Crystal structure and crystal chemistry of biehlite, $Sb_{1.79}As_{0.21}MoO_6$

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Abstract. The new mineral biehlite was found in the Tsumeb mine, Namibia and has the composition $Sb_{1.79}As_{0.21}MoO_6$. It crystallizes monoclinic, space group $C2/c$ with lattice parmeters $a = 18.076(5)$ Å, $b = 5.920(5)$ Å, $c = 5.083(5)$ Å, $\beta = 96.97(1)°$. Refinement led to a final $R(F)$ value of 0.065 for 679 symmetrically independent reflections.

$[MoO_6]^{6-}$ octahedra share common edges and form zig-zag chains which run parallel to the c direction. The octahedra are flanked by a $[Sb_2O_2]^{2+}$ group on each side and infinite ribbons of composition $[Sb_4Mo_2O_{12}]$ are obtained. Neighbouring ribbons are only held together by weak Sb—O bonds in the directions of a and b.

The $[MoO_6]^{6-}$ octahedra are strongly distorted with Mo—O distances ranging from 1.700(5) to 2.248(6) Å and O—Mo—O angles between 72.1(2)° and 105.3(4)°. The common O—O edge (2.492(8) Å) is shortened with respect to the remaining edges of the octahedra (2.704(8) Å–2.899(8) Å).

The Sb-cation forms three short bonds with oxygen at distances slightly smaller than 2 Å. Six further oxygen atoms are located at distances ranging from 2.910(6) to 3.470(6) Å. Calculated distance for the lone-pair is 1.18 Å. Part of the Sb^{3+} is substituted by the smaller As^{3+} ion.

The relationship of the new mineral to similar structures – especially to the mineral stibivanite and the synthetic compound Sb_2MoO_6 – is discussed.

Introduction

Biehlite was found in the Tsumeb mine, Namibia, and has been accepted by the I. M. A. Commission on New Minerals and Mineral Names in December 1999. Chemical analysis yielded the composition $Sb_{1.79}As_{0.21}MoO_6$ [1].

Chemistry and lattice parameters (see Table 1) of biehlite[1] suggested close relationship to the synthetic compound Sb_2MoO_6. This compound was supposed to crystallize in space group $P\bar{1}$ with a unit cell volume of 505.8 Å^3 [2] yet more recent investigations [3] showed weak superstructure reflections which led to a four times larger unit cell volume (2022.6 Å^3).

The structure of synthetic Sb_2MoO_6 is closely related to the Aurivillius phases $(Bi_2O_2)(A_{n-1}M_nX_{3n+1})$ [4] on which a lot of structural investigations has been carried out, due to the fact that special members of this family are selective catalysts for alkene oxidation or exhibit

Table 1. Lattice parameters and chemical composition of related compounds.

	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å^3]	space group	Lit.
Biehlite: $Sb_{1.79}As_{0.21}MoO_6$	18.076(5)	5.920(5)	5.083(5)		96.97(1)		540.3	$C2/c$	this work
Sb_2MoO_6	7.481(2)	7.504(1)	10.120(2)	70.43(2)	70.91(2)	83.35(2)	505.8	$P\bar{1}$	[2]
Sb_2MoO_6	11.192(2)	9.960(1)	18.282(2)	90.33(3)	97.03(2)	90.19(2)	2022.6	$P\bar{1}$	[3]
$Sb_2Mo_{10}O_{31}$	20.03(2)	8.09(1)	7.17(1)				1161.8	$Pma2$	[13]
Sb_2WO_6	5.554(1)	4.941(2)	9.209(3)	90.05(3)	96.98(2)	90.20(2)	250.8	$P1$	[14]
Sb_2WO_6	11.132(1)	9.896(4)	18.482(7)	90.20(4)	96.87(8)	90.21(5)	2021.4	$F\bar{1}$	[15]
$Sb_2W_{0.75}V_{0.25}O_{5.75}$	5.529(3)	4.914(2)	9.193(5)		96.04(4)		248.4	$P2_1/a$	[16]
Stibivanite: Sb_2VO_5	17.989(6)	4.7924(7)	5.500(2)		95.15(3)		472.3	$C2/c$	[17]
Stibivanite −2O: Sb_2VO_5	17.916(3)	4.790(1)	5.509(1)				472.8	$Pmcn$	[18]
$KSbMo_2O_8$	5.015(2)	7.4216(6)	10.304(1)	90.45(1)	100.29(2)	107.79(1)	358.5	$P\bar{1}$	[19]
$LiSbMo_2O_8$	21.640(6)	4.9305(7)	5.5448(6)		100.35(1)		582.0	$C2/c$	[20]
$Bi_2(MoO_4)_3$	7.685(6)	11.49(2)	11.93(1)		115.40(2)		951.6	$P2_1/c$	[21]
Koechlinite: Bi_2MoO_6	5.487(2)	16.226(6)	5.506(2)				490.2	$Pca2_1$	[5]
Koechlinite: Bi_2MoO_6	5.4896(3)	16.2266(7)	5.5131(3)				491.1	$Pca2_1$	[6]
γ-Bi_2MoO_6	5.4822(3)	16.1986(8)	5.5091(3)				489.2	$Pna2_1$	[22]

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[1] Transformation of the lattice parameters of biehlite to the triclinic setting given for synthetic Sb_2MoO_6 by [2] led to $a = 7.804$ Å; $b = 7.804$ Å; $c = 9.514$ Å; $\alpha = 80.73°$; $\beta = 71.87°$; $\gamma = 81.29°$.

Crystal system	monoclinic
Space group	$C2/c$
a [Å]	18.076(5)
b [Å]	5.920(5)
c [Å]	5.083(5)
β [°]	96.97(1)
Lattice parameters from	12699 reflections
in θ range	$1.0° \leq \theta \leq 27.5°$
V [Å^3]	539.91
μ [mm^{-1}]	12.47
Diffractometer	Nonius area detector
Wavelength [Å]	0.71073
range in ω	$0-360°$
Rotation per frame	$2°$
Exposure time per frame	120 sec
Mosaicity	$1.639°$
Zero sigma/profile test	7
sigma cutoff	121
High resolution limit	88
θ range	$1° < \theta < 27.5°$
$hkl_{min} - hkl_{max}$	$\overline{23},\overline{7},\overline{6} - 23,7,6$
Number of full reflections	143
Number of partial reflections	18342
Data completeness	99.9
Number of unique reflections	679
$R(F^2)_{int}$	0.073
Crystal size [mm]	$0.007 \times 0.007 \times 0.03$
Absorption correction	none
Structure solution	Sir92 [23]
Structure refinement	Shelxl93 [24]
$R(F)$	0.065
$R(F) \geq 4\sigma$	0.044
$wR(F^2)$	0.067
Number of variable parameters	45
Extinction correction	Shelxl93 [24]
Extinction coefficient	0.0005(1)
Difference density maximum	1.181
Difference density minimum	-1.025
Weighting scheme	$w = 1/[\sigma^2(F_{obs})^2 + 7.8434 \cdot P]$
with	$P = (\text{Max}(F_{obs}^2) + 2F_{calc}^2)/3$

interesting physical properties like ferroelectricity, piezo-electricity, pyroelectricity and non-linear dielectric susceptibility.

The structure of these phases is characterized by $[Bi_2O_2]^{2+}$ layers interweaved with perovskite like layers. For $n = 1$, M=Mo and X=O the perovskite layer is reduced to $[MoO_4]^{2-}$ and the well investigated mineral koechlinite, Bi_2MoO_6 [5, 6], is formed. If $n = 1$, M=W and X=O the mineral russelite, Bi_2WO_6 [7, 8, 9], is obtained.

The structure of the synthetic compounds Sb_2MO_6 (M=Mo, W) on the other hand is obtained if one substitutes the $[Bi_2O_2]^{2+}$ layers for layers of composition $[Sb_2O_2]^{2+}$ and leaves the perovskite like $[MO_4]^{2-}$ part of the structure basically unchanged.

Surprisingly however, the powder diffraction pattern of biehlite showed little similarities with the synthetic compound Sb_2MoO_6 — and consequently with the Aurivillius phases — and suggested a new structure type. Furthermore, the volume of the unit cell of biehlite was significantly larger than that of the average structure of synthetic Sb_2MoO_6 (540 Å^3 and 506 Å^3, respectively) although the incorporation of the smaller As^{3+} ion suggested the opposite.

Taking into account the importance of a new structure type in this type of systems for possible future applications, we thought it prudent to carry out a full structural analysis of the new mineral biehlite as well as a detailed study of its crystal chemistry and its relationship to other — chemically or structurally related — compounds.

Experimental

Diffraction intensities of a very small needle-like crystal (0.007 mm × 0.007 mm × 0.03 mm) of biehlite were measured using a Kappa CCD (Nonius). Due to the small crystal size we did not think it necessary to carry out an absorption correction. Further experimental details, lattice parameters and selected data concerning the refinement are given in Table 2.

Sb^{3+} and As^{3+} are distributed statistically on one site; refinement of the occupation parameters led to the empirical formula $Sb_{1.84}As_{0.16}MoO_6$ which is in good agreement with composition obtained from microprobe analysis ($Sb_{1.79}As_{0.21}MoO_6$; [1]).

Table 3. Fractional atomic coordinates, occupation factors and equivalent displacement parameters; L.P. = lone-pair electron (position calculated according to [10]).

Atom	x	y	z	Occ.	U_{eq}
Mo	0.0	0.1929(2)	0.25	0.5	0.0158(4)
Sb	0.16349(3)	0.2018(1)	0.6976(1)	0.92(2)	0.0233(3)
As	0.16349(3)	0.2018(1)	0.6976(1)	0.08(3)	0.0233(3)
O1	0.1950(3)	0.0857(1)	0.3709(11)	1.0	0.0257(15)
O2	0.0594(3)	0.0974(1)	0.5824(11)	1.0	0.0195(13)
O3	0.0656(3)	0.3670(1)	0.1473(15)	1.0	0.0246(15)
L.P.	0.177	0.382	0.791		

Table 4. Distances and angles in the MoO$_6$ octahedra with e.s.d.'s in parentheses.

	[Å]		[Å]
Mo — O3	1.700(5)	O2 — O2^{ii}	2.492(8)
— O3^i	1.700(5)	O3 — O3^i	2.704(8)
— O2	1.972(6)	O2 — O3	2.741(8)
— O2^i	1.972(6)	O3 — O2^{iii}	2.770(8)
— O2^{ii}	2.248(6)	O2 — O2^{iii}	2.791(8)
— O2^{iii}	2.248(6)	O2 — O3^i	2.894(8)
	1.973	O2^{ii} — O2^{iii}	2.899(8)

	[°]		[°]
O2 — Mo — O2^{ii}	72.1(2)	O3 — Mo — O2^i	103.8(3)
O2^{ii} — Mo — O2^{iii}	80.3(3)	O3 — Mo — O3^i	105.3(4)
O2 — Mo — O2^{iii}	82.5(2)	O2 — Mo — O2^i	146.7(3)
O3 — Mo — O2^{iii}	88.0(3)	O3 — Mo — O2^{ii}	164.3(3)
O3 — Mo — O2	96.3(2)		

Table 5. Sb—O distances and selected angles around the Sb atom with e.s.d.'s in parentheses; L.P. = lone pair electron (position calculated according to [10]).

	[Å]		[Å]
Sb — O1	1.945(6)	Sb — O3^{vii}	3.209(6)
— O1^{iv}	1.968(6)	— O3	3.273(6)
— O2	1.999(5)	— O2^{iv}	3.376(6)
— O1^v	2.910(6)	— O1^{vii}	3.470(6)
— O3^{vi}	3.099(6)	Sb — Sb^{iii}	3.488(3)
Sb — L.P.	1.18		

	[°]		[°]
O1 — Sb — O1^{iv}	88.8(2)	O1^{iv} — Sb — O2	94.3(2)
O1 — Sb — O2	90.2(2)	Sb — O1 — Sb^{iii}	126.1(3)

Symmetry operators for generating equivalent atoms
(i) $-x, y, \frac{1}{2} - z$; (ii) $-x, -y, 1 - z$; (iii) $x, -y, -\frac{1}{2} + z$;
(iv) $x, -y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (vi) $x, 1 - y, \frac{1}{2} + z$; (vii) $x, y, 1 + z$

Atomic coordinates, isotropic displacement parameters, as well as selected distances and angles are given in Tables 3, 4 and 5[2].

Description of the structure

The structure of biehlite is a typical chain structure in which the bonds formed within the chain are considerably stronger than the ones connecting neighbouring chains.

The Mo^{6+} ions are coordinated by the oxygen atoms in the form of highly distorted octahedra. These octahedra

share common edges and zigzag chains of composition [Mo$_2$O$_8$]$^{4-}$ are formed which run parallel to the crystallographic c direction (see Figure 1, 4a). Each antimony ion forms one short bond with oxygen O2 of the octahedra (Sb—O2: 1.999(5) Å) and has moreover two short bonds to O1 (1.945(6) Å and 1.968(6) Å; see Figure 1; Table 5). The [Mo$_2$O$_8$]$^{4-}$ zigzag chain of octahedra is in this way flanked by a [Sb$_2$O$_2$]$^{2+}$ group on each side and infinite ribbons of composition [Sb$_4$Mo$_2$O$_{12}$] are obtained which run parallel to the c direction.

Neighbouring ribbons are only held together by weak Sb—O bonds in the directions of a and b (Sb—O1: 2.910(6) Å; Sb—O3: 3.099(6) Å; see Figures 1 and 4a) thus macroscopically resulting in the very pronounced needle like appearance of the mineral.

The [MoO$_6$]$^{6-}$ octahedra are strongly distorted with Mo—O distances ranging from 1.700(5) to 2.248(6) Å and O—Mo—O angles between 72.1(2)° and 105.3(4)° (see Figure 2; Table 4). The observed Mo—O distances in the

Table 6. Mo−O bond lengths and bond valence sums (BVS) in biehlite and comparable compounds with octahedral coordination for the Mo^{6+} ion.

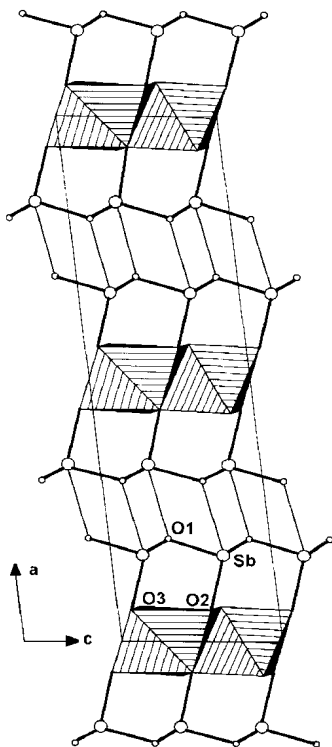| Compound	Min. [Å]	Max. [Å]	Mean [Å]	BVS [v.u.]	Lit.
Biehlite	1.700(5)	2.248(6)	1.973	5.97	this work
Sb_2MoO_6	1.762(7)	2.246(7)	1.959	5.90	[3]
	1.745(7)	2.249(7)	1.952	6.07	
	1.751(7)	2.239(7)	1.957	5.98	
	1.743(7)	2.267(7)	1.968	5.85	
	1.747(7)	2.233(7)	1.945	6.09	
	1.741(7)	2.244(7)	1.958	5.99	
	1.760(7)	2.243(7)	1.939	6.19	
	1.739(7)	2.243(7)	1.943	6.26	
$Sb_2Mo_{10}O_{31}$	1.66(4)	2.33(3)	1.975	5.73	[13]
	1.69(4)	2.39(4)	1.985	5.67	
	1.67(4)	2.37(3)	1.992	6.36	
	1.73(3)	2.41(4)	1.948	6.18	
	1.67(5)	2.35(4)	1.903	7.16	
	1.69(4)	2.41(5)	1.990	5.65	
$KSbMo_2O_8$	1.700(3)	2.451(3)	1.973	5.96	[19]
$LiSbMo_2O_8$	1.729(5)	2.210(5)	1.962	6.00	[20]
Koechlinite	1.75(2)	2.24(2)	1.96	5.92	[5]
Koechlinite	1.780(1)	2.299(11)	1.961	5.93	[6]
γ-Bi_2MoO_6	1.75(1)	2.28(1)	1.955	6.07	[22]

Fig. 1. *a-c*-Projection of the crystal structure of biehlite; octahedra around Mo are shown; Sb^{3+} ions are shown as circles; short Sb−O bonds are shown as thick lines, longer bonds are indicated as thin lines. Drawn with STRUPLO84 [23].

Fig. 2. The distorted $[MoO_6]^{2-}$ octahedra; lengths are given in [Å]. Drawn with ORTEP-3 for Windows [27].
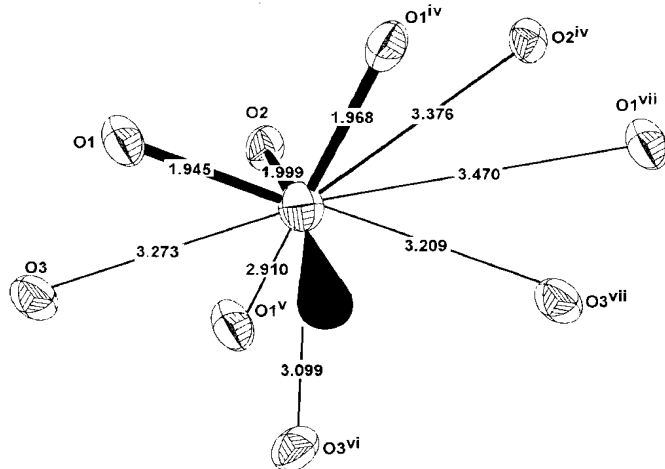
Fig. 3. The surrounding of the Sb^{3+} ion; lengths are given in [Å]. Drawn with ORTEP-3 for Windows [27].

new mineral are within the range which is generally observed for this type of bond in other compounds and the bond valence sum for the Mo^{6+} ion is 5.97 v.u., very close to the ideal value (see Table 6).

All the related compounds which are listed in Table 6 are similarly characterized by the occurrence of $[MoO_6]^{6-}$ octahedra. Yet in most of them the octahedra are corner connected, either forming the perovskite like layers of the Aurivillius phases or, as in the case of $Sb_2Mo_{10}O_{31}$ — resulting in hexagonal channels of edge linked octahedra.
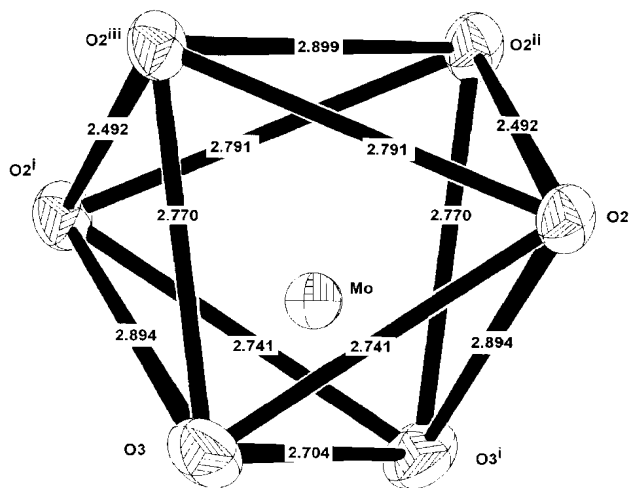
Only in $KSbMo_2O_8$ one observes $[MoO_6]^{6-}$ octahedra forming chains of skew edge shared octahedra. The geometry of the octahedra in $KSbMo_2O_8$ and in biehlite are

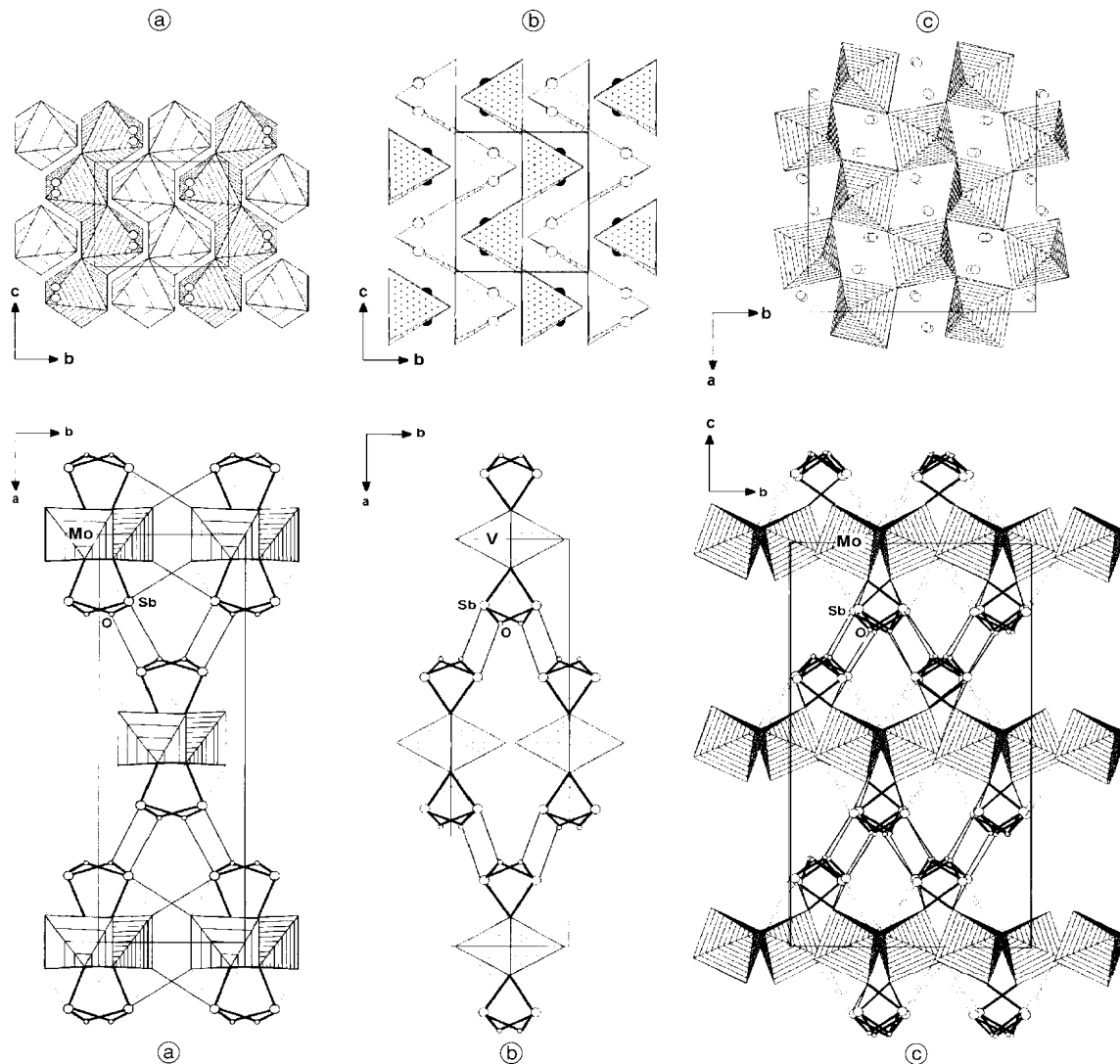**Fig. 4.** Comparison between the structure of **a)** biehlite (above: *b-c*-projection; below: *a-b*-projection); **b)** stibivanite (above: *b-c*-projection; below: *a-b*-projection; coordinates from [17]); **c)** Sb_2MoO_6 (above: *a-b*-projection; below: *b-c*-projection; coordinates from [3]).

Octahedra/tetragonal pyramids around Mo/V are shown; large circles: Sb^{3+}; small circles: oxygen atoms; short Sb—O bonds are drawn as thick lines, longer bonds are indicated as thin lines. Drawn with STRUPLO84 [26].

very similar and in both structures one observes a pronounced shortening of the common O—O edge with respect to the other O—O edges of the octahedra. Thus in our mineral the common edge has a value of 2.492(8) Å while the remaining edges range from 2.704(8) Å to 2.899(8) Å; in $KSbMo_2O_8$ the O—O distance for the common edge is 2.424 Å compared to values between 2.635 Å and 2.949 Å for the other distances.

The environment of the Sb^{3+} ion is rather complicated (see Figure 3 and Table 5) and the cation shows the typical one-sided coordination of a lone-pair atom. The position of the lone-pair electron of the Sb^{3+} was calculated according to [10] and is indicated in the Figure. The distance of the lone-pair to the Sb^{3+} which is obtained from this calculation is 1.18 Å and compares nicely with the distance of 1.06 Å given by [11].

The first coordination sphere of the Sb-cation is representated by three oxygen atoms at distances which are

slightly smaller than 2 Å. Six further oxygen atoms at distances ranging from 2.910(6) to 3.470(6) Å form the second coordination sphere. The overall coordination is thus best described by 3 + 6.

Refinement of the occupation factor for Sb/As yielded the composition $Sb_{1.84}As_{0.16}MoO_6$ which agrees nicely with the values from chemical analysis ($Sb_{1.79}As_{0.21}MoO_6$). Effective ionic radii as given by [12] are 0.76 Å for Sb^{3+} with coordination number six and 0.58 Å for As^{3+}. As a result the incorporation of the smaller As^{3+} ion into the structure should lead to shortening of the Sb—O bond lengths and consequently to higher bond valence values. In fact, a comparison of the bond valence sums of the Sb^{3+} in biehlite and in other related compounds shows in general a higher bond valence sum of the former (see Table 7). This effect can be seen even better if one concentrates on the three smallest Sb—O bond distances which in the mineral are shorter than in all other comparable com-

	Min.	Max.	Coord.	BVS[III]	BVS	Lit.
Biehlite	1.945(6)	3.470(6)	3 + 6	3.03	3.26	this work
Sb_2MoO_6	1.993(8)	3.266(8)	3 + 4	2.51	3.05	[3]
	1.968(7)	3.164(8)	3 + 4	2.65	3.15	
	1.989(7)	3.242(6)	3 + 4	2.70	3.18	
	1.971(7)	3.250(7)	3 + 4	2.58	3.18	
	1.983(7)	3.177(8)	3 + 4	2.62	3.08	
	1.979(7)	3.272(7)	3 + 4	2.62	3.23	
	1.978(7)	3.271(7)	3 + 4	2.44	3.00	
	1.980(7)	3.233(8)	3 + 4	2.71	3.21	
	2.025(7)	3.187(6)	3 + 4	2.52	3.06	
	1.980(7)	3.225(7)	3 + 4	2.44	2.98	
	1.992(7)	3.248(7)	3 + 4	2.45	2.98	
	2.016(7)	3.239(7)	3 + 4	2.49	3.05	
	1.980(7)	3.255(7)	3 + 4	2.54	3.11	
	1.946(7)	3.165(7)	3 + 4	2.73	3.30	
	2.014(7)	3.221(7)	3 + 4	2.54	3.08	
	1.940(7)	3.273(8)	3 + 4	2.69	3.24	
Sb_2WO_6	1.981(8)	3.247(8)	3 + 4	2.63	3.14	[15]
	1.991(8)	3.235(8)	3 + 4	2.61	3.13	
	1.985(8)	3.258(8)	3 + 4	2.62	3.13	
	1.986(8)	3.252(8)	3 + 4	2.66	3.12	
Sb_2WO_6	2.000(1)	3.166(9)	3 + 3	2.50	3.00	[14]
	1.931(8)	3.305(9)	3 + 4	2.93	3.43	
	2.023(9)	3.301(9)	3 + 4	2.21	2.71	
Sb_2VO_5 (−2M)	1.963(5)	3.370(5)	3 + 3	2.83	3.14	[17]
Sb_2VO_5 (−2O)	1.988(5)	3.384(6)	3 + 3	2.78	3.10	[18]
$Sb_2Mo_{10}O_{31}$	1.85(5)	3.08(3)	3 + 4	2.89	3.32	[13]
	1.96(5)	3.07(3)	3 + 4	2.31	2.79	
$Sb_2W_{0.75}V_{0.25}O_{5.75}$	1.978(8)	3.340(8)	3 + 4	2.56	3.13	[16]
$KSbMo_2O_8$	1.990(3)	3.042(3)	3 + 4	2.45	3.13	[19]

Table 7. Sb—O bond distances in [Å] and bond valence sums (according to [25]) in [v.u.] in biehlite and comparable compounds; Min. = minimum Sb—O distance; Max. = maximum Sb—O distance; Coordination of the Sb^{3+}-ion; BVS[III] = bond valence sums taking into account only the three shortest Sb—O distances; BVS = bond valence sums taking into account all Sb—O distances.

pounds and, as a consequence, a significantly higher bond valence is observed when one takes into account only the first coordination sphere of the Sb^{3+} ion[3].

Unlike most of the so far reported structures of similar chemical characteristics biehlite can not be described as a structure of intergrown layers but is clearly a one-dimensional chain structure.

Figure 4 illustrates the similarities and differences between biehlite on one hand and the two related structures of stibivanite and synthetic Sb_2MoO_6 on the other hand. In the figure one clearly sees the striking resemblance of the $[Sb_2O_2]^{2+}$ part of the three structures (of course one has to take into account that in Sb_2MoO_6 the unit cell volume is four times larger!).

The mineral stibivanite, Sb_2VO_5 (see Figure 4b) is probably the compound which provides the closest structural similarities with biehlite. Stibivanite is built up by tetragonal $[VO_5]^{6-}$ pyramids which share a common edge and thus form chains of composition $[V_2O_6]^{4-}$. As in the new mineral, groups of $[Sb_2O_2]^{2+}$ flank this chain on both sides and ribbons of composition $[Sb_4V_2O_{10}]$ are formed which extend in the z direction.

In contrast to this, the structure of synthetic Sb_2MoO_6 (see Figure 4c), related to the Aurivillius family, can be described as a layer structure composed of two different types of layers. As mentioned before, the $[MoO_6]^{6-}$ octahedra share common corners and form perovskite like

$[MoO_4]^{2-}$ layers which are interwoven with $[Sb_2O_2]^{2+}$ layers (see figure 4c).

Finally, it is not clear why biehlite does not assume the structure of the synthetic Sb_2MoO_6 and instead crystallizes in this new structure type. The Tsumeb mine is known to be a place which provided very special conditions (there are up to date 43 minerals which have been observed only there!) and the clue to the formation of the new structure type can probably be given by a detailed study of the associated minerals thus elucidating the building conditions. Yet it is also possible that the incorporation of the smaller As^{3+} ion is the key of understanding why a new structure type is formed. Here only detailed investigations in the system $Sb_2MoO_6 - As_2MoO_6$ can give a definite answer. Further studies of the physical properties will of course also be interesting with respect to possible future applications of this new compound.

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