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$La_5Mo_4O_{16}$: A New Structural Type Related to Perovskite with Extremely Short Mo–Mo Bonds

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The structure of $La_5Mo_4O_{16}$ has been determined using single crystal X-ray diffraction methods. Samples, prepared by fused salt electrolysis, were found to crystallize with monoclinic symmetry, space group $C2/m$, $a = 7.9638(7)$, $b = 7.9958(5)$, $c = 10.3345(7)$ Å, $\beta = 95.067(6)°$. Atomic parameters were refined to $R = 0.031$ and $R_w = 0.034$. The structure is closely related to that of perovskite, with ReO_3-like layers parallel to (001) containing two types of MoO_6 octahedra. These layers are connected to each other through Mo_2O_{10} units, formed by two edge-sharing MoO_6 octahedra. In these units, an exceptionally short Mo–Mo distance (2.406 Å) is observed. The separation of perovskite-like layers by Mo_2O_{10} units may impart quasi-low-dimensional electronic properties to this mixed valence phase. The valence of the three independent molybdenum atoms is discussed. Lanthanum atoms are located in two different cages: La(1) is at the center of an incomplete perovskite cage with 12 oxygen atoms as nearest neighbors, while La(2) is in a cage bounded by four Mo_2O_{10} units with a distorted cubic coordination. Two of the oxygen atoms were found to be crystallographically disordered, yielding a local triclinic symmetry which through averaging becomes monoclinic.

Introduction

The synthesis of lanthanum molybdenum oxides by fused salt electrolysis (*1*) has produced a variety of low and mixed valence compounds with unusual structural and electronic properties. In addition to the Mo(IV) oxide $La_2Mo_2O_7$, an electronically low-dimensional compound which exhibits a layer structure of edge- and corner-sharing MoO_6 octahedra (*2–4*), several other members of this lanthanum molybdenum oxide family are characterized by a valence state of molybdenum less than 4. Indeed, the most highly reduced compounds reveal a rich molybdenum metal atom cluster chemistry: bioctahedral Mo_{10} clusters are observed in $LaMo_5O_8$ (*5*), Mo_8 clusters corresponding to bifaced capped Mo_6 octahedra are found in $LaMo_{7.7}O_{14}$ (*6*), and trigonal Mo_3 clusters are evidenced in the modulated structure of the hollandite type oxide $La_{1.16}Mo_8O_{16}$ (*7*).

During the investigation of the La–Mo–O system by fused salt electrolysis, another reduced phase, $La_5Mo_4O_{16}$, with a very unusual mixed valence state for molybdenum, intermediate between 4 and 5, was isolated (*1*). This paper presents the results of X-ray single crystal structure determination of this phase.

Experimental

Single crystals of the title compound were prepared by the electrolysis of a melt prepared from a mixture of sodium molybdate, molybdenum trioxide, and lanthanum sesquioxide in a molar ratio of 3.00 : 2.50 : 1.00 at 1100°C. Both electrodes were made of platinum. A porcelain crucible was used as the container for this particular batch, al-

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TABLE I

EXPERIMENTAL DATA AND STRUCTURE REFINEMENT PARAMETERS FOR $La_5Mo_4O_{16}$

Crystal shape and size	Sample bounded by {001}, {010}, and {100} forms, $176 \times 34 \times 22$ μm
Lattice parameters (T = 294K)	a = 7.9638(7), b = 7.9958(5), c = 10.3345(7) Å, β = 95.067(6)°, V = 655.5(1) Å^3
Space group	$C\,2/m$ (No 12)
D_c; Z	6.77 gcm^{-3}; 2
Data collection technique	CAD4 Enraf Nonius diffractometer
Scan mode	$\omega - \theta$
Wavelength	$\lambda MoK\alpha = 0.71069$ Å
$(\sin \theta/\lambda)_{max}$	0.995 Å^{-1}
Number of measured reflections	2914, $-15 < h < 15, 0 < k < 15, 0 < l < 20$
Number of reflections used in refinement	1539 with $I > \sigma(I)$
Absorption corrections	Based on the crystal morphology
Absorption coefficient	μ (Mo$K\alpha$) = 199 cm^{-1}
Extremal transmission factors	0.66; 0.48
Weighting scheme	Unitary
R, R_w	0.031, 0.034
$(\text{Shift/error})_{max}$	<0.01

though alumina crucibles can be used without effect. An emission spectrographic analysis of a sample prepared in a porcelain crucible showed the presence of less than 100 ppm of Si, indicating that the use of this type of crucible posed no synthetic problem. Details of the preparative method have been described elsewhere (*1*). The thin, black, plate-like crystals of $La_5Mo_4O_{16}$ were produced along with lesser amounts of $LaMo_2O_5$ and $La_3Mo_4SiO_{14}$, but because of their morphology, they are readily separated mechanically from these contaminants.

A previous X-ray diffraction study using precession photography found a triclinic cell for this compound with a = 5.64 Å, b = 5.64 Å, c = 20.70 Å, α = 93.5°, β = 86.5°, and γ = 90.0° (*1*). However, a careful study of the spot distribution on the Weissenberg photographs used in the current study reveal a monoclinic symmetry with the **a** and **b** oriented approximately 45° to the previous ones and the length of the third edge divided by 2 (Table I) with β = 95.067(6)°. For this basis, the only systematic absence observed is $h + k = 2n + 1$ for all hkl, leading to the three possible space groups $C2/m$, Cm, or $C2$. The centrosymmetric space group $C2/m$ was chosen to solve the structure from 1539 unique measure intensities with $I > 3\sigma(I)$ corrected for Lorentz, polarization, and absorption factors (Table I).

Both Patterson function analysis and direct methods were used to determine the position of the heavy atoms. Two La and three Mo, all symmetrically independent, were thus found. Seven oxygen atoms were located by difference synthesis. Successive refinement cycles of atomic parameters with anisotropic thermal coefficients for the heavy atoms led to a correct convergence with Δ/σ less than 0.01. At this stage, the fit between the observed and calculated structure factors seemed satisfactory, since the classical R values were R = 0.037 and R_w = 0.042. However, the O(6) oxygen atoms, which were confined to lie on a two-fold axis, and O(7), which lay in a mirror plane, showed abnormally high thermal B factors, 6.3(5) and 2.7(2), respectively. Conversely, the B values of the other oxygens ranged between 0.46(7) and 0.89(9). A difference synthesis performed in the surroundings of O(6) and O(7) revealed a splitting of their electron densities which removed them

TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	Site	x	y	z	B (Å)^2
La(1)	8j	0.27297(4)	0.24497(5)	0.21054(3)	0.773(4)
La(2)	2c	0	0	$\frac{1}{2}$	0.581(8)
Mo(1)	2a	0	0	0	0.59(1)
Mo(2)	2b	$\frac{1}{2}$	0	0	0.39(1)
Mo(3)	4i	0.56078(8)	0	0.39747(6)	0.324(7)
O(1)	8j	0.0375(5)	0.2630(6)	0.3585(4)	0.61(5)
O(2)	4i	0.2863(7)	$\frac{1}{2}$	0.3263(5)	0.49(7)
O(3)	4i	0.3087(7)	0	0.4314(6)	0.54(8)
O(4)	4i	0.4601(8)	0	0.1889(6)	0.57(8)
O(5)	4i	0.0729(9)	0	0.1740(7)	0.92(9)
O(6)[a,b]	8j	0.046(1)	0.250(1)	0.000(1)	1.1(1)
O(7)[b,c]	8j	0.246(1)	0.967(1)	0.9574(9)	1.1(2)

[a] Displaced from ideal site 4g (0, y, 0).

[b] Occupancy factor = 0.5.

[c] Displaced from ideal site 4i (x, 0, z).

from the above-mentioned symmetry elements. Taking these peculiarities into account, final refinements were performed ($R = 0.031$; $R_w = 0.035$) by placing O(6) and O(7) in the general position, each with an occupancy of 50%, and considering anisotropic thermal parameters for all atoms (Table II). For O(6), the final position is shifted by 0.37 Å from the twofold axis in the [100] direction, while O(7) is shifted by 0.26 Å from the mirror in the [010] direction.

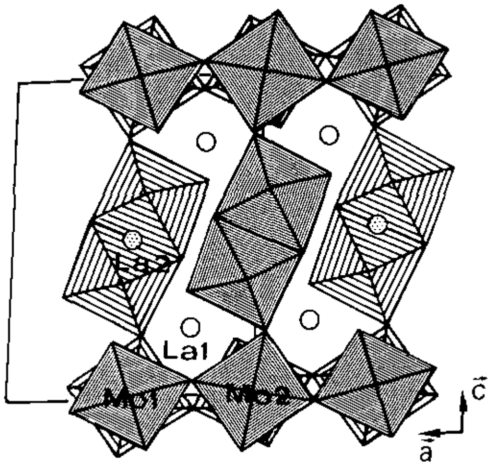

FIG. 1. Projection of the structure along [010] showing the Mo_2O_{10} clusters and their linkages to the ReO_3-like layers.

Description of the Structure and Discussion

The projection of the structure of $La_5Mo_4O_{16}$ along the [010] direction (Fig. 1) shows that the octahedral host lattice $[Mo_4O_{16}]_\infty$ forms cages where the lanthanum cations are located. The framework of corner- and edge-sharing MoO_6 octahedra is closely related to that of the perovskite structure. Indeed, it consists of distorted ReO_3-type layers parallel to (001) (Fig. 2) and connected to each other along **c** through Mo_2O_{10} units formed by two edge-sharing MoO_6 octahedra (Fig. 1).

In the ReO_3 type layers, one observes two kinds of MoO_6 octahedra, labeled Mo(1)O_6 and Mo(2)O_6, respectively. The Mo(1)O_6 octahedra exhibit two free apexes, sharing only the corners of their basal planes with four Mo(2)O_6 octahedra. The Mo(2)O_6 octahedra are linked to six other octahedra: they share their equatorial apexes with four Mo(I)O_6 octahedra in the (001) plane and their apical apexes along **c** with two Mo(3)O_6 octahedra belonging to the Mo_2O_{10} units.

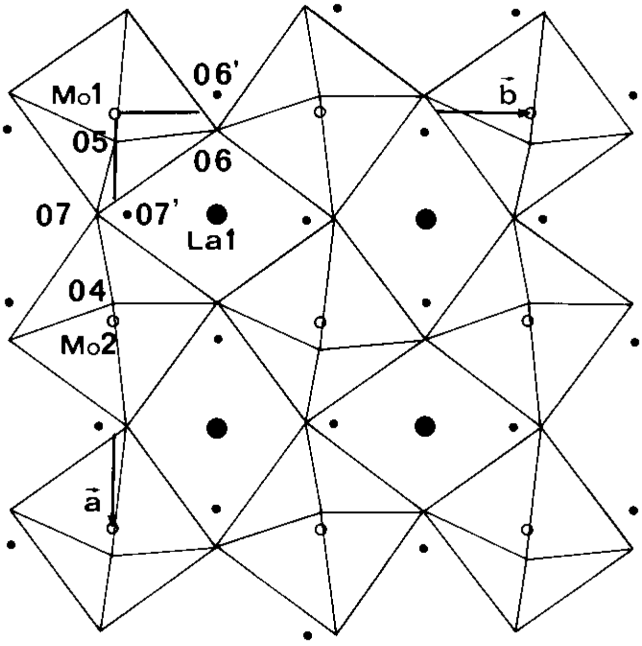

FIG. 2. A layer of the ReO_3 type. The two positions of the split atoms O(6) and O(7) are indicated. One of the two possible orientations of the MoO_6 octahedra is shown; the other is symmetrical with respect to a (010) mirror. Note that these two structural models are inverse with respect to one another.

Thus, in the ReO_3 type layers one $Mo(1)O_6$ octahedron alternates with one $Mo(2)O_6$ octahedron along both **a** and **b**.

The splitting of the O(6) and O(7) atoms, which correspond to the basal plane of the Mo(1)O6 and Mo(2)O6 octahedra, leads to a diamond-shaped configuration of the windows instead of the square ones found in the ideal ReO_3 type structure. Indeed, the simultaneous participation of the O(6) and O(7′) (or O(7) and O(6″)) in the same "O_6" octahedron would lead to unrealistically short O–O distances of 2.407(9) and 2.423(9) Å, so that we have to consider the octahedra as being built up either with O(6) and O(7) or with O(6′) or O(7′) separately. The two orientations for $Mo(1)O_6$ on the one hand and $Mo(2)O_6$ on the other hand are symmetrical with respect to the (010) mirror plane passing through the origin, since Mo(1) and Mo(2) are precisely located in the plane of the mirror, as are O(4) and O(5), which close the octahedra. Thus, the Mo–O distances are unchanged in the two orientations.

The 12 O–O edges in a $Mo(1)O_6$ octahedron range from 2.684(7) to 2.971(9) Å with a mean value of 2.802(8) Å, and in a $Mo(2)O_6$ octahedron from 2.792(7) to 2.954(9) Å, but with a mean value of 2.867(8) Å, which is significantly greater. This illustrates that the $Mo(1)O_6$ and $Mo(2)O_6$ octahedra are not identical. Indeed, both are tilted with respect to the **c** axis, but the $Mo(1)O_6$ octahedron is significantly flattened along this axis since the diagonal distance O(5)–O(5) is 3.680(9) Å while the corresponding distance O(4)–O(4) in the $Mo(2)O_6$ octahedron is 4.011(8) Å. In both octahedra, the O–Mo–O angles do not stray much from 90° since they range from 87.1(3)° to 92.9(3)°. The Mo–O distances of the $Mo(2)O_6$ octahedron, ranging from 2.005(4) to 2.046(6) Å, show that this octahedron is the most regular, in agreement with the fact that its six corners are shared with six other octahedra. In addition, the lengths of their Mo–O bonds are typical of those found for octahedrally coordinated Mo(IV). In contrast, the $Mo(1)O_6$

TABLE III

Selected Interatomic Distances

Mo(1)–O(5)	1.840(5) (×2)	La(1)–O(1)	2.526(3)
–O(6)	2.034(7) (×2)	–O(1)	2.492(3)
–O(7)	2.065(6) (×2)	–O(2)	2.362(2)
Mo(2)–O(4)	2.005(4) (×2)	–O(3)	3.002(3)
–O(6)	2.032(7) (×2)	–O(4)	2.483(3)
–O(7)	2.046(6) (×2)	–O(4)	3.212(3)
Mo(3)–O(1)	1.943(3) (×2)	–O(5)	2.532(3)
–O(2)	2.000(4)	–O(5)	3.188(4)
–O(3)	1.970(4)	–O(6)	2.699(7)
–O(3)	2.069(4)	–O(6)	2.714(7)
–O(4)	2.232(4)	–O(7)	3.425(7)
		–O(7)	2.880(7)
Mo(1)–La(1)	3.5301(2) (×4)	–O(6′)	3.200(7)
	3.5856(3) (×4)	–O(6′)	3.210(7)
Mo(2)–La(1)	3.5405(2) (×4)	–O(7′)	2.478(7)
	3.5753(3) (×4)	–O(7′)	3.108(7)
Mo(3)–La(1)	3.3649(4) (×2)		
–La(1)	3.4698(5) (×2)	La(2)–O(1)	2.594(3) (×4)
–La(1)	3.5642(1)	–O(2)	2.362(4) (×2)
–La(2)		–O(3)	2.618(4) (×2)
Mo(3)–Mo(3)	2.406(1)		

octahedron exhibits two abnormally short Mo–O distances of 1.84 Å, corresponding to the apical free apexes. This behavior can be compared to that of Mo(V).

Indeed, the recent crystallographic study of numerous molybdenum(V) phosphates (*8*) has shown that Mo(V) is off-centered in its octahedron and systematically exhibits one abnormally short Mo–O distance of 1.65 Å, characteristic of a molybenyl ion and corresponding to a free apex of a MoO_6 octahedron. In this respect, the apical Mo–O bonds of Mo(1) can be considered intermediate between that of Mo(IV) and Mo(V). Valence calculations using the empirical bond length–bond strength relationships of Brown and Wu (*9*) lead to values of 4.68 and 3.84 for Mo(1) and Mo(2), respectively. This suggests the tendency of Mo(1) to accept a higher valence close to 5, whereas Mo(2) sites would tend to be occupied by Mo(IV).

The Mo_2O_{10} units share only two corners with other $Mo(2)O_6$ octahedra, so that each $Mo(3)O_6$ octahedron exhibits three free or unshared apexes. Consequently, they are significantly distorted. The 12 O–O edges in a $Mo(3)O_6$ octahedron range from 2.618(4) to 3.245(8) Å, the latter value being relative to the common edge of two adjacent octahedra. The O–Mo–O angles have a large spread, ranging from 77.3(8)° to 106.9(1)°. The largest Mo–O distance is 2.232(4) Å (Table III) and corresponds to the O(4) oxygen shared with a $Mo(2)O_6$ octahedron. The other Mo–O distances correspond to the free apexes O(2) and O(1), and to O(3) oxygens of the O(3)–O(3) edge common to the two octahedra in Mo_2O_{10}. The Mo–O bond lengths for this group are between 1.94 and 2.07 Å and are typical of tetravalent molybdenum. This observation is supported by the bond valence calculation which leads to a value of 4.05 for Mo(3).

In orthorhombic $La_2Mo_2O_7$, Mo_2O_{10} units constitute the basic building block of the whole structure in which they share corners with identical blocks through six oxygen atoms, giving rise to Mo_2O_7 layers that are held together by La^{3+}. In both structures the Mo_2O_{10} units (Fig. 3) exhibit a striking similarity of geometry; one observes in particular a common edge of the octahedra, which is the longest O–O distance, and a very short intermetallic Mo–Mo distance, which occurs because the molybdenum atoms have moved off center toward each other in their respective octahedra.

Further, this exceptionally short Mo–Mo distance of 2.406 Å observed for $La_5Mo_4O_{16}$ is significantly shorter than that observed in $La_2Mo_2O_7$ (2.478 Å) and is, to our knowledge, the shortest Mo–Mo bond observed for molybdenum clusters in oxides. Theoretical studies of the latter compound show significant amounts of both π and ∂ contributions to the Mo–Mo bonding (*4*) and one might expect even larger contributions of these two orbital types in $La_5Mo_4O_{16}$.

The cohesion of the $[Mo_4O_{16}]_\infty$ framework is ensured by the lanthanum ions sitting in two different positions. La(1) is located at the center of an incomplete perovskite cage from which two opposite MoO_6 are absent in the same (001) plane. The distribution of the oxygen atoms which limit this perovskite-like cage are not greatly disturbed by

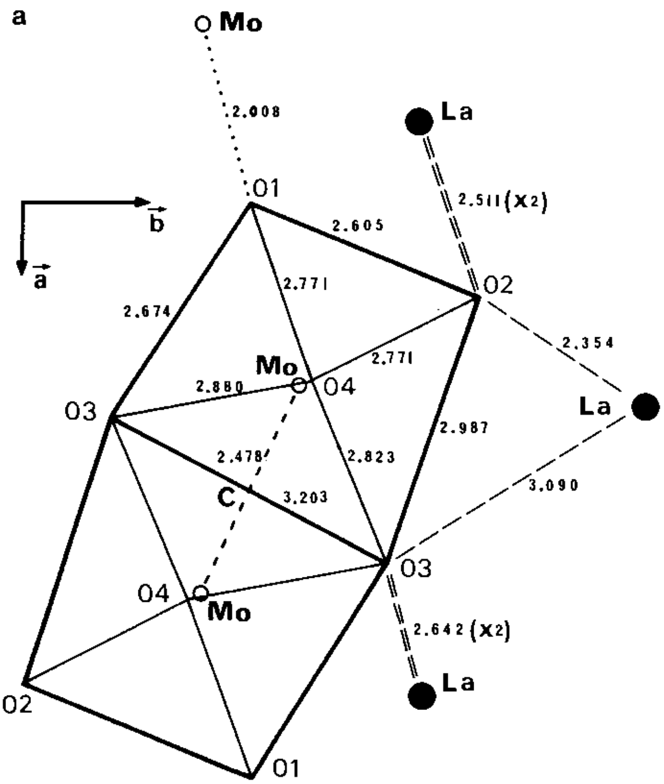

FIG. 3. Comparison of the features of the Mo_2O_{10} units in (a) $La_2Mo_2O_7$ and (b) $La_5Mo_4O_{16}$.

this absence and La(1) has 12 oxygen atoms as its nearest neighbors. However, owing to the splitting of the O(6) and O(7) sites, the La(1) atoms exhibit two slightly different 12-fold coordinations according to whether the involved couple is O(6)–O(7) or O(6′)–O(7′). Of course, both configurations occur in the same cell. Eight of the La–O distances are the same, but in the first case, two O(6) are at 2.699 and 2.714 Å from La with two O(7) at 2.880 and 3.425 Å, while in the second case, two O(6′) are at 3.200 and 3.210 Å from La and two O(7′) are at 2.478 and 3.108 Å. The bond valence calculations yield 3.08 and 3.07 respectively for the two conditions. On the other hand, La(2) sits in a cage limited by four Mo_2O_{10} units and exhibits a distorted cubic coordination, with the La–O distances ranging from 2.362 to 2.618 Å, typical of values found for eight-fold coordinate La. The calculated valence for La(2) is 2.97.

Although the structure is clearly three dimensional in a crystallographic sense, the lack of cross-linking between Mo_2O_{10} units and the long Mo(3)–O(4) distance of 2.232 Å would appear to relegate any metallic or semimetallic conductivity, which might be expected for this mixed valent compound, to the ReO_3-like layers. Indeed, the similar Mo_2O_{10} units found in $La_2Mo_2O_7$ have been predicted to be insulating in the **ab** plane by the theoretical studies of Whangbo and Canadel (*4*) which have, in part, been confirmed by experiment (*3*). We will attempt to grow more substantial crystals in the near future with a view to measuring the electrical conductivity of this compound as a function of crystallographic direction.

From a symmetry viewpoint, the most

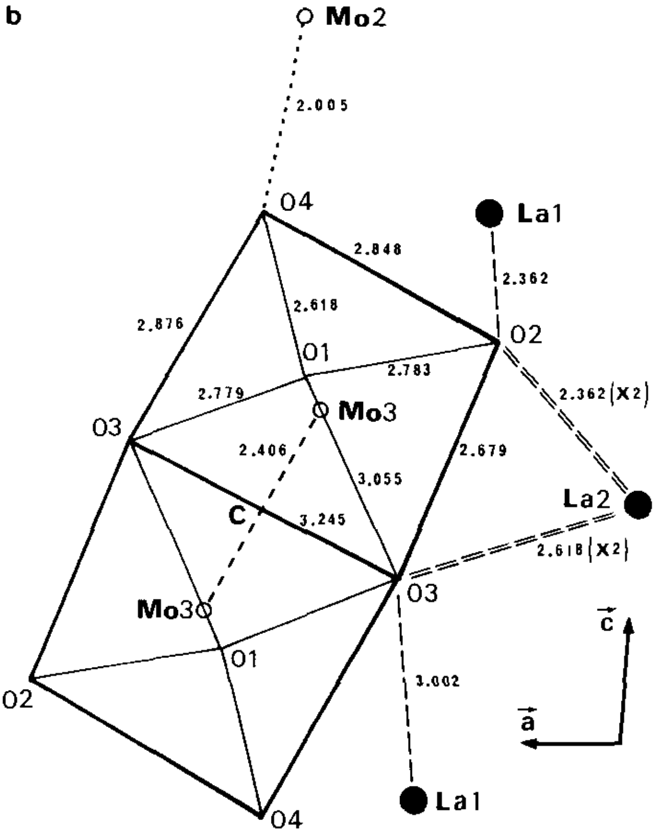

FIG. 3—*Continued*

surprising result is that all the atoms have positions according to *C2/m* except the oxygen atoms O(6) and O(7), which are split. If only O(6) did not sit on the twofold axis while O(7) sat in the mirror plane, then the *Cm* group would describe the whole structure, the splitting being due to the treatment in the centrosymmetric group. In the same manner, if only O(7) lay outside of the mirror plane while O(6) sat on the twofold axis, then the possible group would be *C2* with the same average effect. The symmetry should be monoclinic in both cases. However, the simultaneous shift of these two atoms out of the symmetrical elements leads to a structure of lower triclinic symmetry. Moreover, since for the other atoms no deviation from the positions of *C2/m* is detected within the limits of our X-ray investigation, either these positions are actual or the atomic displacements are too small to be detected. In the first case, averaging of two variants of equal probability would occur throughout the whole crystal, leading to monoclinic symmetry. In the second case, only one variant would be favored, giving rise to a triclinic structure characterized by a stressed monoclinic pseudosymmetry.

Conclusions

The structural study of $La_5Mo_4O_{16}$ has revealed a new structural type in which perovskite-like units are separated by Mo_2O_{10} units, similar to but more isolated than those found in $La_2Mo_2O_7$. This insertion may impart quasi-low-dimensional electronic properties to this mixed valence oxide, which also has the shortest Mo–Mo distance yet observed for molybdenum in oxide systems.

References

1. W. H. McCarroll, C. Darling, and G. Jakubicki, *J. Solid. State Chem.* **48,** 189 (1983).
2. A. Moini, M. A. Subramanian, A. Clearfield, F. J. DiSalvo, and W. H. McCarroll, *J. Solid State Chem.* **66,** 136 (1986).
3. B. T. Collins, M. Greenblatt, W. H. McCarroll, and G. W. Hull, *J. Solid State Chem.* **73,** 507 (1988).
4. M.-H. Whangbo and E. Canadell, *Inorg. Chem.* **26,** 842 (1987).
5. S. J. Hibble, A. K. Cheetham, A. R. L. Bogle, H. R. Wakerley, and D. E. Cox, *J. Amer. Chem. Soc.* **110,** 3295 (1988).
6. H. Leligny, M. Ledésert, Ph. Labbé, B. Raveau, and W. H. McCarroll, *J. Solid State Chem.* **87,** 35 (1990).
7. H. Leligny, Ph. Labbé, M. Ledésert, B. Raveau, C. Valdez, and W. H. McCarroll, *Acta Crystallogr. Sect. B* **48,** 134 (1992).
8. G. Costentin, Thesis, Caen, June (1992).
9. I. D. Brown and K. K. Wu, *Acta Crystallogr. Sect. B* **32,** 1957 (1976).