The vacuum oven is insufficient for the task of melting these salts, and a new method must be developed for breaking and storing the salts inside the glovebox. Future development will most likely not include ammonium-bifluoride and instead use HF/H_2 sparging.

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APPENDIX A. EQUIPMENT

Equipment	**Manufacturer**	**Model**
Glovebox	MBraun	MBraun Labmaster^{Pro} SP
Scale	Mettler Toledo	MS304TB/00
Ceramic Tube	McDaniels	50.8-mm Alumina Tube
Furnace	Watlow	VC404AOGA 120-volt
Furnace Controller	Thermal Solutions of Texas	TSOT-13
Thermocouple Reader	Omega	HH306A
Vacuum Furnace	MBraun	MB-VOH-600
XRD	Rigaku	MiniFlex II