Preparation, Crystal Structure, and Luminescence of Magnesium Molybdate and Tungstate Monohydrates, MgMoO$_4$ · H$_2$O and MgWO$_4$ · H$_2$O

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Triclinic MgMoO$_4$ · H$_2$O and the isomorphous MgWO$_4$ · H$_2$O have been prepared under mild hydrothermal conditions in single crystalline form and the crystal structure of MgMoO$_4$ · H$_2$O has been determined by X-ray diffraction. The structure is compared to a model deduced earlier for MgWO$_4$ · H$_2$O from topotaxy data, with which the general topology agrees, but there is an important difference in the orientation of MoO$_4$-tetrahedra. The X-ray powder diffraction data, thermal dehydration behavior, as well as the luminescence properties are reported and the latter compared with data of related phases. Crystal data are: Triclinic, space group $P -1$; MgMoO$_4$ · H$_2$O: $a = 5.665$ Å, $b = 5.869$ Å, $c = 6.875$ Å, $\alpha = 100.80°$, $\beta = 95.05°$, $\gamma = 106.57°$; MgWO$_4$ · H$_2$O: $a = 5.681$ Å, $b = 5.887$ Å, $c = 6.870$ Å, $\alpha = 100.85°$, $\beta = 95.44°$, $\gamma = 106.55°$. © 1988 Academic Press, Inc.

Introduction

In an earlier paper (*1*), we have described the crystal structure of magnesium tungstate dihydrate, MgWO$_4$ · 2H$_2$O, and from a study of the topotaxy of its dehydration, a model for the crystal structure of the monohydrate, MgWO$_4$ · H$_2$O, has been deduced. We have now succeeded in preparing the monohydrate directly in crystalline form by hydrothermal synthesis under mild conditions, as well as the isomorphous magnesium molybdate monohydrate, MgMoO$_4$ · H$_2$O, and have determined the crystal structure of the latter from single crystal X-ray diffraction data (*2*). The present paper compares this structure with the model suggested in (*1*), pointing out a difference in the orientation of MoO$_4$-tetrahedra, and describes the dehydration behavior of the two compounds, as well as their luminescence properties, which are compared to those of related phases. The data presented help in understanding the structural chemistry of magnesium molybdates and tungstates as a family of related compounds.

Preparation of Samples

(a) MgWO$_4$ · H$_2$O: Equal volumes of 0.75 *M* solutions of Na$_2$WO$_4$ and Mg(NO$_3$)$_2$ in

water are mixed at room temperature and filled into Pyrex tubes to approximately two-thirds of their volume. The closed tubes are put in upright position into an oven and kept at 155°C for 3 days. The crystalline product is filtered, washed with water and ethanol, and dried in air at 90°C.

(b) MgMoO$_4$ · H$_2$O: Equal volumes of 1 M solutions of Na$_2$MoO$_4$ and MgCl$_2$ in 0.5 M HCl are mixed at room temperature (pH = 6) and filled into Pyrex tubes to approximately two-thirds of their volume. The closed tubes are put in upright position into an oven and kept at 155°C for 3 days. The crystalline product is filtered, washed with water and ethanol, and dried in air at 90°C.

X-ray Powder Diffraction

Whereas the magnesium tungstate monohydrate prepared by dehydration of the dihydrate was of a relatively low degree of crystallinity and heavily twinned, as reported in (1), the materials prepared according to the above procedures are much more crystalline, and therefore yield diffraction patterns with more and better resolved lines (Guinier-De Wolff camera, CuKα_1). Following the single crystal experiments (see below), these could be indexed by means of a triclinic unit cell which is four times smaller than the pseudo-monoclinic cell proposed in (1). (Lattice constants were calculated by least-squares refinement of powder data; see Table I. Intensities were measured photometrically.) The true symmetry was hidden in the dehydrated samples due to the intense twinning, which hindered a recognition of the systematic absences. The pseudomonoclinic and the triclinic cells are related as follows:

$$a_{tric} = 0.5a_{mono} + 0.25b_{mono} + 0.25c_{mono},$$

$$b_{tric} = -0.5a_{mono} + 0.25b_{mono} + 0.25c_{mono},$$

$$c_{tric} = -0.5b_{mono} + 0.5c_{mono}.$$

TABLE I

X-RAY POWDER DIFFRACTION PATTERNS OF MgMoO$_4$ · H$_2$O AND MgWO$_4$ · H$_2$O

MgMoO$_4$ · H$_2$O		MgWO$_4$ · H$_2$O			
d(Å)	I/I_0	d(Å)	I/I_0	$h\ k\ l_{tric}$	$h\ k\ l_{mono}$
6.648	12	6.618	5	0 0 1	0 1 1
5.472	52	5.477	51	0 1 0	−1 1 1
5.349	11	5.386	6	1 0 0	
4.783	17	4.787	30	0 1−1	−1 2 0
4.610	65	4.614	58	1−1 0	2 0 0
4.529	54	4.543	62	1 0−1	1 2 0
3.899	65	3.893	78	1−1 1	1 0 2
3.833	20	3.831	17	0 1 1	−2 1 1
3.691	27	3.701	28	1−1−1	2 1 1
3.350	80	3.357	50	1 1 0	0 2 2
3.331	100	3.329	100	0 0 2	0 3 1
3.313	80			1 1−1	
3.179	49	3.181	35	0 1−2	−1 2 2
2.815	55	2.826	47	1−2 0	−3 1 1
2.780	22	2.777	55	1−1 2	3 1 1
2.770	61			2−1 0	
2.768	65	2.769	47	0 2−1	
2.753	41	2.750	25	1 1 1/0 2 0	0 1 3/−2 2 2
2.695	40	2.705	22	1 1−2	0 4 0
2.681	45	2.688	34	2 0 0	231/−113/113
2.629	23	2.636	11	1−1−2	
2.605	16	2.602	16	0 1 2	
2.598	14	2.608	12	2−1−1	−1 4 0
2.520	7	2.519	9	2−1 1	0 2 3
2.465	4			1−2−1	
2.395	11	2.402	3	0 2−2	
2.371	8			2 0 1	
2.359	18	2.359	18	0 2 1	−2 4 0
2.334	23	2.334	15	1−2 2	2 1 3
2.306	7			2−2 0	
2.263	13	2.275	13	2 0−2	0 4 2
2.241	11	2.243	10	0 1−3	
2.226	26	2.221	13	0 0 3	0 3 3
2.194	28	2.204	14	2 1−1	−1 3 3
		2.187	12	1 2 0/2−1−2	
2.177	9	2.177	9	1 0−3	
		2.166	5	2 1 0	
2.142	11	2.149	10	2−2−1	0 0 4
2.135	8	2.128	6	1 1 2	
2.089	29	2.095	11	1 1−3	0 5 1
		2.085	12	2−1 2	
2.068	28	2.076	14	1 2−2	−3 4 0
2.052	5	2.047	4	1−1 3	
2.017	18	2.026	8	2 1−2	1 5 1
2.011	22	2.013	15	1−2−2	

Note. MgMoO$_4$ · H$_2$O: a = 5.665 Å, b = 5.869 Å, c = 6.875 Å, α = 100.80°, β = 95.05°, γ = 106.57°; MgWO$_4$ · H$_2$O: a = 5.681 Å, b = 5.887 Å, c = 6.870 Å, α = 100.85°, β = 95.44°, γ = 106.55°.

The indexed powder diffraction patterns for both MgWO$_4$ · H$_2$O and MgMoO$_4$ · H$_2$O are listed in Table I and compared to the former monoclinic indexing. Table I clearly shows that the two patterns are virtually identical.

TABLE II

Atomic parameters for MgMoO$_4$ · H$_2$O

Atom	x	y	z	$U_{eq}{}^a$
Mo	0.25802(4)	0.12151(4)	0.25128(3)	0.007
Mg	0.3594(1)	0.2926(1)	−0.1944(1)	0.009
O(1)	0.3744(3)	0.3625(3)	0.1229(2)	0.010
O(2)	0.3640(3)	−0.1288(3)	0.1674(2)	0.016
O(3)	0.3653(4)	0.2341(3)	0.5050(2)	0.019
O(4)	−0.0715(3)	0.0239(3)	0.2123(3)	0.015
OW	0.0969(3)	0.4764(3)	−0.2215(3)	0.024
HW(1)	0.1237	0.6493	−0.1984	0.060
HW(2)	−0.0404	0.4229	−0.1815	0.060

Anisotropic temperature factors[b]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	0.00602(7)	0.00534(7)	0.00585(7)	0.00219(5)	0.00183(5)	0.00092(5)
Mg	0.0081(3)	0.0073(3)	0.0070(3)	0.0018(2)	0.0015(2)	0.0015(2)
O(1)	0.0115(7)	0.0068(6)	0.0084(6)	0.0034(5)	0.0022(5)	−0.0006(5)
O(2)	0.0131(7)	0.0113(7)	0.0166(8)	0.0032(6)	0.0029(6)	0.0072(6)
O(3)	0.0232(9)	0.0179(8)	0.0078(7)	0.0030(6)	0.0015(6)	0.0037(7)
O(4)	0.0078(6)	0.0119(7)	0.0195(9)	0.0055(6)	0.0038(6)	0.0014(5)
OW	0.0146(8)	0.0152(9)	0.033(1)	0.0082(8)	0.0056(8)	0.0074(7)

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

[b] The U_{ij} are defined by $\exp[-2\pi^2(U_{11} a^{*2} h^2 + U_{22} b^{*2} k^2 + U_{33} c^{*2} l^2 + 2U_{23} b^* c^* kl + 2U_{13} a^* c^* hl + 2U_{12} a^* b^* hk)]$.
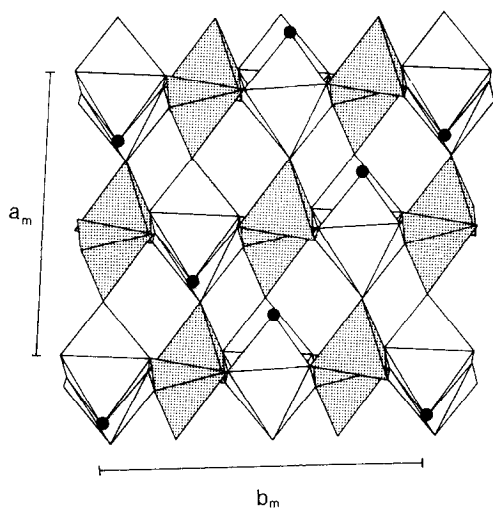
FIG. 1. View (1 1 1)$_{\text{triclinic}}$ (equivalent to (0 0 1)$_{\text{monoclinic}}$) of the crystal structure of MgMoO$_4$ · H$_2$O, to be compared with Fig. 3b in (1). (Drawn with STRUPLO (7)). Black dots: H$_2$O molecules. MoO$_4$-tetrahedra shaded. Axes indicated belong, for ease of comparison, to the monoclinic unit cell. a_{mono} corresponds to $(a_{\text{tric}} - b_{\text{tric}})$, b_{mono} to $(a_{\text{tric}} + b_{\text{tric}} - c_{\text{tric}})$.

nation shows that in reality, at least for the crystals prepared directly as MgMoO$_4$ · H$_2$O, the tetrahedra within one and the same row point alternatingly up and down (Fig. 1). The need for such a reorientation of the tetrahedra is the most probable cause for the high disorder (low degree of crystallinity) and intense twinning of the MgWO$_4$ · H$_2$O prepared by dehydration of MgWO$_4$ · 2H$_2$O (alternatively, it might be argued that the dehydrated material may differ in its structure from the prepared crystals, which may not be completely ruled out in view of the diffuseness of its powder X-ray diffraction pattern which prevents an accurate comparison of intensities).

Thermal Dehydration

The thermal dehydration behavior of MgWO$_4$ · H$_2$O essentially corresponds to that described in (1), with the difference

TABLE III

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
		Interatomic distances and angles for MgMoO$_4$ · H$_2$O			
Mg–O(1)	2.130(2)	Mo–O(1)	1.802(2)	OW–HW(1)	0.961(2)
Mg–O(1)'	2.088(2)	Mo–O(2)	1.757(2)	OW–HW(2)	0.842(2)
Mg–O(2)'	2.069(3)	Mo–O(3)	1.730(2)		
Mg–O(3)'	2.034(2)	Mo–O(4)	1.768(2)	Mg–Mg'	3.191(2)
Mg–O(4)'	2.066(2)			Mg–Mo	3.441(1)
Mg–OW	2.084(3)			Mo–Mo'	4.061(1)

Atoms	Angle (°)	Atoms	Angle (°)
O(1)–Mg–O(1)'	81.69(8)	O(2)'–Mg–OW	176.66(9)
O(1)–Mg–O(2)'	89.19(9)	O(3)'–Mg–O(4)'	94.50(9)
O(1)–Mg–O(3)'	176.93(9)	O(3)'–Mg–OW	90.7(1)
O(1)–Mg–O(4)'	88.02(8)	O(4)'–Mg–OW	88.95(9)
O(1)–Mg–OW	91.1(1)	O(1)–Mo–O(2)	111.19(9)
O(1)'–Mg–O(2)'	90.72(8)	O(1)–Mo–O(3)	108.31(9)
O(1)'–Mg–O(3)'	95.95(8)	O(1)–Mo–O(4)	110.1(1)
O(1)'–Mg–O(4)'	168.45(9)	O(2)–Mo–O(3)	108.7(1)
O(1)'–Mg–OW	86.03(9)	O(2)–Mo–O(4)	109.25(9)
O(2)'–Mg–O(3)'	88.9(1)	O(3)–Mo–O(4)	109.2(1)
O(2)'–Mg–O(4)'	94.39(9)	HW(1)–OW–HW(2)	103.5(3)

X–H · · · Y	H · · · Y (Å)	X · · · Y (Å)	X–H · · · Y (°)
		Hydrogen bonded contacts (Calculated with ORFFE3 (6))	
OW–HW(1) · · · O(4)"	2.038(2)	2.962(3)	161.0(1)
OW–HW(2) · · · O(2)	2.152(2)	2.920(3)	151.4(2)

Atom	Symmetry code	Atom	Symmetry code	Atom	Symmetry code
Mo	x,y,z	O(2)	x,y,z	O(4)'	$-x,-y,-z$
Mo'	$-x,-y,-z$	O(2)'	$1-x,-y,-z$	O(4)"	$-x,1-y,-z$
Mg	x,y,z	O(3)	x,y,z	OW	x,y,z
Mg'	$1-x,1-y,-z$	O(3)'	$x,y,-1+z$	HW(1)	x,y,z
O(1)	x,y,z	O(4)	x,y,z	HW(2)	x,y,z
O(1)'	$1-x,1-y,-z$				

that the anhydrous product, which corresponds to literature data for a "high temperature" modification (8), yields much clearer X-ray powder and pseudo-single-crystal diffraction patterns, when prepared from the monohydrate instead of the dihydrate, because its immediate precursor is obviously single crystalline and not severely twinned as when starting from the dihydrate. It now seems feasible to interpret the topotactic reaction from MgWO$_4$ · H$_2$O to "high temperature" MgWO$_4$ and to deduce a crystal structure model for this phase too (9). A high resolution electron microscopic study of this material is in progress.

In the case of MgMoO$_4$ · H$_2$O, dehydration first leads at 190°C to a poorly crystalline material, which corresponds already roughly to the known structure of MgMoO$_4$ and recrystallizes to this phase in well-crystallized form above 600°C.

Luminescence Properties

We have recently reported the luminescence of magnesium tungstate dihydrate, MgWO$_4$ · 2H$_2$O (10). In view of the structural results on the monohydrates MgWO$_4$ · H$_2$O and MgMoO$_4$ · H$_2$O, it seemed interesting to investigate also the luminescence of these two compounds and to compare the results for the dihydrates, the monohydrates, and the anhydrous compounds.

The optical instrumentation used is the same as mentioned in (10), and consists essentially of a Perkin–Elmer spectrofluorometer MPF-3 equipped with a Xe lamp and a helium cryostat. The spectral data obtained are very similar to those reported for MgWO$_4$ · 2H$_2$O as far as band shape is concerned.

MgWO$_4$ · 2H$_2$O shows two different emissions which are independent of each other, viz., a blue emission which is related to the presence of water, and a greenish emission from the tungstate tetrahedron. The latter is due to a charge transfer transition in the tungstate group. None of the other samples shows the blue emission, whatever the temperature or excitation wavelength may be. This seems to indicate that the blue emission is not due to intrinsic water molecules, but rather to water (or hydroxide groups) on the surface (see Ref. (10) and references cited herein).

All molybdate and tungstate samples show broadband excitation spectra like those reported for the tungstate luminescence of MgWO$_4$ · 2H$_2$O (10). No luminescence was observed for MgMoO$_4$ · 2H$_2$O, not even at 4.2 K. According to the literature, water-free MgMoO$_4$ does not luminesce at 77 K (11). We prepared MgMoO$_4$ as described in (11) and observed at 4.2 K an orange emission, which persists up to 250 K. In Table IV we have compiled our results by presenting the maxima of the emission bands, the maxima of the excitation bands, the Stokes shifts of the emissions, and the thermal quenching temperatures of the emissions of the compounds under investigation. For those that do not luminesce, the position of the optical band edge estimated from the reflectance spectrum is given. This value can be compared with the position of the excitation maxi-

TABLE IV

LUMINESCENCE PROPERTIES OF SEVERAL MOLYBDATES AND TUNGSTATES

Compound	Emission maximum (nm)	Excitation maximum (nm)	Stokes shift (10^3 cm^{-1})	Quenching temp. (K)	Ref.
MgWO$_4$ · 2H$_2$O	480	270	17	200	(10)
MgWO$_4$ · H$_2$O	465	250	19	300	*
MgWO$_4$ (wolframite)	470	295	13.5	450	(10)
SrWO$_4$ (scheelite)	460	245	19.5	300	(10)
MgMoO$_4$ · 2H$_2$O	—	320^a	—	—	*
MgMoO$_4$ · H$_2$O	540	270	19	150	*
MgMoO$_4$ (α-MnMoO$_4$)^b	{ ~520 / ~620	~275 / ~310	~17	~250	*
Mg(W,Mo)O$_4$ (wolframite)	680	360	13.5	—	(11)
SrMoO$_4$ (scheelite)	530	280	17.5	200	(12)

* This work.

^{a} No luminescence, see text.

^{b} There is a weak additional emission with a maximum at ~700 nm and an excitation maximum at ~340 nm.

mum, since the excitation and absorption bands correspond to the same electronic transition, viz., the charge-transfer transition of the molybdate group. The previous results and some literature data are added to this table. According to spectral analysis, the monohydrates are contaminated by a few percent of dihydrate. Our optical measurements are more sensitive in this aspect than X-ray powder diffraction analysis.

The luminescence properties of $MgWO_4 \cdot H_2O$ are different from those of $MgWO_4 \cdot 2H_2O$. In the monohydrate the spectral bands are at higher energy and the quenching temperature is higher. The properties of $MgWO_4 \cdot H_2O$ are very similar to those of the scheelite $SrWO_4$.

In (10) it was argued that the low-energy position of the spectral band of $MgWO_4 \cdot 2H_2O$ (which implies a low quenching temperature) is due to the unsaturated character of O(3). This in turn is a consequence of the layer structure of $MgWO_4 \cdot 2H_2O$, the O(3) ion being an oxygen ion which is only bonded to tungsten and not to magnesium. The crystal structure of $MgWO_4 \cdot H_2O$ is different, because every oxygen ion is bonded to tungsten as well as to magnesium. This results from the fact that the layer character of the dihydrate structure is lost in the monohydrate. It is satisfying to note that the spectra of the monohydrate move to higher energy and become similar to those for a compound with a three-dimensional lattice like $SrWO_4$.

It is well known that the molybdate group has its spectral features at considerably lower energy than the tungstate group and that the molybdate luminescence has, consequently, a lower quenching temperature (12, 13). This can also be observed in Table IV. The luminescence of $MgMoO_4 \cdot H_2O$, which is similar to that of $SrMoO_4$, is at lower energy and has a lower quenching temperature that that of the isomorphous $MgWO_4 \cdot H_2O$.

The dihydrates have very similar crystal structures (1, 14), although their symmetry is slightly different. For our present purposes we can neglect this small difference. This means that we are able to estimate the emission maximum of $MgMoO_4 \cdot 2H_2O$ by using the data of $MgWO_4 \cdot 2H_2O$ and the value of the optical band edge of the molybdate. This yields an emission maximum of about 700 nm. Obviously the nonradiative rate exceeds the radiative rate considerably, because no luminescence could be observed.

A comparison with the water-free compounds is difficult. In $MgWO_4$ (wolframite), the tungsten coordination is octahedral instead of tetrahedral. The charge-transfer absorption moves to lower energy with an increasing number of coordinating ligands (see Table IV) and the Stokes shift decreases (9). In fact, $MgWO_4$ is a commercially applied luminescent material. A comparison with $MgMoO_4$ makes no sense, since $MgMoO_4$ has the α-$MnMoO_4$ structure with tetrahedral MoO_4-groups (15, 16). Kröger (11) has reported the luminescence of the molybdate group diluted in the wolframites $MgWO_4$ and $ZnWO_4$ (see Table IV). His data show in comparison to those of $MgWO_4$ the trends indicated above.

The data illustrate also that the thermal quenching temperature of broadband luminescence decreases if the energy levels shift to low energy and if the Stokes shift is large. This is a direct consequence of the configurational coordinate diagram (17).

Finally we consider $MgMoO_4$, which has a rather complicated crystal structure (15, 16). The two emission bands with the corresponding excitation spectra are assigned to the two crystallographically different molybdate groups in the crystal structure (15). It is impossible to separate these two emissions spectrally which makes the data in Table IV rather inaccurate. The additional emission (see Table IV) is ascribed to a defect molybdate group, following similar ob-

servations for CaMoO$_4$ (*18*). It is satisfying to note that the averaged values for the molybdate luminescence of MgMoO$_4$ are about equal to those for MgMoO$_4$ · H$_2$O and SrMoO$_4$, as is to be expected from the structural analogy (three-dimensional molybdate lattice).

Acknowledgments

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