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$Bi_3ScMo_2O_{12}$: the difference from $Bi_3FeMo_2O_{12}$

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$Bi_3ScMo_2O_{12}$, tribismuth(III) scandium molybdate(VI), has a framework structure derived from that of scheelite. It is nearly isotypic with $Bi_3FeMo_2O_{12}$; while in the latter the Fe^{III} atom is tetrahedrally coordinated by O atoms, the Sc atom in the title compound has a distorted octahedral coordination, and is substituted by Bi to a very minor extent (*ca* 4%). The change in coordination is achieved predominantly by shifts of two O atoms. The average Sc—O and Mo—O bond lengths are 2.162 and 1.775 Å, respectively. The environments of the two eight-coordinated Bi sites are very similar to those in $Bi_3FeMo_2O_{12}$. All atoms are on general positions except Sc and one Bi (both of which have site symmetry 2).

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mo–O) = 0.003 Å
Disorder in main residue
R factor = 0.022
wR factor = 0.052
Data-to-parameter ratio = 21.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

During flux growth preparation in air of compounds in the system Sc_2O_3–Al_2O_3–TiO_2–SiO_2, the title compound was obtained as a by-product. $Bi_3ScMo_2O_{12}$, tribismuth(III) scandium molybdate(VI), belongs to a small group of $Bi_3M^{III}Mo_2O_{12}$ compounds, all of which have space group $C2/c$. The structure of the Fe^{III} member, $Bi_3FeMo_2O_{12}$, was solved from single-crystal X-ray diffraction data by Jeitschko

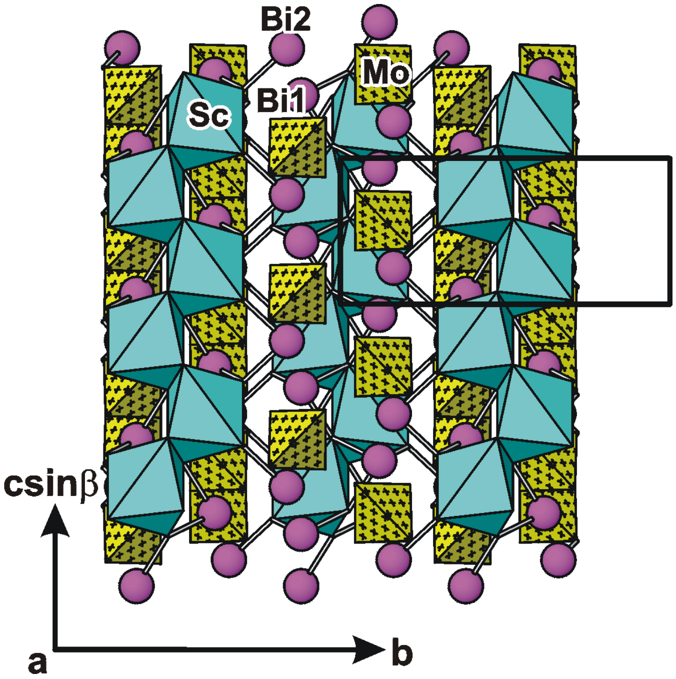

Figure 1
View of the framework structure of $Bi_3ScMo_2O_{12}$ along [100]. Distorted ScO_6 octahedra (blue) share edges to form zigzag chains parallel to [001]. Eight-coordinated Bi atoms (purple) connect these chains to isolated MoO_4 tetrahedra (yellow). Only the strongest Bi—O bonds, *i.e.* those shorter than 2.4 Å, are shown. The unit cell is outlined.

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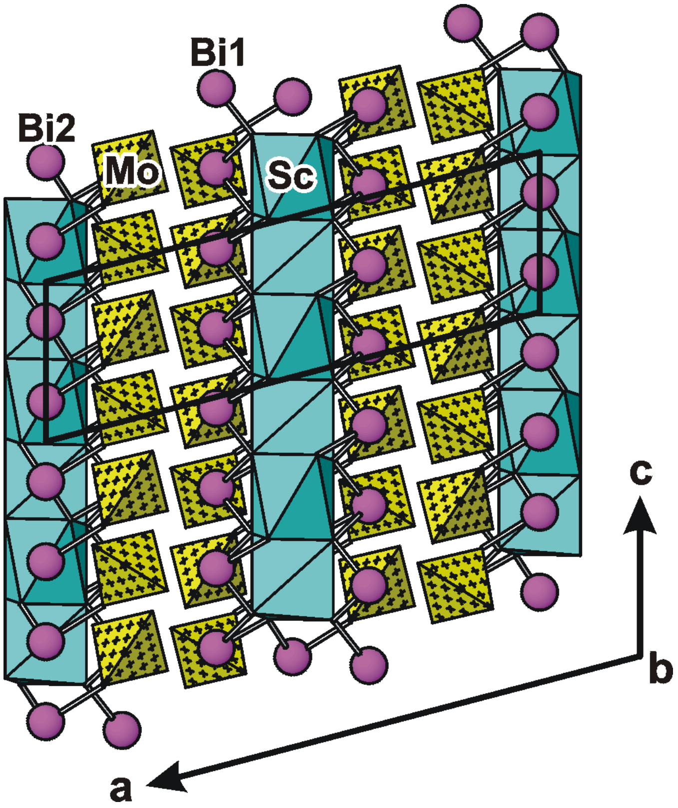

Figure 2
View of the framework structure of $Bi_3ScMo_2O_{12}$ along [010]. For key see Fig. 1.

et al. (1976); they pointed out the unusual tetrahedral coordination of the Fe atom and therefore used the alternative formula $Bi_3(FeO_4)(MoO_4)_2$. They also provided details on the relation of the crystal structure to that of scheelite, $CaWO_4$. The Fe^{III} member is an important catalyst for some organic reactions (*e.g.* Linn & Sleight, 1976; Krenzke & Keulks, 1980). Its conductivity behavior can also be used to detect low concentrations of atmospheric reducing vapors (*e.g.* Sears, 1993). The Ga member, $Bi_3GaMo_2O_{12}$, was reported by Sleight & Jeitschko (1974) and Jeitschko *et al.* (1976), and also later confirmed by Mokhosoev *et al.* (1987). The latter authors prepared two new members, *viz.* $Bi_3InMo_2O_{12}$ and $Bi_3ScMo_2O_{12}$, and reported their X-ray powder diffraction data (see also ICCD-PDF cards 40–413 and 40–414, respectively). Mokhosoev *et al.* (1987) also stated that Al and Cr did not form a phase analogous to $Bi_3FeMo_2O_{12}$.

Apart from $Bi_3FeMo_2O_{12}$, no structure refinement of any other member has been reported so far, although a very crude, Rietveld-related method was used by Kishkin *et al.* (1989) to calculate theoretical X-ray powder diffraction patterns for $Bi_3InMo_2O_{12}$ and $Bi_3ScMo_2O_{12}$, and refine the heavy-atom positions of these two compounds on the basis of measured powder patterns, and using the atomic coordinates of $Bi_3FeMo_2O_{12}$ (Jeitschko *et al.*, 1976) as a starting model. Their work did not include the oxygen positions and they gave a list of the heavy atom coordinates only. No *R* values, s.u.values or any other important experimental details were given, nor were the results discussed. The data in the article of Kishkin *et al.* (1989) imply that the In and Sc atoms in the two studied compounds also show a tetrahedral coordination. However, this is incorrect, as will be shown below.

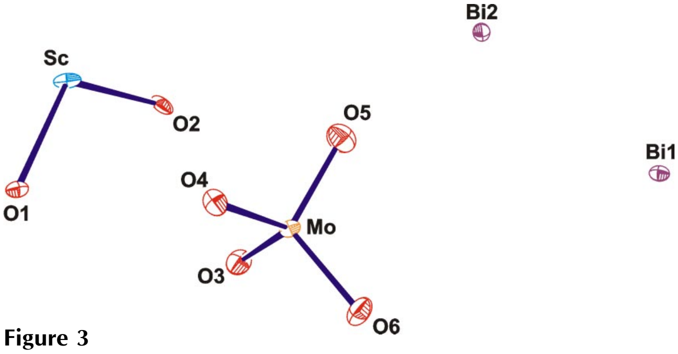

Figure 3
View of the atoms in the asymmetric unit of $Bi_3ScMo_2O_{12}$, shown with displacement ellipsoids at the 70% probability level.

$Bi_3ScMo_2O_{12}$ crystallizes in space group $C2/c$. The framework structure (Figs. 1–3) contains two crystallographically non-equivalent Bi atoms, one Mo atom, one Sc atom and six O atoms. All atoms are on general positions except Bi2 and Sc, both of which have site symmetry 2. The coordinates of the heavy atoms are very similar to those in $Bi_3FeMo_2O_{12}$ (Jeitschko *et al.*, 1976), and those given by Kishkin *et al.* (1989) for $Bi_3ScMo_2O_{12}$. The presently determined unit-cell parameters of the title compound are very close to those refined earlier from X-ray powder diffraction data, $a = 16.992$ (6), $b = 11.604$ (5), $c = 5.322$ (3) Å, $\beta = 104.70$ (5)° and $V = 1015.02$ Å^3 (Mokhosoev *et al.*, 1987; ICDD-PDF 40–414).

The two Bi atoms are each coordinated by eight O atoms. However, Bi1 shows a wide range of Bi—O bond lengths (Table 1), whereas Bi2 clearly has a [4 + 4]-coordination. All features of the two Bi—O polyhedra are fairly similar to those in $Bi_3FeMo_2O_{12}$ (Jeitschko *et al.*, 1976), and a stereochemical activity of the lone electron pairs on the Bi^{III} ions is evident from the geometry of the Bi—O polyhedra (Fig. 2). The Mo atom is tetrahedrally coordinated, with an average Mo—O bond length of 1.775 Å, and only small deviations from ideal tetrahedral angles (Table 1).

The Sc atom is surrounded by six O atoms, resulting in a slightly distorted ScO_6 octahedron (Table 1). A further Sc—O distance, to O4 at 3.259 (3) Å, is too long to be considered as a bond. The ScO_6 octahedron shares two edges with adjacent octahedra, thus forming zigzag chains parallel to [001] (Figs. 1 and 2).

Occupancy refinements of the heavy atom sites show that Bi1, Bi2, and Mo are fully occupied, whereas the Sc site must also be the host of minor amounts of an element distinctly heavier than Sc. It was assumed that Bi partially substitutes for Sc, and an occupancy refinement gave a Sc:Bi ratio of 0.9589 (17):0.0411 (17). The Bi-for-Sc substitution is also indicated by a bond-valence analysis of the structure, using the parameters of Brese & O'Keeffe (1991) for Bi—O and Mo—O bonds, and the parameters of Brown (1996) for Sc—O bonds. If the bond-valence sum for the Sc site is calculated using only the Sc—O parameters, a fairly low value of 2.73 valence units (v.u.) is obtained. If the refined Sc:Bi occupancy is taken into account, the bond-valence increases to a more reasonable value of 2.82 v.u. A substitution of Mo^{VI} or other elements for Sc^{III} can be excluded because a necessary charge balance is missing, and the chemical analysis revealed no impurity contents.

For the Bi1, Bi2, and Mo sites, bond-valence sums of 3.16, 3.11, and 5.74 v.u. are calculated, respectively; these values are close to ideal valences. For the six O atoms O1 to O6, values of 2.07, 2.13, 1.90, 2.06, 1.79, and 1.92 v.u. are obtained, respectively. The relatively low value of O5, 1.79 v.u., may be explained as the result of a poor fit of the bond-valence parameters around short Mo—O as much as around long Bi—O bonds, although it could also indicate some internal strain.

The octahedral coordination of Sc in $Bi_3ScMo_2O_{12}$ contrasts with the tetrahedral coordination of Fe^{III} in $Bi_3FeMo_2O_{12}$ (average Fe—O 1.91 Å; Jeitschko *et al.*, 1976). In the Fe^{III} member, the Fe atom is coordinated by two O1 [at a distance of 1.93 (2) Å] and two O2 atoms [1.90 (2) Å], whereas in the Sc compound, the O ligands are four O1 atoms [2 × 2.134 (3) Å and 2 × 2.274 (3) Å] and two O2 atoms [2 × 2.079 (3) Å]. A careful comparison of the atomic coordinates demonstrates that the change in coordination number is predominantly achieved by shifts of the O atoms O1 and O2. Interestingly, the 'tendency' of a higher coordination of Fe^{III} in $Bi_3FeMo_2O_{12}$ is already indicated by two additional very long distances to O1 at 2.851 Å each (Jeitschko *et al.*, 1976). The present results suggest that the coordination of the In atom in isostructural $Bi_3InMo_2O_{12}$ is also octahedral (six-coordinated In^{III} has an average In—O bond length of 2.141 Å, similar to the corresponding value for Sc^{III}, 2.105 Å, and distinctly larger than the value for Fe^{III}, 2.011 Å; Baur, 1981). As result of the octahedral coordination of the Sc atom, the O1 atom now has a fourfold coordination, unlike the situation in $Bi_3FeMo_2O_{12}$, where all O atoms show threefold coordination (Jeitschko *et al.*, 1976).

The strong influence of the ionic radius of M^{III} atoms on the stability of Bi oxides is also evident in the case of $Bi_2M^{III}{}_4O_9$ compounds (*e.g.* $Bi_2Al_4O_9$; Arpe & Müller-Buschbaum, 1977; Abrahams *et al.*, 1999), in which there is one tetrahedrally and one octahedrally coordinated M^{III} site. This structure type is stable only for M^{III} = Al, Fe, and Mn, but not for In, Sc, or Cr, or any lanthanide element. This is in agreement with the general observation that trivalent Al, Fe, and Mn can be tetrahedrally coordinated by O, but not the other listed elements.

Experimental

The title compound crystallized from a Bi-rich flux as a major component of the matrix (experimental parameters: 4 g Bi_2O_3, 2 g MoO_3, 0.2618 g Sc_2O_3, 0.0716 g Al_2O_3; Pt crucible covered with lid, T_{max} 1423 K, holding time 6 h, cooling rate 1.5 K min^{-1}, T_{min} = 1173 K, slow cooling to room temperature after switching off furnace; weight loss 2.0%). $Bi_3ScMo_2O_{12}$ formed large, anhedral, transparent grains with yellow color and strong luster. The grains were accompanied by smoky, short, prismatic, transparent crystals of α-Al_2O_3, a large colorless plate of $Sc_2(MoO_4)_3$, and small pale yellow to white laths of the high-temperature modification of Bi_2MoO_6 (*e.g.* Chen & Smith, 1975; Buttrey *et al.*, 1994); the latter may have been stabilized by the incorporation of Sc^{III} ions, but it is also reported to be easily quenched to room temperature (Watanabe *et al.*, 1987). Chemical analyses of the title compound with standard SEM–EDS showed the presence of only Bi, Sc, and Mo metals (Al was not detectable even when counting times of 200 s were used). This indicates that the Al present in the flux has completely partitioned into α-Al_2O_3, while all of the Sc has formed Sc molybdate compounds. It is also in agreement with the observation of Mokhosoev *et al.* (1987) that Al does not form a compound analogous to $Bi_3FeMo_2O_{12}$.

Crystal data

$Bi_{3.04}Sc_{0.96}Mo_2O_{12}$
M_r = 1055.78
Monoclinic, $C2/c$
a = 16.996 (3) Å
b = 11.601 (2) Å
c = 5.319 (1) Å
β = 104.67 (3)°
V = 1014.6 (3) $Å^3$
Z = 4

D_x = 6.912 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1881 reflections
θ = 2.0–32.6°
μ = 54.94 mm^{-1}
T = 293 (2) K
Irregular fragment, yellow
0.06 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.052, T_{max} = 0.064
3569 measured reflections

1833 independent reflections
1777 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 32.6°
$h = -25 \rightarrow 25$
$k = -17 \rightarrow 17$
$l = -8 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.052
S = 1.14
1833 reflections
86 parameters

$w = 1/[\sigma^2(F_o{}^2) + (0.025P)^2 + 7.1P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 3.57 e $Å^{-3}$
$\Delta\rho_{min}$ = −3.08 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00384 (9)

Table 1
Selected geometric parameters (Å, °).

$Bi1—O1^{i}$	2.211 (3)	$Bi2—O5^{vii}$	2.913 (4)
$Bi1—O2^{ii}$	2.218 (3)	$Bi2—O5^{viii}$	2.955 (4)
$Bi1—O1^{iii}$	2.335 (3)	$Sc—O2^{vii}$	2.079 (3)
$Bi1—O4^{i}$	2.492 (3)	$Sc—O1^{vii}$	2.134 (3)
$Bi1—O3^{ii}$	2.591 (3)	$Sc—O1^{ix}$	2.274 (3)
$Bi1—O6^{iv}$	2.612 (3)	Mo—O5	1.737 (3)
$Bi1—O6^{v}$	2.651 (3)	Mo—O3	1.762 (3)
$Bi1—O3^{vi}$	2.775 (3)	Mo—O6	1.767 (3)
$Bi2—O2^{ii}$	2.151 (3)	Mo—O4	1.834 (3)
$Bi2—O4^{i}$	2.344 (3)		
$O2^{vii}—Sc—O2$	102.43 (18)	$O1^{ix}—Sc—O1^{x}$	106.66 (16)
$O2^{vii}—Sc—O1^{vii}$	115.98 (11)	O5—Mo—O3	108.03 (16)
$O2—Sc—O1^{vii}$	92.01 (12)	O5—Mo—O6	112.91 (16)
$O1^{vii}—Sc—O1$	135.63 (17)	O3—Mo—O6	105.82 (16)
$O2^{vii}—Sc—O1^{ix}$	77.16 (11)	O5—Mo—O4	106.92 (16)
$O2—Sc—O1^{ix}$	166.06 (11)	O3—Mo—O4	112.13 (14)
$O1^{vii}—Sc—O1^{ix}$	76.02 (8)	O6—Mo—O4	111.08 (15)
$O1—Sc—O1^{ix}$	77.91 (12)		

Symmetry codes: (i) $x, 1-y, z-\frac{1}{2}$; (ii) $x, 1-y, \frac{1}{2}+z$; (iii) $x, 1+y, z$; (iv) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $-x, y, \frac{1}{2}-z$; (viii) $-x, 1-y, -z$; (ix) $-x, -y, 1-z$; (x) $x, -y, z-\frac{1}{2}$.

The highest peak and deepest hole in the final difference map are 0.74 Å from the Bi2 site and 0.73 Å from the Bi1 site, respectively.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL*

DENZO (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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