PHASE EQUILIBRIA IN MOLTEN SALT

BREEDER REACTOR FUELS.

I. THE SYSTEM $LiF-BeF_2-UF_4-ThF_4$

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OAK RIDGE NATIONAL LABORATORY
operated by
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CONTENTS

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ABSTRACT

The phase equilibrium relationships for the systems limiting the quaternary system LiF-BeF$_2$-UF$_4$-ThF$_4$ 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,

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[1]S. Glasstone, Principles of Nuclear Reactor Engineering, p 841, Van Nostrand, Princeton, N.J., 1955.
[2]H. G. MacPherson, p 567 in Fluid Fuel Reactors, ed. by J. A. Lane, H. G. MacPherson, and F. Maslan, Addison-Wesley, Reading, Mass., 1958.
[3]W. 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

[4]Ibid., p 588.
[5]Ibid., p 570.
[6]MSR Quar. Prog. Rep. Jan. 31, 1958, ORNL-2474, p 1.
[7]H. G. MacPherson, ORNL, personal communication.
[8]W. 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 $LiF-BeF_2-UF_4-ThF_4$ 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 $LiF-BeF_2-UF_4-ThF_4$ 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

[9]C. J. Barton et al., J. Am. Ceram. Soc. 41, 63–69 (1958).
[10]C. J. Barton et al., J. Phys. Chem. 62, 665 (1958).
[11]H. A. Friedman, J. Am. Ceram. Soc. 42, 284–85 (1959).
[12]P. A. Tucker and E. F. Joy, Am. Ceram. Soc. Bull. 36, 52–54 (1957).
[13]L. 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 thermocouple[11] 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 UF_4 was a product of Mallinckrodt Chemical Works. The ThF_4 was obtained from Iowa State College and from National Lead Company. The BeF_2 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.

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

Because thorium[15] and uranium fluorides are easily converted to ox-
ides 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, $NH_4F \cdot HF$
was added to the mixture before melting. As such mixtures are heated
the water evaporates from the system. Trace quantities of oxide impuri-
ties are converted to products which have not yet been identified but
which are likely to be ammonium "fluometallates."[16,17] Upon further heat-
ing the ammonium "fluometallates" and the excess $NH_4F \cdot HF$ 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 des-
iccant. They were ground to pass a 100-mesh screen and used in the
quenching experiments. The heating cycles were conducted in closed cap-
sules 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 high-
est atomic number range. It might, therefore, be expected that the di-
verse 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

[15]R. W. M. D'Eye, J. Chem. Soc. 1958, 196.
[16]MSR Quar. Prog. Rep. Apr. 30, 1959, ORNL-2723, p 93.
[17]B. 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]

[a]T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4824 (1954).

[b]R. E. Thoma et al., "Phase Equilibria in the Systems BeF_2-ThF_4 and LiF-BeF_2-ThF_4," J. Phys. Chem., in press.

[c]D. M. Roy, R. Roy, and E. F. Osborn, J. Am. Ceram. Soc. 36, 185 (1953).

[d]M. P. Boryenkova et al., Zhur. Neorg. Khim. 1, 2071 (1956).

[e]R. E. Thoma et al., J. Phys. Chem. 63, 1266 (1959).

[f]J. Asker, E. R. Segnit, and A. W. Wylie, J. Chem. Soc. 1952, 4470.

[g]A. J. Darnell and F. J. Keneshea, Jr., J. Phys. Chem. 62, 1143 (1958).

[h]H. 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 BeF_2 is analogous to that of SiO_2, as was predicted by Goldschmidt;[19] all known modifications crystallize as SiO_2-type structures. Being similar to SiO_2, BeF_2 readily forms a glass upon cooling from the liquid state. For this reason, establishing solid-state equilibria with BeF_2, in which devitrification of this glass must be accomplished, is often a very slow process.

Optical and crystallographic properties for the compounds LiF, BeF_2, ThF_4, and UF_4 may be found in Appendix A. Their x-ray diffraction data are listed in Appendix B.

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

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

3.2 The Systems BeF$_2$-ThF$_4$ and BeF$_2$-UF$_4$

The systems BeF$_2$-ThF$_4$[20] (Fig. 1) and BeF$_2$-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
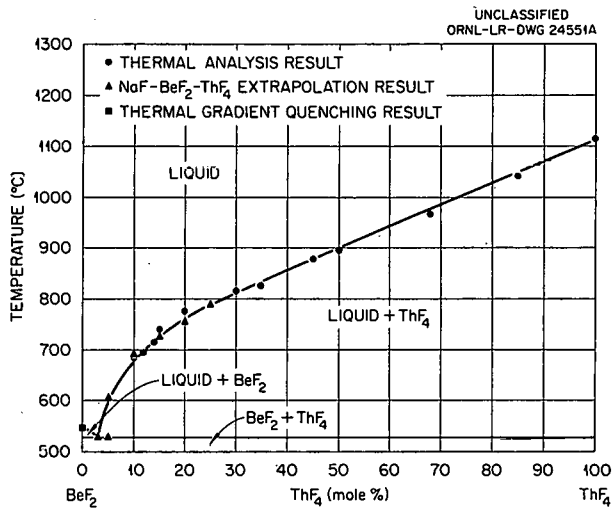
Fig. 1. The System BeF$_2$-ThF$_4$.

[20]R. E. Thoma et al., "Phase Equilibria in the Systems BeF$_2$-ThF$_4$ and LiF-BeF$_2$-ThF$_4$," J. Phys. Chem., in press.
[21]T. B. Rhinehammer, P. A. Tucker, and E. F. Joy, Phase Equilibria in the System BeF$_2$-UF$_4$, MLM-1082 (to be published).
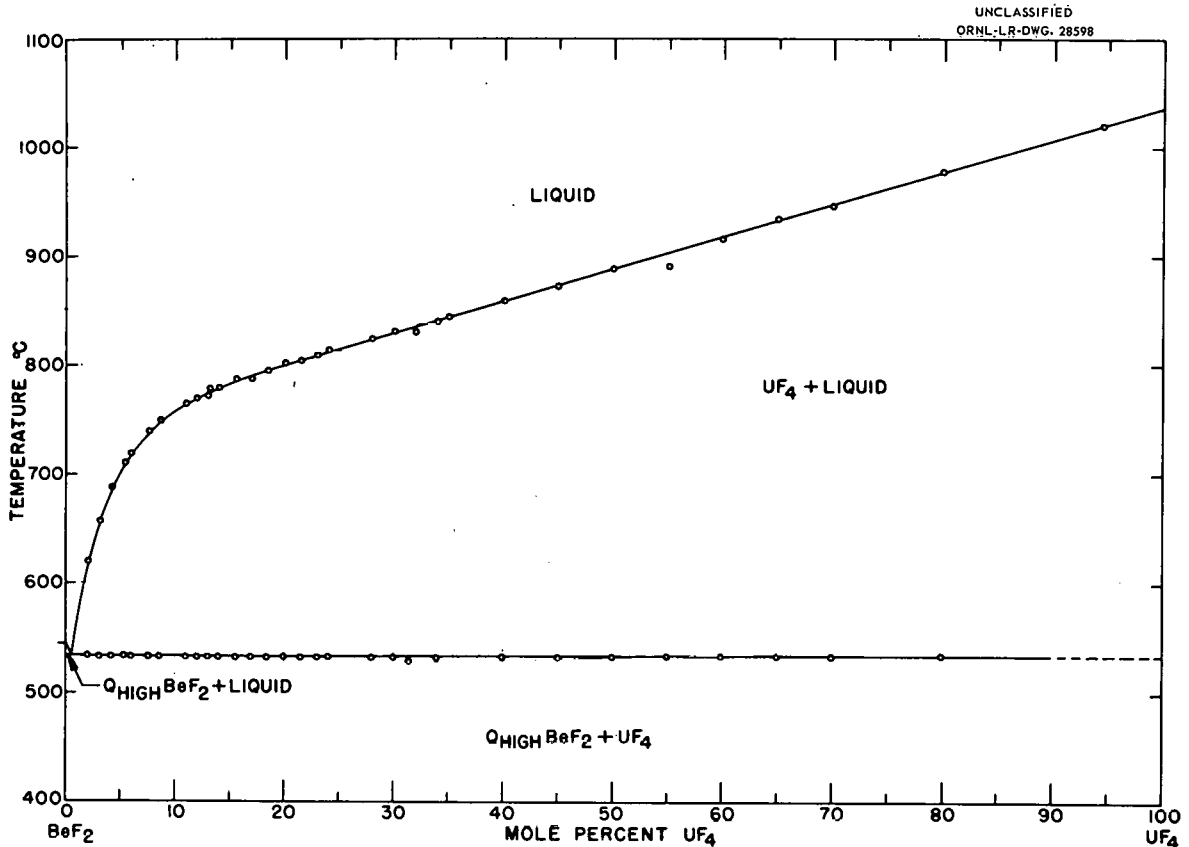
Fig. 2. The System BeF$_2$-UF$_4$.

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 $LiF-BeF_2$

A phase diagram of the system $LiF-BeF_2$[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

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[22]R. E. Thoma (ed.), Phase Diagrams of Nuclear Reactor Materials, ORNL-2548, p 33 (Nov. 2, 1959).
[23]R. E. Moore, C. J. Barton, R. E. Thoma, and T. N. McVay, ORNL, unpublished data.
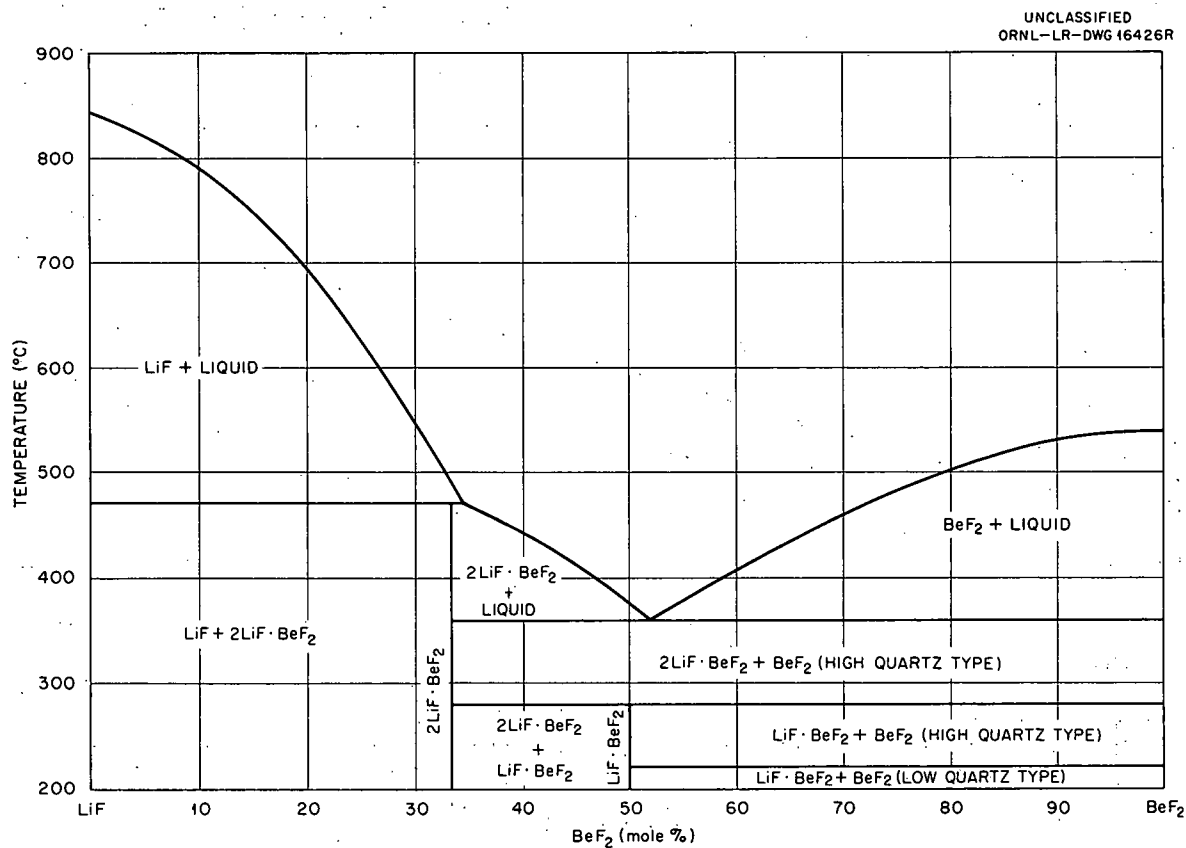
Fig. 3. The System $LiF-BeF_2$.

Mound Laboratory.[24] These diagrams are revisions of those published by earlier investigators.[25-27] Two equilibrium compounds occur in the system LiF-BeF$_2$, the incongruently melting compound 2LiF·BeF$_2$ and the subsolidus compound LiF·BeF$_2$. Unsuccessful attempts have been made by the authors to produce the reported compounds 3LiF·2BeF$_2$[28] and LiF·2BeF$_2$[25] by devitrification of LiF-BeF$_2$ glass and by solid-state equilibration of mixtures of BeF$_2$ and 2LiF·BeF$_2$. Because the special purification techniques described earlier in this report were not used by other investigators[25,28] reports of the existence of 3LiF·2BeF$_2$ and LiF·2BeF$_2$ should be considered tentative.

The optical properties, crystallographic properties, and x-ray diffraction data for the compounds 2LiF·BeF$_2$ and LiF·BeF$_2$ 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-BeF$_2$*

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

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

Cooling mixtures of LiF and BeF$_2$ slowly from the liquid to the solid state rarely produces equilibrium solids, for the subsolidus reaction

[24]J. F. Eichelberger, C. R. Hudgens, L. V. Jones, and T. B. Rhinehammer, Mound Laboratory, unpublished data.
[25]D. M. Roy et al., J. Am. Ceram. Soc. 37, 300 (1954).
[26]A. V. Novoselova et al., J. Phys. Chem. (USSR) 26, 1244 (1952).
[27]J. L. Speirs, Ph.D. thesis, University of Michigan, May 29, 1952.
[28]E. Thilo and H. A. Lehmann, Z. anorg. Chem. 258, 332–55 (1949); Ceram. Abstr. 1950, 82f.

$Li_2BeF_4 + BeF_2 \rightarrow 2LiBeF_3$ proceeds very slowly. The compound $LiF \cdot BeF_2$ 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 $LiF\text{-}BeF_2$ 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 $2LiF \cdot BeF_2$ 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 gases[37] in $LiF\text{-}BeF_2$ solvents have been reported. The reactions M + HF (M = Fe, Cr, or Ni),[38] CeF_3 + BeO,[39] and CeF_3 + H_2O[40] in $LiF\text{-}BeF_2$ solvents have been investigated, as have the exchange reactions between CeF_3 and CeO_2 and between HfC and HfF_4.[41]

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

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

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

[32]Ibid., p 44.

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

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

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

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

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

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

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

[40]Ibid., p 88.

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

3.4 The System LiF-ThF$_4$

One congruently melting compound (3LiF·ThF$_4$) and three incongruently melting compounds (7LiF·6ThF$_4$, LiF·2ThF$_4$, and LiF·4ThF$_4$) are formed in the system LiF-ThF$_4$[42] (Fig. 4). Optical properties, crystallographic 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-ThF$_4$ mixtures containing more than 25 and less than 66.7 mole % ThF$_4$ regularly contain 3LiF·ThF$_4$ and LiF·2ThF$_4$ if cooled from the liquid state under non-equilibrium conditions.[43] The solidification temperature is not significantly changed by the failure of 7LiF·6ThF$_4$ to form.[42] The equilibrium

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Fig. 4. The System LiF-ThF$_4$.

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[42]R. E. Thoma et al., J. Phys. Chem. **63**, 1266 (1959).
[43]R. 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-ThF$_4$*

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

*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 (4LiF·UF$_4$, 7LiF·6UF$_4$, and LiF·4UF$_4$) are formed in the system LiF-UF$_4$[9] (Fig. 5). The metastable

Fig. 5. The System LiF-UF$_4$.

compound 3LiF·UF$_4$ is readily formed from melts containing approximately 25 mole % UF$_4$ at temperatures above the incongruent melting point of 4LiF·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.
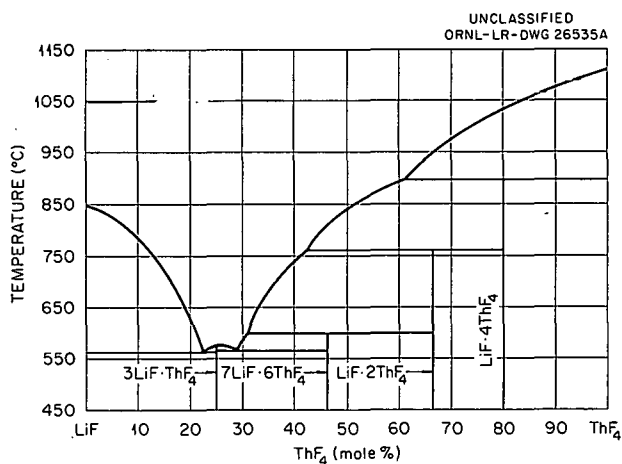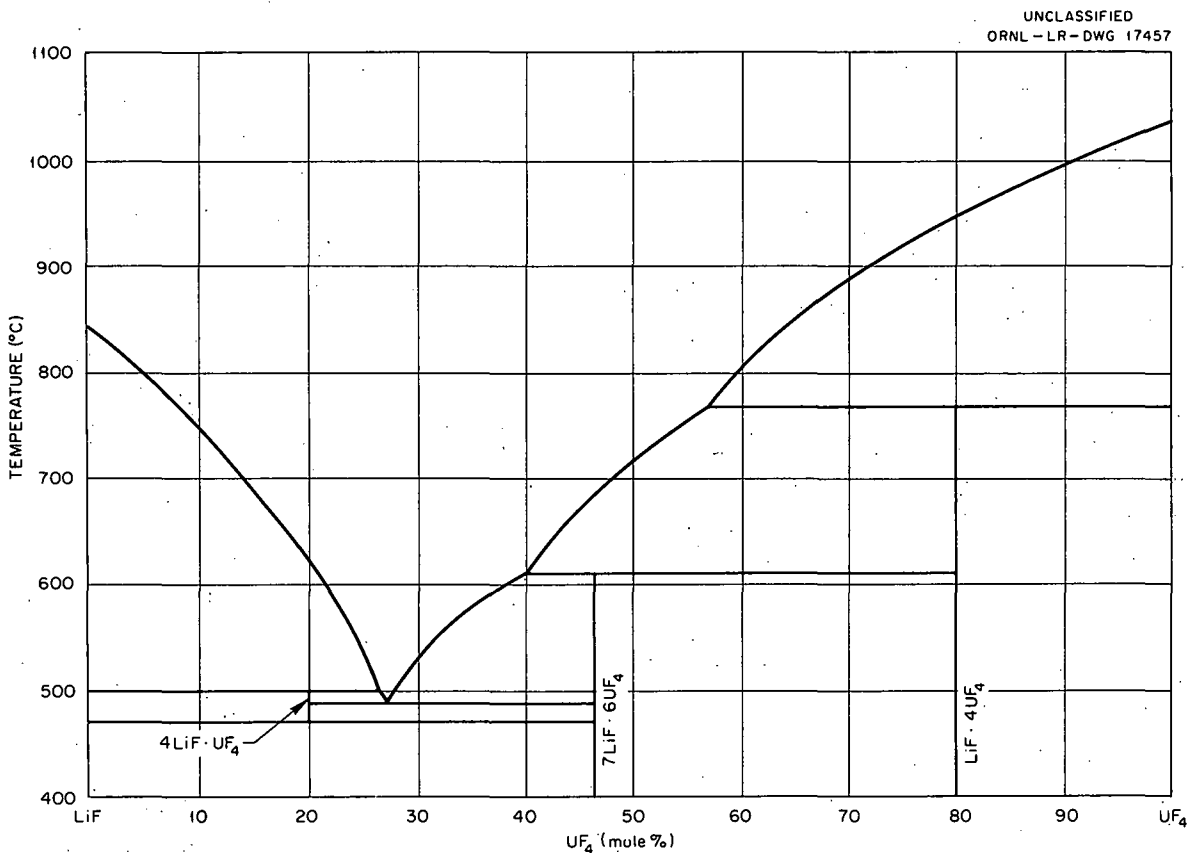
The optical properties (except for $3LiF \cdot UF_4$), crystallographic properties, and x-ray diffraction data for these compounds may be found in Appendixes A and B. The compositions and temperatures of the four invariant points and the lower temperature limit of stability for $4LiF \cdot UF_4$ may be found in Table 4. The systems $LiF-ThF_4$ and $LiF-UF_4$ are similar

Table 4. Invariant Equilibria in the System $LiF-UF_4$*

Mole % UF₄ in Liquid	Invariant Temperature (°C)	Type of Equilibrium	Phases Present
—	470	Lower stability limit for $4LiF \cdot UF_4$	LiF, $4LiF \cdot UF_4$, $7LiF \cdot 6UF_4$
26	500	Peritectic	LiF, $4LiF \cdot UF_4$, liquid
27	490	Eutectic	$4LiF \cdot UF_4$, $7LiF \cdot 6UF_4$, liquid
40	610	Peritectic	$7LiF \cdot 6UF_4$, $LiF \cdot 4UF_4$, liquid
57	775	Peritectic	$LiF \cdot 4UF_4$, 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 $7LiF \cdot 6ThF_4$ and $7LiF \cdot 6UF_4$ form a continuous series of solid solutions as do the compounds $LiF \cdot 4ThF_4$ and $LiF \cdot 4UF_4$. 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 $LiF-UF_4$ solvents have been investigated. The vapor pressures of $LiF-UF_4$ mixtures containing 10 and 20 mole % LiF have been reported.[48]
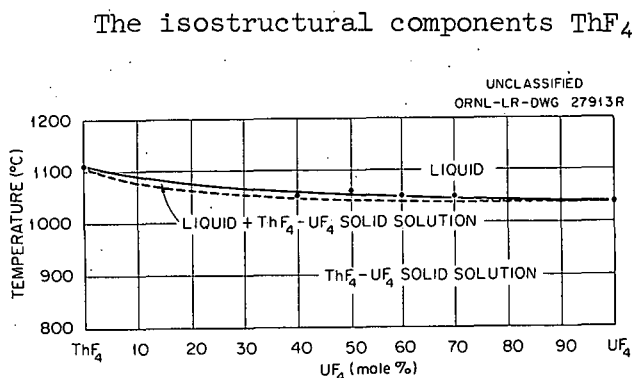
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[44]R. E. Thoma et al., J. Am. Ceram. Soc. 42, 21–26 (1959).

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

[46]Ibid., p 102.

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

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

3.6   The System UF$_4$-ThF$_4$

The isostructural components ThF$_4$ and UF$_4$ form a continuous series

Fig. 6.   The System UF$_4$-ThF$_4$.

of solid solutions without maximum or minimum[49] (Fig. 6). The indices of refraction of the ThF$_4$-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 LiF-BeF$_2$-UF$_4$

No ternary compounds form within the system LiF-BeF$_2$-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 LiF-BeF$_2$-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]

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

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

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

[52]R. 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).

[53]R. 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).

[54]R. 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.
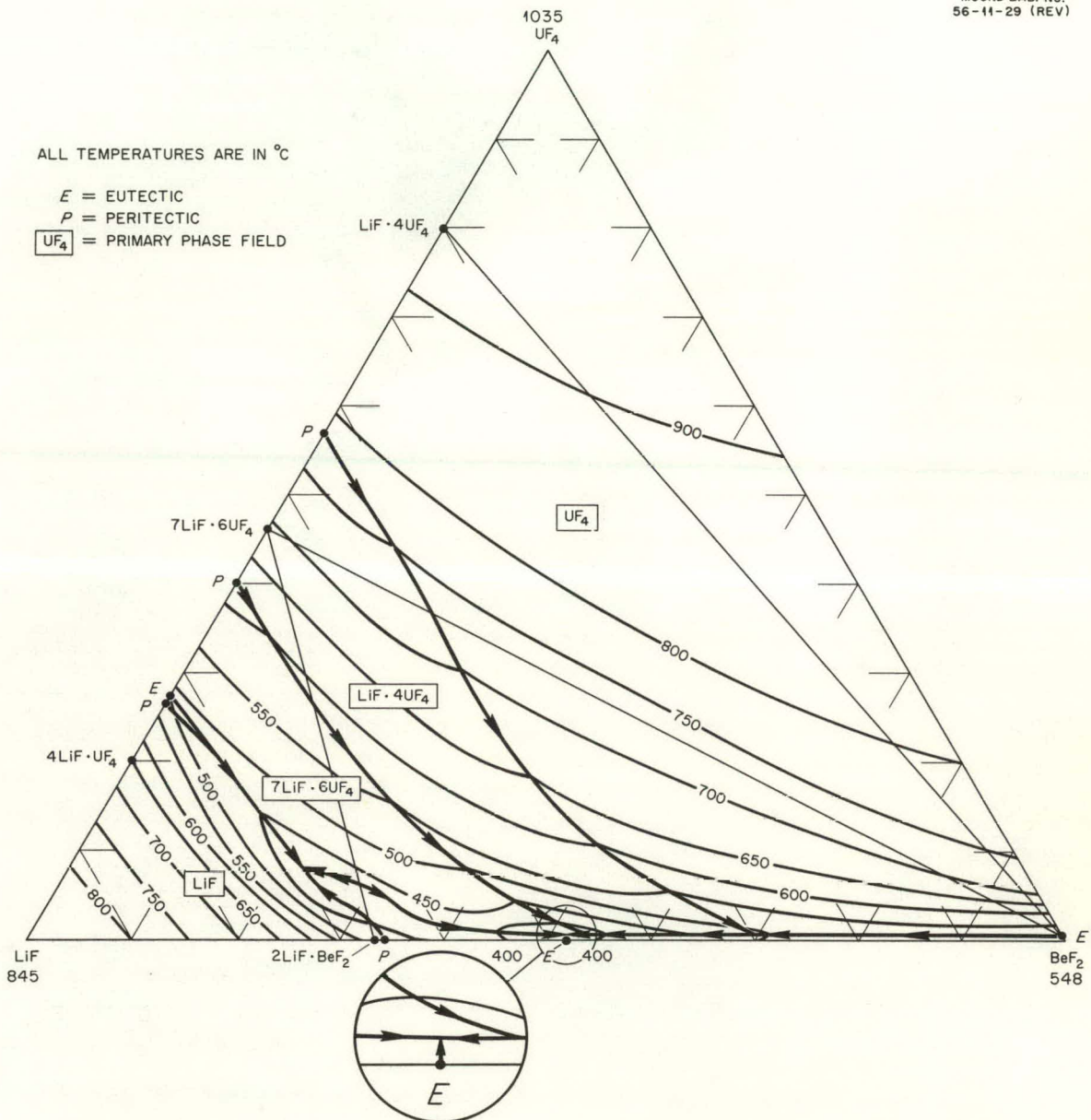
Fig. 7. The System LiF-BeF$_2$-UF$_4$.

Numerous investigations of the interactions of molten mixtures of LiF, BeF$_2$, and UF$_4$ with other substances have been reported. The solu-
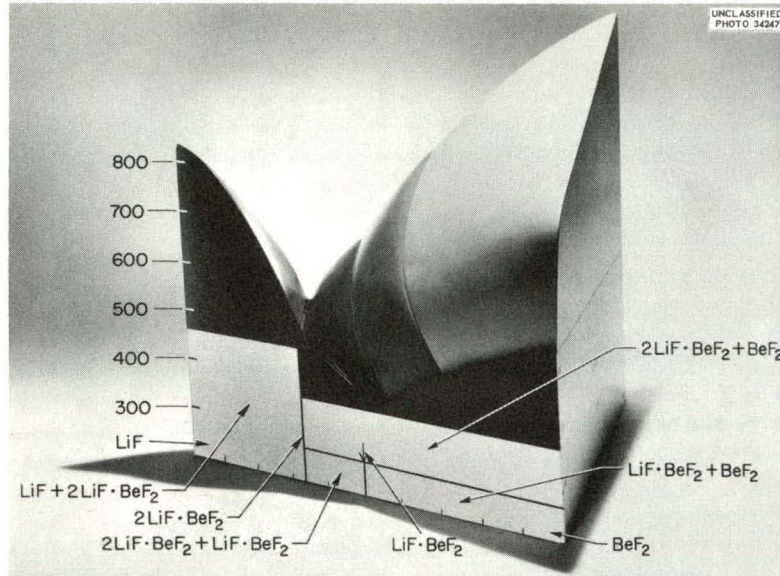
Fig. 8.   The System LiF-BeF$_2$-UF$_4$.

Table 5.   Invariant Equilibria in the System LiF-BeF$_2$-UF$_4$*

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-BeF$_2$-UF$_4$ 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 $LiF-BeF_2-UF_4$ solvents and the reactions of BeO[56] and steam[57] 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 $LiF-UF_4-BeF_2$ 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 purification[64] have been reported for $LiF-UF_4-BeF_2$ mixtures.

3.8 The System $LiF-BeF_2-ThF_4$

The phase equilibria in the system $LiF-BeF_2-ThF_4$ (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 $3LiF \cdot ThF_4$ 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

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

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

[57] Ibid., p 87.

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

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

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

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

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

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

[64] J. E. Eorgan et al., Reactor Chem. Ann. Prog. Rep. Jan. 31, 1960, ORNL-2931, p 64.
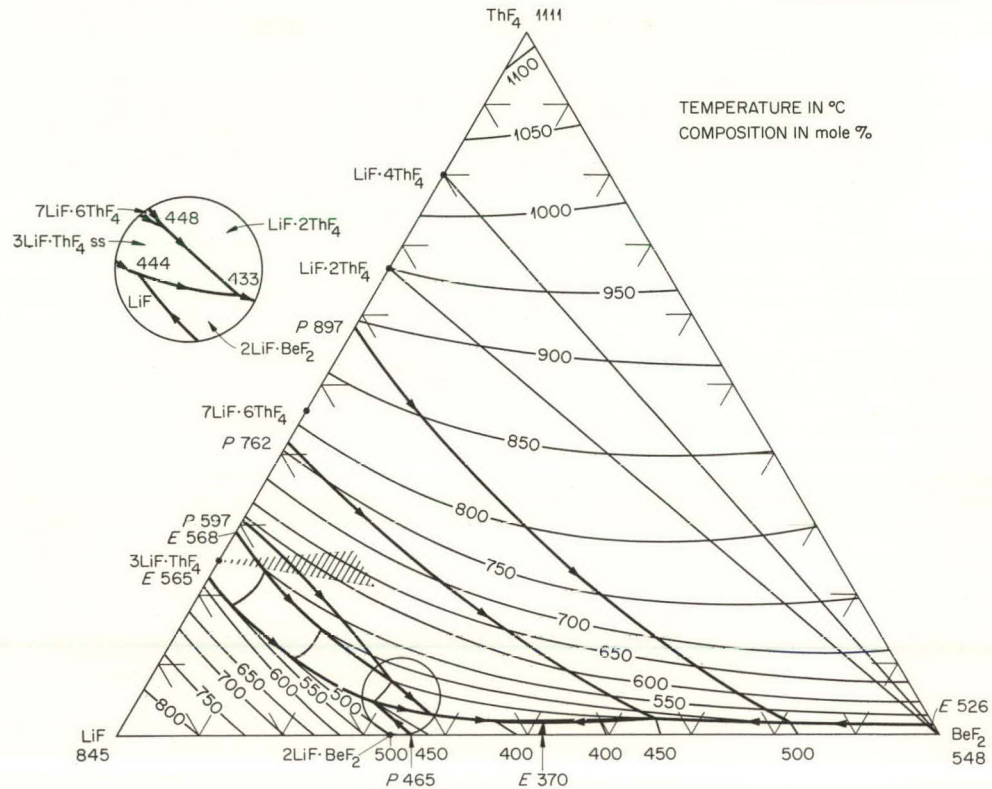
Fig. 9. The System LiF-BeF$_2$-ThF$_4$.

Table 7. Limits of Single-Phase
3LiF·ThF$_4$ 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).

in 3LiF·ThF$_4$ 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-BeF$_2$ 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. Consequently, all the solid phases formed in the system, except for members of the 3LiF·ThF$_4$ 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.
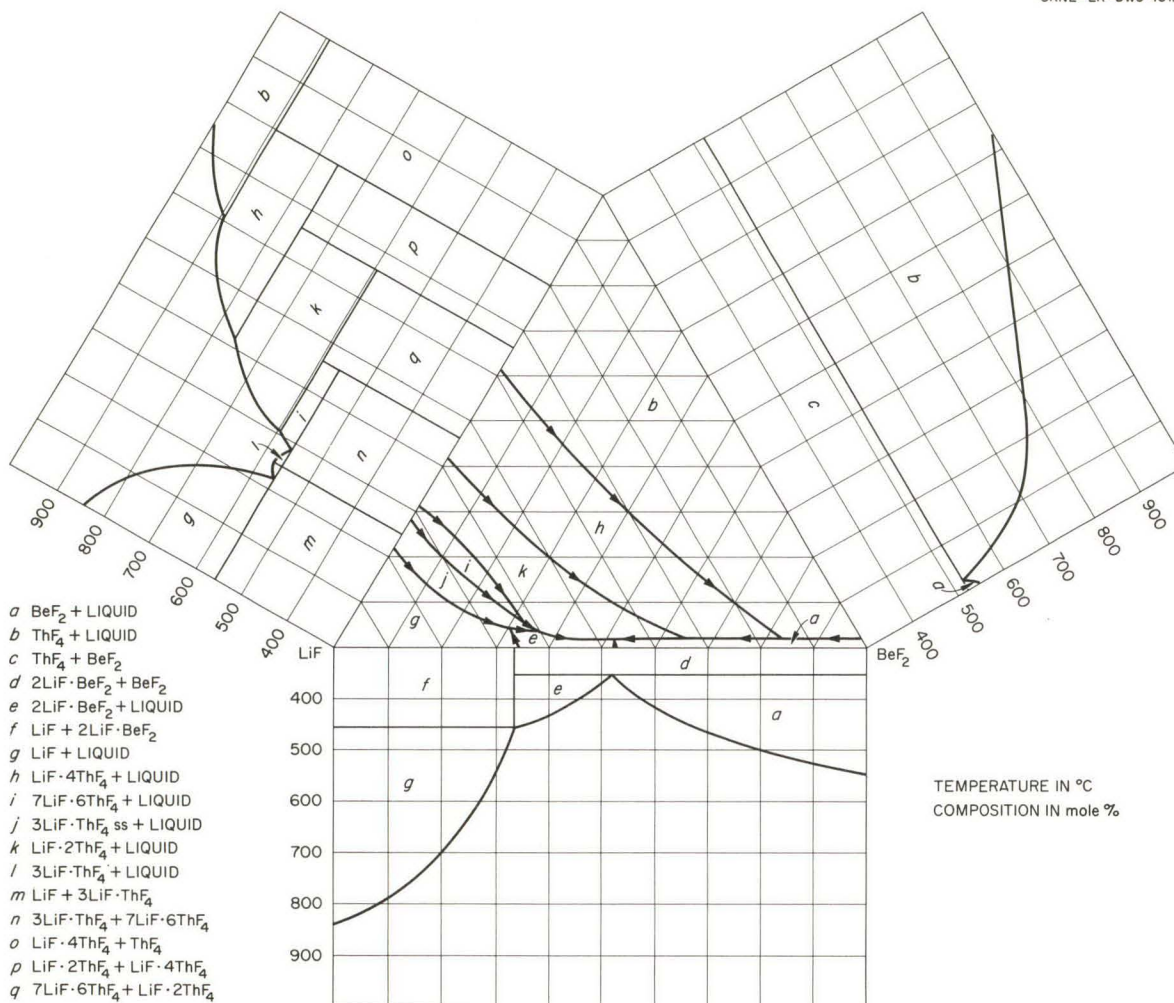
Fig. 10.   The System LiF-BeF$_2$-ThF$_4$.

The equilibrium phase behavior which will occur in several selected LiF-BeF$_2$-ThF$_4$ compositions is described in Table 9.

When mixtures of LiF-BeF$_2$-ThF$_4$ 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]

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

[66]R. 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).
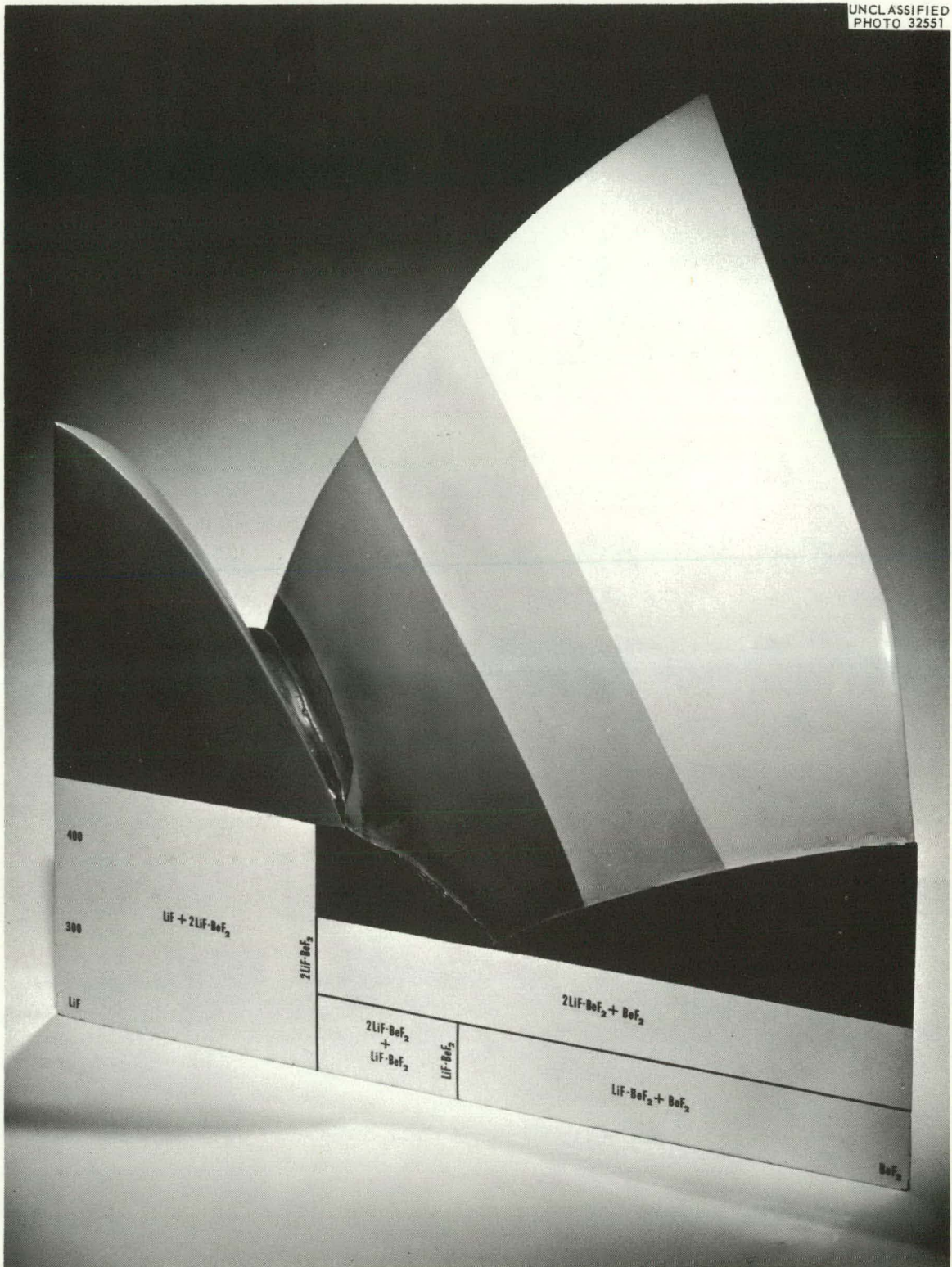
Fig. 11. The System LiF-BeF$_2$-ThF$_4$.
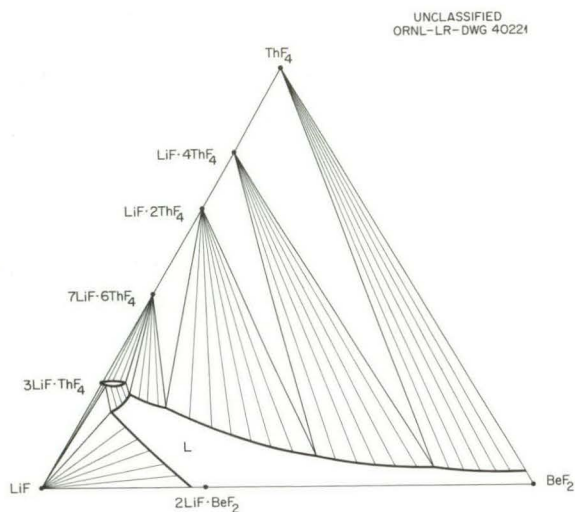
Fig. 12. The System LiF-BeF$_2$-ThF$_4$: 550°C Isotherm.
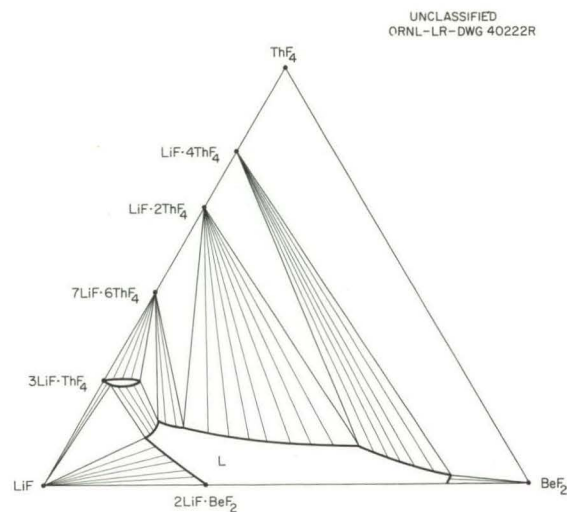
Fig. 13. The System LiF-BeF$_2$-ThF$_4$: 497°C Isotherm.
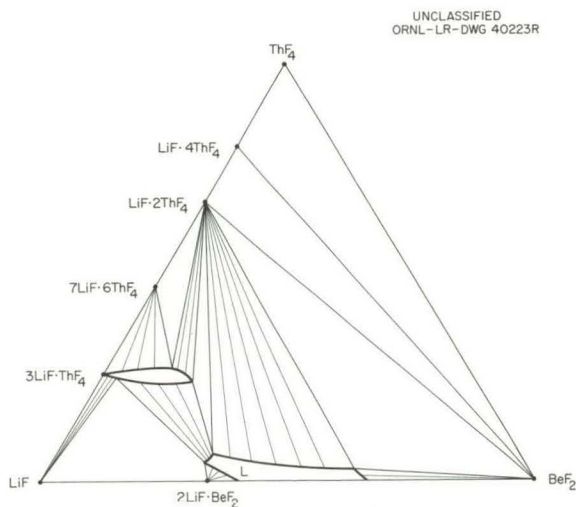
Fig. 14. The System LiF-BeF$_2$-ThF$_4$: 444°C Isotherm.
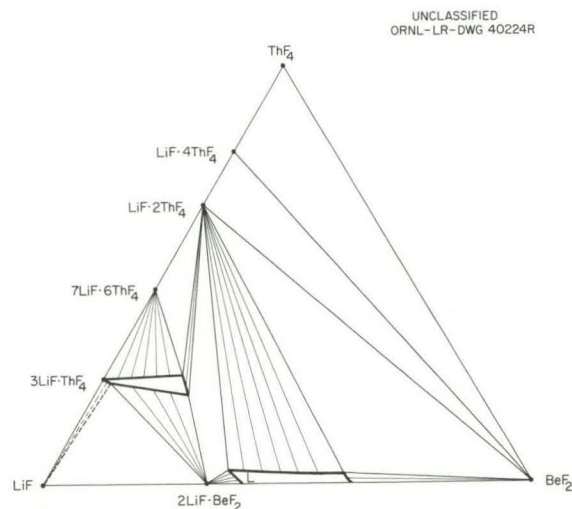
Fig. 15. The System LiF-BeF$_2$-ThF$_4$: 433°C Isotherm.

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-BeF$_2$-ThF$_4$ and LiF-BeF$_2$-UF$_4$ are very similar. In both, the primary phase fields of the LiF-BeF$_2$ compounds occupy a small area, and the lowest liquidus temperatures are very near those in the system LiF-BeF$_2$. 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-BeF$_2$-ThF$_4$*

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-BeF$_2$-ThF$_4$ 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-BeF$_2$-ThF$_4$ (67.5-17.5-15 Mole %), BeLT-15, ORNL CF-59-4-49 (Apr. 13, 1959).

system LiF-BeF$_2$-ThF$_4$ tend to occur at somewhat higher temperatures than those in the system LiF-BeF$_2$-UF$_4$.

Several investigations of the interactions of molten mixtures of LiF, BeF$_2$, and ThF$_4$ have been reported. The precipitation of ThO$_2$ from LiF-BeF$_2$-ThF$_4$ mixtures by steam[40] has been studied. Attempts to remove barium from LiF-BeF$_2$-ThF$_4$ mixtures by adding Cr$_2$O$_3$ or BeO were unsuccessful, as were attempts to remove cerium by adding BeO or Al$_2$O$_3$.[41] The segregation effect of thermal cycling on LiF-BeF$_2$-ThF$_4$ mixtures has been reported.[60,63]

3.9 The System BeF$_2$-ThF$_4$-UF$_4$

The great similarity of the binary systems BeF$_2$-UF$_4$ and BeF$_2$-ThF$_4$ (Sec 3.2) and the continuous solid solution between UF$_4$ and ThF$_4$ (Sec 3.6)

indicate that the phase equilibria in the system BeF_2-ThF_4-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
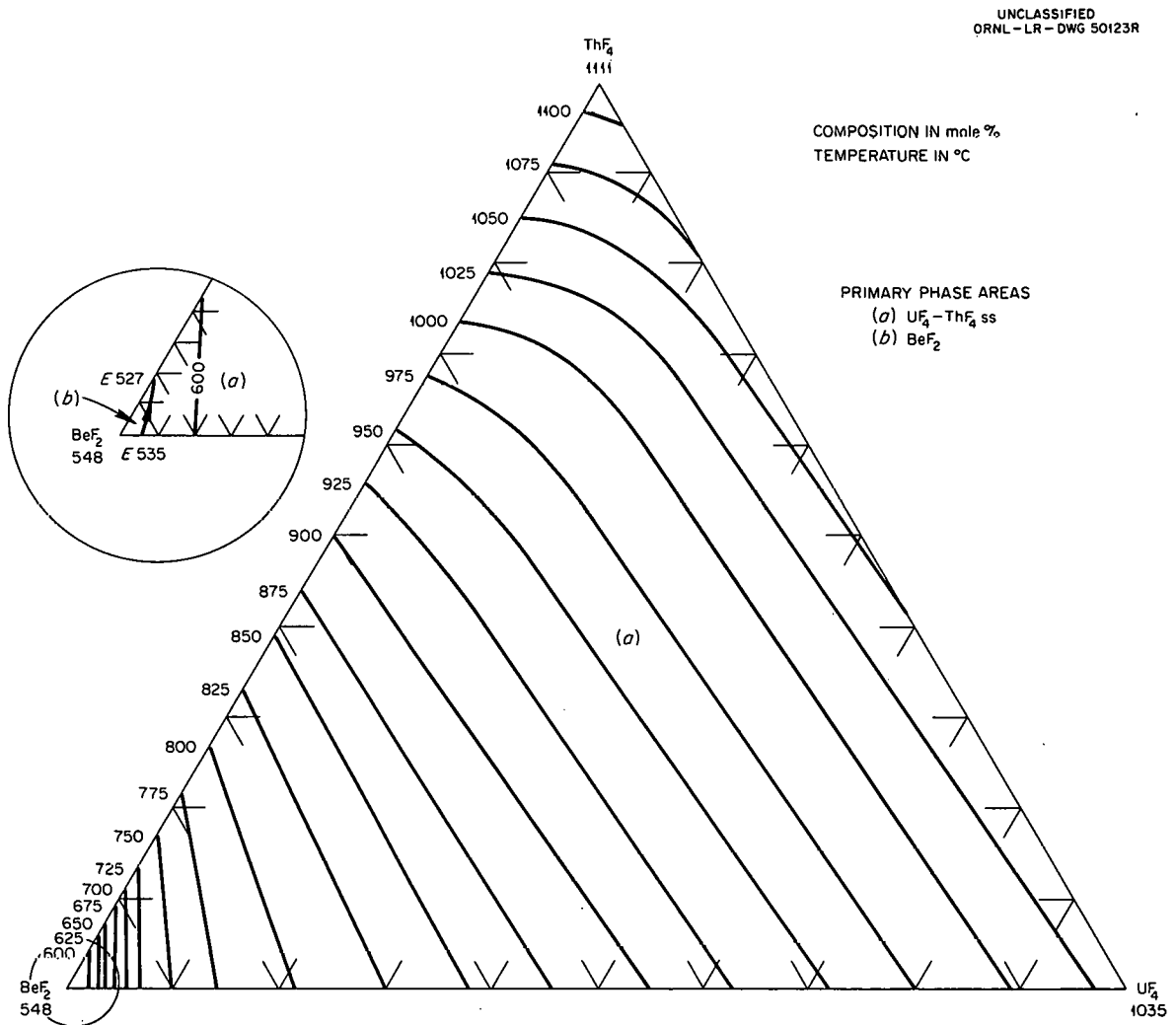
Fig. 16. The System BeF_2-UF_4-ThF_4.

area of the UF_4-ThF_4 solid solution. The only solid phases existing at equilibrium are BeF_2 and the UF_4-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

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[67]C. 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 $LiF-UF_4-ThF_4$

The system $LiF-UF_4-ThF_4$[49] (Figs. 17 and 18) is characterized by extensive ternary solid solutions[68] which are shown in Figs. 19–22. The

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[68]The phrase "ternary solid solution" as used here implies that the solid solution composition lies within the system $LiF-UF_4-ThF_4$. 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.
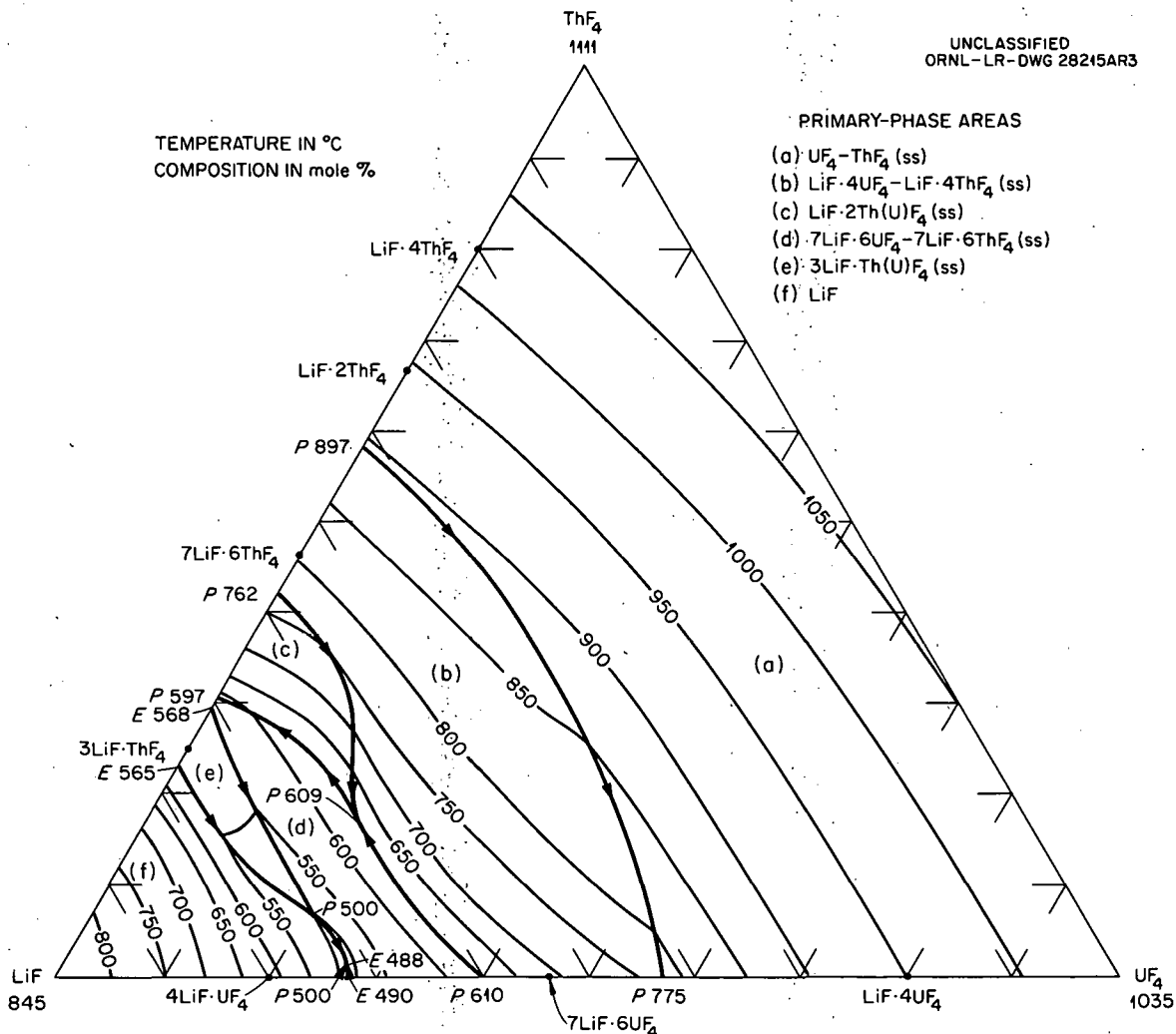
Fig. 17. The System $LiF-UF_4-ThF_4$.
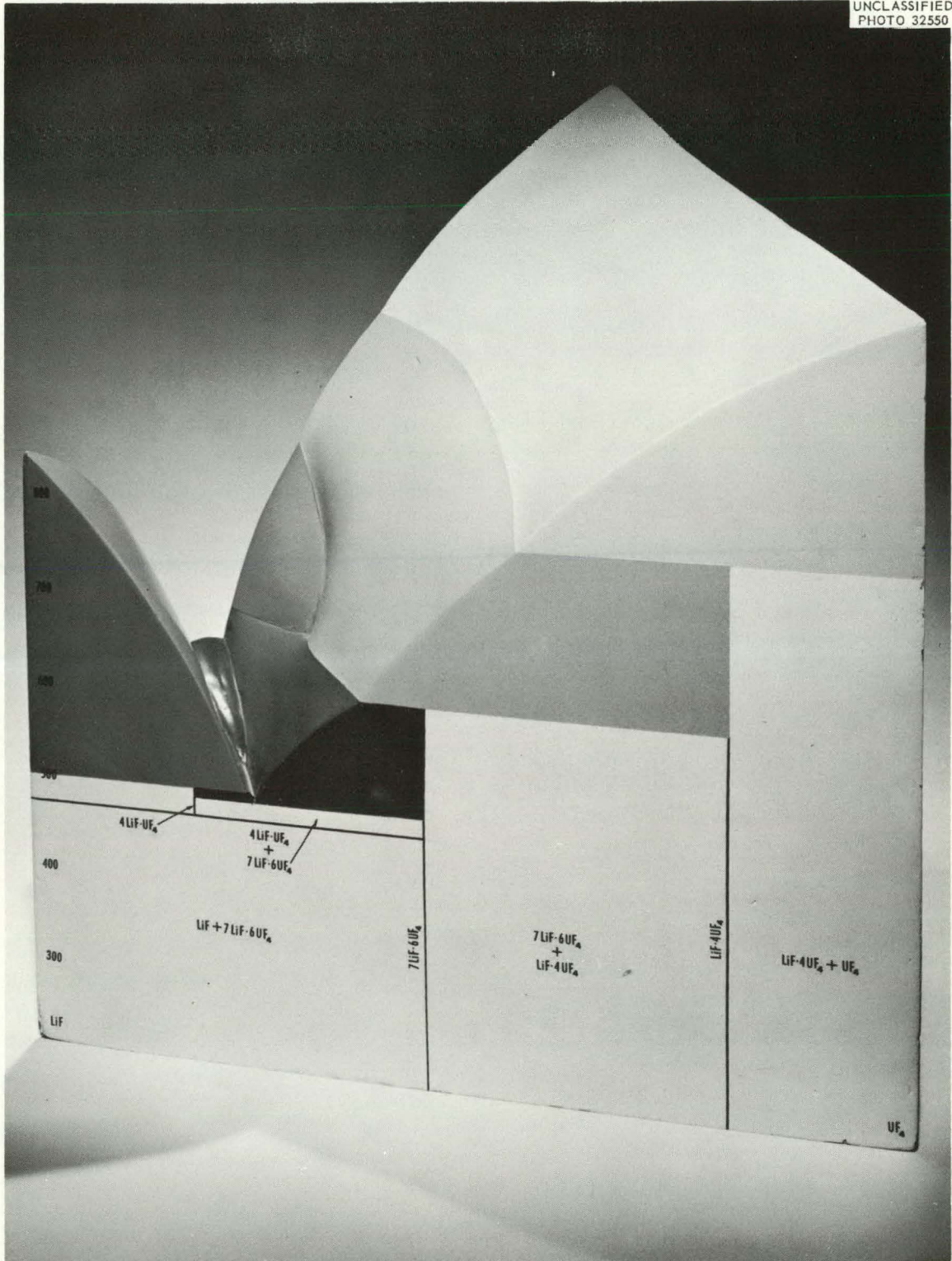
Fig. 18. The System LiF-UF$_4$-ThF$_4$.
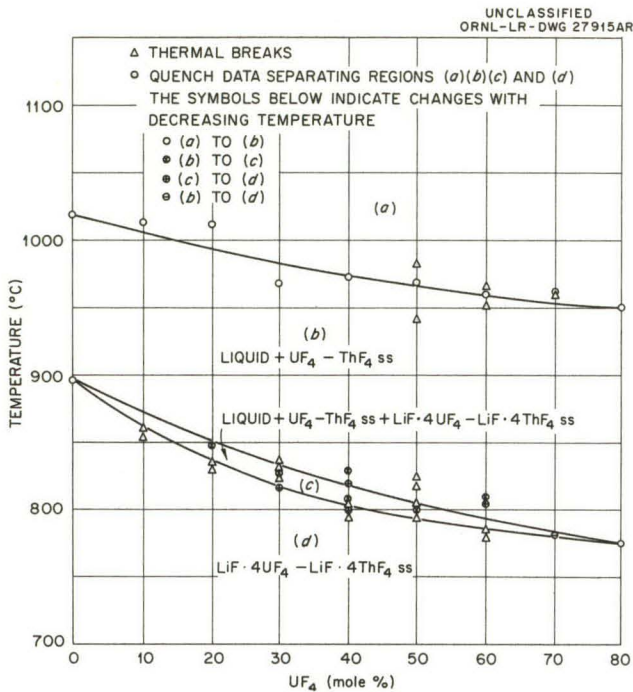
Fig. 19. The System LiF-UF₄-ThF₄: 20 Mole % LiF Section.

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.

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.

(*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
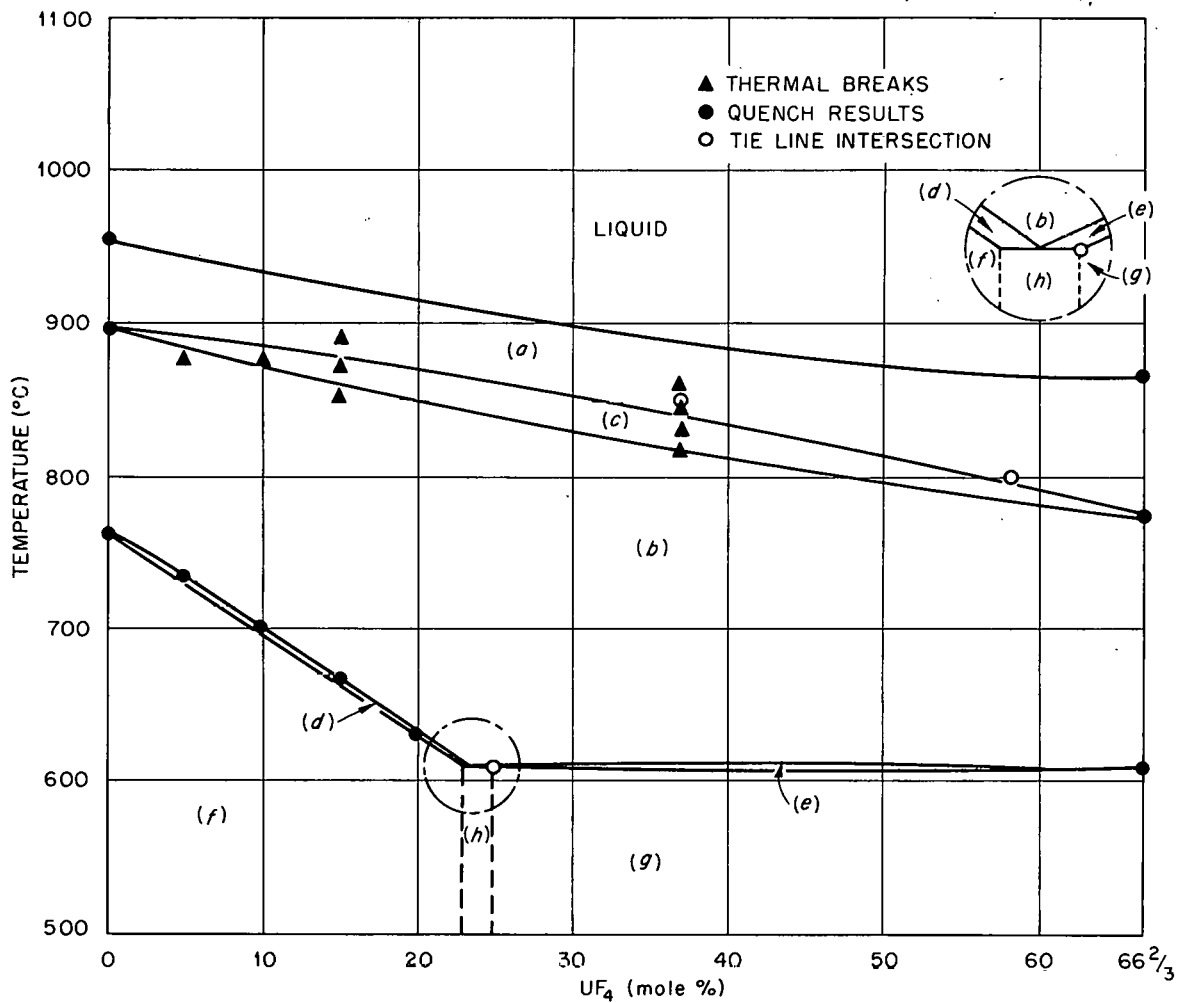
Fig. 20. The System $LiF-UF_4-ThF_4$: 33-1/3 Mole % LiF Section.
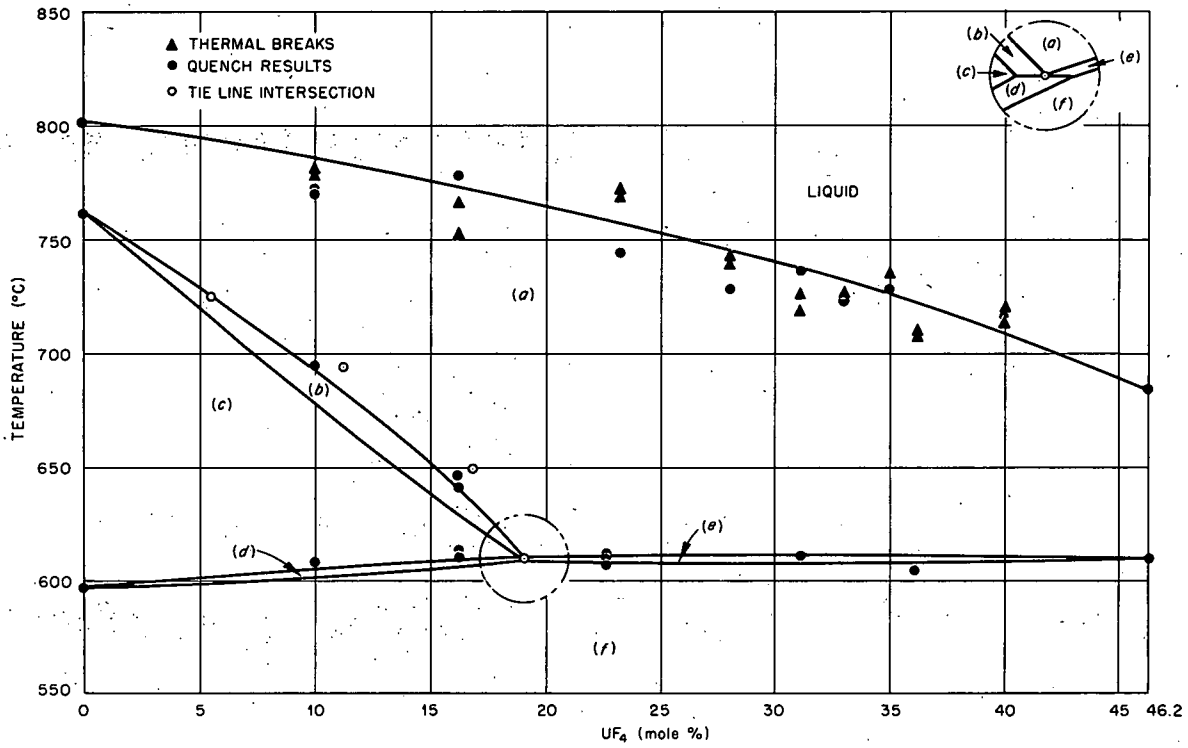
Fig. 21. The System LiF-UF$_4$-ThF$_4$: 53.8 Mole % LiF Section.

(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
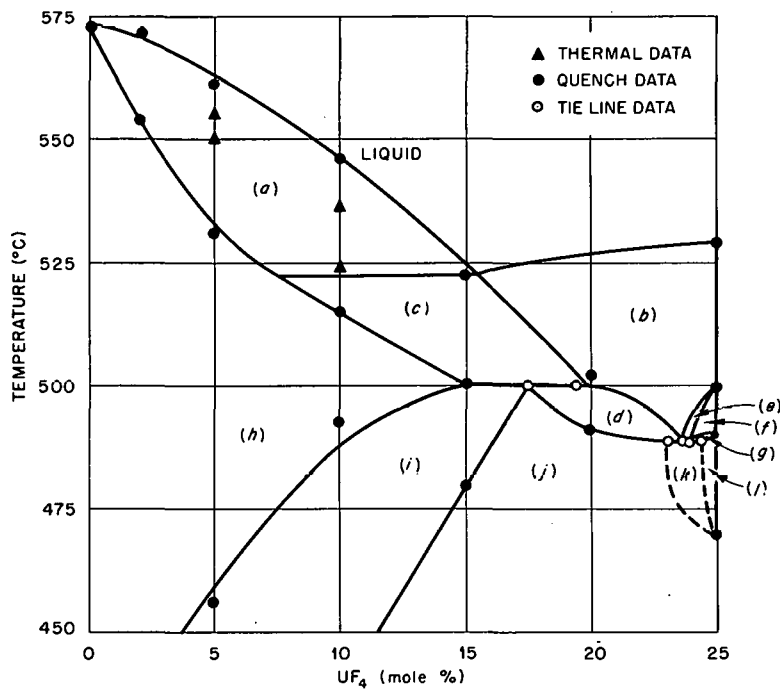
Fig. 22. The System LiF-UF₄-ThF₄: 75 Mole % LiF Section.
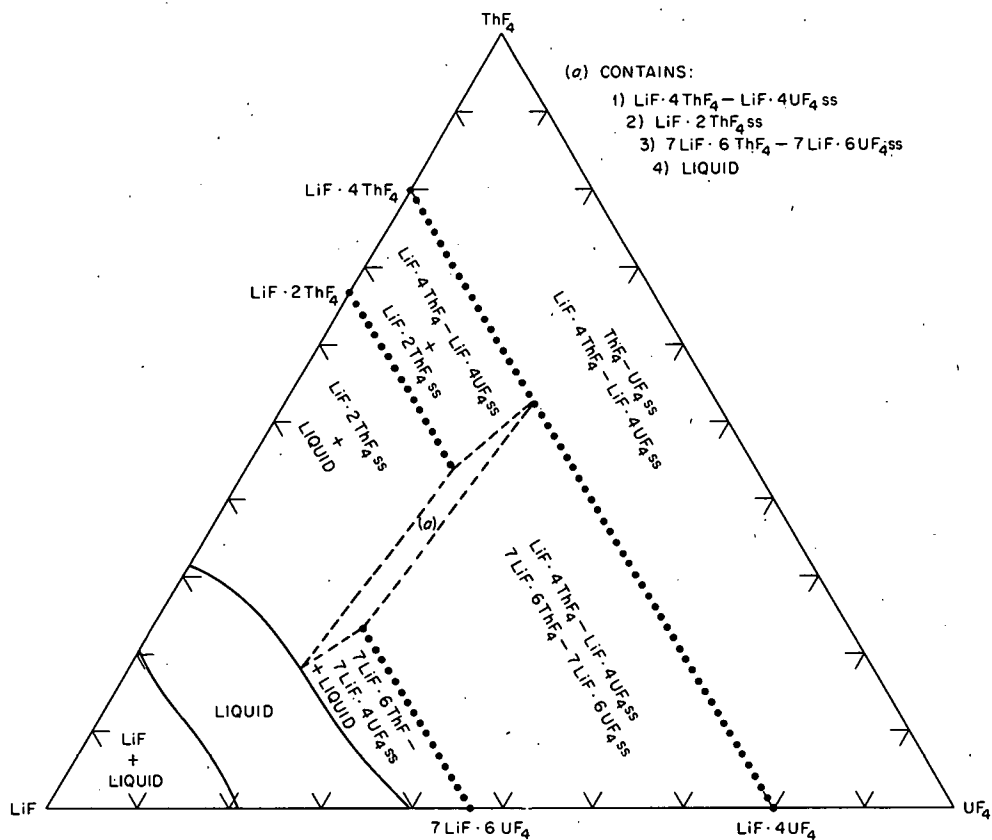
Fig. 23. The System LiF-UF$_4$-ThF$_4$: 609°C Isothermal Section.
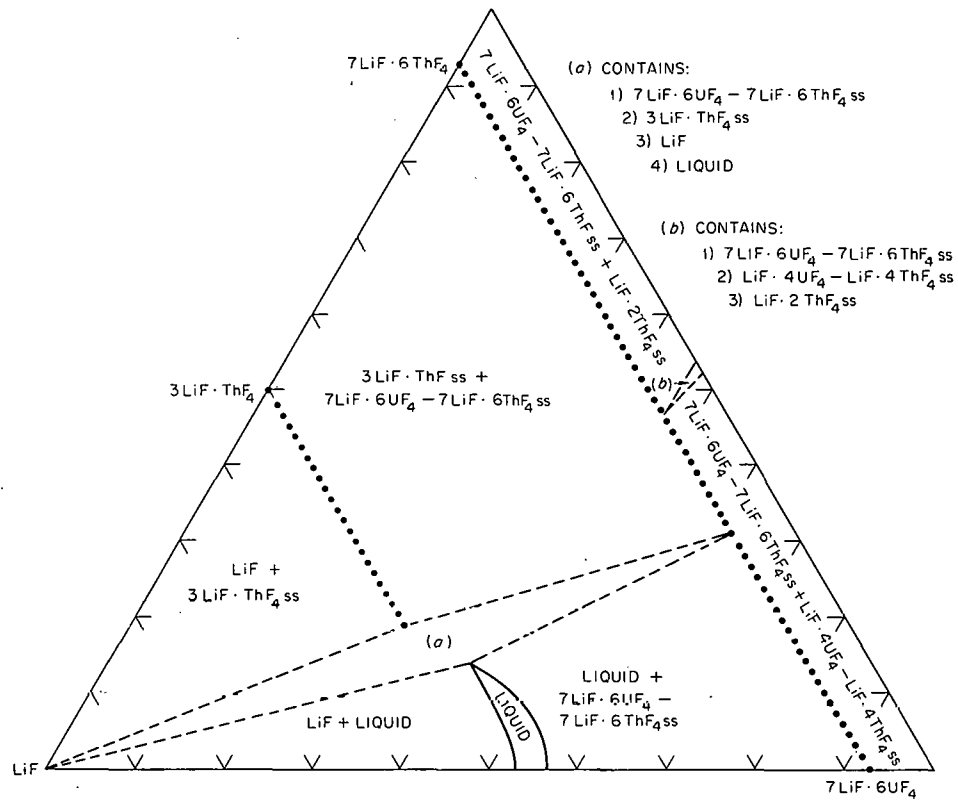
Fig. 24. The System LiF-UF$_4$-ThF$_4$: 500°C Isothermal Section.
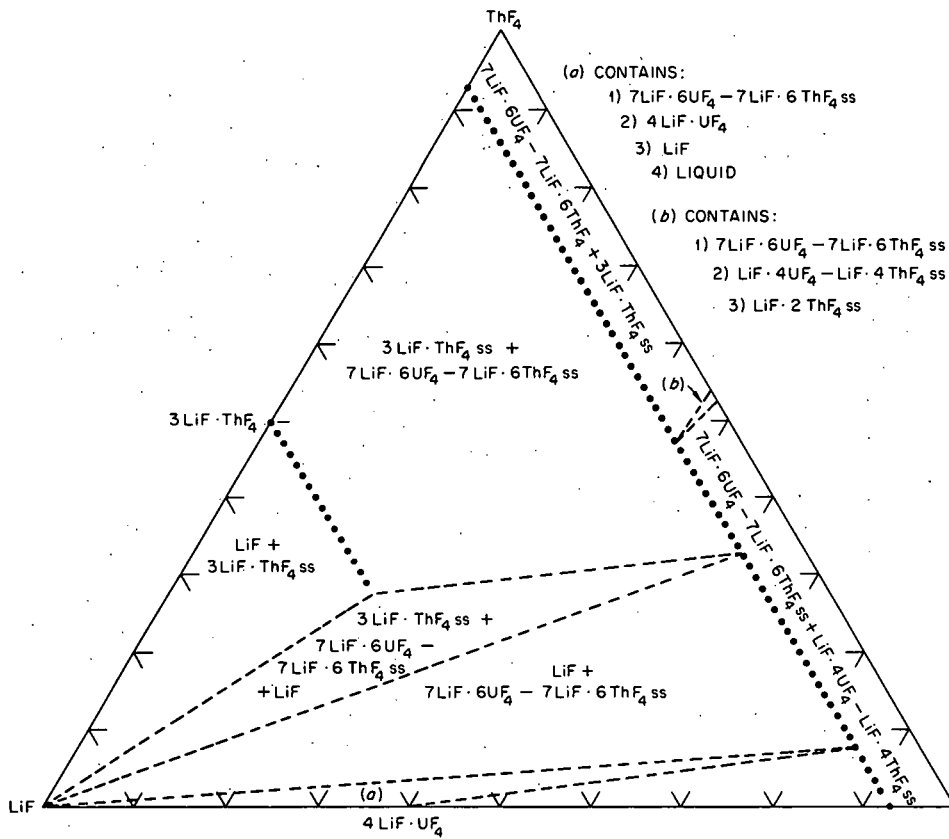
Fig. 25. The System LiF-UF$_4$-ThF$_4$: 488°C Isothermal Section.
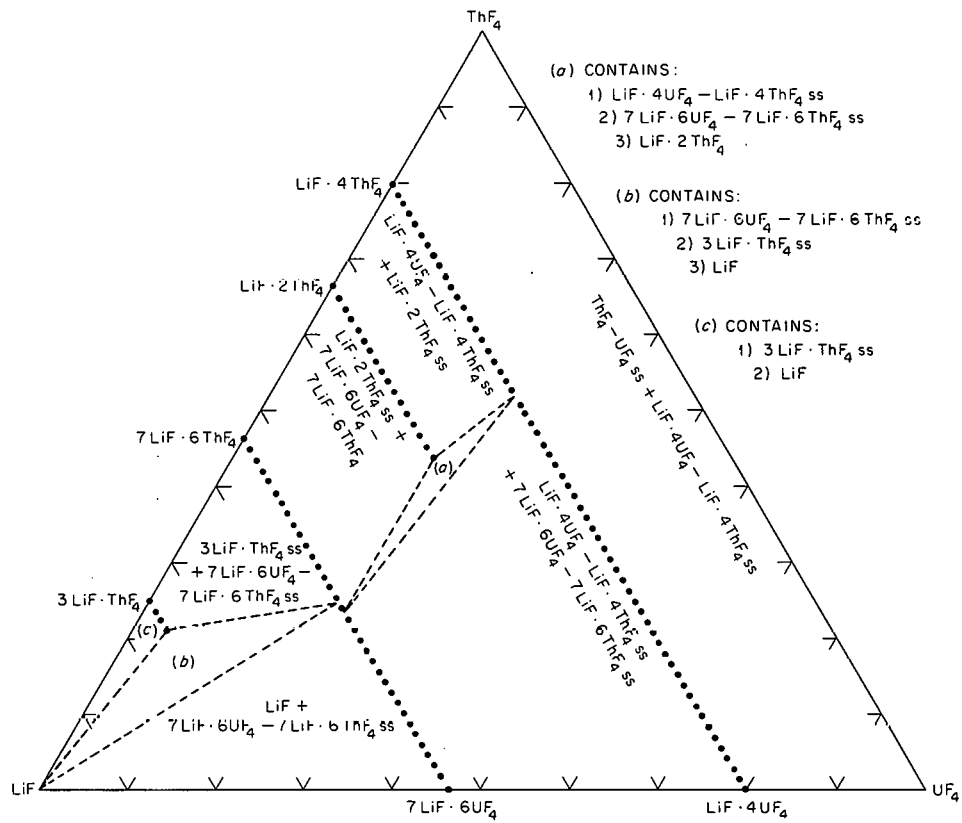
Fig. 26. The System LiF-UF_4-ThF_4: 450°C Isothermal Section.
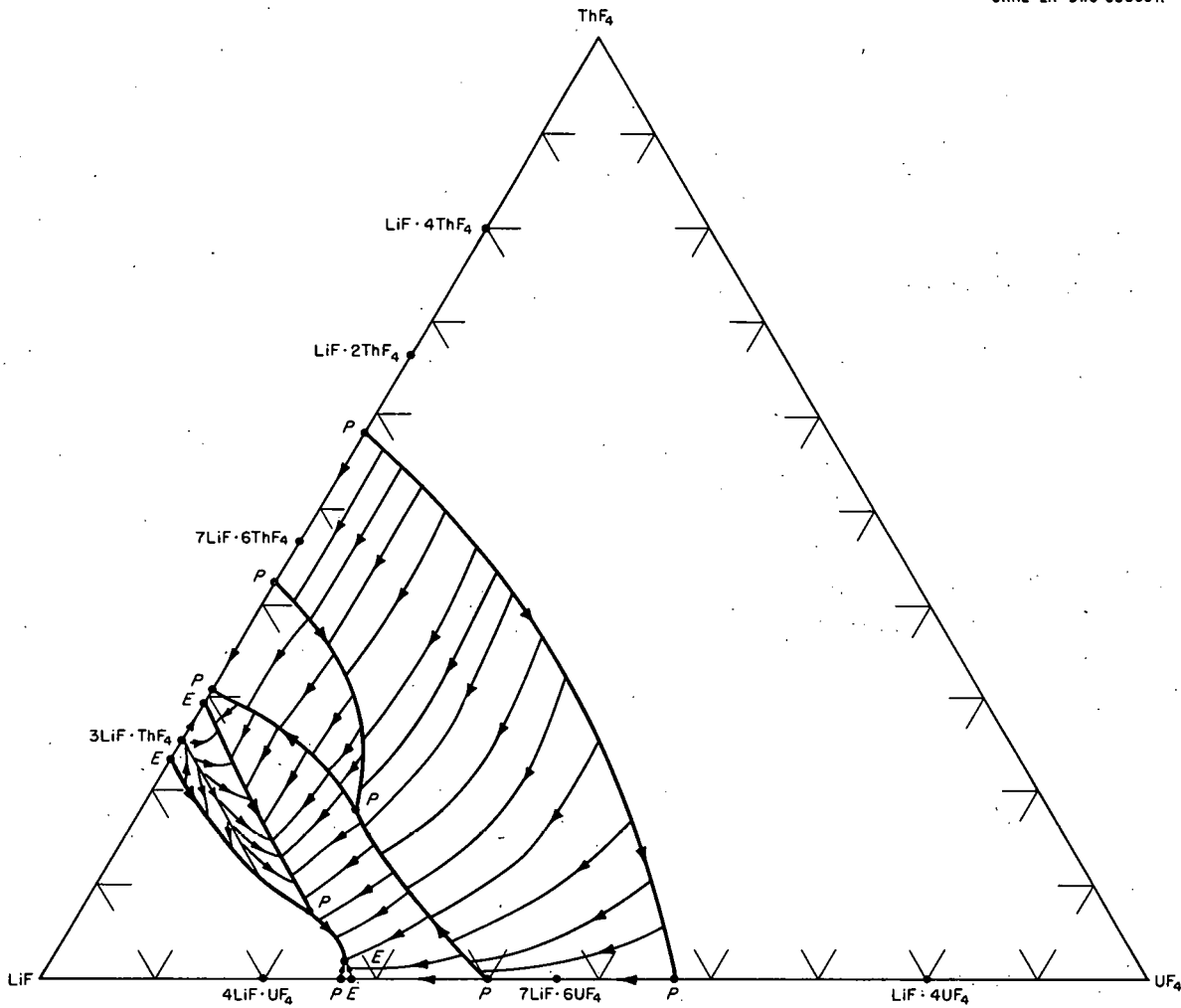
Fig. 27. The System LiF-UF₄-ThF₄: Fractionation Paths.
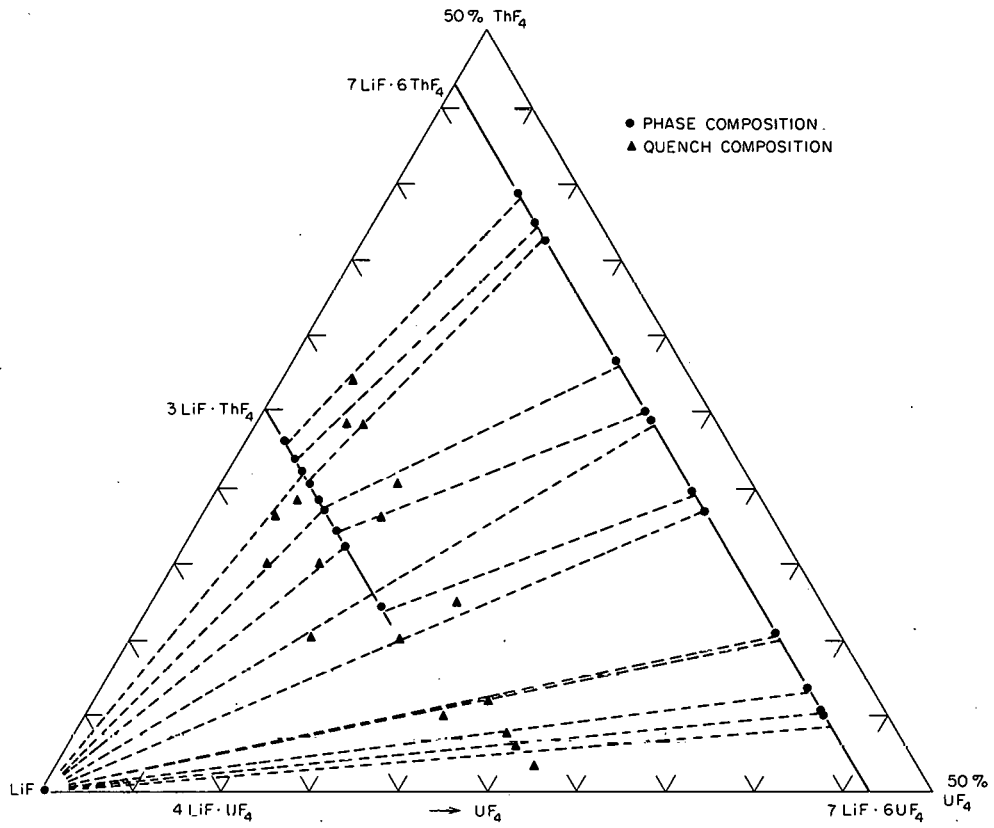
Fig. 28.   The System LiF-UF$_4$-ThF$_4$:   Tie Lines.

Table 10. Invariant Equilibria in the System $LiF-UF_4-ThF_4$*

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	$LiF \cdot 4ThF_4$-$LiF \cdot 4UF_4$ss containing 28 mole % UF_4, $LiF \cdot 2Th(U)F_4$ss containing 23 mole % UF_4, $7LiF \cdot 6ThF_4$-$7LiF \cdot 6UF_4$ss containing 23 mole % UF_4
72.5	20.5	7	500	Peritectic	$7LiF \cdot 6ThF_4$-$7LiF \cdot 6UF_4$ss containing 31 mole % UF_4, $3LiF \cdot Th(U)F_4$ss containing 15.5 mole % UF_4, LiF
72	26.5	1.5	488	Eutectic	$7LiF \cdot 6ThF_4$-$7LiF \cdot 6UF_4$ss containing 42.5 mole % UF_4, $4LiF \cdot UF_4$, LiF

*C. F. Weaver et al., Phase Equilibria in the Systems UF_4-ThF_4 and $LiF-UF_4-ThF_4$, ORNL-2719 (Aug. 17, 1959); J. Am. Ceram. Soc. 43, 213 (1960).
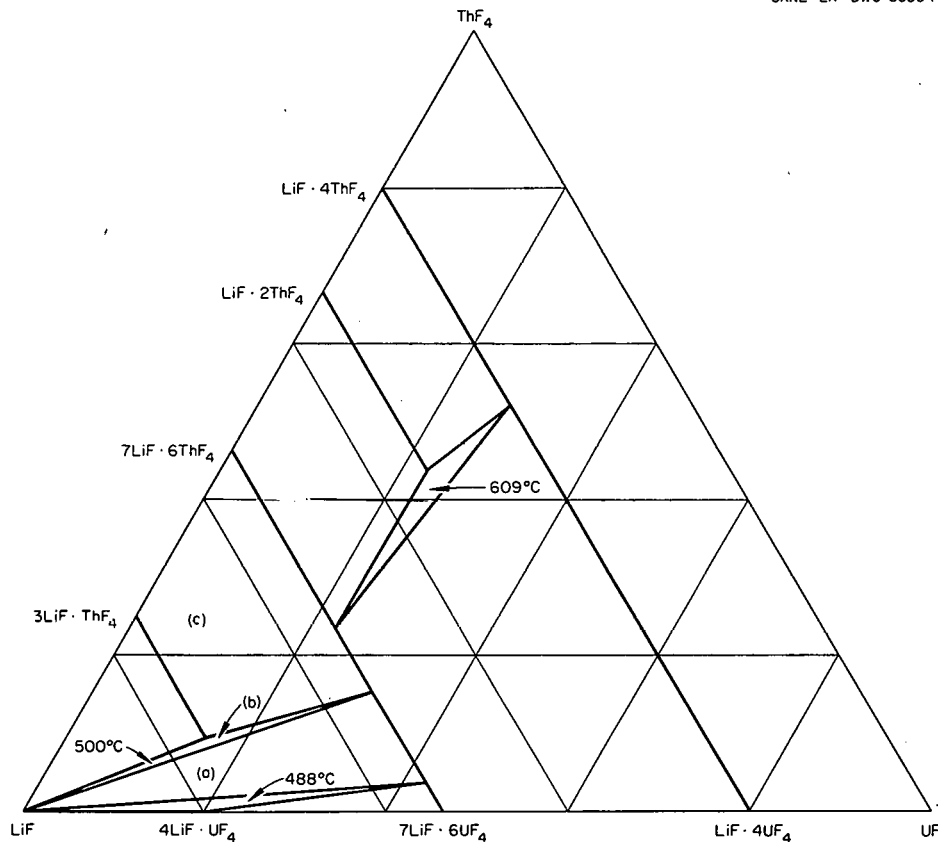
Fig. 29. The System LiF-UF$_4$-ThF$_4$: Compatibility Triangles.

3.11 The System LiF-BeF$_2$-UF$_4$-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 LiF-BeF$_2$-UF$_4$-ThF$_4$ is no exception in this respect, and consequently the experimental work was directed toward compositions which posses sufficiently low liquidus and viscosity values to be of project interest.

The similarities between the systems BeF$_2$-ThF$_4$ and BeF$_2$-UF$_4$, the systems LiF-ThF$_4$ and LiF-UF$_4$, and the systems LiF-BeF$_2$-ThF$_4$ and LiF-BeF$_2$-UF$_4$ have been discussed in Secs 3.2, 3.5, and 3.8 of this report. Within the systems UF$_4$-ThF$_4$ and LiF-UF$_4$-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 $LiF-BeF_2-ThF_4$ and $LiF-BeF_2-UF_4$. 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 $7LiF \cdot 6(U,Th)F_4$ 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 $LiF-BeF_2-ThF_4$ (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 % UF_4 + ThF_4 in the range 30–38 mole % BeF_2 have liquidus values close to those of the system $LiF-BeF_2$. These compositions differ from the $LiF-BeF_2$ 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 $LiF-BeF_2-UF_4-ThF_4$

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$_4$)

47

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 $2LiF \cdot BeF_2$
62	36.5	0.5	1	448 ± 3	L and $2LiF \cdot BeF_2$	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4 ss$
62	36.5	0.5	1	~433	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4 ss$	$2LiF \cdot BeF_2$ and $7LiF \cdot 6(U,Th)F_4 ss$
63	35	1	1	450 ± 3	L	L and $2LiF \cdot BeF_2$
63	35	1	1	438 ± 3	L and $2LiF \cdot BeF_2$	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4 ss$
63	35	1	1	416 ± 3	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4 ss$	$2LiF \cdot BeF_2$ and $7LiF \cdot 6(U,Th)F_4 ss$
63	35	2	1	442 ± 2	L	L and $2LiF \cdot BeF_2$
63	35	2	1	438 ± 2	L and $2LiF \cdot BeF_2$	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4 ss$ (23 mole % UF_4)
63	35.5	0.5	1	456 ± 2	L	L and $2LiF \cdot BeF_2$
63	35.5	0.5	1	448 ± 3	L and $2LiF \cdot BeF_2$	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4 ss$
64	32	3	1	446 ± 2	L	L and $2LiF \cdot BeF_2$
64	32	3	1	443 ± 2	L and $2LiF \cdot BeF_2$	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4 ss$
64	33	2	1	442 ± 2	L	L and $2LiF \cdot BeF_2$

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 $2LiF \cdot BeF_2$
65	31	3	1	443 ± 2	L and $2LiF \cdot BeF_2$	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4ss$
65	33	1	1	465 ± 1	L	L and $2LiF \cdot BeF_2$
65	33	1	1	446 ± 2	L and $2LiF \cdot BeF_2$	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4ss$ (22 mole % UF_4)
65	33	1	1	408 ± 2	L, $2LiF \cdot BeF_2$, and $7LiF \cdot 6(U,Th)F_4ss$	$2LiF \cdot BeF_2$ and $7LiF \cdot 6(U,Th)F_4ss$
66.4	24.9	5.4	3.3	446 ± 2	L	L and $7LiF \cdot 6(U,Th)F_4ss$ (21 mole % UF_4)
67	18.5	0.5	14	499 ± 4	L	L and $3LiF \cdot ThF_4ss$
67.5	17.5	3	12	490 ± 3	L	L and $7LiF \cdot 6(U,Th)F_4ss$
67.5	17.5	3	12	480 ± 3	L and $7LiF \cdot 6(U,Th)F_4ss$	L, $7LiF \cdot 6(U,Th)F_4ss$, and $3LiF \cdot ThF_4ss$
67.5	17.5	3	12	429 ± 2	L, $7LiF \cdot 6(U,Th)F_4ss$, and $3LiF \cdot ThF_4ss$	L and $3LiF \cdot ThF_4ss$
67.5	17.5	6.	9	490 ± 3	L	L and $7LiF \cdot 6(U,Th)F_4ss$
67.5	17.5	6	9	462 ± 3	L and $7LiF \cdot 6(U,Th)F_4ss$	L, $7LiF \cdot 6(U,Th)F_4ss$, and $3LiF \cdot ThF_4ss$
67.5	17.5	6	9	429 ± 2	L, $7LiF \cdot 6(U,Th)F_4ss$, and $3LiF \cdot ThF_4$	L, $7LiF \cdot 6(U,Th)F_4ss$, and $2LiF \cdot BeF_2$

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

[a] The uncertainty indicates the temperature difference between the quenched samples.

[b] Only 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."

[c] L = liquid.

[d] This 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-UF$_4$-BeF$_2$ (Fig. 7).
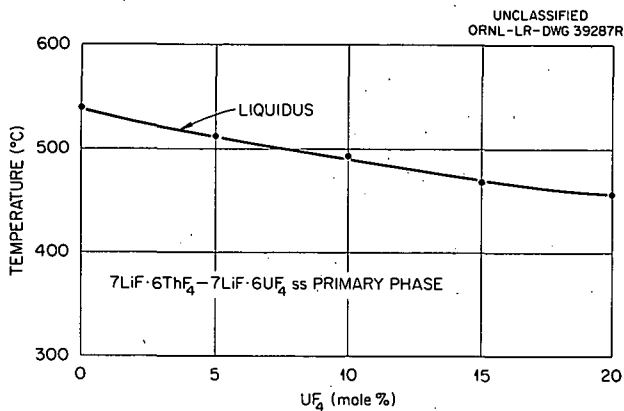
Fig. 30. The Join LiF-BeF$_2$-ThF$_4$ (70-10-20)–LiF-BeF$_2$-UF$_4$ (70-10-20) in the Quaternary System LiF-BeF$_2$-ThF$_4$-UF$_4$.
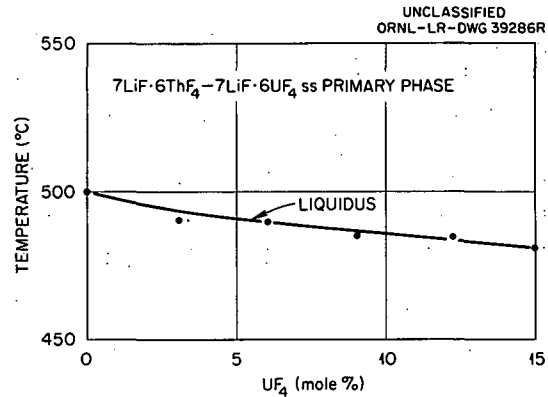
Fig. 31. The Join LiF-BeF$_2$-ThF$_4$ (67.5-17.5-15)–LiF-BeF$_2$-UF$_4$ (67.5-17.5-15) in the Quaternary System LiF-BeF$_2$-UF$_4$-ThF$_4$.
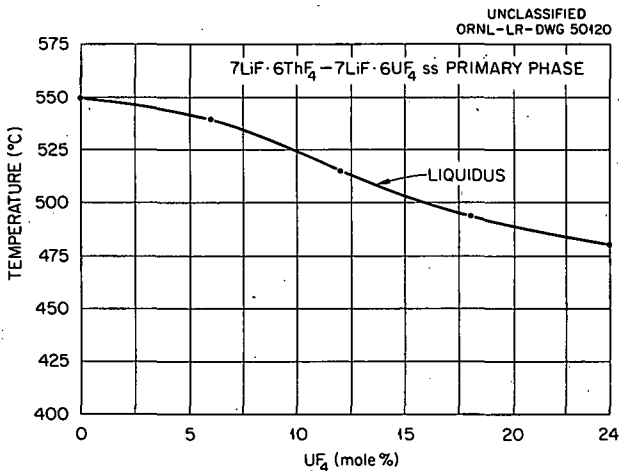
Fig. 32. The Join LiF-BeF$_2$-ThF$_4$ (70-6-24)–LiF-BeF$_2$-UF$_4$ (70-6-24) in the Quaternary System LiF-BeF$_2$-UF$_4$-ThF$_4$.
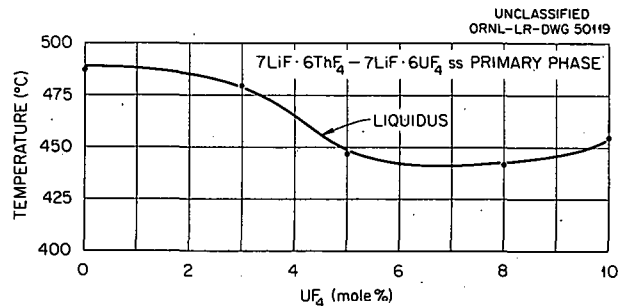
Fig. 33. The Join LiF-BeF$_2$-ThF$_4$ (65-25-10)–LiF-BeF$_2$-UF$_4$ (65-25-10) in the Quaternary System LiF-BeF$_2$-UF$_4$-ThF$_4$.

secondary phases. Liquidus values rise sharply as the UF$_4$ + ThF$_4$ 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 $LiF-UF_4-ThF_4-BeF_2$.

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.
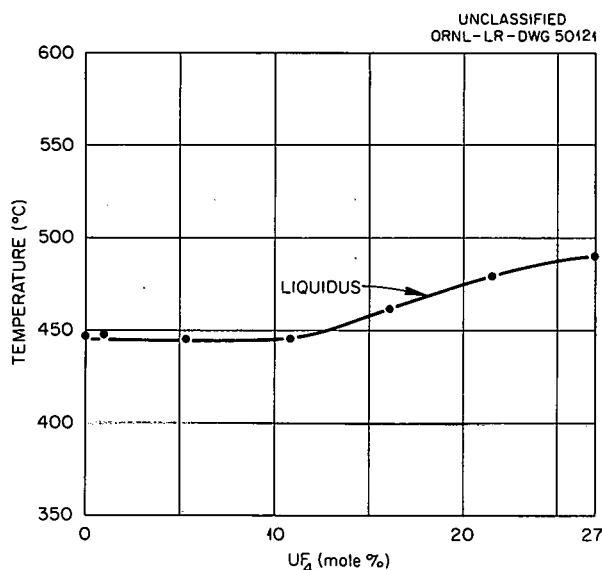
Fig. 34. The Join $LiF-UF_4$ (73-27)–$LiF-BeF_2-ThF_4$ (64.75-31.1-4.15) in the Quaternary System $LiF-BeF_2-UF_4-ThF_4$.

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

[69]F. F. Blankenship, ORNL, personal communication.
[70]MSR 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 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 LiF-BeF_2-UF_4-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-8[73] have been investigated.

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SAMPLE PLACED IN VACUUM DRY BOX, DRIED AT 135°C FOR TWO HOURS, FUSED

Fig. 35. Hydration—Vacuum-Dehydration Cycle for LiF-BeF_2-ThF_4-UF_4 (62-36.5-1-0.5).

4. ACKNOWLEDGMENTS

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

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

[73]J. 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 $LiF-UF_4-ThF_4-BeF_2$ are summarized in Tables A-1 and A-2 respectively. No ternary or quaternary compounds have been observed. The refractive indices of the $LiF-UF_4-ThF_4$ and UF_4-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 $LiF-UF_4-ThF_4-BeF_2$

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	~60°	−	1.552	1.598	Green
ThF_4[b]	Biaxial	~60°	−	1.500	1.534	Colorless
$2LiF \cdot BeF_2$[b]	Uniaxial		+	1.312	1.319	Colorless
$LiF \cdot BeF_2$	Biaxial	Large		1.35 (average)		Colorless
$4LiF \cdot UF_4$[b]	Biaxial	~10°	−	1.560	1.472	Green
$7LiF \cdot 6UF_4$[b]	Uniaxial		−	1.554	1.551	Green
$LiF \cdot 4UF_4$[b]	Biaxial	~10°	−	1.584	1.600	Green
$3LiF \cdot ThF_4$[d,e]	Biaxial	~10°	−	1.480	1.488	Colorless
$7LiF \cdot 6ThF_4$[d]	Uniaxial		+	1.502	1.508	Colorless
$LiF \cdot 2ThF_4$[d]	Uniaxial		−	1.554	1.548	Colorless
$LiF \cdot 4ThF_4$[d,e]	Biaxial	~10°	−	1.528	1.538	Colorless

[a] Am. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 4-0857.

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

[c] W. W. Harris and R. A. Wolters, Optical Properties of UF₄, MDDC-1662 (Nov. 5, 1947); USAEC, Abstracts of Declassified Documents, vol 2, p 103, Technical Information Div., Oak Ridge, Tenn., 1948.

[d] R. E. Thoma et al., J. Phys. Chem. 63, 1266 (1959).

[e] This 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 $LiF-UF_4-ThF_4-BeF_2$

Compound	Crystal System	Lattice Parameters				Space Group	X-Ray Density (g/cc)
		a_0 (A)	b_0 (A)	c_0 (A)	β		
LiF[a]	Cubic (face-centered)	4.0270				O_h^5-Fm3m	2.638
BeF$_2$[b]	Hexagonal	4.72		5.18		D_6^4 = C6$_2$2, D_6^5 = C6$_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			

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

[b] This is the β-quartz form of BeF$_2$ routinely observed in the systems described in this report. The β-quartz and three other forms of BeF$_2$ are described by A. V. Novoselova, Uspekhi Khim 27, 33 (1959).

[c] W. H. Zachariasen, Acta Cryst. 2, 388 (1949).

[d] Am. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 8-428.

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

[f] L. A. Harris, G. D. White, and R. E. Thoma, J. Phys. Chem. 63, 1974 (1959).

[g] Am. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 6-0557; E. Thilo and H. A. Lehmann, Z. anorg. Chem. 258, 332 (1949).
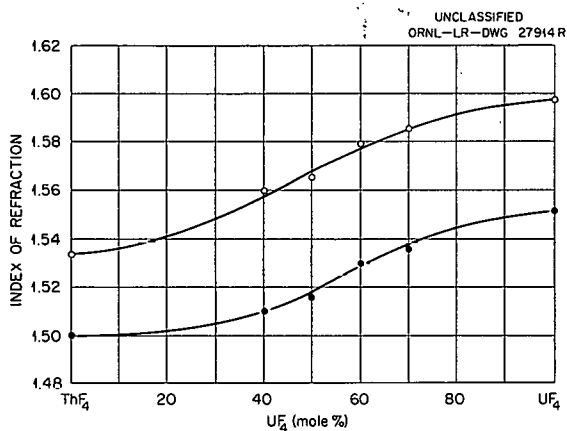
Fig. A-1. Refractive Indices of the UF_4-ThF_4 Solid Solutions.
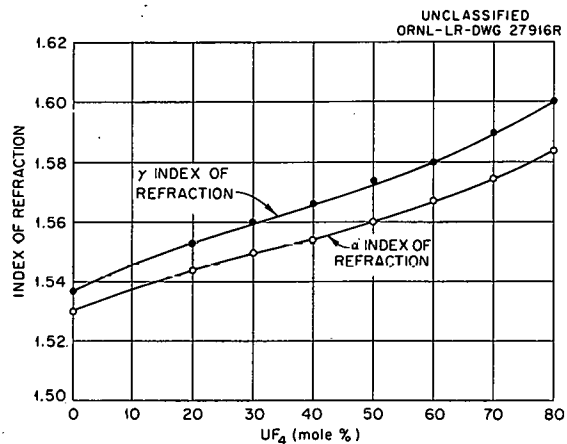
Fig. A-2. Refractive Indices of the $LiF \cdot 4UF_4$-$LiF \cdot 4ThF_4$ Solid Solutions.
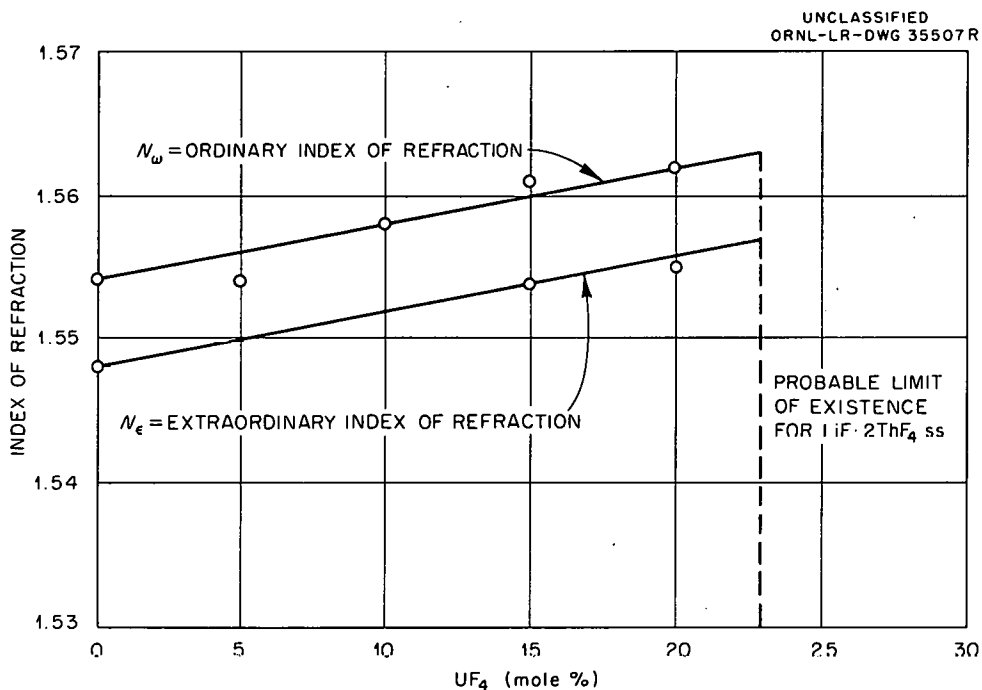
Fig. A-3. Refractive Indices of the $LiF \cdot 2Th(U)F_4$ Solid Solutions.
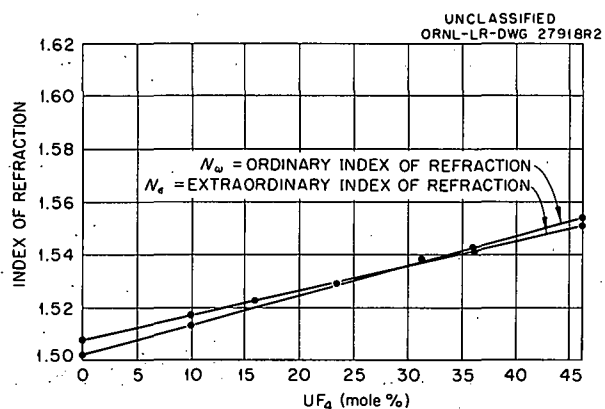
Fig. A-4. Refractive Indices of the $7LiF \cdot 6UF_4 - 7LiF \cdot 6ThF_4$ Solid Solutions.
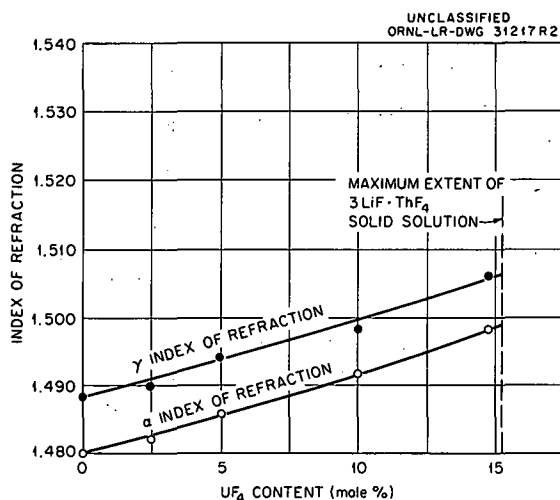
Fig. A-5. Refractive Indices of the $3LiF \cdot Th(U)F_4$ Solid Solutions.

Appendix B

X-RAY DIFFRACTION DATA FOR THE SOLID PHASES OBSERVED IN THE QUATERNARY SYSTEM $LiF-BeF_2-UF_4-ThF_4$

LiF[a]		ThF₄		ThF₄ (continued)	
BeF₂[b]		d (A)	I/I₁	d (A)	I/I₁
d (A)	I/I₁	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
UF₄[c]				1.922	25

Appendix B (continued)

ThF$_4$ (continued)

d (A)	I/I$_1$
1.881	10
1.859	5.5
1.771	10
1.737	10
1.683	20
1.666	10
1.640	10
1.612	10
1.588	5
1.575	10
1.520	20
1.484	5
1.455	20
1.431	10
1.404	5
1.373	10

4LiF·UF$_4$[b]

d (A)	I/I$_1$
5.67	20
5.46	25
5.13	70
4.93	100
4.55	45
4.44	100
4.23	7
3.82	40
3.55	30
3.03	50
2.89	25
2.866	30
2.747	50
2.468	40
2.398	20
2.221	40
2.167	75
2.074	20
2.025	20
1.872	20
1.836	25

3LiF·UF$_4$[b] (metastable)

d (A)	I/I$_1$
4.98	20
4.80	15
4.41	100
4.34	100
3.98	15
3.91	8
3.60	80
3.40	10
3.14	25
3.07	50
2.84	80
2.771	30
2.529	35
2.169	15
2.083	75
2.055	35
1.943	50
1.913	25
1.861	30
1.751	25
1.723	25
1.685	25
1.662	8
1.646	20
1.599	8

7LiF·6UF$_4$[b]

d (A)	I/I$_1$
6.61	6
5.97	20
5.82	15
5.24	90
5.15	10
4.65	10
4.37	13
3.95	55
3.85	13
3.68	20
3.49	75

7LiF·6UF$_4$[b] (continued)

d (A)	I/I$_1$
3.33	90
3.15	70
3.07	10
2.99	95
2.771	30
2.707	30
2.542	25
2.350	13
2.286	25
2.264	13
2.184	10
2.097	30
2.060	30
2.047	75
1.993	25
1.972	20
1.947	25
1.924	15
1.909	30
1.854	45
1.825	20
1.773	20
1.757	25
1.709	15
1.680	15
1.625	15
1.579	25
1.562	8

LiF·4UF$_4$[b]

d (A)	I/I$_1$
7.02	8
6.33	12
6.07	5
5.73	25
4.98	8
4.70	25
4.25	90
3.88	20

Appendix B (continued)

LiF·4UF$_4$[b] (continued)		3LiF·ThF$_4$[d] (continued)		LiF·2ThF$_4$[d]	
d (A)	I/I$_1$	d (A)	I/I$_1$	d (A)	I/I$_1$
				7.97	5
3.78	100	1.701	35	6.37	10
3.52	90	1.661	10	3.96	100
3.16	8	1.618	10	3.57	65
3.13	8	1.547	35	3.25	5
3.06	12	1.520	35	3.21	5
2.84	40			2.97	20
2.771	55	7LiF·6ThF$_4$[d]		2.822	25
2.542	8			2.675	7
2.350	10	d (A)	I/I$_1$	2.528	10
2.310	10			2.388	5
2.226	8	6.07	15	2.123	85
2.000	10	5.91	20	2.053	30
2.088	35	5.36	90	2.001	65
2.016	60	5.25	15	1.787	7
1.991	50	4.95	30	1.701	10
1.888	20	4.85	20	1.689	5
1.819	8	4.75	100	1.603	5
1.767	25	4.01	85	1.519	5
3LiF·ThF$_4$[d]		3.92	15	LiF·4ThF$_4$[d]	
		3.74	15		
d (A)	I/I$_1$	3.55	65	d (A)	I/I$_1$
		3.44	10		
6.42	100	3.39	70	8.34	3
4.46	100	3.29	60	7.76	3
4.37	100	3.03	100	6.51	5
3.62	85	2.814	25	5.80	25
3.09	55	2.747	25	4.62	5
2.866	70	2.578	20	4.33	70
2.788	30	2.430	10	3.88	100
2.542	25	2.392	10	3.60	60
2.327	10	2.302	20	3.25	10
2.189	20	2.137	20	2.92	25
2.104	65	2.018	5	2.822	25
2.071	25	2.001	15	2.603	10
2.036	40	1.892	55	2.398	10
1.959	30	1.859	15	2.137	25
1.933	60	1.804	15	2.053	35
1.877	25	1.680	15	2.040	10
1.771	25	1.653	20	2.018	10
1.743	30	1.600	20	2.005	30

Appendix B (continued)

LiF·4ThF$_4$[d] (continued)		LiF·BeF$_2$[f]		LiF·BeF$_2$[f] (continued)	
d (A)	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
2LiF·BeF$_2$[e]		2.201	100	1.233	1
		2.074	80	1.216	2

[a]Am. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 4-0857.

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

[c]Am. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 8-428.

[d]R. E. Thoma et al., J. Phys. Chem. 63, 1266 (1959).

[e]Am. Soc. Testing Materials, X-Ray Diffraction Data Cards, card No. 6-0557.

[f]E. 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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