Paru dans Powder Diffraction
2, 36-38 (1987)
Tirés à part non reçus

(9)

CRYSTAL DATA FOR TWO MOLYBDATES $M^{IV}(MoO_4)_2$ WITH M^{IV}= ZR,HF :

by M. AURAY, Université Pierre et Marie Curie, Laboratoire de Chimie II, Tour 54, 4, Place Jussieu, 75230 Paris CEDEX 05, France,

M. QUARTON, Université Pierre et Marie Curie, Laboratoire de Chimie Minérale, CNRS-CRL85,Tour 54, 4, Place Jussieu, 75230 Paris CEDEX 05, France,

and P. TARTE, Université de Liège, Institut de Chimie,B-4000 Sart-Tilman par Liège 1, Belgium.

ABSTRACT

Two molybdates $M^{IV}(MoO_4)_2$ (with M^{IV} = Hf or Zr) were synthesized by solid state reaction between $M^{IV}O_2$ and MoO_3. Zirconium molybdate undergoes a reversible phase transition at 952K.

$Hf(MoO_4)_2$ and H.T. $Zr(MoO_4)_2$, obtained as single crystal, are trigonal, space group $P\bar{3}1c$ with Z=6 ; the cell dimensions are respectively a = 10.1005(3), c = 11.7230(5)Å ; V = 1035.76(11)Å^3 ; D_m(298K) = 4.78(4), D_x = 4.792 Mg m^{-3} and a = 10.1409(3), c = 11.7097(5)Å ; V = 1042.88(11)Å^3 ; D_m (298K) = 3.91(4), D_x = 3.926 Mg m^{-3}.

L.T. $Zr(MoO_4)_2$, indexed by Visser automatic indexation program (1969) was found monoclinic, possible space group P2, $P2_1$ or Pm with Z=4 ; the cell dimensions are a = 9.7557(5), b = 7.9373(5), c = 7.4631(4)Å, β = 97.959°(5) ; V = 572.3(5)Å^3; D_m(298K) = 4.74(5), D_x = 4.770 Mg m^{-3}. Powder diffraction data were obtained at 293K on a counter diffractometer with Ni-filtered copper radiation ($\bar{\lambda}$ = 1.5418 Å).

INTRODUCTION

The two molybdates $Hf(MoO_4)_2$ and $Zr(MoO_4)_2$, synthesized by several authors, were found to be isotypic. However, in the structure of $Hf(MoO_4)_2$, reported by Rimsky, Thoret and Freundlich (1968) the bond distances do not match the atomic coordinates and a twelvefold coordination for Hf^{IV} is most unlikely. Therefore, it commands a redetermination of the compound structure which is at the present time in progress.

Furthermore, when $Zr(MoO_4)_2$ was synthesized, we evidenced a low temperature polymorph of this compound, which has been characterized by X-ray diffractometry and vibrational spectroscopy.
This work presents the crystal chemistry of the 2 compounds $Hf(MoO_4)_2$ and $Zr(MoO_4)_2$ (H.T. and L.T. forms).

ORIGIN OF SPECIMENS

The powder samples were obtained by solid state reaction. The initial oxides $M^{IV}O_2$ and MoO_3, well mixed in stoichiometric amounts, were heated in platinum crucibles.

Single crystals of $Hf(MoO_4)_2$ and H.T. $Zr(MoO_4)_2$ were prepared by heating some of the powder sample (MO_2 : $2MoO_3$) with a very large excess of MoO_3. The mixture was quenched after 3 hours at 1123K.

The low temperature form of $Zr(MoO_4)_2$ is obtained, either by direct synthesis at 873K, or by tempering the H.T. form at the same temperature.

The low to high temperature phase transition was investigated by DTA, it appeared as an endothermic peak at 952K for a heating rate of 60°/hr. The reverse transition to the low temperature form could not be observed by DTA. This transition is of the reconstructive type since H.T. $Zr(MoO_4)_2$ crystals reduce to powder.

No low temperature form was obtained for the isomorphous compound $Hf(MoO_4)_2$. However, solid solutions $Zr_{1-x}Hf_x(MoO_4)_2$ can be converted into the low temperature form at least for $x \leq 0.4$. Their study by DTA shows that the transition temperature decreases with increasing values s of x : 952K for x = 0 to 913K for x = 0.4.

CRYSTAL GEOMETRY

$Hf(MoO_4)_2$ and H.T. $Zr(MoO_4)_2$ single crystals appear as colourless hexagonal based prisms flattened along [001]. Distances along a, b and c axes were roughly 0.30; 0.40 and 0.07 mm.

Precession photographs indicated Laue symmetry $\bar{3}m$ and existence conditions ($hh2\bar{h}l$ for $l = 2n$) were consistent with space group $P\bar{3}1c$.

Pycnometric densities were measured in toluene (D = 0.867).

POWDER DATA

Experimental conditions, identical for the three forms are presented in Table 4. $Hf(MoO_4)_2$, H.T. $Zr(MoO_4)_2$ and L.T. $Zr(MoO_4)_2$ powder patterns are given in Tables 5,6 and 7 respectively.

$Hf(MoO_4)_2$ and H.T. $Zr(MoO_4)_2$ were indexed by Freundlich & Thoret (1967) and Trunov & Kovba (1967), but some indices are questionable.

The low temperature form of $Zr(MoO_4)_2$ was indexed by Visser (1969) automatic indexation program, it leads to a monoclinic cell ; the figure of merit is good and all the observed diffraction lines, down to d = 1.56 Å, are indexed. Coincidence of some frequencies in the IR and Raman spectra leads to a non centrosymmetric space group. Consequently, the possible space groups are P2, $P2_1$ and Pm.

No isotypic compound was found for L.T. $Zr(MoO_4)_2$ in the JCPDS data file. Its IR spectrum, very similar to the MoO_3 one with the strongest band at 612 cm^{-1}, suggests the presence of MoO_6 octahedra.

REFERENCES

FREUNDLICH, W. & THORET, J.(1967).C.R.Acad.Sci.,C265,96-98.

RIMSKY, A., THORET, J. & FREUNDLICH, W.(1968).C.R.Acad.Sci.,C267,1468-1470.

SMITH, G.S. & SNYDER, R.L.(1969).J.Appl.Cryst.,12,60-65.

TRUNOV, V.K. & KOVBA, L.M.(1967).Russ.J. of Inorg.Chem.,12,1703.

VISSER, J.W.(1969).J.Appl.Cryst.2,89-95.

WILLIAMS, D.E.(1964).LCR-2 : A Fortran Lattice-constant Refinement Program. USAEC Report US-1052.

Table 1. Unit-cell data of $Hf(MoO_4)_2$

Method of cell detn.	: X-ray diffraction study of single crystal
Cell refinement method	: Least-squares. See Williams(1964)
Cell dimensions	: a = 10.1005(3)Å ; c = 11.7230(5)Å ; V = 1035.8(1)Å^3
Formula weight	: M_r = 498.37 ; Z=6 ; D_m=4.78(4)Mg m^{-3}, D_x=4.792 Mg m^{-3}
Crystal system	: Trigonal
Space group	: P$\bar{3}$1c [163]
Figure of merit	: F_N. See Smith & Synder(1979). F_{30} = 36(0.008,102).

Table 2. Unit-cell data of H.T. $Zr(MoO_4)_2$

Method of cell detn.	: X-ray diffraction study of single crystal
Cell refinement method	: Least-squares. See Williams(1964)
Cell dimensions	: a = 10.1409(3)Å ; c = 11.7097(5)Å ; V = 1042.9(1)Å^3
Formula weight	: M_r = 411.10 ; Z=6 ; D_m=3.91(4)Mg m^{-3}, D_x=3.926 Mg m^{-3}
Crystal system	: Trigonal
Space group	: P$\bar{3}$1c [163]
Figure of merit	: F_N. See Smith & Snyder(1979). F_{30} = 44(0.006,114).

Table 3. Unit cell data of L.T. $Zr(MoO_4)_2$

Method of cell detn.	: X-ray diffraction study of powder specimen and automatic indexation program. See Visser (1969).
Cell refinement method	: Least-squares. See Williams(1964)
Cell dimensions	: a = 9.7557(5)Å ; b = 7.9373(5)Å ; c = 7.4631(4)Å ; β = 97.959(5) ; V = 572.3(5)Å^3
Formula weight	: M = 411.10 ; Z=4 ; D_m=4.74(5) Mg m^{-3}, D_x=4.770 Mg m^{-3}
Crystal system	: Monoclinic
Space group	: P2 [3] , $P2_1$ [4] or Pm [6]
Figure of merit	: F_N. See Smith & Snyder(1979). F_{30} = 49(0.005,113).

Table 4 . X-ray powder technique

Radiation type, source	: X-rays, Cu
λ value used	: 1.5418 Å ($K\bar{\alpha}$)
λ discriminator	: Diffracted beam, Ni filter
λ detector	: Proportional counter (Xe)
Instrument description	: 17 cm vertical diffractometer Philips PW1050/25
Divergence angle	: 1°
Receiving-slid width	: 0.1 mm
Soller slits	: 2 sets (in inc. and diff. beam), aperture q = 1.8
Instrumental profile breadth	: 0.15° (2θ)
Temperature	: 20°C
Specimen form	: Vertically packed powder into a diffractometer holde
Particle size	: < 10μm
Range of 2θ	: From 4° to 60° minimum
Specimen motion	: None
Internal 2θ standard	: Si (a_o = 5.43075 Å)
2θ error correction procedure	: Linear interpolation from nearest 2θ's of standard
Intensity mesuring technique	: Graphic registration, peak heights (error 3%)

Table 5 . X-ray diffraction data of $Hf(MoO_4)_2$

$2\Theta_{exp.}$ (degrees)	I/I_o	d_{exp} (Å)	h k l	$\Delta 2\Theta = 2\Theta_{exp} - 2\Theta_{calc.}$ (degrees)
15.12	7	5.86	0 0 2	0.005
17.56	4	5.05	1 1 0	- 0.001
21.72	1	4.09	2 0 1	0.033
23.26	100	3.824	1 1 2	0.012
24.96	1	3.567	1 0 3	0.004
28.04	1	3.182	2 1 1	- 0.001
30.65	36	2.917	3 0 0	- 0.011
34.34	2	2.611	3 0 2	- 0.010
35.40	22	2.536	1 1 4	- 0.010
38.83	11	2.319	2 2 2	- 0.001
39.81	1	2.264	1 0 5	0.007
43.93	1	2.061	3 1 3	0.003
46.50	2	1.953	0 0 6	0.023
47.54	13	1.9126	2 2 4	0.011
			2 1 5	- 0.002
50.01	5	1.8222	1 1 6	0.
50.23	16	1.8148	4 1 2	0.007
54.46	5	1.6834	3 3 0	0.002
55.85	1	1.6447	1 0 7	0.004
56.64	8	1.6236	3 0 6	- 0.020
57.58	8	1.5994	4 1 4	0.005
			4 0 5	- 0.006
59.80	1	1.5452	2 2 6	0.004
62.08	1	1.4938	2 1 7	0.009
63.44	1	1.4650	0 0 8	0.018
63.79	5	1.4578	6 0 0	0.004
			5 1 3	- 0.006
65.98	1	1.4146	6 0 2	0.009
66.36	2	1.4074	1 1 8	- 0.006
67.96	1	1.3781	3 1 7	0.017
68.67	2	1.3656	6 0 3	- 0.014
			4 1 6	0.001
68.86	5	1.3623	5 2 2	- 0.010

(see following sheet)

Table 5. (continued)

72.06	1	1.3095	3 0 8	0.007
73.44	1	1.2882	1 0 9	0.007
73.61	1	1.2857	3 2 7	0.007
74.30	3	1.2755	3 3 6	- 0.008
74.84	2	1.2676	2 2 8	- 0.011
75.10	4	1.2638	5 2 4	- 0.004
77.23	1	1.2342	4 4 2	0.004
77.86	1	1.2258	4 3 5	0.004
81.80	1	1.1764	4 2 7	0.005
82.47	1	1.1686	6 0 6	- 0.008
83.00	1	1.1624	4 1 8	- 0.006
83.24	2	1.1597	4 4 4	- 0.012
84.82	1	1.1421	1 1 10	- 0.012
85.32	3	1.1367	7 1 2	- 0.003
88.68	2	1.1021	6 3 0	- 0.001

Table 6 . X-ray diffraction data of H.T. $Zr(MoO_4)_2$

$2\Theta_{exp.}$ (degrees)	I/I_o	d_{exp} (Å)	h k l	$\Delta 2\Theta = 2\Theta_{exp.} - 2\Theta_{calc.}$ (degrees)
15.14	2	5.85	0 0 2	0.008
21.62	1	4.11	2 0 1	0.007
23.20	100	3.834	1 1 2	- 0.006
24.96	1	3.567	1 0 3	- 0.004
27.94	1	3.193	2 1 1	0.003
30.55	41	2.926	3 0 0	0.014
			0 0 4	0.014
35.41	19	2.535	2 2 0	0.005
			1 1 4	0.005
38.70	10	2.327	2 2 2	- 0.003
43.81	1	2.066	3 1 3	0.001
			2 0 5	0.001
45.69	1	1.9856	3 2 1	0.0
46.53	1	1.9517	0 0 6	- 0.002
47.53	14	1.9168	4 1 0	- 0.008
			2 2 4	- 0.008
50.03	23	1.8215	4 1 2	- 0.005
			1 1 6	- 0.005
54.24	7	1.6897	3 3 0	0.016
56.65	9	1.6234	3 0 6	0.018
			3 3 2	0.018
57.49	8	1.6016	5 0 3	0.004
			4 0 5	0.004
63.50	8	1.4638	6 0 0	- 0.002
66.42	2	1.4063	1 1 8	- 0.001
			5 2 0	- 0.001
68.56	8	1.3675	5 2 2	- 0.008
			4 1 6	- 0.008
72.08	1	1.3092	6 0 4	0.001
			3 0 8	0.001
73.52	1	1.2870	3 2 7	- 0.001
			1 0 9	- 0.001
74.15	2	1.2777	3 3 6	- 0.001
74.83	5	1.2677	4 4 0	- 0.008
			5 2 4	- 0.008
			2 2 8	- 0.008

Table 7 . X-Ray diffraction data of L.T. $Zr(MoO_4)_2$

$2\Theta_{exp.}$ (degrees)	I/I_o	d_{exp} (Å)	h k l	$\Delta 2\Theta = 2\theta = 2\Theta_{exp.} - 2\Theta_{calc.}$ (degrees)
14.44	55	6.13	1 1 0	- 0.002
16.38	7	5.41	0 1 1	- 0.007
18.38	13	4.83	2 0 0	0.015
22.40	12	3.969	0 2 0	- 0.001
24.08	8	3.696	0 0 2	- 0.001
25.94	35	3.435	2 1 1	- 0.003
26.53	15	3.360	1 2 $\bar{1}$	- 0.006
27.06	8	3.295	1 1 $\bar{2}$	0.008
27.70	4	3.220	3 0 0	0.002
			1 2 1	0.005
28.29	47	3.155	2 0 $\bar{2}$	- 0.010
29.11	100	3.067	2 2 0	- 0.010
29.95	13	2.983	3 1 0	0.009
32.48	10	2.756	2 0 2	0.003
33.11	32	2.705	0 2 2	- 0.012
36.37	6	2.470	2 2 $\bar{2}$	0.018
			1 0 $\bar{3}$	0.008
36.68	2	2.450	3 2 $\bar{1}$	0.003
37.22	3	2.416	4 0 0	- 0.004
38.25	7	2.353	0 1 3	0.001
38.98	13	2.311	4 1 0	0.004
41.74	1	2.164	4 0 $\bar{2}$	- 0.004
42.50	9	2.127	4 1 1	- 0.005
44.31	3	2.044	3 3 0	0.003
45.03	14	2.013	2 1 3	0.0
45.72	7	1.9844	0 4 0	- 0.002
47.88	29	1.8998	4 2 $\bar{2}$	- 0.002
48.78	7	1.8668	1 4 1	0.007
49.02	9	1.8583	4 0 $\bar{3}$	- 0.001
49.31	7	1.8480	0 0 4	- 0.006
50.26	4	1.8137	1 1 $\bar{4}$	0.003
51.50	3	1.7730	3 1 $\bar{2}$	0.001
53.00	8	1.7263	3 3 2	- 0.015

(see following sheet)

Table 7. (continued)

54.06	8	1.6949	4 3 1	0.004
54.60	12	1.6794	2 4 $\bar{2}$	0.004
54.76	11	1.6749	4 3 $\bar{2}$	0.003
			0 2 4	0.010
55.73	8	1.6480	2 2 $\bar{4}$	0.001
57.15	4	1.6104	6 0 0	- 0.003
			2 4 2	0.005
58.19	11	1.5840	4 1 3	- 0.001
59.29	7	1.5572	6 0 $\bar{2}$	0.003