PHASE EQUILIBRIA IN THE LIF-AIF3-Na3AIF6-A1203 SYSTEM

by

Roger T. Cassidy

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APPROVED:

J. J. Brown, Jr., Chairman

W. R. Hibbard, Jr.

L. H. Slack

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Blacksburg, Virginia

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I. INTRODUCTION

Aluminum is the most abundant metal and the third most abundant element in the earth's crust. It is too active chemically to occur in nature in the elemental state and is usually found combined with oxygen or in complex alumino-silicates such as clays or feldspars. In view of the wide distribution of aluminum minerals and the fast growing demand for the metal, it is surprising that the isolation of aluminum was so relatively recent. High energy of reaction and the lack of naturally occurring materials capable of reducing aluminum compounds to the elemental metal were the two main problems in the development of aluminum metallurgy. Direct smelting of aluminum from its ores requires a temperature that would immediately vaporize the aluminum produced.

Today aluminum is commercially produced by a two step process. The first step involves purification of Al_20_3 which is done in the Bayer process. The Bayer process is basically the treatment of bauxite ore $(Al_20_3 \cdot 2H_20)$ to obtain Al_20_3 . Impurities such as Fe₂0₃ and SiO₂ are removed by reacting bauxite with caustic soda.

The second step of aluminum production is known as the Hall process which was developed simultaneously but independently by Charles M. Hall of the United States and Paul L. T. Héroult of France in 1886. Basically the process involves the electrolysis of alumina which has been dissolved in a molten bath of fused cryolite. Although minor changes and adjustments have been made since the discovery of the Hall process, the basic procedure has remained the same.

The electrolytic process for obtaining aluminum takes place in a large carbon lined steel tank. Dimensions of industrial tanks range from 16 x 9 x 3 feet deep to 25 x 12 x 3 feet deep with the carbon lining varying from 6 to 10 inches thick. The steel tank acts as the cathode and is backed by a thin layer of insulating brick. The anode is a series of pressed carbon rods that extends down into the electrolvte bath. Some modern industrial cells use the continuous Soderberg electrode which consists of a single anode in which a mixture of carbon and pitch is continuously fed from above the cell through a rectangular box. The heat of the cell bakes the carbon-pitch mixture thus forming a single continuous graphite electrode. A second type of anode used is the multiple prebaked block system which involves up to two dozen carbon blocks suspended into the molten fluoride bath $^{(1)}$. In both anode systems, the carbon must be kept 5-6 inches above the bottom of the tank.

The major component of the molten electrolyte bath is cryolite, Na₃AlF₆. Alumina, Al₂O₃, is dissolved in amounts of between 5 and 10 weight % in the bath. Other components of the bath include lithium fluoride, added to increase the electrical conductivity of the electrolyte, and aluminum fluoride. During smelting, a small amount of the fluoride content of the bath is consumed by combining with the soda impurity in the alumina and lost by hydrolysis from moisture in the air. Aluminum fluoride is added to maintain maximum operating efficiency⁽²⁾.

To reduce the alumina dissolved in the bath, a large electrical current is passed through the electrolyte. A current of between 50,000 and 125,000 amps is applied to a group of cells which are connected in series⁽³⁾. Operating voltage is between $6\frac{1}{2}$ and 7V and the current density is approximately 1000 A/ft² of cathode⁽⁴⁾. The temperature of the cell is between 900 and 1000° C.

As the large current is applied, Al_2O_3 is reduced. Molten aluminum metal is deposited at the bottom of the tank and becomes the cathode. The metal is tapped or siphoned at the bottom of the cell. Oxygen is released at the graphite rod anodes and immediately combines with the carbon to form CO and CO₂ gases. The reduction process is continuous and as aluminum is deposited at the bottom of the tank, alumina must be added at the top of the cell. If the Al_2O_3 content falls below 2 weight %, the electrolyte no longer wets the anode and fluorine gas is released at the anode forming a thin insulating film. This action, which causes a sharp increase in voltage (from 6V to 30V), is known as the anode effect. Because of the large amounts of current wasted during the anode effect, the crust of the cell must be broken and alumina is added.

During the addition of alumina, the electrolyte must be stirred to help dissolve the alumina. Although the bubbling action of the CO and CO_2 gases at the carbon anodes helps agitate the electrolyte, mechanical stirring is also done in industrial cells. Fluorite, CaF_2 , is also added to the bath with alumina. Small amounts of fluorite increase the density of the electrolyte thus enabling the

alumina to dissolve faster. Additions of over 15% CaF_2 will cause the electrolyte density to become greater than that of molten aluminum (2.29) causing the aluminum to float to the top of the cell and short it out. A typical cell composition used in today's cells is: (in weight %) 80-86 Na_3AlF_6 , 5-6 CaF_2 , 5-10 AlF_3 , 3-5 Al_2O_3 , 0.3-0.5 MgF_2 , 0.1 LiF and less than 0.1 NaF.

Carbon and alumina must both be continuously fed into the bath as aluminum is produced. For every pound of aluminum produced, between 0.6 and 0.8 pounds of carbon are consumed⁽³⁾. Two pounds of alumina are required to produce one pound of aluminum.

An interesting aspect of the Hall cell is the comparison of the theoretical emf of the cell with the actual operating voltage. At the graphite anodes, oxygen is produced and combines with carbon to form CO and CO₂ gases. At cell operating temperatures the gas given off is mostly carbon monoxide. At the cathode, aluminum with a purity of 99+% is deposited. The half cell reactions and their free energy equations can be written as follows:

Anode: $C(gr) + {}^{1}_{2}O_{2}(g) = CO(g)$ $\Delta G^{O} = -28,200 - 20.16T \text{ cal/mole}$ Cathode: $Al_{2}O_{3}(s) = 2Al(l) + 3/2 O_{2}(g)$ $\Delta G^{O} = +401,400 - 77.0T \text{ cal/mole}$

The combined reactions at the electrodes become:

$$A1_{2}0_{3}(s) + 3C(gr) = 2A1(l) + 3CO(g)$$

and its free energy equation is:

 $\Delta G^{\circ} = 316,800 - 137.48T \text{ cal/mole}$

The decomposition potential, ϵ is related to free energy of reaction by the equation:

 $\Delta G^{O} = -nF\varepsilon$

where F = Faraday's constant, and

n = number of equiv transferred/gm atom.

At 900°C for the above case,

 $\varepsilon = -1.13V.$

The reversible cell potential at 900° C, if the assumption is made that the carbon-oxygen action at the anodes does not affect the cell potential, is -2.24V for the decomposition of alumina to liquid aluminum and gaseous oxygen. As mentioned previously, a typical cell operating voltage is in the 6-7V range. The additional voltage is caused by over-voltage at the anode and ohmic drop through the bus bars, cathode lining, electrolyte and anode ⁽³⁾. The decomposition voltage will increase as the alumina activity decreases (as alumina content decreases). Thus for optimum cell operation changes must be made in operating conditions as the cell produces aluminum.

The Hall cell requires vast amounts of energy during operation to maintain the high bath temperature. This is evidenced by the fact that the aluminum industry is the largest user of electricity worldwide. Improvements in cell operation and electrolyte composition have improved the situation somewhat. In 1939, 12 kilowatt-hours (KWH) were required to produce one pound of aluminum whereas 8 KWH were required to produce the same amount of aluminum in 1973⁽⁵⁾.

Phase equilibria studies of the electrolyte components may help reduce the large energy usage of the aluminum industry by locating

lower melting compositions for use in industrial Hall cells. Of particular interest is the industrially important quaternary system $LiF-AlF_3-Na_3AlF_6-Al_2O_3$. The $Li_3AlF_6-Na_3AlF_6-Al_2O_3$ ternary system divides the quaternary system into two separate tetrahedra and is therefore of special interest.

The goals of this study are to learn the phase relations in the $LiF-AlF_3-Na_3AlF_6-Al_2O_3$ system by:

- 1. Studying the $\text{Li}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ system, and
- 2. Determining invariant points in the $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{Al}_2^0_3$ and $\text{LiF}-\text{AlF}_3-\text{Na}_3\text{AlF}_6-\text{Al}_2^0_3$ systems.

II. LITERATURE REVIEW

A. One Component Systems

1. Cryolite

The most important component of the Hall cell process is cryolite, Na₃AlF₆. It is one of the few naturally occurring minerals that will reduce alumina. Because of its importance in the industrial production of aluminum, cryolite has been the subject of many studies. Of particular interest have been heats of transition and melting point. Cryolite exists in at least two polymorphic forms, a low temperature (α -Na₃AlF₆) and a high temperature (β -Na₃AlF₆) polymorph. The temperature of transformation of cryolite has been reported to be between 560 and 572°C⁽⁶⁻⁹⁾. The α - β transition is a rapid reversible transformation and has a heat of transition of 2238 cal/mole associated with it⁽⁶⁾. The low temperature polymorph, α -Na₃AlF₆, is monoclinic with cell parameters a₀ = 5.40Å, b₀ = 5.60Å, c₀ = 7.78Å and β = 90°11'. The β -Na₃AlF₆ polymorph is cubic with a cell parameter of a₀ = 7.962Å⁽¹⁰⁾.

A third polymorphic form of cryolite has been reported. Landon and Ubbelohde⁽⁷⁾ found a transition to exist at 881°C. They denoted the new polymorph as γ -Na₃AlF₆ and the heat of the β - γ transition was set at 0.2 kcal/mole. More recent investigations have failed to confirm the existence of the γ -polymorph.

The melting point of natural Greenland cryolite has been studied numerous times. Earlier values, based on thermal arrest methods, reported values between 997 and $1000^{\circ}c^{(11,12)}$. Later work

involved improved experimental procedures such as inert atmospheres and some form of encapsulation to prevent volatilization. These studies revealed an increase in the melting point of cryolite when compared to earlier thermal arrest results. Phillips et al. ⁽¹³⁾ reported the melting point of cryolite to be 1009° C. Rolin⁽¹⁴⁾ determined melting points for natural and synthetic cryolite. He determined that natural cryolite (with impurities of 1 weight % AlF₃, 1% Al₂O₃ and 0.75% CaF₂) had a melting point of 1006° C. Rolin deduced that pure cryolite should melt at 1009° C.

Foster⁽¹⁵⁾ used a quenching technique to determine the melting point of cryolite. By sealing samples in platinum foil, he determined that cryolite melted at $1004 \pm 1^{\circ}$ C. In 1968 Foster⁽¹⁶⁾ recalculated the melting point of cryolite using the quench method and examining the liquid fraction of natural mineral samples over the melting range. A plot of temperature vs. the reciprocal liquid fraction revealed a melting point of 1009.2°C for natural cryolite and 1012°C for pure cryolite.

The dissociation of cryolite in the liquid state has been the subject of two studies (17,18). Frank and Foster (18) studied several dissociation schemes for cryolite and determined that cryolite dissociated into NaF and NaAlF₄ according to the following equation:

 $Na_3A1F_6 = 2NaF + NaA1F_4$.

2. Aluminum Fluoride

Aluminum fluoride possesses a rhombohedral unit cell with parameters $a_{rh} = 5.039$ Å and $\alpha = 58^{\circ}32' \pm 1'^{(19)}$. The compound is uniaxial positive with refractive indices of 1.3765 and 1.3770.

A second polymorph of AlF_3 was reported in 1957 by O'Brien and Kelley⁽⁸⁾. They noted a minor crystalline transformation at 454°C. Confirmation of the transformation was made by Holm and Holm⁽²⁰⁾ who designated the new polymorph as β -AlF₃ and set the transition temperature at 453°C.

Shinn et al.⁽²¹⁾ reported a third polymorph of AlF_3 which they designated γ -AlF₃. The γ -AlF₃ form was formed by heating ammonium hexafluoraluminate. Gamma aluminum fluoride has not been reported in later work involving phase diagrams of the Hall cell electrolyte⁽²⁰⁾. Aluminum fluoride sublimes at $1291^{\circ}c^{(22)}$.

3. Lithium Fluoride

Lithium fluoride exists in one polymorphic form. It has the NaCl cubic structure with an index of refraction of $1.3915^{(22)}$.

The melting point of lithium fluoride has been reported to be between 844 and 870°C. A value of 844°C was reported by Bergman⁽²³⁾, 845° by Botschwar⁽²⁴⁾, 847° by Rolin⁽²⁵⁾, 850° by Schultz⁽²⁶⁾, 860° by Fedotieff⁽²⁷⁾ and a value of 870°C by Counts⁽²⁸⁾.

Foster⁽²⁹⁾ attempted to determine the melting point of lithium fluoride by using quenching techniques. This method proved to be inadequate when samples above and below the liquidus temperature appeared identical when examined under the microscope. By employing

molar concentration units, the liquidus curve in the LiF-Na₃AlF₆ diagram was determined to be nearly linear from the eutectic to 100% LiF. Foster's extrapolated value of the melting point of LiF was 847[°]C.

4. Aluminum Oxide

Aluminum oxide, Al_20_3 , possesses seven crystalline modifications arbitrarily designated α -, γ -, δ -, η -, θ -, κ -, and χ -alumina⁽³⁰⁾. The most common form of alumina is α -Al₂0₃ (corundum) which has a hexagonal unit cell with parameters a = 4.758Å and c = 12.991Å⁽³¹⁾.

One other form of alumina besides corundum has been reported in phase studies of the Hall electrolyte. Foster ⁽³²⁾ reported the presence of η -Al₂0₃ in portions of the Na₃AlF₆-AlF₃-Al₂0₃ diagram. The η -Al₂0₃ phase was distinguished from α -Al₂0₃ by its average refractive index of 1.670 compared to 1.760 for α -Al₂0₃.

Corundum is a uniaxial positive mineral with indices of refraction 1.768 and $1.760^{(22)}$.

B. Two Component Systems

1. System LiF-AlF₃

The numerous investigations (27, 33-40) of the LiF-AlF₃ system are summarized in Table I. Good agreement exists between the reported diagrams. One compound, lithium cryolite (Li₃AlF₆), melts congruently between 782° and 800°C and divides the system into two simple binaries (LiF-Li₃AlF₆ and Li₃AlF₆-AlF₃). The eutectic for the LiF-Li₃AlF₆ system has been reported between 14.5 and 16.5 mole % AlF₃ and between 705° and 715°C. The Li₃AlF₆-AlF₃ system has been reported to

TABLE I

Reported Eutectic Compositions and Temperatures in the System LiF-AlF _3 and the Melting Point of $\text{Li}_3^{\text{AlF}}_6$

Author(s)	Equilibrium Solid Phases	Liquid Co of Euteci	mposition .tc(Mole%)	Eutectic Temperature (°C)	M.P. Li ₃ AlF ₆ (⁸ C)
Puschin and	LiF,Li3 ^{A1F} 6	14.5 AlF ₃	85.5 LiF	705	800
Baskow	Li3 ^{A1F} 6,A1F3	37 A1F3	63 LiF	690	
Fedotieff and	LiF, Li ₃ AlF ₆	15 Alf ₃	85 LiF	715	790
Timoteeff	Li ₃ AlF ₆ , AlF ₃	36 Alf ₃	64 LiF	710	
Dergunov ⁽³⁵⁾	LiF, Li ₃ AlF ₆	16.5 AlF ₃	83.5 LiF	706	792
	Li ₃ AlF ₆ , AlF ₃				
Thoma et al. ⁽³⁶⁾	LiF, Li ₃ AlF ₆	14.5 AlF ₃	85.5 LiF	711	785
	Li ₃ AlF ₆ , AlF ₃	36 A1F ₃	64 LiF	710	
Rolin et al. ⁽³³⁾	LiF, Li ₃ AlF ₆				782
	Li ₃ AlF ₆ , AlF ₃	35.5 Alf ₃	64.5 LiF		
Malinovsky	LiF, Li ₃ AlF ₆	15 AlF ₃ 8	5 LiF	711	782
et al. (37)	Li ₃ AlF ₆ , AlF ₃	35 A1F ₃	65 LiF	708	
Rolin et al. ⁽³⁸⁾	LiF, Li ₃ AlF ₆	15.5 A1F3	84.5 LiF	711	782
	Li ₃ AlF ₆ , AlF ₃		'		
Matiasovsky and	LiF, Li ₃ A1F ₆	15 A1F3	85 LiF	711	782
Malinovsky ⁽³⁹⁾	Li ₃ AlF ₆ , AlF ₃	35 Alf ₃	65 LiF	708	
Holm ⁽⁴⁰⁾	LiF, Li ₃ AlF ₆	14.5 AlF3	85.5 LiF	710	785
	Li ₃ AlF ₆ , AlF ₃	35.5 A1F ₃	64.5 LiF	709	
Garton and	LiF, Li ₃ AlF ₆				
Wanklyn ⁽⁴¹⁾					
Holm ⁽⁴²⁾					780

contain a eutectic between 35 and 37 mole % AlF_3 and between 690^o and 711^oC.

The representative diagram of the system shown in Figure 1 is that presented by $Holm^{(40)}$ based on TA and DTA data.

The polymorphism and structure of the compound lithium cryolite have been the subject of four studies $^{(41-44)}$. Garton and Wanklyn $^{(41)}$ used high temperature X-ray diffraction and standard DTA methods to identify five polymorphs, α -, β -, γ -, δ -, and ϵ -Li₂AlF₆.

The α - β transition takes place at 210°C. Both forms were reported as hexagonal with cell parameters a = 9.70Å and c = 12.32Å and a =13.71Å and c = 12.32Å respectively. The third polymorph, γ -Li₃AlF₆ is stable between 515° and 604°C where it converts to δ -Li₃AlF₆. Crystallographic data on the γ polymorph conformed with a cubic unit cell, a = 14.2Å (at 596°C). The high temperature polymorph, ε -Li₃AlF₆, was found to be stable from 705° to its melting point at 783°C. No crystallographic data were reported for the δ and ε forms.

Holm⁽⁴²⁾ studied lithium cryolite using DTA methods and powder X-ray diffraction. He found three polymorphs of Li_3AlF_6 and inversion temperatures at 505° and 597°C. The compound was reported to melt at 780°C. The high temperature form was reported to have the garnet structure with a cubic unit cell (a = 12.03 ± 0.05Å at 625 ± 10°C). The low temperature form was orthorhombic with cell dimensions a = 8.39Å, b = 11.92Å and c = 7.82Å. No data were reported on the intermediate temperature polymorph.



Figure 1. System LiF-AlF $_3^{(40)}$.

Burns, Tennissen and Brunton⁽⁴³⁾ used single crystal X-ray diffraction to study α -Li₃AlF₆. They reported an orthorhombic unit cell with parameters a = 9.510, b = 8.2295 and c = 4.8762Å. Their X-ray powder pattern agreed with the pattern reported for α -Li₃AlF₆ by Garton and Wanklyn⁽⁴²⁾.

The discrepancies in all reported parameters led Holm and Jenssen⁽⁴⁴⁾ to reinvestigate the polymorphy and structure of Li_3AlF_6 . DTA heating curves resulted in transformation peaks at 510°C and 597°C. These values were reported as the $\beta \rightarrow \gamma$ -Li₃AlF₆ and $\gamma \rightarrow \delta$ -Li₃AlF₆ inversions. The α -Li₃AlF₆ polymorph was not seen after normal cooling, but was observed along with β -Li₃AlF₆ in samples quenched from 647° and 790°C. The beta polymorph was reported to be orthorhombic with cell parameters a = 11.78Å, b = 8.43Å and c = 7.77Å. It was stable up to 510°C where it converted to the tetragonal gamma form with cell parameters of a = 11.81Å and c = 8.74Å. The final transformation of Li₃AlF₆ took place at 592°C when γ -Li₃AlF₆ converted to a cubic polymorph designated δ . The cell edge of δ -Li₃AlF₆ is a = 11.98Å.

The authors believe that the 705° C peak reported by Garton and Wanklyn⁽⁴²⁾ corresponds to the eutectic in the LiF-AlF₃ system reported in the literature.

2. System LiF-Na₃AlF₆

The system LiF-Na₃AlF₆ has been investigated numerous times^(29,40,45-52) with widely divergent results being reported. Diagrams of a simple eutectic, limited solid solubility of LiF and mutual solubility of both end members have all been reported. The

reported extents of the solid solutions, in particular that of LiF in Na_3AlF_6 , differ by as much as 60 mole %.

After studying the liquidus curve, Chu and Belyaev⁽⁴⁵⁾ reported the eutectic composition as 83.5 mole % LiF with a eutectic temperature of 700°C. Holm⁽⁴⁶⁾ reported a eutectic temperature of 693°C as did Jenssen⁽⁴⁷⁾. Jenssen⁽⁴⁷⁾ located the eutectic composition at 15.4 mole % Na₃AlF₆.

Lewis⁽⁵²⁾ differed with earlier investigators and reported mutual solid solubility of the end members. Approximately 69 mole % LiF is soluble in Na_3AlF_6 and 3 mole % Na_3AlF_6 in LiF. The eutectic was located at 87 mole % LiF and 703°C.

The first investigation reporting the system to exhibit only partial solid solubility of LiF in Na₃AlF₆ was conducted by Matiasovsky and Malinovsky⁽⁴⁹⁾. Using TA and X-ray phase analysis the extent of solution was set at 70 mole % LiF and the eutectic was located at 14.4 mole % Na₃AlF₆ and 700°C. Holm⁽⁵⁰⁾ reinvestigated the system and found the amount of LiF soluble in Na₃AlF₆ to be considerably less. The extent of solid solution was 12 mole % LiF and the eutectic was placed at 15 mole % Na₃AlF₆ and 694°C. Kostenska⁽⁵¹⁾ further reduced the solubility of LiF to 6 mole % Na₃AlF₆ and 696°C.

Holm⁽⁴⁰⁾ used TA, DTA, quenching techniques and X-ray diffraction to study the system (Figure 2). He found the subsolidus region below 550° C to be a pseudobinary due to the presence of only two phases, α -Na₃AlF₆ and LiF. He reported the solid-liquid region to be part of the ternary reciprocal system





$$3LiF + Na_3AlF_6 \stackrel{\uparrow}{\downarrow} Li_3AlF_6 + 3NaF$$

as a result of a formation of solid solutions between Li_3AlF_6 and Na_3AlF_6 .

Foster $^{(29)}$, realizing the problem of volatization, encapsulated his samples in sealed platinum tubes. Working under carefully controlled conditions and employing both quench methods and refractive index measurements, he determined mutual solubility of both end members. By assuming Raoult behavior, the amount of LiF soluble in Na₃AlF₆ was calculated to be 14.4 mole %. Cryolite was found to be soluble in LiF up to 6.8 mole %. The eutectic was located at 85.3 mole % LiF. The diagram is shown in Figure 3.

3. System Na₃AlF₆-Li₃AlF₆

The Na₃AlF₆-Li₃AlF₆ system has been studied many times with little agreement between investigators (53-59). The first study was made in 1936 by Drossbach (53). Using thermal methods he reported a continuous solid solution between the end members. Solidus temperatures ranged from 10 to 15° C below the liquidus and a thermal minimum was located at 70 mole % Li₃AlF₆.

Mashovets and Petrov⁽⁵⁴⁾ found the system to be a simple eutectic with no solid solution. Thermal and optical studies were employed and the eutectic was found at 710° C and 62 mole % Li₃AlF₆.

Another study⁽⁵⁵⁾ reported three compounds to exist corresponding to the formulas $\text{Li}_3\text{Na}_6\text{Al}_3\text{F}_{18}$, $\text{Li}_6\text{Na}_3\text{Al}_3\text{F}_{18}$ and $\text{Li}_{15}\text{Na}_3\text{Al}_6\text{F}_{36}$. No compound having the formula of the naturally occurring mineral cryolithionite, $\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$, was reported.



Rolin and Muhlethaler⁽³³⁾ used cooling curves to examine the system. They found a continuous series of solid solutions on the Li_3AlF_6 side up to the eutectic point of 62.3 mole % Li_3AlF_6 and 713°C. Solid solution extended to 36 mole % Li_3AlF_6 on the Na_3AlF_6 side.

Garton and Wanklyn⁽⁵⁶⁾ used X-ray analysis, quenching techniques, and DTA results in studying the system. Two compounds were found, one corresponding to the natural mineral cryolithionite, $Na_3Li_3Al_2F_{12}$ and another compound of the formula Na_2LiAlF_6 . Cryolithionite was found to exist as a nonstoichiometric solid solution which decomposed to Li_3AlF_6 and a phase of Na_3AlF_6 at $680^{\circ}C$. The second compound, Na_2LiAlF_6 was found to decompose at $500^{\circ}C$.

Holm and Holm⁽⁵⁷⁾ used DTA and high temperature X-ray analyses to confirm the existence of the two compounds. Each existed up to approximately 500°C. Na₂LiAIF₆ was found to exist in two polymorphic forms. The α polymorph was indexed on the basis of a monoclinic unit cell with parameters a = 7.538Å, b = 7.516Å and c = 7.525Å. On heating, α -Na₂LiAIF₆ converted to cubic β -Na₂LiAIF₆ (a = 7.639Å at 445°C). The transformation could not be detected by DTA but high temperature X-ray diffraction showed the inversion to be complete at 420°C. Na₃Li₃Al₂F₁₂ was identical to naturally occurring cryolithionite (a = 12.127Å at 20°C). The study also revealed one new phase present between 560°C and 630°C from 90 to 99 mole % Li₃AIF₆. The new phase was indexed based on a tetragonal unit cell with parameters a = 11.97Å and c = 8.73° (625°C). Although no solid solution was found at room temperature, an extensive amount was reported at high temperatures. The liquidus curve reached a minimum at 64 mole % Li₃AlF₆ and 710°C.

Baylor et al.⁽⁵⁸⁾ found $\text{Li}_{3}\text{AlF}_{6}$ to be soluble in $\text{Na}_{3}\text{AlF}_{6}$ up to a maximum of 18 mole %. Cryolithionite and $\text{Na}_{2}\text{LiAlF}_{6}$ were reported to decompose between 500 and 600°C. Stinton and Brown⁽⁵⁹⁾ used DTA and X-ray diffraction to study the system. Samples were sealed in platinum tubes to prevent volatilization during firing and DTA experiments. Their liquidus curve agreed well with that of Holm and Holm⁽⁵⁷⁾. The eutectic was placed at 64 mole % $\text{Li}_{3}\text{AlF}_{6}$ and 713°C and no solid solution was reported below 500°C. An intermediate solid solution denoted $\alpha'-\text{Na}_{3}\text{AlF}_{6}$ was found to be stable between 530°C and 758°C and 10 and 38 mole % $\text{Li}_{3}\text{AlF}_{6}$. Their diagram is pictured in Figure 4.

4. System Li₃AlF₆-Al₂O₃

The first study of the system $\text{Li}_3\text{AlF}_6-\text{Al}_20_3$ was made in 1936 by Drossbach⁽⁵³⁾. Using thermal methods he reported a simple eutectic system with the invariant point at 782°C and 1 wt. % Al_20_3 . Mashovets and Petrov⁽⁵⁴⁾ used samples containing up to 6 wt. % Al_20_3 to revise the eutectic location to 775 \pm 3°C and 1.1 weight % Al_20_3 . Their diagram is pictured in Figure 5.

5. System Na₃AlF₆-Al₂O₃

Early published phase diagrams of the Na₃AlF₆-Al₂O₃ system differ as to eutectic location and amount of Al₂O₃ soluble in Na₃AlF₆, if any. Drossbach⁽⁵³⁾ employed cooling curves to determine the system and reported Al₂O₃ to be soluble in Na₃AlF₆ up to approximately 10 weight %. A eutectic was located at 937°C and 18 weight % Al₂O₃.





Phillips et al. ⁽¹³⁾ determined the liquidus curve for the system by making visual observations during cooling of the melts. Super cooling was noted on the Al_20_3 side of the eutectic and showed a maximum of $5^{\circ}C$. They located the eutectic at 10 weight $% Al_20_3$ and $962^{\circ}C$. The authors also noted that above 10 weight $% Al_20_3$, the cooling curves exhibited no break corresponding to the first appearance of crystals from the melt. Slowness of crystal formation and the steepness of the liquidus curve were cited as possible explanations. Cooling rates of less than $0.1^{\circ}C/minute$ were employed to help alleviate the problem.

The problem encountered by Phillips et al.⁽¹³⁾ lead Foster to employ a quenching technique to determine the system⁽⁶⁰⁾. After quenching encapsulated samples, index of refraction measurements were taken to determine the phase(s) in equilibrium with liquid at the quench temperature. X-ray diffraction was also employed to supplement the optical microscopy findings. The result of Foster's work is shown in Figure 6. The eutectic was located at 961°C and 10.5 weight % $Al_2^0_3$.

6. System Na₃AlF₆-AlF₃

Phase studies of the Na₃AlF₆-AlF₃ system have been reported numerous times^(14,17,61-65) with good agreement on the high cryolite side of the diagram (up to 30 weight % AlF₃). All studies report the existence of an incongruently melting compound, Na₅Al₃F₁₄, chiolite. Chiolite decomposes by a peritectic reaction to Na₃AlF₆ and liquid at a temperature between 730° and 741°C^(14,17,61-65). The existence of



Figure 6. System $\operatorname{Na}_3\operatorname{AlF}_6\operatorname{-Al}_2\operatorname{O}_3^{(60)}$.

a second compound, NaAlF₄, has also been reported ^(17,64). Grjotheim⁽¹⁷⁾ reported NaAlF₄ as a congruently melting compound whereas Ginsberg and Wefers⁽⁶⁴⁾ reported NaAlF₄ to melt incongruently at 710° C.

Holm⁽⁶³⁾ studied the stability of NaAlF₄ in the solid phase. Solid NaAlF₄ was gathered from the vapor over a melt of the same composition⁽⁶⁵⁾. DTA of the sample revealed that the reaction

$$5$$
NaAlF₄ = Na₅Al₃F₁₄ + 2AlF₃

was complete at 500° C demonstrating the instability of NaAlF₄ at this temperature.

Foster⁽⁶⁵⁾ examined the system to determine if $NaAlF_4$ was stable as a solid phase and to determine the phases in equilibrium with liquid. Samples of compositions in the $NaAlF_4$ area were sealed in platinum tubes and quenched into water. Those samples that were quenched from regions of all liquid or liquid plus a solid phase contained $NaAlF_4$. Samples quenched from solid phase regions showed only chiolite and AlF_3 in equilibrium with no $NaAlF_4$ present. These results led Foster to conclude that $NaAlF_4$ is not stable in the solid phase and is only found in liquid phase regions. His diagram is pictured in Figure 7.

C. Three Component Systems

1. System LiF-AlF3-Na3AlF6

Holm and Holm⁽⁶⁶⁾ worked near the $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{LiF}$ portion of the ternary diagram in 1973. They found a ternary eutectic at 684°C and 83 mole % LiF, 7% AlF₃ and 10% Na₃AlF₆. Thoma et al.⁽³⁶⁾ studied



the NaF-LiF-AlF₃ ternary system and found the LiF-AlF₃-Na₃AlF₆ portion of the diagram to contain a eutectic in each of the two compatibility triangles Na₃AlF₆-AlF₃-Li₃AlF₆ and Na₃AlF₆-LiF-Li₃AlF₆. No evidence of either Na₂LiAlF₆ or Na₃Li₃Al₂F₁₂ was reported.

Rolin and Muhlethaler ⁽³³⁾ presented a diagram of the Na₃AlF₆-Li₃AlF₆-AlF₃ ternary system (Figure 8) showing a peritectic at 647^oC and 47 weight % Na₃AlF₆, 34.5% Li₃AlF₆ and 18.5% AlF₃ and a eutectic at 36 weight % Na₃AlF₆, 41% Li₃AlF₆ and 23% AlF₃ and 607^oC.

To avoid the problem of volatilization, Stinton and Brown⁽⁶⁷⁾ encapsulated all samples in platinum tubes. DTA, quench methods, and X-ray analyses were employed to determine the system shown in Figure 9. Seven compatibility triangles, three eutectics, one peritectic, a reaction point and two regions of cryolite - $\text{Li}_3\text{AlF}_{6(\text{ss})}$ (Na₃AlF_{6(ss)}-Na₅Al₃F₁₄ and Na₃AlF_{6(ss)}-LiF) were identified.

2. System Li₃AlF₆-Na₃AlF₆-Al₂O₃

Drossbach⁽⁵³⁾ first investigated this system in 1936. Working near the Na₃AlF₆-Li₃AlF₆ side of the ternary, he determined a boundary curve extending from 10 weight % Al₂O₃ on the Na₃AlF₆-Al₂O₃ binary at 937^oC to 38 weight % Li₃AlF₆ on the Na₃AlF₆-Li₃AlF₆ join at 810^oC. No Li₃AlF₆ primary phase field was indicated.

Mashovets and Petrov⁽⁵⁴⁾ also worked in the Na₃AlF₆-Li₃AlF₆ side of the ternary and found a boundary curve extending from 15 weight % Al₂O₃ on the Na₃AlF₆-Al₂O₃ join to 7 weight % Al₂O₃ on the Li₃AlF₆-Al₂O₃ join.







Figure 9. System LiF-AlF₃-Na₃AlF₆⁽⁶⁷⁾.

Rolin and Muhlethaler⁽³³⁾ obtained similar results in their study of the diagram. Using data obtained from thermal arrest cooling curves they found a single boundary curve separating Al_20_3 from the cryolitelithium cryolite solid solution. The boundary curve paralleled the $Na_3AlF_6-Li_3AlF_6$ binary within 1 weight % from 45 to 100 weight % Li_3AlF_6 . No ternary compounds were reported.

3. System Na₃AlF₆-AlF₃-Al₂O₃

Several studies of the $Na_3AlF_6-AlF_3-Al_2O_3$ system have been reported in the literature. Fenerty and Hollingshead ⁽⁶²⁾ and Rolin ⁽⁶⁸⁾ reported similar results for compositions of low AlF₃. Fenerty and Hollingshead ⁽⁶²⁾ reported a boundary curve between Na_3AlF_6 and Al_2O_3 which breaks quickly to low Al_2O_3 contents at AlF₃ contents of greater than 25%. The ternary peritectic point was located near 0.5% Al_2O_3 .

Rolin⁽⁶⁸⁾ reported a boundary curve between Na_3AlF_6 and Al_2O_3 which does not have the steep slope to the peritectic that Fenerty and Hollingshead reported. Rolin located the ternary peritectic at 5 weight % Al_2O_3 , 28.4% AlF_3 and 66.6% Na_3AlF_6 and a ternary eutectic at 3.3% Al_2O_3 , 36.7% AlF_3 and 60% Na_3AlF_6 .

Foster $^{(32)}$ used a combination of quench technique, optical microscopy and X-ray diffraction during his study of the system. Samples were prepared along the 5, 10, 14, 18, 20, 25, 30, 32, 35, 37, and 40% AlF₃ isopleths and sealed in platinum tubes to insure no loss of fluorine during heat treatments. The alumina content was varied between 0 and 14%. The results of the study are seen in Figure 10. One interesting point of the diagram is the n-Al₂0₃ phase


field at AlF_3 contents of 20% or more. The study revealed a ternary peritectic point at 28.3% AlF_3 , 4.4% Al_2O_3 and 67.3% Na_3AlF_6 at 723°C. A ternary eutectic point was located at 37.3% AlF_3 , 3.2% Al_2O_3 and 59.5% Na_3AlF_6 .

III. EXPERIMENTAL PROCEDURE

A. Materials

Starting materials used in the study of the $\text{LiF-AlF}_3-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ system were reagent grade lithium fluoride*, aluminum fluoride trihydrate*, hand picked natural Greenland cryolite** and aluminum oxide*. Weight loss factors were determined for Al_20_3 , LiF, and $\text{AlF}_3\cdot3\text{H}_20$ by heating small samples of each material at different temperatures until a constant weight was reached. The materials were fired in open silica crucibles. Aluminum fluoride was found to show a sharp increase in weight loss at temperatures above 500°C indicating volatization.

B. Subsolidus Equilibria

Subsolidus equilibria data at 500° C were determined for the Li₃AlF₆-Al₂O₃ binary, the Li₃AlF₆-Na₃AlF₆-Al₂O₃ ternary and the LiF-AlF₃-Na₃AlF₆-Al₂O₃ quaternary systems. Selected compositions in each of the binary, ternary and quaternary systems were weighed to \pm 0.1 mg on a Sartorius analytical balance and hand mixed under acetone in a glass mortar and pestle until near dryness. Each sample was heat treated at 300°C overnight in an open silica crucible to drive off the chemically held water of AlF₃ and adsorbed water on Al₂O₃ and LiF. The calcined samples were then sealed in platinum tubes to prevent volatization of AlF₃. Approximately 0.03 gm samples were encapsulated

*Matheson, Coleman and Bell Manufacturing Chemists, Norwood, Ohio.

^{**}Supplied by ALCOA, New Kensington, PA. Impurities in weight %: SiO₂ 0.14, KF 0.55, CaF₂ 0.01, and LiF 0.035.

in 0.125 cm OD tubes 2 cm in length. The tubes were hermetically sealed with a Burell arc welder and placed in a 500°C furnace for 48 hours. After the samples were removed from the furnace, the tubes were examined to determine if any breakage had occurred during firing. Broken tubes were distinguishable by the presence of white powder on the outside of the tube. Broken tube samples were refired in newly sealed tubes.

In previous studies in which a sealed tube experimental procedure has been employed, the effect of the vapor pressure inside the tube on liquidus temperatures has been questioned. Foster $^{(32)}$ determined that for pressures within rupture limits of the tubes (4 atms) the liquidus temperatures would be affected by only $0.03^{\circ}/atm$. Using the Clausius-Clapeyron equation

 $dT = T(v_{\rho} - v_{\rho})/q \, dp,$

he found for pure cryolite

 $dT = 0.03^{\circ}/atm dp$.

In this study, capsules that were determined to have good seals were opened and the contents were crushed in an agate mortar with pestle. The sample was X-rayed to determine if complete reaction had taken place. Samples where equilibrium had not yet been reached were resealed and refired until relative amounts of phases present remained constant. At this point it was assumed that equilibrium had been reached.

C. Liquidus Equilibria

Liquidus data were determined for the $\text{Li}_3\text{AlF}_6\text{-Al}_2^0_3$ binary diagram and the $\text{Li}_3\text{AlF}_6\text{-Na}_3\text{AlF}_6\text{-Al}_2^0_3$ ternary diagram. Compositions at 10 mole % intervals along the $\text{Li}_3\text{AlF}_6-\text{Al}_20_3$ binary join and selected compositions from all areas of the $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ system were studied. In the $\text{LiF}-\text{AlF}_3-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ quaternary system compositions in each of the seven quaternary tetrahedra were studied to locate quaternary invariant points. Compositions on the 5 mole % Al_20_3 plane and at the l:l:l:l locations in each of the seven quaternary tetrahedra were prepared.

Each composition was weighed to 0.1 mg and mixed under acetone until near dryness in the same manner as samples studied in the subsolidus. Calcination was done by heat treating samples in open silica crucibles at 300°C overnight. Calcined samples were sealed in platinum tubes in the same manner as subsolidus compositions. Liquidus temperatures were obtained by running a differential thermal analysis (DTA) on each composition. DTA runs revealed subsolidus reaction points, phase transformations and in some cases liquidus temperatures. To verify the liquidus temperatures, samples sealed in platinum tubes were placed in a vertical tube quench furnace. The temperature in the furnace was controlled to $\pm 3^{\circ}$ C by a Tem Pres controller. Each capsule was heated just above the liquidus temperature obtained from the DTA runs (when liquidus was seen) and held for 1 hour. The sample was then quenched into ice water. After examining the capsules for breakage or leakage during firing, the tube was opened and the contents were removed and crushed in an agate mortar and pestle. A small amount of each sample was viewed under a petrographic microscope. From the overall appearance of the quenched

material it was possible to determine if liquid had been present at the firing temperature. The presence of liquid was distinguishable by irregular shapes, small crystals and cracks and bubbles. Capsules that contained liquidus samples also exhibited wetting on their interior walls. These samples had white powder on the walls where liquid had been present. The sample itself was more difficult to remove from the tube once melting had taken place.

The Becké line method was used to determine what primary phase was present in each sample. Those samples quenched from just below the liquidus surface exhibited rapidly crystallized liquid and well developed crystals of the primary phase field composition. These crystals were easily distinguishable from the recrystallized liquid and were identified on the basis of their refractive indices.

D. Equipment

1. X-Ray Diffraction

General phase analysis of each sample was done by standard X-ray powder diffraction techniques. A Norelco diffractometer with CuK_{α} nickel filtered radiation, a graphite crystal monochrometer and pulse height analyzer was used for identification. A scan speed of $1^{\circ}2\theta/minute$ was used for standard identification. A scan speed of $\frac{1}{2}\theta/minute}{1}$ was used for precise peak locations.

The unit was checked against a standard silicon disk for accuracy. Runs at $\frac{1}{4}^{O}2\theta$ /minute were made and peak locations were averaged. The unit was found to be accurate within 0.05^O20.

2. DTA Equipment

The DTA equipment consisted of a small platinum wound furnace* programmed by an automatic controller**. All samples were heated at a rate of 3° C/minute. The encapsulated samples and standard (calcined Al₂0₃) were placed directly on the Pt-Pt/10Rh thermocouple beads. The differential emf's were recorded versus millivolts on an x-y recorder*** The scales used on the recorder were 2 millivolts/inch on the y-axis and 1 millivolt/inch on the x-axis. The scales were checked before each DTA run with a Leeds and Northrup potentiometer. The DTA was calibrated against the melting point of NaCl (800.8°C) and Na₂SO₄ (884.8°C).

3. Quench Furnace

The quench furnace consisted of a vertical tube furnace controlled by a Tem Pres control unit. Temperatures were accurate to $\pm 3^{\circ}$ C. Calibration of the unit was done with a Pt/Pt-10Rh thermocouple and a Leeds and Northrup potentiometer.

4. Microscope

The microscope used for optical examination of samples was a Reichert-Wien universal camera microscope model MeF₂ equipped with polarizers. Cagill index of refraction liquids were used in the Becké line method.

*R. L. Stone, Austin, Texas **Leeds and Northrup Controllall.

IV. RESULTS AND DISCUSSION

A. The Li₃AlF₆-Al₂O₃ System

The phase relations in the lithium cryolite-alumina binary system must be established in order to study the $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ ternary system and the $\text{LiF}-\text{AlF}_3-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ quaternary systems. Existing publications involving the lithium cryolite-alumina diagram are few and in most cases present conflicting results. Unlike the other two boundary binary diagrams in the ternary system, no study of this system has been conducted using sealed tubes.

Samples at 10 mole % increments were prepared along the Li_3AlF_6 -Al₂0₃ join by mixing lithium fluoride, aluminum fluoride and alumina. Following a 48 hour heat treatment at 500°C, the phases present in the samples were determined by X-ray diffraction techniques. The results are shown in Table II. All binary samples contained only α -Li₃AlF₆ and Al₂0₃. Several samples were resealed and refired for 24 hours. Examination of these samples revealed that the relative amounts of α -Li₃AlF₆ and Al₂0₃ present were the same as after 48 hours of firing. This indicated a simple binary system between the two end members. A check for solid solution was made by scanning samples at $\frac{1}{4}^{\circ}20/\text{minute}$ and measuring the location of the most intense peak of both α -Li₃AlF₆ and α -Al₂0₃. No solid solution was detected.

TABLE II

DTA and X-Ray Diffraction Results of Samples in the ${\rm Li_3^{AlF}_6^{-Al}_20_3}$ System

Sample Composition	Heat Treatment (^O C/Hours)	Phases Present	DTA Pea ks ([°] C)
10% Li ₃ AlF ₆ 90% Al ₂ 0 ₃	500/48	$^{A1}2^{0}_{3}$ $^{\alpha-Li}3^{A1F}_{6}$	706,765
^{20% Li₃^{AlF}₆ 80% Al₂0₃}	500/48	$^{A1}2^{0}_{3}_{\alpha-Li}^{3}_{3}^{A1F}_{6}$	668,756
^{30% Li₃AlF₆ 70% Al₂0₃}	500/72	$^{A1}2^{0}_{3}$ $^{\alpha-Li}3^{A1F}_{6}$	235,658,756
40% Li ₃ AlF ₆ 60% Al ₂ 0 ₃	500/72	α-Li3 ^{AlF} 6 Al ₂ 03	667,754
^{50% Li₃AlF₆ 50% Al₂0₃}	500/48	α-Li3 ^{A1F} 6 ^{A1} 2 ⁰ 3	677,754
^{60% Li} 3 ^{A1F} 6 40% A1 ₂ 0 ₃	500/72	α-Li3 ^{A1F} 6 ^{A1} 2 ⁰ 3	515,696,754
70% Li ₃ AlF ₆ 30% Al ₂ 0 ₃	500/48	$\overset{\alpha-\text{Li}_3\text{AlF}_6}{\overset{\text{Al}_2^0}{_3}}$	503,588, 692,755
80% Li ₃ AlF ₆ 20% Al ₂ 0 ₃	500/48	α-Li ₃ AlF ₆ Al ₂ 0 ₃	696,760
90% Li ₃ AlF ₆ 10% Al ₂ 0 ₃	500/48	$\overset{\alpha-\text{Li}_{3}\text{Alf}_{6}}{\text{Al}_{2}^{0}{}_{3}}$	- 507, 693,759
100% Li ₃ A1F ₆	500/48	α-Li ₃ AlF ₆	223,515,605, 698,780

Several binary samples were quenched from temperatures where the higher polymorphs of Li_3AlF_6 are stable (above 600°C) in an effort to obtain other polymorphs of Li_3AlF_6 . After quenching, these samples contained only β -Li_3AlF₆. This result agrees well with previous studies which reported α - and β -Li_3AlF₆ as the only polymorphs seen at room temperature.

Following the X-ray investigations, DTA experiments were conducted using heating and cooling rates of $3^{\circ}C/minute$ to help locate the eutectic temperature of the system. The results are shown in The lower temperatures represent smaller peaks and agree Table II. well with the polymorphic transformation temperatures of Li₃AlF₆. DTA results also revealed a peak in all binary samples in the 750-760°C range. This peak was larger than the minor peaks associated with Li_3A1F_6 polymorphic changes. The peak in the 750-760°C range could not be explained by a polymorphic inversion and was taken to represent the eutectic temperature. Samples of high lithium cryolite compositions exhibited larger peaks than those samples with medium or low Li_3AlF_6 compositions. This indicated the location of the eutectic to be near the Li_3AlF_6 side of the diagram. In an effort to determine the eutectic, samples containing 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, and 7.0 mole % Al₂0₃ were prepared. The DTA results of these samples are shown in Table III.

Although DTA experiments were conducted to temperatures over 1000° C, most samples showed no peaks on heating curves above the 750-760°C range or above the eutectic temperature. This phenomena

TABLE III

Liquidus Temperatures as Determined by Quenching Methods in the ${\rm Li_3}^{\rm A1F}{\rm 6}^{\rm -A1}{\rm _20}{\rm _3}$ System

Sample Composition (Mole %)	DTA Peaks (°C)	Liquidus Determined from Quench (^O C)
0.5% A1 ₂ 0 ₃	490,596	771
99.5% Li ₃ AlF ₆	678,756	
1.0% A1 ₂ 0 ₃	495,596	eutectic
99.0% Li ₃ AlF ₆	688,757	
1.5% Al ₂ 0 ₃	491,593	770
98.5% Li3AlF ₆	688,752	
2.0% Al ₂ 03	495,596	785
98.0% Li ₃ AlF ₆	691,750	
3.0% Al ₂ 0 ₃		797
97.0% Li3 ^{AlF} 6	706,754	
5.0% Al ₂ 03	511,591	830
95.0% Li ₃ AlF ₆	699,750	
7.0% Al ₂ 03	510, -	-
93.0% Li ₃ AlF ₆	701,756	

has been noted in the literature in many systems which contain alumina. These systems have failed to exhibit peaks corresponding to liquidus temperatures in heating and cooling curves. In this study, a change in heating and cooling rates of the DTA furnace from 3[°]C/minute to approximately 1.5[°]C/minute failed to reveal definite liquidus peaks on either heating or cooling curves.

Quench experiments were used to determine the liquidus temperatures to an accuracy of $\pm 3^{\circ}$ C. Examination of the sample in the tube after quenching as well as microscopic viewing of the sample revealed relative amounts of melting. The results of the quench work are shown in Table III. The binary diagram is shown in Figure 11. The eutectic was located at 754°C and 1.0 mole % Al₂0₂.

Compositions on the alumina side of the eutectic did not exhibit DTA peaks corresponding to liquidus temperatures. By determining liquidus temperatures from quench data, the steepness of the liquidus curve can be seen (Figure 11). This steepness is probably the cause of no liquidus peaks being seen on heating. On cooling, small, broad peaks were found at temperatures $5-10^{\circ}$ C below the liquidus value determined from the quench work. Because of their broad, flat shape, these peaks revealed little useful information in determining liquidus values. A change in cooling rate from 3° C/minute to 1.5° C/minute failed to improve the shape of the liquidus peak.

The presence of supercooling has been seen in other phase equilibria studies of systems involving the Hall cell electrolyte and is, in fact, quite common.





B. The Li₃AlF₆-Na₃AlF₆-Al₂O₃ System

The introduction of alumina into the LiF-AlF3-Na3AlF6 system can be expected to provide information that is interesting from both a theoretical and practical point of view. The effects of adding Al_20_3 such as solubility, possible quaternary compounds and solid solution will be of special interest. A study of the $Li_3AlF_6-Na_3AlF_6-Al_2O_3$ system is an excellent first step in determining the phase relations in the LiF-AlF₃-Na₃AlF₆-Al₂ 0 ₃ quaternary system since it divides the quaternary into two separate tetrahedra. A particular point of interest is the behavior of the two binary compounds that exist on the Na_3AlF_6 - Li_3AlF_6 join (Na₂LiAlF₆ and Na₃Li₃Al₂F₁₂). There is no study in the literature where the reactions between these two compounds and alumina have been reported. The possibility of phase fields for one or both of these incongruently melting compounds cannot be overlooked. However. since Na_2LiAlF_6 has been reported to decompose at 543°C⁽⁶⁷⁾, it is doubtful that it will ever be present in equilibrium with liquid.

1. Subsolidus Equilibria

Compositions from all parts of the Li₃AlF₆-Na₃AlF₆-Al₂O₃ diagram were prepared in order to determine the compatibility relations. Samples were sealed in platinum tubes and heat treated at 500[°]C for 48 hours. The results of the subsolidus study are shown in Table IV. The subsolidus diagram is shown in Figure 12. X-Ray diffraction data revealed three compatibility triangles and one two phase region to be present. No ternary compounds were found to exist.

TABLE IV

Compositions Used to Determine Compatibility Relations in the System $\text{Li}_3\text{AlF}_6\text{-Na}_3\text{AlF}_6\text{-Al}_2^0_3$

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Composition (Mole %)		Firing Time	Phases Present		
Li3 ^{AlF} 6	^{Na} 3 ^{A1F} 6	A12 ⁰ 3	(Hrs)		
5	5	90	48	A1203, Na3Li3A12F12	
10	25	65	48	$A1_20_3$, Na_2LiAlF_6 , Na_3AlF_6 (ss)	
30	15	55	48	β -Li ₃ AlF ₆ , Na ₃ Li ₃ Al ₂ F ₁₂ , Al ₂ O ₃	
15	50	35	48	$A1_20_3$, $Na_3A1F_6(ss)$, Na_2LiA1F_6	
15	65	20	48	$A1_{20_3}$, $Na_3A1F_{6(ss)}$, Na_2LiA1F_6	
30	50	20	48	$A1_20_3$, Na_2LiAlF_6 , $Na_3Li_3A1_2F_{12}$	
50	30	20	48	Li3AlF6, Na3Li3Al2F12, Al2O3	
70	10	20	48	Li ₃ AlF ₆ , Na ₃ Li ₃ Al ₂ F ₁₂ , Al ₂ O ₃	
10	85	5	48	$^{\text{Na}}3^{\text{AlF}}6(\text{ss}), ^{\text{Al}}2^{0}3$	
50	45	5	48	$Na_{3}Li_{3}Al_{2}F_{12}$, $Al_{2}O_{3}$, $Li_{3}AlF_{6}$	
80	15	5	48	Na3Li3A12F12, A1203, Li3A1F6	
40	50	10	48	Na ₂ LiAlF ₆ , Na ₃ Li ₃ Al ₂ F ₁₂ , Al ₂ O ₃	
35	55	10	48	Na_2LiAlF_6 , $Na_3Li_3Al_2F_{12}$, Al_2O_3	
50	40	10	48	^{Na} 3 ^{Li} 3 ^{A1} 2 ^F 12, Li3 ^{A1F} 6, A12 ⁰ 3	
40	30	30	48	^{Na} 3 ^{Li} 3 ^{A1} 2 ^F 12, ^{A1} 2 ⁰ 3, ^{Li} 3 ^{A1F} 6	
25	25	50	48	$A1_{2}0_{3}$, $Na_{3}Li_{3}A1_{2}F_{12}$	
10	35	55	48	$Na_3^{A1F}_{6(ss)}$, $A1_2^{0}_3$, $Na_2^{LiA1F}_{6}$	
15	20	65	48	Na_2LiAlF_6 , $Na_3Li_3Al_2F_{12}$, Al_2O_3	
33 .33	33.33	33.33	48	$A1_{2}0_{3}$, $Na_{3}Li_{3}A1_{2}F_{12}$	
30	40	30	48	Na ₂ LiA1F ₆ , Na ₃ Li ₃ A1 ₂ F ₁₂ , A1 ₂ 0 ₃	
25	35	40	48	Na ₂ LiAlF ₆ , Na ₃ Li ₃ Al ₂ F ₁₂ , Al ₂ O ₃	
20	30	50	48	Na2LiAlF6, Na3Li3A12F12, A1203	
35	45	20	48	Na ₂ LiAlF ₆ , Na ₃ Li ₃ Al ₂ F ₁₂ , Al ₂ O ₃	
18.6	36.4	45	48	Al ₂ 0 ₃ , Na ₂ LiAlF ₆	
8.6	16.4	75	48	Al ₂ 0 ₃ , Na ₂ LiAlF ₆	
30.2	59.8	10	48	Al ₂ 0 ₃ , Na ₂ LiAlF ₆	



Figure 12. Subsolidus compatibility relations at 500° C in the $Li_3^{A1F}6^{-Na}3^{A1F}6^{-A1}2^{0}3^{\circ}$ system.

As can be seen from the diagram, the only solid solution in the system is on the $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6$ join. X-Ray diffraction scan speeds of $\frac{1}{4}^020/\text{minute}$ of samples were made to determine if solid solution existed in either the $\text{Al}_20_3-\text{Na}_2\text{LiAlF}_6$ or the $\text{Al}_20_3-\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$ system. The slow speed scans revealed no shift in the location of the most intense peak of either of the binary compounds or alumina.

Baylor et al.⁽⁵⁸⁾ reported Li_3AlF_6 to be soluble in Na_3AlF_6 up to 18 mole % Li_3AlF_6 at 500°C. Measurement of the most intense cryolite peak was made to determine the extent of solid solution. As more Li_3AlF_6 went into solution with Na_3AlF_6 , the d₍₂₂₀₎ value for cryolite decreased from 1.942 to 1.929Å.

Seven samples were prepared in the interior of the ternary system near the line connecting Al_2O_3 and 18% Li_3AlF_6 on the Na_3AlF_6-Li_3AlF_6 join. These samples were heat treated at 500°C for 100 hours to insure the attainment of equilibrium. X-Ray diffraction data revealed whether the composition was located in the two phase region or in the Na_3AlF_6(ss)-Na_2LiAlF_6-Al_2O_3 three phase region. As more Li_3AlF_6 was added, entry into the three phase region was indicated by the presence of Na_2LiAlF_6. The results of the seven samples examined are shown in Table V. The amount of Li_3AlF_6 soluble in cryolite was found to be 16 mole %. This agrees well with the findings of Baylor et al.⁽⁵⁸⁾ The discrepancy is found to be small when comparing d₍₂₂₀₎ values. At 18%, Baylor reported a d₍₂₂₀₎ value of 1.929. Measurements of d₍₂₂₀₎ values in the present study revealed a value of 1.931. The discrepancy is

TABLE V

Samples Studied to Determine the Location of the $\frac{Na_3AIF}{3}6(ss)^{-A1}2^03$ Two Phase Region

Composition (Mole %) Li ₃ AlF ₆ Na ₃ AlF ₆ Al ₂ O ₃		Heat Treatment (^O C/Hrs)	Phases Present	
5	50	45	500/100	^{Na} 3 ^{A1F} 6(ss), ^{A1} 2 ⁰ 3
10	60	30	500/100	$^{Na}3^{A1F}_{6(ss)}, ^{A1}2^{0}_{3}$
10	75	15	500/100	$^{Na}3^{A1F}6(ss), ^{A1}2^{0}3$
12	63	25	500/100	$Na_3^{A1F}_{6(ss)}, A1_2^{0_3},$ $Na_2^{LiA1F}_{6}$
13	62	25	500/100	$Na_3^{AlF}_{6(ss)}, Al_2^{0}_3,$ $Na_2^{LiAlF}_6$
15	65	20	500/100	$^{\text{Na}}3^{\text{AlF}}6(\text{ss}), \text{Al}_2^03$
10	85	5	500/100	$Na_3^{AlF}_{6(ss)}, Al_2^0_3$

probably due to the difference in experimental procedure. Baylor fired at 500° C in open air as opposed to the present study where sealed tubes were used.

Subsolidus relations above 500°C differ from those at 500°C. At 543°C Na₂LiAlF₆ decomposes to cryolite and an intermediate solid solution of cryolite⁽⁶⁷⁾. Therefore, at 543°C the subsolidus diagram contains two three-phase regions and one two-phase region. Attempts to verify this by quenching samples from 600°C proved useless because the higher temperature phases are non-quenchable. All compositions in the Na₃AlF_{6(ss)}-Na₃AlF₆-Al₂O₃ portion of the diagram that were quenched from 600°C contained Na₂LiAlF₆.

2. Liquidus Equilibria

Liquidus equilibria for the $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ system were determined by a combination of DTA, quench techniques and optical microscopy. Compositions from all parts of the diagram were prepared and analyzed by DTA with heating and cooling rates of 3°C/minute. The majority of samples studied to determine liquidus data were low in Al_20_3 content (<40% Al_20_3) because preliminary examination of DTA patterns for high Al_20_3 content samples failed to reveal liquidus temperatures. The amounts of alumina soluble in Na_3AlF_6 and Li_3AlF_6 (18.5 and 1 mole %, respectively) suggests the location of the cryolite-alumina and lithium cryolite-alumina boundary curves to be near the Na_3AlF_6-Li_3AlF_6 join. In addition, the results of the subsolidus equilibria presented earlier (which verify the absence of any ternary compounds) rule out the presence of any new phase fields in the high Al_20_3 portion of the diagram. It was felt that any existing phase field for either Na_2LiAlF_6 or $Na_3Li_3Al_2F_{12}$ would most likely be near the $Na_3AlF_6-Li_3AlF_6$ join.

Preliminary investigations of DTA patterns revealed no new or unexplainable peaks below the reported dissocation temperature of Na_2LiAlF_6 , $543^{o}C^{(67)}$. Therefore, the presence of a phase field for Na_2LiAlF_6 was ruled out. Two peaks were noted in the 670-685^oC range which could not be explained by known subsolidus invariant points on the cryolite-lithium cryolite join or by polymorphic inversions. Since $Na_3Li_3Al_2F_{12}$ decomposes at $693^{o}C^{(67)}$, these temperatures could be an indication of cryolithionite being in equilibrium with liquid. If a phase field was not present for $Na_3Li_3Al_2F_{12}$, then the ternary system would have to consist of a simple eutectic system. Examination of DTA patterns revealed that this was not the case.

To prove or disprove the existence of a cryolithionite phase field, compositions near the $Na_3AlF_6-Li_3AlF_6$ join were prepared with an emphasis being placed on compositions near $Na_3Li_3Al_2F_{12}$. These samples were heat treated below the liquidus temperature for 1 hour and quenched into ice water. The firing temperature was determined from DTA results of samples close in chemical composition. Examination of the platinum tube after quenching and microscopic viewing of the samples revealed if the composition was in the primary phase field during heat treatment. Those samples that were found to contain no sign of liquid were resealed and fired at a higher temperature until liquid and a single primary phase could be identified. The results of the quench work are shown in Table VI. A phase field for cryolithionite was located near the $Na_3AlF_6-Li_3AlF_6$ side of the diagram. The extent of this phase field was determined by the quench work presented in Table VI.

A sample located in the cryolithionite phase field was easily identified because $Na_3Li_3Al_2F_{12}$ is isotropic (it shows extinction under cross nicols during a 360° rotation of the microscopic stage). Since this is the only cubic phase present in the Li_3AlF_6 - $Na_3AlF_6-Al_2O_3$ diagram, it was not difficult to pick out cryolithionite under the microscope. The $Na_3Li_3Al_2F_{12}$ grains were distinguished by their rounded boundary edges and cubic characteristics. All samples in the cryolithionite phase field were verified by the Becké line technique. Cryolithionite grains were matched with an oil of refractive index 1.340. This agrees well with the value given for cryolithionite in the literature of $1.3395^{(22)}$. A photomicrograph of a sample in the cryolithionite phase field is shown in Figure 13. The primary phase is characterized by its rounded grain appearance. The liquid present is marked by small bubbles and cracks.

The $Na_3Li_3Al_2F_{12}$ grains seen in the quenched samples were compared with $Na_3Li_3Al_2F_{12}$ grains heat treated below the liquidus temperature. A sample of the cryolithionite composition was prepared from Na_3AlF_6 , LiF and AlF_3 and heat treated at $600^{\circ}C$ for 48 hours. Examination under the microscope revealed a single cubic phase with an index of refraction of 1.340. This single phase possessed identical characteristics to the cubic phase seen in quenched liquid and primary

TABLE VI

Samples Examined to Determine Location of Primary Phase Fields

Compos	ition (Mole	%)	Primary Phase as Seen Using
Li3 ^{AlF} 6	^{Na} 3 ^{A1F} 6	A12 ⁰ 3	an Optical Microscope
50	45	5	^{Na} 3 ^{AlF} 6(ss)
50	40	10	A1203
48	50	2	^{Na} 3 ^{A1F} 6(ss)
63	36	1	$^{Na}3^{A1F}_{6}(ss)$
72	27	1	Li ₃ A1F ₆
60	37	3	Na ₃ Li ₃ A1 ₂ F ₁₂
56	41	3	Na ₃ Li ₃ Al ₂ F ₁₂
64	33	3	Na ₃ A1F ₆ (ss)
65	28	7	A1203
66	32	2	Li ₃ AlF ₆
67	30	3	Li ₃ A1F ₆
60	34	6	Na ₃ Li ₃ Al ₂ F ₁₂
62	28	10	Al ₂ 0 ₃
70	24	6	A1203
62	31	7	A1203
64	30	6	Undistinguishable
56	39	5	Na ₃ Li ₃ Al ₂ F ₁₂
58	37	5	Na ₃ Li ₃ Al ₂ F ₁₂
53	39	8	Na ₃ Li ₃ Al ₂ F ₁₂
56	35	9	Al ₂ 0 ₃
59	31	10	A1203



Figure 13. Photomicrograph of a sample quenched from the cryolithionite primary phase field (composition 56 mole % Li_3AlF_6 , 39% Na_3AlF_6 and 5% $\text{Al}_2^{\circ}_3$) (160X).

phase samples. Cryolithionite appeared as a rounded, sometimes oblong grain with an index of refraction of 1.340. A photomicrograph of cryolithionite prepared by solid state reaction is shown in Figure 14.

The location of the alumina phase field was not difficult. Corundum has an average refractive index of 1.765 which is much higher than any other compound in the system. The crossing of a boundary curve into the corundum field was marked by a drastic change in the index of refraction.

Cryolite is reported in the literature as having indices of refraction $\alpha = 1.338$, $\beta = 1.338$, and $\gamma = 1.339^{(22)}$. However, Stinton⁽⁶⁹⁾ reported an increase in the average index of refraction of cryolite to 1.360 as Li_3AlF_6 went into solid solution with cryolite. This was seen in the present study with indices of refraction between 1.340 and 1.350 being determined for samples in the cryolite phase field. The cryolite grains exhibited sharp, jagged grain edges when viewed under the microscope.

Once the cryolithionite phase field was located, DTA results were reviewed again to locate liquidus isotherms. Those samples high in alumina content were used to determine temperatures on boundary curves. Liquidus temperatures for these samples were too high to be detected on DTA experiments that were conducted to 1100[°]C.

Unlike the Li₃AlF₆-Al₂O₃ binary system, samples in the alumina phase field revealed a very small, flat liquidus peak on heating. Liquidus peaks were seen in corundum phase field samples that were located near the boundary curve. All platinum tubes and their contents



Figure 14. Photomicrograph of cryolithionite grains fired at 600° C for 48 hours (160X).

Yes,

were inspected after DTA experiments. Those samples that had contained an appreciable amount of liquid revealed a small amount of wetting on the interior walls of the capsule. The sample itself appeared as a hard, densely packed material which proved difficult to remove from the tube because of adherence to the walls.

The results of the DTA work are shown in Table VII. Two representative DTA diagrams are shown in Figure 15. The first pattern represents a sample in the $Na_3Li_3Al_2F_{12}-Na_3AlF_6-Al_2O_3$ portion of the diagram. As can be seen, the crystallization path for this sample terminates at the peritectic temperature, $683^{\circ}C$. The second pattern is representative of a sample in the $Li_3AlF_6-Na_3Li_3Al_2F_{12}-Al_2O_3$ portion of the diagram. Samples in this area follow crystallization paths that end at the $670^{\circ}C$ eutectic temperature where corundum, cryolithionite and lithium cryolite are in equilibrium with liquid.

The $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ phase diagram is shown in Figure 16. The diagram contains a large phase field for corundum with comparably smaller fields for cryolite, lithium cryolite and cryolithionite. A ternary peritectic exists at 683°C and 51 mole % Li_3AlF_6 , 42.5% Na_3AlF_6 , and 6.5% Al_20_3 . A ternary eutectic point exists at 670°C and 66 mole % Li_3AlF_6 , 29% Na_3AlF_6 and 5% Al_20_3 where cryolithionite, lithium cryolite and corundum are in equilibrium with liquid. A reaction point exists at 65 mole % Li_3AlF_6 , 33% Na_3AlF_6 and 2% Al_20_3 which signifies the decomposition of cryolithionite at 693°C .

TABLE VII

Invariant Points, Boundary Curve Temperatures and Liquidus Temperatures as Determined by DTA

.

Sample	e Composit: (Molo %)	ion				
Li3 ^{A1F} 6	Na 3 ^{A1F} 6	A12 ⁰ 3	Eutectic	Peritectic	Boundary	Liquidus
5	5	90	-	673	719	-
10	25	65	-	676	800	-
30	15	55	622	678	696	-
15	35	50	-	678	838	-
15	65	20	-	684	847	876
30	50	20	-	678	736	843
50	30	20	669	-	681	-
70	10	20	671	-	718	_
10	85	5	-	683	893	974
50	45	5	667	688	691	703
80	15	5	669	-	717	735
40	50	10	-	681	702	793
35	55	10	· 🕳	668	712	764
50	40	10	663	687	-	698
40	30	30	664	683	695	-
25	25	50	-	679	695	-
10	35	55	-	681	845	-
15	20	65	-	671	723	-
33.3	33.3	33.3	-	687	697	-
30	40	30	-	670	705	-
20	30	50	-	674	710	-
35	45	20	-	680	707	830
18.5	36.5	45	-	683	876	-
8.5	16.5	75	-	683	859	-
30	60	10	-	690	731	815
63	36	1	669	-	693	709
72	27	1	669	_	694	726
48	50	2	-	681	693	731



Figure 15. Representative DTA patterns in the $\text{Li}_3^{\text{A1F}}6^{-\text{Na}}3^{\text{A1F}}6^{-\text{A1}}2^03$ system.



MOLE %

Figure 16. System Li₃AlF₆-Na₃AlF₆-Al₂O₃

C. The LiF-AlF₃-Na₃AlF₆-Al₂0₃ System

The seven compatibility tetrahedra seen in Figure 17 were established for the LiF-AlF₃-Na₃AlF₆-Al₂O₃ system. Fourteen samples were mixed and fired at 500° C for 48 hours. Two samples were prepared in each of the seven tetrahedra. One sample contained a composition located at the center of the tetrahedra (25 mole % of each of the 4 corner members) while the second sample had a composition at the center of the 5 mole % Al₂O₃ plane.

After firing the samples were examined by X-ray diffraction. No new compounds were detected thus verifying the seven compatibility tetrahedra. They are:

1.
$$Al_2 O_3 - LiF - Li_3 AlF_6 - Na_3 Li_3 Al_2 F_{12}$$

2. $Al_2 O_3 - Li_3 AlF_6 - Na_3 Li_3 Al_2 F_{12} - AlF_3$
3. $Al_2 O_3 - Na_3 Li_3 Al_2 F_{12} - AlF_3 - Na_5 Al_3 F_{14}$
4. $Al_2 O_3 - LiF - Na_3 Li_3 Al_2 F_{12} - Na_2 LiAlF_6$
5. $Al_2 O_3 - Na_3 Li_3 Al_2 F_{12} - Na_2 LiAlF_6 - Na_5 Al_3 F_{14}$
6. $Al_2 O_3 - LiF - Na_2 LiAlF_6 - Na_3 AlF_6$
7. $Al_2 O_3 - Na_3 AlF_6 - Na_5 Al_3 F_{14} - Na_2 LiAlF_6$

Each of the 14 samples was examined on the DTA. Samples were heated and cooled at 3° C/minute. The DTA results were insufficient to draw any positive conclusions about quaternary invariant points. Examination of DTA patterns for the 5 mole % Al₂0₃ samples revealed a small change (<5°C) in eutectic temperatures from those reported by Stinton⁽⁶⁷⁾ in the LiF-AlF₃-Na₃AlF₆ system. These findings are preliminary because of the minimal amount of data drawn from the 14 samples prepared in the quaternary.



Figure 17. Compatibility relations in the LiF-AlF₃- $Na_3AlF_6-Al_2O_3$ system.

V. SUMMARY

The phase equilibria relations in the systems $\text{Li}_3\text{AlF}_6-\text{Al}_2^0{}_3$, $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{Al}_2^0{}_3$ and $\text{LiF}-\text{AlF}_3-\text{Na}_3\text{AlF}_6-\text{Al}_2^0{}_3$ have been examined at 500°C and on the liquidus surface. The major points of special interest include:

- 1. In the binary system, a eutectic was located at 1 mole $\% \frac{A1}{20_3}$ and 754°C.
- In the ternary system a phase field was located for the incongruently melting compound, Na₃Li₃Al₂F₁₂.
- 3. A ternary eutectic was located at 66 mole % Li_3AlF_6 , 29% Na_3AlF_6 and 5% Al_20_3 .
- Seven compatibility tetrahedra were located in the quaternary system at 500°C.

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APPENDIX

Suggestions for Future Research

Because of the scope of the research undertaken in this study, the extent of the work in the LiF-AlF₃-Na₃AlF₆-Al₂O₃ system was basically exploratory in nature. The foundation has been laid with the completion of the LiF-AlF₃-Na₃AlF₆ and the Li₃AlF₆-Na₃AlF₆-Al₂O₃ ternary systems at Virginia Polytechnic Institute and State University. The seven subsolidus compatibility tetrahedra could give rise to seven invariant points involving liquid. The location of these points could be very beneficial to the aluminum industry and should therefore be determined. Several suggestions for future work in the system are: A. Phase Equilibria

- Determination of boundary ternary phase diagrams using a sealed tube experimental procedure. In particular, diagrams involving alumina should be explored since these are not found in the literature. From the results of this study, it would be suggested to emphasize the low-alumina portion of the diagrams.
- 2. Location of quaternary invariant points.
- 3. Incorporation of other Hall electrolyte components such as MgF_2 and CaF_2 into the present system and the determination of the resulting phase diagrams.

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B. Electrical Conductivity

Since LiF is added to the Hall electrolyte to raise the electrical conductivity, electrical measurements should be carried out on molten samples in the system. The determination of an optimun composition from an electrical conductivity point of view would be beneficial.

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PHASE EQUILIBRIA IN THE LIF-Alf3-Na3Alf6-Al203 SYSTEM

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Roger T. Cassidy

(ABSTRACT)

The phase equilibria relationships in the $\text{Li}_3\text{AlF}_6-\text{Al}_20_3$ binary system, the $\text{Li}_3\text{AlF}_6-\text{Na}_3\text{AlF}_6-\text{Al}_20_3$ ternary system and the $\text{LiF}-\text{AlF}_3 \text{Na}_3\text{AlF}_6-\text{Al}_20_3$ quaternary system have been investigated using a combination of X-ray powder diffraction, DTA, quenching and optical microscopy techniques. The compatibility relations at 500°C for the ternary and quaternary systems, the $\text{Li}_3\text{AlF}_6-\text{Al}_20_3$ binary system and the ternary liquidus surface were determined. The binary system was found to have a eutectic at 754°C and 1 mole % Al_20_3 . The liquidus surface was found to contain the following three invariant points:

- 1. eutectic 66 mole % Li₃AlF₆, 29% Na₃AlF₆, 5% Al₂O₃ and 670^oC
- 2. peritectic 51 mole % Li_3AlF_6 , 42.5% Na_3AlF_6 , 65% Al_2O_3 and 683°C
- 3. reaction point 65 mole % Li_3AlF_6 , 33% Na_3AlF_6 , 2% Al_2^0 and 693°C.

The 500° C isothermal section contains three 3-phase regions and one 2-phase region. The quaternary system contains 7 compatibility tetrahedra at 500° C.