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THE SYSTEMS NbF_5-RbF AND NbF_5-CsF

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SUMMARY

NbF_5 systems (M=Rb,Cs) are investigated by differential thermal analysis and X ray powder diffraction. Six types of ternary fluorides are found, and lattice parameters calculated for most of them. Comparison with the NbF_5-TlF system is carried out.

INTRODUCTION

The present work extends to rubidium and cesium the study of the systems NbF_5-MF (M=alcalis, thallium, ammonium) which have been carried out previously in our laboratory. Results with M=Li,Na,K [1] and Tl [2] have been published before ; those with M=NH_4^+ will be published later.

We present here the phase diagrams of NbF_5-RbF (CsF) and X-ray powder diffraction data for several new compounds, then, we draw comparison between these systems and the NbF_5-TlF binary.

EXPERIMENTAL

NbF_5 was obtained as a commercial product and refined by distillation under vacuum. RbF and CsF are obtained by the action of 40% aquous hydrogene fluoride with the appropriate carbonate, evaporation of the solution, and drying of the solid under an argon stream at 600°C.

Reactions between NbF_5 and MF are carried out in sealed nickel tubes, at 20°C below the temperature of the lowest thermal change (transition, eutectic,...) observed for the mixture.

For differential thermal analysis we use tight nickel crucibles up to 1000°C. We note heating temperatures (accuracy $\mp$ 5°C). Special sample holders are available for X-ray powder diffraction up to 200°C.

We have not found a suitable fluid for density measurements on powders because the fluids examined reacted, or traces of water caused hydrolysis. We have used the theoretic density as a function of starting materials densities and composition, and we assume that actual density is not very different.

RESULTS

The systems NbF_5-TlF, NbF_5-RbF and NbF_5-CsF exhibit the following ternary fluoride species : MNb_4F_{21} (for M = Cs only), MNb_3F_{16} (for M = Tl and Rb), MNb_2F_{11}, $MNbF_6$, M_2NbF_7, M_3NbF_8 (all for M = Tl, Rb, Cs). In every case, the powders obtained are pale grey, very hygroscopic, and we never detect the presence of single crystals.

Before our study, the $MNbF_6$ fluorides were the subject of important cristallographic work by Bode and Von Döhren [3] , Cox [4] and Kemmitt and Col. [5] , on single crystals formed by the action of BrF_3 upon a mixture of niobium pentoxyde and the alcali metal fluoride. These authors found that the $MNbF_6$ compounds, for M = Tl,Rb,Cs, are isostructural with a rhomboedral lattice of the $KOsF_6$ type, space groupe $R\bar{3}$, with one formula weight per unit cell.

The X-ray powder diffraction patterns of $\alpha TlNbF_6$, $\alpha RbNbF_2$ and $\alpha CsNbF_6$, obtained by direct reaction between NbF_5 and MF are accuratly indexed with lattice parameters given by these authors except for $TlNbF_6$ (a = 5.21 Å instead of 5.14 Å).

In this work, except for the $MNbF_6$ type, we have indexed most of the X-ray diffraction patterns by calculations and trials, because of the lack of single crystals.

These crystal data are therefore tentative only ; nevertheless, the use of the theoretic density and lattice parameters assigned to various phases leads,to the numbers of formula weight per unit cell very consistently.

Figure 1 exhibits the NbF_5-RbF and NbF_5-CsF phase diagrams which relevant data listed below. Table I collects the crystallographic parameters of different compounds, and interplanar lengths and hkl values are listed in Table II.

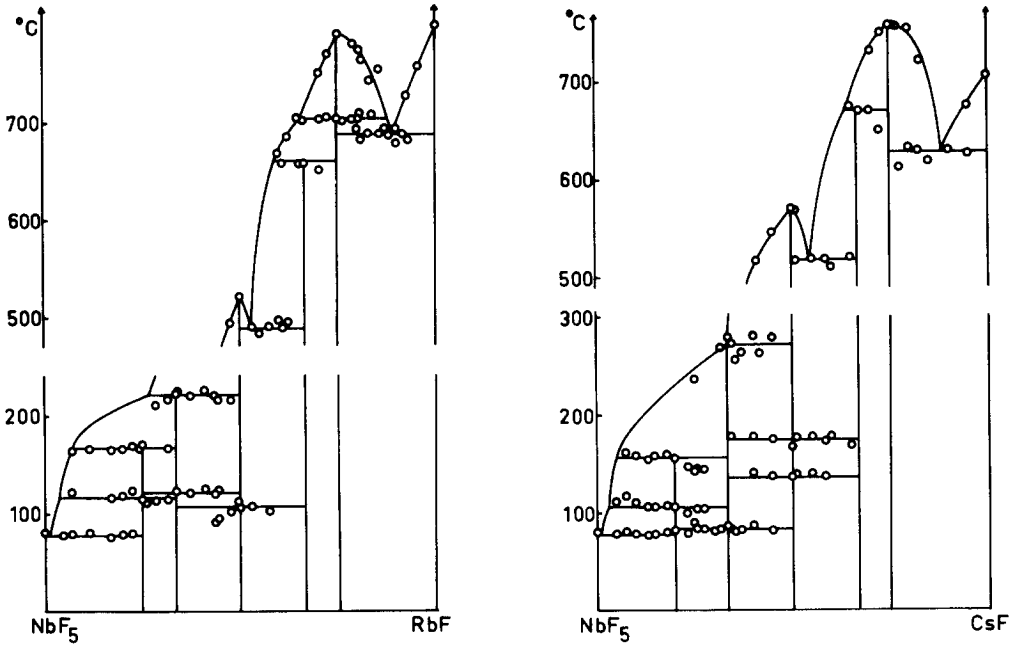

Figure 1. NbF_5-RbF and NbF_5-CsF phase diagrams.

% RbF	temp.	phenomena	% CsF	temp.	phenomena
0	80	NbF_5 melting	0	80	NbF_5 melting
3	77	Eutectic	2	78	Eutectic
25	115	$\alpha RbNb_3F_{16} \rightleftarrows \beta$	20	105	$\alpha CsNb_4F_{21} \rightleftarrows \beta$
	166	$RbNb_3F_{16}$		157	$CsNb_4F_{21}$ peritexy
33.3	120	$\alpha RbNb_2F_{11} \rightleftarrows \beta$	33.3	86	$\alpha CsNb_2F_{11} \rightleftarrows \beta$
	220	$RbNb_2F_{11}$peritexy		272	$CsNb_2F_{11}$ peritexy
50	106	$\alpha RbNbF_6 \rightleftarrows \beta$	50	137	$\alpha CsNbF_6 \rightleftarrows \beta$
	520	$RbNbF_6$ melting		174	$\beta \rightleftarrows \gamma$
53	488	Eutectic		570	$CsNbF_6$ melting
66.6	660	Rb_2NbF_7	55	518	Eutectic
75	702	$\alpha Rb_3NbF_8 \rightleftarrows \beta$	66.6	670	Cs_2NbF_7 peritexy
	788	Rb_3NbF_8melting	75	756	Cs_3NbF_8 melting
89	686	Eutectic	88	628	Eutectic
100	796	RbF melting	100	704	CsF melting

TABLE I

NbF_5/MF	TlF	RbF	CsF
4			α $CsNb_4F_{21}$ rhomb. a=9.52 Å α=88.8° d=3.56 Z=2 β $CsNb_4F_{21}$ non obtained X-ray pattern.
3	$TlNb_3F_{16}$ Intricate X-Ray pattern.	$RbNb_3F_{16}$ Intricate X-Ray pattern. $RbNb_3F_{16}$ rhomb. a=11.30 Å α=95° d=3.38 Z=4	
2	α $TlNb_2F_{11}$ rhomb. a=10.70 Å α=94.5° d=5.10 Z=6 β $TlNb_2F_{11}$ cubic a=7.42 Å (t=145°)	α $RbNb_2F_{11}$ rhomb. a=12.76 Å α=91.20° d=3.32 Z=9 β $RbNb_2F_{11}$ cubic a=7.38 Å	α $CsNb_2F_{11}$ rhomb. a=12.47 Å α=91°30 d=3.56 Z=8 β $CsNb_2F_{11}$ rhomb. d=12.73 Å =91°7
1	α $TlNbF_6$ rhomb. a=5.21 Å α=96.37° β $TlNbF_6$ cub. a=5.28 Å (t=104°C)	α $RbNbF_6$ rhomb. a=5.14 Å α=96.4° β $RbNbF_6$ cub. a=5.27 Å (t=120°C)	α $CsNbF_6$ rhomb. a=5.32 Å α=95.8° β $CsNbF_6$ cub. a=5.41 Å (t=145°C) γ $CsNbF_6$ no observed.
1/2	Tl_2NbF_7 rhomb. a=10.97 α=9.25° d=6.66 Z=8	Rb_2NbF_7 monoclinic a=10.60 Å b=10.10 Å c= 9.65 Å β=99.5° d= 3.10 Z=5	Cs_2NbF_7 monoclinic a=11.50 Å b=10.97 Å c= 9.08 Å β=95° d= 3.57 Z=5
1/3	Tl_3NbF_8 hexagonal a=8.59 Å c=6.69Å d=7.06 Z=2	Rb_3NbF_8 monoclinic a=10.65 Å b=9.40 Å c= 8.58 Å β=91°2 d= 3.04 Z=3	Cs_3NbF_8 monoclinic a=11.20 Å b=9.85 Å c= 8.93 Å β=91°5 d= 3.57 Z=3

TABLE II

α $CsNb_4F_{21}$			$TlNb_3F_{16}$		α $RbNb_3F_{16}$		β $RbNb_3F_{16}$		
d	I/I_o	h k l	d	I/I_o	d	I/I_o	d	I/I_o	h k l
6.75	4	1 1 0	7.25	35	7 24	4	5.52	50	2 0 0
5.59	5	1 1 1	-	-	6.08	8	4.18	100	$\bar{2}$ 2 0
4.31	2	2 1 0	-	-	5.67	13	3.914	8	$\bar{2}$ 2 1
4.20	7	$\bar{2}$ 1 0	-	-	5.09	5	3.785	95	2 2 0
3.965	100	2 1 1	-	-	4.90	10	3.706	30	3 0 0
3.860	24	$\bar{2}$ 1 1	4.44	6	4.43	24	3.639	8	$\bar{3}$ 1 0
3.383	6	2 2 0	4.15	10	4.16	92	2.957	24	2 2 2
3.311	4	$\bar{2}$ 2 0	-	-	4.07	13	2.808	5	4 0 0
3.241	2	2 2 1	4.011	100	3.980	36	2.772	5	$\bar{4}$ 1 0
3.170	4	3 0 0	3.931	10	3.907	100	2.646	15	4 1 0
2.923	2	3 1 1	3.887	50	3.873	25	2.332	28	$\bar{2}$ 2 4
2.846	4	$\bar{3}$ 1 1	3.738	6	3.767	13	2.149	5	4 3 0
2.756	12	$\bar{2}$ 2 2	3.613	72	3.607	62	2.124	7	4 2 2
2.576	7	3 2 1	-	-	3.553	18	2.091	16	$\bar{4}$ 4 0
2.304	8	$\bar{4}$ 1 0	3.424	8	3.504	26	1.985	8	3 3 3
2.279	15	3 3 0	-	-	3.202	12	1.871	16	6 0 0
2.241	7	$\bar{4}$ 1 1	-	-	3.140	10			
2.030	4	$\bar{3}$ 3 2	-	-	3.099	9			
1.982	9	4 2 2	-	-	3.027	9			
1.894	3	4 3 1	2.947	7	2.930	6			
			2.723	4	2.802	7			
			2.673	8	2.673	8			
			-	-	2.624	4			
			2.546	12	2.547	8			
			2.396	5	2.406	8			
			2.228	9	2.253	10			
			2.212	9	2.211	17			

TABLE II (continued)

∝ $TlNb_2F_{11}$			∝ $RbNb_2F_{11}$			∝ $CsNb_2F_{11}$		
d	I/I_o	h k l	d	I/I_o	h k l	d	I/I_o	h k l
7.28	70	1 1 0	7.24	8	1 1 1	7.13	6	1 1 1
4.033	100	2 1 1	5.60	9	2 1 0	4.207	100	$\bar{2}$ 2 1
3.904	52	$\bar{2}$ 2 0	5.28	9	$\bar{2}$ 1 1	3.972	25	$\bar{3}$ 1 0
3.717	7	$\bar{2}$ 2 1	5.10	14	2 1 1	3.890	42	$\bar{3}$ 1 0
3.616	81	2 2 0	4.19	3	2 2 1	3.636	80	$\bar{2}$ 2 2
3.435	8	$\bar{3}$ 1 0	3.987	83	3 1 0	3.545	21	2 2 2
3.358	4	$\bar{3}$ 1 1	3.870	42	$\bar{3}$ 1 1	3.097	12	4 0 0
2.957	12	$\bar{3}$ 2 1	3.831	19	$\bar{1}$ 3 1	2.864	3	$\bar{1}$ 3 3
2.829	2	2 2 2	3.705	13	$\bar{2}$ 2 2	2.757	2	4 2 0
2.680	14	$\bar{3}$ 2 2	3.601	100	2 2 2	2.642	13	3 3 2
2.615	2	$\bar{3}$ 3 0	3.417	15	$\bar{1}$ 3 2	2.539	10	$\bar{4}$ 3 0
2.553	21	$\bar{3}$ 3 1	2.925	15	$\bar{1}$ 3 3	2.415	7	$\bar{3}$ 3 3
2.509	7	4 1 0	2.744	4	4 2 1	2.353	7	3 3 3
2.402	16	3 3 0	2.715	4	$\bar{2}$ 3 3	2.290	15	5 2 0
2.359	12	$\bar{3}$ 3 2	2.671	9	3 3 2	2.241	4	5 2 1
2.234	11	$\bar{4}$ 2 2	2.544	17	5 0 0	2.199	6	4 4 0
2.219	11	$\bar{4}$ 3 0	2.509	6	4 3 0	2.174	5	$\bar{4}$ 3 3
2.197	7	4 2 1	2.400	8	3 3 3	2.092	13	4 3 3
2.173	7	$\bar{4}$ 3 1	2.371	9	$\bar{2}$ 3 4	2.005	6	6 1 1
2.111	8	5 0 0	2.355	11	5 2 0	1.983	4	5 3 2
2.004	16	$\bar{5}$ 2 1	2.339	12	4 3 2	1.929	11	5 4 0
1.909	4	3 3 3	2.221	12	4 4 0			
1.850	10	5 2 1	2.208	14	5 2 2			
			2.164	7	5 3 0			
			2.112	10	6 0 0			

TABLE II (continued)

β $TlNb_2F_{11}$			β $RbNb_2F_{11}$		β $CsNb_2F_{11}$		
d	I/I_o	h k l	d	I/I_o	d	I/I_o	h k l
7.29	7	1 0 0	7.25	1	7.14	10	1 1 1
5.24	3	1 1 0	5.22	23	5.30	9	$\bar{2}$ 1 1
4.27	15	1 1 1	4.19	14	4.33	43	$\bar{2}$ 2 1
3.711	100	2 0 0	3.685	100	3.972	33	3 1 0
-	-	2 1 1	3.019	3	3.907	8	$\bar{3}$ 1 1
2.622	17	2 2 0	2.615	8	3.745	100	3 1 1
2.343	6	3 1 0	2.330	4	3.572	33	$\bar{3}$ 2 0
2.141	51	2 2 2	2.136	39	3.062	10	4 1 0
1.982	3	3 2 1	-	-	2.656	7	3 3 2
1.855	15	4 0 0	1.850	15	2.584	15	$\bar{4}$ 3 3
					2.484	3	5 1 0
					2.375	22	3 3 3
					2.294	4	4 3 2
					2.209	13	4 4 0
					2.165	16	4 4 1
					2.083	6	6 1 0
					1.981	3	6 2 0
					1.933	5	4 4 3
					1.872	5	6 2 2

TABLE II (continued)

α $TlNbF_6$		α $RbNbF_6$		α $CsNbF_6$		
d	I/I_o	d	I/I_o	d	I/I_o	h k l
5.14	6	5.09	11	-	-	1 0 0
3.847	100	3.834	100	3.945	100	$\bar{1}$ 1 0
3.432	91	3.396	94	3.520	95	1 1 0
3.076	3	3.060	2	-	-	$\bar{1}$ 1 1
2.666	8	2.634	5	2.747	8	1 1 1
2.560	17	2.544	17	2.627	18	2 0 0
2.400	15	2.391	8	2.461	10	$\bar{2}$ 1 0
2.217	14	2.213	13	2.274	13	$\bar{2}$ 1 1
2.189	4	-	-	-	-	2 1 0
2.129	36	2.118	52	2.187	42	$\bar{1}$ 2 1
-	-	1.918	11	-	-	$\bar{2}$ 2 0
1.918	15	1.894	8	1.972	16	2 1 1
1.715	6	-	-	-	-	2 2 0

β $TlNbF_6$		β $RbNbF_6$		β $CsNbF_6$		
d	I/I_o	d	I/I_o	d	I/I_o	h k l
5.29	5	5.27	8	5.39	4	1 0 0
3.741	100	3.726	100	3.825	100	1 1 0
3.056	6	-	-	3.105	9	1 1 1
2.646	13	2.636	10	2.718	16	2 0 0
2.346	10	-	-	2.403	6	2 1 0
2.158	33	2.151	46	2.201	39	2 1 1
1.867	12	1.865	14	1.918	9	2 2 0

TABLE II (continued)

Tl_2NbF_7			Rb_2NbF_7			Cs_2NbF_7		
d	I/I_o	h k l	d	I/I_o	h k l	d	I/I_o	h k l
5.15	3		5.40	14	1 1 1	5.67	5	2 0 0
5.03	4	$\bar{2}$ 1 0	5.24	42	2 0 0	5.48	9	0 2 0
3.965	4	$\bar{2}$ 2 0	5.03	12	0 2 0	4.51	4	0 0 2
3.795	71	2 2 0	4.74	20	0 0 2	4.51	4	0 0 2
3.735	45	$\bar{2}$ 2 1	3.938	100	2 1 1	3.972	100	2 2 0
3.550	66	$\bar{3}$ 1 0	3.834	51	$\bar{2}$ 0 2	3.795	45	3 0 0
3.415	100	3 1 0	3.782	20	1 1 2	3.735	26	$\bar{2}$ 2 1
3.376	38	$\bar{3}$ 1 1	3.659	74	2 2 0	3.556	40	2 2 1
3.106	21	$\bar{3}$ 2 0	3.482	8	3 0 0	3.358	46	0 3 1
2.993	2	$\bar{3}$ 2 1	3.373	34	0 3 0	3.297	24	1 2 2
2.733	10	4 0 0	3.310	12	3 1 0	3.151	23	3 2 0
2.712	4	$\bar{3}$ 2 2	3.195	56	1 3 0	3.013	20	0 0 3
2.634	2	4 1 0	3.056	6	$\bar{1}$ 1 3	2.919	11	2 2 2
2.563	2	$\bar{3}$ 3 1	2.984	32	1 3 1	2.501	15	3 2 2
2.502	16	3 3 0	2.911	20	1 0 3	2.458	32	2 4 0
2.381	10	$\bar{3}$ 3 2	2.342	28	1 4 0	2.412	15	$\bar{3}$ 1 3
2.342	6	4 2 1	2.194	23	4 2 1	2.384	15	4 2 1
2.235	35	3 3 2	2.085	44	5 0 0	2.303	25	5 0 0
2.191	12	5 0 0				2.273	19	3 0 3
2.151	19	4 2 2				2.194	14	0 5 0
2.083	17	4 3 1				2.169	30	4 3 1
1.955	3	4 3 2				2.102	6	2 3 3
1.912	8	$\bar{4}$ 3 3				1.983	6	4 4 0
1.888	11	4 4 0				1.916	16	6 0 0

TABLE II (continued)

Tl_3NbF_8			Rb_3NbF_8			Cs_3NbF_8	
d	I/I_o	h k l	d	I/I_o	h k l	d	I/I_o
3.726	27	2 0 0	5.39	9	2 0 0	-	-
3.587	5	1 1 1	4.72	12	0 2 0	-	-
3.348	33	0 0 2	4.29	8	0 0 2	-	-
3.250	100	2 0 1	-	-	1 0 2	4.11	5
3.052	5	1 0 2	-	-	1 2 1	3.965	6
2.637	5	1 1 2	3.674	42	$\bar{1}$ 1 2	3.840	32
2.593	10	2 1 1	3.612	17	1 1 2	3.760	18
2.486	23	2 0 2	3.386	55	$\bar{2}$ 0 2	3.559	47
2.320	6	3 0 1	3.333	100	3 1 0	3.477	100
2.147	20	2 2 0	-	-	2 2 1	3.386	20
1.901	22	2 0 3	3.170	74	0 2 2	3.309	85
1.857	4	4 0 0	-	-	0 3 1	3.082	8
1.805	24	2 2 2	2.822	8	3 2 0	2.953	9
1.668	6	0 0 4	2.656	24	4 0 0	2.782	20
1.662	3	4 0 2	-	-	4 0 1	2.656	5
			-	-	$\bar{4}$ 1 1	2.599	5
			2.617	5	3 1 2	-	-
			2.402	3	$\bar{3}$ 2 2	-	-
			2.354	19	0 4 0	2.463	11
			2.220	10	$\bar{4}$ 1 2	2.322	5
			2.140	53	0 0 4	2.229	43
			1.979	25	2 0 4	2.076	19
			1.872	17	0 5 0	1.967	11
			1.849	6	$\bar{2}$ 2 4	1.924	5
			1.806	35	2 2 4	1.886	28

DISCUSSION

An important analogy is found between the three diagrams NbF_5-MF. All of the compounds rich in NbF_5 (NbF_5/MF > 1) decompose by peritexy and show a crystal transition, except $TlNb_3F_{16}$. Both of the compounds $MNbF_6$ and M_3NbF_8 melt congruently, the first type having one or two crystal transitions. The M_2NbF_7 type decomposes in the solid state (M=Tl) or melts incongruently. Cesium is unique in showing the MNb_4F_{21} type structure.

From crystallographic data, we observe the following :
The $MNbF_6$ compounds are isostructural : "low temperature" phases are rhombohedral, as seen above, and "high temperature" phases are cubic with $a_{cubic} = a_{rhomb.}$ for the same compound. We can consider that the conversion consists in a slight distorsion from the cubic cell into a rhombohedral cell without variation of a nor Z.

From Rb_3NbF_8 and Cs_3NbF_8 X ray diffraction patterns, these compounds appear to be monoclinic and isostructural. This is different from Rb_2NbF_7 and Cs_2NbF_7, both of which are monoclinic but not isostructural. Tl_2NbF_7 is rhombohedral.

$\alpha TlNb_2F_{11}$ and $\alpha RbNb_2F_{11}$ are quite similar but it is not possible to index the second with the lattice constants of the first. The $\alpha CsNb_2F_{11}$ X-ray pattern is different. Nevertheless, the three compounds have rhombohedral lattices. $TlNb_2F_{11}$ and $RbNb_2F_{11}$ undergo crystalline conversion and the β forms are cubic and isostructural.

Thallium compounds seem slightly different from the analogous rubidium or cesium salts.

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