Journal of Solid State Chemistry **159,** 223–227 (2001)
doi:10.1006/jssc.2001.9189, available online at http://www.idealibrary.com on IDEAL®

Ab Initio Structure Determination of Lanthanum Cyclo-tetratungstate α-$La_2W_2O_9$ from X-ray and Neutron Powder Diffraction

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Received January 3, 2001; in revised form March 13, 2001; accepted March 26, 2001

Lanthanum tungstate α-$La_2W_2O_9$ has been successfully synthesized by the ceramic route. Its crystal structure was determined *ab initio* from neutron diffraction data (space group $P\bar{1}$ No. 2; $a = 7.2489(1)$ Å, $b = 7.2878(1)$ Å, $c = 7.0435(1)$ Å, $\alpha = 96.367(1)°$, $\beta = 94.715(1)°$, $\gamma = 70.286(1)°$; $Z = 2$; reliability factors: $R_p = 6.0\%$, $R_{wp} = 6.9\%$, $R_B = 3.0\%$). The structure exhibits isolated $[W_4O_{18}]^{12-}$ groups in the form of rings involving $[WO_6]$ octahedra alternating with $[WO_5]$ trigonal bipyramids sharing corners. These rings are inserted in the 3D framework built by the 9- and 10-fold coordination polyhedra of the lanthanum atoms. © 2001 Academic Press

Key Words: **lanthanum; tungstate; oxide; *ab initio* structural determination; refinement from X-rays and neutron powder diffraction pattern; Monte Carlo.**

INTRODUCTION

Several previous studies on compounds with $Ln_2M_2O_9$ formulation (M = Mo with Ln = La, Sm, Tb, Er, Lu (1–7) and M = W with Ln = La, Pr, Nd, Sm, Eu, Gd (8–14) have been done. In this oxide family with lanthanum (M = Mo, W) an α of which crystal structure is unknown and a β cubic phase at low and high temperature, respectively, are evidenced. This is also the case for $Ce_2W_2O_9$. All the other compounds $Ln_2W_2O_9$ are monoclinic and crystallize in the $P2_1/c$ space group (see for instance $Pr_2W_2O_9$ (13)). The crystal structure of $Ln_2Mo_2O_9$ compounds is unknown, except for the high-temperature form β-$La_2Mo_2O_9$, whose crystal structure and interesting fast oxide-ion conduction properties were characterized (3–5). The low-temperature form α-$La_2Mo_2O_9$ exhibits a $2 \times 3 \times 4$ superstructure of the cubic form and was suspected to be monoclinic with a slight distortion (4).

We now report the chemical preparation and the crystal structure of α-$La_2W_2O_9$ which has been determined using X-ray and neutron powder diffraction.

EXPERIMENTAL

Synthesis

Elaboration of powder samples of α-$La_2W_2O_9$ was achieved by solid-state reaction from pure reagents: La_2O_3 and WO_3. La_2O_3 powder was dried at 1000°C overnight and stored in a dessicator prior to use. Appropriate amounts of each of the oxides were weighted, ground together in an agate mortar and then placed in an alumina crucible. The powder was reacted 5 days at 1100°C with several intermediate grindings. The final product is white.

Structural Characterization

The X-ray and neutron powder diffraction patterns of α-$La_2W_2O_9$ were recorded on a Bragg–Brentano X-ray diffractometer (Bruker-AXS D8) and Debye-Scherrer neutron diffractometer (ILL D2B high-resolution powder diffractometer), respectively. The details of the data collections are presented in Table 1. The atomic arrangement was determined through direct methods, Fourier syntheses, and Monte Carlo (see below), alternatively using programs FULLPROF (15), SHELXS86 (16), SHELXL93 (17), and ESPOIR 3.5 (18).

CRYSTAL STRUCTURE DETERMINATION

The reflection positions of the X-ray powder pattern were determined by means of the program EVA (available in the Socabim PC software package DIFFRAC-AT supplied by Siemens, derivative method) after stripping $K\alpha_2$. Auto-indexing was performed using the program TREOR (19), which was applied to the first 20 detected lines for α-$La_2W_2O_9$. Only one triclinic solution was found with the parameters $a = 7.238(4)$ Å, $b = 7.269(8)$ Å, $c = 7.026(3)$ Å, $\alpha = 96.45(6)°$, $\beta = 94.27(6)°$, $\gamma = 70.28(4)°$ and characterized by the conventional figures of merit $M_{20} = 24$ and $F_{20} = 39$ (0.015, 34) (20, 21).

X-ray diffraction pattern could be fitted on the basis of this triclinic cell with space group $P\bar{1}$. Direct methods were

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0022-4596/01 $35.00

TABLE 1
Conditions of X-ray and Neutron Data Collection and Confidence Factors for α-$La_2W_2O_9$

Diffractometer	Bruker AXS D8	D2B (ILL)
Radiation	X-ray Cu*K*α	Neutron 1.5939 Å
Angular range [°2θ]	10–140	10–160
Step scan increment [°2θ]	0.015	0.05
Counting time [s/step]	60	2h30 (total)
Number of reflections	1317	1366
Number of refined parameters	58	69
Peak shape	Pseudo-Voigt	Pseudo-Voigt
R_{Bragg}	11.4%	3.0%
R_{P}	15.6%	6.0%
R_{wp}	18.6%	6.9%
$R_{\mathrm{exp.}}$	6.4%	1.9%
χ^2	8.6%	1.6%

then applied to the observed intensities as extracted from the X-ray data by the program FULLPROF (Le Bail method) using SHELXS86 and allowed to locate two lanthanum and two tungsten sites. However, oxygen atoms could not be located. We first believed that the structure could be acentric, so that 18 oxygen atoms would have to be found, a very difficult task owing to their weak contribution. Indeed, no solution was obtained in the $P1$ space group. A neutron pattern was then recorded. With neutron diffraction, the weights of all atoms are similar, and moreover, the resolution is relatively poor with minimal full width at half maximum close to 0.30°(2θ), so that the direct methods failed again. Trying Fourier syntheses from the known positions of La and W did not allow the oxygen atoms location. A hypothesis of WO_4 tetrahedra was used in a program able to locate rigid-body fragments by a Monte Carlo and simulated annealing search: ESPOIR (18). The tetrahedra were rotated around the fixed W atom X-ray positions using the neutron data, whereas the La atoms were kept at fixed positions too. This was not satisfying, since it was not possible to obtain a $R_{\mathrm{P(F)}}$ factor lower than 25% ($R_{\mathrm{P(F)}}$: the calculation is made on a powder pattern generated from the structure factor amplitudes instead of the intensities). In an ultimate test, the La and W atom positions were fixed at the positions obtained from the X-ray data, and the ESPOIR program searched the 9 oxygen atoms by a random approach. A $R_{\mathrm{P(F)}} = 6.2\%$ was obtained in $P\bar{1}$ from the 150 first reflections of the neutron powder pattern, after 200,000 oxygen atom random moves (669 accepted). Drawing the structure showed that the two tungsten atom sites have different coordinations, explaining the failure of tetrahedron hypothesis. The whole neutron powder pattern was then used for refining that model by the Rietveld method, leading quickly to R Bragg $\sim 3\%$. Finally, it was understood that the X-ray pattern was affected probably by the multipreferred orientation effect, in spite of efforts to avoid it (anti-orientation sample holder, sifting through a 63-μm sieve on silicon grease). This was the reason for not finding clearly the oxygen atoms by Fourier difference synthesis from the X-ray data, and this explains the poor fit quality with high R factors in Table 1.

Refinement conditions with the corresponding reliability factors are summarized in Table I for X-ray and neutron data. The neutron diffraction pattern is given Fig. 1. The

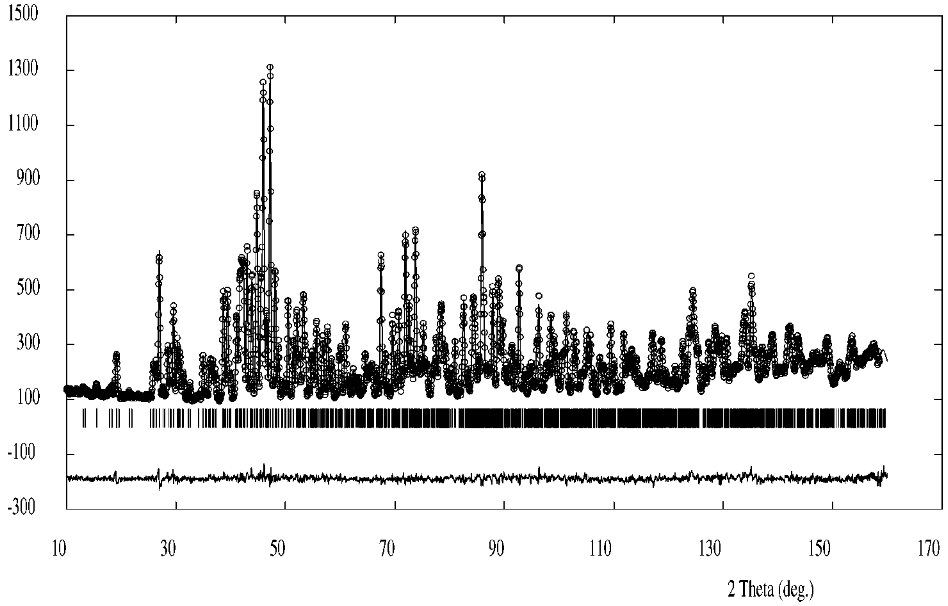

FIG. 1. Final profile refinement of α-$La_2W_2O_9$: observed (points), calculated (line), and difference (bottom) profiles for neutron diffraction data. Vertical lines are reflection positions.

TABLE 2
Cristallographic Parameters of α-$La_2W_2O_9$

	x	y	z	B_{iso} (Å^2)
La1	0.8480(3)	0.7410(3)	0.1568(3)	0.33(3)
La2	0.5837(3)	0.7297(3)	0.6258(3)	0.57(3)
W1	0.6479(4)	0.2037(5)	0.8445(5)	0.52(5)
W2	− 0.0635(4)	0.2716(4)	0.2798(4)	0.41(5)
O1	0.1900(4)	0.9065(4)	0.7250(4)	0.85(5)
O2	0.0930(4)	0.4157(4)	0.1883(4)	0.59(5)
O3	0.4630(4)	0.2918(4)	0.0204(4)	0.72(4)
O4	0.1913(4)	0.0526(4)	0.1415(4)	0.78(5)
O5	0.4738(4)	0.0969(4)	0.6830(4)	0.48(4)
O6	0.2552(4)	0.5066(4)	0.6561(4)	0.76(5)
O7	0.0942(4)	0.2237(4)	0.4919(4)	0.93(5)
O8	0.1564(4)	0.7195(4)	0.0113(4)	0.61(5)
O9	0.3510(4)	0.6481(4)	0.3426(4)	0.76(4)

Note. Space group $P\bar{1}$; $a = 7.2489(1)$ Å, $b = 7.2878(1)$, $c = 7.0435(1)$, $\alpha = 96.367(1)°$, $\beta = 94.715(1)°$, $\gamma = 70.286(1)°$; $Z = 2$.

atomic coordinates and thermal parameters refined from the neutron data are reported in Table 2. Selected interatomic distances and angles deduced from the neutron refinement are listed in Table 3.

TABLE 3
Selected Bond Distances (Å) and Bond Angles (°) for α-$La_2W_2O_9$

Tungsten polyhedra

W1	O3	O4	O5	O8	O9
O3	**1.806(4)**	3.078(4)	2.623(4)	2.759(4)	3.124(4)
O4	114.8(2)	**1.846(4)**	2.575(4)	2.584(4)	3.223(4)
O5	89.2(2)	86.0(2)	**1.929(4)**	3.800(4)	2.608(4)
O8	97.0(1)	87.8(2)	172.7(2)	**1.878(4)**	2.634(4)
O9	120.3(2)	124.5(2)	88.8(1)	81.6(2)	**1.796(5)**

W2	O1	O2	O4	O6	O7	O8
O1	**1.821(5)**	3.724(4)	2.902(4)	2.783(4)	2.822(4)	2.626(4)
O2	158.5(1)	**1.970(5)**	2.489(4)	2.692(4)	2.680(4)	2.588(4)
O4	91.7(2)	72.9(1)	**2.207(4)**	3.944(4)	2.675(4)	2.720(4)
O6	101.2(2)	91.6(2)	162.8(2)	**1.781(4)**	2.833(4)	2.805(4)
O7	102.6(2)	90.6(2)	83.2(1)	104.7(1)	**1.796(4)**	3.847(4)
O8	83.6(2)	78.7(1)	78.1(1)	91.9(1)	160.5(2)	**2.107(4)**

Lanthanum polyhedra

La1	O1	2.541(3)	La2	O1	2.818(3)
	O2	2.456(3)		O2	2.541(3)
	O2	2.573(3)		O3	2.571(3)
	O3	2.556(3)		O4	2.931(4)
	O4	2.659(3)		O5	2.517(3)
	O5	2.528(3)		O5	2.570(3)
	O6	2.675(4)		O6	2.557(3)
	O7	2.475(3)		O7	2.677(4)
	O8	2.485(4)		O9	2.653(3)
				O9	2.664(3)

Note. Standard deviations are given in parentheses.

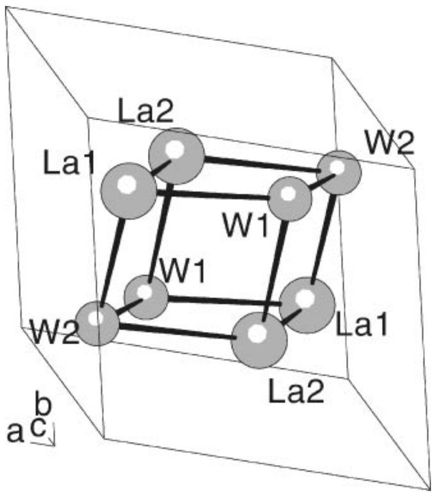

FIG. 2. The cubic cationic arrangement in α-$La_2W_2O_9$.

DISCUSSION

If we compare the cell parameters between α-$La_2W_2O_9$ ($a = 7.2489(1)$ Å, $b = 7.2878(1)$ Å, $c = 7.0435(1)$ Å, $\alpha = 96.367(1)°$, $\beta = 94.715(1)°$, $\gamma = 70.286(1)°$) and β-$La_2Mo_2O_9$ ($a = 7.2014(5)$ Å), the two structures are related: the a, b, α, and β parameters are quite close between the two structures. Only the c axis differs but is compensated by the decrease of the γ angle. A cubic arrangement for the cations is observed in the two structures (Fig. 2).

A projection of the refined structure of α-$La_2W_2O_9$ is shown in Fig. 3. W1 is surrounded by five oxygen atoms which build up a trigonal bipyramid, whereas W2 is in six-fold octahedral coordination. Two octahedra share two corners with two trigonal bipyramids in order to form

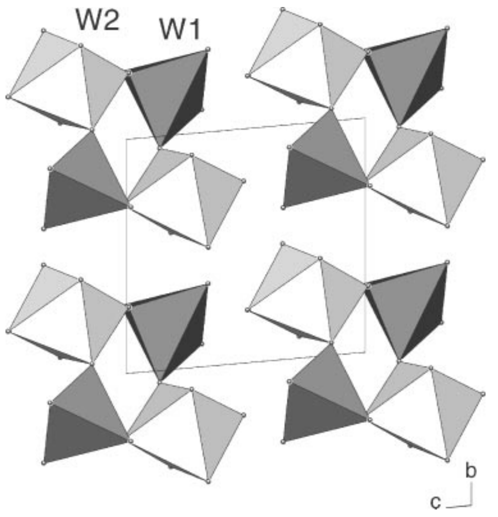

FIG. 3. Projection of the crystal structure of α-$La_2W_2O_9$.

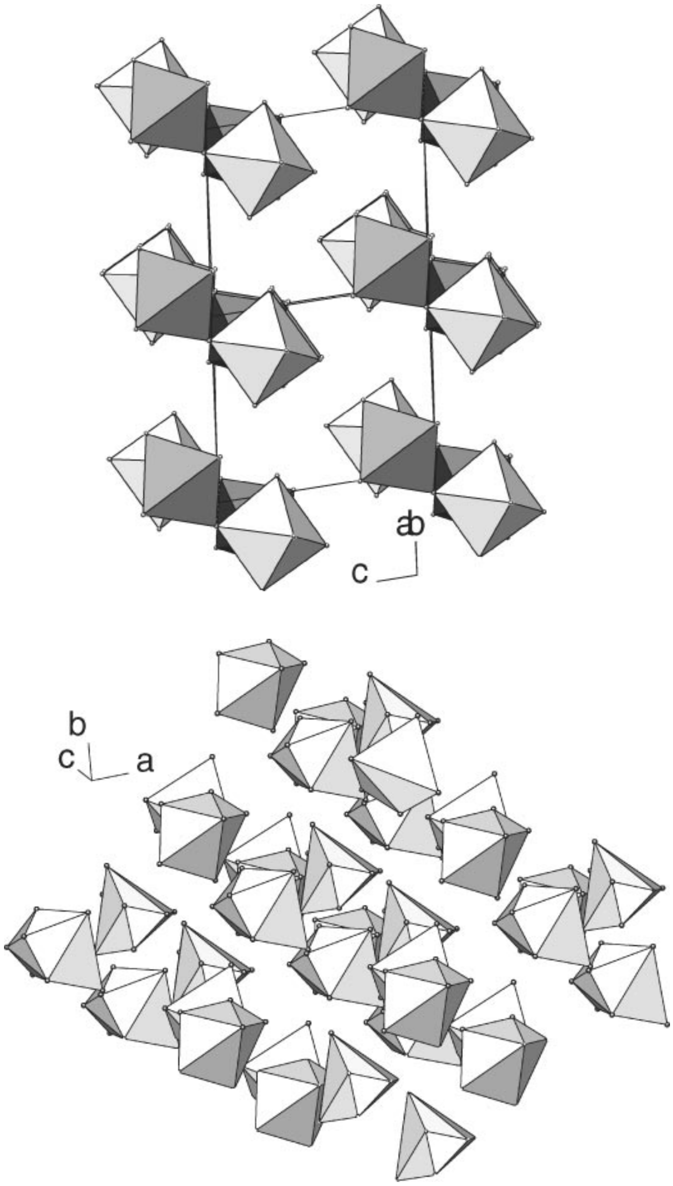

FIG. 4. Perspective views of the crystal structures of α-$La_2W_2O_9$ (top) and β-$La_2Mo_2O_9$ (bottom).

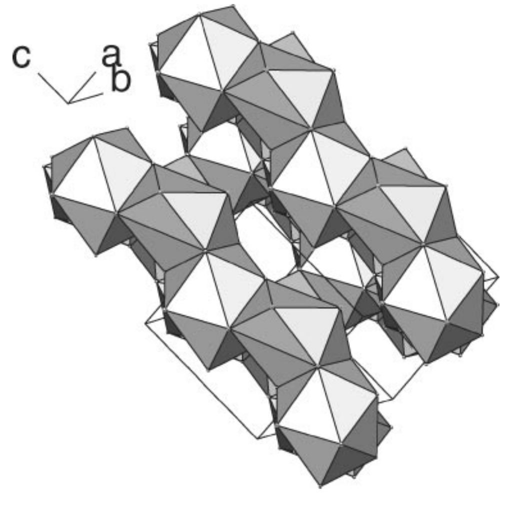

FIG. 5. The lanthanum polyhedra network.

a four-member ring with $[W_4O_{18}]^{12-}$ formulation. All the nine oxygen atom sites are involved in one isolated cluster. For the sake of comparison, in β-$La_2Mo_2O_9$ the molybdenum atom is approximatively in trigonal bipyramid surrounding with statistical occupancy for two on the three oxygen sites. These entities are isolated in β-$La_2Mo_2O_9$.

A perspective view of the structure of α-$La_2W_2O_9$ is given Fig. 4 (top). The isolated clusters could build up successive layers exactly as in β-$La_2Mo_2O_9$ (Fig. 4) (bottom) if they were connected.

The presence of $[W_4O_{18}]^{12}$ α-rings allows to described α-$La_2W_2O_9$ as a cyclo-tungstate. Cyclo-tungstates seem to be less numerous than poly-tungstates (Keggin phases). We could find a pentacesium monoammonium dodecakis (isothiocyanato) cyclo-tetratungstate (22) with tetrameric units of corner-sharing $[WO_3N_3]$ octahedra. Cyclo-fluorometallates are known with $[M_4F_{20}]^{8-}$ (M = Fe, Al) tetrameric units of octahedra connected by corners, for instance $Ba_3Al_2F_{12}$, $Pb_3Fe_2F_{12}$, $Pb_3Al_2F_{12}$ (23–25), and the transition metal pentafluorides showing neutral tetramers with two structural types, the RhF_5 type, and the MoF_5 type (26, 27). The rings may be in either a parallel or an orthogonal configuration. In α-$La_2W_2O_9$ the rings are parallel.

The two lanthanum atoms exhibit two different surrounding, respectively, with 9 and 10 oxygens. La1 is connected with all oxygen atoms except O9 and La1 with all except O8. The $La(1)O_9$ polyhedron is an acceptable tricapped trigonal prism, whereas the $La(2)O_{10}$ polyhedron is more difficult to define, it looks like a distorted cube with two capped adjacent faces. These polyhedra are connected one to each other by edges and corners to build up a three-dimensional network (Fig. 5).

ACKNOWLEDGMENT

The authors thank E. SUARD (Institut Laüe-Langevin – Grenoble) for neutron diffraction pattern measurements.

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