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A New Mixed Oxide with $(Bi_{12}O_{14})_n$ Columns: $PbBi_{12}Mo_5O_{34}$

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Abstract

The title compound, lead(II) dodecabismuth(III) pentamolybdenum(VI) oxide, was prepared by solid-state methods. The structure consists of $(Bi_{12}O_{14})_n^{8n+}$ columns surrounded by $(MoO_4)^{2-}$ tetrahedra. The Pb atoms occupy specific sites between four tetrahedra.

Comment

This work was carried out as part of our studies of M^*–(V,Mo,W)–O systems with ns^2 lone-pair elements M^* (Galy, Enjalbert, Millan & Castro, 1993; Castro, Millan, Enjalbert, Snoeck & Galy, 1994; Sorokina, Enjalbert, Baules, Castro & Galy, 1996). In the Aurivillius-type series $(Bi_2O_2)_2V_{2-x}^{5+}V_{2x}^{4+}O_{7-x}$, the $(Bi_2O_2)_{2n}$ layers alternate with $(V_2O_{7-x})_n$ layers. Oxygen non-stoichiometry, with the simultaneous presence of vanadium(IV) and vanadium(V) in VO_6 octahedra and VO_5 square pyramids, is responsible for their ionic conduction properties. In order to modify these interesting physical properties, we have considered the possible alteration of the two types of layers: on the one hand, the association of lone-pair elements Bi and Pb, and on the other, the association of transition metals V and Mo.

The new compound synthesized, $PbBi_{12}Mo_5O_{34}$, is not a layered structure as expected, but contains columns of $(Bi_{12}O_{14})_n$, MoO_4 tetrahedra and specific sites for the Pb atoms. The projection of the structure onto the the (010) plane (Fig. 1) shows the organization of the $(Bi_{12}O_{14})_n$ columns in the form of roses formed by Bi and O atoms. One rose is surrounded by ten MoO_4 tetrahedra, two of which are disordered.
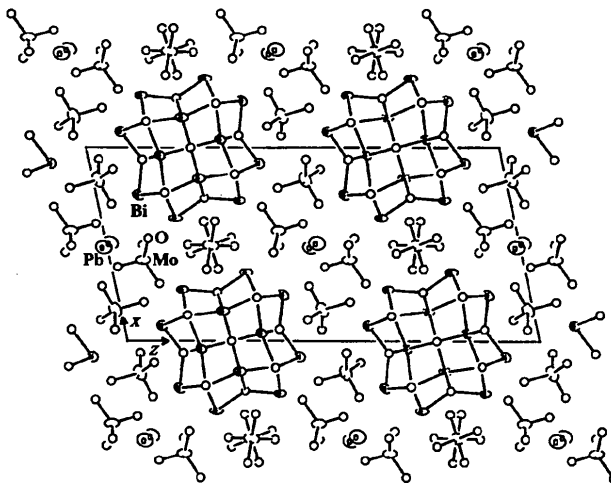

Fig. 1. Projection of the structure onto the (010) plane.

The Pb atoms are disordered around the $2b$ site at 1/2,1/2,0 with 50% site occupancy. The distance between the two potential crystallographic sites is 0.43 Å. The partial view in Fig. 2, slightly tilted for clarity, specifies the atomic numbering scheme.

The roses are the projections of infinite $(Bi_{12}O_{14})_n$ columns along the [010] direction. The Bi1 and Bi2 atoms in the rose are bonded to four O atoms (Bi—O < 2.43 Å). The external Bi3, Bi4, Bi5 and Bi6 atoms are bonded to three O atoms (Bi—O < 2.20 Å). Their environment is completed by other O atoms belonging to the tetrahedra. The coordination number of Bi^{3+} increases from 4 to 6 if Bi—O distances of up to 2.72 Å are included.

The Bi atoms are at the corners of Bi_6 octahedra. Two such octahedra share an edge in the equatorial plane (Fig. 3a). Pairs of such Bi_6 octahedra are then stacked along the [010] direction after a 90° rotation (Fig. 3b). The residual densities lie around Bi atoms at 0.7–0.8 Å from their crystallographic sites indicating possible small displacements. The O atoms of the MoO_4 tetrahedra exhibit relatively large displacement parameters indicative of an important libration. This phenomenon could be reasonably related to the properties of anionic conduction exhibited by these types of compounds. This disorder was evident in the refinement only for the tetrahedron associated with the Mo1 atom
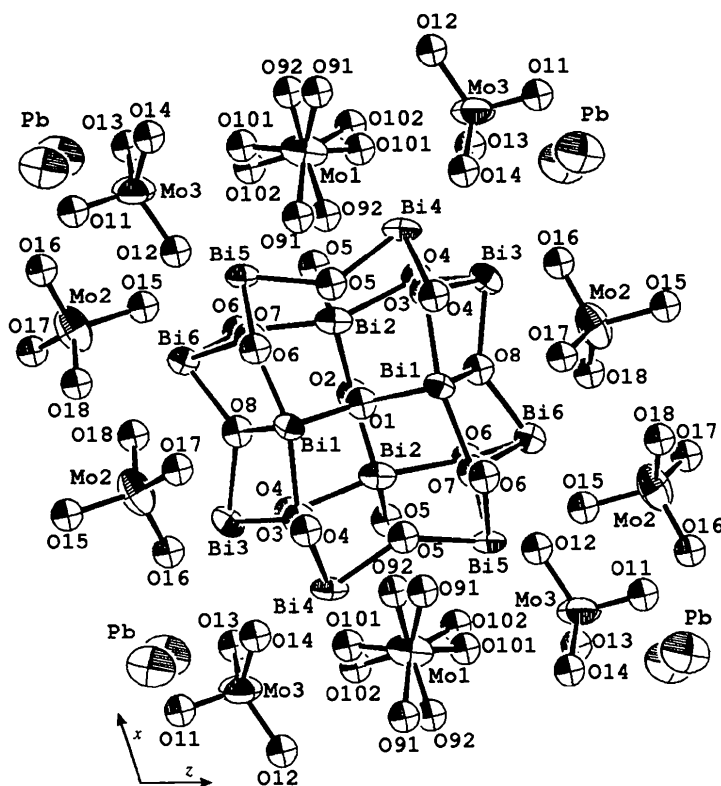
Fig. 2. Detail of MoO$_4$ tetrahedra surrounding the Bi$_{12}$O$_{14}$ rose. Displacement ellipsoids are plotted at the 98% probability level. (U_{iso} values for the O atoms are fixed at 0.013 Å^2.)
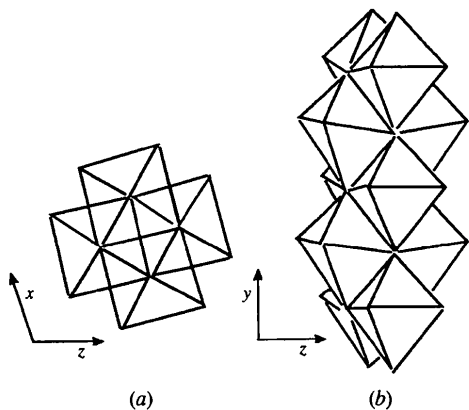

(a)   (b)

Fig. 3. Arrangement of the Bi atoms at the corners of octahedra in the (Bi$_{12}$O$_{14}$)n columns.

(2f site). The Mo atoms are apparently in a distorted cube of partially occupied O-atom sites. The Pb atoms are inserted between the four Mo2O$_4$ and Mo3O$_4$ tetrahedra.

This compound was decided upon following the results of an extensive investigation of Bi$_{13}$Mo$_4$VO$_{34}$ and Bi$_{13}$Mo$_{4.66}$Al$_{0.33}$O$_{34}$ (Enjalbert, Hasselmann &

Galy, 1996). PbBi$_{12}$Mo$_5$O$_{34}$ is isostructural with the Bi$_{26}$Mo$_{10}$O$_6$ compound studied by Vannier, Mairesse, Abraham & Nowogrocki (1996), and represents further proof that the formula and the non-stoichiometry suggested by Vannier and co-workers are not in agreement with the detailed structure of this family (see the discussion developed by Enjalbert et al., 1996).

Experimental

The samples were prepared by solid-state reactions from mixtures of Bi$_2$O$_3$, MoO$_3$ and PbO powders of analytical grade (99.99% Sigma Aldrich). The mixtures, ground in an agate mortar, were placed in a platinum crucible, heated in air and cooled slowly. After each thermal treatment the products were reground and examined by X-ray powder diffraction. The details of the experiment are: heating at 823 K for 24 h, quenching to room temperature, heating at 1123 K for 24 h and cooling at 50 K h^{-1}. Single crystals were obtained by slow cooling after melting: 1223 K for 1 h, followed by cooling to 1173 K at 2 K h^{-1}, then to 1123 K at 10 K h^{-1}, and finally to room temperature at 50 K h^{-1}. The yellow crystals obtained were parallelepipeds, some reaching 3 mm in length.

Crystal data

PbBi$_{12}$Mo$_5$O$_{34}$
M_r = 3738.65

Mo $K\alpha$ radiation
λ = 0.71069 Å

O16	0.287 (4)	0.429 (8)	0.460 (2)	0.070 (12)
O17	0.113 (3)	0.781 (8)	0.453 (2)	0.066 (11)
O18	0.064 (4)	0.300 (9)	0.475 (2)	0.074 (12)

† Site occupancy = 0.50.   ‡ Site occupancy = 0.30.   § Site occupancy = 0.70.

Monoclinic
P2/c
a = 11.715 (4) Å
b = 5.800 (2) Å
c = 24.694 (9) Å
β = 102.10 (3)°
V = 1640.6 (10) Å^3
Z = 2
D_x = 7.568 Mg m^{-3}
D_m not measured

Cell parameters from 25
reflections
θ = 6.3–24.8°
μ = 71.145 mm^{-1}
T = 293 (2) K
Parallelepiped
0.175 × 0.0875 ×
0.025 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4
diffractometer
ω–2θ scans
Absorption correction:
numerical (Coppens, Leis-
erowitz & Rabinovich,
1965)
T_{min} = 0.0087, T_{max} =
0.1044
3455 measured reflections

3367 independent reflections
R_{int} = 0.1879
θ_{max} = 33.96°
h = 0 → 18
k = 0 → 9
l = −38 → 36
3 standard reflections
every 150 reflections
frequency: 60 min
intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.168
S = 0.904
3366 reflections
164 parameters
$w = 1/[\sigma^2(F_o^2) + (0.14P)^2 + 197P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.020

$\Delta\rho_{max}$ = 12.556 e Å^{-3}
$\Delta\rho_{min}$ = −5.675 e Å^{-3}
Extinction correction:
*SHELXL*93 (Sheldrick,
1993)
Extinction coefficient:
0.00046 (6)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

U_{iso} for O atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{iso}/U_{eq}
Bi1	0.03995 (8)	0.4229 (2)	0.32675 (5)	0.0129 (2)
Bi2	0.15749 (8)	−0.0786 (2)	0.24496 (5)	0.0144 (2)
Bi3	0.24259 (9)	0.0160 (2)	0.39911 (5)	0.0147 (2)
Bi4	0.35929 (8)	0.5090 (2)	0.32165 (5)	0.0150 (2)
Bi5	0.26961 (8)	0.5092 (2)	0.15871 (5)	0.0137 (2)
Bi6	0.08118 (8)	0.0132 (2)	0.09135 (5)	0.0137 (2)
Pb†	0.5103 (7)	0.485 (2)	0.0087 (2)	0.0368 (12)
Mo1	1/2	0.0156 (8)	1/4	0.0211 (8)
Mo2	0.1641 (2)	0.5184 (6)	0.48774 (13)	0.0210 (6)
Mo3	0.4244 (2)	−0.0053 (6)	0.07977 (14)	0.0226 (6)
O1	0	0.251 (5)	1/4	0.013 (5)
O2	0	−0.268 (6)	1/4	0.017 (6)
O3	0.2293 (19)	0.274 (4)	0.3332 (11)	0.021 (5)
O4	0.2351 (17)	0.770 (4)	0.3349 (10)	0.015 (4)
O5	0.2571 (19)	0.597 (5)	0.2423 (11)	0.023 (5)
O6	0.1306 (17)	0.757 (4)	0.1524 (10)	0.015 (4)
O7	0.1357 (17)	0.265 (4)	0.1576 (10)	0.016 (4)
O8	0.0601 (16)	0.070 (4)	0.3685 (9)	0.015 (4)
O91‡	0.382 (8)	0.211 (18)	0.221 (5)	0.03 (2)
O92§	0.377 (4)	0.185 (8)	0.249 (2)	0.035 (9)
O101‡	0.520 (9)	−0.05 (2)	0.184 (5)	0.04 (2)
O102§	0.4784 (4)	−0.187 (9)	0.198 (2)	0.048 (12)
O11	0.377 (4)	0.064 (9)	0.011 (2)	0.072 (12)
O12	0.305 (3)	−0.019 (7)	0.107 (2)	0.055 (9)
O13	0.504 (3)	−0.274 (9)	0.083 (2)	0.070 (12)
O14	0.532 (4)	0.18 (1)	0.108 (2)	0.084 (15)
O15	0.200 (3)	0.553 (8)	0.5575 (19)	0.061 (11)

Table 2. *Selected bond lengths (Å)*

Bi1—O1	2.105 (15)	Bi6—O8^i	2.13 (2)
Bi1—O8	2.28 (2)	Bi6—O7	2.18 (2)
Bi1—O3	2.35 (2)	Bi6—O12	2.57 (4)
Bi1—O7^i	2.36 (2)	Bi6—O17^{vii}	2.66 (4)
Bi1—O2^{ii}	2.58 (2)	Bi6—O18^i	2.68 (5)
Bi2—O2	2.17 (2)	Pb—O13^{ii}	2.31 (5)
Bi2—O5^{iii}	2.22 (2)	Pb—O16^{iv}	2.36 (4)
Bi2—O4^{iii}	2.38 (2)	Pb—O13^{viii}	2.54 (5)
Bi2—O6^{iii}	2.43 (2)	Pb—O16^{vi}	2.68 (4)
Bi2—O1	2.68 (2)	Mo1—O102	1.72 (6)
Bi3—O4^{iii}	2.12 (2)	Mo1—O102^{iv}	1.72 (6)
Bi3—O8	2.14 (2)	Mo1—O92^{iv}	1.74 (4)
Bi3—O3	2.19 (3)	Mo1—O92	1.74 (4)
Bi3—O17^{iii}	2.62 (4)	Mo1—O101	1.74 (12)
Bi4—O3	2.11 (2)	Mo1—O101^{iv}	1.74 (12)
Bi4—O5	2.13 (3)	Mo1—O91^{iv}	1.82 (10)
Bi4—O4	2.17 (2)	Mo1—O91	1.82 (10)
Bi4—O92	2.65 (5)	Mo2—O15	1.70 (4)
Bi4—O14^{iv}	2.71 (6)	Mo2—O18	1.71 (5)
Bi4—O102^v	2.72 (5)	Mo2—O17	1.79 (5)
Bi5—O7	2.11 (2)	Mo2—O16	1.79 (4)
Bi5—O6	2.15 (2)	Mo3—O12	1.68 (4)
Bi5—O5	2.16 (3)	Mo3—O14	1.69 (5)
Bi5—O15^{vi}	2.49 (5)	Mo3—O11	1.73 (5)
Bi5—O91	2.50 (11)	Mo3—O13	1.81 (5)
Bi6—O6^{iii}	2.11 (2)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, 1 + y, z$; (iii) $x, y - 1, z$; (iv) $1-x, y, \frac{1}{2}-z$; (v) $1-x, 1+y, \frac{1}{2}-z$; (vi) $x, 1-y, z-\frac{1}{2}$; (vii) $-x, y-1, \frac{1}{2}-z$; (viii) $1 - x, -y, -z$.

The crystal system was determined using the precession method with Mo $K\alpha$ radiation. The monoclinic cell parameters were refined by optimization of the setting angles of 25 *hkl* reflections on the diffractometer. The intensities of the measured reflections were corrected for Lorentz and polarization factors. An absorption correction was applied using the numerical method (Coppens, Leiserowitz & Rabinovich, 1965) with 001, 00Ī, 10Ī, Ī02, 012 and 0Ī2 as limiting faces. The Bi atoms were located by the Patterson technique and the other atoms from a series of refinements and Fourier syntheses (Sheldrick, 1985).

The Bi, Pb and Mo atoms were refined anisotropically and the O atoms isotropically. The occupancies of O atoms O91, O92, O101 and O102 were originally fixed at 50% but refinement holding U_{iso} constant showed that the occupancies of the atoms O91 and O101 are close to 30%, and those of O92 and O102 are close to 70%. Holding site occupancies fixed at these values and varying U_{iso} led to more homogeneous values of U_{iso} (0.031 for O91, 0.035 for O92, 0.042 for O101 and 0.048 for O102). The very large absorption coefficient, which made an accurate absorption correction difficult, is responsible for the relatively large values of R and $\Delta\rho_{max}$. However, the bond lengths and angles, as well as the displacement parameters, appear to be satisfactory.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CADAK* (Savariault, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *OR-TEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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