

## Classification and search for novel binary acentric molybdate and wolframate crystals

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**Abstract** The model of the shortest chemical bonds is applied for the classification of acentric simple and binary Mo(VI) and W(VI) oxides. It is shown that on the plane of the shortest chemical bonds the compounds are located into the rosette of three intersected ellipses. The correlation between the optical nonlinearity and combination of the bond lengths is discussed.

**Key words** Molybdates, Wolframates, Bond length, Property

### 1. Introduction

The search for new acentric crystals is a perpetual objective in present because the materials possess such practically valuable properties as second order optical nonlinearity, ferro- and piezoelectricity [1]. Molybdate and wolframate oxides are among the compounds most promising for high "acentric" properties. The Mo(VI) and W(VI) cation are related to  $d^0$ -type and characterized by enhanced ability to form continuously chained metal-oxygen octahedra distorted by unequal bonds between metal and oxygen ions due to second-order Jahn-Teller (SOJT) effect [2]. Presently known oxide crystals with Mo(VI) and W(VI) cations are widely used as laser active ion hosts efficient for laser-diode pumping and stimulated Raman scattering (SRS) [3-14]. Recently, an idea to combine in one compound the  $(\text{IO}_3)^+$  groups with nonbonding but stereochemically active electrons and  $d^0$  transition metal has been tested yielding two new oxides  $\text{AMoO}_3(\text{IO}_3)$  ( $A = \text{Rb}, \text{Cs}$ ) with high second order nonlinearity [15]. Theoretical methods are also developed to predict the nonlinearity over one crystal family of  $\beta\text{-Gd}_2(\text{MoO}_4)_3$  on the basis of structure data [16, 17]. Nevertheless, the known analytical methods may give only version forecast for the properties of new designed compounds, particularly the presence or absence of inversion center in crystal lattice. Respectively, empirical correlations are of great importance for creation of new materi-

als because the methods are based on real properties of the compounds known already.

The absence of inversion center in crystal lattice is defined by two factors, namely the distortion of oxygen environment around cation M and asymmetric linkage of  $\text{MO}_x$  groups with the oxygen polyhedra containing another cations. As to Mo and W cations, they forms  $\text{MO}_6$  octahedra distorted due to SOJT effect and the distortion evidently increases with increase of the apparent oxidation state of the metals [18, 19]. In parallel, the lengths of the bonds between Mo and W ions and oxygens become shorter. As it seems, the length of the shortest chemical bond  $L(\text{M-O})$  can be used as a reasonable parameter to characterize the acentricity of  $\text{MO}_6$  octahedra. However, the rules governing the regularities of linkage of the octahedra and polyhedra of another cations in crystal lattice are less clear now and only for few oxide families with related structure the transformations of the lattice construction induced by cation change are described. Earlier it has been shown that the shortest chemical bond lengths  $L(\text{E-O})$  and  $L(\text{B-O})$  in binary oxides of  $\text{B}_n\text{E}_m\text{O}_p$ ,  $\text{B}_n\text{B}_m\text{O}_p$  and  $\text{E}_n\text{E}_m\text{O}_p$  types can be related with the acentric properties of compounds [20-23]. Here the cations E and B are defined by the relation  $123.5 < L(\text{E-O}) < 197 < L(\text{B-O})$  pm. It has been shown that acentric binary oxide crystals have maximum refractivity  $R$ , NLO susceptibility  $\chi^{(2)}$ , electrooptic ( $r$ ), piezoelectric ( $d$ ) coefficients and spontaneous polarization  $P_s$  at  $L(\text{E-O}) = 125\text{-}127$  pm (N-O, C-O bond) or at  $L(\text{E-O}) = 196$  pm (Ti-O bond), and minimum  $\chi^{(2)}$ ,  $r$ ,  $d$  and  $P_s$  at  $L(\text{E-O}) = 160$  pm (Si-O bond). In any case  $\chi^{(2)}$  is zero for binary oxide crystals with all bonds outside the in-

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terval  $123.5 < L(E-O) < 197$ , namely at  $L(E-O) < 123.5$  and  $L(B-O) > 197$  pm. So, this study is aimed to consider the formation of simple and binary Mo(VI) and W(VI) oxides without center of inversion taking the criteria of the shortest bond length as a key parameter. For this purpose the body of available experimental data on the structure and known physical properties of the compounds has been observed.

## 2. Data Selection

Only published results on the structure and values of  $d$ ,  $P_s$  and  $\chi^{(2)}$  were taken. Powder or single-crystal data reported in X-ray or neutron studies are included only if  $R(F) < 0.15$ . Binary or ternary oxides are considered. There are few specific cases. For ternary molybdate  $CsMo_6O_{10}(Mo_2O_7)_3(PO_4)_2$  the group  $Mo_6O_{10}(PO_4)_2$  was specified as “one cation” to reduce the number of formal cations to two. In  $Mo_4O_{11}$  crystal two different Mo positions with different  $L$  were revealed by structure analysis and for this compound the Mo ions were considered as two particular cations. In some compounds, molybdenum or tungsten bronzes for example, definite lattice positions are settled by different cations in scattered manner. The position was considered as “one cation” and are described by one  $L$  value.

## 3. Results and Discussion

The available findings for acentric binary and simple molybdates and wolframates along with its structure, shortest bond lengths, symmetry and properties are collected respectively in Table 1 and Table 2. To keep the length of the manuscript, the citations are not included in the text. In the Tables a star marks the theoretical calculation and two stars mark SHG powder data. In Fig. 1 the Mo(VI) acentric oxides are shown as points on the plane of the shortest chemical bonds. On the plane any binary molybdate is displayed by two points positioned symmetrically in reference to the bisectrix of the coordinate angle. The points related to simple molybdates lie on the bisectrix. This way was used because of arbitrariness in the choice of the first cation in chemical formula of binary molybdate. All experimental points are covered by a rosette of three crossing ellipses. It is interesting that the axis proportion for horizontal and vertical ellipses 0.5 are similar to that obtained previously for lateral ellipses of binary germanates, titanates [24], niobates and tantalates. The length of the central ellipse lying along the bisectrix is defined by  $KMo_4O_6$ . The number and position of molybdates already synthesized in this part of the plane not enough to govern the shape of the ellipse directly and on this cause the axis ratio was taken as 0.7, that is the value observed by us for the

Table 1  
Structure and properties of acentric Mo(VI) molybdates

No	Chemical formula	Symmetry	L, pm		d pC/N	$P_s$ $\mu C/cm^2$	$\chi^{(2)}$ pm/V
			M-O	E-O			
1	$Mo_4O_{11}$	$C_{2v}$	173.6	175			
2	$Li_2Zr(MoO_4)_3$	$C_{2v}$	210	201			
3	$LiMoO_2AsO_4$	$C_{2v}$	202	168.1			
4	$Na_{0.9}Mo_6O_{17}$	$C_2$	246.8	186.6			
5	$Na_2In_2Mo_5O_{16}$	$C_{3v}$	227	209.7			
6	$NaMoO_2AsO_4$	$C_{2v}$	234.5	160.2			
7	$KMo_4O_6$	$S_4$	277.0	277.0			
8	$\beta-K_2Mg_2(MoO_4)_3$	$D_2$	267	199			
9	$KMgIn(MoO_4)_3$	$C_2$	264	205			
10	$K_5(Mg_{0.5}Zr_{1.5})(MoO_4)_6$	$C_{3v}$	271.5	205.5			
11	$\beta-K_5In(MoO_4)_4$	$C_s$	299.7	208.8			
12	$K_3Sc(MoO_4)_3$	$C_{2v}$	265	200.3			
13	$K_2Pb(MoO_4)_2$	$C_2$	266.1	250.9			
14	$K_5(Mn_{0.5}Zr_{1.5})(MoO_4)_6$	$C_{3v}$	275	207.5			
15	$RbLiMoO_4$	$T_d$	291.5	186			
16	$\alpha-Rb_5Al(MoO_4)_4$	$C_s$	283.7	189.7			
17	$Rb_3O_2(MoO)_4(PO_4)_4$	$D_2$	271.5	151.7			
18	$RbMoO_3(IO_3)$	$C_{2v}$	289.4	181.1			23**
19	$Cs_{0.25}MoO_3$	$C_2$	276	276			
20	$CsLiMoO_4$	$T_d$	319	185.6			

Table 1  
Continued

No	Chemical formula	Symmetry	L, pm		d pC/N	P <sub>s</sub> μC/cm <sup>2</sup>	χ <sup>(2)</sup> pm/V
			M-O	E-O			
21	Cs <sub>6</sub> Zn <sub>5</sub> (MoO <sub>4</sub> ) <sub>8</sub>	T <sub>d</sub>	327.3	197.5			
22	Cs <sub>2</sub> Hf(MoO <sub>4</sub> ) <sub>3</sub>	C <sub>c</sub>	298	206			
23	CsMo <sub>6</sub> O <sub>10</sub> (Mo <sub>2</sub> O <sub>7</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	D <sub>2d</sub>	308	147			
24	$\tilde{N}$ <sub>5</sub> Bi(MoO <sub>4</sub> ) <sub>4</sub>	C <sub>s</sub>	281	214			0.8**
25	CsMoO <sub>3</sub> (IO <sub>3</sub> )	C <sub>2v</sub>	298.5	179.8			23**
26	α-Cs <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> ]	C <sub>2v</sub>	307	176.5			
27	Cu <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub>	C <sub>2v</sub>	179	179			
28	Cu <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub>	C <sub>2v</sub>	179.5	179.5			
29	Cu <sub>4-x</sub> Mo <sub>3</sub> O <sub>12</sub>	D <sub>2</sub>	194.6	192.8			
30	Cu <sub>3.85</sub> Mo <sub>3</sub> O <sub>12</sub>	D <sub>2</sub>	193	193			
31	Cu <sub>2</sub> Th <sub>4</sub> (MoO <sub>4</sub> ) <sub>9</sub>	T <sub>d</sub>	243	194			
32	α-AgIn(MoO <sub>4</sub> ) <sub>2</sub>	C <sub>4</sub>	234	208			
33	AgSm(MoO <sub>4</sub> ) <sub>2</sub>	S <sub>4</sub>	242.2	242.2			
34	AgYb(MoO <sub>4</sub> ) <sub>2</sub>	S <sub>4</sub>	241.9	241.9			
35	BaMo <sub>2</sub> O <sub>5</sub> (SeO <sub>3</sub> ) <sub>2</sub>	C <sub>2v</sub>	276.7	169.9			
36	CdTeMoO <sub>6</sub>	D <sub>2d</sub>	215.9	200.2			
37	Tl <sub>2</sub> MoO <sub>4</sub>	C <sub>2v</sub>	256	256			5.5**
38	Sb <sub>2</sub> Mo <sub>10</sub> O <sub>31</sub>	C <sub>2v</sub>	185	185			
39	Bi <sub>2</sub> MoO <sub>6</sub>	C <sub>2v</sub>	215	215			
40	Bi <sub>1/2</sub> TeMo <sub>3</sub> V <sub>2</sub> O <sub>34</sub>	C <sub>2</sub>	207	166			
41	Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2</sub>	190	190			
42	CoTeMoO <sub>6</sub>	D <sub>2</sub>	206.0	195.9			
43	La <sub>3</sub> MoO <sub>7</sub>	D <sub>2</sub>	232.5	232.5			
44	La <sub>2</sub> MoO <sub>6</sub>	D <sub>2d</sub>	225	225			
45	La <sub>4</sub> (MoO <sub>4</sub> ) <sub>3</sub> (ReO <sub>4</sub> ) <sub>6</sub>	T <sub>d</sub>	251	170			
46	La <sub>5</sub> Mo <sub>3.31</sub> Co <sub>0.69</sub> O <sub>15.8</sub>	C <sub>1</sub>	237.5	204.1			
47	α-Nd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub> , C <sub>2v</sub>	249.2	249.2			3.28**
48	β-Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>	227.2	227.2		20	2.98
49	Gd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	D <sub>2d</sub>	229	229			
50	β-Tb <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>	225.6	225.6		19	2.9
51	β-ThMo <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	C <sub>3h</sub>	234	234			
52	U <sub>2</sub> MoO <sub>8</sub>	D <sub>2</sub>	206	206			
53	Rb <sub>2</sub> Mg <sub>2</sub> Mo <sub>3</sub> O <sub>12</sub>	D <sub>2</sub>					3.36
54	Rb <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	D <sub>2</sub>					
55	Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	T			5		
56	Sm <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				24	
57	Eu <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				14	
58	Gd(Mo <sub>0.85</sub> W <sub>0.15</sub> O <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				20	
59	Gd <sub>1.6</sub> Y <sub>0.4</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				21	
60	Gd <sub>1.94</sub> Nd <sub>0.06</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				21	
61	Gd <sub>0.5</sub> Tb <sub>1.5</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				23	
62	Gd <sub>1.6</sub> Eu <sub>0.4</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				14	
63	Gd <sub>1.8</sub> Eu <sub>0.2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				22	
64	Tl <sub>2</sub> PbMo <sub>2</sub> O <sub>8</sub>	C <sub>3v</sub>				50	3.36
65	Tb <sub>1.8</sub> Eu <sub>0.2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				15	
66	TbEu(MoO <sub>4</sub> ) <sub>3</sub>	C <sub>2v</sub>				9	

central ellipse in silicates, phosphates, borates, aluminates and gallates. It is seen that acentric Mo(VI) oxides are positioned on the strongly restricted area on the plane of the shortest bonds. It is reasonable to reveal the positions of molybdates with high optical nonlinearity. Evidently the experimental data for this oxide family are

very scarce, but all compounds with measured χ<sup>(2)</sup> are positioned on or near the long axis of central or lateral ellipses. So, it may be supposed that this tendency for optimal bond lengths in molybdates (VI) would be used for cation choice to generate new compounds with high χ<sup>(2)</sup>.

Table 2  
Structure and properties of acentric W(VI) wolframates

No	Chemical formula	Symmetry	L, pm		d pC/N	P, $\mu\text{C}/\text{cm}^2$	$\chi^{(2)}$ pm/V
			M-O	E-O			
1	$\epsilon\text{-WO}_3$	$C_s$	170	170			
2	$\text{LiCsWO}_4$	$T_d$	328.6	189.7			
3	$(\text{Li}_{11}\text{Fe})[\text{WO}_4]_3[\text{W}_4\text{O}_{16}]$	$T_d$	199	198			
4	$\text{Na}_2\text{W}_2\text{O}_7(\text{II})$	$C_{2v}$	238.5	238.5			
5	$\text{Na}_{0.33}\text{WO}_3$	$D_{2d}$	221	186			
6	$\text{Na}_2\text{ZrW}_3\text{O}_{12}$	$C_4$	226	205			
7	$\text{Na}_{1.3}(\text{Mo}^{\text{V}}_{0.15}\text{W}^{\text{V}}_{0.15}\text{W}^{\text{VI}}_{1.7})_2\text{O}_5\text{PO}_4$	$D_2$	211	152			
8	$\text{K}_{0.26}\text{WO}_3$	$C_6$	293	293			
9	$\text{K}_2\text{MgWO}_2(\text{PO}_4)_2$	$C_1$	258.8	149.5			
10	$\text{K}_2\text{NiWO}_2(\text{PO}_4)_2$	$D_4$	262.1	151.3			
11	$\text{Rb}_{22}\text{W}_{32}\text{O}_{107}$	$C_4$	294	294			
12	$\text{Rb}_{0.3}\text{Ga}_{0.1}\text{W}_{0.9}\text{O}_3$	$C_{2v}$	306	160			
13	$\text{Rb}_{0.3}\text{Nb}_{0.3}\text{W}_{0.7}\text{O}_3$	$C_{2v}$	312	165			
14	$\text{Cs}_{0.06}\text{WO}_3$	$D_2$	324.5	324.5			
15	$\text{Cs}_6\text{W}_{11}\text{O}_{36}$	$C_s$	294	294			
16	$\text{CsVW}_4\text{O}_9\text{WO}_4(\text{PO}_4)_4$	$C_{2v}$	300	149			
17	$\text{Cs}_2(\text{WO}_3)_3\text{SeO}_3$	$C_6$	300.6	172.7			
18	$\text{Cu}_2\text{WO}_4$	$C_1$	175.3	175.3			
19	$\text{CuBiW}_2\text{O}_8$	$C_1$	220.6	178.7			
20	$\text{Ag}_8\text{W}_4\text{O}_{16}$	$C_{2v}$	220	220			
21	$\text{Ca}_6[\text{Al}_{12}\text{O}_{24}](\text{WO}_4)_2$	$C_{2v}$	230	173			
22	$\text{Ba}_2\text{Cr}_2\text{WO}_9$	$D_{3h}$	207	201			
23	$\text{Al}_2(\text{WO}_4)_3$	$C_2$	171.8	171.8			
24	$\text{Ge}_{0.24}\text{WO}_3$	$D_6$	225.3	225.3			
25	$\beta\text{-SnWO}_4$	$T$	221.4	221.4			
26	$\text{WPO}_5$	$C_{2v}$	146.2	146.2			
27	$\text{Sb}_2\text{WO}_6$	$C_1$	193.1	193.1			
28	$\text{Bi}_2\text{WO}_6$	$C_{2v}$	221	221	40	42*	4**
29	$\text{Nb}_7\text{W}_{10}\text{O}_{47}$	$D_2$	171.1	174.5			
30	$\text{WNb}_{12}\text{O}_{33}$	$C_2$	185	185			
31	$\text{W}_5\text{Nb}_{16}\text{O}_{55}$	$C_2$	181	181			
32	$\text{W}_8\text{Nb}_9\text{O}_{47}$	$D_2$	188	154			
33	$\text{V-Y}_2\text{WO}_6$	$D_2$	223	223			
34	$\epsilon\text{-Y}_2\text{WO}_6$	$D_2$	212	212			
35	$\delta\text{-Nd}_2\text{WO}_6$	$D_2$	229	229			
36	$\text{V-Gd}_2\text{WO}_6$	$D_2$	226	226			
37	$\text{V-Er}_2\text{WO}_6$	$D_2$	222	222			
38	$\text{LiNbWO}_6$	$C_{4v}$					60**
39	$\text{LiSm}_5(\text{WO}_4)_8$	$C_2$					
40	$\text{RbNbWO}_6$	$C_{4v}$					2.5**
41	$\text{TlLiWO}_6$	$C_{2v}$					5.65*
42	$\text{TlNbWO}_6$	$C_{4v}$					4**

In Fig. 2 the plane of the shortest chemical bonds with the points related to acentric wolframates are shown. The total number of the wolframates is lower than that of molybdates, nonetheless it is clearly seen that the topology of the field for W(VI) acentric oxides is the same as for the molybdates. Specifically, in Fig. 2 the central ellipse is greatly longer, the length is defined by the point related to  $\text{Cs}_{0.06}\text{WO}_3$  bronze. The only point

not covered by the ellipse rossete is  $\text{WPO}_5$  but in this compound the valence of W ions is questionable. Next time the only compound for which the bond lengths and  $\chi^{(2)}$  are known is positioned on the axis of the central ellipse. So, for both acentric molybdates and wolframates we see the same correlation between the set of the shortest chemical bonds and the level of optical non-linearity.

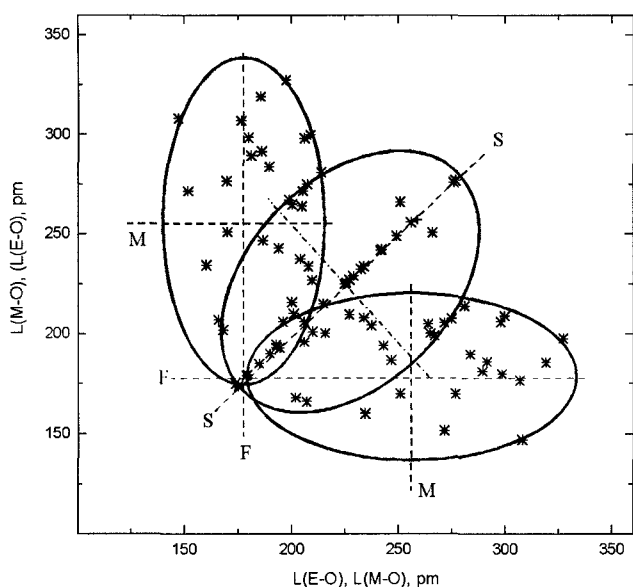


Fig. 1. The plane of the shortest chemical bonds for acentric Mo(VI) oxides.

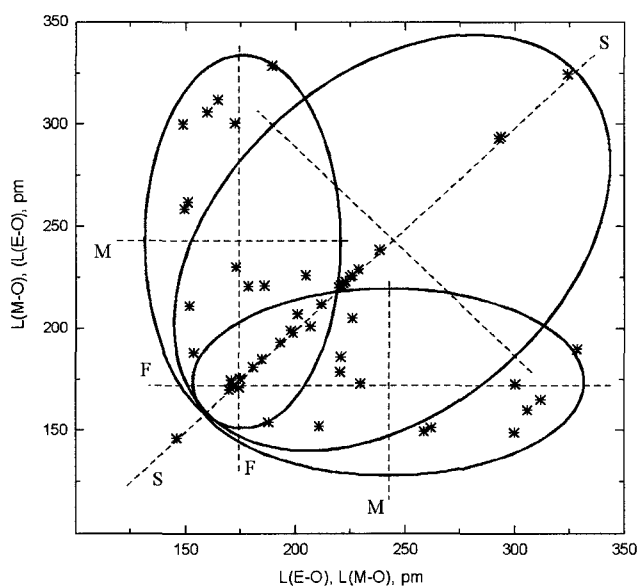


Fig. 2. The plane of the shortest chemical bonds for acentric W(VI) oxides.

#### 4. Conclusions

The set of the known acentric Mo(VI) and W(VI) oxides is considered with using criteria of the shortest chemical bond between additive cations and oxygens. On the plane of the shortest bonds the points represented the compounds from the oxide families are positioned in the restricted field covered by a rosette of three intersected ellipses. The points related to the compounds with high optical nonlinearity are lying near the long axes of the ellipses. So, in design of new com-

pounds with strong  $\chi^{(2)}$  the cations should be taken in such manner that the point is near the axes of the ellipses.

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