

OXYHALIDE PRECURSORS

Field of the Invention

5 The present invention relates to certain precursors for the vapor deposition of certain Group VI-containing materials, a method for their preparation, and novel crystal structures thereof.

Background of the Invention

10 In consequence of its characteristics of extremely high melting point, low coefficient of thermal expansion, low resistivity, and high thermal conductivity, Group VI metals such as molybdenum and tungsten are increasingly utilized in the manufacture of semiconductor devices, including use in diffusion barriers, electrodes, photomasks, power electronics substrates, low-resistivity gates, and interconnects.

15 Such utility has motivated efforts to achieve deposition of molybdenum and tungsten films for such applications that is characterized by high conformality of the deposited film and high deposition rate to accommodate efficient high-volume manufacturing operations. This in turn has motivated efforts to develop improved molybdenum and tungsten source reagents useful in vapor deposition operations, as well as improved process parameters utilizing such reagents.

20 Molybdenum pentachloride is most commonly used as a molybdenum source for chemical vapor deposition of molybdenum-containing material. Another source reagent or precursor is MoO_2Cl_2 , but there remains a need to prepare such reagents in high yield and purity, along with other oxyhalides such as WOCl_4 , WO_2Cl_2 , MoOCl_4 , and the like.

25 Summary of the Invention

 The invention provides a process for preparing certain Group VI metal oxyhalide compounds which are useful in the deposition of Group VI containing films on various surfaces of microelectronic devices. In the process of the invention, a molybdenum or tungsten trioxide is heated in either a solid state medium or in a melt-phase reaction
30 comprising a eutectic blend comprising one or more alkaline and/or alkaline earth metal salts. The molybdenum or tungsten oxyhalide thus formed may be isolated as a vapor and crystallized to provide highly pure crystalline oxyhalides such as MoO_2Cl_2 and WO_2Cl_2 to provide another aspect of the invention.

Brief Description of the Drawings

Figure 1 is a crystal structure depiction of the MoO_2Cl_2 unit cell.

Figure 2 depicts a thermogravimetric analysis of MoO_3 and LiCl/KCl mixtures displaying appreciable mass loss upon combination of MoO_3 and LiCl/KCl . Residual mass (%) is plotted versus Temperature ($^{\circ}\text{C}$)

Figure 3 depicts a thermogravimetric analysis comparing commercially available MoO_2Cl_2 and synthesized MoO_2Cl_2 using the method of the invention. Residual mass (%) is plotted versus Temperature ($^{\circ}\text{C}$).

Figure 4 is an FTIR comparison of purchased MoO_2Cl_2 versus MoO_2Cl_2 prepared using the method of the invention.

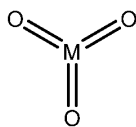
Figure 5 is a plot of the experimental X-ray powder diffraction of MoO_2Cl_2 crystals compared to the calculated spectra (black lines) using the obtained MoO_2Cl_2 unit cell parameters.

Figure 6 is the X-ray powder diffraction of hydrated MoO_2Cl_2 with the simulated MoO_2Cl_2 illustrated below as solid vertical lines.

Figure 7 is a simultaneous thermogravimetric analysis coupled with differential scanning calorimetry (STA-DSC) of the described method. This data shows that a melting point occurs at a temperature slightly different than at the LiCl/KCl eutectic alone.

Detailed Description of the Invention

In a first aspect, the invention provides a process for preparing compounds of the formula MO_yX_z , wherein M is chosen from molybdenum, and tungsten, and X is chosen from chloro, fluoro, bromo, and iodo, y is 1 or 2, and z is 2 or 4, which comprises contacting a compound of the formula



with at least one compound of the formula A-X, wherein A is chosen from elements of Group 1, Group 2, transition metals, and main-group elements of the Periodic Table, at a temperature of about 200° to about 900° C.

As set forth herein, A can be any element capable of forming a halide.

In one embodiment, A is chosen from alkali and alkaline earth metals.

In one embodiment, A is chosen from lithium, sodium, and potassium. In another embodiment, A is chosen from magnesium, calcium, strontium, barium, beryllium, scandium, titanium, vanadium, and chromium. In another embodiment, A is lithium or potassium.

In one embodiment, X is chloro.

5 In another embodiment, the at least one compound of the formula A-X is a mixture of two or more compounds, and in certain embodiments, said compounds are chosen so as to form a eutectic mixture.

10 In the process of the invention, while the interaction of the compound of the formula A-X and the compound of the formula MO_3 can occur while A-X is in a solid state throughout the temperature range of about 200° to about 900° , the compounds of the formula A-X can also be advantageously chosen from those alkali metal halides and alkaline earth metal halides which form eutectic blends. In this manner, eutectic blends of two or more compounds of the formula A-X allow for the practice of the process of the invention in the melt phase at processing temperatures lower than the melting point of each individual alkali
15 metal halide or alkaline earth metal halide, while at the same time providing a melt phase reaction environment which facilitates the sublimation of the compounds of the formula MO_yX_z as formed, which can then be removed and allowed to cool to provide a pure crystalline form. Various blends of compounds of the formula A-X may be chosen and in varying proportions in order to provide a suitable reaction medium and halide source while
20 providing at the same time a sufficiently high temperature melt phase to facilitate sublimation of the desired product as it is formed. In certain embodiments, the proportions of the individual alkali metal halides and alkaline earth metal halides may be approximately 1:1, but may also be varied from 10:1 or 1:10, depending on whatever concentration of either component of the blend is necessary to provide a melt phase reaction medium in the desired
25 temperature range. In other embodiments, the mixture defined by the formula A-X may comprise three or more species which form a eutectic blend which forms a melt phase within the desired temperature range for the formation and sublimation of the products of the formula MO_yX_z .

30 Many compounds of the formula A-X are known to form eutectic blends, for example, LiCl/KCl, as recited in the experimental section below, along with those set forth in "Molten Salts: Volume 4, Part 2 Chlorides and Mixtures - electrical conductance, density, viscosity, and surface tension data", G.J. Janz et al., Journal of Physical and Chemical Reference Data 4, 871 (1975).

In one embodiment, the compounds of the formula A-X are a mixture of lithium chloride and potassium chloride, which form a eutectic mixture having a melting point of about 357° C, in proportions of about 44 weight percent of lithium chloride to about 56 weight percent of potassium chloride.

5 In certain embodiments, the process is conducted utilizing inert carrier gasses such as nitrogen, argon, *etc.*, either at atmospheric pressure or under reduced pressure, such parameters chosen to facilitate the sublimation of the desired reaction products of the formula MO_yX_z , as well as to minimize thermal decomposition of the desired product. Additionally, in one embodiment, the stoichiometric amount of the starting material of the formula MO_3 is
10 chosen so as to lead to a higher production of compounds of the formula MO_yX_z , when Y is 1 and Z is 4. In another embodiment, the stoichiometric amount of the starting material of the formula MO_3 is chosen so as to lead to a higher production of compounds of the formula MO_yX_z , when Y is 2 and Z is 2. In a further embodiment, the process is conducted under a regime of fractional sublimation, while varying the pressure and temperature so as to generate
15 a given species at different pressure/temperature combinations. In this manner, species of desired product where Y and Z are 2 can be separated from species of desired product where Y is 1 and Z is 4, each forming a pure crystalline form upon cooling.

In a second aspect, the invention provides compounds having the formula MO_yX_z in crystalline form, wherein M is chosen from molybdenum and tungsten, X is chosen from
20 chloro, fluoro, bromo, and iodo, and y is 1 or 2, and z is 2 or 4.

In one embodiment, the compound of the formula MO_yX_z is MoO_2Cl_2 . In another embodiment, the crystalline form of the compound of the formula MoO_2Cl_2 possesses a crystal structure as depicted in Figure 1; this crystalline form of MoO_2Cl_2 is anhydrous. In another embodiment, the crystalline form of the compound of the formula
25 MoO_2Cl_2 possesses an orthorhombic crystal system, and unit cell dimensions of about

$$\begin{aligned} a &= 13.552(5) \text{ \AA} & \alpha &= 90^\circ \\ b &= 5.456(2) \text{ \AA} & \beta &= 90^\circ \\ c &= 5.508(2) \text{ \AA} & \gamma &= 90^\circ. \end{aligned}$$

30

The approximate bond lengths in the crystalline form of the compound of the formula MoO_2Cl_2 have been determined to be as follows:

$$\text{Mo--Cl} \quad 2.278(2) \text{ \AA}$$

Mo--O 1.706(5) - 2.239(5) Å
 Cl--Mo--Cl 151.78(7) Å
 O--Mo--O 79.08-102.90 Å.

5 As used herein the term "unit cell" refers to the smallest and simplest volume element of a crystal that is completely representative of the unit of pattern of the crystal. The dimensions of the unit cell are defined by six numbers: dimensions a, b, and c and angles α , β , and γ . A crystal is an efficiently packed array of many unit cells.

10 As used herein, the term "orthorhombic unit cell" refers to a unit cell wherein $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$.

As used herein, "crystal lattice" refers to the array of points defined by the vertices of packed unit cells, as determined by single-crystal x-ray diffraction analysis.

15 As used herein, "space group" refers to the symmetry of a unit cell. In a space group designation (*e.g.*, C2) the capital letter indicates the lattice type and the other symbols represent symmetry operations that can be carried out on the unit cell without changing its appearance.

20 In another embodiment, the crystalline form of MoO_2Cl_2 exhibits a powder XRD pattern with one or more peaks at 12.94, 23.64, 26.10, 39.50, and/or 40.28 ± 0.04 degrees 2-theta. In a further embodiment, the crystalline form of MoO_2Cl_2 has a powder XRD pattern as depicted in Figure 5. In another embodiment, crystalline MoO_2Cl_2 has a powder XRD pattern with one or more peaks as determined from the single crystal unit cell parameters listed in Table 4.

25 In another embodiment, the compound of the formula MO_yX_z in crystalline form is WO_2Cl_2 .

30 This invention can be further illustrated by the following examples of certain embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

30 Examples

Example 1. Synthesis of MoO_2Cl_2

A (44/56 by weight) mixture of lithium chloride and potassium chloride was combined with MO_3 in a stainless steel ampule and evacuated under reduced pressure (20

mTorr). The ampule was heated to 475° C inside a tube furnace. The resulting MoO₂Cl₂ vapor was collected via a short-path tube equipped with a round bottom flask. FTIR and STA analysis supports the synthesis of MoO₂Cl₂.

- 5 Table 1. 4 (ICP-MS data on MoO₂Cl₂ synthesized using the described method. Data reported in parts-per-million (ppm)).

Element list	D.L.	Sample A*	Sample B	Sample C
Aluminum	0.041	0.523	0.354	0.571
Antimony	0.027	0.786	0.690	0.606
Barium	0.018	0.019	<0.018	<0.018
Calcium	1.851	1.851	1.272	0.919
Chromium	0.027	<0.027	<0.027	<0.027
Cobalt	0.026	<0.026	<0.026	<0.026
Copper	0.028	<0.028	<0.028	<0.028
Iron	0.028	0.482	0.404	0.704
Lead	0.023	<0.023	<0.023	<0.023
Lithium	0.036	0.238	0.067	0.133
Magnesium	0.032	0.081	0.065	0.092
Manganese	0.021	<0.021	<0.021	<0.021
Nickel	0.022	0.033	0.056	0.045
Potassium	0.019	1.019	2.259	2.731
Silver	0.027	<0.027	<0.027	<0.027
Sodium	0.066	0.083	0.165	0.329
Tin	0.043	0.115	0.119	0.409

Titanium	0.067	<0.067	<0.067	0.068
Vanadium	0.027	<0.027	<0.027	<0.027

*Each of samples A, B, and C were taken from the same lot.

Table 2 Crystal data and structure refinement for MoO₂Cl₂

5

Identification code	NB00657
Empirical formula	Cl ₂ Mo O ₂
Formula weight	198.84
Temperature	100.0 K
10 Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Cmc21
Unit cell dimensions	a = 13.552(5) Å α = 90°. b = 5.456(2) Å β = 90°. c = 5.508(2) Å γ = 90°.
15 Volume	407.2(3) Å ³
Z	4
Density (calculated)	3.243 Mg/m ³
Absorption coefficient	4.342 mm ⁻¹
20 F(000)	368
Crystal size	0.27 x 0.22 x 0.2 mm ³
Theta range for data collection	3.006 to 28.284°.
Index ranges	-17 ≤ h ≤ 17, -7 ≤ k ≤ 5, -7 ≤ l ≤ 7
Reflections collected	1579
25 Independent reflections	523 [R(int) = 0.0274]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.2627 and 0.1831
Refinement method	Full-matrix least-squares on F ²
30 Data / restraints / parameters	523 / 1 / 28

	Goodness-of-fit on F^2	1.144
	Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0216$, $wR2 = 0.0540$
	R indices (all data)	$R1 = 0.0234$, $wR2 = 0.0556$
	Absolute structure parameter	0.12(5)
5	Extinction coefficient	n/a
	Largest diff. peak and hole	1.383 and -0.853 e.Å ⁻³

10 Table 3. Bond lengths [Å] and angles [°] for MoO₂Cl₂.

	Mo(1)-Cl(1)#1	2.2783(17)
	Mo(1)-Cl(1)	2.2783(17)
	Mo(1)-O(1)	1.715(5)
15	Mo(1)-O(1)#2	2.234(6)
	Mo(1)-O(2)	1.706(5)
	Mo(1)-O(2)#3	2.239(5)
	Cl(1)#1-Mo(1)-Cl(1)	151.78(7)
20	O(1)#2-Mo(1)-Cl(1)	79.41(4)
	O(1)-Mo(1)-Cl(1)#1	98.91(5)
	O(1)-Mo(1)-Cl(1)	98.91(5)
	O(1)#2-Mo(1)-Cl(1)#1	79.41(4)
	O(1)-Mo(1)-O(1)#2	88.36(11)
25	O(1)#2-Mo(1)-O(2)#3	79.1(3)
	O(1)-Mo(1)-O(2)#3	167.4(3)
	O(2)-Mo(1)-Cl(1)#1	98.54(5)
	O(2)#3-Mo(1)-Cl(1)	78.92(4)
	O(2)#3-Mo(1)-Cl(1)#1	78.92(4)
30	O(2)-Mo(1)-Cl(1)	98.54(5)
	O(2)-Mo(1)-O(1)	103.0(4)
	O(2)-Mo(1)-O(1)#2	168.6(3)
	O(2)-Mo(1)-O(2)#3	89.57(6)
	Mo(1)-O(1)-Mo(1)#4	149.9(4)

Mo(1)-O(2)-Mo(1)#5 173.8(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,z #2 -x+1,-y+1,z+1/2 #3 -x+1,-y,z+1/2

5 #4 -x+1,-y+1,z-1/2 #5 -x+1,-y,z-1/2

Table 4.

0.5(Cl ₄ Mo ₂ O ₄) MoO ₂ Cl ₂ .cif							MoO ₂ Cl ₂
0.5(Cl ₄ Mo ₂ O ₄)							Orthorhombic: Cmc21 (36) [M=8]
CELL: 13.552 x 5.456 x 5.508 <90.0 x 90.0 x 90.0> Vol=407.3, Z=4, Dx=3.2428, I/Ic=8.14							oC20
See Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.							
_cell_measurement_reflns_used= 1075, _cell_measurement_temperature= 100(2), _cell_measurement_theta_max= 28.28, _cell_measurement_theta_min= 3.01							
99 Merged Lines in 0.0-90.0 degs >= 0.0%, I/Ic=8.14 (m = merged line):							[Diffractometer LP] [U(i,j)] [F'+F"]
#	(hkl)	2-Theta	d(Å)	I(f)	Theta	1/(2d)	2pi/d m
1	(200)	13.055	6.776	57.9	6.527	0.0738	0.9273
2	(110)	17.508	5.0612	0.1	8.754	0.0988	1.2414
3	(111)	23.857	3.7268	100.0	11.929	0.1342	1.6860
4	(310)	25.580	3.4795	0.3	12.790	0.1437	1.8058
5	(400)	26.283	3.3880	8.8	13.142	0.1476	1.8545
6	(311)	30.360	2.9417	10.5	15.180	0.1700	2.1359
7	(2)	32.485	2.7540	8.0	16.242	0.1816	2.2815
8	(20)	32.803	2.7280	12.3	16.401	0.1833	2.3032
9	(202)	35.146	2.5513	7.3	17.573	0.1960	2.4627
10	(220)	35.443	2.5306	1.3	17.722	0.1976	2.4829
11	(21)	36.734	2.4446	0.1	18.367	0.2045	2.5702
12	(510)	37.004	2.4274	0.0	18.502	0.2060	2.5885
13	(112)	37.136	2.4191	0.7	18.568	0.2067	2.5974
14	(221)	39.143	2.2995	0.5	19.571	0.2174	2.7324
15	(600)	39.880	2.2587	13.5	19.940	0.2214	2.7818
16	(511)	40.582	2.2212	19.0	20.291	0.2251	2.8287
17	(312)	41.797	2.1594	0.4	20.898	0.2315	2.9096
18	(402)	42.256	2.1370	4.4	21.128	0.2340	2.9401
19	(420)	42.510	2.1248	0.6	21.255	0.2353	2.9571
20	(421)	45.730	1.9824	0.3	22.865	0.2522	3.1695
21	(22)	46.837	1.9381	10.8	23.419	0.2580	3.2419

22	(222)	48.835	1.8634	8.5	24.418	0.2683	3.3719
23	(710)	49.945	1.8245	0.0	24.973	0.2740	3.4437
24	(512)	50.049	1.8210	0.2	25.025	0.2746	3.4504
25	(130)	50.599	1.8025	0.0	25.299	0.2774	3.4858
26	(602)	52.344	1.7464	3.6	26.172	0.2863	3.5977
27	(620)	52.561	1.7397	5.5	26.280	0.2874	3.6116
28	(711)	52.814	1.7320	9.8	26.407	0.2887	3.6277
29	(113)	53.013	1.7259	5.6	26.507	0.2897	3.6404
30	(131)	53.442	1.7131	9.7	26.721	0.2919	3.6677
31	(800)	54.094	1.6940	1.3	27.047	0.2952	3.7091
32	(330)	54.334	1.6871	0.2	27.167	0.2964	3.7243
33	(422)	54.501	1.6823	5.7	27.250	0.2972	3.7349
34	(621)	55.333	1.6590	0.0	27.666	0.3014	3.7874
35	(313)	56.637	1.6238	8.1	28.319	0.3079	3.8694
36	(331)	57.048	1.6131	1.6	28.524	0.3100	3.8951
37	(23)	60.758	1.5232	0.1	30.379	0.3283	4.1251
38	(712)	60.853	1.5210	0.1	30.426	0.3287	4.1309
39	(530)	61.336	1.5102	0.0	30.668	0.3311	4.1605
40	(132)	61.426	1.5082	0.0	30.713	0.3315	4.1660
41	(223)	62.442	1.4861	0.1	31.221	0.3365	4.2280
42	(622)	63.163	1.4708	7.2	31.581	0.3399	4.2718
43	(513)	63.477	1.4643	3.0	31.739	0.3415	4.2909
44	(531)	63.861	1.4564	4.6	31.930	0.3433	4.3141
45	(910)	64.103	1.4515	0.0	32.052	0.3445	4.3287
46	(802)	64.533	1.4429	1.0	32.266	0.3465	4.3546
47	(820)	64.723	1.4391	0.4	32.361	0.3474	4.3660
48	(332)	64.748	1.4386	0.2	32.374	0.3476	4.3676
49	(911)	66.570	1.4036	0.9	33.285	0.3562	4.4765
50	(821)	67.177	1.3924	0.1	33.589	0.3591	4.5126
51	(423)	67.350	1.3892	0.1	33.675	0.3599	4.5228
52	(4)	68.029	1.3770	0.4	34.014	0.3631	4.5630
53	(40)	68.767	1.3640	1.8	34.384	0.3666	4.6064
54	(10,0,0)	69.277	1.3552	0.3	34.639	0.3689	4.6364
55	(204)	69.617	1.3494	1.8	34.808	0.3705	4.6562
56	(240)	70.348	1.3372	0.8	35.174	0.3739	4.6988
57	(114)	70.864	1.3287	0.0	35.432	0.3763	4.7288
58	(730)	71.059	1.3255	0.0	35.529	0.3772	4.7401
59	(532)	71.143	1.3242	0.0	35.571	0.3776	4.7450
60	(41)	71.153	1.3240	0.1	35.577	0.3776	4.7456
61	(241)	72.711	1.2994	0.3	36.355	0.3848	4.8353
62	(713)	73.054	1.2942	1.8	36.527	0.3863	4.8550
63	(731)	73.412	1.2887	3.4	36.706	0.3880	4.8755
64	(133)	73.578	1.2862	1.6	36.789	0.3887	4.8849
65	(912)	73.723	1.2841	0.0	36.861	0.3894	4.8932

66	(314)	73.971	1.2804	0.1	36.986	0.3905	4.9073
67	(404)	74.291	1.2757	1.6	37.145	0.3920	4.9254
68	(822)	74.304	1.2755	1.9	37.152	0.3920	4.9262
69	(440)	75.003	1.2653	0.5	37.501	0.3952	4.9657
70	(623)	75.174	1.2628	0.1	37.587	0.3959	4.9754
71	(333)	76.643	1.2423	3.1	38.322	0.4025	5.0579
72	(441)	77.311	1.2332	0.2	38.656	0.4055	5.0951
73	(24)	77.603	1.2293	0.3	38.802	0.4067	5.1113
74	(42)	78.130	1.2223	1.2	39.065	0.4091	5.1405
75	(10,0,2)	78.616	1.2160	0.6	39.308	0.4112	5.1673
76	(10,2,0)	78.791	1.2137	0.1	39.396	0.4120	5.1769
77	(224)	79.115	1.2095	2.6	39.558	0.4134	5.1947
78	(242)	79.639	1.2029	1.3	39.820	0.4157	5.2234
79	(11,1,0)	79.730	1.2017	0.0	39.865	0.4161	5.2284
80	(514)	80.053	1.1977	0.0	40.027	0.4175	5.2460
81	(732)	80.321	1.1944	0.0	40.160	0.4186	5.2606
82	(10,2,1)	81.068	1.1853	0.0	40.534	0.4218	5.3011
83	(604)	81.864	1.1757	0.4	40.932	0.4253	5.3441
84	(11,1,1)	82.000	1.1741	1.6	41.000	0.4259	5.3514
85	(640)	82.557	1.1676	2.0	41.279	0.4282	5.3812
86	(533)	82.667	1.1663	1.1	41.334	0.4287	5.3871
87	(930)	83.233	1.1598	0.0	41.617	0.4311	5.4173
88	(424)	83.610	1.1556	2.4	41.805	0.4327	5.4373
89	(442)	84.128	1.1498	1.1	42.064	0.4349	5.4648
90	(641)	84.812	1.1422	0.1	42.406	0.4377	5.5008
91	(913)	85.141	1.1387	2.1	42.571	0.4391	5.5181
92	(931)	85.486	1.1349	0.4	42.743	0.4406	5.5361
93	(823)	85.701	1.1326	0.0	42.851	0.4414	5.5474
94	(12,0,0)	86.013	1.1293	0.9	43.006	0.4427	5.5636
95	(10,2,2)	87.827	1.1106	1.1	43.913	0.4502	5.6574
96	(11,1,2)	88.750	1.1014	0.0	44.375	0.4539	5.7045
97	(714)	88.988	1.0991	0.0	44.494	0.4549	5.7166
98	(43)	89.421	1.0949	0.0	44.710	0.4567	5.7385
99	(134)	89.491	1.0942	0.1	44.745	0.4569	5.7421

Table 4 is the simulated Powder X-ray Diffraction (PXRD) spectra using the unit cell (MoO₂Cl₂ crystal structure) using commercially-available software to model and simulate PXRD data.

Table 5

Hydrated MoO ₂ Cl ₂							Peak Search Report	
SCAN: 10.0/90.0/0.032/43.5(sec), Cu, I(p)=8121, 05/22/19 11 :28p								
PEAK: 1 5(pts)/Parabolic Filter, Threshold=3.0, Cutoff=0.1 %, BG=3/1 0, Peak-To..								
NOTE: Intensity = Counts, 2T(0)=0.0(deg), Wavelength to Compute d-Spacing = ...								
#	2-Theta	d(Å)	BG	Height	H%	Area	A%	FWHM
1	12.854	6.8817	1670	876	13.1	8314	15.6	0.258
2	16.045	5.5194	1458	6663	100.0	53209	100.0	0.217
3	19.349	4.5836	1328	1428	21.4	10284	19.3	0.196
4	24.786	3.5891	1403	1421	21.3	10676	20.1	0.204
5	25.738	3.4586	1432	1641	24.6	12382	23.3	0.205
6	26.191	3.3997	1418	1875	28.1	15407	29.0	0.223
7	32.051	2.7902	1292	579	8.7	5877	11.0	0.276
8	32.486	2.7539	1269	181	2.7	3136	5.9	0.472
9	35.509	2.5260	1159	112	1.7	2723	5.1	0.660
10	36.011	2.4920	1122	174	2.6	2305	4.3	0.361
11	44.499	2.0344	1089	251	3.8	3794	7.1	0.411

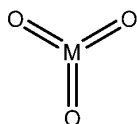
Table 5 depicts the experimental X-ray powder diffraction of hydrated MoO₂Cl₂ obtained after exposure of MoO₂Cl₂ to ambient atmosphere for several hours.

In the drawings and specification, there have been disclosed certain embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.

Claims

1. A compound having the formula MO_yX_z in crystalline form, wherein M is chosen from molybdenum and tungsten, X is chosen from chloro, fluoro, bromo, and iodo, and y is 1 or 2, and z is 2 or 4.
2. The compound of claim 1, wherein M is molybdenum.
3. The compound of claim 1, wherein M is tungsten.
4. The compound of claim 1, wherein M is molybdenum and X is chloro.
5. The compound of claim 1, wherein M is tungsten and X is chloro.
6. A compound having the formula MoO_2Cl_2 in crystalline form and having the x-ray crystallographic structure as shown in Figure 1.
7. The compound of claim 6, having an orthorhombic crystal system, and unit cell dimensions of about
- | | |
|-----------------------------|---------------------|
| $a = 13.552(5) \text{ \AA}$ | $\alpha = 90^\circ$ |
| $b = 5.456(2) \text{ \AA}$ | $\beta = 90^\circ$ |
| $c = 5.58(2) \text{ \AA}$ | $\gamma = 90^\circ$ |
8. The compound of claim 6, which exhibits a powder XRD pattern with one or more peaks at 12.94, 23.64, 26.10, 39.50, and/or 40.28 ± 0.04 degrees 2-theta.
9. The compound of claim 6, which has a powder XRD pattern as depicted in Figure 5.
10. A compound having the formula WO_2Cl_2 in crystalline form.

11. A process for preparing compounds of the formula MO_yX_z , wherein M is chosen from molybdenum and tungsten, and X is chosen from chloro, fluoro, bromo, and iodo, y is 1 or 2, and z is 2 or 4, which comprises contacting a compound of the formula



5 with at least one compound of the formula A-X, wherein A is chosen from elements of Group 1, Group 2, transition metals, and main-group elements, at a temperature of about 200° to about 900° C.

10 12. The process of claim 11, wherein A is chosen from lithium, sodium, and potassium.

13. The process of claim 11, wherein X is chloro.

14. The process of claim 11, wherein A is chosen from magnesium, calcium, strontium, barium, beryllium, scandium, titanium, vanadium, and chromium.

15 15. The process of claim 11, wherein the compounds of the formula A-X are comprised of a mixture of lithium chloride and potassium chloride.

20 16. The process of claim 11, further comprising collecting the compound of the formula MO_yX_z as a vapor and allowing said vapor to cool, thereby forming a crystalline form of the the compound of the formula MO_yX_z .

17. The process of claim 11, wherein the compound of the formula MO_yX_z is MoO_2Cl_2 .

25 18. The process of claim 11, wherein the compound of the formula MO_yX_z is MoOCl_4 .

19. The process of claim 11, wherein the compound of the formula MO_yX_z is WO_2Cl_2 .

30 20. The process of claim 11, wherein the compound of the formula MO_yX_z is WOCl_4 .