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Phase Equilibria in the System Sodium Fluoride–Yttrium Fluoride

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A phase diagram of the condensed system $NaF-YF_3$ was constructed from data obtained in cooling-curve and quenching experiments. The number and identity of phases co-existing at equilibrium were determined by use of the X-ray diffractometer and the petrographic microscope. Two compounds, $NaF \cdot YF_3$ and $5NaF \cdot 9YF_3$, were formed from the components. Each compound exists in two polymorphic forms, the high-temperature form in both cases crystallizing from molten mixtures as fluorite-like cubic crystals. The two cubic phases form a continuous solid solution with a maximum melting temperature of 975° at the composition $5NaF \cdot 9YF_3$. Lattice parameters and refractive indices of the solid solution appear to be linear functions of the YF_3 content, $a = 5.447–5.530$ Å., refractive index 1.430–1.470. Pure crystals of $NaF \cdot YF_3$ invert from the fluorite cubic form, on cooling below 691°, to a hexagonal form which is isostructural with β_2-Na_2ThF_6, with lattice constants $a = 5.95$, $c = 3.52$ Å. The five primary phase fields below the liquidus were found to be NaF, hexagonal $NaF \cdot YF_3$, $NaF \cdot YF_3$–$5NaF \cdot 9YF_3$ ss, and two forms of YF_3. Two eutectics occur in association with these primary phases, at 29 and 75 mole % YF_3 and at 638 and 947°, respectively. Because of the isomorphism of YF_3 with the trifluorides of the rare earths samarium–lutetium and the similarity of their cation sizes, the system $NaF-YF_3$ is predicted to be an approximate model for each of the binary systems SmF_3–LuF_3 with NaF.

Introduction

The objectives of this investigation were (1) to provide important information on the relationship between cation radius ratio and complex fluoride compound formation and (2) to resolve discrepancies arising from previous investigations of the $NaF-YF_3$ system.

The senior author has shown the relation of cation sizes to the formation and character of complex compounds in binary systems of alkali fluorides with fluorides of metals in groups I to IV.[2] To extend this relation to include phase equilibrium behavior, the $NaF-YF_3$ system was chosen as a model binary system in order to predict phase behavior in the $NaF-MF_3$ system where M is any rare earth from Sm to Lu. The closeness of ionic size between Y^{3+} and the heavier trivalent rare earth cations is the basis for believing that the $NaF-YF_3$ system will be suitable as such a model.

Previous investigations[3–5] of phase relationships in the system $NaF-YF_3$ differ markedly. The only investigation of the liquid–solid equilibria was conducted by Dergunov, who constructed a phase diagram of the system and other binary systems with the alkali fluorides, based primarily on cooling-curve studies. Although Dergunov concluded that NaF and YF_3 produced a continuous solid solution and no intermediate compounds, Hund subsequently showed that the compound $NaF \cdot YF_3$ existed and could be produced either from anhydrous molten fluoride mixtures or in aqueous solutions. He reported the compound to be dimorphic, occurring as a high-temperature cubic phase, "β-$NaYF_4$," and as a low-temperature phase, "α-$NaYF_4$," of lower but undetermined symmetry. Hund's study showed that β-$NaYF_4$ crystallizes in a cubic structure of fluorite type, which is capable of accommodating a substantial amount of additional YF_3 within the lattice. Hund[4] and Roy[6] observed substitution limits of YF_3 in $NaYF_4$ to be approximately 50%. In an attempt to produce a cubic form of YF_3 by precipitation of YF_3 in an aqueous NaF solution, Nowacki prepared crystals which he believed to be a polymorph of YF_3 and with an X-ray powder pattern he indexed as primitive cubic. Zalkin and Templeton[7] have speculated that this primitive cubic phase is that of the compound $NaF \cdot 3YF_3$. In the absence of a consensus regarding the solid phase relationships among $NaF-YF_3$ phases, it was evident that further investigation of this important system was indeed worthwhile.

Experimental

Materials.—The mixtures used in these equilibrium studies were prepared from commercially available reagent grade sodium fluoride and specially purified yttrium fluoride. Equilibrium data were obtained from mixtures which contained YF_3 converted from the oxide by ammonium bifluoride. The oxygen concentration in YF_3 thus produced was found to be 600 p.p.m., by the bromine trifluoride method of analysis. Additional data were obtained with YF_3 produced by gaseous hydrofluorination of Y_2O_3. The small amount of oxide remaining in this product (1600 p.p.m.) seriously affected the results of the quenching experiments (see Table IV), especially those designed to determine the composition limits of the $NaF-YF_3$ fluorite solid solution. It was necessary to maintain <500 p.p.m. of oxygen in the $NaF-YF_3$ mixtures in order to obtain reproducible and consistent results. These methods of purification and analysis of YF_3 mixtures were discussed previously.[8]

Apparatus and Methods.—The techniques and apparatus employed in studying $NaF-YF_3$ equilibrium relationships as well as the methods for identifying phases were discussed pre-

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[1] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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

[3] E. P. Dergunov, *Dokl. Akad. Nauk SSSR*, **60**, 1185 (1948).

[4] F. Hund, *Z. anorg. Chem.*, **261**, 106 (1950); F. Hund, *ibid.*, **263**, 102 (1950).

[5] W. Nowacki, *Z. Krist.*, **100**, 242 (1938).

[6] D. M. Roy and R. Roy, Paper No. 12-B-62, presented at the 64th Annual Meeting of the American Ceramic Society, April 29–May 2, 1962; Abstract: *Bull. Am. Ceram. Soc.*, **41**, 221 (1962).

[7] A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75**, 2453 (1953).

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

viously.[9,10] A useful and often necessary method of protecting purified fluoride mixtures from contamination by adsorbed water consists in avoiding exposure to the atmosphere during all handling procedures following purification with ammonium bifluoride. The same mixtures used in the cooling-curve experiments were homogenized and reused in quenching experiments. Grinding and loading were done in an inert-atmosphere glove box. The water content of the atmosphere was maintained at 50 p.p.m. or less. Data from cooling-curve experiments were used for preliminary estimations of composition–temperature relationships. Liquidus data for the primary phase fields of NaF and YF_3 were best obtained from cooling-curve data, while solid-state transition data were best obtained from specimens annealed in a thermal gradient and quenched. The reliability of the determination of phase transitions of molten salts is increased if temperatures determined from quench studies coincide with inflection temperatures observed from cooling curves. However, for NaF–YF_3 mixtures containing from 45 to 65 mole % YF_3, cooling curves were not, in general, useful in estimating the temperatures of crystallization. Also, inversion reactions of the NaF–YF_3 cubic solid solutions could not be determined by cooling curves because little heat is evolved and equilibrium crystallization frequently does not occur. Consequently, equilibrium data were obtained principally from specimens which were equilibrated in a thermal gradient at high temperatures for various periods ranging from 2 days to 1 month and were then quenched. The equilibration periods were varied according to the transition investigated; *e.g.*, specimens were equilibrated for 1 to 7 days if liquid–solid transitions were expected and 2 to 4 weeks if solid-state transitions were expected. In the absence of cooling-curve inflections, verification of the equilibrium phase transitions was obtained by reproducing the transition with specimens which before equilibration contained, in one case, the crystalline phases found above the transition temperature and, in the other case, the crystalline phases found below the transition temperature.

Results and Discussion

The phase diagram of the system NaF–YF_3 is presented in Fig. 1. Invariant and singular points in the system are given in Table I. Phase transition data obtained from thermal gradient quenching and cooling-curve experiments are presented in Tables II and III. Phase equilibria in the system NaF–YF_3 involve the components and two intermediate compounds, $NaF{\cdot}YF_3$ and $5NaF{\cdot}9YF_3$. The phase diagram of the system NaF–YF_3 contains several features which have seldom if ever been observed in phase behavior of salt mixtures. Of particular interest are the equilibrium phase reactions involving the two intermediate compounds, $NaF{\cdot}YF_3$ and $5NaF{\cdot}9YF_3$, which crystallize from the melt as fluorite-like cubic crystals, form a continuous series of solid solutions with a maximum melting temperature at the latter composition, and invert to other forms at low temperatures. Crystals of the stoichiometric cubic phases, $NaF{\cdot}YF_3$ and $5NaF{\cdot}9YF_3$, may also be formed from molten mixtures of NaF and YF_3: $NaF{\cdot}YF_3$ from mixtures containing 32 to 41 mole % YF_3 and $5NaF{\cdot}9YF_3$, at its composition. Refractive indices and lattice parameters of the cubic solid solutions were found to be functions of the YF_3 content (Fig. 2). At temperatures below 691°, cubic $NaF{\cdot}YF_3$ inverts to a hexagonal form. The hexagonal phase persisted in specimens annealed for 4 weeks at temperatures as low as 350°, the practical minimum for this study. At temperatures below 710°, cubic $5NaF{\cdot}9YF_3$ inverts to a phase which appears to be an ordered form of the compound. The ordered phase is stable in the temperature interval 710 to 537°; at equilibrium, it is unstable below 537°, decomposing on cooling into hexagonal $NaF{\cdot}YF_3$ and YF_3.

Table I

Invariant and Singular Points in the System NaF–YF_3

Compn., mole % YF_3	Temp., °C.	Type of equil. at invariant temp.	Equilibrium reaction
28	638	Eutectic	L $\rightleftharpoons$ NaF + hexagonal $NaF{\cdot}YF_3$
32	691	Peritectic	Cubic $NaF{\cdot}YF_3$ + L $\rightleftharpoons$ hexagonal $NaF{\cdot}YF_3$ + L
58.5	665	Eutectoid	Fluoride ss $\rightleftharpoons$ hexagonal $NaF{\cdot}YF_3$ ss + orthorhombic YF_3
64.28	975	Congruent m.p. for $5NaF{\cdot}9YF_3$	L $\rightleftharpoons$ cubic $5NaF{\cdot}9YF_3$
64.28	710	Inversion of $5NaF{\cdot}9YF_3$	Disordered cubic $5NaF{\cdot}9YF_3$ $\rightleftharpoons$ ordered $5NaF{\cdot}9YF_3$
64.28	537	Dec. of $5NaF{\cdot}9YF_3$	$5NaF{\cdot}9YF_3$ $\rightleftharpoons$ hexagonal $NaF{\cdot}YF_3$ ss + YF_3 (orthorhombic)
75	947	Eutectic	L $\rightleftharpoons$ cubic $5NaF{\cdot}9YF_3$ ss + orthorhombic YF_3
91	1052	Peritectic	L + high-temperature YF_3 $\rightleftharpoons$ L + orthorhombic YF_3

Solid Phase Boundaries.—In previous investigations of fluoride systems, the composition of pure solid phases was established by synthesizing a single crystalline phase at a unique composition.[11] This method was also used in the present work to establish the properties of the phases at the composition of the compounds $NaF{\cdot}YF_3$ and $5NaF{\cdot}9YF_3$. In addition, the parametric method of extrapolating lattice constants and refractive indices was used in determining the solid solution phase boundaries. The disappearing phase method was also applied in an attempt to determine whether the compound formula, $NaF{\cdot}YF_3$, could be confirmed by this X-ray method. Fourteen slowly cooled NaF–YF_3 mixtures were used, varying in composition from 2.5 to 47 mole % YF_3. The diminution in intensities of NaF lines for the specimens in this composition range was regular enough to confirm that the hexagonal phase has the formula $NaF{\cdot}YF_3$, though not sufficiently regular to prove the absence of the phase region $Na_{1+x}YF_{4-x}$.

Crystallization from Slowly Cooled Melts.—Equilibrium crystallization from NaF–YF_3 melts, cooling at rates of 1 to 3°/min., occurred only for compositions containing 0 to 32 mole % YF_3. Mixtures containing greater than 32 mole % YF_3 produced crystals of the

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(9) C. J. Barton, *et al.*, *J. Am. Ceram. Soc.*, **42**, 63 (1958).

(10) H. A. Friedman, G. M. Hebert, and R. E. Thoma, "Thermal Analysis and Gradient Quenching Apparatus and Techniques for the Investigation of Fused Salt Phase Equilibria," Oak Ridge National Laboratory report No. ORNL-3373 (Dec. 18, 1962).

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

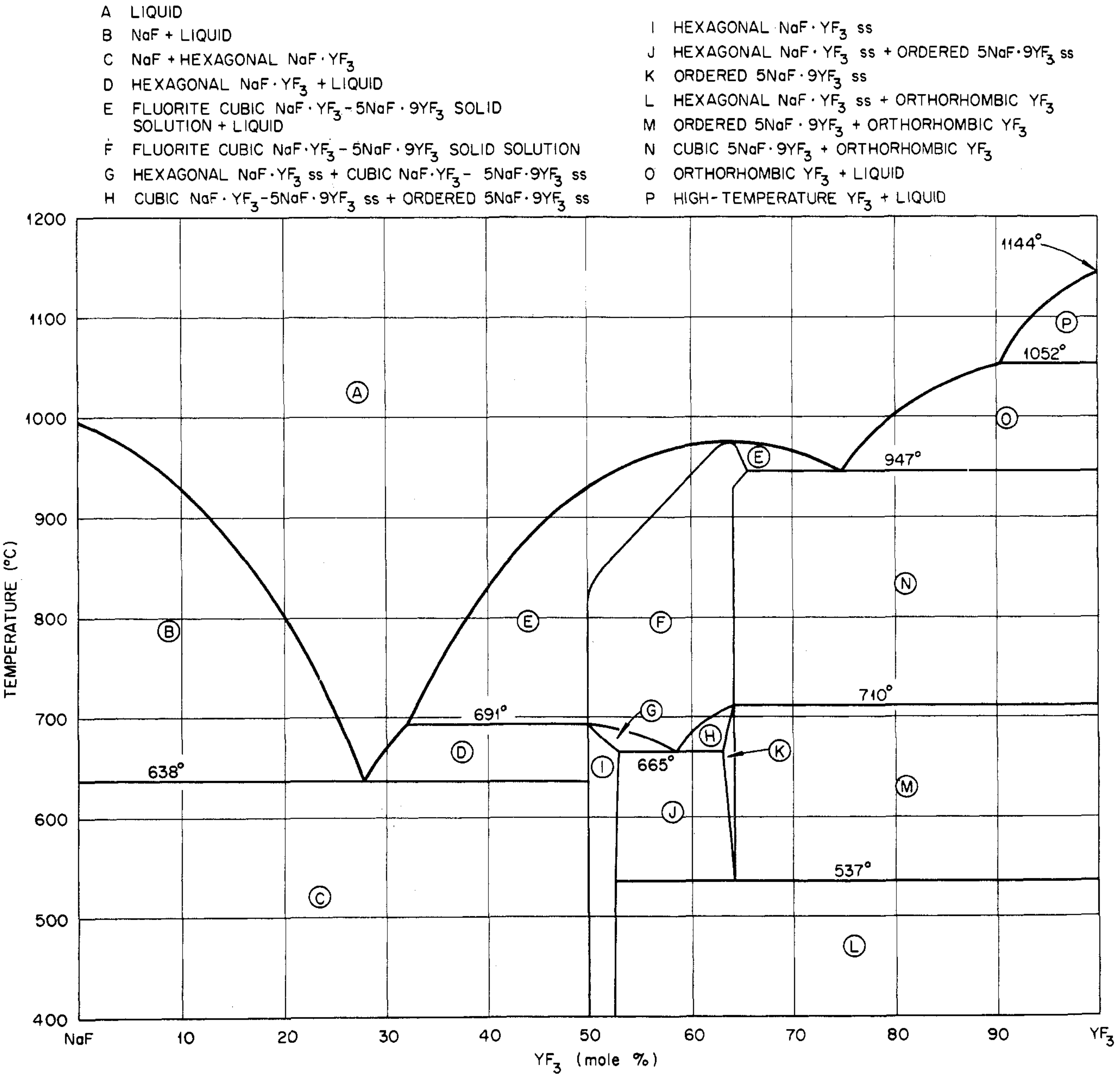

Fig. 1.—The system NaF–YF$_3$.

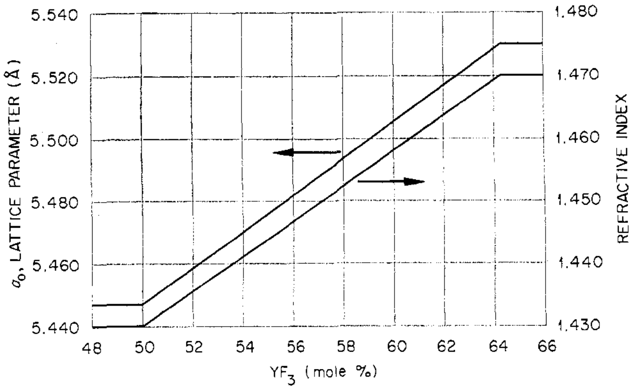

Fig. 2.—Lattice parameter and refractive indices of NaF–YF$_3$ fluorite solid solutions.

fluorite cubic phase as the primary phase, which inverted to hexagonal crystals only after cooling well below the equilibrium transition temperature at compositions of 32 to 54 mole % YF$_3$. At greater YF$_3$ concentrations, the cubic phase inverted to the hexagonal form only partially (55 to 57 mole % YF$_3$) or not at all ($>58\%$). As the cubic solid solution at 55 to 57 mole % YF$_3$ began to invert, hexagonal NaF·YF$_3$ was formed and the YF$_3$ concentration of the remaining unconverted cubic phase increased and became that of the eutectoid composition (58.5%). That this phase change occurred in the slowly cooled melts is shown by the high refractive index of the cubic phases remaining in the cooled melts. The fluorite solid solution was retained in cooled melts having compositions of 58 to 64 mole % YF$_3$ as the single phase remaining on cooling. At the composition 5NaF·9YF$_3$, slowly cooled melts produced a single phase, the ordered form of 5NaF·9YF$_3$. At all compositions greater than 64.5 mole % two phases remained on cooling, crystals of the fluorite cubic form of 5NaF·9YF$_3$ and orthorhombic YF$_3$.

TABLE II

PHASE TRANSITION DATA OBTAINED FROM QUENCHED NaF–YF_3 MIXTURES

Compn. mole % YF_3	Transition temp., °C.	Type transition[a]	Solid phases above transition temp.	n_D of cubic phase	Solid phases below transition temp.	n_D of cubic phase	a_0 of cubic phase
2.5	970 ± 3[b]	L	. . .		NaF		
5.0	948 ± 4	L	. . .		NaF		
	638 ± 3	S	NaF		NaF, H-1:1[c]		
15.0	864 ± 4	L	. . .		NaF		
19.0	778 ± 4	L	. . .		NaF		
	638 ± 3	S	NaF		NaF, H-1:1		
22.5	742 ± 3	L	. . .		NaF		
	639 ± 4	S	NaF		NaF, H-1:1		
25.0	629 ± 3	L	. . .		NaF		
	641 ± 3	S	NaF		NaF, H-1:1		
29.0	654 ± 3	L	. . .		H-1:1		
	635 ± 3	S	H-1:1		H-1:1, NaF		
30.0	639 ± 4	S	H-1:1		H-1:1, NaF		
33.3	726 ± 2	L	. . .		Cubic[d]	1.430	
37.0	788 ± 2	L	. . .		Cubic	1.422	
	690 ± 3	P	Cubic	1.426	H-1:1		
	645 ± 4	S	H-1:1		H-1:1, NaF		
48.0	908 ± 4	L	. . .		Cubic	1.446	
	803	. .[e]			Cubic	1.432	
	739	. .			Cubic	1.428	
	690 ± 3	P	Cubic	1.426	H-1:1		
	632 ± 4	S	H-1:1		H-1:1, NaF		
50.0	930 ± 3	L	. . .		Cubic	1.448	
	904	. .			Cubic	1.444	
	888	. .			Cubic	1.440	
	852	. .			Cubic	1.438	
	830 ± 3	S	Cubic	1.438	Cubic	1.432	5.4473
	814	. .			Cubic	1.432	5.4473
	740	. .			Cubic	1.430	5.4473
	694 ± 3	I	Cubic	1.430	H-1:1		
52.0	697 ± 3	I	Cubic	1.434	Cubic, H-1:1		
	670 ± 3	I	Cubic, H-1:1		H-1:1		
54.0	703 ± 3	I	Cubic	1.440	Cubic, H-1:1		
	678 ± 3	I	Cubic, H-1:1	1.440	H-1:1		
55.0	964 ± 4	L	. . .		Cubic	1.456	
	890 ± 5	S	Cubic	1.458	Cubic	1.452	
	705	. .				1.446	
	685 ± 3	I	Cubic	1.446	Cubic, H-1:1	1.450	
	659 ± 3	I	Cubic, H-1:1	1.450	H-1:1, O-5:9[f]		
58.0	970 ± 4	L	. . .		Cubic	1.460	
	960 ± 5	L	. . .		Cubic	1.459	
	903 ± 4	S	Cubic	1.456	Cubic	1.454	5.4986
60.0	970 ± 10	L	. . .		Cubic		
	961 ± 6	L	. . .		Cubic	1.462	
	930 ± 6	S	Cubic	1.460	Cubic	1.459	5.5060
	666 ± 6	I	Cubic	1.464	Cubic, H-1:1	1.464	5.5060
62.0	974 ± 5	L	. . .		Cubic	1.466	
	946 ± 5	L	. . .		Cubic	1.466	5.5150
62.5	970 ± 5	L	. . .		Cubic	1.470	
	945 ± 5	S	Cubic	1.470	Cubic	1.468	
	645 ± 4	I	Cubic	1.467	Cubic, O-5:9		
	638 ± 4	I	Cubic, O-5:9	1.470	O-5:9		
	539 ± 2	D	O-5:9		H-1:1, YF_3		
63.0	682 ± 4	I	Cubic	1.468	Cubic, O-5:9		
	651 ± 4	I	Cubic, O-5:9		O-5:9		
	538 ± 3	I	O-5:9		O-5:9, H-1:1		
63.5	970 ± 4	L	. . .		Cubic	1.472	5.5240
	717 ± 3	I	Cubic	1.470	O-5:9, cubic		
	659 ± 4	I	O-5:9, cubic		O-5:9, H-1:1		
	538 ± 4	D	O-5:9		H-1:1, YF_3		
64.0	972 ± 4	L	. . .		Cubic	1.470	5.5300
	946 ± 5	S	Cubic		Cubic	1.470	5.5300
64.28	974 ± 5	L	. . .		Cubic	1.470	5.5300
	696 ± 4	I	Cubic	1.470	O-5:9		
	537 ± 2	D	O-5:9		O-5:9, H-1:1, YF_3		
65.5	975 ± 4	L	. . .		Cubic	1.470	
	945 ± 4	S	Cubic	1.470	Cubic	1.472	

TABLE II (*Continued*)

Compn., mole % YF_3	Transition temp., °C.	Type transition[a]	Solid phases above transition temp.	n_D of cubic phase	Solid phases below transition temp.	n_D of cubic phase	a_0 of cubic phase
66.7	976 ± 2	L	...		Cubic	1.472	5.5300
	944 ± 6	S	Cubic	1.473	Cubic, YF_3	1.473	
	963 ± 5	L	...		Cubic	1.472	
	852	..			Cubic	1.471	
	557 ± 4	D	O-5:9		H-1:1, YF_3		
68.0	953 ± 5	L	...		Cubic	1.474	
	934 ± 10	S	Cubic	1.474	Cubic, YF_3	1.472	
	557 ± 4	D	O-5:9		H-1:1, YF_3		
70.0	975 ± 5	L	...		Cubic		5.53
	956 ± 5	S	Cubic		Cubic, YF_3	1.476	5.53
	940 ± 5	S	Cubic	1.470	Cubic, YF_3	1.471	
	850	..				1.470	
72.5	955 ± 4	L	...		Cubic	1.478	
	942 ± 5	S	Cubic	1.478	Cubic, YF_3	1.478	
75.0	947 ± 5	E	...		Cubic, YF_3	1.477	
	840	..				1.474	5.53
77.5	973 ± 5	L	...		YF_3		
	938 ± 5	S	YF_3		YF_3, cubic	1.474	
80.0	994 ± 5	L	...		YF_3		
85.0	1022 ± 4	L	...		YF_3		
90.0	1048 ± 4	L	...		YF_3		
95.0	1127 ± 5	L	...		YF_3		

[a] The symbols L, S, I, D, and E refer to the liquidus, solidus, decomposition, and eutectic transitions, respectively. [b] The uncertainty in temperatures shown in column 2 indicates the temperature differences between the quenched samples from which the values were obtained. [c] H-1:1 refers to the hexagonal form of $NaF\cdot YF_3$ or to solid solutions of the hexagonal form. [d] Cubic refers to cubic solid solutions of $NaF\cdot YF_3$ and $5NaF\cdot 9YF_3$ or the compounds themselves. [e] Items not designating phase transitions are included to show variation of refractive indices with temperature. [f] O-5:9 refers to the low-temperature ordered form of $5NaF\cdot 9YF_3$.

Very little if any heat was associated with solid transitions occurring in the composition range 50 to 91 mole % YF_3. Consequently, many of the equilibrium transitions could be determined only through the use of the static methods.

Crystalline Phases in Quenched Specimens.—Solid-state boundaries in the system NaF–YF_3 were determined from the number and identity of solids preserved in specimens quenched from high temperatures. These experiments were uniquely adaptable for a study of equilibrium relationships involving the compounds $NaF\cdot YF_3$ and $5NaF\cdot 9YF_3$.

The composition–temperature limits of cubic $NaF\cdot YF_3$–$5NaF\cdot 9YF_3$ solid solutions were observed to be at 50 ± 0.5 and 64.5 ± 0.5 mole % YF_3 through a temperature interval from just below the solidus to that of the lower stability temperature, 538°. At temperatures just above and below the $5NaF\cdot 9YF_3$–YF_3 947° solidus, $5NaF\cdot 9YF_3$ dissolved a small amount of orthorhombic YF_3 in the solid state, extending the fluorite phase limit to 65.5 mole % YF_3. The inference that the phase limit at 64.5 mole % YF_3 indicates the existence of the compound $5NaF\cdot 9YF_3$ is based on these facts: (1) the experimental phase boundary virtually coincides with the stoichiometric ratio, $5NaF\cdot 9YF_3$, (2) the phase boundary is vertical as a function of temperature, and (3) the phase $5NaF\cdot 9YF_3$ melts congruently.

Solubility relationships between $NaF\cdot YF_3$ and $5NaF\cdot 9YF_3$ in the temperature range 500 to 700° were determined from X-ray and optical examinations. X-Ray data provided evidence that the ordered form of $5NaF\cdot 9YF_3$ has variable composition, with maximum variation at the eutectoid temperature, at which temperature the phase apparently can become slightly deficient in YF_3. The phase boundaries were based on the change in observed intensities of the $5NaF\cdot 9YF_3$ superlattice lines as a function of temperature for compositions adjacent to that of the compound $5NaF\cdot 9YF_3$. Qualitative estimates of the fraction of optically birefringent material present in the same specimens as a function of temperature correlated well with the X-ray intensity data. Variable composition in the hexagonal form of $NaF\cdot YF_3$ was determined from the measured increase in refractive index and from determinations of the number and identity of phases in the quenched specimens.

Equilibrium phases were not isolated under some conditions of this study. Crystals of the high-temperature form of YF_3 were not preserved by quenching methods. The fact that the inversion is highly energetic[8] suggests that it will be possible to characterize the pure phase only at high temperatures. It was found that the refractive index of the fluorite-type cubic phase in slowly cooled preparations is generally higher than the refractive index of primary phase crystals of the same composition. The difference is probably due to the fact that slow cooling has an annealing effect which results in a slightly greater ordering and densification. Rapidly cooled mixtures containing 35 to 40 mole % YF_3 occasionally produced a solid phase, metastable with respect to NaF–YF_3 equilibrium solid phases. Pure crystals of the phase have not yet been isolated. The principal X-ray diffraction maxima for this metastable phase were found at 6.24, 3.88, and 2.91 Å.

TABLE III

PHASE TRANSITION DATA OBTAINED FROM NaF–YF_3 MIXTURES COOLED AT 1 TO 3°/MIN.

Compn., mole % YF_3	Liquidus, °C.	Solidus, °C.	Inversion temp., °C.	Solids produced in cooled melt	n_D of fluorite cubic	a_0 of fluorite cubic
2.5	917	606	...	NaF, H-1:1[a]		
5.0	952	608	...	NaF, H-1:1		
8.0	942	...	...	NaF, H-1:1		
10.0	927	616	...	NaF, H-1:1		
13.0	888	...	...	NaF, H-1:1		
15.0	875	625	...	NaF, H-1:1		
19.0	905	628	...	NaF, H-1:1		
22.5	744	622	...	NaF, H-1:1		
25.0	695	628	...	NaF, H-1:1		
29.0	...	632	...	NaF, H-1:1		
32.0	...	620	...	NaF, H-1:1		
33.3	...	625	652	NaF, H-1:1		
35.0	735	615	...	NaF, H-1:1		
37.0	806	629	...	NaF, H-1:1		
40.0	862	620	...	NaF, H-1:1		
41.0						
45.0	...	615	650	NaF, H-1:1		
48.0	928	...	...	NaF, H-1:1		
49.5	938	...	646	NaF, H-1:1		
49.75	930	...	638	NaF, H-1:1		
50.0	941	...	653	H-1:1		
52.0[b]	...	...	...	H-1:1		
53.0[b]	...	...	...	H-1:1		
54.0	955	...	...	H-1:1		
55.0	...	...	590	H-1:1, cubic[c]	1.454	
56.0[b]	...	...	...	H-1:1, cubic	1.463	
58.0	965	...	630	H-1:1, cubic	1.457	5.4980
60.0	969	...	691	Cubic	1.459	5.5040
62.0	970	...	...	Cubic	1.466	5.5167
62.5	...	...	...	Cubic, YF_3	1.468	
63.0	...	...	...	Cubic	1.470	
63.5	...	...	...	Cubic	1.472	
64.0	973	...	...	O-5:9,[d] cubic	1.4705	5.5260
64.28	988	935	...	O-5:9, cubic	1.476	
64.5	...	952	...	Cubic		
65.0	...	...	...	Cubic, YF_3	1.472–1.476	
66.7	965	940	...	Cubic, YF_3	1.472	5.5240
68.0	...	...	...	Cubic, YF_3	1.473	
70.0	1079	945	...	Cubic, YF_3	1.4705	
72.5	...	952	...	Cubic, YF_3	1.474	
75.0	961	947	...	Cubic, YF_3	1.470–1.472	
77.5	982	...	...	Cubic, YF_3	1.470–1.473	
85.0	1038	940	...	Cubic, YF_3	1.490–1.493	
90.0	1070	915	1006, 613	Cubic, YF_3	1.490	
95.0	1102	940	1052	Cubic, YF_3	1.490	

[a] H-1:1 refers to the hexagonal form of NaF·YF_3 or to solid solutions of the hexagonal form. [b] These preparations were cooled too slowly to allow detection of changes in cooling rates. [c] Cubic refers to cubic solid solutions of NaF·YF_3 and 5NaF·9YF_3 or the compounds themselves. [d] O-5:9 refers to the low-temperature ordered form of 5NaF·9YF_3 or to solid solutions of the ordered phase.

Effects of Hydrolysis in Phase Transitions.—Previous investigators were probably unable to obtain equilibrium phase data because of the difficulty of obtaining oxygen-free YF_3 and NaF–YF_3 crystal phases. In early stages of our investigation it was not apparent that small amounts of hydrolysis products, occasionally present, markedly affected the results of experiments designed to determine the upper YF_3 composition limit of the fluorite solid solution. Reliable phase transition data were obtained only after oxide-free YF_3 was employed and purified NaF–YF_3 mixtures were protected from all further exposure to water-laden atmospheres. Like many heavy metal fluorides, NaF–YF_3 mixtures are easily hydrolyzed at high temperatures by small amounts of water, usually absorbed at low temperature during routine transfer operations. An optically cubic form of YOF is produced on hydrolysis of YF_3 and is soluble in the fluorite solid solution. Our preliminary results, and almost certainly those of other investigators, were adversely affected by YOF dissolved in the fluorite phase. The refractive index of cubic YOF is 1.78 and that of the fluorite solid solution 1.430 to 1.473 ± 0.002. Therefore, contamination of the fluorite solid solution by dissolved YOF can be detected by small changes in refractive index for YOF concentration levels as low as 350 to 550 p.p.m. Whereas our first estimate of the solubility limit of YF_3 in NaF·YF_3 was 75 mole % YF_3, equivalent to

TABLE IV

PHASE TRANSITION DATA OBTAINED FROM QUENCHED IMPURE NaF–YF_3 MIXTURES

Compn., mole % YF_3	Transition temp., °C.		Type of transition	Solid phases above trans. temp.	n_D of cubic phase		Solid phases below trans. temp.	n_D of cubic phase		Estd. concn. of oxide ion, p.p.m.
	Obsd.	Equil.			Obsd.	Equil.		Obsd.	Equil.	
52	>1000	945	L	. . .			Cubic	1.488		1650
	842	857	S	Cubic	1.474		Cubic	1.442	1.436	
55	>925	958	L	. . .			Cubic	1.472	1.456	960
	891	891	S	Cubic	1.458		Cubic	1.458	1.444	
60	1011	970	L	. . .			Cubic	1.492	~1.470	1140
	953	938	S	Cubic	1.466	1.458	Cubic	1.464	1.458	
62	1023	972	L	. . .	1.470		Cubic	1.498	~1.470	1545
	945	957	S	Cubic	1.474	1.463	Cubic	1.474	1.463	
70	975	965	L	. . .			Cubic	1.480	~1.470	1200
	956	947	S	Cubic	1.480	1.472	Cubic + Y	1.480	1.472	
75	958	947	S	. . .			Cubic + YF_3	1.478	1.472	900
80	958	947	S	YF_3			Cubic + YF_3	1.496	1.472	3600
85	962	947	S	YF_3			Cubic + YF_3	1.518	1.472	6900
90	957	947	S	YF_3			Cubic + YF_3	1.487	1.472	750
95	970	945	S	YF_3			Cubic + YF_3	1.496	1.472	3600

that estimated by Hund, the limit determined for specimens which were essentially oxide-free was 64.5 mole % YF_3 at temperatures below 950° and up to 65.5 mole % YF_3 at the solidus. Small amounts of hydrolysis products also affected NaF–YF_3 liquid–solid transitions sharply. Solidus transitions obtained using YF_3, for which analytical results indicated an oxygen content of 1600 p.p.m., are shown in Table IV. The effect on the transition temperatures as well as on the refractive index of the fluorite cubic phase is apparently related to the quantity of contaminating oxide.

Transitions in 5NaF·9YF_3.—A molten mixture of the composition 35.72NaF–64.28YF_3 (mole %) crystallizes completely at 975° to form crystals of the cubic phase, 5NaF·9YF_3, with a_0 = 5.530 ± 0.005 Å., refractive index 1.470. Mixtures containing more than 65.5 mole % YF_3 retain cubic crystals having refractive indices of 1.470 to 1.473 after quenching from temperatures near that of the eutectic, 947°. The highest refractive indices were observed at the eutectic temperature, indicating that a small amount of YF_3 may be dissolved in 5NaF·9YF_3 in the solid state; this solubility is indicated in Fig. 1.

Crystals of the ordered form of 5NaF·9YF_3 were prepared by slowly cooling (1 to 3°/min.) a molten solution of the stoichiometric composition. Other molten NaF–YF_3 mixtures containing >60 mole % YF_3 retained fluorite-type cubic phases on slow cooling (1 to 3°/min.). These mixtures, when annealed in the temperature range 538 to 710° for 2 to 3 weeks and quenched, contained crystals of a uniaxial phase which produced an X-ray powder diffraction pattern of an ordered phase, distinguished from that of the high-temperature cubic form of 5NaF·YF_3 by additional lines typical of a superlattice. Crystals of this low-temperature ordered form of 5NaF·9YF_3 are uniaxial negative, with refractive indices N_α 1.465, N_ω 1.478. The phase has no equilibrium stability below 537°. Information leading to an understanding of the mechanism of ordering which occurs between the high- and low-temperature forms of 5NaF·9YF_3 must be obtained from single crystals. A study of this ordering mechanism has been initiated.

The formation of the ordered 5NaF·9YF_3 phase bears a close resemblance to the behavior of UO_2 under high-temperature oxidation. As UO_2 is oxidized, oxygen enters the fluorite lattice and occupies octahedral holes until a saturating composition corresponding to $UO_{2.25}$ is reached. At this composition and at temperatures below 1400°, the stable crystal phase is ordered and is related to the UO_2 fluorite solid solution by producing additional X-ray lines, indicating the occurrence of a superlattice.[12] As an ordered phase, the material is considered to be $U_4O_{9\pm x}$. Recent descriptions of the UO_2 fluorite solid solution phase boundary such as that given by Alexander and Shevlin[13] indicate that it, like the fluorite phase boundary in the system NaF–YF_3, is essentially vertical through a wide range of temperatures. This striking similarity between the fluorides and oxides with respect to the types of phase transitions and the persistence of a phase boundary which does not change significantly with temperature strongly suggests that the phase boundary in the UO_{2+x} solid solution indicates the existence of U_4O_9 as a high-temperature cubic phase which forms solid solutions with UO_2. This conclusion appears to be supported by the results of recently reported work by Lynds, *et al.*,[14] which showed that the lattice constants measured for oxidized and quenched specimens of UO_2 followed "two separate linear functions, one characteristic of UO_{2+x} and the other of U_4O_{9-y}." Density data were consistent with an oxygen vacancy model for U_4O_{9-y}.

Structures of NaF–YF_3 Crystal Phases.—Eight crystal phases are formed in the system NaF–YF_3. Of these, four are polymorphic forms of the two interme-

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(12) P. B. Belbeoch, C. Piekarski, and P. Perio, *Acta Cryst.*, **14**, 837 (1961).

(13) C. A. Alexander and T. A. Shevlin, Paper No. 14, in "Nuclear Reactor Chemistry, Second Conf., Gatlinburg, Tenn., Oct. 10–12, 1961," TID-7622, p. 139.

(14) L. Lynds, W. A. Young, J. S. Mohl, and G. G. Libowitz, Paper No. 9, Division of Inorganic Chemistry, 141st National Meeting of the American Chemical Society, Washington, D. C., March 20–29, 1962.

diate compounds, $NaF\cdot YF_3$ and $5NaF\cdot 9YF_3$; one is an unidentified metastable compound of probable formula $5NaF\cdot 3YF_3$; the other three include NaF and two forms of YF_3. Yttrium trifluoride crystallizes from the molten phase in an unknown crystal form which inverts on cooling below 1052° to the orthorhombic form described by Zalkin and Templeton.[7] Lattice parameters and refractive indices of the cubic $NaF\cdot YF_3$–$5NaF\cdot 9YF_3$ solid solution crystals are given in Fig. 2. Inversion of cubic $NaF\cdot YF_3$ crystals results in the formation of uniaxial (+) hexagonal crystals having refractive indices N_ω 1.464, N_ϵ 1.486, with $a = 5.95 \pm 0.03$ Å. and $c = 3.52 \pm 0.03$ Å.[15] The calculated density of these crystals with 1.5 formula weights per unit cell is 4.22 g./cc., as compared with a measured value of 4.2 g./cc. Because of the similarity of stoichiometry and unit-cell dimensions, the hexagonal phase was deduced to be isostructural with β_2-Na_2ThF_6. Although the powder pattern of the ordered form of $5NaF\cdot 9YF_3$ can be indexed assuming a primitive cubic cell with $a = 5.530$ Å., a larger cell is required by stoichiometry; moreover, a noncubic symmetry is indicated by optical data since the crystals are uniaxial (−), with N_α 1.465, N_ω 1.478. An explanation consistent with these observations is that the unit cell is tetragonal with the unique axis being some integral multiple of the pseudo-cubic cell edge, but single-crystal data are needed to test this hypothesis. Evidence that the low-temperature form of $5NaF\cdot 9YF_3$ exists over a small but finite composition range was observed in the powder diffraction patterns at 63.5 and 64 mole % YF_3; through the temperature interval 710 to 537°, the intensities of the superlattice lines were reduced in proportion to the extent that the composition $5NaF\cdot 9YF_3$ deviated from the stoichiometric ratio. The primitive lattice reported by Nowacki[5] is very similar to that of the ordered form of $5NaF\cdot 9YF_3$ and, though slightly larger in apparent cell size, is not deducible as identical. The lattice parameter assigned to the "primitive cubic YF_3" observed by Nowacki was 5.655 ± 0.003 Å. Although Zalkin and Templeton inferred that the primitive cubic phase was $NaF\cdot 3YF_3$,[7] no conclusions can be drawn with respect to the relationship of this phase to the ordered form of $5NaF\cdot 9YF_3$ because crystals observed in our study have never exhibited so large a unit-cell parameter and because quantitative intensity data are not available for comparison.

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[15] J. H. Burns and D. J. Duchamp, "Reactor Chemistry Division Annual Progress Report for Period Ending Jan. 31, 1962," ORNL-3262, p. 15.

CONTRIBUTION FROM THE GOODYEAR ATOMIC CORPORATION,
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Hexafluorides of Molybdenum, Tungsten, and Uranium. II. Reactions with Nitryl Fluoride, Nitrosyl Fluoride, and Nitrosyl Chloride[1,2]

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Reactions of three metal hexafluorides with nitrosyl and nitryl fluorides resulted in solid compounds of the composition $NO_xF\cdot MF_6$ where x is 1 or 2 and M is W, Mo, or U. Infrared absorption data for these compounds indicate that the ionic form $NO_x{}^+MF_7{}^-$ and the molecular form $NO_xF\cdot MF_6$ contribute to the structure of the solid. Nitrosyl chloride does not act as do the nitrogen oxyfluorides with the hexafluorides but, like nitric oxide,[3] it reduces molybdenum and uranium to complex nitrosyl fluorides of Mo(V) and U(V), with the formation of chlorine. Tungsten hexafluoride does not react with nitrosyl chloride.

Introduction

The study of the action of various nitrogen-containing compounds on the hexafluorides of molybdenum, tungsten, and uranium has been continued in this laboratory. The action of nitrous oxide and nitric oxide toward the hexafluorides has been reported previously.[3] That work suggested that reaction occurred between the hexafluorides and nitrosyl fluoride. In the present investigation the reaction stoichiometry between the hexafluorides and nitryl fluoride, nitrosyl fluoride, or nitrosyl chloride and the physical and chemical properties of the reaction products were determined.

Experimental

Materials.—Purification of the hexafluorides and nitrosyl fluoride has been described.[3] Hydrogen fluoride was purified by the method of Jarry and Davis.[4] Boron trifluoride was used as obtained commercially from the Matheson Company.

Nitryl fluoride was prepared by allowing a slight excess (over

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[1] This work was performed under Contract AT-(33-2)-1 with the U. S. Atomic Energy Commission.

[2] Paper presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., September 14, 1960.

[3] J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 661 (1962).

[4] R. L. Jarry and W. Davis, *J. Phys. Chem.*, **57**, 60 (1953).