is shown in projection in Figure 5. Qualitative comparison of X-ray powder intensities suggests that this interpretation is not unreasonable.

The collapse of this structure along the *c* axis to the α-AlF_3 structure follows readily, forming an almost cubic structure, with the Al–Al distance of 3.52 A directly comparable to the 3.55 and 3.59 A of its precursors. The fluorides revert to a complete octahedral configuration, the Al–F distances having remained at 1.76–1.79 A during the series. Comparison is simplified if the sixfold primitive hexagonal cell, a = 4.914, c = 12.449 A, is used for α-AlF_3. The edges of the pseudo-cube (the Al–Al directions) then lie along the $[2\bar{2}1]$, $[42\bar{1}]$, and $[241]$ directions of the hexagonal cell. The vacancies in γ-AlF_3 correspond to those in α-AlF_3, the latter lying at the centers of the pseudo-cubes.

It is interesting to note that there is a report of different forms of gallium fluoride, one obtained by thermal decomposition of ammonium hexafluorogallate and one by fluorination of oxide at 600°.[28]

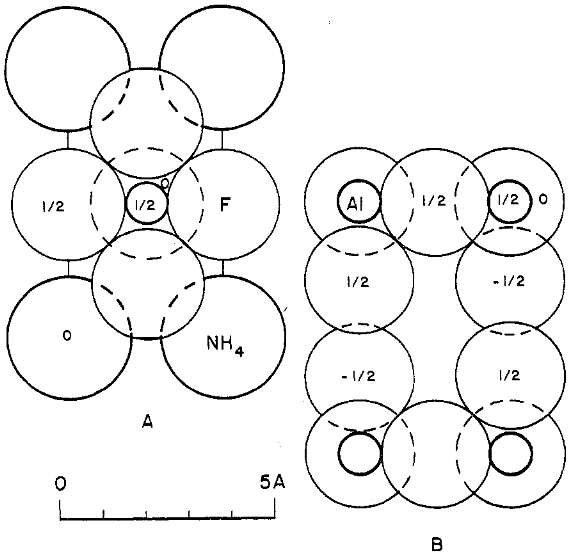

Figure 5.—Structural relation between NH_4AlF_4 and γ-AlF_3: A, NH_4AlF_4; B, γ-AlF_3. The figures are projected along the *a* axis; numbers within the circles give the fractional distances in terms of cell axes of atoms above (or below) the plane of protection. Note that the drawing of γ-AlF_3 is not that of the unit cell.

NOTE ADDED IN PROOF.—We have recently become aware of a patent[29] on the synthesis of vinyl fluoride, in which one of the claims is for the preparation of a new catalytic form of aluminum fluoride by dehydration of α-aluminum fluoride trihydrate. The powder pattern cited is quite similar to that for the γ-aluminum fluoride presented in this paper but contains a number of lines not present in our material, including a strong line at 3.465 A. The low calculated density indicates an open structure, and it is believed that the product reported in the patent is the open γ-AlF_3 of this paper with a small amount of water remaining in the holes. No analysis is given in the patent, and there is no evidence to indicate complete removal of water.

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[28] O. Hannebohn and W. Klemm, *Z. Anorg. Allgem. Chem.*, **229**, 337 (1936); R. Hoppe, unpublished work, 1955–1956; Dissertation, Münster, 1958. See C. Hebecker and R. Hoppe, *Naturwissenschaften*, **53**, 104 (1966).

[29] F. J. Christoph, Jr., and G. Teufer, U. S. Patent 3,178,483 (1965).

CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
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The Sodium Fluoride–Scandium Trifluoride System[1]

BY R. E. THOMA AND R. H. KARRAKER[2]

Received May 20, 1966

The equilibrium phase diagram of the condensed system NaF–ScF_3 was constructed from data obtained using standardized methods of thermal analysis and thermal gradient quenching, and also by direct observation of crystallizing melts. Crystallographic properties of the solid phases were measured by petrographic and X-ray diffraction techniques. Equilibria among the condensed phases in the system were established through the temperature interval from the liquidus to approximately 400°. Two equilibrium compounds were observed to form from NaF and ScF_3—the cryolite-like phase, $3NaF \cdot ScF_3$, and a hexagonal phase, $NaF \cdot ScF_3$, with lattice constants a = 12.97 A, c = 9.27 A. Four invariant points were found to occur in the system NaF–ScF_3: the eutectic at 17 mole % ScF_3 and at 800°, a peritectic at 35 mole % ScF_3 and at 680°, associated with a solid-state transition in $3NaF \cdot ScF_3$, a eutectic at 38 mole % ScF_3 and at 650°, and a peritectic at 42 mole % ScF_3 and at 660°. The equilibrium character of the system NaF–ScF_3 is contrasted with that of NaF–AlF_3 and with those of the sodium fluoride–rare earth trifluoride systems.

Introduction

Variability in stoichiometry, structure, and stability among the complex compounds formed in the binary systems of the alkali fluorides and the lanthanide trifluorides is influenced chiefly by two factors: (a) disparity in size between the monovalent and trivalent ions[3] and (b) relative charge density of the lanthanide ions. Results of the recent investigation of the sodium fluoride–lanthanide trifluoride systems[4] showed

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[1] Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] Summer Research Participant, 1964–1965.

[3] R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

[4] R. E. Thoma, G. M. Hebert, and H. Insley, *ibid.*, **5**, 1222 (1966).

that among the heavier lanthanide systems the effects of charge density were more pronounced than those which were attributable strictly to size disparity. It was therefore significant to investigate the systems which would permit the behavior in the lanthanide trifluoride systems to be contrasted with that produced by the reactions of the alkali fluorides with the trifluorides of metals whose cationic radii are nearest those of the heavier lanthanides.

The current study was initiated to compare compound formation in the NaF–ScF_3 system with that in the systems NaF–LuF_3 and NaF–AlF_3. The only previously known work on the NaF–ScF_3 system at that time was the investigation of NaF freezing point depression by Cantor and Ward.[5] The results of an investigation of the system NaF–ScF_3 by Fedorov, Sklyarenko, and Petrov[6] appeared shortly thereafter; more recently, Babaev and Bukhalova[7] have again described the phase diagram of the system in a report which takes no cognizance of the earlier work by Fedorov, *et al.* Since each of these prior investigations is either incomplete or erroneous, we continued the investigation of the NaF–ScF_3 system[8] as described in the present report.

Experimental Section

Apparatus and Methods.—Phase transition data were obtained from heating and cooling curve experiments, by direct observation of melts crystallizing at known temperatures, and by identification of the equilibrium phases formed in quenched specimens. The techniques used for measurement of the temperatures which define the NaF–ScF_3 phase diagram, as well as the X-ray and microscopic techniques used in identifying phases, have been discussed previously.[9–11] Phase transitions were determined principally from the results of thermal gradient quenching experiments. For these experiments, 5-g specimens of the proper compositions were prepared from commercially available reagent grade sodium fluoride and from pure scandium fluoride which was prepared in this laboratory by reaction of ammonium bifluoride with high-purity scandium oxide.[12] NaF–ScF_3 mixtures were also treated with ammonium bifluoride for 16 hr at temperatures of 150 to 200° in dry helium atmospheres and then heated to approximately 1000° for 15 min. After cooling to room temperature, the samples were powdered (again in dry helium atmospheres), examined microscopically for traces of oxides or oxyfluoride contaminants, and then used to fill sample tubes for use in thermal gradient quenching experiments.

Attempts to obtain single crystals of the low-temperature form of $3NaF \cdot ScF_3$ at the compound composition were unsuccessful. The cubic high-temperature form of the compound undergoes a strongly energetic solid-state transition on cooling below 680° and routinely produces poorly crystallized and highly twinned material as it inverts. Larger single crystals of the low-temperature form could not be preserved in quenched specimens; in all attempts the seed crystals became twinned. This problem was avoided by crystallizing β-$3NaF \cdot ScF_3$, the low-temperature form, from a molten NaF–ScF_3 mixture in which it was the primary phase (at about 30 mole % ScF_3). In this manner, crystals of β-$3NaF \cdot ScF_3$ were formed which had not inverted and were of sufficiently good quality for X-ray diffraction single-crystal studies. In similar manner, crystals of $NaF \cdot ScF_3$ were grown from an NaF–ScF_3 mixture of approximately 41 mole % ScF_3.

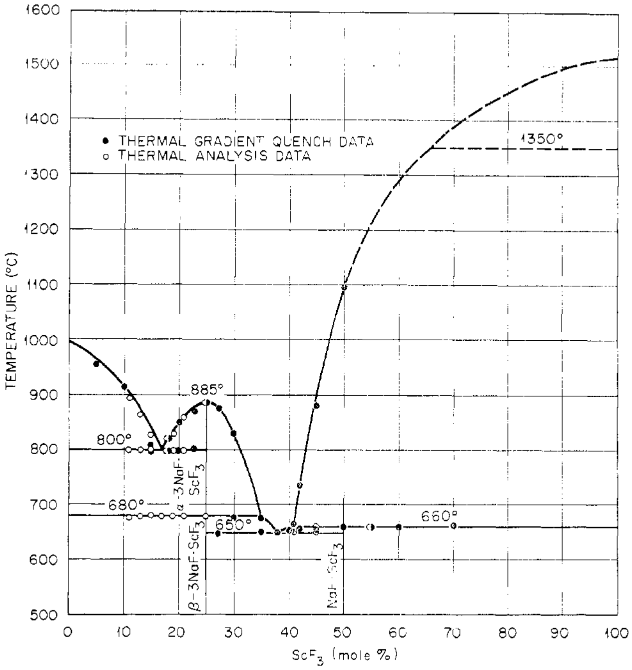

Figure 1.—The system NaF–ScF_3.

Results and Discussion

Equilibrium phase behavior in the NaF–ScF_3 system is described by the phase diagram in Figure 1. Two intermediate compounds, $3NaF \cdot ScF_3$ and $NaF \cdot ScF_3$, are formed in the system. Crystallographic properties of these compounds, measured as part of the current study, are given in Table I. Compositions and temperatures of singular points and invariant equilibrium reactions among NaF–ScF_3 phases are listed in Table II. Phase transition temperature data obtained from thermal analysis and thermal gradient quenching experiments are given in Tables III and IV.

Equilibria in the system NaF–ScF_3 may be described in terms of the two subsystems NaF–$3NaF \cdot ScF_3$ and $3NaF \cdot ScF_3$–ScF_3. The former is remarkably similar to the sodium fluoride–cryolite system in that both consist of simple eutectic systems of NaF with complex components which are isomorphous in each of their dimorphic modifications; in contrast, the $3NaF \cdot ScF_3$–ScF_3 and $3NaF \cdot AlF_3$–AlF_3 subsystems are dissimilar, differing principally in the formulas and crystal symmetries of the intermediate compounds which are produced.

Crystal properties of the NaF–ScF_3 intermediate phases, $3NaF \cdot ScF_3$ and $NaF \cdot ScF_3$, have not been described previously. The compound $3NaF \cdot ScF_3$ bears a marked resemblance to $3NaF \cdot AlF_3$ with respect to crystal symmetry. Both phases crystallize from melts

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[5] S. Cantor and W. T. Ward, *J. Phys. Chem.*, **67**, 2766 (1963).

[6] N. Y. Fedorov, S. I. Sklyarenko, and E. S. Petrov, *Akad. Nauk Sibirsk. SSSR*, **1**, 104 (1964).

[7] E. P. Babaev and G. A. Bukhalova, *Zh. Neorgan. Khim.*, **10**, 1455 (1965).

[8] R. H. Karraker and R. E. Thoma, *J. Tenn. Acad. Sci.*, **40**, 67 (1965).

[9] H. A. Friedman, G. M. Hebert, and R. E. Thoma, "Thermal Analysis and Gradient Quenching Apparatus and Techniques for the Invesitgation of Fused Salt Phase Equilibria," ORNL-3375, Dec 18, 1962.

[10] C. J. Barton, *et al.*, *J. Am. Ceram. Soc.*, **42**, 65 (1958).

[11] G. D. Robbins, R. E. Thoma, and H. Insley, *J. Inorg. Nucl. Chem.*, **27**, 559 (1965).

[12] F. H. Spedding and A. H. Daane, "The Rare Earths," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 78.

TABLE I

OPTICAL AND X-RAY DIFFRACTION DATA FOR $NaF-ScF_3$ COMPOUNDS

β-$3NaF \cdot ScF_3$

Equilibrium stability range: <680°
Optical character: uniaxial (+), $2V \cong 0°$
Refractive indices: $N_\omega = 1.368$, $N_\epsilon = 1.374$

X-Ray diffraction data

Symmetry: monoclinic, $P2_1/n$
$a = 5.60 \pm 0.02$ A, $b = 5.81 \pm 0.02$ A, $c = 8.12 \pm 0.02$ A, $\beta = 90° 45 \pm 5'$
Density: 2.87 (calcd, $z = 2$)

d, A			
Obsd	Calcd	*I*	*hkl*
4.68	4.72	97	011
4.57	4.64	30	$10\bar{1}$
4.54	4.58	58	101
4.00	4.06	94	002
	4.03		110
2.88	2.91	65	020
2.86	2.87	97	$11\bar{2}$
2.83	2.85	100	112
2.78	2.80	30	200
2.51	2.52	55	210
	2.45		121
2.44	2.45	47	013
	2.45		$10\bar{3}$
	2.42	65	103
2.41	2.42		$21\bar{1}$
2.35	2.36	12	022
2.23	2.24	28	113
2.17	2.18	25	$12\bar{2}$
2.02	2.03	63	004
2.01	2.02	75	220
1.97	1.98	16	023
1.95	1.96	10	$22\bar{1}$
1.88	1.88	10	031
1.87	1.87	13	$12\bar{3}$
	1.86		123
1.83	1.83	16	130
	1.81		114
1.80	1.81	30	301
	1.81		$22\bar{2}$
	1.78		131
1.78	1.79	25	$13\bar{1}$
	1.78		310
1.73	1.73	10	311
	1.67		$13\bar{2}$
1.66	1.66	50	024
	1.67		132
1.63	1.63	47	204
1.62	1.62	25	312

$NaF \cdot ScF_3$

Equilibrium stability range: <660°
Optical character: uniaxial (−)
Refractive indices: $N_\omega = 1.442$, $N_\epsilon = 1.431$

X-Ray diffraction data

Symmetry: hexagonal, $P3_1 12$, $P3_2 12$, $P3_1 21$, or $P3_2 21$
$a = 12.97 \pm 0.03$ A, $c = 9.27 \pm 0.02$ A
Density: 3.01 (calcd), $z = 18$

d, A			
Obsd	Calcd	*I*	*hkl*
6.46	6.49	20	110
5.29	5.31	38	111
3.74	3.77	25	112
	3.74		030
3.45	3.47	14	031
3.08	3.09	16	003
3.06	3.06	100	221
2.90	2.91	6	032
2.79	2.79	7	113
2.36	2.37	8	141
2.18	2.18	7	051
	2.18		114
	2.03		124
2.02	2.02	5	052
	2.02		150
1.95	1.96	11	332
1.91	1.92	13	143
1.88	1.87	76	060
1.86	1.86	25	134
1.76	1.76	6	025
	1.61		162
1.60	1.60	7	350
	1.60		070
	1.60		063
1.59	1.60	28	441
	1.59		135

TABLE II

INVARIANT EQUILIBRIA IN THE SYSTEM $NaF-ScF_3$

Compn, mole % ScF_3	Invariant temp, °C	Type of equilibrium	Phase reaction (invariant temp)
17	800	Eutectic	$L \rightleftharpoons NaF + \alpha\text{-}3NaF \cdot ScF_3$[a]
25	885	Congruent melting point	$L \rightleftharpoons \alpha\text{-}3NaF \cdot ScF_3$
35	680	Peritectic inversion of $3NaF \cdot ScF_3$	$\alpha\text{-}3NaF \cdot ScF_3 \rightleftharpoons \beta\text{-}3NaF \cdot ScF_3$
38	650	Eutectic	$L \rightleftharpoons \beta\text{-}3NaF \cdot ScF_3 + NaF \cdot ScF_3$
42	660	Peritectic	$L + ScF_3 \rightleftharpoons L + NaF \cdot ScF_3$

[a] L refers to liquid.

TABLE III

$NaF–ScF_3$ PHASE TRANSITION TEMPERATURE DATA OBTAINED FROM THERMAL GRADIENT QUENCHING EXPERIMENTS

Compn, mole % ScF_3	Liquidus temp, °C	Solidus temp, °C
0	995	
5	954	
10	913	
15	809	797
18	820	797
20	850	796
23	870	803
25	885	
27	878	647
30	830	665
35	680	650
36	674	651
37	652	652
38	657	657
40	653	653
41	668	652
42	738	657
45	880	659
50	1097	660
55		648
60		648
70		663

TABLE IV

$NaF–ScF_3$ PHASE TRANSITION TEMPERATURE DATA OBTAINED FROM THERMAL ANALYSIS

Compn, mole % ScF_3	Liquidus temp, °C	Solidus temp, °C	Other transition temp, °C
11	893	800	678
13	865	800	680
15	828	801	681
17	821	799	681
19	828	799	680
21	860	798	680
23	878	794	680
25	885	885	679
45		650	660
55		660	

and invert with little or no hysteresis to isomorphous, monoclinic, low-temperature forms. Indication of the solid-state transformation was confirmed by cooling curves and by data obtained on investigation of this compound with a high-temperature diffractometer. Results of these experiments indicate that the high-temperature form of $3NaF \cdot ScF_3$ is isomorphous with the high-temperature form of cryolite[13,14] and is a member of a group of complex fluorides which in their high-temperature forms adopt the ideal perovskite structure but which on cooling invert to a number of distorted forms whose structures are of lower symmetry.[15]

Within the subsystem $3NaF \cdot ScF_3$–ScF_3, three invariant equilibrium points occur: a peritectic at 35 mole % ScF_3 and at 680° associated with the solid-state transition in $3NaF \cdot ScF_3$, the eutectic at 38 mole % ScF_3 and at 650°, and a peritectic at 42 mole % ScF_3 and at 660°. The compound $NaF \cdot ScF_3$ melts incongruently at 660° to form ScF_3 and liquid. In a single-crystal X-ray diffraction study of $NaF \cdot ScF_3$, the phase was found to be hexagonal with $a = 12.97$ A and $c = 9.27$ A. The space group is one of the enantiomorphic pairs, $P3_112$, $P3_212$, $P3_121$, or $P3_221$. The reaction to form $NaF \cdot ScF_3$ from the melt is slow and the rate is controlled by solution of ScF_3 in the melt. Cooled melts in the region 42–50 mole % ScF_3 were generally found to contain a considerable amount of incompletely resorbed ScF_3 crystals. In order for the reaction between the liquid and ScF_3 to be completed, it was necessary to equilibrate the salt mixtures at or above the eutectic temperature for 10 or more days.

The results obtained in the current study of the $NaF–ScF_3$ system agree within experimental error with the liquidus curve of the NaF primary phase reported by Cantor and Ward.[5] The phase diagram described here affords an interesting contrast with that reported during the course of this investigation by Fedorov and associates,[6] who believed that the formula of the congruently melting intermediate phase in the system was $2NaF \cdot ScF_3$. The reasons for the remarkable difference between the two diagrams are not deducible from the literature. Scandium trifluoride, like many metal fluorides, is very easily hydrolyzed at high temperatures by traces of moisture in the atmosphere. Hydrolysis reactions such as

$$2Na_3ScF_6 + 2H_2O \rightleftharpoons 2NaF \cdot ScOF + 4NaF + 4HF$$

would account for the anomalous activity of NaF reported by Fedorov, *et al.*,[6] at low ScF_3 concentrations and for a 2:1 oxyfluoride phase not encountered in either our measurements or those of the more recent Russian investigators,[7] a phase which might have been inferred to be Na_2ScF_5.

The liquidus curve for compositions greater than 50 mole % ScF_3 is tentative and, because it occurs at temperatures which are intractably high for determination by the methods used in this study, was inferred by extrapolation to the reported melting point of ScF_3, 1515°.[12,16]

The phase diagram of the $NaF–ScF_3$ system, as well as the symmetry of the $3NaF \cdot ScF_3$ phase, shows that cation size and polarizability are the principal controlling factors in determining the character of interactions between pairs of ionic component salts. A consideration of the size of Na^+ and Sc^{3+} alone leads to the expectation that the $NaF–ScF_3$ system should have hybrid character and would resemble both the $NaF–LuF_3$[4] and $NaF–AlF_3$[17] systems. However, the molar refraction, a measure of polarization, for the crystalline phase $3NaF \cdot ScF_3$ is 18.0 cm³, much closer to that for cryolite (20.22 cm³) than to that for the equimolar $NaF–LuF_3$ crystalline phases (12.20 cm³). We infer this to mean that the effect of the lanthanide contraction on the sodium fluoride–lanthanide trifluoride crystalline

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(13) S. v. Naray-Szabo and K. Sasvari, *Z. Krist.*, **99**, 27 (1938).

(14) E. G. Steward and H. P. Rooksby, *Acta Cryst.*, **6**, 49 (1953).

(15) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962.

(16) L. N. Komissarova and B. I. Pokrovskii, *Dokl. Akad. Nauk SSSR*, **149**, 599 (1963).

(17) P. P. Fedotieff and W. P. Iljinskii, *Z. Anorg. Chem.*, **80**, 121 (1913).

phases was to reduce the polarizability of the rare earth cations significantly, whereas in the absence of this effect, relative polarizability of Sc^{3+} and Al^{3+} is great, and strongly bonded complex compounds with little compositional variability may be formed.[18] On the basis of this inference, phase diagrams of the binary systems of NaF with the group III fluorides, GaF_3, InF_3, and possibly TlF_3, should resemble that for NaF–ScF_3 rather than those of NaF with the heavier lanthanide trifluorides.

Acknowledgments.—The authors are pleased to acknowledge the assistance of G. M. Hebert and H. A. Friedman in the experimental work, T. N. McVay and H. Insley for measurements of optical properties, and J. H. Burns, G. D. Brunton, and D. R. Sears for assistance with the X-ray measurements.

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[18] The relationship between polarizabilities in complex fluorides was discussed in ref 4.

CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
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Equilibrium Dimorphism of the Lanthanide Trifluorides[1a]

BY R. E. THOMA AND G. D. BRUNTON

Received June 3, 1966

The lanthanide trifluorides SmF_3 to LuF_3 and YF_3 were found to undergo high-temperature dimorphism, inverting from hexagonal to orthorhombic crystals on cooling. Equilibrium inversion temperatures were determined for this group using a controlled-atmosphere, high-temperature X-ray diffractometer and were found to lie in the temperature range from 555° for SmF_3 to 1075° for ErF_3. Dimorphism was not observed for the compounds LaF_3 to NdF_3. A hexagonal modification of yttrium trifluoride, not heretofore described, was found to be the stable phase above 1052° and below the melting point. Although the hexagonal and orthorhombic forms of the lanthanide trifluorides SmF_3 to HoF_3 correspond to those described earlier by Zalkin and Templeton,[1b] hexagonal crystals of YF_3 and the lanthanide trifluorides ErF_3 to LuF_3, observed at high temperatures, were not isomorphous with tysonite, as was previously believed.

Introduction

The occurrence of dimorphism among the lanthanide trifluorides was first recognized by Zalkin and Templeton.[1b] They observed that at room temperature the trifluorides LaF_3 to NdF_3 occurred only in a hexagonal form, that SmF_3, EuF_3, HoF_3, and TmF_3 could be obtained either as the hexagonal ($P\bar{3}c1$) or orthorhombic form (Pnma), and that only an orthorhombic form of GdF_3, TbF_3, DyF_3, ErF_3, YbF_3, and LuF_3 could be produced. Melting points of the lanthanide trifluorides were determined later by Spedding and Daane,[2] who noted that SmF_3, GdF_3, ErF_3, YbF_3, and LuF_3 produced thermal effects at temperatures below the melting points. They inferred that these effects were the result of solid-stage crystalline inversions. Evidence of dimorphism was noted by both groups of investigators for SmF_3, by one or the other for EuF_3 to LuF_3, and by neither for LaF_3 to NdF_3, TbF_3, or DyF_3.

In recent investigations of the alkali fluoride–lanthanide trifluoride systems[3] we found that, as NaF–GdF_3 and NaF–TbF_3 mixtures crystallize from the molten state, the trifluoride components invert from the hexagonal (high-temperature) to the orthorhombic (low-temperature) form at 918 and 950°, respectively. Although these values are somewhat lower than those reported by Spedding and Daane for the transition temperatures, they are in sufficiently close agreement to suggest that the thermal effects they observed in the solid state resulted from the hexagonal–orthorhombic transition. We were unable to preserve hexagonal modifications of DyF_3, ErF_3, YbF_3, and LuF_3 on rapid cooling of NaF–LnF_3 mixtures. The results obtained in recent investigations of these and the LiF–LnF_3 systems at this laboratory strongly suggested that all of the lanthanide trifluorides may exhibit equilibrium dimorphic transitions at high temperatures. To test this possibility, we investigated the high-temperature behavior of each of the lanthanide trifluorides (excluding PmF_3) and YF_3 in a controlled-atmosphere X-ray diffractometer.

Experimental Section

The lanthanide trifluorides used in the present study were prepared and purified in this laboratory by conversion of the commercial oxides with ammonium bifluorides. Yttrium fluoride was obtained by the same procedures, described earlier,[4,5] which assure that the oxide contamination does not exceed approximately 300 ppm. The lanthanide oxides used for preparing the trifluorides were obtained from several commercial vendors; cationic purity nominally exceeded 99.9%. The results of

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[1] (a) Research supported by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.; (b) A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75**, 2453 (1953).

[2] F.H. Spedding and A. H. Daane, Ed., "The Rare Earths," John Wiley and Sons, Inc., New York, N. Y., 1961, p 78.

[3] R. E. Thoma, H. Insley, and G. M. Hebert, *Inorg. Chem.*, **5**, 1222 (1966).

[4] J. Walker and E. Olson, "Preparation of Yttrium Fluoride Using Ammonium Bifluoride," USAEC, IS-2, 1959.

[5] R. E. Thoma, *et al.*, *J. Phys. Chem.*, **65**, 1096 (1961).