



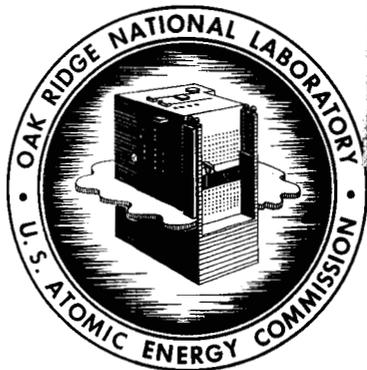
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ORNL-2896
UC-4 - Chemistry-General

PHASE EQUILIBRIA IN MOLTEN SALT
BREEDER REACTOR FUELS.

I. THE SYSTEM $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$

C. F. Weaver
R. E. Thoma
H. Insley
H. A. Friedman



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REACTOR CHEMISTRY DIVISION

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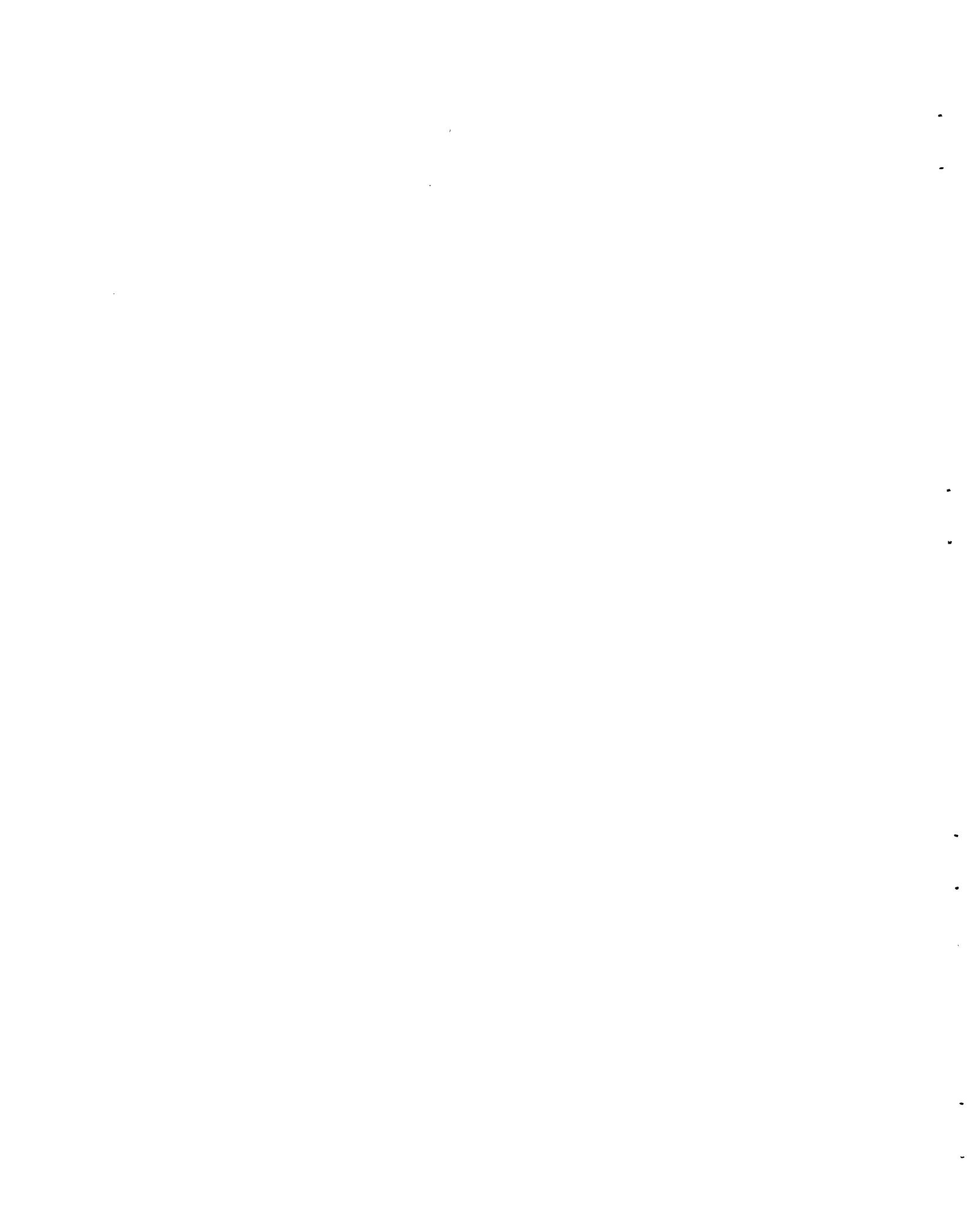


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I. THE SYSTEM LiF-BeF₂-UF₄-ThF₄

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ABSTRACT

The phase equilibrium relationships for the systems limiting the quaternary system LiF-BeF₂-UF₄-ThF₄ are described in detail along with available information on the quaternary system itself. The implications of the extensive solid solutions in the limiting systems are discussed and experimental information supporting the conclusions is presented. The optical properties, crystallographic properties, and x-ray diffraction patterns for the phases occurring in these systems are tabulated. Specific compositions of project interest to which references have been made in the ORNL literature are given special attention. Reference is made to literature reporting properties of these materials other than those discussed in this report.

1. INTRODUCTION

Fluoride fused salts have attracted general interest for use in high-temperature reactors because: (1) fluorine has a very low thermal neutron absorption cross section,¹ (2) fluorides have low vapor pressures at temperatures and compositions of interest,² (3) molten fluorides are very resistant to damage by nuclear emissions,² and (4) there are no serious corrosion problems between many fluorides and nickel-based structural material.² Specifically, uranium tetrafluoride, a fissile material, is of interest because it is the only nongaseous fluoride of uranium which does not incur serious metal container corrosion and/or fuel inhomogeneity as an effect of high-temperature disproportionation.³ Thorium tetrafluoride,

¹S. Glasstone, Principles of Nuclear Reactor Engineering, p 841, Van Nostrand, Princeton, N.J., 1955.

²H. G. MacPherson, p 567 in Fluid Fuel Reactors, ed. by J. A. Lane, H. G. MacPherson, and F. Maslan, Addison-Wesley, Reading, Mass., 1958.

³W. R. Grimes et al., p 577 in Fluid Fuel Reactors, ed. by J. A. Lane, H. G. MacPherson, and F. Maslan, Addison-Wesley, Reading, Mass., 1958.

a fertile material, is the only fluoride of thorium.⁴ The fluorides PbF_2 , BiF_3 , Li^7F , NaF , ZrF_4 , and BeF_2 have sufficiently low thermal neutron absorption cross sections, vapor pressures, and melting points to allow their use as diluents for the UF_4 and ThF_4 . However, PbF_2 and BiF_3 are unsuitable because the cations are readily reduced to the metallic state by structural metals such as iron and chromium.⁵ The lower thermal neutron absorption cross section of Li^7 as compared with that of sodium allows the design of reactors which have a smaller holdup of fissile material and superior breeding performance.⁶

Fluid salt mixtures containing high concentrations of ZrF_4 are not regarded as attractive reactor fluids because of significant vapor pressure of ZrF_4 above 500°C . In a reactor system sublimation of ZrF_4 followed by deposition as a solid limits the temperatures at which long operating times are permissible. Comparable limitations do not occur in mixtures containing BeF_2 rather than ZrF_4 .⁷ Molten salt reactor systems which are designed to operate at sufficiently high temperatures that alkali fluoride- ZrF_4 solvents containing 30-40 mole % ZrF_4 can be employed may offer advantages in the future, but present preference must be given to BeF_2 on the basis of sublimation.⁸ Consequently, mixtures containing Li^7F , BeF_2 , UF_4 , and ThF_4 which have liquidus values several hundred degrees below the ThF_4 and UF_4 melting points are the most promising core materials for a fused salt thermal breeder/converter reactor. A knowledge of the liquidus values of such mixtures is necessary since as reactor fluids they must remain wholly in the liquid state during reactor operation. Liquidus data alone are insufficient because mixtures of solids and liquids will be formed during some fuel handling operations. A knowledge of the nature of the melting-freezing process, of the uranium-thorium partition or phase separation during this process, and of the identity of

⁴Ibid., p 588.

⁵Ibid., p 570.

⁶MSR Quar. Prog. Rep. Jan. 31, 1958, ORNL-2474, p 1.

⁷H. G. MacPherson, ORNL, personal communication.

⁸W. R. Grimes et al., p 582-84 in Fluid Fuel Reactors, ed. by J. A. Lane, H. G. MacPherson, and F. Maslan, Addison-Wesley, Reading, Mass., 1958.

solids formed on cooling of molten mixtures is also necessary. Thus, the phase equilibrium relationships for the quaternary system must be understood, especially near liquidus temperatures and at compositions which may afford attractive core or blanket materials. Before the determinations of the phase relationships can be made in a quaternary system, the 14 limiting unary, binary, and ternary systems must be understood. All these limiting systems for the quaternary system $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$ have been reported and are described in detail in the body of this report along with the available data on the quaternary system itself. It is remarkable that these studies have not disclosed the existence of ternary or of quaternary compounds.

The majority of the information included in this report was derived in the High Temperature Phase Equilibrium Group of the Reactor Chemistry Division at the Oak Ridge National Laboratory. Some of the preliminary studies of the phase equilibria in the limiting binary and ternary systems were begun as early as 1951.

2. EXPERIMENTAL METHODS

2.1 Techniques and Apparatus

The experimental techniques and apparatus used in the studies of $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$ phase equilibria have been described in detail elsewhere.⁹⁻¹³ In general, the data were obtained by thermal analysis of slowly cooled melts and by quenching mixtures which had been equilibrated at known temperatures. Commonly, fused-salt diagrams are based entirely on information from cooling curves (temperature of the sample plotted as a function of time). Changes in the slope of the cooling curve reflect phase changes which occur on cooling, but are prone to give misleading or irrelevant indications because of the impossibility of maintaining equilibrium during the cooling process. Consequently, predominant use

⁹C. J. Barton *et al.*, J. Am. Ceram. Soc. 41, 63-69 (1958).

¹⁰C. J. Barton *et al.*, J. Phys. Chem. 62, 665 (1958).

¹¹H. A. Friedman, J. Am. Ceram. Soc. 42, 284-85 (1959).

¹²P. A. Tucker and E. F. Joy, Am. Ceram. Soc. Bull. 36, 52-54 (1957).

¹³L. J. Wittenberg, J. Am. Ceram. Soc. 42, 209-11 (1959).

has been made of the much more effective method of quenching equilibrium samples and identifying the phases by examination with a polarizing light microscope and by x-ray diffraction techniques.

A thermal gradient furnace with a single moving thermocouple¹¹ is used for equilibration in the temperature range 650–1200°C. Five other thermal gradient furnaces, operating at a maximum temperature of 900°C, incorporate 18 thermocouples each. The independent readings from these are used to determine a temperature calibration curve of the thermal gradient within the annealing area of the furnace. Malfunction of a single thermocouple becomes readily apparent. In quenching studies made at temperatures below 900°C, sample tubes are distributed among the five furnaces randomly, to achieve maximum reproducibility among independent temperature readings. The region of temperature overlap, 650–900°C, is used to monitor the single high-temperature furnace. In the absence of supercooling effects, the completely separate measurements in the thermal analysis furnaces agree within 5°C with those from the thermal gradient furnaces. This interlocking system, by which multiple thermocouples within five of the furnaces and three types of furnaces are used, provides a continuous check on the proper function of the equipment.

The accuracy of the temperature measurements is limited by the characteristics of the Chromel-Alumel thermocouples used.¹⁴ The invariant point temperature data are so precise that a standard deviation of 1 or 2° is obtained.

2.2 Materials

The LiF used for this work was reagent grade obtained from Foote Mineral Company and from Maywood Chemical Works. The UF₄ was a product of Mallinckrodt Chemical Works. The ThF₄ was obtained from Iowa State College and from National Lead Company. The BeF₂ was a product of Brush Beryllium Company. No impurities were found in any of these materials by x-ray diffraction or microscopic analysis. Spectroscopic analysis indicates less than 0.25 wt % impurities.

¹⁴J. F. Potts, Thermocouple Research - Cold Work, ORNL CF-59-6-61 (June 15, 1959).

Because thorium¹⁵ and uranium fluorides are easily converted to oxides or oxyfluorides at elevated temperatures it was necessary to remove small amounts of water and oxygen as completely as possible from the starting materials. In a few cases the molten mixtures were treated with anhydrous HF. For the vast majority of preparations, however, $\text{NH}_4\text{F}\cdot\text{HF}$ was added to the mixture before melting. As such mixtures are heated the water evaporates from the system. Trace quantities of oxide impurities are converted to products which have not yet been identified but which are likely to be ammonium "fluometallates."^{16,17} Upon further heating the ammonium "fluometallates" and the excess $\text{NH}_4\text{F}\cdot\text{HF}$ decompose. The products are metal fluorides and the gases NH_3 and HF. These gases are quantitatively swept from the system by dry helium. The samples were melted and cooled to obtain thermal analysis data. The purified solids were transferred to an argon-filled dry box which contained BaO as a desiccant. They were ground to pass a 100-mesh screen and used in the quenching experiments. The heating cycles were conducted in closed capsules or under an atmosphere of dry helium or argon.

3. PHASE EQUILIBRIA AND RELATED PHENOMENA

3.1 The Components LiF, BeF_2 , ThF_4 , and UF_4

A special character can be assigned to the behavior of combinations of the four compounds LiF, BeF_2 , ThF_4 , and UF_4 , for in this grouping are to be found a pair of metal cations in the lowest and a pair in the highest atomic number range. It might, therefore, be expected that the diverse physical and chemical properties of these four components would contribute to the occurrence of phase behavior in which a wide variety of phenomena would appear. The melting points of the components are shown in Table 1.

Of the four components, only BeF_2 exhibits polymorphic transitions. The equilibrium melting temperature and the nature of these solid-state

¹⁵R. W. M. D'Eye, J. Chem. Soc. 1958, 196.

¹⁶MSR Quar. Prog. Rep. Apr. 30, 1959, ORNL-2723, p 93.

¹⁷B. J. Sturm, ORNL, personal communication (May 1960).

Table 1. The Melting Points of the Components

Component	Melting Point (°C)
LiF	845 ^a
BeF ₂	548 ^{b-d}
ThF ₄	1111 ^{e-g}
UF ₄	1035 ^h

^aT. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4824 (1954).

^bR. E. Thoma et al., "Phase Equilibria in the Systems BeF₂-ThF₄ and LiF-BeF₂-ThF₄," J. Phys. Chem., in press.

^cD. M. Roy, R. Roy, and E. F. Osborn, J. Am. Ceram. Soc. 36, 185 (1953).

^dM. P. Boryenkova et al., Zhur. Neorg. Khim. 1, 2071 (1956).

^eR. E. Thoma et al., J. Phys. Chem. 63, 1266 (1959).

^fJ. Asker, E. R. Segnit, and A. W. Wylie, J. Chem. Soc. 1952, 4470.

^gA. J. Darnell and F. J. Keneshea, Jr., J. Phys. Chem. 62, 1143 (1958).

^hH. R. Hoekstra and J. J. Katz, p 177 in The Actinide Elements, ed. by G. T. Seaborg and J. J. Katz, McGraw-Hill, New York, 1954.

transitions have been the subject of controversy for several years.¹⁸ The structure of BeF₂ is analogous to that of SiO₂, as was predicted by Goldschmidt;¹⁹ all known modifications crystallize as SiO₂-type structures. Being similar to SiO₂, BeF₂ readily forms a glass upon cooling from the liquid state. For this reason, establishing solid-state equilibria with BeF₂, in which devitrification of this glass must be accomplished, is often a very slow process.

Optical and crystallographic properties for the compounds LiF, BeF₂, ThF₄, and UF₄ may be found in Appendix A. Their x-ray diffraction data are listed in Appendix B.

¹⁸A. V. Novoselova, Uspekhi Khim. 27, 33 (1959).

¹⁹V. M. Goldschmidt, Skrifter Norske Videnskaps-Akad. Oslo. I. Mat.-Naturv. Kl. 1926, No. 8, p 7-156 (1927).

3.2 The Systems $\text{BeF}_2\text{-ThF}_4$ and $\text{BeF}_2\text{-UF}_4$

The systems $\text{BeF}_2\text{-ThF}_4$ ²⁰ (Fig. 1) and $\text{BeF}_2\text{-UF}_4$ ²¹ (Fig. 2) are similar

in that both possess no intermediate equilibrium compounds, have lowest liquidus values between 97 and 100 mole % BeF_2 , have a single eutectic invariant point, and have an abrupt change in the

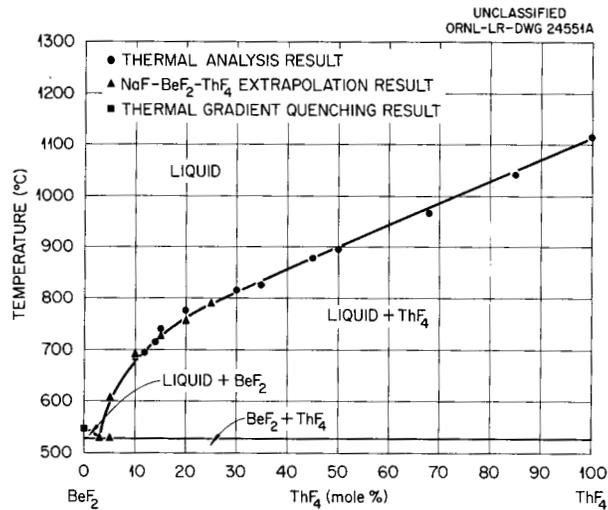


Fig. 1. The System $\text{BeF}_2\text{-ThF}_4$.

²⁰R. E. Thoma et al., "Phase Equilibria in the Systems $\text{BeF}_2\text{-ThF}_4$ and $\text{LiF-BeF}_2\text{-ThF}_4$," J. Phys. Chem., in press.

²¹T. B. Rhinehammer, P. A. Tucker, and E. F. Joy, Phase Equilibria in the System $\text{BeF}_2\text{-UF}_4$, MLM-1082 (to be published).

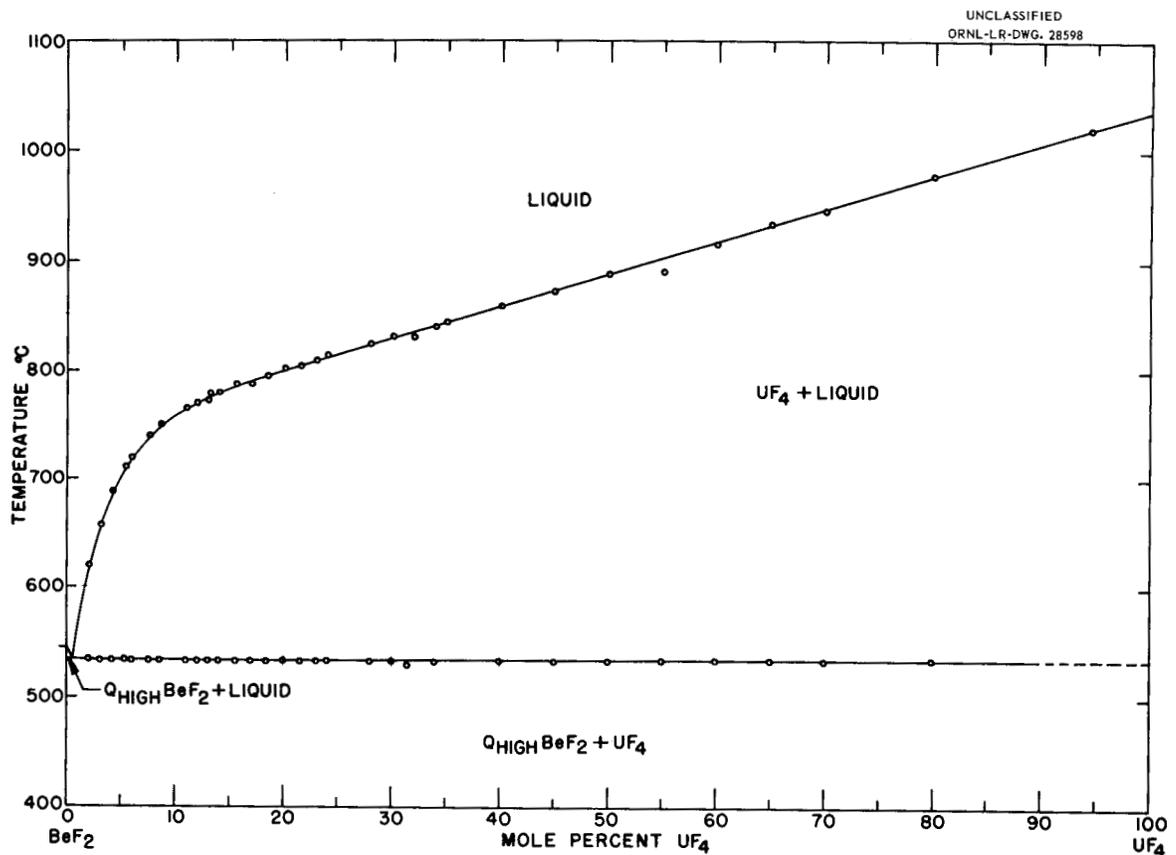


Fig. 2. The System $\text{BeF}_2\text{-UF}_4$.

liquidus slope in the quadrivalent fluoride primary phase region. The eutectic invariant points are at 2 mole % ThF_4 , 527° , and at 0.5 mole % UF_4 , 535° , while the change in slope occurs near 12 mole % ThF_4 and 7 mole % UF_4 in the corresponding systems.

3.3 The System $\text{LiF}-\text{BeF}_2$

A phase diagram of the system $\text{LiF}-\text{BeF}_2$ ^{22,23} (Fig. 3) has been derived at ORNL from the results of thermal gradient experiments. A phase diagram nearly identical with that shown has been derived independently at the

²²R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 33 (Nov. 2, 1959).

²³R. E. Moore, C. J. Barton, R. E. Thoma, and T. N. McVay, ORNL, unpublished data.

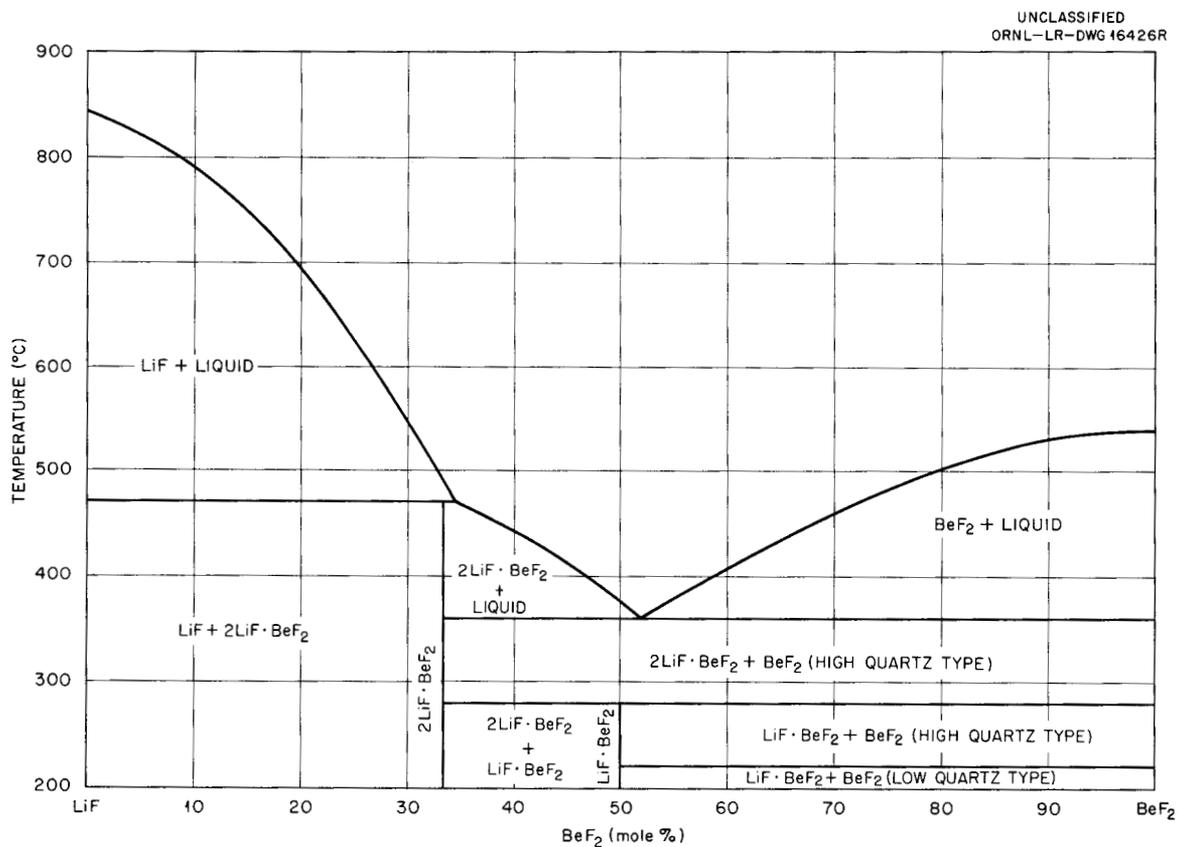


Fig. 3. The System $\text{LiF}-\text{BeF}_2$.

Mound Laboratory.²⁴ These diagrams are revisions of those published by earlier investigators.²⁵⁻²⁷ Two equilibrium compounds occur in the system LiF-BeF₂, the incongruently melting compound 2LiF·BeF₂ and the subsolidus compound LiF·BeF₂. Unsuccessful attempts have been made by the authors to produce the reported compounds 3LiF·2BeF₂²⁸ and LiF·2BeF₂²⁵ by devitrification of LiF-BeF₂ glass and by solid-state equilibration of mixtures of BeF₂ and 2LiF·BeF₂. Because the special purification techniques described earlier in this report were not used by other investigators^{25,28} reports of the existence of 3LiF·2BeF₂ and LiF·2BeF₂ should be considered tentative.

The optical properties, crystallographic properties, and x-ray diffraction data for the compounds 2LiF·BeF₂ and LiF·BeF₂ are listed in Appendixes A and B. The compositions and temperatures of the two invariant points and one upper limit of stability may be found in Table 2.

Table 2. Invariant Equilibria in the System LiF-BeF₂*

Mole % BeF ₂ in Liquid	Invariant Temperature (°C)	Type of Equilibrium	Phase Reaction at Invariant Temperature
33.5	454	Peritectic	$L + \text{LiF} \rightleftharpoons 2\text{LiF} \cdot \text{BeF}_2$
52	355	Eutectic	$L \rightleftharpoons 2\text{LiF} \cdot \text{BeF}_2 + \text{BeF}_2$
-	280	Upper temperature of stability for LiF·BeF ₂	$2\text{LiF} \cdot \text{BeF}_2 + \text{BeF}_2 \rightleftharpoons \text{LiF} \cdot \text{BeF}_2$

*R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 33 (Nov. 6, 1959).

Cooling mixtures of LiF and BeF₂ slowly from the liquid to the solid state rarely produces equilibrium solids, for the subsolidus reaction

²⁴J. F. Eichelberger, C. R. Hudgens, L. V. Jones, and T. B. Rhinehammer, Mound Laboratory, unpublished data.

²⁵D. M. Roy et al., J. Am. Ceram. Soc. 37, 300 (1954).

²⁶A. V. Novoselova et al., J. Phys. Chem. (USSR) 26, 1244 (1952).

²⁷J. L. Speirs, Ph.D. thesis, University of Michigan, May 29, 1952.

²⁸E. Thilo and H. A. Lehmann, Z. anorg. Chem. 258, 332-55 (1949); Ceram. Abstr. 1950, 82f.

$\text{Li}_2\text{BeF}_4 + \text{BeF}_2 \rightarrow 2\text{LiBeF}_3$ proceeds very slowly. The compound $\text{LiF}\cdot\text{BeF}_2$ may be observed to grow slowly into solid mixtures of LiF and BeF_2 which are held for several days at temperatures just below 280°C . The formation of $\text{LiF}\text{-BeF}_2$ glass which devitrifies slowly also prevents compositions rich in BeF_2 from reaching equilibrium rapidly. Mixtures of LiF and BeF_2 containing more than 33.3 mole % BeF_2 regularly contain only $2\text{LiF}\cdot\text{BeF}_2$ and the low-quartz form of BeF_2 if they are cooled under nonequilibrium conditions.^{29,30}

The compositions, liquidus temperatures, and primary phases for mixtures of LiF and BeF_2 which have been referred to in the ORNL literature as C-74, C-112, and C-132 may be found in Appendix C.

Solubilities of NaF ,³¹ RbF ,³² ZrF_4 ,³³ PuF_3 ,³⁴ CeF_3 ,³⁵ HF ,³⁶ and the noble gases³⁷ in $\text{LiF}\text{-BeF}_2$ solvents have been reported. The reactions $\text{M} + \text{HF}$ ($\text{M} = \text{Fe}, \text{Cr}, \text{or Ni}$),³⁸ $\text{CeF}_3 + \text{BeO}$,³⁹ and $\text{CeF}_3 + \text{H}_2\text{O}$ ⁴⁰ in $\text{LiF}\text{-BeF}_2$ solvents have been investigated, as have the exchange reactions between CeF_3 and CeO_2 and between HfC and HfF_4 .⁴¹

²⁹R. E. Thoma, X-Ray Diffraction Results, ORNL CF-56-6-25, item T-1437 (June 4, 1956).

³⁰R. E. Thoma, Results of X-Ray Diffraction Phase Analyses of Fused Salt Mixtures, ORNL CF-58-2-59, item 1894 (Feb. 18, 1958).

³¹R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 42 (Nov. 2, 1959).

³²Ibid., p 44.

³³MSR Quar. Prog. Rep. Jan. 31 and Apr. 30, 1960, ORNL-2973, p 65.

³⁴C. J. Barton et al., Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 12.

³⁵W. T. Ward, R. A. Strehlow, and G. M. Watson, Chem. Ann. Prog. Rep. June 20, 1958, ORNL-2584, p 82.

³⁶J. H. Shaffer and G. M. Watson, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 31.

³⁷N. V. Smith et al., Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 28.

³⁸C. M. Blood et al., Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 39.

³⁹J. H. Shaffer, G. M. Watson, and W. R. Grimes, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 86.

⁴⁰Ibid., p 88.

⁴¹J. H. Shaffer and G. M. Watson, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 82-84.

3.4 The System LiF-ThF₄

One congruently melting compound (3LiF·ThF₄) and three incongruently melting compounds (7LiF·6ThF₄, LiF·2ThF₄, and LiF·4ThF₄) are formed in the system LiF-ThF₄⁴² (Fig. 4). Optical properties, crystallographic

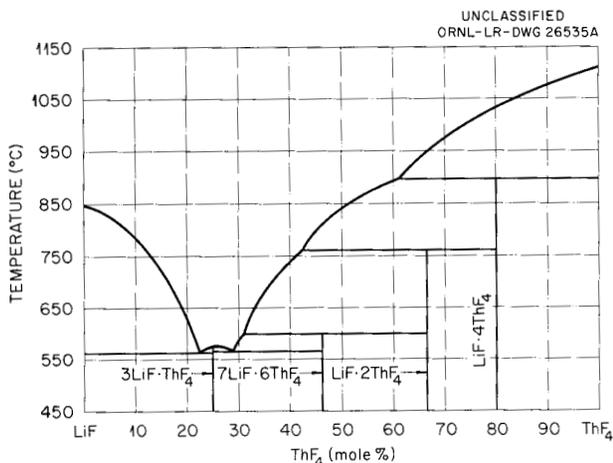


Fig. 4. The System LiF-ThF₄.

properties, and x-ray diffraction data for these compounds are listed in Appendixes A and B. The compositions and temperatures of the five invariant points and one congruent melting point may be found in Table 3.

Binary LiF-ThF₄ mixtures containing more than 25 and less than 66.7 mole % ThF₄ regularly contain 3LiF·ThF₄ and LiF·2ThF₄ if cooled from the liquid state under non-

equilibrium conditions.⁴³ The solidification temperature is not significantly changed by the failure of 7LiF·6ThF₄ to form.⁴² The equilibrium

⁴²R. E. Thoma *et al.*, J. Phys. Chem. 63, 1266 (1959).

⁴³R. E. Thoma, *Results of X-Ray Diffraction Phase Analyses of Fused Salt Mixtures*, ORNL CF-58-2-59, items 1854, 1873, and 1894 (Feb. 18, 1958).

Table 3. Invariant Equilibria in the System LiF-ThF₄*

Mole % ThF ₄ in Liquid	Invariant Temperature (°C)	Type of Equilibrium	Phase Reaction at Invariant Temperature
23	565	Eutectic	$L \rightleftharpoons \text{LiF} + 3\text{LiF} \cdot \text{ThF}_4$
25	573	Congruent mp	$L \rightleftharpoons 3\text{LiF} \cdot \text{ThF}_4$
29	568	Eutectic	$L \rightleftharpoons 3\text{LiF} \cdot \text{ThF}_4 + 7\text{LiF} \cdot 6\text{ThF}_4$
30.5	597	Peritectic	$\text{LiF} \cdot 2\text{ThF}_4 + L \rightleftharpoons 7\text{LiF} \cdot 6\text{ThF}_4$
42	762	Peritectic	$\text{LiF} \cdot 4\text{ThF}_4 + L \rightleftharpoons \text{LiF} \cdot 2\text{ThF}_4$
58	897	Peritectic	$\text{ThF}_4 + L \rightleftharpoons \text{LiF} \cdot 4\text{ThF}_4$

*R. E. Thoma *et al.*, J. Phys. Chem. 63, 1267 (1959).

condition will be readily established if the LiF-ThF_4 mixtures are held for a short time at temperatures just below the solidus.

The composition, liquidus temperature, and primary phases for the mixture of LiF and ThF_4 referred to in the ORNL literature as C-128 may be found in Appendix C.

3.5 The System LiF-UF_4

Three incongruently melting compounds ($4\text{LiF}\cdot\text{UF}_4$, $7\text{LiF}\cdot 6\text{UF}_4$, and $\text{LiF}\cdot 4\text{UF}_4$) are formed in the system LiF-UF_4 ⁹ (Fig. 5). The metastable

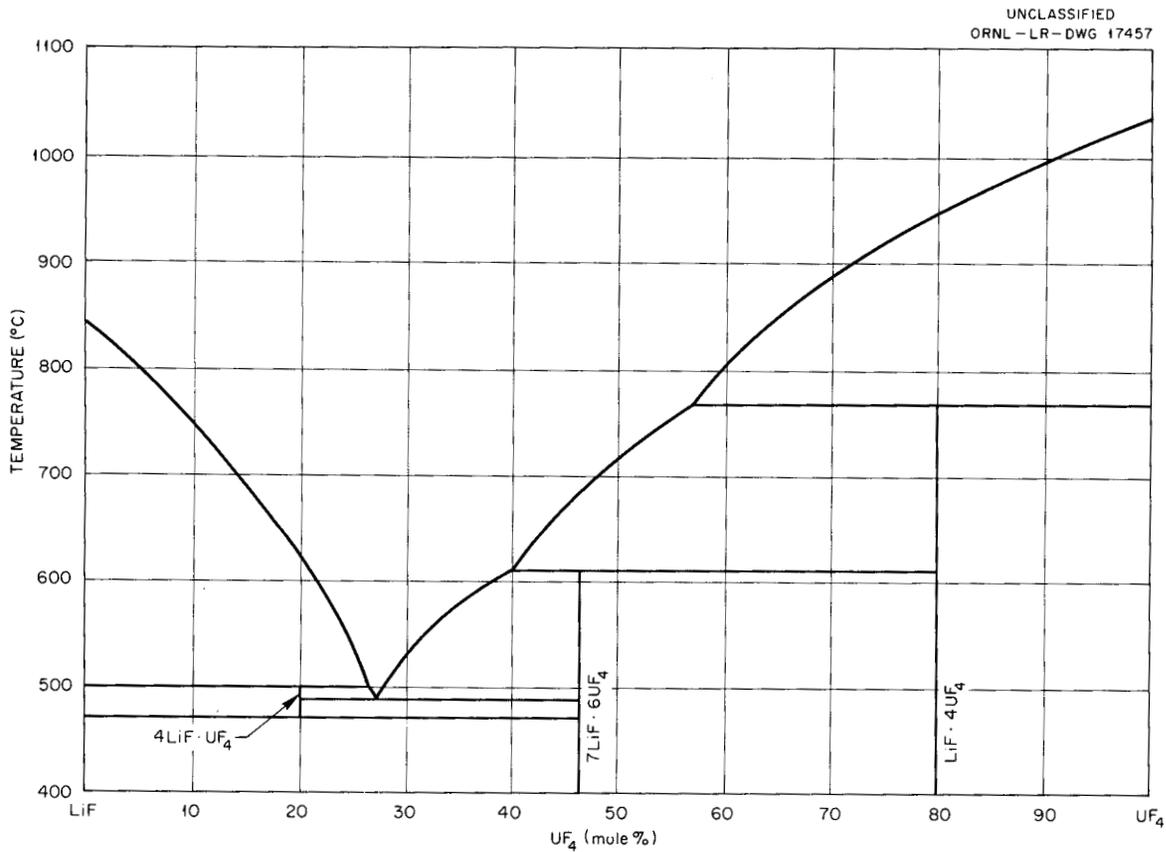


Fig. 5. The System LiF-UF_4 .

compound $3\text{LiF}\cdot\text{UF}_4$ is readily formed from melts containing approximately 25 mole % UF_4 at temperatures above the incongruent melting point of $4\text{LiF}\cdot\text{UF}_4$ when these mixtures are rapidly cooled from the liquid state. The cooling curves of samples in this composition range differ remarkably from one another depending upon the maximum temperature of the mixture just prior to cooling.

The optical properties (except for $3\text{LiF}\cdot\text{UF}_4$), crystallographic properties, and x-ray diffraction data for these compounds may be found in Appendixes A and B. The compositions and temperatures of the four invariant points and the lower temperature limit of stability for $4\text{LiF}\cdot\text{UF}_4$ may be found in Table 4. The systems $\text{LiF}\text{-ThF}_4$ and $\text{LiF}\text{-UF}_4$ are similar

Table 4. Invariant Equilibria in the System $\text{LiF}\text{-UF}_4$ *

Mole % UF_4 in Liquid	Invariant Temperature (°C)	Type of Equilibrium	Phases Present
—	470	Lower stability limit for $4\text{LiF}\cdot\text{UF}_4$	LiF , $4\text{LiF}\cdot\text{UF}_4$, $7\text{LiF}\cdot6\text{UF}_4$
26	500	Peritectic	LiF , $4\text{LiF}\cdot\text{UF}_4$, liquid
27	490	Eutectic	$4\text{LiF}\cdot\text{UF}_4$, $7\text{LiF}\cdot6\text{UF}_4$, liquid
40	610	Peritectic	$7\text{LiF}\cdot6\text{UF}_4$, $\text{LiF}\cdot4\text{UF}_4$, liquid
57	775	Peritectic	$\text{LiF}\cdot4\text{UF}_4$, UF_4 , liquid

*C. J. Barton et al., J. Am. Ceram. Soc. 41, 63-69 (1958).

in that in each the lowest liquidus temperatures are found between 70 and 80 mole % LiF , and in both systems compounds with alkali fluoride ratios of 3:1, 7:6, and 1:4 are formed. The compounds $7\text{LiF}\cdot6\text{ThF}_4$ and $7\text{LiF}\cdot6\text{UF}_4$ form a continuous series of solid solutions as do the compounds $\text{LiF}\cdot4\text{ThF}_4$ and $\text{LiF}\cdot4\text{UF}_4$. These solid solutions are described in Sec 3.10 and Appendix A.

The solubilities of NaF ,⁴⁴ KF ,⁴⁵ RbF ,⁴⁶ and UF_3 ⁴⁷ in $\text{LiF}\text{-UF}_4$ solvents have been investigated. The vapor pressures of $\text{LiF}\text{-UF}_4$ mixtures containing 10 and 20 mole % LiF have been reported.⁴⁸

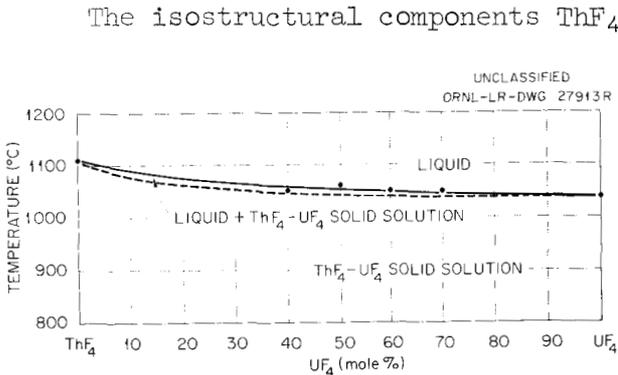
⁴⁴R. E. Thoma et al., J. Am. Ceram. Soc. 42, 21-26 (1959).

⁴⁵R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 98 (Nov. 6, 1959).

⁴⁶Ibid., p 102.

⁴⁷C. J. Barton et al., Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 26.

⁴⁸S. Langer, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 51.

3.6 The System $\text{UF}_4\text{-ThF}_4$ Fig. 6. The System $\text{UF}_4\text{-ThF}_4$.

of solid solutions without maximum or minimum⁴⁹ (Fig. 6). The indices of refraction of the $\text{ThF}_4\text{-UF}_4$ solid solutions change regularly with composition but not linearly. The optical properties for these solid solutions may be found in Appendix A.

3.7 The System $\text{LiF-BeF}_2\text{-UF}_4$

No ternary compounds form within the system $\text{LiF-BeF}_2\text{-UF}_4$ ^{50, 51} (Figs. 7 and 8). Consequently, the solid phases occurring in the system are those of the components or binary compounds described above (Secs 3.1, 3.2, 3.3, and 3.5). The compositions and temperatures of the five invariant points may be found in Table 5. The equilibrium phase behavior of selected compositions of $\text{LiF-BeF}_2\text{-UF}_4$ is given in Table 6 and in Appendix C. When mixtures of LiF , BeF_2 , and UF_4 cool slowly from the liquid state, equilibrium is rarely, if ever, achieved. In the compositions C-75, C-126, C-130, C-131, and C-136 solids have been routinely observed in the cooled melts which are indicative of nonequilibrium cooling.⁵²⁻⁵⁴

⁴⁹C. F. Weaver et al., Phase Equilibria in the Systems $\text{UF}_4\text{-ThF}_4$ and $\text{LiF-UF}_4\text{-ThF}_4$, ORNL-2719 (Aug. 17, 1959); J. Am. Ceram. Soc. **43**, 213 (1960).

⁵⁰L. V. Jones et al., Phase Equilibria in the $\text{LiF-BeF}_2\text{-UF}_4$ Ternary Fused Salt System, MLM-1080 (Aug. 24, 1959).

⁵¹R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 108-9 (Nov. 6, 1959).

⁵²R. E. Thoma, Results of Examinations of Fused Salt Mixtures by Optical and X-Ray Diffraction Methods, ORNL CF-58-11-40, item 1925 (Nov. 14, 1958).

⁵³R. E. Thoma, Results of X-Ray Diffraction Phase Analyses of Fused Salt Mixtures, ORNL CF-58-2-59, items 1873 and 1894 (Feb. 18, 1958).

⁵⁴R. E. Thoma, Results of Examinations of Fused Salt Mixtures by Optical and X-Ray Diffraction Methods, ORNL CF-59-10-18, items 2006, 2019, 2036, 2056, 2061, and 2074 (Oct. 7, 1959).

Solid-state equilibrium is readily established if the solid mixture is annealed for a short time at temperatures near the solidus.

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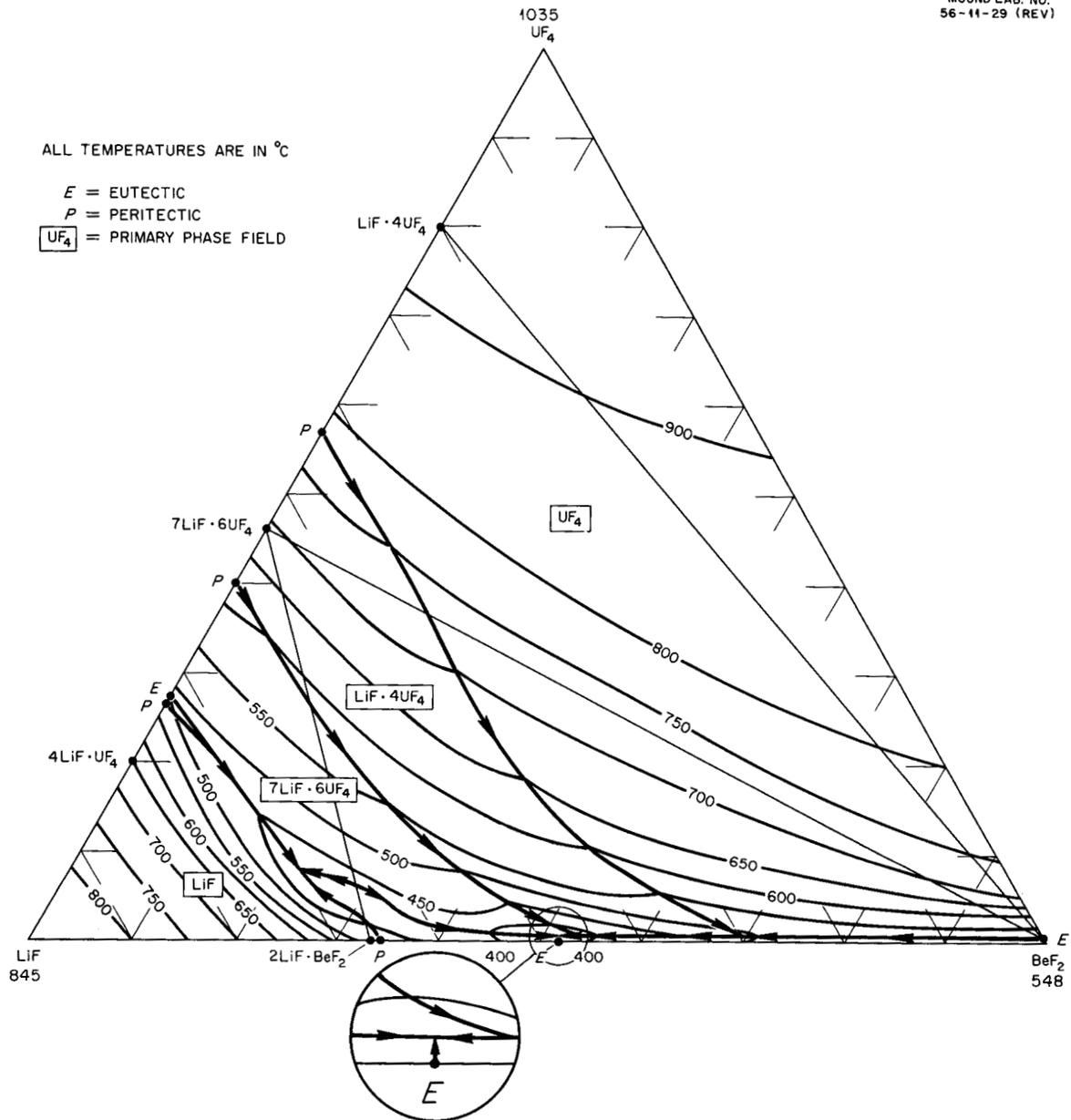
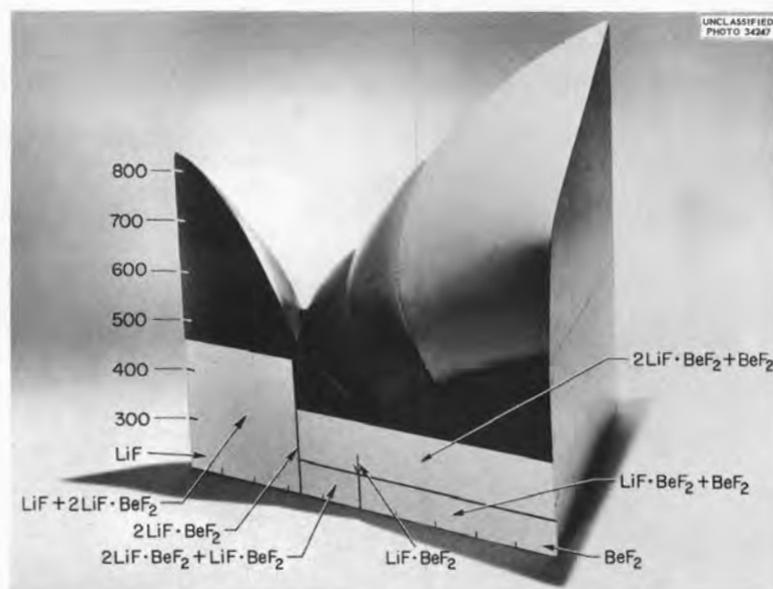


Fig. 7. The System LiF-BeF₂-UF₄.

Numerous investigations of the interactions of molten mixtures of LiF, BeF₂, and UF₄ with other substances have been reported. The solu-

Fig. 8. The System LiF-BeF₂-UF₄.Table 5. Invariant Equilibria in the System LiF-BeF₂-UF₄*

Composition of Liquid (mole %)			Temperature (°C)	Type of Equilibrium	Solid Phases Present at Invariant Temperature
LiF	BeF ₂	UF ₄			
72	6	22	480	Peritectic (decomposition of 4LiF·UF ₄ in the ternary system)	4LiF·UF ₄ , LiF, and 7LiF·6UF ₄
69	23	8	426	Eutectic	LiF, 2LiF·BeF ₂ , and 7LiF·6UF ₄
48	51.5	0.5	350	Eutectic	7LiF·6UF ₄ , 2LiF·BeF ₂ , and BeF ₂
45.5	54	0.5	381	Peritectic	LiF·4UF ₄ , 7LiF·6UF ₄ , and BeF ₂
29.5	70	0.5	483	Peritectic	UF ₄ , LiF·4UF ₄ , and BeF ₂

*R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 109 (Nov. 6, 1959).

Table 6. Phase Behavior of Selected LiF-BeF₂-UF₄ Compositions

Temperature (°C)	Phases Present
C-75: 67 LiF-2.5 UF ₄ -30.5 BeF ₂ (Mole %)	
464-450	LiF and liquid
450-426	LiF, 2LiF·BeF ₂ , and liquid
Below 426	LiF, 2LiF·BeF ₂ , and 7LiF·6UF ₄
C-126: 53 LiF-1 UF ₄ -46 BeF ₂ (Mole %)	
400-350	2LiF·BeF ₂ , 7LiF·6UF ₄ , and liquid
350-280	2LiF·BeF ₂ , 7LiF·6UF ₄ , and BeF ₂
Below 280	2LiF·BeF ₂ , 7LiF·6UF ₄ , and LiF·BeF ₂
C-130: 62 LiF-1 UF ₄ -37 BeF ₂ (Mole %)	
440-414	2LiF·BeF ₂ and liquid
414-381	2LiF·BeF ₂ , 7LiF·6UF ₄ , and liquid
381-280	2LiF·BeF ₂ , 7LiF·6UF ₄ , and BeF ₂
Below 280	2LiF·BeF ₂ , 7LiF·6UF ₄ , and LiF·BeF ₂
C-131: 60 LiF-4 UF ₄ -36 BeF ₂ (Mole %)	
450-415	7LiF·6UF ₄ and liquid
415-381	7LiF·6UF ₄ , 2LiF·BeF ₂ , and liquid
381-280	7LiF·6UF ₄ , 2LiF·BeF ₂ , and BeF ₂
Below 280	7LiF·6UF ₄ , 2LiF·BeF ₂ , and LiF·BeF ₂
C-136: 70 LiF-20 UF ₄ -10 BeF ₂ (Mole %)	
500-465	7LiF·6UF ₄ and liquid
465-426	7LiF·6UF ₄ , LiF, and liquid
Below 426	7LiF·6UF ₄ , LiF, and 2LiF·BeF ₂

bilities of PuF_3 ,¹² CeF_3 ,⁵⁵ LaF_3 ,⁵⁵ and SmF_3 ⁵⁵ in $\text{LiF}-\text{BeF}_2-\text{UF}_4$ solvents and the reactions of BeO ⁵⁶ and steam⁵⁷ on these solvents have been investigated. The exchange of SmF_3 (dissolved) and CeF_3 (solid),⁵⁸ the exchange of Hf in HfF_4 and HfC ,⁵⁹ and the effect of AlF_3 ⁵⁸ on the solubility of the rare-earth trifluorides in $\text{LiF}-\text{UF}_4-\text{BeF}_2$ molten mixtures have been studied. In addition the effect of thermal cycling on segregation,⁶⁰ the effect of radiation on static corrosion of graphite and of INOR-8,⁶¹ graphite permeation,⁶² dehydration,⁶³ and purification⁶⁴ have been reported for $\text{LiF}-\text{UF}_4-\text{BeF}_2$ mixtures.

3.8 The System $\text{LiF}-\text{BeF}_2-\text{ThF}_4$

The phase equilibria in the system $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ (Figs. 9-15) have been described in a recent report.²⁰ One aspect of the phase equilibria in this system which is of significance is the formation of a solid solution in which beryllium replaces both lithium and thorium in the $3\text{LiF}\cdot\text{ThF}_4$ lattice. The single-phase composition area for this solid solution is limited as indicated in Table 7. This results in the formation of phases at the solidus whose compositions are not so diverse as those which would have been formed if the substitutional solid solution

⁵⁵R. A. Strehlow *et al.*, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 77.

⁵⁶J. H. Shaffer, G. M. Watson, and W. R. Grimes, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 84.

⁵⁷Ibid., p 87.

⁵⁸R. A. Strehlow *et al.*, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 77-80.

⁵⁹J. H. Shaffer and G. M. Watson, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 83.

⁶⁰G. J. Nessel and J. Truitt, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 17-19.

⁶¹W. E. Browning and H. L. Hemphill, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 74-75.

⁶²R. J. Sheil *et al.*, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 69.

⁶³C. J. Barton *et al.*, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 20.

⁶⁴J. E. Eorgan *et al.*, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 64.

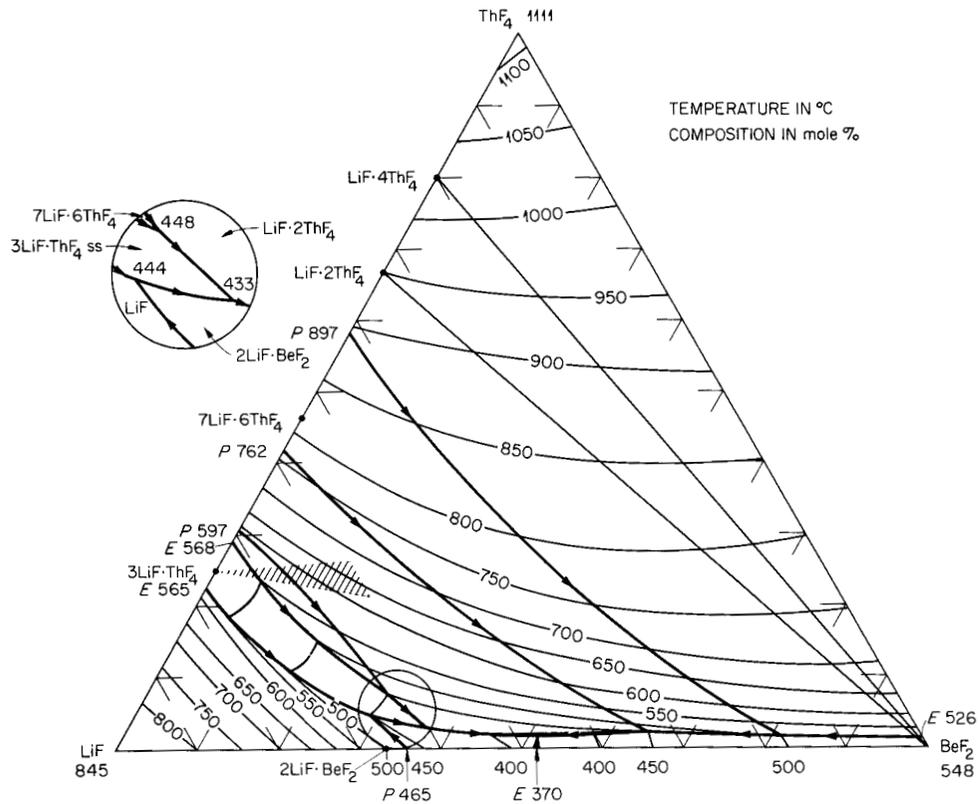


Fig. 9. The System LiF-BeF₂-ThF₄.

Table 7. Limits of Single-Phase 3LiF·ThF₄ Solid Solution*
Composition in mole %

LiF	BeF ₂	ThF ₄
75	0	25
58	16	26
59	20	21

*R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 81 (Nov. 6, 1959).

Consequently, all the solid phases formed in the system, except for members of the 3LiF·ThF₄ solid solution, are the components or binary compounds described above (Secs 3.1, 3.2, 3.3, and 3.4). The compositions and the temperatures of the six invariant points may be found in Table 8.

in 3LiF·ThF₄ were not to occur. This is a way of saying that when such mixtures are used as reactor fuels, the segregation of the thorium-containing phase or phases from the LiF-BeF₂ solvent on cooling will be less than one would expect without a knowledge of the solid solution.

No ternary compounds are formed in the system. Conse-

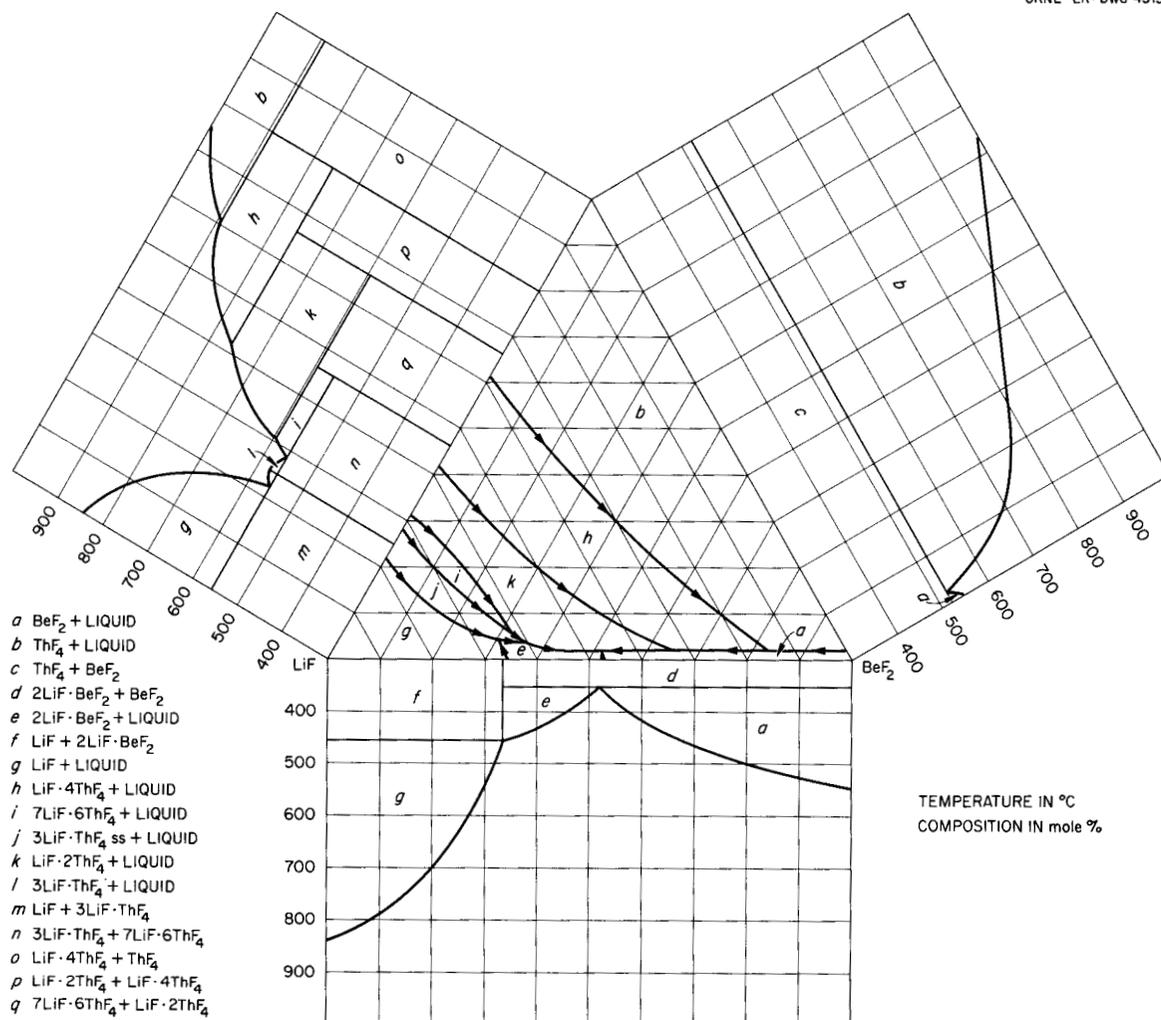


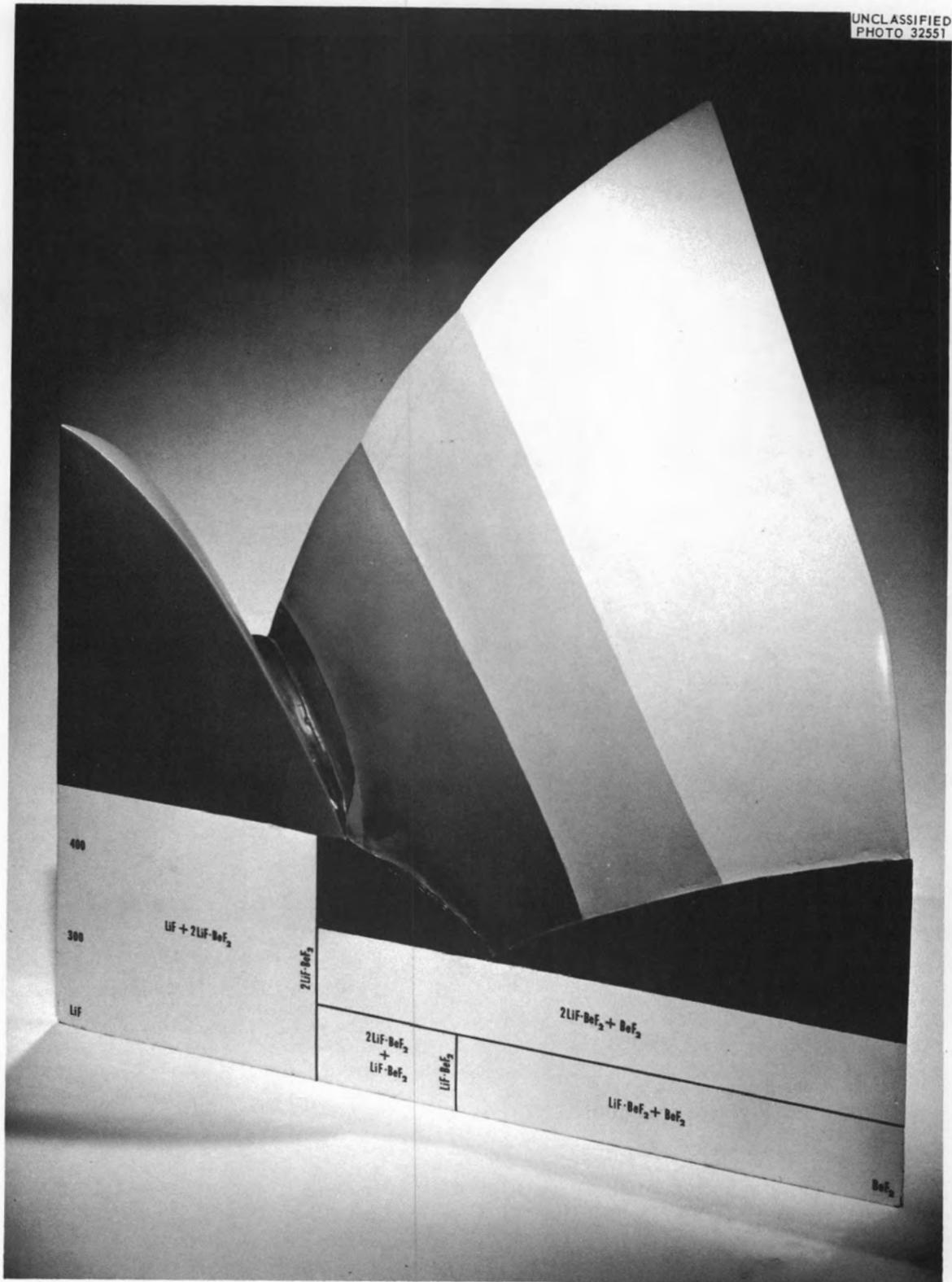
Fig. 10. The System LiF-BeF₂-ThF₄.

The equilibrium phase behavior which will occur in several selected LiF-BeF₂-ThF₄ compositions is described in Table 9.

When mixtures of LiF-BeF₂-ThF₄ are cooled slowly from the liquid state, equilibrium is rarely, if ever, achieved. In compositions C-127, C-133 (or C-111a), and BeLT-15, solids have been routinely observed in the cooled melts which are indicative of nonequilibrium cooling.^{65, 66}

⁶⁵R. E. Thoma, Results of X-Ray Diffraction Phase Analyses of Fused Salt Mixtures, ORNL CF-58-2-59, item 1854 (Feb. 18, 1958).

⁶⁶R. E. Thoma, Results of Examinations of Fused Salt Mixtures by Optical and X-Ray Diffraction Methods, ORNL CF-59-10-18, item 2095 (Oct. 7, 1959).

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PHOTO 32551Fig. 11. The System $\text{LiF}-\text{BeF}_2-\text{ThF}_4$.

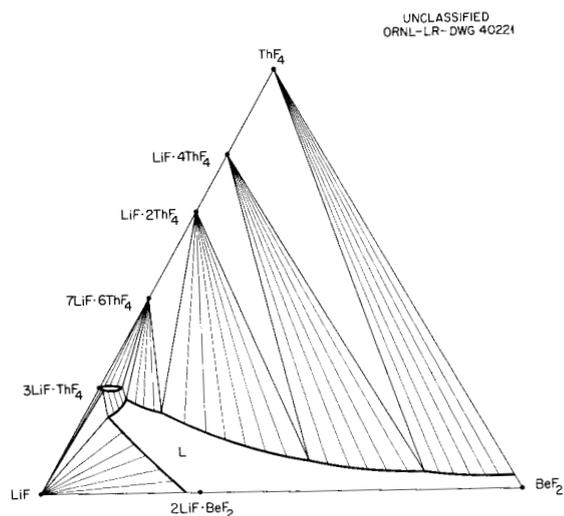


Fig. 12. The System LiF-
BeF₂-ThF₄: 550°C Isotherm.

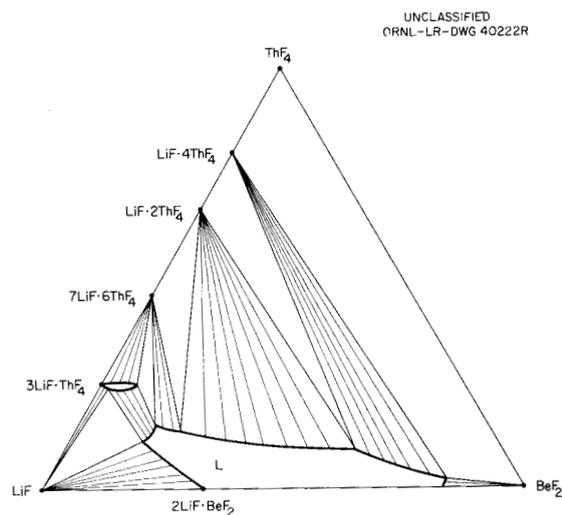


Fig. 13. The System LiF-
BeF₂-ThF₄: 497°C Isotherm.

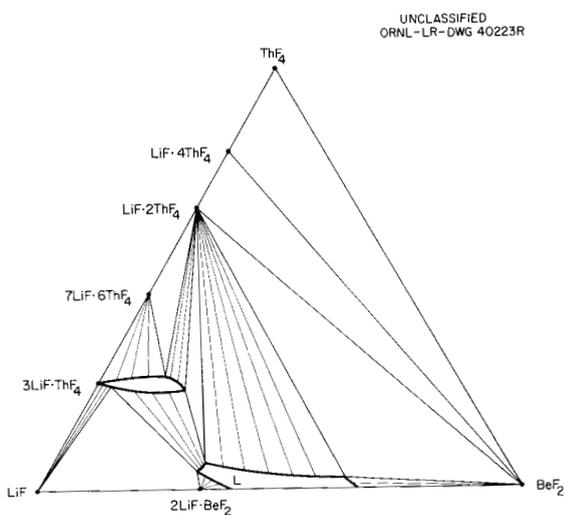


Fig. 14. The System LiF-
BeF₂-ThF₄: 444°C Isotherm.

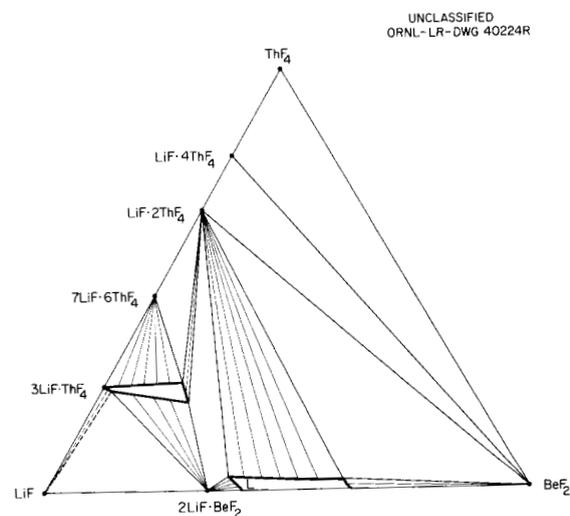


Fig. 15. The System LiF-
BeF₂-ThF₄: 433°C Isotherm.

Solid-state equilibrium is readily established if the solid mixture is annealed for a short time at temperatures near the solidus.

The system pairs LiF-BeF₂-ThF₄ and LiF-BeF₂-UF₄ are very similar. In both, the primary phase fields of the LiF-BeF₂ compounds occupy a small area, and the lowest liquidus temperatures are very near those in the system LiF-BeF₂. A rather low temperature region exists on the liquidus surfaces in the vicinity of 70 mole % LiF. The liquidus surfaces in the

Table 8. Invariant Equilibria in the System LiF-BeF₂-ThF₄*

Composition of Liquid (mole %)			Invariant Temperature (°C)	Type of Invariant	Solids Present at Invariant Point
LiF	BeF ₂	ThF ₄			
15	83	2	497 ± 4	Peritectic	ThF ₄ , LiF·4ThF ₄ , and BeF ₂
33.5	64	2.5	455 ± 4	Peritectic	LiF·4ThF ₄ , LiF·2ThF ₄ , and BeF ₂
47	51.5	1.5	356 ± 6	Eutectic	2LiF·BeF ₂ , LiF·2ThF ₄ , and BeF ₂
60.5	36.5	3	433 ± 5	Peritectic	LiF·2ThF ₄ , 3LiF·ThF ₄ ss, and 2LiF·BeF ₂
65.5	30.5	4	444 ± 4	Peritectic	LiF, 2LiF·BeF ₂ , and 3LiF·ThF ₄ ss
63	30.5	6.5	448 ± 5	Peritectic	3LiF·ThF ₄ ss, 7LiF·6ThF ₄ , and LiF·2ThF ₄

*R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 80 (Nov. 6, 1959).

Table 9. Phase Behavior of Selected LiF-BeF₂-ThF₄ Compositions

Temperature (°C)	Phases Present
C-127: 58 LiF-7 ThF ₄ -35 BeF ₂ (Mole %)	
460-430	LiF·2ThF ₄ and liquid
430-356	LiF·2ThF ₄ , 2LiF·BeF ₂ , and liquid
356-280	LiF·2ThF ₄ , 2LiF·BeF ₂ , and BeF ₂
Below 280	LiF·2ThF ₄ , 2LiF·BeF ₂ , and LiF·BeF ₂
C-133: 71 LiF-13 ThF ₄ -16 BeF ₂ (Mole %)	
500-470	3LiF·ThF ₄ ss and liquid
470-444	3LiF·ThF ₄ ss, LiF, and liquid
Below 444	3LiF·ThF ₄ ss and 2LiF·BeF ₂
BeLT-15:* 67.5 LiF-15 ThF ₄ -17.5 BeF ₂ (Mole %)	
500-465	3LiF·ThF ₄ ss, 7LiF·6ThF ₄ , and liquid
465-440	3LiF·ThF ₄ ss and liquid
Below 440	3LiF·ThF ₄ ss and 2LiF·BeF ₂

*R. E. Thoma, Crystallization Reactions in the Mixture LiF-BeF₂-ThF₄ (67.5-17.5-15 Mole %), BeLT-15, ORNL CF-59-4-49 (Apr. 13, 1959).

system LiF-BeF₂-ThF₄ tend to occur at somewhat higher temperatures than those in the system LiF-BeF₂-UF₄.

Several investigations of the interactions of molten mixtures of LiF, BeF₂, and ThF₄ have been reported. The precipitation of ThO₂ from LiF-BeF₂-ThF₄ mixtures by steam⁴⁰ has been studied. Attempts to remove barium from LiF-BeF₂-ThF₄ mixtures by adding Cr₂O₃ or BeO were unsuccessful, as were attempts to remove cerium by adding BeO or Al₂O₃.⁴¹ The segregation effect of thermal cycling on LiF-BeF₂-ThF₄ mixtures has been reported.^{60, 63}

3.9 The System BeF₂-ThF₄-UF₄

The great similarity of the binary systems BeF₂-UF₄ and BeF₂-ThF₄ (Sec 3.2) and the continuous solid solution between UF₄ and ThF₄ (Sec 3.6)

indicate that the phase equilibria in the system $\text{BeF}_2\text{-ThF}_4\text{-UF}_4$ ⁶⁷ are essentially predictable from the limiting systems. This has been confirmed experimentally (Fig. 16). The system is dominated by the primary phase

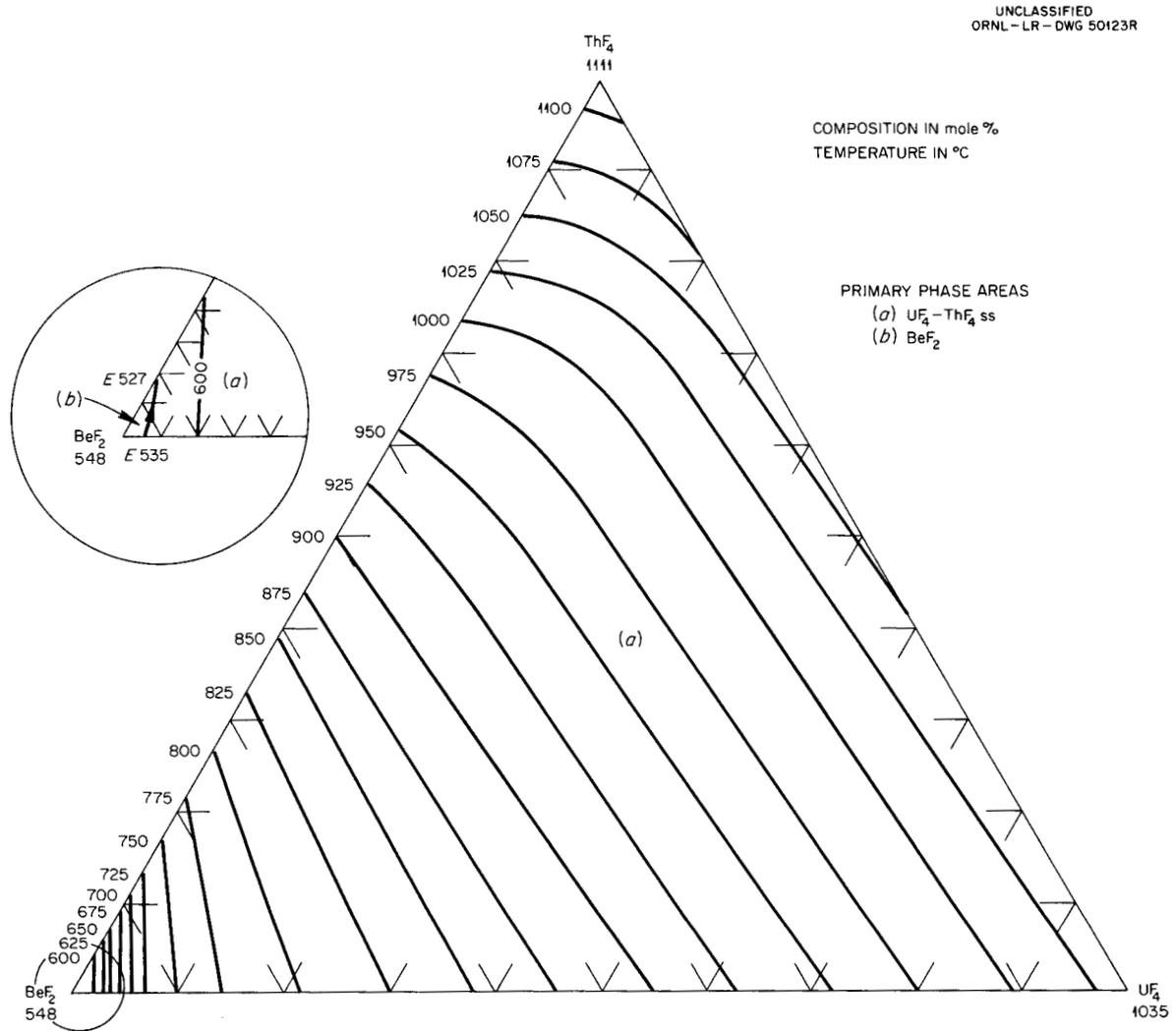


Fig. 16. The System $\text{BeF}_2\text{-UF}_4\text{-ThF}_4$.

area of the $\text{UF}_4\text{-ThF}_4$ solid solution. The only solid phases existing at equilibrium are BeF_2 and the $\text{UF}_4\text{-ThF}_4$ solid solution. The properties of these solids are given in Secs 3.1 and 3.6 and in Appendixes A and B. The system possesses a single boundary path and no ternary invariant

⁶⁷C. F. Weaver, R. E. Thoma, H. A. Friedman, and H. Insley, J. Am. Ceram. Soc., in press.

points. All mixtures with liquidus temperatures below 550°C contain more than 97 mole % BeF_2 .

3.10 The System $\text{LiF-UF}_4\text{-ThF}_4$

The system $\text{LiF-UF}_4\text{-ThF}_4$ ⁴⁹ (Figs. 17 and 18) is characterized by extensive ternary solid solutions⁶⁸ which are shown in Figs. 19-22. The

⁶⁸The phrase "ternary solid solution" as used here implies that the solid solution composition lies within the system $\text{LiF-UF}_4\text{-ThF}_4$. Each of the solid solutions in this system, however, may be formed from mixtures of two end members and in this sense is a binary series.

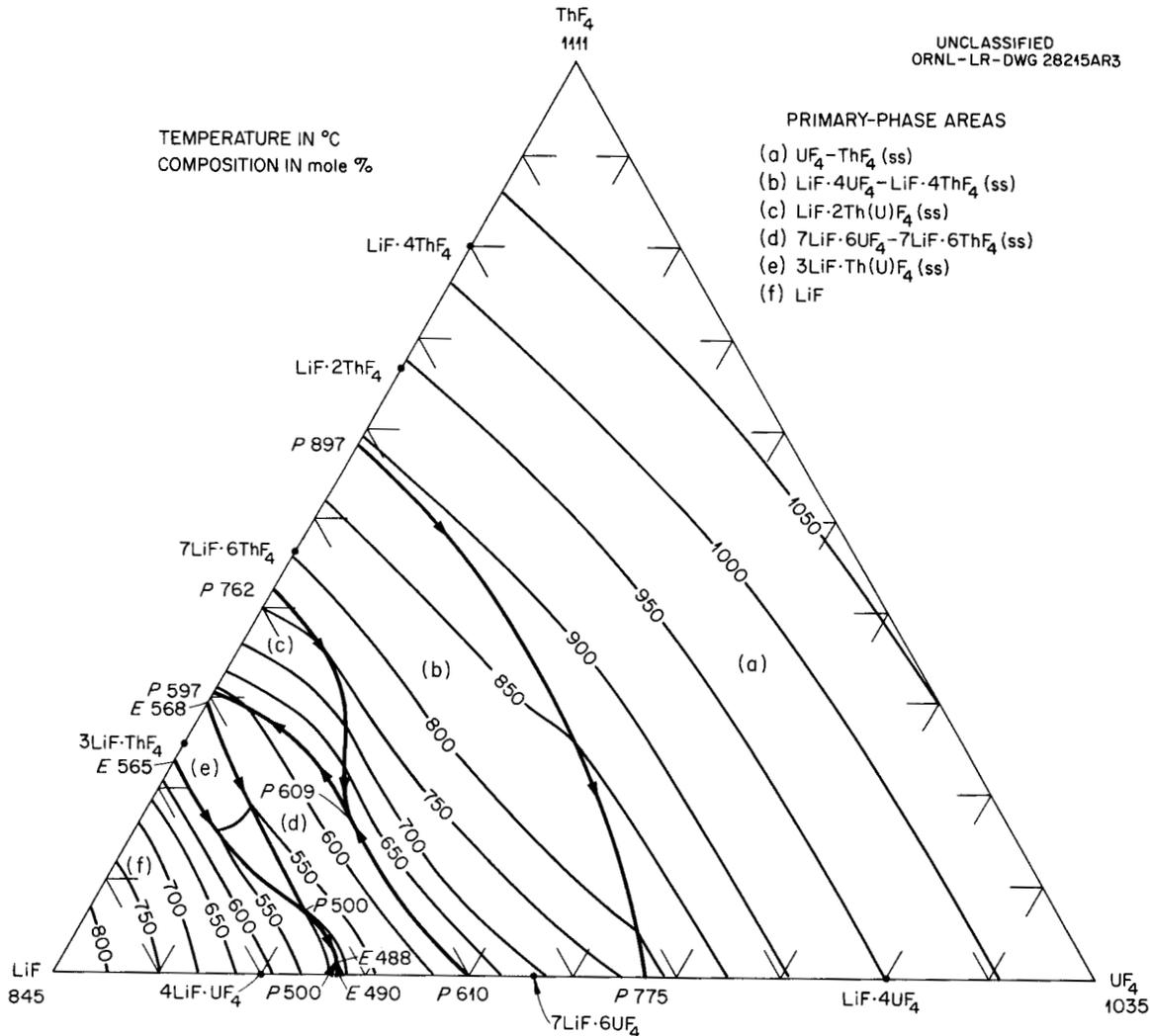
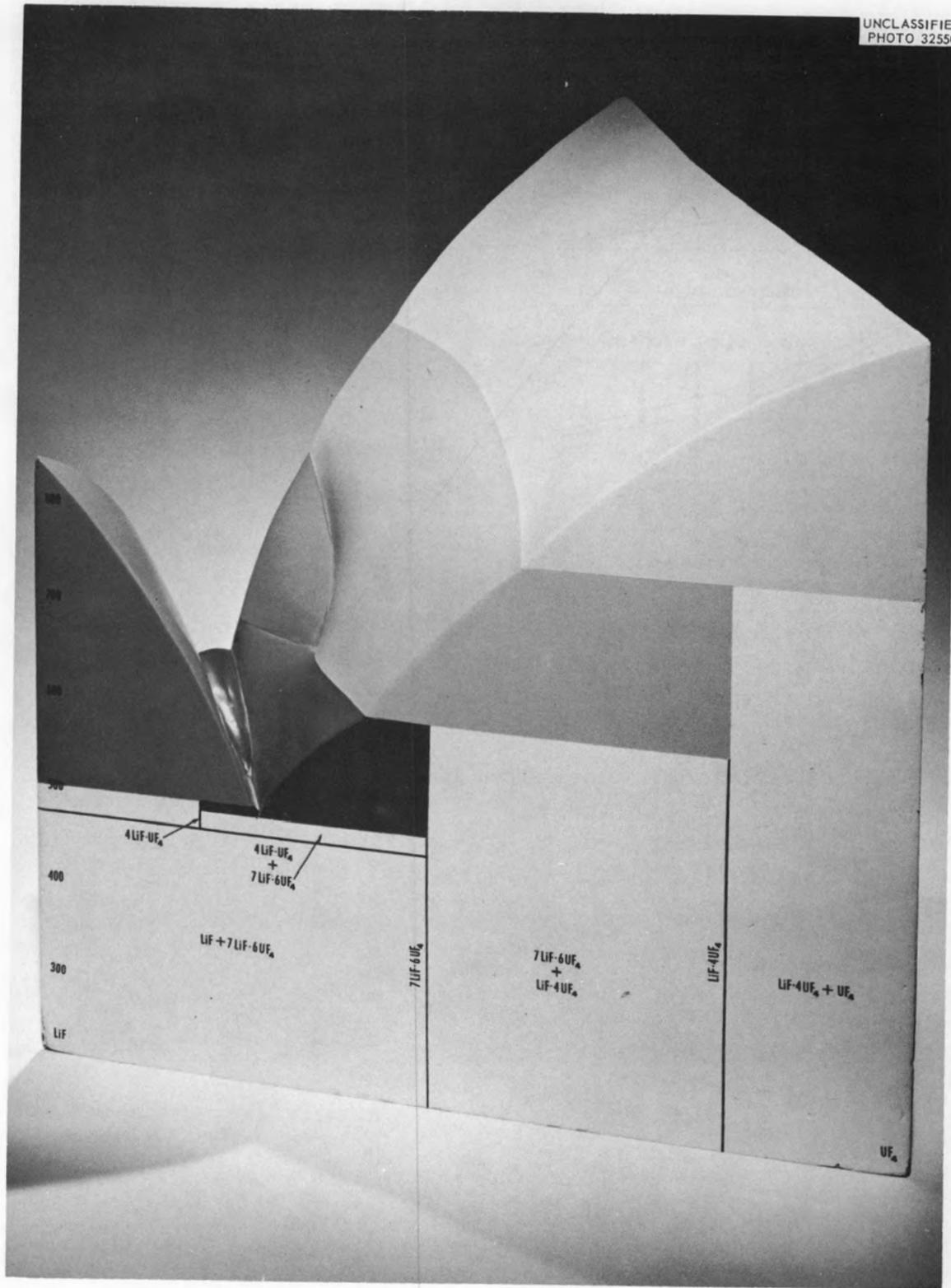


Fig. 17. The System $\text{LiF-UF}_4\text{-ThF}_4$.

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PHOTO 32550Fig. 18. The System $\text{LiF-UF}_4\text{-ThF}_4$.

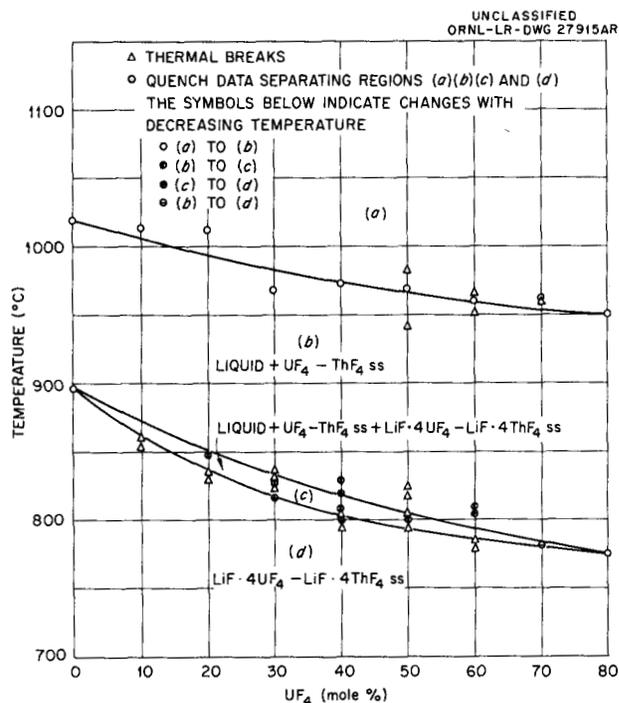


Fig. 19. The System LiF- UF_4 - ThF_4 : 20 Mole % LiF Section.

The temperatures and compositions of the three ternary invariant points are listed in Table 10. The compatibility triangles associated with these invariant points are shown in Fig. 29 and Table 10.

equilibrium phase behavior of a ternary system involving solid solutions can be clearly and unambiguously described only by an extensive series of isothermal sections, fractionation paths in the primary phase areas, and tie lines in the subsolidus regions. Four isothermal sections which illustrate the invariant and the subsolidus phenomena are shown in Figs. 23-26. The fractionation paths for the primary phase areas of the solutions may be found in Fig. 27. Tie lines for three of the subsolidus two-phase regions are shown in Fig. 28.

- (a) $UF_4 - ThF_4$ ss + LIQUID
 (b) $LiF \cdot 4UF_4 - LiF \cdot 4ThF_4$ + LIQUID
 (c) $UF_4 - ThF_4$ ss + LIQUID + $LiF \cdot 4UF_4 - LiF \cdot 4ThF_4$ ss
 (d) $LiF \cdot 2ThF_4$ ss + LIQUID + $LiF \cdot 4UF_4 - LiF \cdot 4ThF_4$ ss
 (e) $LiF \cdot 4UF_4 - LiF \cdot 4ThF_4$ ss + LIQUID + $7LiF \cdot 6UF_4 - 7LiF \cdot 6ThF_4$ ss
 (f) $LiF \cdot 2ThF_4$ ss
 (g) $LiF \cdot 4UF_4 - LiF \cdot 4ThF_4$ ss + $7LiF \cdot 6UF_4 - 7LiF \cdot 6ThF_4$ ss
 (h) $LiF \cdot 4UF_4 - LiF \cdot 4ThF_4$ ss + $7LiF \cdot 6UF_4 - 7LiF \cdot 6ThF_4$ ss + $LiF \cdot 2ThF_4$ ss

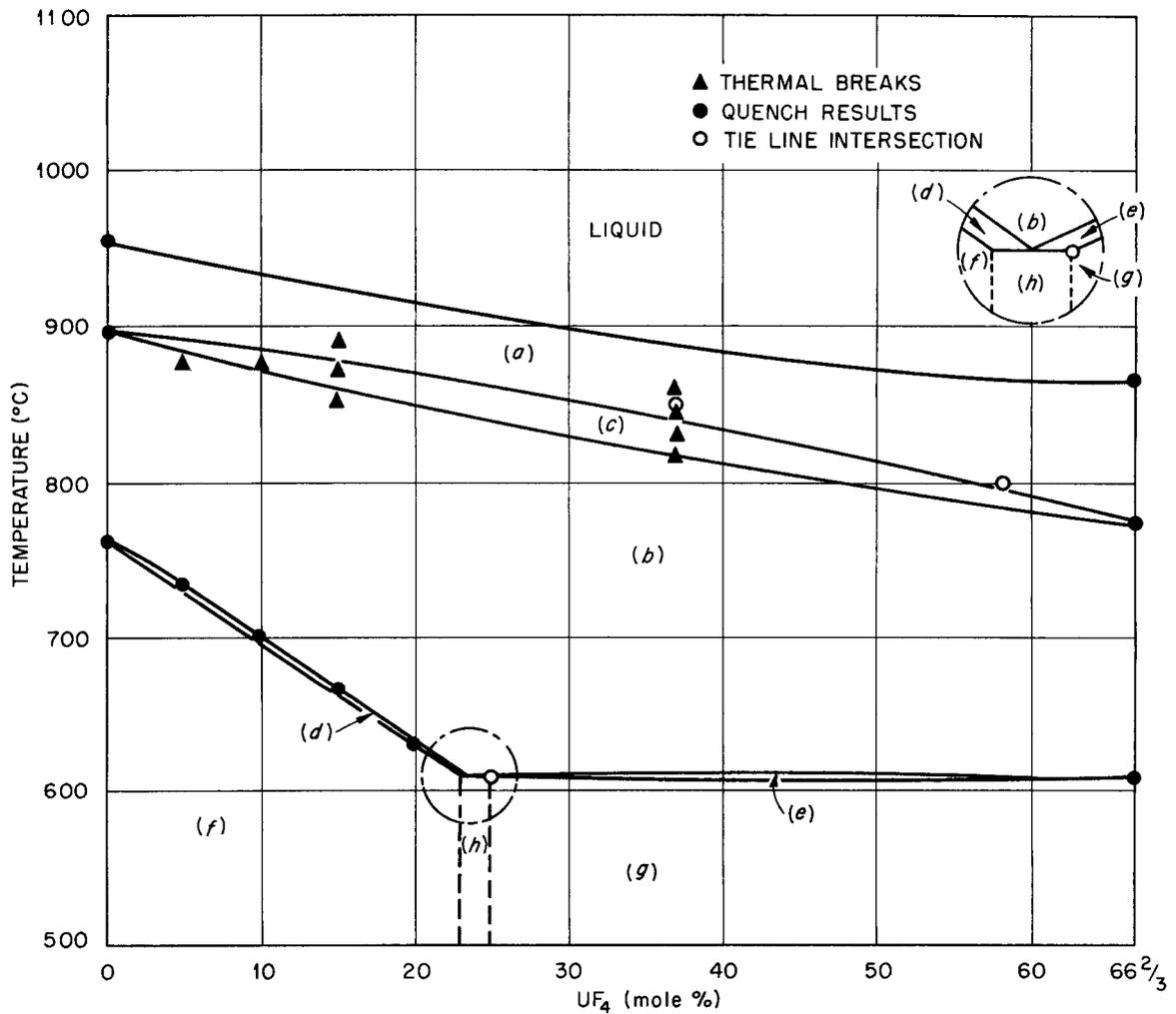
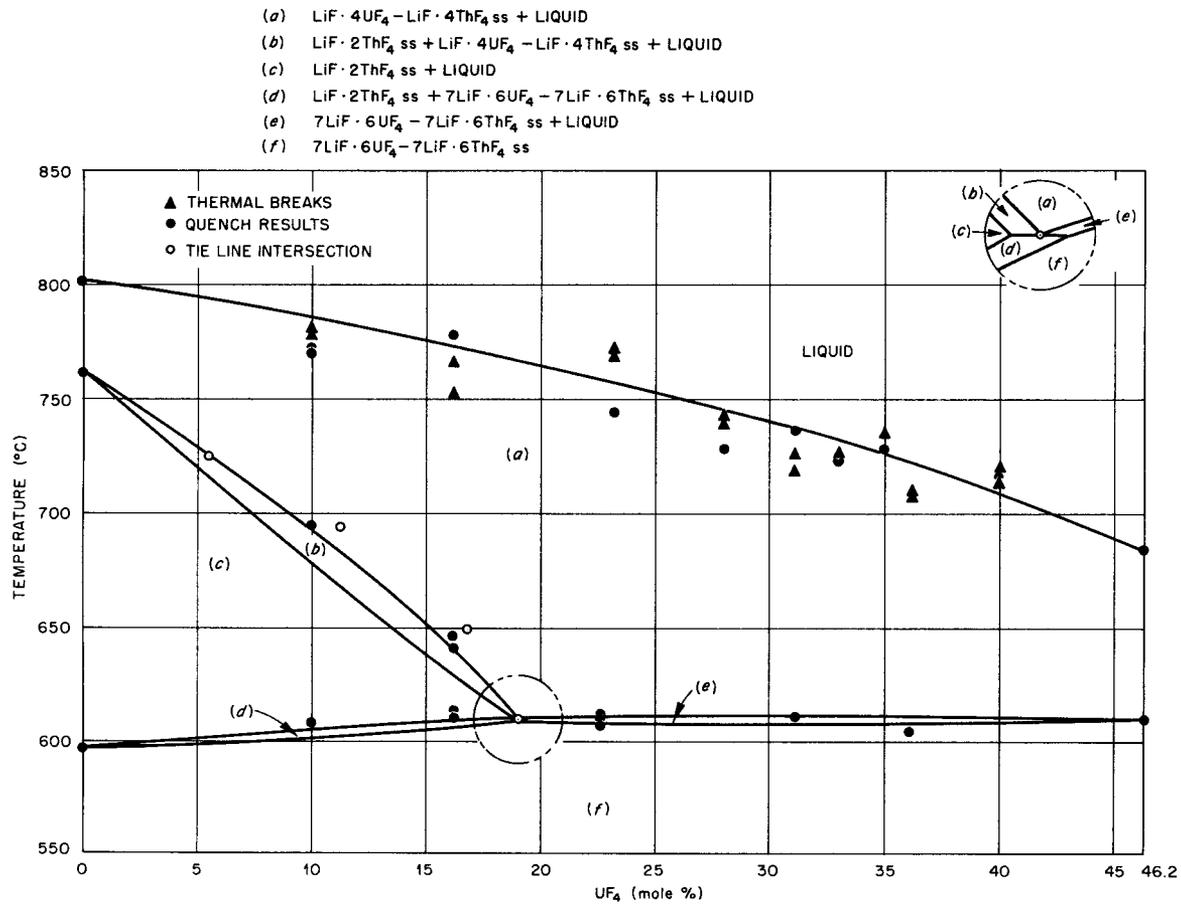


Fig. 20. The System $LiF-UF_4-ThF_4$: $33\frac{1}{3}$ Mole % LiF Section.

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ORNL-LR-DWG 27917ARFig. 21. The System $\text{LiF}-\text{UF}_4-\text{ThF}_4$: 53.8 Mole % LiF Section.

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- (a) LIQUID + 3 LiF · ThF₄ ss
 (b) LiF + LIQUID
 (c) LiF + 3 LiF · ThF₄ ss + LIQUID
 (d) LiF + 7 LiF · 6 ThF₄ - 7 LiF · 6 UF₄ ss + LIQUID
 (e) 4 LiF · UF₄ + LIQUID + LiF
 (f) 4 LiF · UF₄ + LIQUID
 (g) 4 LiF · UF₄ + 7 LiF · 6 ThF₄ - 7 LiF · 6 UF₄ ss + LIQUID
 (h) 3 LiF · ThF₄ ss
 (i) 3 LiF · ThF₄ ss + 7 LiF · 6 ThF₄ - 7 LiF · 6 UF₄ ss + LiF
 (j) LiF + 7 LiF · 6 ThF₄ - 7 LiF · 6 UF₄ ss
 (k) LiF + 4 LiF · UF₄ + 7 LiF · 6 ThF₄ - 7 LiF · 6 UF₄ ss
 (l) 4 LiF · UF₄ + 7 LiF · 6 ThF₄ - 7 LiF · 6 UF₄ ss

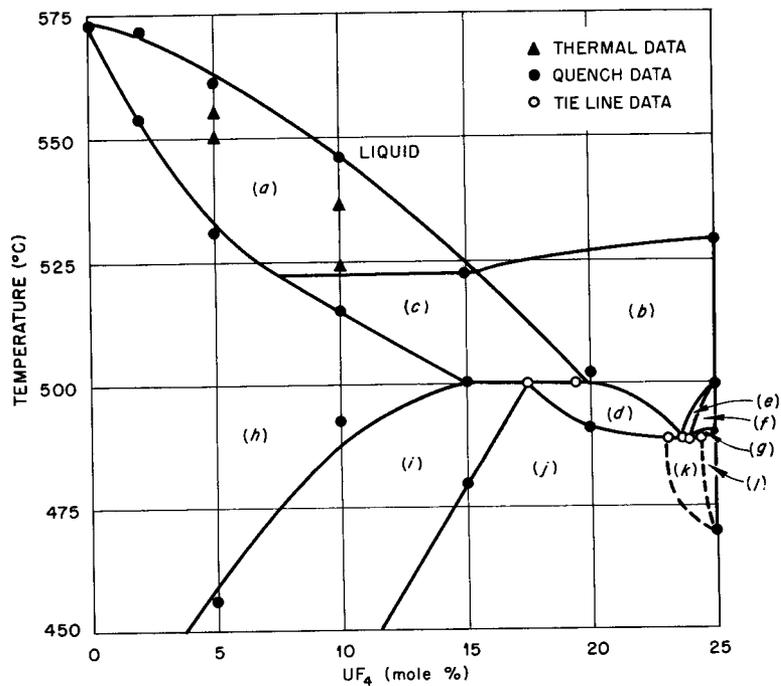


Fig. 22. The System LiF-UF₄-ThF₄: 75 Mole % LiF Section.

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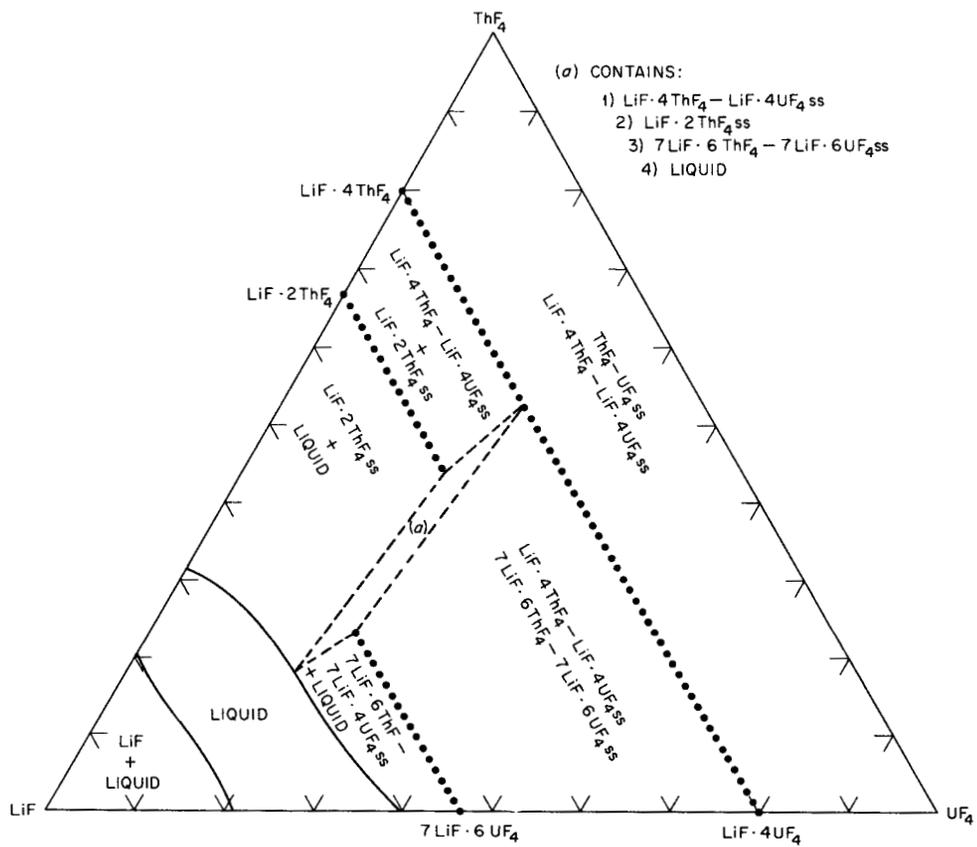


Fig. 23. The System $\text{LiF}-\text{UF}_4-\text{ThF}_4$: 609°C Isothermal Section.

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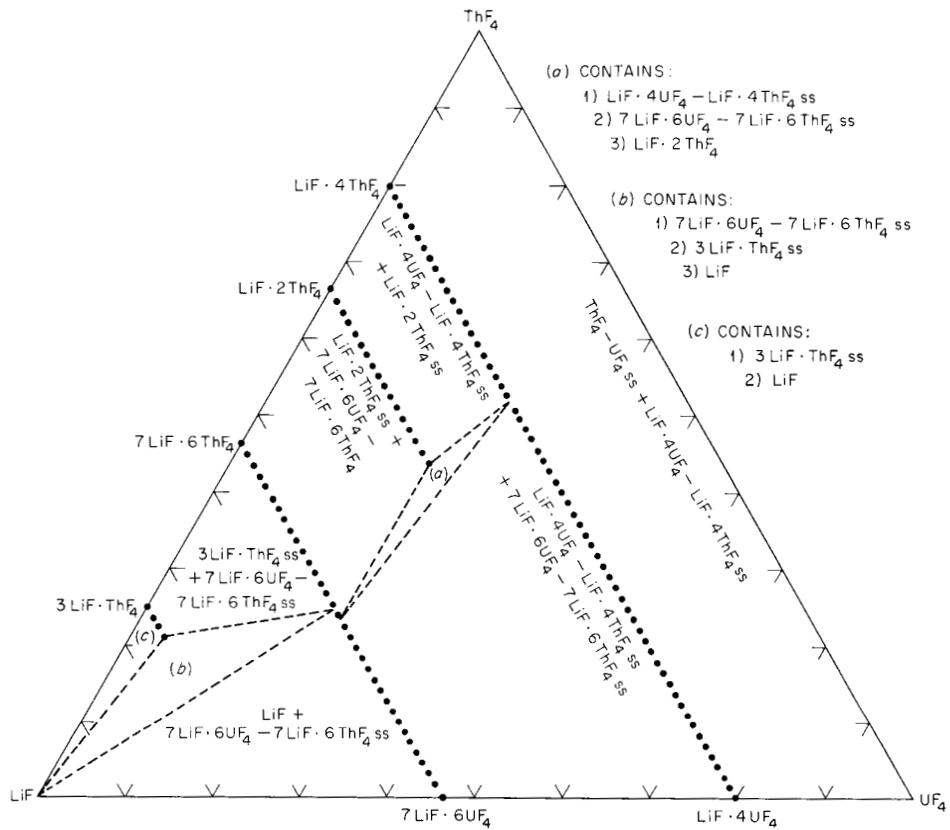


Fig. 26. The System $\text{LiF}-\text{UF}_4-\text{ThF}_4$: 450°C Isothermal Section.

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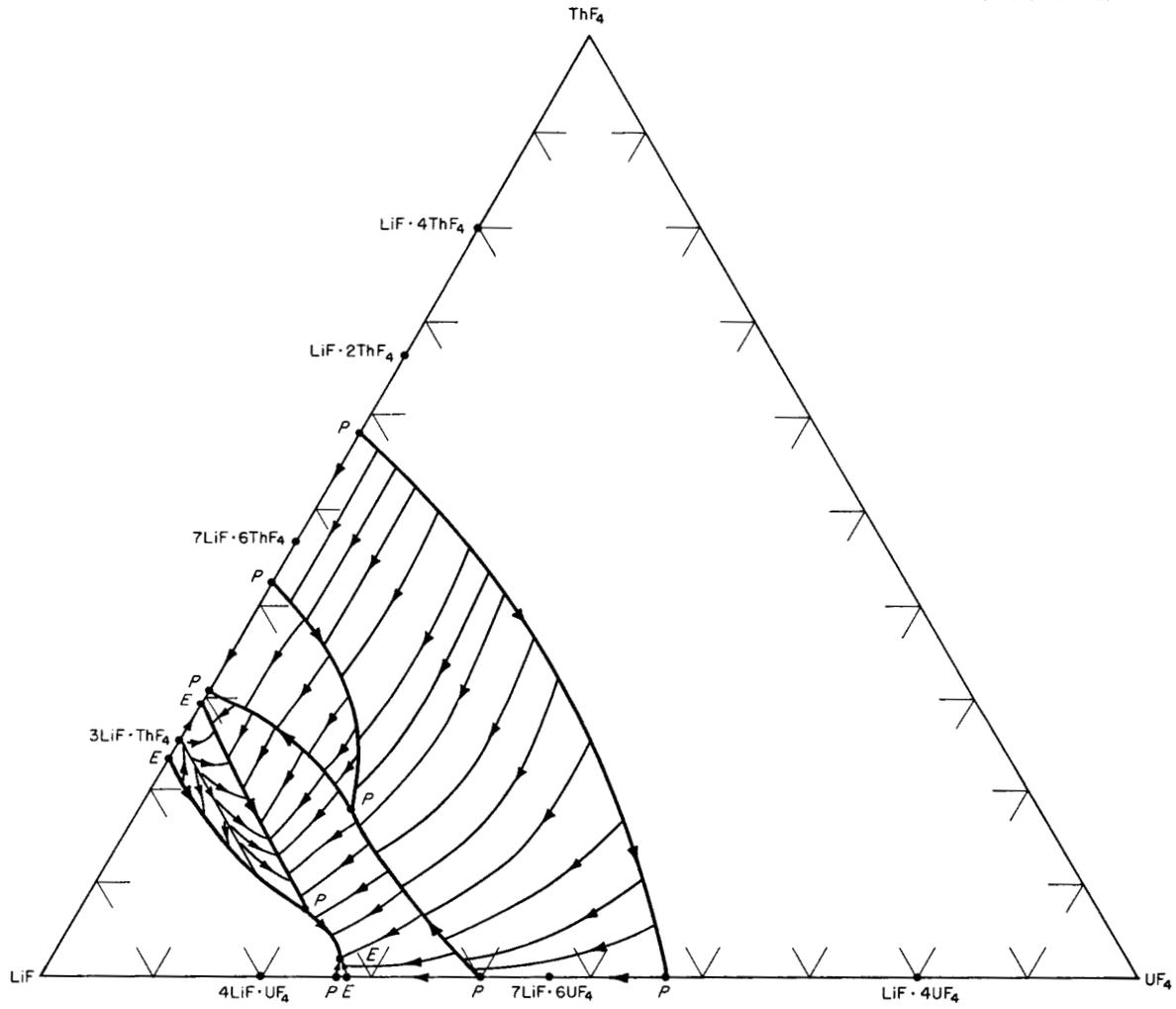


Fig. 27. The System $\text{LiF-UF}_4\text{-ThF}_4$: Fractionation Paths.

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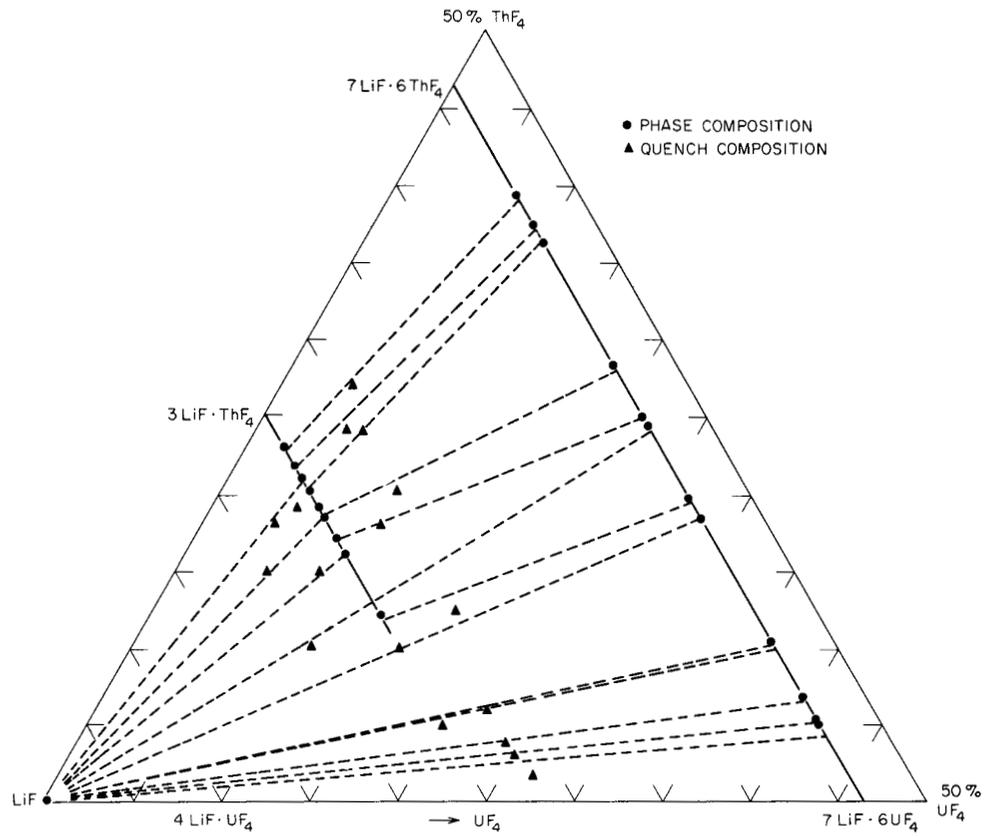


Fig. 28. The System $\text{LiF}-\text{UF}_4-\text{ThF}_4$: Tie Lines.

Table 10. Invariant Equilibria in the System LiF-UF₄-ThF₄*

Composition of Invariant Point (mole %)			Invariant Temperature (°C)	Type of Equilibrium	Solid Phases in Equilibrium at the Invariant Temperature
LiF	UF ₄	ThF ₄			
63	19	18	609	Peritectic	LiF·4ThF ₄ -LiF·4UF ₄ ss containing 28 mole % UF ₄ , LiF·2Th(U)F ₄ ss containing 23 mole % UF ₄ , 7LiF·6ThF ₄ -7LiF·6UF ₄ ss containing 23 mole % UF ₄
72.5	20.5	7	500	Peritectic	7LiF·6ThF ₄ -7LiF·6UF ₄ ss containing 31 mole % UF ₄ , 3LiF·Th(U)F ₄ ss containing 15.5 mole % UF ₄ , LiF
72	26.5	1.5	488	Eutectic	7LiF·6ThF ₄ -7LiF·6UF ₄ ss containing 42.5 mole % UF ₄ , 4LiF·UF ₄ , LiF

*C. F. Weaver et al., Phase Equilibria in the Systems UF₄-ThF₄ and LiF-UF₄-ThF₄, ORNL-2719 (Aug. 17, 1959); J. Am. Ceram. Soc. 43, 213 (1960).

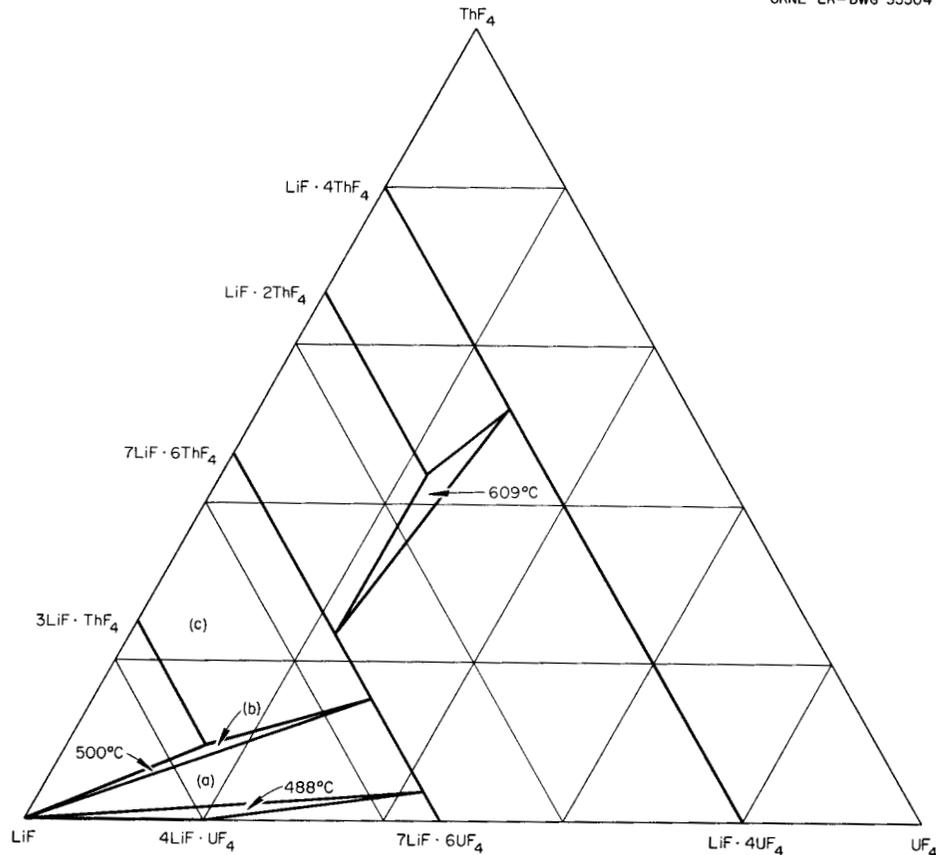


Fig. 29. The System $\text{LiF-UF}_4\text{-ThF}_4$: Compatibility Triangles.

3.11 The System $\text{LiF-BeF}_2\text{-UF}_4\text{-ThF}_4$ (Selected Portions)

Detailed phase equilibrium studies for an entire quaternary system require such a vast amount of time and money that they are usually completed over a number of years if at all. The system $\text{LiF-BeF}_2\text{-UF}_4\text{-ThF}_4$ is no exception in this respect, and consequently the experimental work was directed toward compositions which possess sufficiently low liquidus and viscosity values to be of project interest.

The similarities between the systems $\text{BeF}_2\text{-ThF}_4$ and $\text{BeF}_2\text{-UF}_4$, the systems LiF-ThF_4 and LiF-UF_4 , and the systems $\text{LiF-BeF}_2\text{-ThF}_4$ and $\text{LiF-BeF}_2\text{-UF}_4$ have been discussed in Secs 3.2, 3.5, and 3.8 of this report. Within the systems $\text{UF}_4\text{-ThF}_4$ and $\text{LiF-UF}_4\text{-ThF}_4$ extensive solid solutions are formed between corresponding compounds. The existence of these similar systems and of solid solutions between analogous compounds leads to the hypothesis

that UF_4 and ThF_4 are very nearly interchangeable in the quaternary mixtures with respect to their liquidus values and that the phase relationships in the quaternary system will be very much like those in the ternary systems $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ and $\text{LiF}-\text{BeF}_2-\text{UF}_4$. Four sections of constant mole per cent LiF and BeF_2 were studied experimentally as a means of partially verifying this hypothesis. These sections contain 70 LiF and 10 BeF_2 , 67.5 LiF and 17.5 BeF_2 , 70 LiF and 6 BeF_2 , and 65 LiF and 25 BeF_2 (mole %). The first two sections include the compositions C-136 and BeLT-15 (see Appendix C). The experimental results of these experiments may be found in Table 11. The liquidus values along the first three joins are nearly linear functions of the composition (Figs. 30-32). The deviation from linearity in the fourth join (Fig. 33) is in the direction of lower liquidus temperatures. The ThF_4 -containing end member has the maximum liquidus temperature for all the joins, while the UF_4 -containing end member has the minimum liquidus temperature for three of the four joins. The solid solution $7\text{LiF}\cdot 6(\text{U,Th})\text{F}_4$ is the primary phase for all the compositions on the joins listed above. The interchangeability of UF_4 and ThF_4 implies that a breeder blanket selected from the quaternary system or its limiting systems will contain the maximum concentration of ThF_4 for a given temperature only if no UF_4 is present. In other words, if UF_4 is added an approximately equal amount of ThF_4 must be removed to maintain the same liquidus temperature.

Mixtures containing a maximum amount of ThF_4 for a given temperature are found in the system $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ (Figs. 9-11) up to 568°C . Above 568° the mixtures must contain no BeF_2 ; thus they will be binary mixtures of LiF and ThF_4 .

The members of a second series contain a small total mole percentage of UF_4 and ThF_4 (Table 11). They represent the breeder fuels, such as C-134, BULT 4-0.5U, and BULT 4-1U. Compositions containing up to 5 mole % $\text{UF}_4 + \text{ThF}_4$ in the range 30-38 mole % BeF_2 have liquidus values close to those of the system $\text{LiF}-\text{BeF}_2$. These compositions differ from the $\text{LiF}-\text{BeF}_2$ binary mixtures in that their liquidus values are slightly lower and solid solutions containing UF_4 and ThF_4 precipitate as primary or

Table 11. Thermal Gradient Quench Data for the System LiF-BeF₂-UF₄-ThF₄

Composition (mole %)				Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
LiF	BeF ₂	UF ₄	ThF ₄			
55	35	3	7	427 ± 3	L ^c and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
56	35	2	7	432 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
57	35	3	5	488 ± 3	L	L and LiF·2ThF ₄ ss
57	35	3	5	480 ± 3	L and LiF·2ThF ₄ ss	L and 7LiF·6(U,Th)F ₄ ss
57	35	3	5	433 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
58	35	2	5	498 ± 3	L	L and LiF·2ThF ₄ ss (15 mole % UF ₄)
58	35	2	5	460 ± 2	L and LiF·2ThF ₄ ss	L and 7LiF·6(U,Th)F ₄ ss (11 mole % UF ₄)
58	35	2	5	433 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
59	35	3	3	479 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss (22 mole % UF ₄)
59	35	3	3	434 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
60	35	2	3	449 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss
60	35	2	3	440 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
60	35	2	3	~425	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂	2LiF·BeF ₂ and 7LiF·6(U,Th)F ₄ ss (20 mole % UF ₄)

Table 11 (continued)

Composition (mole %)				Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
LiF	BeF ₂	UF ₄	ThF ₄			
60	36	3	1	449 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss
60	36	3	1	432 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄
60	37	2	1	434 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss
60	37	2	1	431 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
60	38	1	1	442 ± 2	L	L and 2LiF·BeF ₂
60	38	1	1	433 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss (20 mole % UF ₄)
61	36	2	1	437 ± 2	L	L and 2LiF·BeF ₂
61	36	2	1	434 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss (23 mole % UF ₄)
61	37.5	0.5	1	439 ± 3	L	L and 2LiF·BeF ₂
62	34	3	1	446 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss
62	34	3	1	443 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
62	36	1	1	446 ± 2	L	L and 2LiF·BeF ₂
62	36	1	1	438 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss
62	36	1	1	~420	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss	2LiF·BeF ₂ and 7LiF·6(U,Th)F ₄ ss

Table 11 (continued)

Composition (mole %)				Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
LiF	BeF ₂	UF ₄	ThF ₄			
62	36.5	0.5	1	452 ± 2	L	L and 2LiF·BeF ₂
62	36.5	0.5	1	448 ± 3	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F _{4ss}
62	36.5	0.5	1	~433	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F _{4ss}	2LiF·BeF ₂ and 7LiF·6(U,Th)F _{4ss}
63	35	1	1	450 ± 3	L	L and 2LiF·BeF ₂
63	35	1	1	438 ± 3	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F _{4ss}
63	35	1	1	416 ± 3	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F _{4ss}	2LiF·BeF ₂ and 7LiF·6(U,Th)F _{4ss}
63	35	2	1	442 ± 2	L	L and 2LiF·BeF ₂
63	35	2	1	438 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F _{4ss} (23 mole % UF ₄)
63	35.5	0.5	1	456 ± 2	L	L and 2LiF·BeF ₂
63	35.5	0.5	1	448 ± 3	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F _{4ss}
64	32	3	1	446 ± 2	L	L and 2LiF·BeF ₂
64	32	3	1	443 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F _{4ss}
64	33	2	1	442 ± 2	L	L and 2LiF·BeF ₂

Table 11 (continued)

Composition (mole %)				Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
LiF	BeF ₂	UF ₄	ThF ₄			
64	33	2	1	440 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss (22 mole % UF ₄)
65	25	3	7	477 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss
65	25	3	7	437 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
65	25	5	5	447 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss (22 mole % UF ₄)
65	25	5	5	437 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss
65	25	5	5	430 ± 3	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss	7LiF·6(U,Th)F ₄ ss and 2LiF·BeF ₂
65	25	8	2	442 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss
65	25	8	2	432 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss (36 mole % UF ₄), and 2LiF·BeF ₂
65	25	8	2	424 ± 2	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂	LiF, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
65	30	1	4	448 ± 2	L	L, 2LiF·BeF ₂ , and 3LiF·ThF ₄ ss
65	30	1	4	423 ± 2	L, 2LiF·BeF ₂ , and 3LiF·ThF ₄ ss	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss (9 mole % UF ₄)
65	30.5	0.5	4	453 ± 1	L	L and 3LiF·ThF ₄ ss
65	30.5	0.5	4	448 ± 2	L and 3LiF·ThF ₄ ss	L, 3LiF·ThF ₄ ss, and 2LiF·BeF ₂

Table 11 (continued)

Composition (mole %)				Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
LiF	BeF ₂	UF ₄	ThF ₄			
65	31	3	1	449 ± 2	L	L and 2LiF·BeF ₂
65	31	3	1	443 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss
65	33	1	1	465 ± 1	L	L and 2LiF·BeF ₂
65	33	1	1	446 ± 2	L and 2LiF·BeF ₂	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss (22 mole % UF ₄)
65	33	1	1	408 ± 2	L, 2LiF·BeF ₂ , and 7LiF·6(U,Th)F ₄ ss	2LiF·BeF ₂ and 7LiF·6(U,Th)F ₄ ss
66.4	24.9	5.4	3.3	446 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss (21 mole % UF ₄)
67	18.5	0.5	14	499 ± 4	L	L and 3LiF·ThF ₄ ss
67.5	17.5	3	12	490 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss
67.5	17.5	3	12	480 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss
67.5	17.5	3	12	429 ± 2	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss	L and 3LiF·ThF ₄ ss
67.5	17.5	6	9	490 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss
67.5	17.5	6	9	462 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss
67.5	17.5	6	9	429 ± 2	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂

Table 11 (continued)

Composition (mole %)				Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
LiF	BeF ₂	UF ₄	ThF ₄			
67.5	17.5	9	6	484 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss
67.5	17.5	9	6	438 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
67.5	17.5	12	3	484 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss
67.5	17.5	12	3	433 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 2LiF·BeF ₂
68	18.7	10.8	2.5	446 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss (34 mole % UF ₄)
69.7	12.4	16.2	1.7	461 ± 2	L	L, LiF, and 7LiF·6(U,Th)F ₄ ss (38 mole % UF ₄)
70	6	6	18	540 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss
70	6	6	18	531 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss
70	6	12	12	516 ± 2	L	L and 7LiF·6(U,Th)F ₄ ss (16 mole % UF ₄)
70	6	12	12	503 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss
70	6	18	6	494 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss (30 mole % UF ₄)
70	6	18	6	476 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and LiF
70	6	24	0 ^d	480 ± 3	L	L and 7LiF·6UF ₄
70	6	24	0 ^d	462 ± 2	L and 7LiF·6UF ₄	L, 7LiF·6UF ₄ , and LiF

Table 11 (continued)

Composition (mole %)				Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
LiF	BeF ₂	UF ₄	ThF ₄			
70	10	5	15	512 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss (6 mole % UF ₄)
70	10	5	15	510 ± 3	L and 7LiF·6(U,Th)F ₄ ss (6 mole % UF ₄)	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss
70	10	5	15	485 ± 3	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss	L and 3LiF·ThF ₄ ss
70	10	10	10	493 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss
70	10	10	10	489 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss
70	10	10	10	455 ± 3	L, 7LiF·6(U,Th)F ₄ ss, and 3LiF·ThF ₄ ss	L, 7LiF·6(U,Th)F ₄ ss, and LiF
70	10	15	5	475 ± 3	L	L and 7LiF·6(U,Th)F ₄ ss (28 mole % UF ₄)
70	10	15	5	471 ± 3	L and 7LiF·6(U,Th)F ₄ ss	L, 7LiF·6(U,Th)F ₄ ss (28 mole % UF ₄), and LiF
71	16	1	12	513 ± 2	L	L and 3LiF·ThF ₄ ss
71.4	6.2	21.6	0.8	483 ± 1	L	L and 7LiF·6(U,Th)F ₄ ss (13 mole % UF ₄)
71.4	6.2	21.6	0.8	480 ± 2	L and 7LiF·6(U,Th)F ₄ ss	L, LiF, and 7LiF·6(U,Th)F ₄ ss

^aThe uncertainty indicates the temperature difference between the quenched samples.

^bOnly phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."

^cL = liquid.

^dThis ternary mixture is included here because its liquidus temperature, as measured at ORNL, differs somewhat from that found on the Mound Laboratory diagram for the system LiF-UF₄-BeF₂ (Fig. 7).

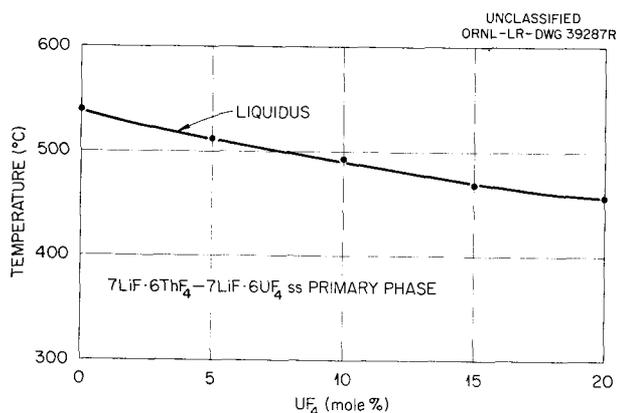


Fig. 30. The Join LiF-BeF₂-ThF₄ (70-10-20)-LiF-BeF₂-UF₄ (70-10-20) in the Quaternary System LiF-BeF₂-ThF₄-UF₄.

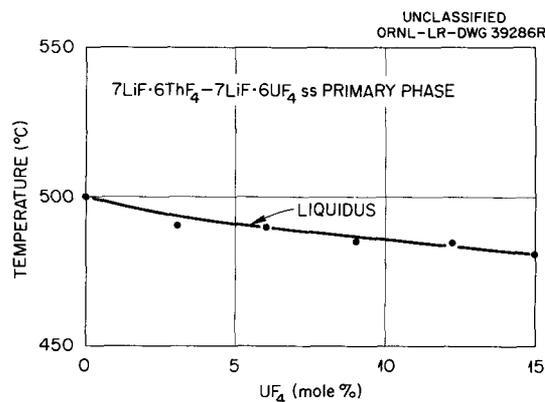


Fig. 31. The Join LiF-BeF₂-ThF₄ (67.5-17.5-15)-LiF-BeF₂-UF₄ (67.5-17.5-15) in the Quaternary System LiF-BeF₂-UF₄-ThF₄.

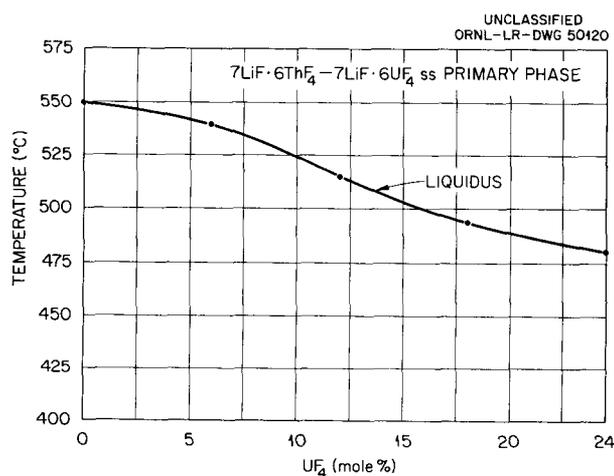


Fig. 32. The Join LiF-BeF₂-ThF₄ (70-6-24)-LiF-BeF₂-UF₄ (70-6-24) in the Quaternary System LiF-BeF₂-UF₄-ThF₄.

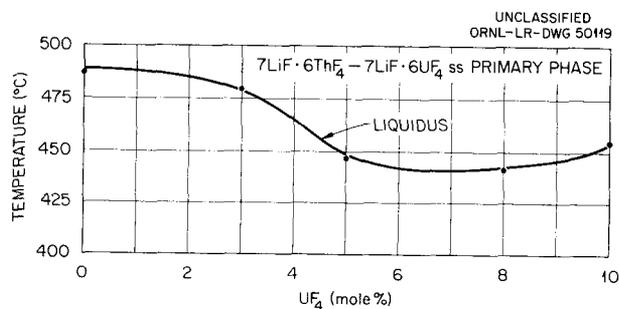


Fig. 33. The Join LiF-BeF₂-ThF₄ (65-25-10)-LiF-BeF₂-UF₄ (65-25-10) in the Quaternary System LiF-BeF₂-UF₄-ThF₄.

secondary phases. Liquidus values rise sharply as the UF₄ + ThF₄ concentration is increased beyond 5 mole %.

The compositions referred to in the ORNL literature by code comprise a third series, which overlaps the group above. Their equilibrium behavior is described in Table 11 and Appendix C.

Melts which have been cooled slowly, rather than annealed and quenched, frequently contain nonequilibrium combinations of stable phases,

metastable phases, and glass. Consequently the phase analysis of slowly cooled melts cannot be relied upon to yield subsolidus equilibrium data. Supercooling is also observed and so affects the thermal analysis that this technique for studying heterogeneous equilibria cannot be used for the system $\text{LiF-UF}_4\text{-ThF}_4\text{-BeF}_2$.

It has been suggested that the uranium concentration in a molten salt reactor might be increased by adding the eutectic mixture of LiF and UF_4 .⁶⁹ Consequently, phase relationships in the quaternary section between 73 LiF -27 UF_4 and 64.75 LiF -4.15 ThF_4 -31.1 BeF_2 have been investigated. This join contains the fuel mixture 65 LiF -30 BeF_2 -4 ThF_4 -1 UF_4 (BULT 4-1U), and all the compositions which may be produced by mixing 73 LiF -27 UF_4 and 64.75 LiF -4.15 ThF_4 -31.1 BeF_2 . The results of thermal gradient quenching experiments may be found in Table 11. The liquidus values are shown as a function of composition in Fig. 34.

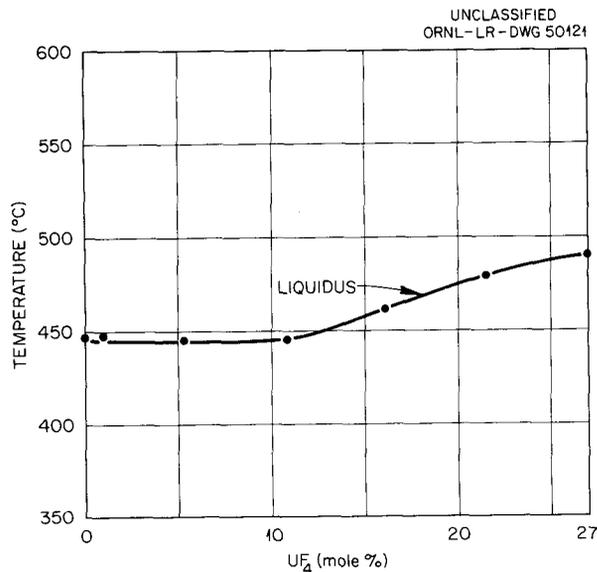


Fig. 34. The Join LiF-UF_4 (73-27)- $\text{LiF-BeF}_2\text{-ThF}_4$ (64.75-31.1-4.15) in the Quaternary System $\text{LiF-BeF}_2\text{-UF}_4\text{-ThF}_4$.

Purified samples of this material were exposed to water-saturated air at room temperature, vacuum-dried at 135°C, and melted under vacuum

Throughout the investigated portions of the quaternary system, the compositions of the solid solutions precipitating as primary phases indicate that the U/Th ratio is less in the solid which first appears than it is in the liquid phase. However, the concentration of uranium in these precipitates is frequently much higher than in the liquid phase.

Quaternary mixtures such as 62 LiF -36.5 BeF_2 -0.5 UF_4 -1 ThF_4 (mole %) (C-134) are hygroscopic and are prone to hydrolyze.⁷⁰

⁶⁹F. F. Blankenship, ORNL, personal communication.

⁷⁰MSR Quar. Prog. Rep. Oct. 31, 1959, ORNL-2890, p 63.

(Fig. 35). The cooled melts contained appreciable amounts of UO_2 , which was detected by polarized light microscopy.^{63,70} These results indicate

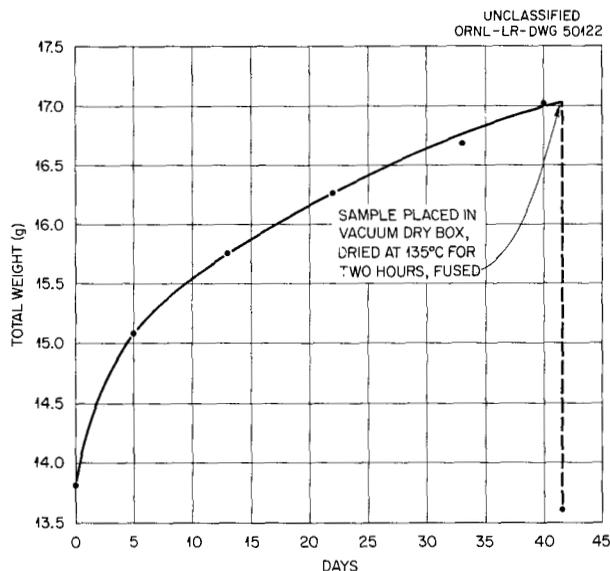


Fig. 35. Hydration-Vacuum-Dehydration Cycle for $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$ (62-36.5-1-0.5).

that a simple drying operation cannot be used with such mixtures and that to prevent hydrolysis these reactor fuels must be protected from water vapor even at room temperature.

Several investigations of the interaction of molten mixtures of LiF , BeF_2 , UF_4 , and ThF_4 with other substances may be found in the ORNL literature.

The solubility of CeF_3 ⁷¹ in $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$ liquids and the reactions of BeO ⁷² and steam on these solvents have been reported. The exchange of CeF_3 (dissolved in a quaternary solvent) and LaF_3 (solid) has been studied.⁵⁸ The segregation effect of thermal cycling,⁶⁰ graphite compatibility,⁶² and the leaching of chromium from INOR-8⁷³ have been investigated.

4. ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of G. M. Hebert, who prepared a number of the quenched samples. We are especially grateful to J. H. Burns, F. F. Blankenship, H. G. MacPherson, and J. E. Ricci for suggestions and advice concerning many phases of the investigation.

⁷¹R. A. Strehlow *et al.*, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 79.

⁷²J. H. Shaffer, G. M. Watson, and W. R. Grimes, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 86.

⁷³J. E. Eorgan *et al.*, Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 67.

Appendix A

OPTICAL AND CRYSTALLOGRAPHIC PROPERTIES

The optical and crystallographic properties of the compounds which occur in the system $\text{LiF-UF}_4\text{-ThF}_4\text{-BeF}_2$ are summarized in Tables A-1 and A-2 respectively. No ternary or quaternary compounds have been observed. The refractive indices of the $\text{LiF-UF}_4\text{-ThF}_4$ and $\text{UF}_4\text{-ThF}_4$ solid solutions may be found in Figs. A-1 through A-5.

Table A-1. Optical Properties of the Components and Binary Compounds in the System $\text{LiF-UF}_4\text{-ThF}_4\text{-BeF}_2$

Compound	Optical Character	Optic Angle, 2V	Optic Sign	Refractive Indices		Color
				N_ω or N_α	N_ϵ or N_γ	
LiF^a	Isotropic			1.3915		Colorless
BeF_2^b	Uniaxial		+	1.325		Colorless
UF_4^c	Biaxial	$\sim 60^\circ$	-	1.552	1.598	Green
ThF_4^b	Biaxial	$\sim 60^\circ$	-	1.500	1.534	Colorless
$2\text{LiF}\cdot\text{BeF}_2^b$	Uniaxial		+	1.312	1.319	Colorless
$\text{LiF}\cdot\text{BeF}_2$	Biaxial	Large		1.35 (average)		Colorless
$4\text{LiF}\cdot\text{UF}_4^b$	Biaxial	$\sim 10^\circ$	-	1.560	1.472	Green
$7\text{LiF}\cdot 6\text{UF}_4^b$	Uniaxial		-	1.554	1.551	Green
$\text{LiF}\cdot 4\text{UF}_4^b$	Biaxial	$\sim 10^\circ$	-	1.584	1.600	Green
$3\text{LiF}\cdot\text{ThF}_4^{d,e}$	Biaxial	$\sim 10^\circ$	-	1.480	1.488	Colorless
$7\text{LiF}\cdot 6\text{ThF}_4^d$	Uniaxial		+	1.502	1.508	Colorless
$\text{LiF}\cdot 2\text{ThF}_4^d$	Uniaxial		-	1.554	1.548	Colorless
$\text{LiF}\cdot 4\text{ThF}_4^{d,e}$	Biaxial	$\sim 10^\circ$	-	1.528	1.538	Colorless

^aAm. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 4-0857.

^bH. Insley et al., Optical Properties and X-Ray Diffraction Data for Some Inorganic Fluoride and Chloride Compounds, ORNL-2192 (Oct. 23, 1956).

^cW. W. Harris and R. A. Wolters, Optical Properties of UF_4 , MDDC-1662 (Nov. 5, 1947); USAEC, Abstracts of Declassified Documents, vol 2, p 103, Technical Information Div., Oak Ridge, Tenn., 1948.

^dR. E. Thoma et al., J. Phys. Chem. 63, 1266 (1959).

^eThis routinely observed biaxiality appears to be a function of strain, since the crystal type is tetragonal as determined by x-ray diffraction measurements (see Table A-2).

Table A-2. Crystallographic Properties of the Components and the Binary Compounds Which Occur in the System LiF-UF₄-ThF₄-BeF₂

Compound	Crystal System	Lattice Parameters				Space Group	X-Ray Density (g/cc)
		a ₀ (Å)	b ₀ (Å)	c ₀ (Å)	β		
LiF ^a	Cubic (face-centered)	4.0270				O _h ⁵ -Fm3m	2.638
BeF ₂ ^b	Hexagonal	4.72		5.18		D _{6h} ⁴ = C6 ₂ 2, D _{6h} ⁵ = C6 ₄ 2	
ThF ₄ ^c	Monoclinic	13.1	11.01	8.6	126°	C _{2h} ⁶ -C2/c	5.71
UF ₄ ^{c,d}	Monoclinic	12.82	10.74	8.41	126°10'	C _{2h} ⁶ -C2/c	6.70
7LiF·6UF ₄ ^e	Tetragonal	10.48		5.98		I4 ₁ /a	
3LiF·ThF ₄ ^f	Tetragonal	6.206		6.470		P4/nmm or P4/n	5.143
7LiF·6ThF ₄ ^f	Tetragonal	15.10		6.60		I4 ₁ /a	5.387
LiF·2ThF ₄ ^f	Tetragonal	11.307		6.399		Body-centered(?)	
LiF·4ThF ₄ ^f	Tetragonal	12.984		11.46			
2LiF·BeF ₂ ^g	Hexagonal	13.23		8.87			

^aAm. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 4-0857; H. E. Swanson and E. Tatge, J C Fel. Reports, NBS 1949.

^bThis is the β-quartz form of BeF₂ routinely observed in the systems described in this report. The β-quartz and three other forms of BeF₂ are described by A. V. Novoselova, Uspekhi Khim 27, 33 (1959).

^cW. H. Zachariasen, Acta Cryst. 2, 388 (1949).

^dAm. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 8-428.

^eL. A. Harris, The Crystal Structures of 7:6 Type Compounds of Alkali Fluorides with Uranium Tetrafluoride, ORNL CF-58-3-15 (Mar. 6, 1958).

^fL. A. Harris, G. D. White, and R. E. Thoma, J. Phys. Chem. 63, 1974 (1959).

^gAm. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 6-0557; E. Thilo and H. A. Lehmann, Z. anorg. Chem. 258, 332 (1949).

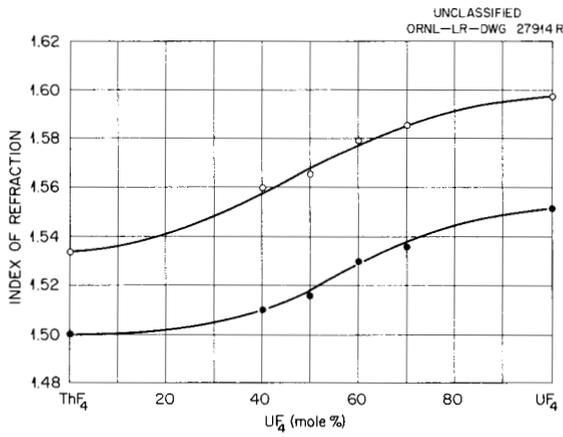


Fig. A-1. Refractive Indices of the UF₄-ThF₄ Solid Solutions.

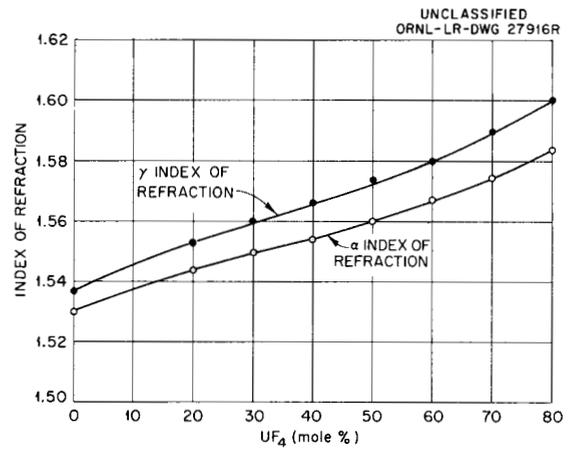


Fig. A-2. Refractive Indices of the LiF·4UF₄-LiF·4ThF₄ Solid Solutions.

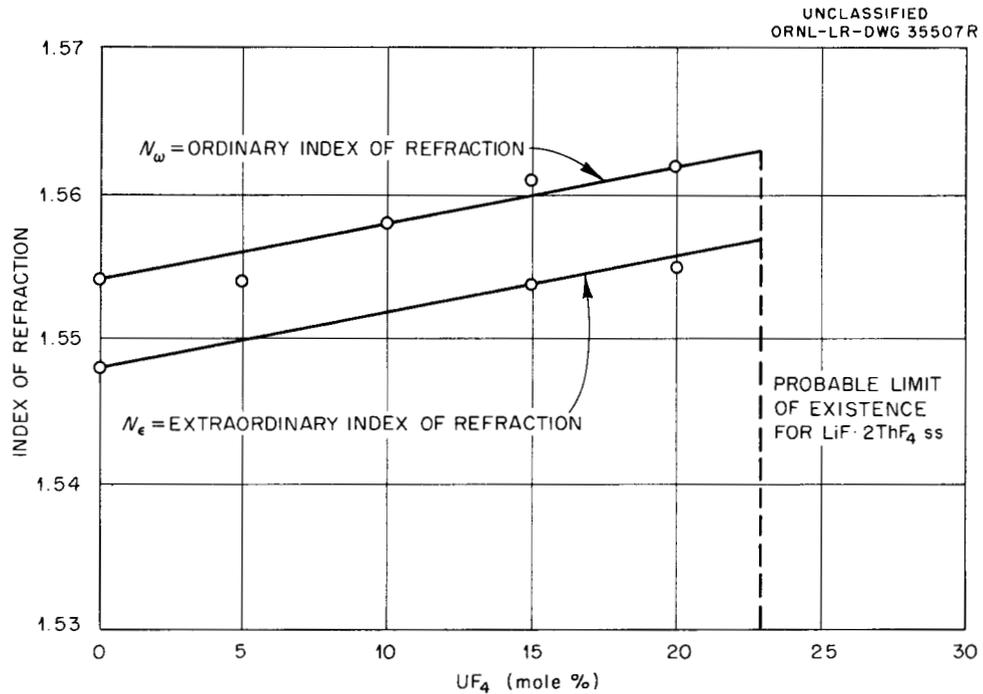


Fig. A-3. Refractive Indices of the LiF·2Th(U)F₄ Solid Solutions.

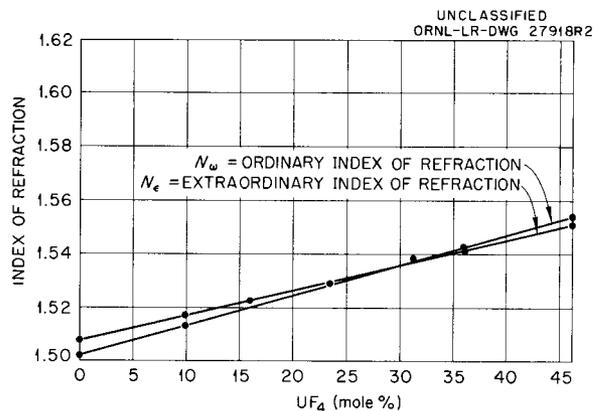


Fig. A-4. Refractive Indices of the $7\text{LiF}\cdot 6\text{UF}_4$ - $7\text{LiF}\cdot 6\text{ThF}_4$ Solid Solutions.

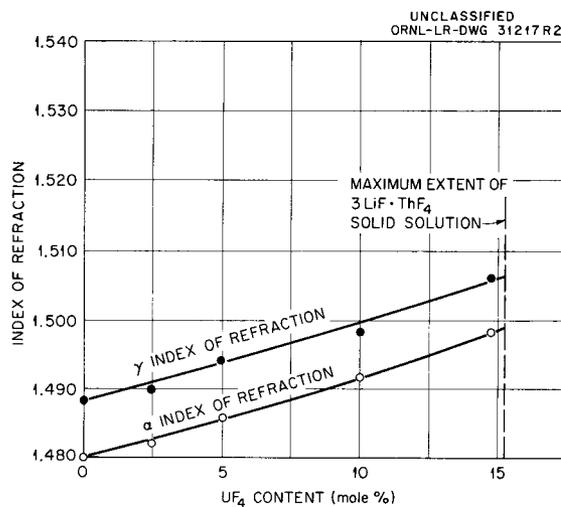


Fig. A-5. Refractive Indices of the $3\text{LiF}\cdot\text{Th(U)F}_4$ Solid Solutions.

Appendix B

X-RAY DIFFRACTION DATA FOR THE SOLID PHASES OBSERVED IN THE QUATERNARY SYSTEM $\text{LiF}-\text{BeF}_2-\text{UF}_4-\text{ThF}_4$

LiF^a		ThF_4		ThF_4 (continued)	
BeF_2^b		d (Å)	I/I_1	d (Å)	I/I_1
d (Å)	I/I_1				
		7.63	10	2.528	12
		5.24	10	2.495	12
4.09	70	4.75	20	2.361	5
3.21	100	4.46	12	2.350	10
2.367	100	4.29	20	2.338	10
2.189	100	4.02	60	2.259	5
2.154	100	3.80	100	2.242	5
1.905	70	3.72	5	2.196	5
1.748	50	3.63	50	2.156	15
1.606	35	3.43	15	2.132	35
1.591	20	3.35	50	2.113	35
1.550	30	3.04	5	2.067	5
1.484	30	2.848	5	2.040	20
1.320	30	2.796	5	2.023	20
1.233	15	2.747	15	1.985	35
1.208	15	2.723	5	1.965	15
		2.629	5	1.937	15
UF_4^c				1.922	25

Appendix B (continued)

ThF ₄ (continued)		3LiF·UF ₄ ^b (metastable)		7LiF·6UF ₄ ^b (continued)	
d (A)	I/I ₁	d (A)	I/I ₁	d (A)	I/I ₁
1.881	10	4.98	20	3.33	90
1.859	5.5	4.80	15	3.15	70
1.771	10	4.41	100	3.07	10
1.737	10	4.34	100	2.99	95
1.683	20	3.98	15	2.771	30
1.666	10	3.91	8	2.707	30
1.640	10	3.60	80	2.542	25
1.612	10	3.40	10	2.350	13
1.588	5	3.14	25	2.286	25
1.575	10	3.07	50	2.264	13
1.520	20	2.84	80	2.184	10
1.484	5	2.771	30	2.097	30
1.455	20	2.529	35	2.060	30
1.431	10	2.169	15	2.047	75
1.404	5	2.083	75	1.993	25
1.373	10	2.055	35	1.972	20
4LiF·UF ₄ ^b		1.943	50	1.947	25
d (A)	I/I ₁	1.913	25	1.924	15
5.67	20	1.861	30	1.909	30
5.46	25	1.751	25	1.854	45
5.13	70	1.723	25	1.825	20
4.93	100	1.685	25	1.773	20
4.55	45	1.662	8	1.757	25
4.44	100	1.646	20	1.709	15
4.23	7	1.599	8	1.680	15
3.82	40	7LiF·6UF ₄ ^b		1.625	15
3.55	30	d (A)	I/I ₁	1.579	25
3.03	50	6.61	6	1.562	8
2.89	25	5.97	20	LiF·4UF ₄ ^b	
2.866	30	5.82	15	d (A)	I/I ₁
2.747	50	5.24	90	7.02	8
2.468	40	5.15	10	6.33	12
2.398	20	4.65	10	6.07	5
2.221	40	4.37	13	5.73	25
2.167	75	3.95	55	4.98	8
2.074	20	3.85	13	4.70	25
2.025	20	3.68	20	4.25	90
1.872	20	3.49	75	3.88	20
1.836	25				

Appendix B (continued)

$\text{LiF}\cdot 4\text{UF}_4^{\text{b}}$ (continued)		$3\text{LiF}\cdot \text{ThF}_4^{\text{d}}$ (continued)		$\text{LiF}\cdot 2\text{ThF}_4^{\text{d}}$	
d (A)	I/I ₁	d (A)	I/I ₁	d (A)	I/I ₁
3.78	100	1.701	35	7.97	5
3.52	90	1.661	10	6.37	10
3.16	8	1.618	10	3.96	100
3.13	8	1.547	35	3.57	65
3.06	12	1.520	35	3.25	5
2.84	40			3.21	5
2.771	55			2.97	20
2.542	8	$7\text{LiF}\cdot 6\text{ThF}_4^{\text{d}}$		2.822	25
2.350	10			2.675	7
2.310	10	d (A)	I/I ₁	2.528	10
2.226	8			2.388	5
2.000	10	6.07	15	2.123	85
2.088	35	5.91	20	2.053	30
2.016	60	5.36	90	2.001	65
1.991	50	5.25	15	1.787	7
1.888	20	4.95	30	1.701	10
1.819	8	4.85	20	1.689	5
1.767	25	4.75	100	1.603	5
		4.01	85	1.519	5
		3.92	15		
		3.74	15	$\text{LiF}\cdot 4\text{ThF}_4^{\text{d}}$	
		3.55	65	d (A)	I/I ₁
		3.44	10		
		3.39	70	8.34	3
		3.29	60	7.76	3
		3.03	100	6.51	5
		2.814	25	5.80	25
		2.747	25	4.62	5
		2.578	20	4.33	70
		2.430	10	3.88	100
		2.392	10	3.60	60
		2.302	20	3.25	10
		2.137	20	2.92	25
		2.018	5	2.822	25
		2.001	15	2.603	10
		1.892	55	2.398	10
		1.859	15	2.137	25
		1.804	15	2.053	35
		1.680	15	2.040	10
		1.653	20	2.018	10
		1.600	20	2.005	30
$3\text{LiF}\cdot \text{ThF}_4^{\text{d}}$					
d (A)	I/I ₁				
6.42	100				
4.46	100				
4.37	100				
3.62	85				
3.09	55				
2.866	70				
2.788	30				
2.542	25				
2.327	10				
2.189	20				
2.104	65				
2.071	25				
2.036	40				
1.959	30				
1.933	60				
1.877	25				
1.771	25				
1.743	30				

Appendix B (continued)

LiF·4ThF ₄ ^d (continued)		LiF·BeF ₂ ^f		LiF·BeF ₂ ^f (continued)	
d (Å)	I/I ₁	d (kX)	I/I ₁	d (kX)	I/I ₁
1.937	20	4.353	20	2.040	20
1.820	20	3.180	50	1.829	10
1.778	3	3.084	30	1.691	10
1.725	5	2.926	20	1.558	5
1.719	5	2.836	5	1.488	2
1.666	5	2.780	50	1.439	2
1.605	5	2.739	10	1.324	10
1.595	5	2.455	40	1.303	1
1.563	5	2.259	50	1.244	2
		2.201	100	1.233	1
		2.074	80	1.216	2
2LiF·BeF ₂ ^e					

^aAm. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 4-0857.

^bH. Insley et al., Optical Properties and X-Ray Diffraction Data for Some Inorganic Fluoride and Chloride Compounds, ORNL-2192 (Oct. 23, 1956).

^cAm. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 8-428.

^dR. E. Thoma et al., J. Phys. Chem. 63, 1266 (1959).

^eAm. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 6-0557.

^fE. Thilo and H. A. Lehmann, Z. anorg. Chem. 258, 332-55 (1949).

Appendix C

LIQUIDUS TEMPERATURES AND PRIMARY PHASES FOR SPECIFIC COMPOSITIONS

Code	Composition (mole %)				Liquidus Temperature (°C)	Primary Phase or Phases
	LiF	BeF ₂	UF ₄	ThF ₄		
C-9		100			548	BeF ₂
C-10	100				845	LiF
C-74	69	31			530	LiF
C-75	67	30.5	2.5		464	LiF
C-111	71	16	1	12	505	3LiF·ThF ₄ ss
C-112	50	50			370	2LiF·BeF ₂
C-126	53	46	1		400	2LiF·BeF ₂
C-127	58	35		7	460	LiF·2ThF ₄
C-128	71			29	568*	3LiF·ThF ₄ and 7LiF·6ThF ₄
C-130	62	37	1		440	2LiF·BeF ₂
C-131	60	36	4		450	7LiF·6UF ₄
C-132	57	43			420	2LiF·BeF ₂
C-133 (111-a)	71	16		13	505	3LiF·ThF ₄ ss
C-134	62	36.5	0.5	1	445	2LiF·BeF ₂
C-136	70	10	20		500	7LiF·6UF ₄
BeLT-15	67	18		15	500	7LiF·6ThF ₄ and 3LiF·ThF ₄ ss
BULT 4-0.5U	65	30.5	0.5	4	453	3LiF·ThF ₄ ss
BULT 4-1U	65	30	1	4	448	2LiF·BeF ₂ and 3LiF·ThF ₄ ss
BULT 14-0.5U	67	18.5	0.5	14	500	7LiF·6(Th,U)F ₄ ss and 3LiF·ThF ₄ ss
FULi 73	73		27		490*	4LiF·UF ₄ and 7LiF·6UF ₄

*The solidus and liquidus coincide, since these are eutectic compositions.

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