Indexing of X-Ray Powder Diffraction Data for Potassium Hexafluorovanadate(III)

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Synopsis. X-Ray powder diffraction data for K_3VF_6 are presented; the α form is monoclinic with a=1.2102(1), b=1.7456(2), c=1.2007(2) nm, β=92.58(1)° at 298 K; the β form is monoclinic with a=1.714(2), b=1.237(1), c=0.5479(2) nm, β=91.49(3)° at 453 K; the γ form is tetragonal with a=1.3708(5), c=0.8752(5) nm at 483 K; the low-temperature γ form, which contains a small amount of sodium ion, is tetragonal with a=1.3570(3), c=0.8671(2) nm at 298 K.

TABLE 1. X-RAY DIFFRACTION DATA FOR THE α FORM (Cu $K\alpha$ RADIATION)

No.	I/I_0	$2\theta_{obsd}$/°	d_{obsd}/nm	d_{calcd}/nm	hkl
1	1	16.893	0.5244	0.5241	031
2	81	17.839	0.4968	0.4974	220
3	24	20.323	0.4366	0.4368	040
4	5	21.213	0.4185	0.4180	032
5	1	22.200	0.4001	0.4000	23$\bar{1}$
6	1	22.635	0.3925	0.3923	231
7	2	23.495	0.3783	0.3785	31$\bar{1}$
8	1	25.137	0.3540	0.3542	240
9	1	25.689	0.3465	0.3464	321
10	4	26.534	0.3357	0.3357	31$\bar{2}$
11	7	26.895	0.3312	0.3316	330
12	2	27.581	0.3231	0.3227	33$\bar{1}$
13	34	28.888	0.3088	0.3086	24$\bar{2}$
14	100	29.533	0.3022	0.3020	052
15	2	30.284	0.2949	0.2949	33$\bar{2}$
16	2	30.594	0.2920	0.2919	251
17	2	31.205	0.2864	0.2864	41$\bar{1}$
18	2	32.387	0.2762	0.2762	16$\bar{1}$
19	2	34.044	0.2631	0.2632	053
20	2	34.581	0.2592	0.2588	15$\bar{3}$
21	21	36.121	0.2485	0.2487	440
22	11	36.636	0.2451	0.2454	44$\bar{1}$
23	10	37.533	0.2394	0.2394	50$\bar{1}$
24	9	38.276	0.2350	0.2352	501
25	2	38.677	0.2326	0.2329	36$\bar{1}$
26	5	39.051	0.2305	0.2305	07$\bar{2}$
27	7	39.629	0.2272	0.2272	43$\bar{3}$
28	8	39.894	0.2258	0.2257	172
29	6	40.374	0.2232	0.2233	451
30	53	41.322	0.2183	0.2184	080
31	2	42.749	0.2113	0.2114	45$\bar{2}$
32	27	43.201	0.2092	0.2090	31$\bar{5}$
33	1	44.491	0.2035	0.2031	50$\bar{3}$
34	2	44.952	0.2015	0.2014	27$\bar{3}$
35	18	45.606	0.1987	0.1987	53$\bar{3}$
36	2	46.219	0.1963	0.1963	43$\bar{4}$
37	2	46.462	0.1953	0.1953	28$\bar{2}$
38	3	46.897	0.1936	0.1935	28$\bar{2}$
39	2	47.763	0.1903	0.1903	54$\bar{3}$
40	3	48.058	0.1892	0.1891	19$\bar{1}$
41	1	48.674	0.1869	0.1870	63$\bar{1}$
42	2	49.346	0.1845	0.1845	27$\bar{4}$
43	2	49.798	0.1830	0.1830	53$\bar{4}$
44	25	51.598	0.17699	0.1769	603
45	11	52.798	0.17325	0.1732	64$\bar{2}$
46	2	53.530	0.17105	0.1710	60$\bar{4}$
47	7	54.642	0.16783	0.1678	27$\bar{5}$
48	3	54.847	0.16725	0.1673	42$\bar{6}$
49	4	55.434	0.16561	0.1657	12$\bar{7}$
50	4	56.947	0.16157	0.1616	73$\bar{2}$
51	1	58.236	0.15829	0.1583	662
52	6	59.850	0.15441	0.1545	75$\bar{1}$
53	1	60.630	0.15260	0.1526	2 11 $\bar{1}$
54	10	61.297	0.15110	0.1511	605
55	2	62.990	0.14744	0.1475	29$\bar{5}$
56	2	63.694	0.14598	0.1459	4 10 2
57	3	63.905	0.14555	0.1455	29$\bar{5}$
58	2	64.247	0.14486	0.1449	61$\bar{6}$
59	3	65.086	0.14319	0.1432	81$\bar{3}$
60	3	65.307	0.14276	0.1428	68$\bar{2}$
61	1	65.945	0.14153	0.1415	72$\bar{5}$
62	1	66.207	0.14104	0.1410	63$\bar{6}$
63	1	67.181	0.13923	0.1392	73$\bar{5}$
64	4	67.803	0.13810	0.1381	2 12 $\bar{2}$
65	3	68.142	0.13750	0.1375	68$\bar{3}$
66	2	70.449	0.13355	0.1336	18$\bar{7}$

Monoclinic; a=1.2102(1), b=1.7456(2), c=1.2007(2) nm, β=92.579(10)° at 289 K

The previous paper[1] has revealed that K_3VF_6 has four polymorphic forms and the transition points are 431, 473, and 491 K. When it contains a small amount of sodium ion, the γ and δ froms remain stable even at room temperature. This work was undertaken to present the X-ray powder diffraction data for the α, β, and γ forms, and to index their diffraction patterns.

Experimental

The potassium hexafluorovanadate(III) was prepared from V_2O_3 and KHF_2 of a special reagent grade in the manner reported previously.[1] The γ form which remains stable at room temperature—hereafter, designated the low-temperature γ form—was prepared using reagent-grade KHF_2. The X-ray diffraction pattern of the α form was taken with an X-ray diffractometer, Rigaku Denki Model SG-7, with

TABLE 2. X-RAY DIFFRACTION DATA FOR THE β FORM (Cu $K\alpha$ RADIATION)

No.	I/I_0	$2\theta_{obsd}$/°	d_{obsd}/nm	d_{calcd}/nm	hkl
1	31	17.677	0.5017	0.5015	220
2	10	20.330	0.4368	0.4370	21$\bar{1}$
3	21	20.766	0.4277	0.4281	211
4	1	26.516	0.3361	0.3363	32$\bar{1}$
5	3	26.627	0.3348	0.3344	330
6	28	28.904	0.3089	0.3092	23$\bar{1}$
7	100	29.240	0.3054	0.3059	231
8	15	35.789	0.2509	0.2508	440
9	6	37.082	0.2424	0.2424	341
10	4	37.692	0.2387	0.2389	222
11	6	39.601	0.2276	0.2274	32$\bar{2}$
12	11	39.743	0.2268	0.2268	13$\bar{2}$
13	10	39.951	0.2257	0.2256	132
14	4	40.311	0.2237	0.2239	15$\bar{1}$
15	72	41.301	0.2184	0.2185	42$\bar{2}$
16	15	42.220	0.2139	0.2140	422
17	6	45.279	0.2001	0.2000	52$\bar{2}$
18	28	51.406	0.17760	0.1777	21$\bar{3}$
19	7	51.946	0.17588	0.1759	213
20	3	52.366	0.17457	0.1747	12$\bar{3}$
21	10	54.555	0.16807	0.1681	64$\bar{2}$
22	6	59.832	0.15445	0.1544	523
23	7	60.472	0.15297	0.1530	46$\bar{2}$
24	13	60.582	0.15272	0.1525	34$\bar{3}$
25	1	63.841	0.14568	0.1457	63$\bar{3}$

Monoclinic; a=1.7136(19), b=1.2368(7), c=0.5479(2) nm, β=91.485(28)° at 453 K.

TABLE 3. X-RAY DIFFRACTION DATA FOR THE γ FORM (Cu $K\alpha$ RADIATION)

No.	I/I_0	$2\theta_{obsd}$/°	d_{obsd}/nm	d_{calcd}/nm	hkl
1	35	17.652	0.5024	0.5021	121
2	5	20.308	0.4373	0.4376	002
3	13	20.488	0.4335	0.4335	130
4	100	28.996	0.3079	0.3080	132
5	67	29.184	0.3060	0.3065	240
6	17	35.711	0.2512	0.2511	242
7	3	36.700	0.2447	0.2444	251
8	5	38.219	0.2353	0.2351	350
9	8	39.408	0.2285	0.2285	060
10	55	41.256	0.2186	0.2188	004
11	68	41.635	0.2167	0.2167	260
12	2	43.633	0.2073	0.2071	352
13	2	45.342	0.1998	0.1998	053
14	27	51.266	0.17806	0.1781	244
15	48	51.516	0.17725	0.1772	172
16	2	54.463	0.16834	0.1683	215
17	5	54.853	0.16723	0.1669	181
18	17	60.038	0.15397	0.1540	264
19	10	60.457	0.15300	0.1533	480

Tetragonal; a=1.3708(5), c=0.8752(5) nm at 483 K.

TABLE 4. X-RAY DIFFRACTION DATA FOR THE LOW-TEMPERATURE γ FORM (Cu $K\alpha$ RADIATION)

No.	I/I_0	$2\theta_{obsd}$/°	d_{obsd} / nm	d_{calcd} / nm	hkl
1	37	17.842	0.4971	0.4972	121
2	8	20.487	0.4335	0.4336	002
3	10	20.691	0.4293	0.4291	130
4	100	29.276	0.3051	0.3050	132
5	67	29.458	0.3032	0.3034	240
6	2	31.615	0.2830	0.2827	103
7	3	34.595	0.2591	0.2590	051
8	17	36.105	0.2486	0.2486	242
9	2	36.884	0.2435	0.2436	033
10	5	37.104	0.2421	0.2420	251
11	5	38.664	0.2327	0.2327	350
12	2	39.263	0.2293	0.2292	233
13	2	39.683	0.2269	0.2268	152
14	2	39.793	0.2263	0.2262	060
15	35	41.632	0.2168	0.2168	004
16	45	42.062	0.2146	0.2146	260
17	3	44.121	0.2051	0.2051	352
18	2	45.161	0.2006	0.2005	062
19	2	45.811	0.1979	0.1979	053
20	2	46.900	0.1936	0.1935	134
21	2	47.830	0.1900	0.1899	253
22	15	51.778	0.17641	0.1764	244
23	25	52.048	0.17556	0.1755	172
24	2	53.727	0.17046	0.1709	543
25	2	55.027	0.16674	0.1668	215
26	5	55.546	0.16530	0.1652	181
27	2	58.075	0.15869	0.1586	354
28	10	60.664	0.15252	0.1525	264
29	5	61.071	0.15160	0.1517	480
30	2	63.603	0.14616	0.1461	055
31	2	63.923	0.14551	0.1455	183
32	2	64.103	0.14514	0.1451	291
33	2	68.461	0.13693	0.1370	316

Tetragonal; a=1.3570(3), c=0.8671(2) nm at 298 K.

Cu K_α radiation monochromated by pyrolytic graphite at a scanning speed of 0.0167°/s (1°/min) and a chart speed of 1.67×10^{-4} m/s (10 mm/min). The X-ray diffraction patterns of the β, γ and low-temperature γ forms were taken on the same diffractometer with a Ni-filtered Cu K_α radiation at the same scanning speed and the same chart speed as for the X-ray diffraction pattern of the α form. The diffraction angles were corrected by those of silicon added to the K_3VF_6 powder as an internal standard. Indexing of the diffraction patterns was made with the aid of the computer program, Program ITO, Version 9, originally developed by Visser[2] and improved by Johnson Jr. The lattice parameters were refined by a least-squares method. The wavelengths used were 0.154178 nm (Cu $K\alpha$) for $2\theta \leqq 51°$ and 0.154051 nm (Cu K_{α_1}) for $2\theta > 51°$ respectively.

Results

Tables 1—4 show the X-ray diffraction data for the α, β, γ and low-temperature γ forms, respectively. The α form is simple monoclinic with a=1.2102(1), b=1.7456(2), c=1.2007(2) nm, β=92.58(1)° at 298 K; the β form is simple monoclinic with a=1.714(2), b=1.237(1), c=0.5479(2) nm, β=91.49(3)° at 453 K; the γ form is body-centered tetragonal with a=1.3708(5), c=0.8752(5) nm at 483 K; the low-temperature γ form is body-centered tetragonal with a=1.3570(3), c=0.8671(2) nm at 298 K.

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References

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