On the Lacunar Structure of Pyrochlore-Type WO3

ALI COUCOU, ALI DRIOUICHE, MICHEL FIGLARZ,*
AND MARCEL TOUBOUL

*Laboratoire de Réactivité et de Chimie des Solides, URA CNRS 1211,
Université de Picardie, 33, rue Saint-Leu, 80039 Amiens Cedex, France*

AND GÉRARD CHEVRIER

*Laboratoire Léon Brillouin (CEA CNRS), CEN Saclay, 91191 Gif-sur-Yvette
Cedex, France*

Pyrochlore-type tungsten trioxide has been prepared by H^+/NH_4^+ exchange of ammonium pyrochlore-type tungstate. IR studies and density measurements of pyrochlore-type tungsten trioxide show the presence of H_3O^+ ions and W=O terminal groups in the oxide and an experimental density which is more than 20% lower than the calculated one. These findings have conducted us to investigate a structural lacunar model. A powder X-ray diffraction study led to a model with W and O vacancies and protons to maintain the global electroneutrality. This model has been refined by a powder neutron diffraction study, and protons have been localized in 96h sites; the best model was obtained with an $H_{0.65}W_{1.635}O_{5.23}$ formula with 18% and 13% of W and O vacancies, respectively, in comparison with stoichiometric WO_3. H and O contents can vary under thermal treatment in the temperature range 100–350°C, due to reaction of protons with O of the framework. But stoichiometric pyrochlore WO_3 can never be obtained because the reaction is complete only at about 400°C, the temperature at which the transformation pyrochlore $WO_3 \rightarrow$ monoclinic WO_3 occurs. © 1992 Academic Press, Inc.

Introduction

Over the last years several works have been published on a new form of tungsten trioxide with a pyrochlore-type structure, p.WO3 (1–5). Different preparation routes have been proposed and structural data have been obtained by X-ray studies performed on powders (1–4) or single crystals (5). They all consider the same pyrochlore W–O matrix with a WO_3 stoichiometric composition. The results thus obtained are reported in Table I.

The necessity of a more elaborate model, with the same pyrochlore W–O matrix but which takes into account tungsten and oxygen vacancies, has been pointed out by two of us (2, 7). The aim of this paper is to present the experimental evidence obtained for such a lacunar model and the results of an X-ray powder diffraction study (6) and of a neutron diffraction study which have allowed us to determine the lacunar structure of pyrochlore tungsten trioxide.

Preparation

p.WO3 preparation is done in two steps: we first prepared pyrochlore-type tung-

* To whom correspondence should be addressed.

TABLE I

Structural Data for p.WO$_3$ · 0.5H$_2$O Obtained by Different Authors Using the Hypothesis of a Stoichiometric Oxide

Ref.		A. Coucou and M. Figlarz (2)	R. Nedjar et al. (4)	J. R. Günter et al. (5)
Method		powder	powder	single crystal
a(Å)		10.270(3)	10.206(3)	10.305(3)
d_{exp}(g cm^{-3})		—	6.12	—
d_{cal}(g cm^{-3})		5.91	6.03	5.85
W	site	16c	16c	16c
	B(Å^2)	2.8	4.9	1.55(4)
O	site 48f	$x = 0.324$	$x = 0.418$	$x = 0.312$
	B(Å^2)	1	2.3	1.0(4)
O(H$_2$O)	site	8b	8a	8b
	B(Å^2)	4.9	0.5	4(2)
R		$R_I = 0.05$	$R_I = 0.07$	$R = 0.0426$
Number of reflections used in refinement		13	15	109

states which are subsequently submitted to cationic exchange in acidic aqueous solutions. Pyrochlore-type tungstates can be prepared in several different ways (2, 6, 7) but p.WO$_3$ can best be prepared from ammonium tungstate pyrochlore.

Ammonium tungstate pyrochlore is obtained by treatment of a suspension of ammonium tungstate, (NH$_4$)$_{10}$W$_{12}$O$_{41}$·5H$_2$O, in an acidic solution of ethylene glycol (2, 7). The exchange of NH$_4$ is obtained in 6N HNO$_3$ aqueous solutions; 10 successive 1-hr operations were necessary to achieve complete NH$_4$ exchange. The completely ion-exchanged samples do not show any detectable residual amount of ammonium, as determined by means of chemical analysis by Kjeldal's method. All the samples were white.

Characterization

Chemical analyses were performed on several samples of hydrated p.WO$_3$. Their tungsten content was determined by atomic absorption spectroscopy (Perkin–Elmer 3030) and water content by thermogravime-

tric analysis (Mettler TC11). The results are reported in Table II.

IR spectra (FTIR Nicolet 510) were obtained with the KBr pellet method. They show (Fig. 1) the presence of water molecules (bands at 1630 and 3500 cm^{-1}) and H$_3$O$^+$ ions (shoulders in the H$_2$O bands and bands at 2900 and 1200 cm^{-1} (8, 9)). All the stretching and bending vibration bands of W–O are present, but the unexpected result is the observation of a relatively intense and sharp vibration band at 980 cm^{-1}. This band can be assigned to W=O terminal bonds (10, 11). The existence of terminal W=O groups, which is found in all the pyrochlore-type tungstates (6), is not consistent with a complete W–O skeleton as it has been postulated in the first structural study. This

TABLE II

Analytical Characteristics of Hydrated Pyrochlore Tungsten Trioxide Used for the X-ray Diffraction Study

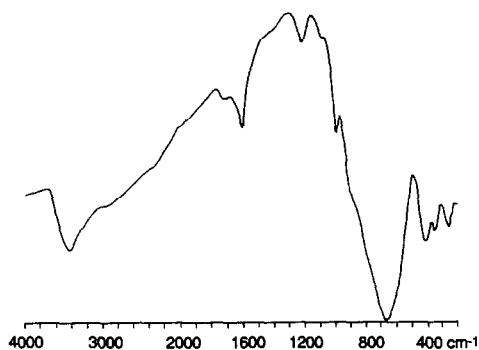| W(g%)	a(Å)	d(g cm^{-3})	$\Delta m\%$ (TG at 600°C)
72.1	10.237(2)	4.61	9.2

FIG. 1. Infrared spectrum of hydrated pyrochlore-type tungsten trioxide.

is a main argument which led us to consider a lacunar pyrochlore structure with W and eventually O vacancies. Another experimental evidence for such a lacunar structure is found in the experimental density of p.WO₃. Indeed the density, determined by Barker's method (*12*), led with reproducibility to a value of 4.61 g cm⁻³ as opposed to 5.91 g cm⁻³ calculated for stoichiometric p.WO₃.

All these results can only be interpreted if we consider a structural model with the pyrochlore W–O matrix with W and possibly O vacancies, and with protons to compensate W and O vacancies. This lacunar structural model has been studied by X-ray diffraction and neutron diffraction.

X-ray Diffraction Study

A hydrated p.WO₃ powder sample, at equilibrium with atmospheric water at room temperature and with the characteristics reported in Table II, was used for this study.

The X-ray diffraction data were collected on a PW1050 Philips diffractometer, in reflection mode, using monochromatized $CuK\alpha$ radiation and a scanning rate of 0.001° 2θ sec⁻¹. The diffracted intensities were evaluated by planimetry of peak recording.

Refinements were achieved in space group $Fd3m$. We first considered a structural model only with W vacancies (*6*). Although the refinement led to a final R-value of 0.050, this model cannot be accepted because the calculated density, 5.41 g cm⁻³, is still different from the experimental one.

The second structural model introduces both W and O vacancies. By comparison with the precursor pyrochlore ammonium tungstate (*6*) and taking into account the characteristics reported in Table II, it is then possible to write the lacunar pyrochlore tungsten trioxide as $H_2W_{1.5}O_{5.5}H_2O$. We do not differentiate here between H_2O molecules and H_3O^+ ions. The comparison between experimental and calculated values of lacunar p.WO₃ for this model shows good agreement particularly $d_{cal} = 4.53$ compared with $d_{exp} = 4.61$ g cm⁻³.

Refinements were achieved with tungsten and oxygen atoms located in the 16c and 48f sites, respectively. For the water molecules, the hydrogen atoms were not taken into account; the oxygen atoms have been located either in 8b or in 32e sites. That led to final R-values of 0.041 and 0.039, respectively, and therefore it is impossible to choose between these two hypotheses. The final parameters are listed in Table III. Comparison between observed and calculated intensities shows a good agreement (Table IV).

The small number of reflections, 13, used for the refinement compared to the number of variable parameters to refine, makes this model rather imprecise. Nevertheless this lacunar structural model with 25 and 8% vacancies for W and O, respectively, is supported by all the experimental data and can be considered as a good approximation. We have tried to go further in the structural determination by conducting a neutron diffraction study.

Neutron Diffraction Study

In order to confirm this lacunar model p.WO₃, a complementary study by neutron diffraction was performed.

TABLE III

FINAL PARAMETERS OF A STRUCTURAL MODEL WITH W AND O VACANCIES

	Site	Occ. factor	x	y	z	$B_{eq}(\text{Å}^2)$	R
W	$16c$	0.750	0	0	0	2.6(3)	
O	$48f$	0.917	0.324	$\frac{1}{8}$	$\frac{1}{8}$	3(1)	
O(H_2O, H_3O^+)	$8b$	1.000	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	12(3)	0.041
O(H_2O, H_3O^+)	$32e$	0.250	0.403	0.403	0.403	3(2)	0.039

It is well known that incoherent scattering of hydrogen leads to a high background in the neutron powder diffraction patterns of hydrated materials. Therefore, contrary to the X-ray diffraction study, we have used a dehydrated sample for the neutron diffraction study. We have shown that in p.WO$_3$, water has a zeolitic-type behavior and can be removed easily (13). In other respects, the thermal behavior study of lacunar $H_xW_yO_z$ pyrochlore oxide has shown that part of the protons can react with oxygen of the W–O matrix leading to phases of compo-

sition $H_{x-\alpha}W_yO_{z-\alpha/2}$. The α-values depend on the temperature (6). Unfortunately, it is impossible to obtain stoichiometric p.WO$_3$ by thermal treatment because this reaction is complete only at about 400°C, the temperature at which the pyrochlore W–O matrix is broken down and a new structure is reconstructed: the monotropic phase transition, lacunar p.WO$_3$ → monoclinic WO$_3$, then occurs. For the neutron diffraction study p.WO$_3$ has been heated at 300°C in air for 2 hr and at 200°C under primary vacuum for 3 hr; in order to avoid rehydration the sample was transferred in a vanadium container into a water-free glove box. We used then a lacunar pyrochlore oxide with an $H_{x'}W_yO_{z'}$ composition ($x' = x - \alpha$ and $z' = z - \alpha/2$).

The neutron diffraction patterns have been obtained with the two-axes diffractometer 3T2 of the Leon Brillouin Laboratory (Orphée Reactor, CEN Saclay) with a wavelength of 1.2268 Å, at 300 K. The data have been collected between 6 and 110° (2θ) in

TABLE IV

OBSERVED AND CALCULATED X-RAY DIFFRACTION LINE INTENSITIES FOR THE LACUNAR MODEL OF HYDRATED PYROCHLORE TUNGSTEN TRIOXIDE

hkl	I_{obs}	I_{calc}[a]
111	100.0	100.0
220	—	0.1
311	62.5	61.7
222	59.9	59.7
400	14.0	14.3
331	11.0	12.2
422	—	0.6
511–333	15.6	16.0
440	24.3	24.9
531	18.6	16.1
620	—	0.1
533	8.3	6.2
622	19.2	19.4
444	6.2	4.5
711–551	8.5	9.0
642	—	0.0
731–553	6.7	9.5

[a] H_2O located in $8b$.

TABLE V

RIETVELD ANALYSIS OF LACUNAR PYROCHLORE TUNGSTEN TRIOXIDE $H_{0.65}W_{1.635}O_{5.23}$ FROM NEUTRON DIFFRACTION STUDY

$a(\text{Å})$	10.2143(6)
u	1.023(58)
v	−0.745(49)
w	0.247(11)
η	0.868(21)
Asymmetry	0.027(4)
R_B	9.03%
R_F	6.65%

TABLE VI

POSITIONAL PARAMETERS (esd) FOR $H_{0.65}W_{1.635}O_{5.23}$ (NEUTRON DIFFRACTION STUDY)

Atom	Site	x	y	z	Occupation factor	$B(Å^2)$
W	$16c$	0.0	0.0	0.0	0.82	3.3(1)
O	$48f$	0.3113(2)	0.1250	0.1250	0.87	1.0(1)
H	$96h$	0.0	0.118(3)	0.882(3)	0.05	10.8(38)

steps of 0.05° with a counting rate of 180 sec.

Least-squares structure refinements were performed with the Rietveld analysis program DBW 3.2S (*14*). The scattering amplitudes of H, W, and O were taken as -0.3740, 0.4770, and 0.5805×10^{-12} cm, respectively.

The calculated intensities take into account the pseudo-Voïgt function, the FWHM parameters with $FWHM = u tg^2\theta + v tg\theta + w$, the assymetry for the reflection profile ($2\theta < 30°$) and cell, atomic, and anisotropic thermal parameters.

All the refinements were done in $Fd3m$ space group considering a lacunar pyrochlore of $H_{x'}W_yO_{z'}$ composition with W and O located in $16c$ and $48f$ sites, respectively. The position of the proton was tested in possible sites corresponding to its size; the best result was obtained with H in the $96h$ site. In order to determine the occupancy factors of W, O, and H several attempts were performed: first with W vacancies alone, then with W and O vacancies; but

always with a W/O/H correlation to keep global electroneutrality. The analytical characteristics (Table II) led us to consider an $H_{0.65}W_{1.635}O_{5.23}$ formula with W and O vacancies. It is with these fixed occupancy values that the best result was obtained for the final refinement (Tables V and VI). The convergence was reached with 19 free parameters with $(D/\sigma)_{max} \leq 0.03$, 85 peaks calculated and $R_B = 9.03\%$. The results obtained are listed in Tables V, VI, and VII; calculated and experimental spectra are given in Fig. 2. Calculated interatomic distances and angles are given in Table VIII.

The neutron diffraction study confirms that pyrochlore tungsten trioxide has a lacunar structure with W and O vacancies in the W–O pyrochlore framework, the global electroneutrality being maintained by the presence of protons. Compared with the X-ray diffraction study the number of data available to refine the parameters is larger and it is therefore not surprising to find different results which are definitely more precise. The W and O vacancies are found to be 18 and 13%, respectively, as opposed to

TABLE VII

ANISOTROPIC THERMAL PARAMETERS $\times 10^3$ (esd) FOR $H_{0.65}W_{1.635}O_{5.23}$ (NEUTRON DIFFRACTION STUDY)

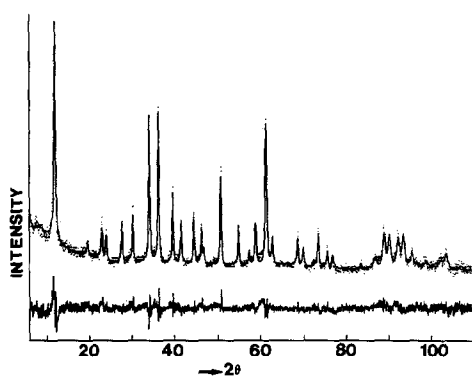|	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	7.9(4)	7.9(4)	7.9(4)	$-4.4(3)$	$-4.4(3)$	$-4.4(3)$
O	3.8(3)	1.8(1)	1.8(1)	0.0	0.0	1.8(3)
H	24(9)	27(9)	27(9)	$-32(8)$	$-32(8)$	34(9)

FIG. 2. Observed and calculated neutron powder diffraction patterns of $H_{0.65}W_{1.635}O_{5.23}$. The lower curve is the difference between observed and calculated profiles. (The list of the observed and calculated intensities may be obtained at the Laboratory).

25 and 8% obtained from the X-ray study. The calculated density inferred from the data of Tables V and VI is 4.80 compared with $d_{exp} = 4.61$ g cm^{-3}, which is quite acceptable.

It is noteworthy that J.R. Günter has tested this lacunar model using the X-ray data collected on single crystal (*15*). Indeed, by leaving the W occupancy factor free for variation in refinement, he has found 18% of W vacancies and the final *R*-value shifting from 0.0426 to 0.0406. Nevertheless he did not find any oxygen vacancies. In other respects we have prepared a rubidium pyrochlore-type tungstate by solid-state reaction between hexagonal WO_3 and rubidium carbonate with a molar ratio W/Rb = 1.5. The

study (*16*) of this pyrochlore-type tungstate leads to a lacunar model with an $Rb_{1.1}W_{1.65}O_{5.5}$ composition. In this tungstate, Rb can be exchanged by protons to obtain the corresponding lacunar $H_{1.1}W_{1.65}O_{5.5}$ oxide. The calculated W vacancies are in agreement with the results obtained from neutron diffraction on the oxide prepared by NH_4 exchange, $H_{0.65}W_{1.635}O_{5.23}$; the differences in H and O contents can be related to the different thermal treatment inducing a difference in the number of protons reacting with O of the W–O pyrochlore framework.

It is interesting to compare the calculated interatomic distances and angles in our lacunar p.WO_3 (Table VIII) and in pyrochlore $HTaWO_6$ compound studied by neutron diffraction by Groult *et al.* (*17*). These values are in good agreement except for the OH distances. Indeed, Groult *et al.* found a value of 0.90 Å compared with 1.40 Å in our case. This low value can be related to the formation of an OH bond. In our lacunar pyrochlore oxide the interaction of protons with O of the framework is different and lies between a hydroxide-type and a hydrogen bond.

Finally, it is noteworthy that the equivalent temperature factor we have found for hydrogen is rather high (Table VI); this is generally the case in X-ray (Table I) and in neutron diffraction studies (*17*).

References

1. A. COUCOU AND M. FIGLARZ, *in* "6th Int. Conf. on Solid State Ionics Garmisch-Partenkirchen, 1987," Ext. Abst., p. 607.
2. A. COUCOU AND M. FIGLARZ, *Solid State Ionics* **28–30,** 1762 (1988).
3. M. FIGLARZ, *Chem. Scr.* **28,** 3 (1988).
4. R. NEDJAR, M. M. BOREL, M. HERVIEU, AND B. RAVEAU, *Mater. Res. Bull.* **23,** 91 (1988).
5. J. R. GÜNTER, M. AMBERG, AND H. SCHMALLE, *Mater. Res. Bull.* **24,** 289 (1989).
6. A. COUCOU, Thèse, Amiens, France (1989).
7. M. FIGLARZ, *Prog. Solid State Chem.* **19,** 1 (1989).
8. R. D. GILLARD AND G. WILKINSON, *J. Chem. Soc.,* 1640 (1964).

TABLE VIII

INTERATOMIC DISTANCES (Å) AND ANGLES (°)
(NEUTRON DIFFRACTION)

W–O: 6 × 1.911(2)	O–W–O: 89.5(1), 90.5(1)
O–O: 4 × 2.691(3)	W–O–W: 141.7(1)
O–O: 4 × 2.714(3)	
W–W: 6 × 3.611(2)	
O–H: 1.404(4)	

9. P. TARTE AND M. T. PAQUES-LEDENT, *Bull. Soc. Chim.*, 1750 (1968).

10. H. J. BECKER, *J. Less-Common Met.* **76**, 169 (1980).

11. M. F. DANIEL, B. DESBAT, J. C. LASSÈGUES, B. GÉRAND, AND M. FIGLARZ, *J. Solid State Chem.* **67**, 235 (1987).

12. W. W. BARKER, *J. Appl. Crystallogr.* **5**, 433 (1972).

13. M. PIJOLAT, M. SOUSTELLE, A. COUCOU, F. PORTEMER, AND M. FIGLARZ, *J. Chim. Phys.* **87**, 1223 (1990).

14. D. B. WILES AND R. A. YOUNG, *J. Appl. Crystallogr.* **14**, 149 (1981).

15. J. R. GÜNTER, private communication.

16. A. DRIOUICHE, F. ABRAHAM, M. TOUBOUL, AND M. FIGLARZ, *Mater. Res. Bull.* **26**, 901 (1991).

17. D. GROULT, J. PANNETIER, AND B. RAVEAU, *J. Solid State Chem.* **41**, 277 (1982).