JOURNAL OF SOLID STATE CHEMISTRY 112, 199–202 (1994)

BRIEF COMMUNICATION

On Low Temperature Preparation of $\delta-K_3REF_6$ (RE = Dy–Lu)

B. N. Wani and U. R. K. Rao

Applied Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

Received August 25, 1993; in revised form November 22, 1993; accepted December 2, 1993

The delta phase of compounds of the type K_3REF_6 where RE = Dy–Lu were prepared by a low temperature solid state reaction of RE_2O_3 with KHF_2. The powder X-ray diffraction patterns of all of these compounds could be better indexed on an orthorhombic unit cell than on a monoclinic cell. © 1994 Academic Press, Inc.

Compounds of the type $[NH_4]_3REF_6$ $1.5H_2O$ where RE = Y, La, Ce, Nd, and Pr were prepared by Patwe *et al.* (1). The corresponding rare earth sesquioxide was mechanically mixed with NH_4HF_2 in a 1 : 6 mole ratio at room temperature in order to obtain the hydrated fluorocomplex but the anhydrous hexafluorocompound could not be obtained by heating since decomposition sets in simultaneously with dehydration. The anhydrous potassium analogues of these compounds, with the general formula K_3REF_6 (RE = Tb–Yb), are reported to exist in three crystallographic modifications (2–5), designated α (monoclinic or orthorhombic), β (tetragonal) and Γ (cubic). Only K_3ErF_6 is reported (3) to exist additionally in a fourth modification designated, δ (monoclinic with β = 90°). The α and δ phases are structurally very similar. The α phase is stable at room temperature.

The δ phase of erbium is prepared (3) by heating a mixture of ErF_3 and KF in a 1 : 3 mole ratio at 900–950°C in dry argon followed by annealing at 500–600°C under dry argon for 600–800 hr and cooling to room temperature. The dry argon cover is necessitated due to the sensitivity of the trifluoride to oxygen at elevated temperatures. This method involves an additional step of preparation of the trifluoride from the rare earth sesquioxide. The present communication describes a very simple method of con-

TABLE 1
XRD Powder Patterns

Serial no.	δ-K_3TbF_6						$\delta-K_3DyF_6$					
	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/I_0	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/I_0
1	1	1	0	5.67	5.65	88	1	1	0	5.65	5.63	81
2	2	0	0	5.427	5.412	71	1	2	0	3.165	3.16	88
3	0	2	0	3.310	3.309	77	1	1	2	3.074	3.08	100
4	3	1	0	3.168	3.168	53	1	2	1	2.900	2.902	40
5	0	2	1	3.019	3.020	100	2	2	1	2.63	2.629	38
6	3	1	2	2.407	2.405	32	4	1	0	2.486	2.488	35
7	4	1	1	2.368	2.372	30	4	1	1	2.354	2.357	40
8	2	0	3	2.241	2.242	30	2	0	3	2.233	2.232	30
9	5	1	0	2.055	2.057	26	4	0	2	2.172	2.170	28
10	0	0	4	1.848	1.848	24	2	3	1	1.963	1.964	28
11	2	3	2	1.786	1.787	25	1	2	3	1.938	1.938	26
12	6	1	0	1.739	1.740	22	0	3	2	1.900	1.890	26
13	5	1	3	1.579	1.579	20	4	2	2	1.814	1.814	26
14	3	4	1	1.474	1.474	18	6	0	0	1.792	1.791	26
15	—			—	—	—	3	4	1	1.470	1.470	20

0022-4596/94 $6.00

TABLE 2
XRD Powder Patterns

Serial no.	δ-K_3HoF_6						δ−K_3TmF_6					
	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/I_0	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/I_0
1	1	1	0	5.65	5.628	71	1	1	0	5.610	5.620	92
2	1	2	0	3.15	3.15	64	2	0	0	5.391	5.391	38
3	1	1	1	3.058	3.05	100	0	0	1	3.621	3.624	33
4	2	0	1	3.015	3.015	65	0	2	0	3.290	3.293	44
5	2	2	0	2.815	2.814	42	3	1	0	3.151	3.155	98
6	4	0	0	2.69	2.71	42	1	1	1	3.048	3.046	100
7	4	1	0	2.502	2.506	20	2	0	1	3.009	3.008	87
8	2	2	1	2.222	2.223	37	4	0	0	2.707	2.699	23
9	5	0	0	2.169	2.169	28	2	2	1	2.221	2.221	43
10	4	2	0	2.10	2.096	28	4	0	1	2.163	2.163	23
11	3	3	0	1.875	1.875	20	3	3	0	1.871	1.873	18
12	1	3	1	1.849	1.850	14	1	3	1	1.850	1.850	14
13	5	1	1	1.791	1.791	25	0	0	2	1.812	1.812	15
14	1	0	2	1.786	1.786	24	6	0	0	1.795	1.797	17
15		—		—	—	—	5	1	1	1.784	1.784	17
16		—		—	—	—	6	2	0	1.581	1.577	11

verting the erbium sesquioxide into the δ-phase in a single step by solid state reaction with KHF_2. In addition, this method is employed to prepare the δ phase of six more members of this series.

The rare earth oxides were of 99.9% purity and the KHF_2 of 98%. A mixture (about 500 mg) of the rare earth oxide and KHF_2 in 1 : 6 mole ratio was homogenized by grinding. It may be added here that KHF_2 is tetragonal (6) at room temperature, becomes cubic at 198°C and melts at 226°C. The powder XRD pattern of the reaction product was recorded using a Ni-filtered Cu$K\alpha$ radiation. The results obtained are discussed below:

All the seven oxides were mixed by grinding them with KHF_2 at room temperature. The reaction occured at room temperature, i.e., in the tetragonal form of KHF_2, with Yb_2O_3 and Lu_2O_3 only. In other cases there was no reac-

TABLE 3
XRD Powder Patterns

Serial no.	δ-K_3YbF_6						δ−K_3LuF_6					
	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/I_0	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I/I_0
1	1	1	0	5.63	5.61	26	1	1	0	5.599	5.596	100
2	2	0	0	5.402	5.391	25	2	0	0	5.389	5.387	69
3	3	1	0	3.157	3.152	24	0	0	1	3.599	3.599	21
4	1	1	1	3.02	3.04	100	0	2	0	3.276	3.274	22
5	3	0	1	2.554	2.551	11	3	1	0	3.151	3.149	57
6	2	2	1	2.215	2.216	17	1	1	1	3.028	3.027	59
7	1	3	1	1.846	1.845	28	2	0	1	2.993	2.993	75
8	4	2	1	1.806	1.806	9	1	2	1	2.361	2.363	13
9	2	3	1	1.764	1.766	8	2	2	1	2.209	2.209	18
10	3	3	1	1.658	1.660	8	5	0	0	2.154	2.154	11
11	0	2	2	1.586	1.585	7	4	2	0	2.081	2.080	5
12	6	2	0	1.574	1.576	17	1	3	1	1.838	1.839	14
13	7	0	0	1.540	1.540	7	0	0	2	1.800	1.800	10
14	4	1	2	1.463	1.465	6	5	1	1	1.779	1.780	11

TABLE 4
XRD Powder Patterns of δ-K_3ErF_6

Serial no.	d_{obs} (Å)	I/I_0	Orthorhombic[a] d_{calc} (Å)	h	k	l	Monoclinic[b] d_{calc} (Å)	h	k	l
1	5.62	100	5.62	1	1	0	5.62	1	1	0
2	5.39	71	5.39	2	0	0	5.39	2	0	0
3	4.89	18	—		—		4.89	0	1	1
4	3.62	18	3.60	3	0	0	3.62	−2	1	1
5	3.29	34	3.29	0	2	0	3.29	0	2	0
6	3.15	60	3.15	1	2	0	3.15	1	2	0
7	3.06	77	3.06	1	1	1	3.06	−1	1	2
8	3.02	49	3.02	2	0	1	3.02	−2	0	2
9	2.497	10	2.497	4	1	0	2.497	4	1	0
10	2.223	32	2.225	2	2	1	2.227	2	2	2
11	2.169	17	2.169	4	0	1	2.169	4	0	2
12	1.823	7	1.823	0	0	2	1.823	0	0	4
13	1.787	15	1.787	5	1	1	1.787	−5	1	2

[a] a_0 = 10.790 Å, b_0 = 6.590 Å, c_0 = 3.646 Å, V = 259 Å^3, figure of merit = 21.
[b] a_0 = 10.790 Å, b_0 = 6.590 Å, c_0 = 7.293 Å, β = 90°, V = 519 Å^3, figure of merit = 16.

tion at all at room temperature. The remaining oxides ground with the bifluoride were heated at 200°C for 4 hr. In the cases of Ho, Er, and Tm, the reaction goes to completion. Thus oxides of Ho, Er, and Tm react with KHF_2 in its cubic form and not in its tetragonal form. However, in the cases of Tb and Dy, even by holding at 200°C for longer period, only partial formation of the product was noticed with unreacted reactants left over. Finally, the last two oxides, i.e., Tb and Dy, were reacted with the melt of bifluoride at 226°C and the reaction goes to completion giving the desired fluorocomplexes.

The XRD patterns of the different δ phases are given in Tables 1–3. Out of all the XRD powder patterns of these fluorocomplexes recorded by us, the pattern of the Er complex is identical to that of the δ-phase of K_3ErF_6 reported by Reshetnikova *et al.* (3). They indexed the pattern on a momoclinic cell with β = 90°. However, the pattern could be better indexed (7) on a smaller orthorhombic unit cell as demonstrated in Table 4. The conditions of preparation of the δ-phase of the seven rare earths fluoride compounds and the unit cell parameters are given in Table 5. It may be added here that no polymorph of K_3LuF_6 is known in the literature. It is interesting to note that although all the rare earth sesquioxides have more or less the same unit cell dimensions and same structure, the reactivity with KHF_2 is different. Some react with KHF_2 in its tetragonal phase, others in its cubic phase only and still others only at its melting point.

TABLE 5
Preparation Conditions and Unit Cell Dimensions of δ-K_3REF_6

Rare earth (*RE*)	Temp. of reaction (°C)	Orthorhombic cell dimension a_0 (Å)	b_0 (Å)	c_0 (Å)	Volume (Å^3)
Tb	225	10.840 ± 0.007	6.625 ± 0.002	7.393 ± 0.003	531.0 ± 0.4
Dy	225	10.754 ± 0.006	6.613 ± 0.005	7.367 ± 0.006	523.9 ± 0.4
Ho	190	10.852 ± 0.007	6.585 ± 0.005	3.634 ± 0.004	259.7 ± 0.4
Er	190	10.811 ± 0.004	6.589 ± 0.002	3.630 ± 0.001	258.6 ± 0.2
Tm	190	10.790 ± 0.006	6.590 ± 0.002	3.627 ± 0.001	257.9 ± 0.2
Yb	28	10.795 ± 0.007	6.564 ± 0.004	3.624 ± 0.001	256.8 ± 0.2
Lu	28	10.782 ± 0.004	6.553 ± 0.002	3.603 ± 0.001	254.6 ± 0.1

ACKNOWLEDGMENT

We thank Dr. P. N. Moorthy, Head, Applied Chemistry Division, for his interest in this work.

REFERENCES

1. S. J. Patwe, B. N. Wani, U. R. K. Rao, and K. S. Venkateswarlu, *Can. J. Chem.* **67,** 1815 (1989).
2. S. Ateonard, M. Labeau, Y. Le Fun, and M. F. Govius, *Mater. Res. Bull.* **8,** 605 (1973).
3. L. Reshetnikova, *Inorg Mater.* **15,** 964 (1979).
4. I. B. Shaimuradov, V. A. Efremov, L. P. Reshetnikova, and L. M. Kovba, *Russ. J. Inorg. Chem.* **18,** 1099 (1973).
5. M. Labeau, S. Aleonard, A. Vedrine, R. Boutonnet and J. C. Cousseius, *Mat. Res. Bull.* **9,** 615 (1974).
6. M. L. Davis and E. F. Westrum, Jr., *J. Phys. Chem.* **65,** 338 (1961).
7. LatPar Program devised by Dr. V. K. Wadhawan, private communication.