

Ab-Initio Determination of La₂Mo₄O₁₅ Crystal Structure from X-rays and Neutron Powder Diffraction

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Received January 4, 2001; in revised form March 22, 2001; accepted March 26, 2001

The structure of La₂Mo₄O₁₅ has been determined from both high resolution X-ray and neutron powder diffraction data. This molybdate crystallizes in a monoclinic space group $P2_1/n$ with cell parameters $a = 9.0357(2) \text{ \AA}$, $b = 12.7737(2) \text{ \AA}$, $c = 10.6408(2) \text{ \AA}$, $\beta = 90.2491(6)^\circ$. The structure consists of molybdenum octahedra [MoO₆] and tetrahedra [MoO], and lanthanum polyhedra [LaO₉]. Molybdenum polyhedra are connected together, forming large units [Mo₆O₂₂], isolated by lanthanum polyhedral chains. This structure is compared with those of already known lanthanide molybdates with formula Ln₂Mo₄O₁₅ (Ln = Ce, Ho). © 2001 Academic Press

Key Words: lanthanum; molybdate; oxide; ab-initio structural determination; coupled refinement; X-rays and neutron powder diffraction.

INTRODUCTION

The lanthanide molybdate compounds form a large family of materials with interesting physical properties. These properties depend on the crystal structures of these oxides and on the oxidation state of molybdenum. In the case of the molybdenum highest oxidation state, + VI, of interest here, one can mention for instance the ferroelectric/ferroelastic properties of Gd₂Mo₃O₁₂ (1), the unusual negative thermal expansion of Ln₂Mo₃O₁₂ (2), the catalytic properties of La₂MoO₆ (3), and our recent discovery of fast oxidation conduction in La₂Mo₂O₉ (4–6). This last finding incited us to reinvestigate the structure and properties of other compositions in the La^{III}–Mo^{VI}–O system. Among those, Alekseev *et al.* (7) pointed out the existence of an Mo-rich phase with composition La₂Mo₄O₁₅, a tetragonal symmetry with cell parameters: $a = 15.85 \text{ \AA}$, $c = 9.595 \text{ \AA}$, and up to now an unknown structure. In an attempt to prepare

this phase, we obtained for this stoichiometry a compound with a different X-ray diagram and undertook a structural determination.

EXPERIMENTAL

Synthesis

The oxide La₂Mo₄O₁₅ can be prepared from a mixture of La₂O₃ and MoO₃ in the stoichiometric proportion 1:4. The weighted powder is mixed in an agate mortar, and then placed in an alumina crucible. This crucible is heated at 570–600°C for 12 h. Attempts to increase the temperature of synthesis failed, the product being unstable above 650–675°C. The final product is white.

Structural Determination

The electron diffraction study was performed on a 200-kV side-entry JEOL 2010 electron microscope with a double-tilt specimen holder operated at room temperature.

Powder diffraction patterns were collected on X-ray and neutron diffractometers (see Table 1). The X-ray pattern was recorded on a Bragg–Brentano diffractometer (Bruker D8) and the neutron pattern on a Debye–Scherrer diffractometer (D2b instrument at the ILL, Grenoble). No absorption correction was applied to the data. For the structural determination the atomic arrangement was found through direct method analysis and Fourier syntheses, using alternatively the programs FullProf (8), ShelxS86, and ShelxL93 (9).

Crystal Symmetry

Using the indexing program TREOR (10), we were not able to find an appropriate crystal cell. The electron diffraction patterns allowed us to evidence an orthorhombic type cell, with cell parameters $a \approx 9.0 \text{ \AA}$, $b \approx 12.8 \text{ \AA}$, $c \approx 10.7 \text{ \AA}$. However, the splitting of some reflections in the high-resolution X-ray diffraction pattern could not be explained with

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TABLE 1
Condition of Acquisition of the Diffraction Patterns
of $\text{La}_2\text{Mo}_4\text{O}_{15}$ and Characteristics of the Refinement

Diffraction	Bruker-AXS D8	D2B (ILL)
Radiation	X-ray $\text{CuK}\alpha$	Neutron 1.594365 Å
2θ Range ($^\circ$)	10–120	0–160
Step-scan	0.01°	0.05°
Counting time	40 s	2 h (total)
R_{BRAGG} (%)	2.8	2.5
R_p (%)	9.7	5.4
R_{wp} (%)	11.6	6.5
R_{exp} (%)	10.9	10.9
χ^2	1.45	0.36
No. of reflections	3645	2428

such a symmetry and rather points toward a slight monoclinic distortion. This can be seen on Fig. 1, which presents a comparison of the pattern-matching fits of the X-ray diagram in both symmetries. The very small departure

($\sim 0.25^\circ$) of the monoclinic angle from 90° explains that it could not be detected on the electron diffraction patterns. However, the observed reflection conditions (see Fig. 2a), $h0l: h + l = 2n$ and $0k0: k = 2n$, suggest a monoclinic space group $P2_1/n$ (No. 14). Note that the weak $0k0$ reflections with $k = 2n + 1$ are observed in the $[100]$ E.D. pattern (Fig. 2b), due to double diffraction effects. The pattern-matching fits, computed from the X-ray data within the 2θ range $[5^\circ\text{--}60^\circ]$, in the orthorhombic $Pmmm$ (No. 59) and monoclinic $P2_1/n$ (No. 14) space groups, led to reliability factors 36.7 and 18.2%, respectively. This definitively rules out the orthorhombic symmetry.

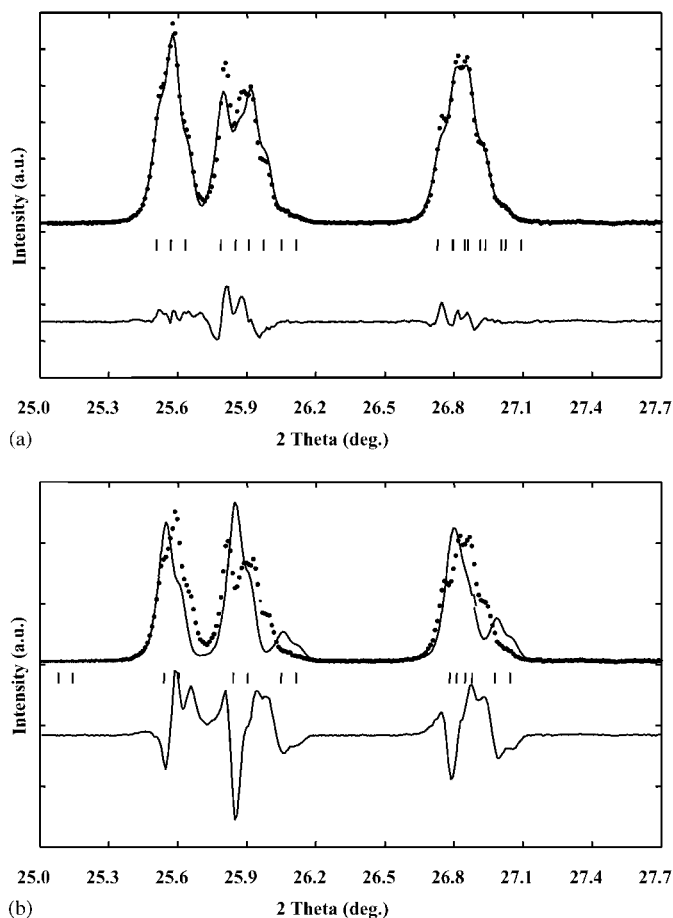


FIG. 1. Details of the pattern-matching fit, for (a) the monoclinic space group $P2_1/n$, and the orthorhombic space group $Pmmm$ (b). Observed (crosses), calculated (line), and difference (lower) patterns are shown.

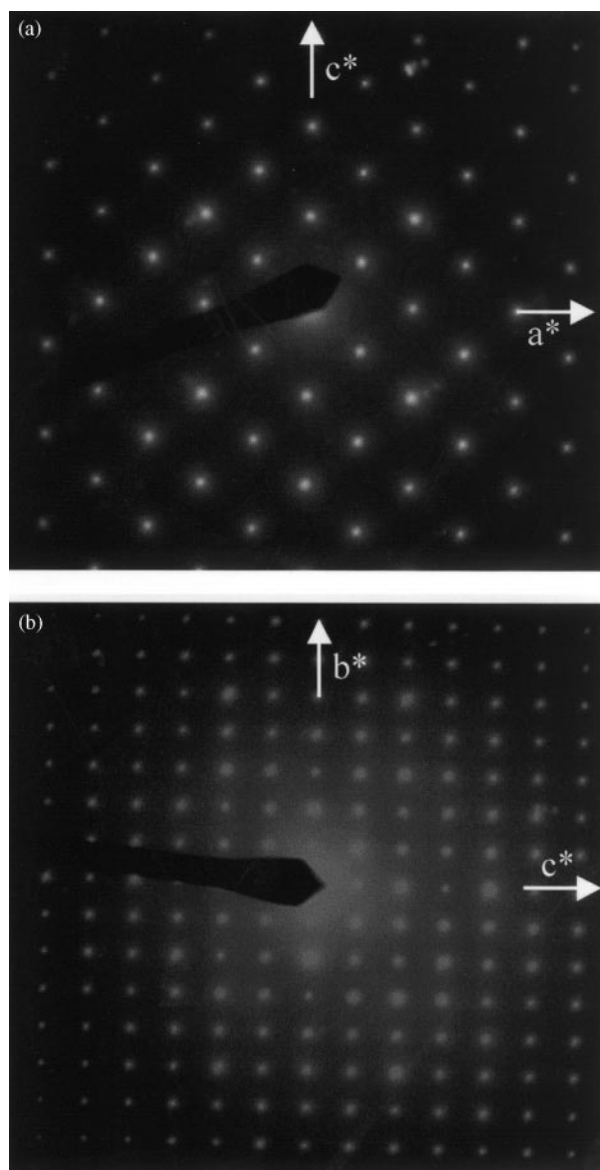


FIG. 2. Electron diffraction pattern of $\text{La}_2\text{Mo}_4\text{O}_{15}$ along $[010]^*$ (a) and $[100]^*$ (b).

Structural Determination

The *ab initio* structural determination was carried out in the monoclinic cell, space group $P2_1/n$. The cell parameters deduced from the electronic diffraction were refined from 16 peak positions in the range 10–25°, with the program UFIT (11). The cell parameters found by this procedure were: $a = 9.039(3)$ Å, $b = 12.777(3)$ Å, $c = 10.644(3)$ Å, $\beta = 90.24(2)^\circ$. Direct methods were applied to the observed intensities, as extracted by the program Fullprof (Profile Matching mode) from the X-ray diffraction pattern. The analysis of positions found by the direct methods (ShelxS86) gave a preliminary solution with four atomic sites attributed to lanthanum and molybdenum in general positions 4e: La1, La2, Mo1, and Mo2. The cation–cation distances obtained from this solution are regular (≈ 3.6 Å). The rest of the atomic sites were located after subsequent cycles of refinement and Fourier syntheses. At the final stage, all the atomic sites and the isotropic thermal factors of the heavy atoms were refined. Under these conditions the lowest R_{Bragg} reliability factor is (8.06%). In order to get a better precision on the oxygen atoms location and to decrease the number of refined parameters versus the number of observed reflections, a structural refinement was performed using both X-ray and neutron diffraction patterns, with a 50%–50% weighting scheme. The simultaneous X-ray and neutron refinement was carried out using the program Fullprof (8). The final atomic positions and refined patterns are given in Table 2 and Fig. 3, respectively.

Structure Analysis

La1 and La2 coordination polyhedra are similar in shape, as through a mirror plane (see Fig. 4), but can hardly be described as regular polyhedra. La1 is surrounded by eight oxygen atoms at distances ranging from 2.36 to 2.57 Å and a ninth oxygen atom at 3.03 Å, while La2 is surrounded by nine oxygen atoms at distances ranging from 2.41 to 2.70 Å (Table 3 and Fig. 4).

The Mo1 coordination polyhedron is an almost regular tetrahedron formed by four oxygen atoms at distances between 1.73 and 1.82 Å. The angles O–Mo1–O range from 105° to 111°. The Mo2 coordination polyhedron is also an almost regular tetrahedron with four oxygen atoms at distances ranging from 1.74 to 1.81 Å, O–Mo2–O angles are between 106.5° and 114°. The Mo3 polyhedron could at first sight be described as an almost regular tetrahedron formed by four oxygen atoms at distances from 1.71 to 1.82 Å, with O–Mo3–O angles ranging from 106° to 116°. In fact, the Mo3 polyhedron has a fifth oxygen neighbor at a much longer distance, 2.53 Å. This polyhedron can be described as a distorted trigonal bipyramid. Mo4 is the only molybdenum atom in the structure to adopt a distorted octahedral coordination formed by six oxygen atoms with distances

TABLE 2
Refined Crystallographic Parameters of $\text{La}_2\text{Mo}_4\text{O}_{15}$ at RT
Space Group: $P2_1/n$ (No. 14), $Z = 4$

Atom	Site	x	y	z	B_{iso} (Å ²)
La1	4e	0.0874(2)	0.3578(2)	0.7724(2)	0.57(5)
La2	4e	−0.3464(2)	0.3728(2)	0.7574(2)	0.62(6)
Mo1	4e	−0.1365(3)	0.3360(2)	0.0915(3)	0.61(6)
Mo2	4e	0.3741(3)	0.3446(2)	0.0605(3)	0.54(6)
Mo3	4e	−0.0747(3)	0.5902(2)	0.6006(3)	0.66(7)
Mo4	4e	0.3060(3)	0.5597(2)	0.6199(3)	0.65(7)
O1	4e	0.378(1)	0.227(1)	0.155(1)	0.8(2)
O2	4e	0.890(1)	0.488(1)	0.711(1)	0.6(2)
O3	4e	0.884(1)	0.551(1)	0.440(1)	0.8(2)
O4	4e	0.829(1)	0.453(1)	0.183(1)	1.3(2)
O5	4e	0.110(1)	0.647(1)	0.607(1)	1.0(2)
O6	4e	0.875(1)	0.366(1)	−0.075(1)	0.7(2)
O7	4e	0.807(1)	0.690(1)	0.636(1)	1.2(2)
O8	4e	0.410(1)	0.663(1)	0.677(1)	1.0(2)
O9	4e	0.349(1)	0.555(1)	0.460(1)	1.1(2)
O10	4e	0.525(1)	0.356(1)	−0.041(1)	1.4(2)
O11	4e	0.384(1)	0.446(1)	0.691(1)	0.9(2)
O12	4e	0.376(1)	0.452(1)	0.160(1)	1.4(2)
O13	4e	0.216(1)	0.351(1)	−0.034(1)	1.2(2)
O14	4e	−0.278(1)	0.247(1)	0.121(1)	1.1(2)
O15	4e	0.023(1)	0.276(1)	0.147(1)	1.3(2)

Note. Cell parameters: $a = 9.0357(2)$ Å, $b = 12.7737(2)$ Å, $c = 10.6408(2)$ Å, $\beta = 90.249(1)^\circ$.

between 1.73 and 2.44 Å, O–Mo4–O angles being distributed between 70° and 107°.

The bond valence calculations were performed using the Brown–Altermatt empirical expression: Valence = $\sum \exp(R_0 - d)/B$ with $B = 0.37$ Å (12). We have used for R_0 the values given in (13), that is $R_0 = 2.172$ Å for La^{3+}

TABLE 3
Selected Bond Distances (Å) for $\text{La}_2\text{Mo}_4\text{O}_{15}$

La1–O1	2.51(1) [× 1]	La2–O1	2.64(1) [× 1]
La1–O2	2.53(1) [× 1]	La2–O2	2.64(1) [× 1]
La1–O3	2.55(1) [× 1]	La2–O6	2.68(1) [× 1]
La1–O4	2.57(1) [× 1]	La2–O7	2.62(1) [× 1]
La1–O6	2.54(1) [× 1]	La2–O9	2.49(1) [× 1]
La1–O13	2.36(1) [× 1]	La2–O10	2.45(1) [× 1]
La1–O14	2.43(1) [× 1]	La2–O11	2.70(1) [× 1]
La1–O8	2.54(1) [× 1]	La2–O12	2.41(1) [× 1]
La1–O11	3.03(1) [× 1]	La2–O15	2.52(1) [× 1]
Mo1–O4	1.81(1) [× 1]	Mo2–O1	1.81(1) [× 1]
Mo1–O6	1.82(1) [× 1]	Mo2–O10	1.75(1) [× 1]
Mo1–O14	1.74(1) [× 1]	Mo2–O12	1.74(1) [× 1]
Mo1–O15	1.73(1) [× 1]	Mo2–O13	1.74(1) [× 1]
Mo3–O2	1.78(1) [× 1]	Mo4–O8	1.73(1) [× 1]
Mo3–O3	1.82(1) [× 1]	Mo4–O9	1.75(1) [× 1]
Mo3–O5	1.82(1) [× 1]	Mo4–O11	1.78(1) [× 1]
Mo3–O7	1.71(1) [× 1]	Mo4–O3	2.31(1) [× 1]
Mo3–O3	2.53(1) [× 1]	Mo4–O4	2.44(1) [× 1]
		Mo4–O5	2.09(1) [× 1]

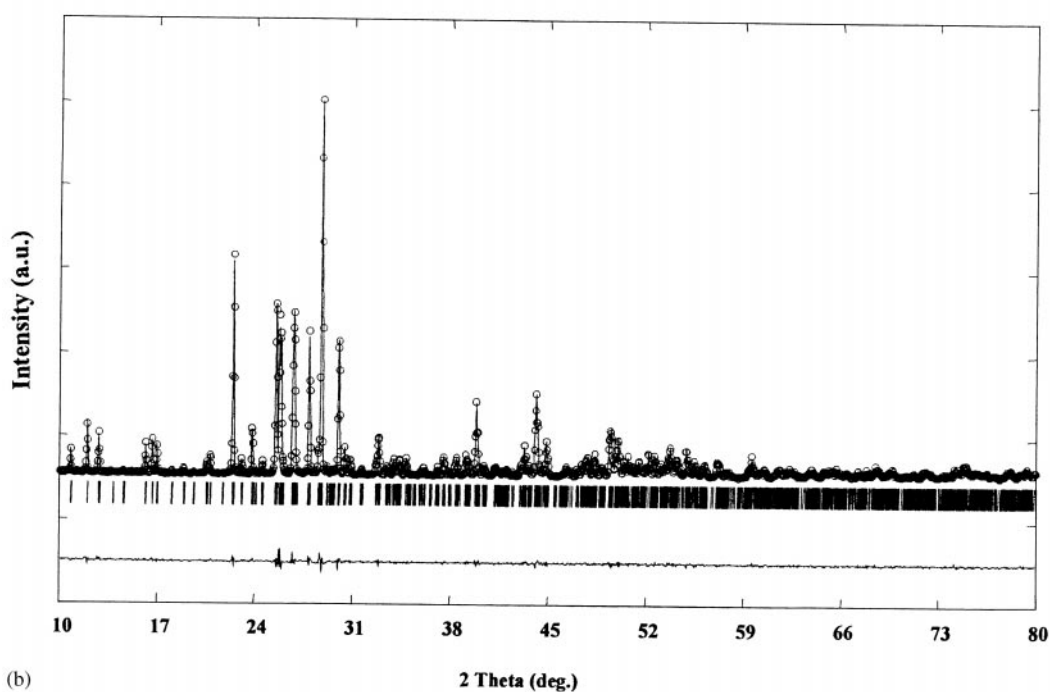
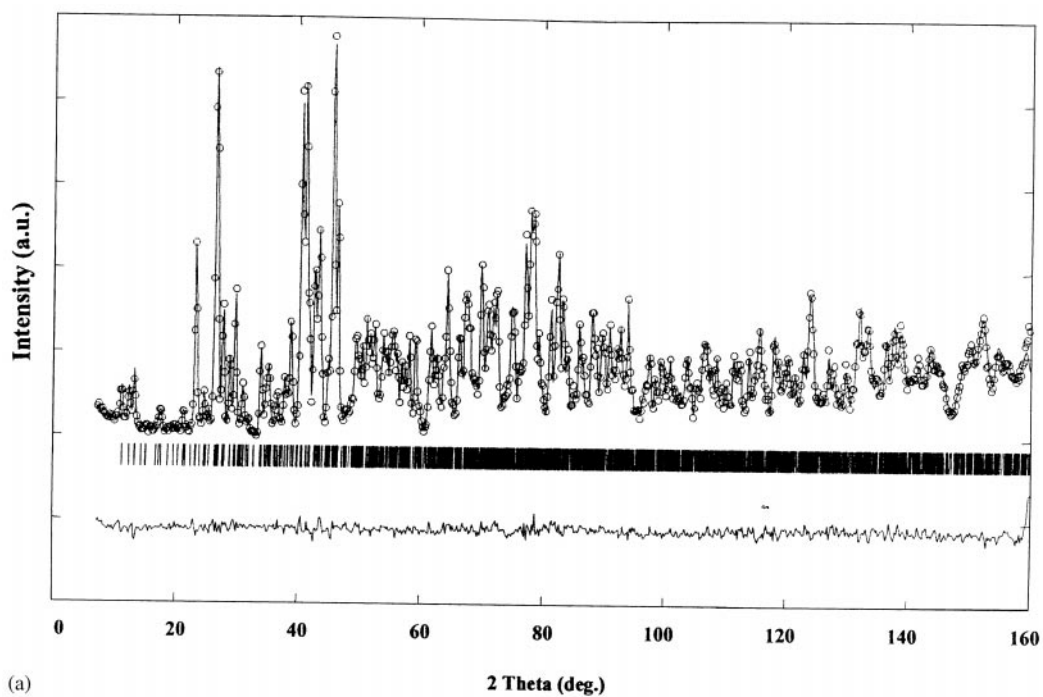


FIG. 3. Final profile refinement of $\text{La}_2\text{Mo}_4\text{O}_{15}$ for (a) the neutron pattern and (b) the X-ray pattern. Observed (crosses), calculated (line), and difference (lower) patterns are shown.

and $R_0 = 1.907 \text{ \AA}$ for Mo^{6+} . The valence calculations for the lanthanum atoms give 3.44(4) and 3.17(4) for La1 and La2, respectively, slightly in excess of the expected + 3. For the molybdenum atoms the valence calculations give 5.75(6),

5.97(6), 5.83(6), and 5.74(6) for Mo1, Mo2, Mo3, and Mo4, respectively, slightly lower than the expected + 6.

The coordination polyhedra of the different cations present some interesting features, some of them sharing one or

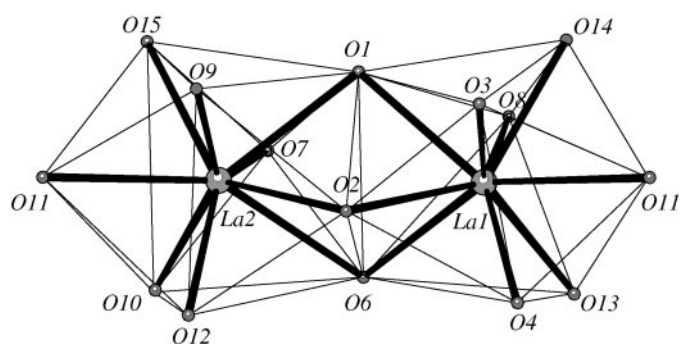


FIG. 4. Coordination polyhedra of La1 and La2 connected together by a face formed by O1, O2, and O6 and by a vertex O11.

several oxygen atoms. The lanthanum coordination polyhedra are connected together alternatively by a face formed by oxygen atoms O1, O2, and O6 and by a vertex O11 (Fig. 4). They are thus forming infinite chains of formula

$[\text{La}_2\text{O}_{14}]_\infty$ running along **a** (see Fig. 5a). The molybdenum coordination polyhedra build up a large unit of formula $[\text{Mo}_6\text{O}_{22}]$ formed by four tetrahedra (Mo3 and Mo1) and two octahedra (Mo4) (Fig. 6a). The structure of $\text{La}_2\text{Mo}_4\text{O}_{15}$ can be described by $[\text{Mo}_6\text{O}_{22}]$ units and twice as many $[\text{MoO}_4]$ isolated tetrahedra (Mo2), surrounding lanthanum files (Fig. 5). These units of tetrahedra and octahedra sharing vertices are not unusual in molybdenum oxides; for instance $\text{Na}_2\text{Mo}_2\text{O}_7$ and $\text{K}_2\text{Mo}_3\text{O}_{10}$ are given by A. F. Wells as displaying the same type of units (14). In the case of other known lanthanide molybdates $\text{Ln}_2\text{Mo}_4\text{O}_{15}$, one can point out the structures of $\text{Ho}_2\text{Mo}_4\text{O}_{15}$ (15) and $\text{Ce}_2\text{Mo}_4\text{O}_{15}$ (16). The structure of the holmium molybdate $\text{Ho}_2\text{Mo}_4\text{O}_{15}$ is built up from $[\text{Mo}_4\text{O}_{15}]$ units which are formed by two bipyramids of formula MoO_5 and two tetrahedra which share their vertices (Fig. 6b). The structure of $\text{Ce}_2\text{Mo}_4\text{O}_{15}$ can be described from infinite chains of formula $[\text{Mo}_4\text{O}_{14}]_\infty$ and isolated $[\text{MoO}_4]$ tetrahedra (Fig. 6c). These infinite chains consist of edge-sharing pairs of $[\text{MoO}_6]$ octahedra bridged by two tetrahedra.

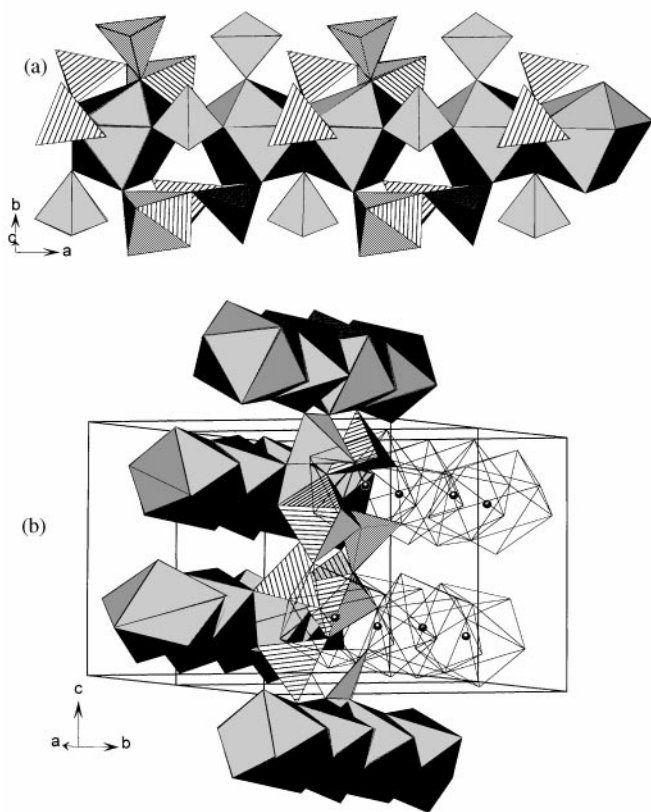


FIG. 5. Details of the $\text{La}_2\text{Mo}_4\text{O}_{15}$ structure in terms of polyhedra: (a) a $[\text{La}_2\text{O}_{14}]_\infty$ chain with its surroundings of molybdenum polyhedra; (b) a $[\text{Mo}_6\text{O}_{22}]$ unit with its surroundings of $[\text{La}_2\text{O}_{14}]_\infty$ chains (for clarity, two of them are open hatched, and La polyhedra are grayed (darker gray), as well as isolated Mo tetrahedra (light gray). The polyhedra of $[\text{Mo}_6\text{O}_{22}]$ units are hatched.

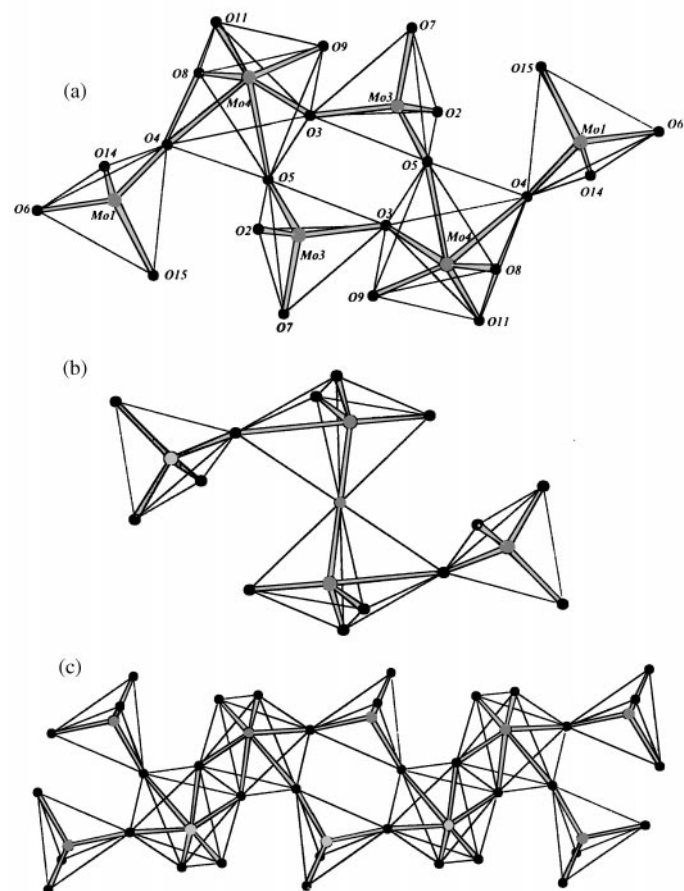


FIG. 6. Different molybdenum coordination polyhedra units observed in (a) $\text{La}_2\text{Mo}_4\text{O}_{15}$, (b) $\text{Ho}_2\text{Mo}_4\text{O}_{15}$, and (c) $\text{Ce}_2\text{Mo}_4\text{O}_{15}$.

CONCLUSION

We have investigated the complex structure of $\text{La}_2\text{Mo}_4\text{O}_{15}$ by means of a coupled refinement of X-ray and neutron powder diffraction pattern. The coupled refinement has permitted to increase the number of data in order to refine the 84 structural parameters. The structure of $\text{La}_2\text{Mo}_4\text{O}_{15}$ is built up from $[\text{Mo}_6\text{O}_{22}]$ units formed by molybdenum octahedra $[\text{MoO}_6]$ and tetrahedra $[\text{MoO}_4]$. These complex units are often present in molybdates, and the comparison of the structures of $\text{Ln}_2\text{Mo}_4\text{O}_{15}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Ho}$) shows a diversity of molybdate units: $[\text{Mo}_6\text{O}_{22}]$, $[\text{Mo}_4\text{O}_{14}]_\infty$, $[\text{Mo}_4\text{O}_{15}]$ for La, Ce, and Ho, respectively. The structural and transport properties of $\text{La}_2\text{Mo}_4\text{O}_{15}$ have been explored. The compound shows a regular thermal expansion with no phase transition up to decomposition, and it does not exhibit any oxide-ion conduction property.

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