Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$Mg_4Sb_2O_9$ of the ilmenite structure type

Yuichi Michiue

National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
Correspondence e-mail: MICHIUE.Yuichi@nims.go.jp

Received 6 August 2008; accepted 1 September 2008

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(Mg–O) = 0.002 Å; disorder in main residue; R factor = 0.032; wR factor = 0.075; data-to-parameter ratio = 45.5.

Single crystals of the title compound, tetramagnesium dianti-monate(V), were obtained by the slow cooling method with K_2CO_3. The structure is isotypic with ilmenite, which is constructed by the alternate stacking of layers consisting of metal–oxygen coordination octahedra. In each layer, the octahedra are connected by sharing edges so as to make holes. One of the two non-equivalent metal sites is fully occupied by Mg (3 symmetry), while the second metal site (3 symmetry) is disordered and occupied by Mg and Sb with occupation factors of 1/3 and 2/3, respectively.

Related literature

For ilmenite structures, see: Wechsler & Prewitt (1984) for $FeTiO_3$ and Wechsler & Von Dreele (1989) for $MgTiO_3$. For further phases in the MgO–Sb_2O_5 system, see: Kasper (1969). For related literature, see: Becker & Coppens (1974); Blasse (1964); Michiue (2007).

Experimental

Crystal data

$Mg_4O_9Sb_2$
M_r = 484.7
Trigonal, $R\overline{3}$
a = 5.1722 (11) Å
c = 14.028 (2) Å
V = 324.99 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 8.73 mm^{-1}
T = 295 K
0.22 × 0.22 × 0.04 mm

Data collection

Rigaku AFC-7R diffractometer
Absorption correction: analytical (*Tompa Analytical*, Rigaku 2004)
T_{min} = 0.210, T_{max} = 0.671
2359 measured reflections
773 independent reflections
715 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
3 standard reflections
every 200 reflections
intensity decay: 4.6%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.074
S = 1.55
773 reflections
17 parameters
$\Delta\rho_{max}$ = 3.78 e Å^{-3}
$\Delta\rho_{min}$ = −3.64 e Å^{-3}

Table 1
Selected bond lengths (Å), M = Mg, Sb.

$M1$—O1	2.0527 (15)	$M1$—O1^{iv}	2.0527 (12)
$M1$—O1^{i}	1.9928 (11)	$M1$—O1^{v}	1.9928 (17)
$M1$—O1^{ii}	2.0527 (19)	Mg2—O1	2.2091 (17)
$M1$—O1^{iii}	1.9928 (18)	Mg2—O1^{vi}	2.0455 (17)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku, 2004); method used to solve structure: structure of the present compound is isotypic with ilmenite; program(s) used to refine structure: *JANA*2000 (Petříček *et al.*, 2000); molecular graphics: *ATOMS* (Dowty, 2005); software used to prepare material for publication: *JANA*2000.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2101).

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–147.
Blasse, G. (1964). *Z. Anorg. Allg. Chem.* **331**, 44–50.
Dowty, E. (2005). *ATOMS*. Shape Software, Kingsport, Tennessee, USA.
Kasper, H. (1969). *Z. Kristallogr.* **128**, 72–84.
Michiue, Y. (2007). *J. Solid State Chem.* **180**, 1840–1845.
Molecular Structure Corporation (1994). *MSC/AFC Diffractometer Control Software*. MSC, The Woodlands, Texas, USA.
Petříček, V., Dušek, M. & Palatinus, L. (2000). *JANA2000*. Institute of Physics, Prague, Czech Republic.
Rigaku (2004). *CrystalStructure* and *Tompa Analytical*. Rigaku Corporation, Tokyo, Japan.
Wechsler, B. A. & Von Dreele, R. B. (1989). *Acta Cryst.* B**45**, 542–549.
Wechsler, B. A. & Prewitt, C. T. (1984). *Am. Mineral.* **69**, 176–185.

supporting information

Acta Cryst. (2008). E**64**, i66 [doi:10.1107/S160053680802789X]

$Mg_4Sb_2O_9$ of the ilmenite structure type

Yuichi Michiue

S1. Comment

A pronounced resemblance of X-ray diffraction patterns for $Mg_4Sb_2O_9$ and the ilmenite $MgTiO_3$ was pointed out by Blasse (1964). In general, ilmenite structure is represented by $A^{2+}B^{4+}O_3$, that is including equal amounts of divalent and tetravalent cations such as $FeTiO_3$ and $MgTiO_3$. Although the chemical composition $Mg_4Sb_2O_9$ is away from that of the typical ilmenite structure, the present analysis has confirmed that the structure of $Mg_4Sb_2O_9$ is deduced from the ilmenite $MgTiO_3$ by replacing the Ti^{4+} ions statistically by 1/3 Mg^{2+} and 2/3 Sb^{5+}, as was supposed by Blasse (1964).

The structure is constructed by the alternate stacking of atomic layers along **c** as shown in Fig. 1. Each of the two nonequivalent metal sites is octahedrally coordinated by six oxygen ions. Two types of layers consisting of edge-shared octahedra are seen in the structure, both of which have holes as illustrated in Fig. 2.

S2. Experimental

Single crystals of the title compound were obtained unintentionally as the product of a synthesis of K-hollandite by the slow cooling method with excess K_2CO_3 (Michiue, 2007).

S3. Refinement

Partial substitution of Sb for Mg at the Mg2 site was checked by refining the occupation factors of Mg and Sb at the site. In the refinement the full occupation at all the metal and oxygen sites was assumed and the charge neutrality of the whole crystal was kept by imposing constraint conditions. The possibility of the existence of Sb ions at the Mg2 site was excluded because the occupation factor of Sb at the site was slightly negative, -0.001, and that of Mg was 1.001 after the refinement. Thus, it was concluded that Sb ions are only at the Mg1/Sb1 site.

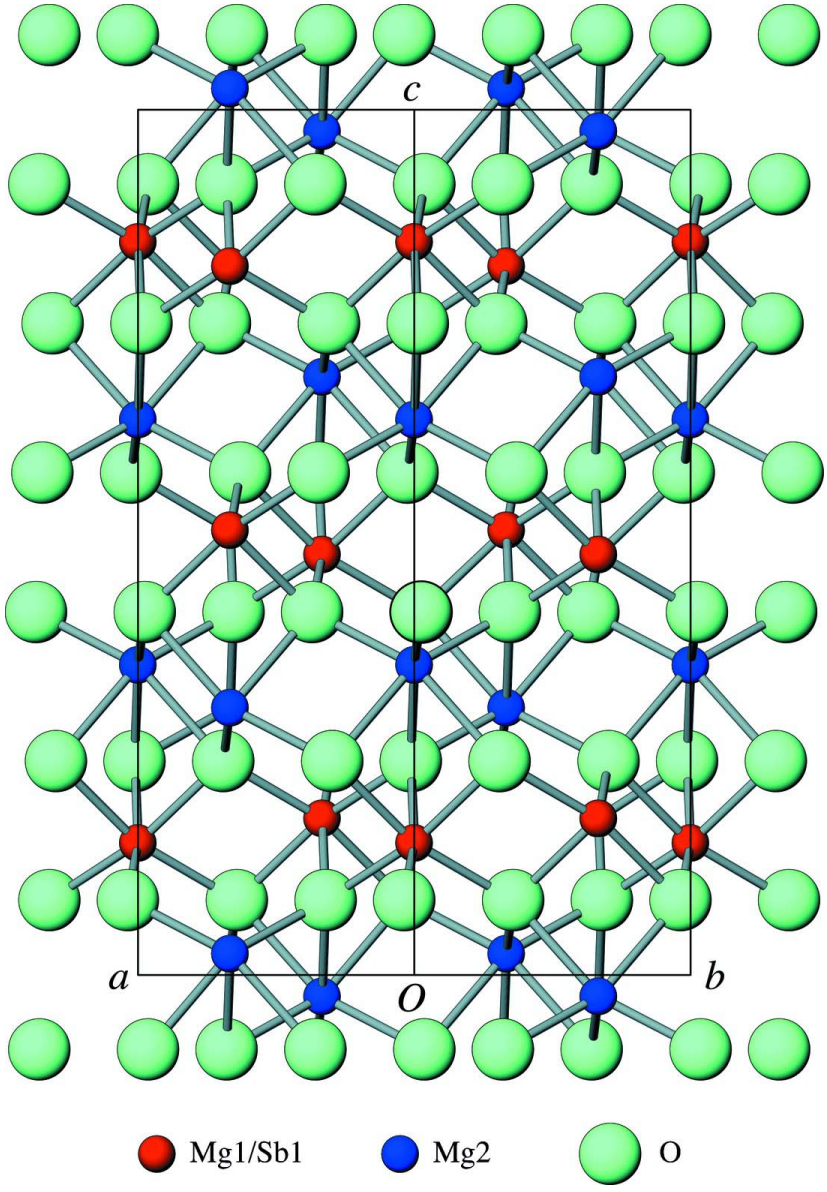
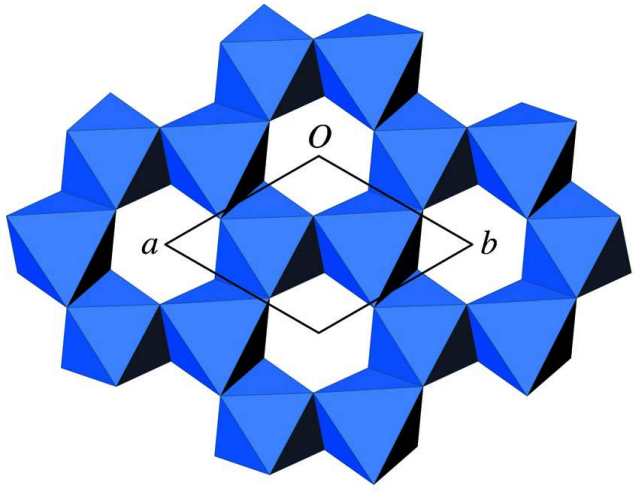
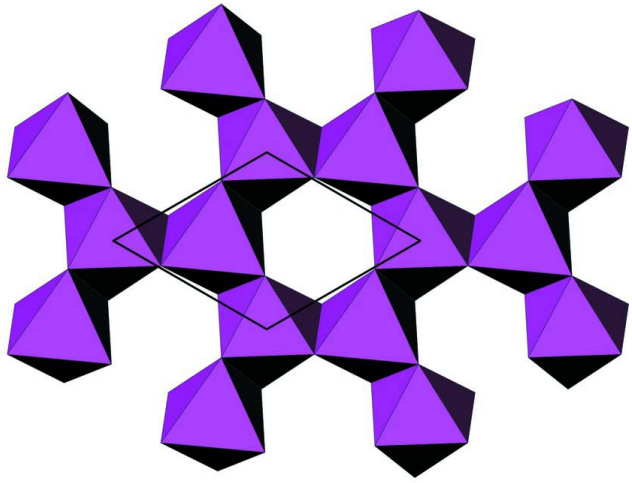


Figure 1

The projection of $Mg_4Sb_2O_9$ along [110].



(a) $Mg2O_6$ layer



(b) $(Mg1/Sb1)O_6$ layer

Figure 2

Layers with holes consisting of (*a*) $Mg2O_6$ octahedra extending around $z = 0$ and (*b*) $(Mg1/Sb1)O_6$ octahedra around $z = 1/6$ in $Mg_4Sb_2O_9$.

tetramagnesium diantimonate

Crystal data

$Mg_4O_9Sb_2$
$M_r = 484.7$
Trigonal, $R\bar{3}$
Hall symbol: -R 3
$a = 5.1722$ (11) Å
$c = 14.028$ (2) Å
$V = 324.99$ (11) Å^3
$Z = 2$
$F(000) = 444$
$D_x = 4.952$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 9.3$–$13.5°$
$\mu = 8.73$ mm^{-1}
$T = 295$ K
Plate, colorless
0.22 × 0.22 × 0.04 mm

Data collection

Rigaku AFC-7R diffractometer
Radiation source: rotating-anode X-ray tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: analytical (Tompa Analytical, Rigaku 2004)
T_{min} = 0.210, T_{max} = 0.671
2359 measured reflections
773 independent reflections
715 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 50.1°, θ_{min} = 4.4°
h = −11→11
k = −11→11
l = 0→30
3 standard reflections every 200 reflections
intensity decay: 4.6%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.075
S = 1.55
773 reflections
17 parameters
0 restraints
Primary atom site location: isomorphous structure methods
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0009I^2)$
$(\Delta/\sigma)_{max}$ = 0.0004
$\Delta\rho_{max}$ = 3.78 e Å^{-3}
$\Delta\rho_{min}$ = −3.64 e Å^{-3}
Extinction correction: B-C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.071 (3)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Mg1	0	0	0.152618 (14)	0.00628 (7)	0.3333
M1	0	0	0.152618 (14)	0.00628 (7)	0.6667
Mg2	0	0	0.35806 (10)	0.0098 (2)	
O1	0.3091 (3)	0.0125 (3)	0.24710 (7)	0.0078 (3)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.00711 (10)	0.00711 (10)	0.00461 (10)	0.00356 (5)	0	0
M1	0.00711 (10)	0.00711 (10)	0.00461 (10)	0.00356 (5)	0	0
Mg2	0.0080 (3)	0.0080 (3)	0.0133 (4)	0.00401 (13)	0	0
O1	0.0097 (4)	0.0073 (4)	0.0069 (3)	0.0047 (3)	−0.0010 (3)	0.0011 (2)

Geometric parameters (Å, º)

M1—O1	2.0527 (15)	Mg2—O1	2.2091 (17)
M1—O1^{i}	1.9928 (11)	Mg2—O1^{vi}	2.0455 (17)
M1—O1^{ii}	2.0527 (19)	Mg2—O1^{ii}	2.209 (2)
M1—O1^{iii}	1.9928 (18)	Mg2—O1^{vii}	2.0455 (14)
M1—O1^{iv}	2.0527 (12)	Mg2—O1^{iv}	2.2091 (15)
M1—O1^{v}	1.9928 (17)	Mg2—O1^{viii}	2.046 (2)
O1—M1—O1^{i}	83.77 (5)	O1—Mg2—O1^{vi}	87.88 (6)
O1—M1—O1^{ii}	82.80 (6)	O1—Mg2—O1^{ii}	75.84 (7)
O1—M1—O1^{iii}	166.22 (6)	O1—Mg2—O1^{vii}	89.32 (5)

O1—M1—O1^{iv}	82.80 (6)	O1—Mg2—O1^{iv}	75.84 (7)
O1—M1—O1^{v}	92.43 (7)	O1—Mg2—O1^{viii}	160.12 (8)
O1^{i}—M1—O1	83.77 (5)	O1^{vi}—Mg2—O1	87.88 (6)
O1^{i}—M1—O1^{ii}	92.43 (5)	O1^{vi}—Mg2—O1^{ii}	160.12 (8)
O1^{i}—M1—O1^{iii}	99.93 (6)	O1^{vi}—Mg2—O1^{vii}	103.48 (8)
O1^{i}—M1—O1^{iv}	166.22 (6)	O1^{vi}—Mg2—O1^{iv}	89.32 (6)
O1^{i}—M1—O1^{v}	99.93 (6)	O1^{vi}—Mg2—O1^{viii}	103.48 (7)
O1^{ii}—M1—O1	82.80 (6)	O1^{ii}—Mg2—O1	75.84 (7)
O1^{ii}—M1—O1^{i}	92.43 (5)	O1^{ii}—Mg2—O1^{vi}	160.12 (8)
O1^{ii}—M1—O1^{iii}	83.77 (7)	O1^{ii}—Mg2—O1^{vii}	87.88 (6)
O1^{ii}—M1—O1^{iv}	82.80 (6)	O1^{ii}—Mg2—O1^{iv}	75.84 (7)
O1^{ii}—M1—O1^{v}	166.22 (5)	O1^{ii}—Mg2—O1^{viii}	89.32 (6)
O1^{iii}—M1—O1	166.22 (6)	O1^{vii}—Mg2—O1	89.32 (5)
O1^{iii}—M1—O1^{i}	99.93 (6)	O1^{vii}—Mg2—O1^{vi}	103.48 (8)
O1^{iii}—M1—O1^{ii}	83.77 (7)	O1^{vii}—Mg2—O1^{ii}	87.88 (6)
O1^{iii}—M1—O1^{iv}	92.43 (7)	O1^{vii}—Mg2—O1^{iv}	160.12 (8)
O1^{iii}—M1—O1^{v}	99.93 (8)	O1^{vii}—Mg2—O1^{viii}	103.48 (7)
O1^{iv}—M1—O1	82.80 (6)	O1^{iv}—Mg2—O1	75.84 (7)
O1^{iv}—M1—O1^{i}	166.22 (6)	O1^{iv}—Mg2—O1^{vi}	89.32 (6)
O1^{iv}—M1—O1^{ii}	82.80 (6)	O1^{iv}—Mg2—O1^{ii}	75.84 (7)
O1^{iv}—M1—O1^{iii}	92.43 (7)	O1^{iv}—Mg2—O1^{vii}	160.12 (8)
O1^{iv}—M1—O1^{v}	83.77 (6)	O1^{iv}—Mg2—O1^{viii}	87.88 (6)
O1^{v}—M1—O1	92.43 (7)	O1^{viii}—Mg2—O1	160.12 (8)
O1^{v}—M1—O1^{i}	99.93 (6)	O1^{viii}—Mg2—O1^{vi}	103.48 (7)
O1^{v}—M1—O1^{ii}	166.22 (5)	O1^{viii}—Mg2—O1^{ii}	89.32 (6)
O1^{v}—M1—O1^{iii}	99.93 (8)	O1^{viii}—Mg2—O1^{vii}	103.48 (7)
O1^{v}—M1—O1^{iv}	83.77 (6)	O1^{viii}—Mg2—O1^{iv}	87.88 (6)

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