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The metallic compound $Sr_{0.44}La_{0.56}Mo_5O_8$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(o–O) = 0.003 Å
Disorder in main residue
R factor = 0.035
wR factor = 0.076
Data-to-parameter ratio = 25.3

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

Strontium lanthanum pentamolybdenum octaoxide, $Sr_{0.44}La_{0.56}Mo_5O_8$, belongs to the $A$$Mo_5O_8$ structure type (A = Ca, Sr, Sn, Pb, Eu, La to Gd). Its crystal structure consists of bioctahedral $Mo_{10}O_{18}$ cluster units interconnected through Mo—Mo bonds of 2.7322 (7) Å to form infinite molybdenum oxide chains. These are linked by corner O atoms to create four-sided channels along [100], in which the La^{3+} and Sr^{2+} cations are statistically distributed over one unique position.

Comment

$A$$Mo_5O_8$ (A = Ca, Sr, Sn, Pb, Eu, La to Gd) phases constitute one of the most interesting series of reduced molybdenum oxides, because these compounds can tolerate a variation of the number of electrons available for metal–metal bonding in the cluster chains (metal cluster electrons, MCE), without a significant change of the basic structural motif. Single-crystal studies of the electronic properties of these compounds have shown the importance of the MCE. Indeed, when the cation A is divalent (A = Ca, Sr, Eu), the $A$$Mo_5O_8$ compounds are semiconducting in the 20–300 K range, whereas for trivalent cations (A = La to Sm), they show anomalous semiconductor-to-metal transitions near 180 K, followed by a re-entrant behavior to the semiconducting state between 30 and 50 K (Gall *et al.*, 1995). Recent work on the solid solution $Sr_{1-x}La_xMo_5O_8$ (x = 0–1) revealed metallic behavior when a few atom percentage of either La or Sr is present (McCarroll *et al.*, 1998). Therefore it was interesting to determine the crystal structure of such a solid solution with its metallic properties from single-crystal data.

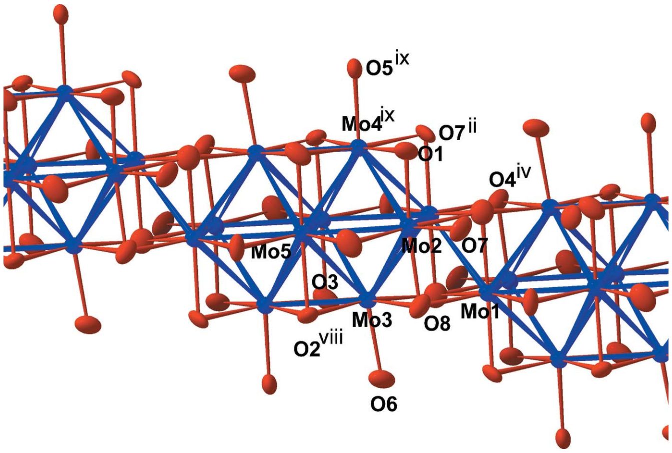

Figure 1
Fragment of a cluster chain in $La_{0.56}Sr_{0.44}Mo_5O_8$. Displacement ellipsoids are drawn at the 97% probability level. Symmetry codes as in Table 1.

The AMo_5O_8 structure type has been described previously (Hibble *et al.*, 1988; Dronskowski & Simon, 1989; Dronskowski *et al.*, 1991; Gougeon *et al.*, 1990, 1991; Gall & Gougeon, 1994*a*,*b*). The principal structural motif consists of a bioctahedral cluster unit $Mo_{10}O_{18}$, which results from the condensation of two Mo_6O_{12} clusters sharing an Mo—Mo edge. The $Mo_{10}O_{18}$ cluster units are linked at opposite edges *via* common O atoms and Mo1—Mo1 intercluster bonds to form infinite chains along [100] (Fig. 1). Neighboring chains are connected through O atoms, establishing four-sided channels where the Sr^{2+} and La^{3+} cations are statistically distributed over one unique position (Fig. 2). Previous X-ray diffraction studies of several AMo_5O_8 compounds have shown that the Mo—Mo bonds most affected by the MCE are those between the Mo_{10} cluster units, *i.e.* the Mo1—Mo1 and Mo1—Mo2 bonds (Gougeon *et al.*, 2003). In the title compound, these distances are 2.7322 (7) and 2.9815 (5) Å, respectively. These values are between those determined in the Sr end-member $SrMo_5O_8$ and the Sr-rich compound $Sr_{0.9}La_{0.1}Mo_5O_8$ and those in the La end-member $LaMo_5O_8$ and the La-rich compound $Sr_{0.11}La_{0.89}Mo_5O_8$, with a quasi-linear behavior in the entire $Sr_{1-x}La_xMo_5O_8$ solid solution series. In the title compound the Mo—O distances range between 1.963 (3) and 2.146 (3) Å (Table 1), with an average Mo—O distance of 2.071 Å. The latter value lies between that in $SrMo_5O_8$ (2.062 Å) and in $LaMo_5O_8$ (2.076 Å).

The metal site in the channels is statistically occupied by La and Sr and has no crystallographically imposed symmetry. It is surrounded by ten O atoms at distances ranging from 2.471 (3) to 2.935 (3) Å, with an additional eleventh O atom at 3.252 (3) Å. The resulting coordination polyhedron can be viewed as a highly distorted cuboctahedron with one vertex removed.

Experimental

Single crystals of $La_{0.56}Sr_{0.44}Mo_5O_8$ were obtained by the electrolysis of a melt formed at 1273 K from a mixture of Na_2MoO_4, MoO_3, $SrMoO_4$ and La_2O_3 in the molar ratio 4.00:0.34:1.00:0.33. The electrolysis was carried out in air using an alumina crucible. The anode was a platinum foil with a surface area of about 1 cm^2 and the cathode a 10-turn spiral platinum wire with a diameter of 0.38 mm. At the end of the run, the electrodes were lifted above the melt to allow rapid cooling to room temperature. Single crystals, which were grown on the cathode in the form of black irregular plates, were obtained by applying a constant current of 20 mA for 24 h. They were separated from the matrix and the cathode by repeated and alternate washings with a hot aqueous solution consisting of 5 wt% K_2CO_3 and 2 wt% ethylenediaminetetraacetic acid (H_4edta) and with 2*M* HCl.

Crystal data

$Sr_{0.44}La_{0.56}Mo_5O_8$
M_r = 724.09
Monoclinic, $P2_1/c$
a = 7.5879 (2) Å
b = 9.1041 (2) Å
c = 9.9342 (2) Å
β = 109.228 (1)°
V = 647.98 (3) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 16.60 mm^{-1}
T = 293 (2) K
0.04 × 0.04 × 0.03 mm

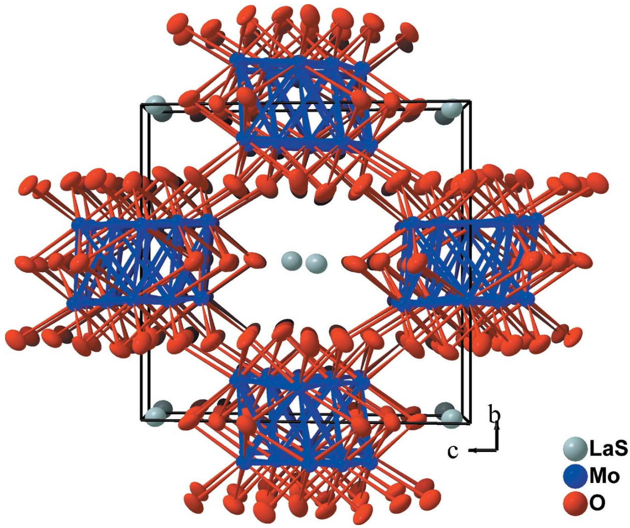

Figure 2
View of $La_{0.56}Sr_{0.44}Mo_5O_8$ along [100]. Displacement ellipsoids are drawn at the 97% probability level.

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995)
T_{min} = 0.545, T_{max} = 0.676
(expected range = 0.475–0.588)
14600 measured reflections
3292 independent reflections
2535 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.077
S = 1.05
3292 reflections
130 parameters
1 restraint
$\Delta\rho_{max}$ = 3.23 e $Å^{-3}$
$\Delta\rho_{min}$ = −2.62 e $Å^{-3}$

Table 1
Selected bond lengths (Å).

La/Sr—$O1^{i}$	2.471 (3)	Mo2—$O8^{ix}$	2.111 (3)
La/Sr—$O1^{ii}$	2.496 (3)	Mo2—O7	2.144 (3)
La/Sr—$O4^{iii}$	2.531 (3)	Mo2—$Mo4^{ix}$	2.7354 (5)
La/Sr—$O7^{ii}$	2.607 (3)	Mo2—Mo5	2.7483 (5)
La/Sr—$O5^{iv}$	2.702 (3)	Mo2—Mo3	2.8217 (5)
La/Sr—$O8^{iii}$	2.736 (3)	Mo3—O3	2.056 (3)
La/Sr—$O2^{i}$	2.739 (3)	Mo3—$O2^{viii}$	2.075 (3)
La/Sr—$O3^{v}$	2.743 (3)	Mo3—$O4^{vii}$	2.076 (3)
La/Sr—$O6^{iii}$	2.908 (3)	Mo3—O6	2.083 (3)
La/Sr—$O2^{vi}$	2.935 (3)	Mo3—O8	2.146 (3)
La/Sr—$O3^{iii}$	3.252 (3)	Mo3—$Mo4^{xi}$	2.6276 (5)
Mo1—$O5^{vii}$	2.039 (3)	Mo3—$Mo5^{xii}$	2.6875 (5)
Mo1—$O7^{viii}$	2.050 (3)	Mo3—Mo5	2.7523 (5)
Mo1—$O4^{vii}$	2.114 (3)	Mo4—$O7^{viii}$	2.061 (3)
Mo1—$O8^{ix}$	2.116 (3)	Mo4—O5	2.065 (3)
Mo1—O8	2.131 (3)	Mo4—$O3^{x}$	2.069 (3)
Mo1—$Mo2^{ix}$	2.6730 (5)	Mo4—$O1^{ix}$	2.073 (3)
Mo1—$Mo1^{ix}$	2.7322 (7)	Mo4—$O2^{xiii}$	2.098 (3)
Mo1—Mo4	2.7657 (5)	Mo4—$Mo5^{x}$	2.7389 (5)
Mo1—$Mo3^{ix}$	2.7854 (5)	Mo4—$Mo5^{ix}$	2.7644 (5)
Mo1—$Mo5^{x}$	2.7975 (5)	Mo5—$O6^{vii}$	2.038 (3)
Mo1—Mo2	2.9815 (5)	Mo5—$O5^{xiv}$	2.041 (3)
Mo1—Mo3	3.0922 (5)	Mo5—$O2^{viii}$	2.074 (3)
Mo2—O1	1.963 (3)	Mo5—$O3^{xii}$	2.075 (3)
Mo2—$O6^{vii}$	1.974 (3)	Mo5—$Mo5^{xii}$	2.8017 (6)
Mo2—$O4^{vii}$	2.038 (3)		

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

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Studies of several crystals with an approximate composition $La_{\sim 0.5}Sr_{\sim 0.5}Mo_5O_8$ revealed a *C*-centered orthorhombic cell ($a \simeq 9.934$ Å, $b \simeq 28.664$ Å, $c \simeq 9.104$ Å; reduced cell $a \simeq 9.934$ Å, $b \simeq 9.104$ Å, $c \simeq 15.176$ Å, $\beta \simeq 109.22^\circ$.). The latter cell is comparable to the cell of other AMo_5O_8 compounds by doubling of the *c* parameter. Owing to a possible La—Sr ordering, attempts were made to solve the structure in the doubled orthorhombic cell. However, no solution was found by using direct methods. Comparison of the reciprocal (010)* plane of $LaMo_5O_8$ and of $La_{\sim 0.5}Sr_{\sim 0.5}Mo_5O_8$ clearly showed that the latter crystals were twinned with a mirror plane perpendicular to *a** as twin element. Subsequently, we were able to select an untwinned single crystal of the title compound and refined the structure with the atomic coordinates of $SrMo_5O_8$ (Gall & Gougeon, 1994*a*) as starting positions. The sum of the individual site occupancies for La and Sr was constrained to unity and the occupancies refined to 0.561 (4) for La and 0.439 (4) for Sr. The highest peak and the deepest hole are located 1.28 Å from La/Sr and 0.62 Å from Mo2, respectively.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); method used to solve structure: coordinates taken from an isotypic compound; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

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