Crystal chemistry of cesium molybdates

A.S. Pakhomova, S.V. Krivovichev

Saint-Petersburg State University, Russian Federation
E-mail: a.s.pakhomova@mail.ru

Cesium molybdates attract special attention as compounds formed during the oxidation of spent nuclear fuel (Fabrichnaya, 2007). Crystal chemical study of these compounds is necessary to study and model the processes that accompany the decay of unstable isotopes of uranium (U-235, U-239).

There are 14 cesium molybdates known to date. Their crystallographic parameters are given below.

Compound	Space Group	Lattice Parameters, Å/º
α-Cs_2MoO_4	*P*nma	*a*=11.608(2) *b*=6.562(2) *c*=8.510(1)
β-Cs_2MoO_4	*h**	*a*=7.19 *c*=9.26
$Cs_2Mo_2O_7$	*o**	*a*=15.54 *b*=7.216 *c*=15.61
$Cs_2Mo_3O_{10}$	*C*2/c	*a*=14.465(1) *b*=8.3997(4) *c*=9.4614(4) *β*=97.74(1)
α-$Cs_2Mo_4O_{13}$	*C*2/c	*a*=45.92(5) *b*=10.418(3) *c*=7.923(8) *β*=97.94(5)
β-$Cs_2Mo_4O_{13}$	*P*1	*a*=8.655(5) *b*=8.396(5) *c*=11.541(4) *α*=117.841(8) *β*=60.069(28) *γ*=109.761(5)
$Cs_2Mo_5O_{16}$	*C*2/c	*a*=21.44(4) *b*=5.559(3) *c*=14.338(7) *β*=122.74(4)
$Cs_2Mo_7O_{22}$	*C*2/c	*a*=21.54(1) *b*=5.537(3) *c*=18.91(1) *β*=122.71(3)
$Cs_6Mo_2O_9$	*h**	*a*=13.10 *c*=8.51
$Cs_{0.14}MoO_3$	$P6_3$/m	*a*=10.620(9) *c*=3.722(2)
$Cs_{0.25}MoO_3$	$P2_1$/m	*a*=6.425(5) *b*=7.543(4) *c*=8.169(5) *β*=96.3
$CsMo_{4-x}O_{12}$ (x≈0.13)	*C*2/m	*a*=19.063(5) *b*=5.5827(23) *c*=12.1147(23) *β*=118.94(2)
$Cs_{0.33}MoO_3$	*C*2/m	*a*=15.862(2) *b*=7.728(2) *c*=6.4080(7) *β*=94.37(1)º
$Cs_{0.3}MoO_3$	*m**	*a*=19.362(8) *b*=7.567(2) *c*=10.506(4) *β*=121.07(3)

* *h* = hexagonal, *o* = orthorhombic, *m* = monoclinic

Cesium molybdates can be divided into two groups: homologous series of molybdates $Cs_2Mo_nO_{3n+1}$ and molybdenum bronzes with general formula $Cs_{1-x}MoO_3$. The peculiarity of the latter is the simultaneous presence of cations Mo^{6+} and Mo^{5+} in their structures.

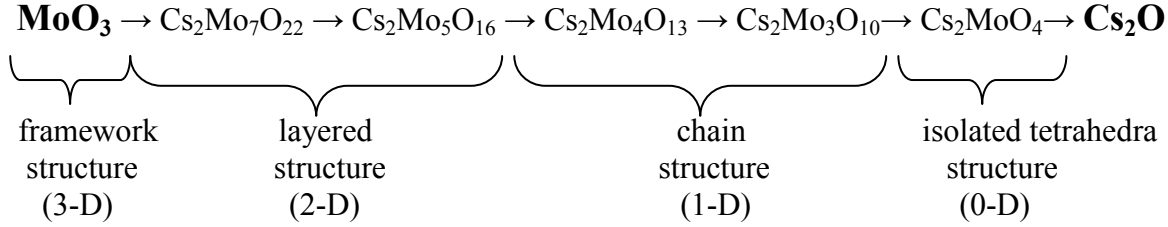
Molybdenum cations may have six-, five-, and also fourfold coordination. The most typical coordination of cation Mo^{6+} is coordination by six oxygen atoms with the formation of distorted octahedra $[MoO_6]^{6-}$. The characteristic of the latter is the distribution of Mo^{6+}-O bonds in 3 groups: 2 short (1.64-1.76 Å), 2 medium (1.87-2.00 Å) and 2 long (2.20-2.43 Å) bonds. The five-coordinated Mo^{6+} can form 2 types of polyhedra: trigonal bipyramid and square pyramid $[MoO_5]^{4-}$. They are also characterized by the distribution of bonds, in this case there are 2 short (1.69-1.71 Å), 2 medium (1.87-1.93 Å) and 1 long (2.05-2.38 Å) bonds. In the fourfold coordination cation Mo^{6+} forms tetrahedrons $[MoO_4]^{2-}$, in which the bond lengths slightly vary from 1.71 to 1.80 Å.

Bond length Mo^{6+}-O is a linear dependence on the coordination number of atom O. In the known cesium molybdates O atoms have coordination numbers from 1 to 4. The average lengths Mo^{6+}-O in the structures are 1.72 Å for $O_{\mu1}$, 1.97 Å for $O_{\mu2}$, 2.10 Å for $O_{\mu3}$ and 2.24 Å for $O_{\mu4}$. Thus, the bond lengths increase together with the increasing of coordination number of oxygen atom. This regularity explains the deviation of molybdenum polyhedra from the regular geometry by connection them with each other.

As a result of crystal chemical study of cesium molybdates belonging to homologous series $Cs_2Mo_nO_{3n+1}$, we can conclude that their structures are based on the principle of dimension reduction. The dimension reduction is characteristic process where ionic components are introduced into a covalent structure (Tulsky, 2001). In this case, cesium molybdates with general formula $Cs_2Mo_nO_{3n+1}$ can be represented as compounds obtained by reaction

$$n\mathrm{MoO_3} + \mathrm{Cs_2O} \rightarrow \mathrm{Cs_2Mo_nO_{3n+1}},$$

where MoO_3 is the "parent" compound with three-dimensional covalent framework, and Cs_2O is the ionic component, decreasing the dimensionality. In the binary system MoO_3-Cs_2O there is the dimension reduction together with the increasing content of ionic component, or a decreasing in the number *n*. This regularity is shown in Scheme 1.



Scheme 1. Dimensional reduction in cesium molybdates belonging to the homologous series $Cs_2Mo_nO_{3n+1}$.

This work was supported by a President of the Russia Federation Grant for Young Doctors of Science (to SVK, grant No. MD-407.2009.5).

References

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