$wR = 0.041$
$S = 2.43$
1571 reflections
104 parameters
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.73$ e Å^{-3}
$\Delta\rho_{\min} = -1.13$ e Å^{-3}

Extinction coefficient: 25936 (709)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K1	0	1/2	1/2	0.036 (1)
K2	0	1/2	0	0.071 (2)
Ga	0.37526 (9)	0.19236 (8)	0.72415 (6)	0.0122 (3)
As1	0.17389 (8)	0.96533 (8)	0.30932 (6)	0.0121 (2)
As2	−0.48212 (8)	0.25386 (7)	0.16579 (6)	0.0119 (3)
O1	−0.0908 (6)	0.8039 (6)	0.2183 (4)	0.016 (2)
O2	0.3361 (6)	0.7913 (6)	0.3308 (5)	0.017 (2)
O3	0.2068 (6)	1.1509 (6)	0.4786 (4)	0.015 (2)
O4	0.2337 (6)	1.1146 (6)	0.1486 (4)	0.017 (2)
O5	0.4469 (7)	0.7384 (6)	0.0285 (4)	0.018 (2)
O6	−0.4286 (7)	0.4979 (6)	0.2852 (5)	0.019 (2)
O7	−0.3102 (7)	0.1238 (6)	0.2775 (5)	0.017 (2)

Table 2. *Selected geometric parameters (Å, °)*

K1—O1	3.206 (4)	Ga—O5^{iii}	2.002 (4)
K1—O2	3.146 (4)	Ga—O6^{ii}	1.936 (4)
K1—O3^{i}	2.841 (4)	Ga—O7^{iv}	1.956 (4)
K1—O6	2.832 (4)	As1—O1	1.669 (3)
K1—O7	2.816 (4)	As1—O2	1.672 (4)
K2—O1	2.738 (4)	As1—O3	1.654 (3)
K2—O2	3.076 (4)	As1—O4	1.765 (3)
K2—O5	2.790 (4)	As2—O4^{v}	1.754 (4)
K2—O6	3.346 (4)	As2—O5^{vi}	1.658 (3)
Ga—O1^{ii}	1.955 (4)	As2—O6	1.654 (4)
Ga—O2^{iii}	1.949 (4)	As2—O7	1.676 (4)
Ga—O3^{i}	1.985 (3)		
O1^{ii}—Ga—O2^{iii}	176.4 (2)	O6^{ii}—Ga—O7^{iv}	177.2 (2)
O1^{ii}—Ga—O3^{i}	88.4 (2)	O1—As1—O2	104.3 (2)
O1^{ii}—Ga—O5^{iii}	92.0 (2)	O1—As1—O3	116.3 (2)
O1^{ii}—Ga—O6^{ii}	88.7 (2)	O1—As1—O4	103.4 (2)
O1^{ii}—Ga—O7^{iv}	90.6 (2)	O2—As1—O3	117.8 (2)
O2^{iii}—Ga—O3^{i}	92.0 (2)	O2—As1—O4	108.1 (2)
O2^{iii}—Ga—O5^{iii}	87.4 (2)	O3—As1—O4	105.9 (2)
O2^{iii}—Ga—O6^{ii}	87.7 (2)	O4^{v}—As2—O5^{vi}	109.6 (2)
O2^{iii}—Ga—O7^{iv}	93.0 (2)	O4^{v}—As2—O6	106.6 (2)
O3^{i}—Ga—O5^{iii}	175.1 (2)	O4^{v}—As2—O7	108.5 (2)
O3^{i}—Ga—O6^{ii}	84.3 (2)	O5^{vi}—As2—O6	114.5 (2)
O3^{i}—Ga—O7^{iv}	93.0 (2)	O5^{vi}—As2—O7	111.3 (2)
O5^{iii}—Ga—O6^{ii}	90.9 (2)	O6—As2—O7	106.1 (2)
O5^{iii}—Ga—O7^{iv}	91.9 (2)	As1—O4—As2^{vii}	119.1 (2)

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

Data collection: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Cell refinement: *NRCVAX*. Data reduction: *NRCVAX*. Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX* and *ORTEP*II (Johnson, 1976).

This work was supported by Institute of Chemistry, Academia Sinica and the National Science Council (NSC85-2113-M-001-017) of the Republic of China.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: KH1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Boughzala, H., Driss, A. & Jouini, T. (1993). *Acta Cryst.* C**49**, 425–427.
Boughzala, H. & Jouini, T. (1995). *Acta Cryst.* C**51**, 179–181.
Chen, J., Li, L., Yang, G. & Xu, R. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1217–1218.
Donnay, G. & Allmann, R. (1970). *Am. Mineral.* **55**, 1003–1015.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Goiffon, A., Jumas, J. C., Maurin, M. & Philippot, E. (1986). *J. Solid State Chem.* **61**, 384–396.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Wilson, S. T., Lok, B. M., Messing, C. A., Cannan, T. R. & Flanigen, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1147.

Acta Cryst. (1996). C**52**, 2389-2393

$LaMo_8O_{14}$

G. Kerihuel, J. Tortelier and P. Gougeon

Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS No. 1495, Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes CEDEX, France. E-mail: patrick.gougeon@univ-rennes1.fr

(*Received 16 January 1996; accepted 25 April 1996*)

Abstract

The crystal structure of lanthanum octamolybdate contains an equal mixture of *cis*-edge-sharing and *trans* bi-face-capped octahedral Mo_8 clusters. These clusters and the O atoms, the arrangement of which derives from close packing with the layer sequence *ABAC*..., form sheets parallel to the (*bc*) plane of the orthorhombic unit cell. The Mo—Mo distances range from 2.5877 (4) to 2.7780 (5) Å and from 2.5961 (5) to 2.8866 (7) Å in the *trans* and *cis*-edge-sharing isomeric clusters, respectively. The shortest Mo—Mo distance between the Mo_8 clusters within the same layer is 3.0807 (4) Å and that between clusters in adjacent layers is 3.6380 (5) Å. The Mo—O distances lie between 2.026 (3) and 2.120 (3) Å in the *trans* isomer and between 1.938 (3) and 2.169 (3) Å in the *cis*-edge-sharing

isomer. The environment of each of the two crystallographically independent $\mathrm{La^{3+}}$ ions consists of twelve O atoms which form a distorted cuboctahedron. The La—O distances lie between 2.593 (3) and 2.927 (3) Å and between 2.489 (3) and 3.029 (3) Å for the La1 and La2 sites, respectively.

Comment

The two related compounds $\mathrm{LaMo_{7.7}O_{14}}$ [space group *Aba*2, *a* = 9.196 (1), *b* = 9.985 (1), *c* = 11.171 (1) Å] and $\mathrm{LaMo_8O_{14}}$ [superspace group $P^{\underline{C2}ca}_{111}$, *a* = 11.129 (1), *b* = 10.000 (1), *c* = 9.218 (1) Å, $q^* = b^*/3$] were obtained by fused-salt electrolysis in the early nineties (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990; Leligny *et al.*, 1993). Single-crystal structure determinations carried out on these compounds revealed that their dominant structural features are layers containing bi-face-capped octahedral $\mathrm{Mo_8}$ clusters which exhibit different configurations and arrangements. In the former compound, the *cis*-edge-sharing isomeric form of the $\mathrm{Mo_8}$ cluster is mainly preponderant, while the statistical formation of either $\mathrm{Mo_7}$ or $\mathrm{Mo_6}$ clusters is expected due to the partial Mo deficiency on the face-capping sites. In the stoichiometric La compound, which was reported to have a modulated structure, *cis*-edge-sharing and *trans* bi-face-capped $\mathrm{Mo_8}$ clusters are observed with an average probability distribution of approximately 65 and 35%, respectively.

Parallel to the work described above, we prepared the $R\mathrm{Mo_8O_{14}}$ (*R* = La, Ce, Pr, Nd and Sm) compounds by solid-state reactions at high temperature (1800–2220 K) (Kerihuel & Gougeon, 1994). Single-crystal structures of the Ce, Pr and Nd compounds thus obtained were reported in recent publications. While $\mathrm{NdMo_8O_{14}}$ [space group *Aba*2, *a* = 9.209 (3), *b* = 10.008 (2), *c* = 11.143 (4) Å] (Gougeon & McCarley, 1991) is isostructural with the molybdenum deficient compound $\mathrm{LaMo_{7.7}O_{14}}$ obtained by fused-salt electrolysis, the Ce [space group *Pbcn*, *a* = 9.1937 (7), *b* = 11.121 (1), *c* = 20.014 (1) Å] and Pr [space group *Pbca*, *a* = 9.2037 (6), *b* = 11.114 (2), *c* = 30.012 (5) Å] compounds crystallize in two different forms (Kerihuel & Gougeon, 1995*a*,*b*). In the Ce and Pr compounds, the Mo-atom network is based on well ordered mixtures of *cis*-edge-sharing and *trans* bi-face-capped octahedral $\mathrm{Mo_8}$ clusters in the ratio 1:1 and 2:1 for $\mathrm{CeMo_8O_{14}}$ and $\mathrm{PrMo_8O_{14}}$, respectively. We present here the crystal structure of the La member synthesized by high-temperature solid-state reaction. Its structure differs from those of the $\mathrm{LaMo_{8-\mathit{x}}O_{14}}$ compounds obtained by fused-salt electrolysis and belongs to the $\mathrm{CeMo_8O_{14}}$ type.

The structure of $\mathrm{LaMo_8O_{14}}$ is characterized by layers in which *cis*-edge-sharing and *trans* bi-face-capped $\mathrm{Mo_8}$ clusters coexist in equal proportions. The two isomeric forms of the $\mathrm{Mo_8}$ cluster are shown in Fig. 1 with their O-atom environments. Each Mo atom of the $\mathrm{Mo_6}$ core is surrounded by five O atoms forming a distorted square pyramid and each of the capping Mo atoms by six O atoms in a distorted octahedron. The perspective view of the structure along the *b* axis [Fig. 2(*a*)] clearly shows that the $\mathrm{Mo_8}$ clusters and the O atoms are arranged in layers parallel to the (*bc*) plane. The O-atom framework is similar to that previously described for all the other $R\mathrm{Mo_8O_{14}}$ forms and derives from a packing of close-packed layers with sequence *ABAC*..., where in the *A* layers a quarter of the O atoms are missing in an ordered way or are substituted by the La ions and the *B* and *C* layers are entirely occupied by O atoms. Within the O-atom network, the Mo atoms occupy half of the octahedral interstices to create the $\mathrm{Mo_8}$ clusters, the arrangement of which in the unit cell is shown in Fig. 2(*b*).

The Mo—Mo distances within the *trans* bi-face-capped $\mathrm{Mo_8}$ cluster range from 2.5877 (4) to 2.7780 (5) Å. These values are close to those determined for the modulated phase [2.54 (1)–2.766 (1) Å] in the region where the probability of the presence of the *trans* form is the largest (*P* = 0.38). The Mo—O distances lie between 2.026 (3) and 2.120 (3) Å, in contrast to 1.89 (2)–2.18 (2) Å for the modulated phase. The discrepancy probably results from the fact that there is no region of the crystal where only the *trans* form occurs. The Mo—Mo distances in the *cis*-edge-sharing isomer cover a range from 2.5961 (5) to 2.8866 (7) Å, slightly wider than in the *trans* isomer as already observed for $\mathrm{CeMo_8O_{14}}$. This augmentation of the dispersion of the intracluster Mo—Mo distances with respect to that found for the *trans* form has also been observed for the modulated form of $\mathrm{LaMo_8O_{14}}$. Indeed, in the region where almost only the *cis* form occurs, the Mo—Mo distances vary between 2.588 (2) and 2.850 (1) Å. It can be seen that the latter range is close to that in $\mathrm{PrMo_8O_{14}}$ [2.595 (1)–2.871 (2) Å], where the *cis* and *trans* $\mathrm{Mo_8}$ clusters are in a 2:1 ratio, very similar to that in the modulated La compound. For $\mathrm{LaMo_{7.7}O_{14}}$, in which only the *cis* isomer occurs, the Mo—Mo distances are spread over a narrower range [2.618 (1)–2.823 (1) Å]. Electronic band-structure calculations would be helpful in understanding these Mo—Mo range variations, which are obviously due to different distributions of the cationic charge between the *trans* and *cis* isomers in the three forms of $\mathrm{LaMo_{8-\mathit{x}}O_{14}}$. The Mo—O distances in the *cis* form vary between 1.938 (3) and 2.169 (3) Å, as opposed to 1.97 (1)–2.15 (1) Å for the modulated phase and 1.932 (6)–2.139 (8) Å for $\mathrm{LaMo_{7.7}O_{14}}$.

The shortest Mo—Mo intercluster distance, which occurs between the Mo3 and Mo8 atoms of the two different isomers within the same layer, is 3.0790 (9) Å and corresponds to that observed for $\mathrm{LaMo_{7.7}O_{14}}$ [3.078 (1) Å]. In the modulated form of $\mathrm{LaMo_8O_{14}}$, the intercluster distances within a given layer vary between 3.043 (9) and 3.083 (2) Å as a function of the occupancy probabilities of the two capping Mo sites. On the other hand, the spacing between Mo_8 clusters of adjacent layers reaches a length of 3.6380 (5) Å and does not change in comparison with those observed in the other forms.

The two crystallographically independent La ions sit either on an inversion centre or on a twofold axis. They are both surrounded by twelve O atoms forming a distorted cuboctahedron. The La—O distances range from 2.593 (3) to 2.927 (3) Å and from 2.489 (4) to 3.029 (3) Å for the La1 and La2 sites, respectively. In $LaMo_{7.7}O_{14}$, where the unique crystallographically independent La ion is located on a twofold axis, the La—O distances are in the range 2.491 (7)–3.045 (6) Å. In the modulated $LaMo_8O_{14}$ phase, the La ions occupy two complementary sites with probabilities ranging from 0.987 to 0.695 for the La1 site and from 0.0 to 0.298 for the La2 site. For the largest occupancy probability of these two sites, the La—O distances range from 2.50 (1) to 3.03 (1) Å and from 2.55 (4) to 2.83 (4) Å, respectively.

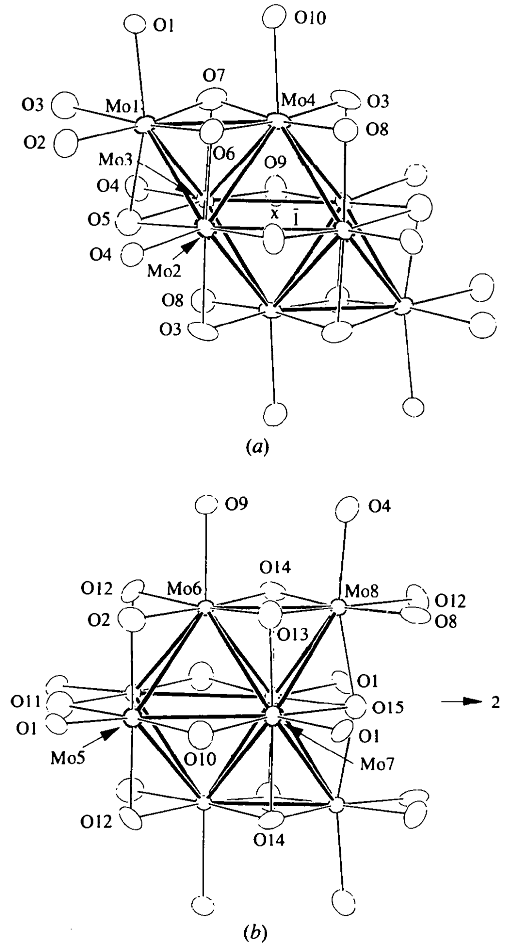

Fig. 1. (a) The *trans* and (b) the *cis*-edge-sharing bi-face-capped Mo_8 clusters with their O-atom environments. Displacement ellipsoids are plotted at the 95% probability level.

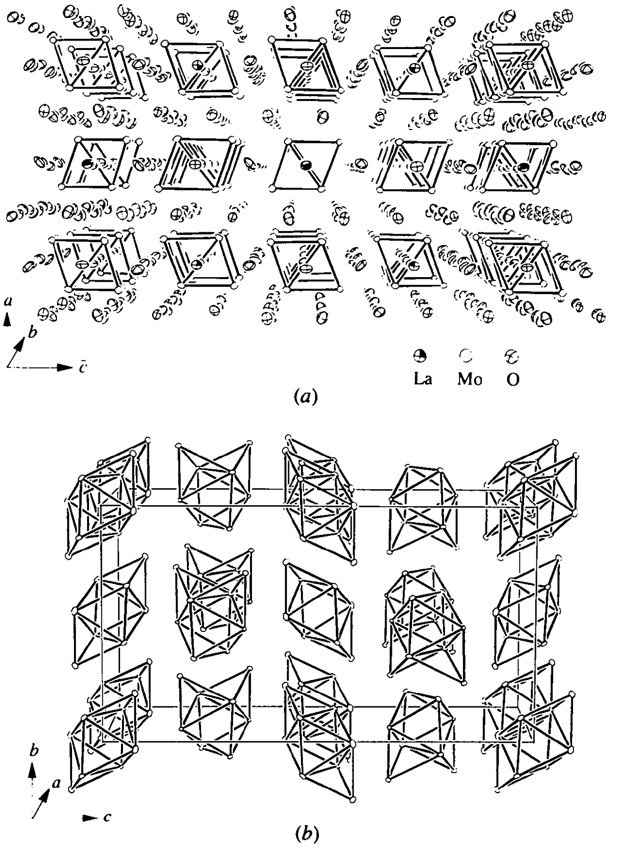

Fig. 2. (a) A perspective view of the structure along the b axis. The Mo_8 clusters are emphasized by bold lines. (b) The arrangement of the Mo_8 clusters within the unit cell. Displacement ellipsoids are plotted at the 95% probability level.

Experimental

Single crystals were obtained by heating a stoichiometric mixture (starting materials: La_2O_3, MoO_3 and Mo) in a sealed molybdenum crucible at *ca* 2220 K for 15 min. The crucible was then cooled at a rate of 100 K h^{-1} down to 1300 K and finally furnace-cooled to room temperature.

Crystal data

$LaMo_8O_{14}$
$M_r = 1130.43$
Orthorhombic
Pbcn
$a = 9.2065\,(4)$ Å
$b = 11.1298\,(9)$ Å
$c = 20.0264\,(8)$ Å
$V = 2052.0\,(2)$ Å^3
$Z = 8$
$D_x = 7.318$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–32°$
$\mu = 13.588$ mm^{-1}
$T = 293\,(2)$ K
Irregular
$0.14 \times 0.12 \times 0.10$ mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans

5847 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 44.93°$

Absorption correction:
 ψ scans of six reflections (North, Phillips & Mathews, 1968)
 $T_{min} = 0.21$, $T_{max} = 0.26$
9237 measured reflections
9237 independent reflections

$h = 0 \rightarrow 18$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 39$
3 standard reflections
 frequency: 90 min
 intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0365$
$wR(F^2) = 0.0816$
$S = 1.142$
7570 reflections
212 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 26.9201P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 3.80$ e Å^{-3}
$\Delta\rho_{min} = -2.24$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00096 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
La1	0	1/2	0	0.00695 (5)
La2	1/2	0.52108 (3)	1/4	0.00644 (5)
Mo1	0.62096 (4)	0.72632 (3)	0.07956 (2)	0.00366 (5)
Mo2	0.62081 (4)	0.62350 (3)	0.45632 (2)	0.00316 (5)
Mo3	0.12313 (4)	0.12476 (3)	0.53667 (2)	0.00315 (5)
Mo4	0.62048 (4)	0.48789 (3)	0.07914 (2)	0.00370 (5)
Mo5	0.61963 (4)	0.87138 (3)	0.212704 (15)	0.00284 (5)
Mo6	0.87879 (4)	0.49661 (3)	0.33003 (2)	0.00261 (5)
Mo7	0.12449 (4)	0.61658 (3)	0.29380 (2)	0.00305 (5)
Mo8	1.12032 (4)	0.72983 (3)	0.167558 (15)	0.00317 (5)
O1	0.2576 (3)	0.2618 (2)	0.83417 (15)	0.0041 (4)
O2	0.5119 (4)	0.8677 (3)	0.1262 (2)	0.0061 (4)
O3	0.7604 (4)	0.3676 (3)	0.03761 (14)	0.0060 (4)
O4	0.2599 (4)	0.7565 (3)	0.5875 (2)	0.0055 (4)
O5	0.9914 (3)	0.7394 (2)	0.00106 (15)	0.0051 (4)
O6	0.9926 (4)	0.1055 (3)	0.36842 (15)	0.0061 (4)
O7	0.2346 (4)	0.6071 (3)	0.4601 (2)	0.0064 (4)
O8	0.5078 (4)	0.3653 (3)	0.37398 (15)	0.0064 (4)
O9	0.2357 (4)	0.4964 (2)	0.0800 (2)	0.0052 (5)
O10	0.2373 (4)	0.0101 (2)	0.8296 (2)	0.0053 (5)
O11	1/2	0.2553 (3)	3/4	0.0063 (6)
O12	0.7578 (4)	0.1312 (2)	0.78953 (14)	0.0051 (4)
O13	0.9886 (3)	0.6092 (2)	0.11821 (15)	0.0045 (4)
O14	0.7359 (3)	0.6146 (3)	0.28770 (14)	0.0045 (4)
O15	1/2	0.2620 (3)	1/4	0.0044 (5)

Table 2. *Selected geometric parameters (Å)*

La1—O7^{i}	2.593 (3)	Mo3—Mo4^{xxiii}	2.7749 (5)
La1—O7^{ii}	2.593 (3)	Mo3—Mo8^{xxii}	3.0807 (4)
La1—O13^{iii}	2.663 (3)	Mo4—O8^{ix}	2.034 (3)
La1—O13^{iv}	2.663 (3)	Mo4—O3	2.036 (3)
La1—O5^{iii}	2.666 (3)	Mo4—O7^{ix}	2.039 (3)
La1—O5^{iv}	2.666 (3)	Mo4—O6^{xi}	2.050 (3)
La1—O9^{v}	2.698 (4)	Mo4—O10^{xiii}	2.120 (3)
La1—O9	2.698 (4)	Mo4—Mo3^{xii}	2.7066 (5)
La1—O3^{iv}	2.758 (3)	Mo4—Mo2^{ii}	2.7545 (5)
La1—O3^{iii}	2.758 (3)	Mo4—Mo3^{xvi}	2.7749 (5)
La1—O2^{vi}	2.927 (3)	Mo4—Mo2^{ix}	2.7780 (5)
La1—O2^{vii}	2.927 (3)	Mo5—O11^{viii}	1.938 (3)
La2—O11^{viii}	2.489 (4)	Mo5—O12^{ii}	1.996 (3)
La2—O14	2.524 (3)	Mo5—O2	1.997 (3)
La2—O14^{ix}	2.524 (3)	Mo5—O10^{viii}	2.048 (3)
La2—O6^{x}	2.552 (3)	Mo5—O1^{viii}	2.087 (3)
La2—O6^{xi}	2.552 (3)	Mo5—Mo5^{ix}	2.6615 (7)
La2—O10^{xii}	2.727 (4)	Mo5—Mo6^{x}	2.7320 (4)
La2—O10^{xiii}	2.727 (4)	Mo5—Mo7^{xvi}	2.7325 (5)
La2—O15	2.883 (4)	Mo5—Mo6^{xi}	2.7553 (5)
La2—O12^{xiv}	2.911 (3)	Mo6—O13^{xxiv}	2.033 (3)
La2—O12^{xv}	2.911 (3)	Mo6—O14	2.043 (3)
La2—O8	3.029 (3)	Mo6—O12^{xv}	2.065 (3)
La2—O8^{ix}	3.029 (3)	Mo6—O2^{xxv}	2.081 (3)
Mo1—O7^{ix}	2.040 (3)	Mo6—O9^{ix}	2.087 (3)
Mo1—O5^{vi}	2.043 (3)	Mo6—Mo8^{xxiv}	2.5961 (5)
Mo1—O1^{viii}	2.062 (3)	Mo6—Mo7^{xxvi}	2.7251 (5)
Mo1—O6^{xi}	2.071 (3)	Mo6—Mo5^{xxvii}	2.7320 (4)
Mo1—O2	2.087 (3)	Mo6—Mo5^{xxv}	2.7553 (5)
Mo1—O3^{x}	2.090 (3)	Mo6—Mo7^{ix}	2.8168 (5)
Mo1—Mo3^{xvi}	2.5877 (4)	Mo7—O1^{ii}	1.997 (3)
Mo1—Mo2^{ix}	2.6039 (5)	Mo7—O10^{xii}	2.030 (3)
Mo1—Mo4	2.6537 (5)	Mo7—O13^{ix}	2.048 (3)
Mo2—O4^{xvii}	2.048 (3)	Mo7—O14^{ix}	2.078 (3)
Mo2—O5^{xviii}	2.049 (3)	Mo7—O15^{xi}	2.169 (3)
Mo2—O6^{x}	2.057 (3)	Mo7—Mo8^{ix}	2.6958 (5)
Mo2—O9^{ix}	2.067 (3)	Mo7—Mo6^{iii}	2.7251 (5)
Mo2—O3^{xix}	2.077 (3)	Mo7—Mo5^{xxiii}	2.7325 (5)
Mo2—Mo1^{ix}	2.6039 (5)	Mo7—Mo6^{ix}	2.8168 (5)
Mo2—Mo4^{xix}	2.7545 (5)	Mo7—Mo8^{iii}	2.8253 (4)
Mo2—Mo3^{xx}	2.7629 (5)	Mo7—Mo7^{i}	2.8866 (7)
Mo2—Mo3^{xiii}	2.7667 (5)	Mo8—O4^{xxviii}	1.951 (3)
Mo2—Mo4^{ix}	2.7780 (5)	Mo8—O8^{xvi}	2.010 (3)
Mo3—O7^{vii}	2.026 (3)	Mo8—O15^{xvi}	2.0203 (7)
Mo3—O9^{xxi}	2.064 (3)	Mo8—O14^{xxiv}	2.049 (3)
Mo3—O5^{xxii}	2.065 (3)	Mo8—O13	2.061 (3)
Mo3—O8^{xiv}	2.084 (3)	Mo8—O12^{xxix}	2.095 (3)
Mo3—O4^{vii}	2.085 (3)	Mo8—Mo6^{xxiv}	2.5961 (5)
Mo3—Mo1^{xxiii}	2.5877 (4)	Mo8—Mo7^{ix}	2.6958 (5)
Mo3—Mo4^{xxi}	2.7066 (5)	Mo8—Mo7^{xxvi}	2.8253 (4)
Mo3—Mo2^{vii}	2.7629 (5)	Mo8—Mo3^{xxx}	3.0807 (4)
Mo3—Mo2^{xiv}	2.7667 (5)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, 1 - y, z - \frac{1}{2}$; (iii) $x - 1, y, z$; (iv) $1 - x, 1 - y, -z$; (v) $-x, 1 - y, -z$; (vi) $x - \frac{1}{2}, \frac{3}{2} - y, -z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (viii) $1 - x, 1 - y, 1 - z$; (ix) $1 - x, y, \frac{1}{2} - z$; (x) $\frac{3}{2} - x, \frac{1}{2} + y, z$; (xi) $x - \frac{1}{2}, \frac{1}{2} + y, \frac{1}{2} - z$; (xii) $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$; (xiii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (xiv) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (xv) $\frac{3}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$; (xvi) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (xvii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (xviii) $\frac{3}{2} - x, \frac{3}{2} - y, \frac{1}{2} + z$; (xix) $x, 1 - y, \frac{1}{2} + z$; (xx) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (xxi) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (xxii) $x - 1, 1 - y, \frac{1}{2} + z$; (xxiii) $x - \frac{1}{2}, y - \frac{1}{2}, \frac{1}{2} - z$; (xxiv) $2 - x, y, \frac{1}{2} - z$; (xxv) $\frac{1}{2} + x, y - \frac{1}{2}, \frac{1}{2} - z$; (xxvi) $1 + x, y, z$; (xxvii) $\frac{3}{2} - x, y - \frac{1}{2}, z$; (xxviii) $\frac{3}{2} - x, \frac{3}{2} - y, z - \frac{1}{2}$; (xxix) $2 - x, 1 - y, 1 - z$; (xxx) $1 + x, 1 - y, z - \frac{1}{2}$.

Data were corrected for Lorentz and polarization effects. The atomic coordinates of Ce, Mo and O from the Ce analogue (Kerihuel & Gougeon, 1995*a*) were used as starting positions for La, Mo and O in the present study. Refinements of the occupancy factors for the La and Mo sites confirmed that they are fully occupied. Calculations were performed on a Digital Pentium Celebris 590 FP for *SHELXL*93 (Sheldrick, 1993) and on a Digital MicroVAX 3100 for the *MolEN* (Fair, 1990) programs.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN*. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Gougeon, P. & McCarley, R. E. (1991). *Acta Cryst.* C**47**, 241–244.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kerihuel, G. & Gougeon, P. (1994). Unpublished results.
Kerihuel, G. & Gougeon, P. (1995*a*). *Acta Cryst.* C**51**, 787–790.
Kerihuel, G. & Gougeon, P. (1995*b*). *Acta Cryst.* C**51**, 1475–1478.
Leligny, H., Labbe, Ph., Ledesert, M., Hervieu, M., Raveau, B. & McCarroll, W. H. (1993). *Acta Cryst.* B**49**, 444–454.
Leligny, H., Ledesert, M., Labbe, Ph., Raveau, B. & McCarroll, W. H. (1990). *J. Solid State Chem.* **87**, 35–43.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2393–2395

Strontium Tetragermanate, $SrGe_4O_9$

Fumito Nishi

Saitama Institute of Technology, 1690 Fusaiji, Okabe, Ohsato-gun, Saitama 369-02, Japan

(*Received 16 January 1996; accepted 21 May 1996*)

Abstract

The structure of tetragermanium strontium nonaoxide, $SrGe_4O_9$, comprises two different types of sheet structure stacked alternately along the *c* axis. One sheet comprises GeO_6 octahedra and SrO_8 polyhedra while the other sheet contains three-membered rings of GeO_4 tetrahedra. In addition, this crystal structure shows a basic unit of the superstructures which are found for $PbGe_4O_9$.

Comment

Three tetragermanates of formula $MeGe_4O_9$ (*Me* = Sr, Pb, Ba) were studied by Robbins & Levin (1961). They showed that these compounds were isostructural on the basis of indexed powder X-ray diffraction patterns. In addition, they discussed a structural relationship with the mineral benitoite, $BaTiSi_3O_9$, the structure of which had been determined by Zachariasen (1930) and was later refined by Fischer (1969). Eulenberger, Wittmann & Nowotny (1962) synthesized two forms of $CaGe_4O_9$ (α and β types) and suggested that the α form was isostructural with the compounds studied by Robbins & Levin (1961).

Robbins, Perloff & Block (1966) determined the crystal structure of $BaGe_4O_9$ by single-crystal X-ray diffraction: a = 11.61, c = 4.74 Å, *P*3, *Z* = 3, final *R* value 6.8% for 327 reflections. Smolin (1969) also studied the structure of the same compound. He reported unit-cell parameters that were consistent with those given by Robbins *et al.* (1966) but gave the space group as *P*321 with a final *R* value of 5.8% for 848 reflections.

Venevtsev *et al.* (1982) studied the structure and physical properties of the four polymorphs (α, β_1, β_2, γ) of $PbGe_4O_9$ and the solid solutions $(Pb_{1-x}M_x)Ge_4O_9$ (*M* = Sr, Ba). Both α- and γ-$PbGe_4O_9$ showed ferroelectric properties, while γ-$PbGe_4O_9$ also displayed ferroelastic properties. We have attempted to solve the crystal structure of $SrGe_4O_9$, which seems to be analogous to $BaGe_4O_9$, and to confirm which space group, *P*3 or *P*321, is correct.

As a result of the structure analysis, the space group of $SrGe_4O_9$ is *P*321, as reported by Smolin (1969) for $BaGe_4O_9$. The crystal structure of $SrGe_4O_9$ has two different types of sheet structure within it. One is formed by a combination of GeO_6 octahedra and SrO_8 polyhedra (Fig. 1) and the other by three-membered rings of GeO_4 tetrahedra (Fig. 2). The sheets are stacked alternately along the *c* axis (Fig. 3).

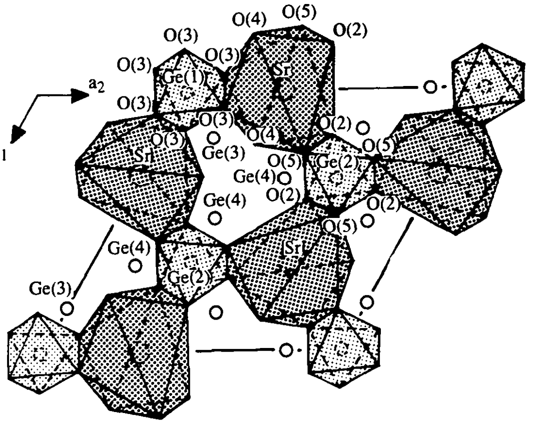

Fig. 1. The arrangement of the GeO_6 octahedra and the SrO_8 polyhedra viewed down the *c* axis.

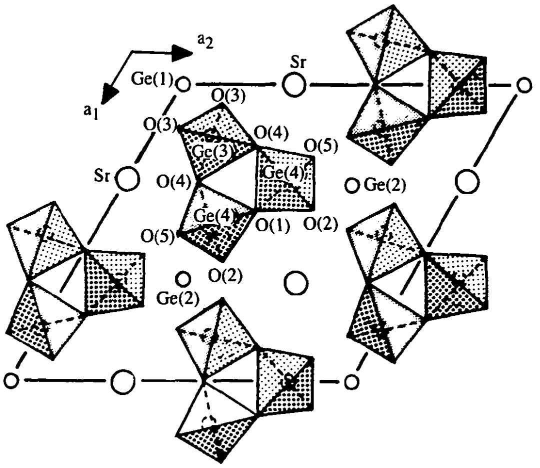

Fig. 2. The arrangement of the three-membered rings of GeO_4 tetrahedra viewed down the *c* axis.