

## Time-of-Flight Neutron Diffraction Study of the Structure of the Perovskite-Type Oxynitride $\text{LaWO}_{0.6}\text{N}_{2.4}$

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The mixed-valence oxynitride  $\text{LaWO}_{0.6}\text{N}_{2.4}$  is a new example of a conductor with the perovskite structure. The time-of-flight neutron diffraction study has shown that this compound possesses a tetragonal symmetry (space group  $I4$ ). Oxygen and nitrogen atoms are disordered and the coordination octahedra around the tungsten atoms are tilted by  $\pm 8^\circ$  along the  $c$  axis. © 1988 Academic Press, Inc.

### Introduction

Oxynitrides of general formula  $AB(\text{O},\text{N})_3$  make up a new family of perovskites in which a great number of  $A/B$  cationic couples can exist because the sum of cationic charges can vary between +6 and +9, depending on the nitrogen content. For example, the barium/tantalum couple corresponds to  $\text{BaTaO}_2\text{N}$  (1, 2), with dielectric properties. The structural study showed it

to possess, even at very low temperature, a cubic symmetry which implies a disorder between oxygen and nitrogen atoms (3).

With the lanthanum/tungsten couple, a nitrogen-rich perovskite was obtained with the formulation  $\text{LaWO}_x\text{N}_{3-x}$ . The value of  $x$  was found by chemical analysis to lie between 0.8 and 0.6 (4); in this phase tungsten has an average oxidation state less than VI, which gives the product conduction properties (5). It was thus interesting to study the structure of this oxynitride in order to determine, in particular, the real symmetry and the existence or nonexis-

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tence of an order between oxygen and nitrogen atoms.

### Experimental

The preparation of the  $\text{LaW}(\text{O},\text{N})_3$  oxynitride is performed by nitridation of the corresponding  $\text{La}_2\text{W}_2\text{O}_9$  tungstate (4) under flowing ammonia in the temperature range 700–900°C. The chemical analysis of nitrogen in the product studied leads to the formulation  $\text{LaWO}_{0.6}\text{N}_{2.4}$ .

The X-ray diffraction powder pattern can be indexed on a cubic unit cell of parameter  $a = 3.994(1) \text{ \AA}$ ; yet, data obtained by this technique are not sufficient to give clearly the true symmetry and the anionic order. The atomic scattering factors of oxygen and of nitrogen are very close and it is not possible to differentiate between the elements with X-rays. On the other hand, by neutron diffraction, the Fermi lengths of O and N are different enough to highlight a possible order.

The neutron diffraction diagram is obtained by the time-of-flight method, using a radial beam of the Melusine 8 MW light-water reactor of the Centre d'Etudes Nucléaires de Grenoble (6). Among the advantages of this method are the very good resolution which enables the detection of very small lattice distortions and the reduced background obtained by using a statistic correlation chopper. Eventually, the refinement is made with a program of diffraction profile analysis which enables the use of a large number of reflections, even if the corresponding diffraction lines are superposed (7).

### Results and Discussion

The precise and numerous data obtained by the previously described method show that the real unit cell does not have cubic symmetry. Additional reflections appear and a systematic study leads to a body-cen-

tered tetragonal unit cell with a very small distortion which may be related to the cubic unit cell by the formula:

$$a_{\text{quad}} = a_{\text{cub}} \sqrt{2}$$

$$c_{\text{quad}} = 2a_{\text{cub}}$$

It will be shown that this distortion could not be observed by X-ray diffraction for the following two reasons:

—The distortion is very small. As a matter of fact, the values of the cubic parameters which are calculated from tetragonal parameters are respectively 3.997 and 4.004 Å, i.e., a ratio of 1.002.

—The heavy atoms La ( $Z = 57$ ) and W ( $Z = 74$ ) are in special positions in the space group with fixed coordinates, and only the atomic coordinates of nitrogen ( $Z = 7$ ) and of oxygen ( $Z = 8$ ) are unfixed. Only these atoms contribute to the superstructure reflections. In this case, Fermi lengths ( $\times 10^{12}$  cm) are as follows:

$$\text{La: } 0.83 \quad \text{N: } 0.94$$

$$\text{W: } 0.477 \quad \text{O: } 0.575.$$

For the  $\text{LaW}(\text{O},\text{N})_3$  stoichiometry, the "weight" of anions is thus greater than that of cations.

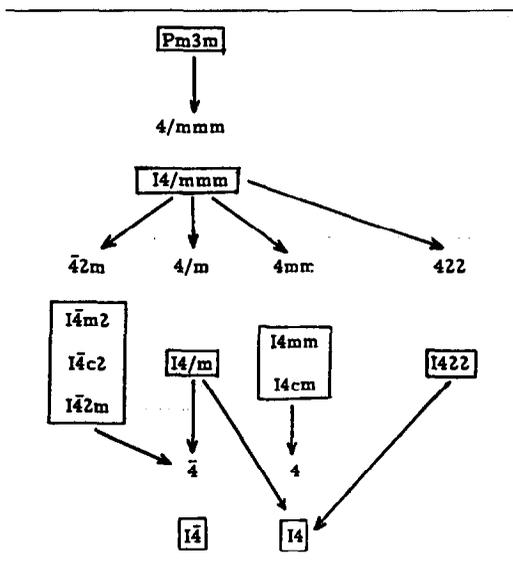
The  $\text{CaTiO}_3$  perovskite is cubic with the space group  $Pm\bar{3}m$ , the symmetry class of which is  $m\bar{3}m$ . Filiations can be derived from this symmetry class in a type I tetragonal system. Table I indicates these filiations and the corresponding space groups.

In the tetragonal unit cell, with the previously determined parameters, the number of formula units is equal to 4. Thus 4 atoms of lanthanum, 4 of tungsten, and 12 anions have to be located.

In the groups  $I4/mmm$  and  $I4/m$ , all atoms are in special positions with fixed coordinates. As a result, structure factors for additional lines are calculated to be equal to zero.

In the symmetry class 422, the anionic displacement induces differing W-(O,N)

TABLE I  
FILIIATIONS AND CORRESPONDING SPACE GROUPS  
FROM THE SYMMETRY CLASS  $m\bar{3}m$  IN A TYPE I  
TETRAGONAL SYSTEM



distances; in the symmetry class  $4mm$ , these distances are equivalent by symmetry but the values of bond angles  $(O,N)-W-(O,N)$  can deviate from  $90^\circ$ .

The existing space groups in the symmetry class  $\bar{4}2m$  are  $I\bar{4}c2$  (No. 120),  $I\bar{4}m2$  (No. 119), and  $I\bar{4}2m$  (No. 121). The positions of the different atoms in the three groups are the following:

	La	W	(O,N) <sub>4</sub>	(O,N) <sub>8</sub>
$I\bar{4}c2$				
Positions	4b	4c	4d	8e
Coordinates	0, 0, 0	$0, \frac{1}{2}, \frac{1}{4}$	$0, \frac{1}{2}, 0$	$x, x, \frac{1}{4}$
$I\bar{4}m2$				
Positions	2a-2b	2c-2d	4f	8h
Coordinates	$0, 0, 0$ $0, 0, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{4}$ $0, \frac{1}{2}, \frac{3}{4}$	$0, \frac{1}{2}, z$	$x, \frac{1}{2} + x, \frac{1}{4}$
$I\bar{4}2m$				
Positions	2a-2b	4d	4c	8i
Coordinates	$0, 0, 0$ $0, 0, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{4}$	$0, \frac{1}{2}, 0$	$x, x, z$

It is to be noted that in the group  $I\bar{4}c2$ , the only unfixed coordinate is the anionic  $x$

value. In the other two groups, the  $z$  coordinate of the anionic position 4 or 8 exists as an additional parameter. Refinement attempts performed in these groups were unsuccessful.

A lowering in symmetry leads to space group  $I\bar{4}$  according to the following positions.

	La	W	(O,N) <sub>4</sub>	(O,N) <sub>8</sub>
$I\bar{4}$				
Positions	2a-2b	2c-2d	4f	8g
Coordinates	$0, 0, 0$ $0, 0, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{4}$ $0, \frac{1}{2}, \frac{3}{4}$	$0, \frac{1}{2}, z$	$x, y, z$

With  $z(O,N)_4 \approx 0$ ,  $x(O,N)_8 \approx y(O,N)_8$ , and  $z(O,N)_8 \approx \frac{1}{4}$ .

In the previous attempts, the  $x(O,N)_8$  value was found to be close to 0.28; from this value, the four positional parameters, the anionic sites occupancy, and the isotropic thermal factors have been refined. The composition  $LaWO_{0.6}N_{2.4}$ , determined by chemical analysis, was kept constant. The final refinement was performed using 51 independent  $hkl$  planes in the range 1-3 Å. A minimum 0.0316 value of the  $R$  profile factor, the definition of which has been previously given (8), is obtained for the parameters listed in Table II.

$$a = 5.6523(6) \text{ \AA}$$

$$c = 8.0084(15) \text{ \AA}$$

Calculations show that oxygen and nitrogen atoms are disordered on sites 4f and 8g.

TABLE II  
ATOMIC PARAMETERS

Atom	Position	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
La <sub>1</sub>	2a	0	0	0	0.15 (64)
La <sub>2</sub>	2b	0	0	$\frac{1}{2}$	0.43 (69)
W <sub>1</sub>	2c	0	$\frac{1}{2}$	$\frac{1}{4}$	0.36 (12)
W <sub>2</sub>	2d	0	$\frac{1}{2}$	$\frac{3}{4}$	0.97 (18)
(O,N) <sub>4</sub>	4f	0	$\frac{1}{2}$	0.0023 (3)	0.44 (8)
(O,N) <sub>8</sub>	8g	0.2815 (3)	0.2865 (4)	0.2439 (6)	0.38 (5)

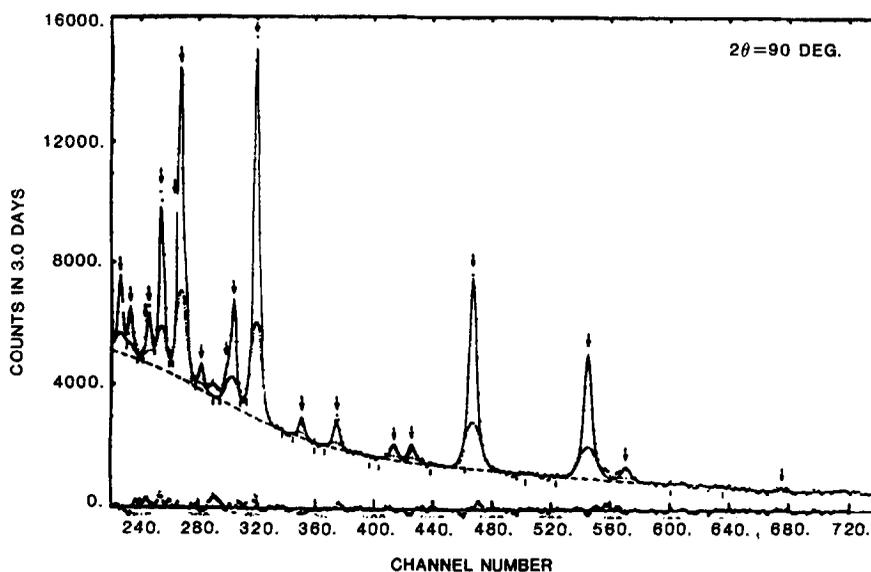


FIG. 1. Neutron diffraction diagram of  $\text{LaWO}_{0.6}\text{N}_{2.4}$ .  $\cdots$ , Observed spectrum;  $\text{---}$ , calculated spectrum;  $\text{---}$ , (along the x-axis) difference between the observed and the calculated curve. The arrows indicate the position of the diffraction lines. Each peak has been described as the sum of two Gaussians; the broken line corresponds to the broadening of the peak base.

The refinement of the occupancies gives the following results:

	O	N
Site 4f	1.47(7)	2.53(7)
Site 8g	0.93(7)	7.07(7)

Figure 1 presents the observed and calculated intensities as well as the difference spectrum of the neutron diffraction diagram. The arrows placed above the diagram indicate the position of the different  $hkl$  planes.

Figure 2 presents a perspective view of the unit cell. Tungsten atoms  $\text{W}_1$  and  $\text{W}_2$  are at the centers of O, N octahedra and the two lanthanum atoms  $\text{La}_1$  and  $\text{La}_2$  are coordinated by 12 oxygen and nitrogen atoms.

The interatomic distances (in Å) are the following:

$\text{W}_1\text{---}(\text{O,N})_4 (\times 2)$ : 1.984(2)	$\text{W}_2\text{---}(\text{O,N})_4 (\times 2)$ : 2.021(2)
$\text{W}_1\text{---}(\text{O,N})_8 (\times 4)$ : 1.997(1)	$\text{W}_2\text{---}(\text{O,N})_8 (\times 4)$ : 2.037(1)
$\text{La}_1\text{---}(\text{O,N})_4 (\times 4)$ : 2.826(0)	$\text{La}_2\text{---}(\text{O,N})_4 (\times 4)$ : 2.826(0)

$$\text{La}_1\text{---}(\text{O,N})_8 (\times 4): 2.681(3) \quad \text{La}_2\text{---}(\text{O,N})_8 (\times 4): 2.607(3)$$

$$\text{La}_1\text{---}(\text{O,N})_8 (\times 4): 2.995(3) \quad \text{La}_2\text{---}(\text{O,N})_8 (\times 4): 3.059(3)$$

The octahedral environment of tungsten atoms  $\text{W}_1$  and  $\text{W}_2$  is nearly regular. In both

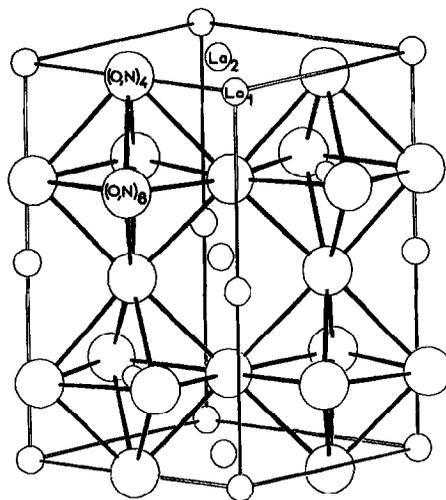


FIG. 2. Perspective view of the unit cell.

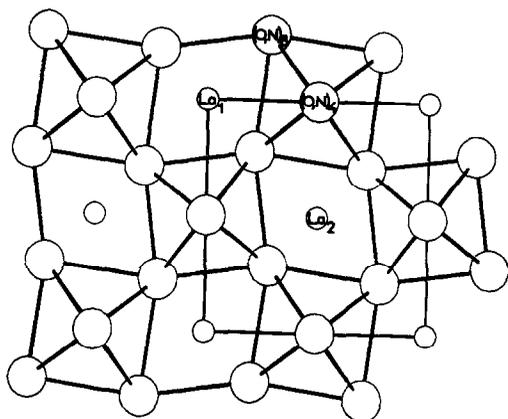


FIG. 3. Projection of the structure along  $c$ .

cases a  $W-(O,N)_4$  distance slightly shorter than the  $W-(O,N)_8$  distance can be observed. This shorter distance is in agreement with a larger O/N ratio in site 4.

The deviation of  $x$  and  $y$   $(O,N)_8$  values from the  $x = y = \frac{1}{4}$  ideal value leads to a rotation of the tungsten coordination octahedra of  $8^\circ$  along the  $c$  axis (Fig. 3). As a result, the environment of the La atoms is distorted. Four  $(O,N)_4$  atoms make up a plane around the lanthanum atoms with a  $La-(O,N)_4$  distance of 2.826 Å. The eight  $La-(O,N)_8$  distances are divided into two groups; four of them are shorter, the four others are longer than the previous  $La-(O,N)_4$  distances.

In conclusion, the neutron diffraction study enabled us to show that:

—The crystal symmetry is tetragonal and not cubic.

—Oxygen and nitrogen atoms are disordered on two positions of the space group.

—The  $W(O,N)_6$  octahedra are tilted by  $\pm 8^\circ$  along the  $c$  axis leading to  $W-(O,N)-W$  angles of  $164^\circ$ , instead of  $180^\circ$  in the cubic perovskites, perpendicular to this axis.

This structural study has been used as a basis for understanding the electrical properties of this compound (5).

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