

Structure of H(D)TaO₃ Determined by Powder X-Ray and Neutron Diffraction

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Pure crystalline samples of HTaO₃ and DTaO₃ have been prepared. The crystal structure has been solved using powder X-ray and neutron diffraction (at 2 K and room temperature) and has been shown to consist of Ta(O,OH)₆ octahedra sharing vertices with the oxygen atoms displaced toward the vacant perovskite A sites. The compound is isomorphous with HNbO₃, D_xWO₃, and D_xReO₃ and contains hydrogen atoms as hydroxide groups. © 1985 Academic Press, Inc.

Introduction

The materials HNbO₃ and HTaO₃ are white crystalline solids obtained from LiNb(Ta)O₃ by ion exchange of lithium by protons (1). The ion exchange results in a structural change of the metal-oxygen framework from rhombohedral to cubic symmetry similar to those found in Li_xReO₃ (2), ZrFeF₆ (3), and possibly Li_xWO₃ (4). The structure of HNbO₃ has been investigated by Fourquet and co-workers and was found to consist of Nb(O,OH)₆ octahedra sharing vertices with the hydrogen atoms statistically distributed over two sites (5). The structure is similar to that determined for the hydrogen insertion compounds H_xWO₃ (6) and H_xReO₃ (7). Hydrogen insertion into the oxides WO₃ and ReO₃ results in a tilting of the MO₆ octahedra of the parent framework and the formation of a skutterudite structure similar to that of In(OH)₃ where all the oxygen atoms are present as

OH groups. In HNbO₃, H_xWO₃, and H_xReO₃ the degree of tilt is considerably less than in In(OH)₃ (8) since only a fraction of the possible hydrogen sites are occupied.

In the present work we have investigated the structure of HTaO₃ by means of powder X-ray diffraction. A sample of DTaO₃ was examined by powder neutron diffraction at room temperature and 2 K to determine proton positions and establish whether ordered occupancy of such sites occurred at low temperatures as had been previously postulated for HNbO₃.

Experimental Methods

Samples of HTaO₃ were prepared by ion exchange of LiTaO₃ with H₂SO₄. LiTaO₃ was prepared by heating a stoichiometric mixture of Li₂CO₃ and Ta₂O₅ at 900°C for 24 hr. A pure single phase of LiTaO₃ was shown to be present by powder X-ray diffraction. Exchange of Li⁺ with H⁺ was effected by stirring 5 g of LiTaO₃ with 9 M H₂SO₄ at 110°C for 7 days. The product was

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washed thoroughly with distilled water until no trace of acid remained and then dried at 120°C for 24 hr. Powder X-ray diffraction confirmed that exchange was complete.

DTaO₃

A sample of DTaO₃ was prepared in an identical method to that employed for HTaO₃ but using deuterated materials in a hydrogen-free glove box. A 9 M solution of D₂SO₄ was prepared by mixing conc. D₂SO₄ (Koch Light 99.7% D) with D₂O (MSD 99.7% D). The degree of deuteration was determined from the infrared spectrum of the product dispersed in a CsI disk. Measurement of the intensity of the -OH deformation band at ~1200 cm⁻¹ and comparison with the -OD deformation at 890 cm⁻¹ indicated that the effective deuteration was >96%. A sample was loaded in a thin-walled vanadium can with an indium wire gasket for the collection of neutron diffraction data.

X-Ray Diffraction

Powder X-ray diffraction data were collected using a Philips vertical diffractometer with an ARM focussing monochromator

TABLE I
HTaO₃ POWDER X-RAY CELL
REFINEMENT

<i>h k l</i>	<i>d</i> _{calc} (Å)	<i>d</i> _{obs} (Å)
2 0 0	3.8112	3.7993
2 2 0	2.6950	2.6936
3 1 0	2.4105	2.4096
2 2 2	2.2004	2.1982
3 2 1	2.0372	2.0372
4 0 0	1.9056	1.9047
4 2 0	1.7044	1.7034
4 2 2	1.5559	1.5553
4 4 0	1.3475	1.3467
4 4 2	1.2704	1.2701
6 2 0	1.2052	1.2054
6 2 2	1.1491	1.1498

TABLE II
HTaO₃ POWDER X-RAY INTENSITY
REFINEMENT

<i>h k l</i>	<i>I</i> _{obs}	<i>I</i> _{calc}
2 0 0	877	906
2 2 0	523	499
1 3 0	12.0	11.6
2 2 2	150	149
3 2 1	5.9	6.8
4 0 0	149	140
4 2 0	322	313
4 2 2	196	201
4 4 0	579	578
6 0 0 / 4 4 2	106	106
6 2 2	595	602
4 4 4	159	149
6 4 0	339	365
6 4 2	683	688

employing CuK α radiation. The pattern was indexed on a cubic unit cell with $a = 7.6225(9)$ Å, twice the value reported by Rice and Jackel. Weak lines with d spacings of 2.410 and 2.036 Å were observed in this work and were indexed as the 310 and 321 reflexions, respectively (see Table I).

The intensities of 15 peaks were measured and a full-matrix least-squares refinement carried out. A program which minimizes the quantity

$$\sum_i w_i (I_{\text{obs}} - I_{\text{calc}})^2$$

was used. The refinement included a scale factor, two temperature factors, and two oxygen positional parameters and the best fit resulted in a R_1 index of 3.23%. Table II shows the observed and calculated intensities and Table III the values of the adjustable parameters at the end of the refinement.

Powder Neutron Refinement

Neutron diffraction spectra were recorded at 300 and 2 K on D1A at the ILL,

TABLE III
POSITIONAL PARAMETERS DERIVED FROM POWDER
X-RAY INTENSITIES

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Ta	0.25	0.25	0.25	1.95(9)
O	0.0	0.222(8)	0.315(6)	3.9(1.0)

Grenoble. The incident wavelength 1.5082 Å was used (calibrated with a nickel standard) and the angular range $\theta = 6\text{--}160^\circ$ scanned in steps of 0.05° .

Room-Temperature Data

The trace showed 30 *hkl* reflexions of reasonable intensity however some of the peaks (211, 532, 611, 127, 255, 633, and 257 reflexions) were considerably broader than the remainder of the peaks. This is probably a result of the method of preparation which involves a twist along the $\langle 111 \rangle$ direction of the product (the hexagonal *c* axis of LiTaO₃) and large displacements of the oxygen atoms. Owing to the breadth of the peaks some difficulty was encountered in calculating their exact intensity and they were therefore omitted from the refinement.

The refinement was carried out using 21 peaks corresponding to 49 reflexions. The initial model was based on that given by Fourquet for HNbO₃ space group *Im*3 (No. 204 International Tables). Oxygen atoms were placed on the 24(*g*) sites and deuterium atoms statistically situated on two 24(*g*) sites corresponding to the edges of the small square of oxygen atoms formed by twisting of the TaO₆ octahedra to form the skutterudite structure. Refinement of the oxygen positional parameters resulted in the atoms being placed along the $\langle 110 \rangle$ direction on sites similar to those found in D_xWO₃. The less symmetrical distortion found in HNbO₃ at room temperature was not apparent here. The oxygen atoms were thus placed on (0, *y*, *z*) with *y* + *z* constrained to equal 0.5. The 48 deuterium

sites in the unit cell are strictly described by $24m$ D in (0, *y*₁, *z*₁) and by $24n$ D in (0, *y*₂, *z*₂) where *m* and *n* are the occupation factors for the two sets of positions. The deuterium atoms were confined to the equivalent sites with 0.5D in (0, *y*, *z*) and 0.5D in (0, 0.5 - *z*, 0.5 - *y*). Refinement of the scale factor, three positional parameters, and three isotropic temperature factors converged to give an *R*₁ of 8.5%. Relaxation of the constraints on the deuterium positions resulted in a shift in position of one of the deuterium atoms to a site slightly outside the smallest square of oxygen atoms but with a degree of deviation away from the O-O line similar to that of the other deuterium site (Fig. 1). Refinement of the scale factor, four positional parameters, and temperature factors converged to give an *R*₁ of 4.9%. Further relaxation of the constraints did not produce any significant changes to the values quoted, though a slight preference of deuterium for the (0, 0.06, 0.345) site was noted. The agreement between observed and calculated intensities is given in Table IV and the positional and thermal parameters in Table V.

2 K Data

The low-temperature profile was similar to that observed at room temperature; no new peaks were observed in contrast to the data for HNbO₃ recorded by Fourquet. The basic model used for refinement was that employed in the room-temperature study.

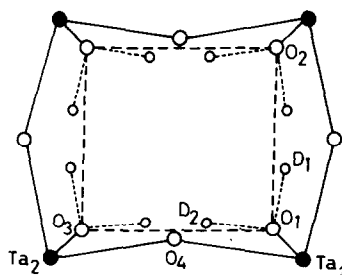


FIG. 1. The average deuterium distribution around (0, 0, $\frac{1}{2}$) at room temperature in HTaO₃.

TABLE IV
POWDER NEUTRON ROOM-TEMPERATURE
REFINEMENT

<i>h k l</i>	<i>I</i> _{calc}	<i>I</i> _{obs}
2 0 0	50.9	48.4
3 1 0	70.5	71.1
4 0 0	56.8	57.7
4 2 0	67.6	74.4
4 2 2	23.5	20.8
4 3 1 / 5 1 0	6.29	5.83
5 2 1	5.35	5.34
4 4 0	18.5	17.4
4 3 3 / 5 3 0	40.2	41.7
6 0 0 / 4 4 2	23.7	23.9
6 2 2	9.96	8.75
4 4 4	4.64	4.76
5 4 3 / 7 1 0 / 5 5 0	22.4	20.1
6 4 2	8.91	9.45
8 2 2 / 6 6 0	53.0	55.8
8 3 1 / 7 4 3 / 5 7 0	20.7	20.6
6 6 2	9.76	9.85
8 3 3 / 9 1 0	1.40	1.45
8 4 2	8.19	7.88
4 6 6	9.38	8.91
8 5 1 / 7 5 4 / 9 3 0	11.8	11.7

A small contraction of the lattice parameter was observed, $a = 7.5957 \text{ \AA}$.

Refinement of the oxygen positions without constraint resulted in a movement of the atom away from the $\langle 110 \rangle$ direction and a distortion similar to that found for HNbO₃. This results in the small square of oxygen atoms being distorted to produce a rectangle with sides measuring 2.91 and 3.13 Å. Deuterium atoms were placed on the room-temperature sites and the occupation factors allowed to vary. This resulted

TABLE V
ATOMIC PARAMETERS FOR HTaO₃ AT ROOM
TEMPERATURE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Occ.
Ta	0.25	0.25	0.25	1.5(1)	1.0
O	0.0	0.1993(5)	0.3007(5)	2.1(1)	3.0
D ₁	0.0	0.236(3)	0.440(6)	4.2(1.0)	0.5
D ₂	0.0	0.060(6)	0.345(3)	4.2(1.0)	0.5

TABLE VI
HTaO₃ POWDER NEUTRON REFINEMENT AT 2 K

<i>h k l</i>	<i>I</i> _{calc}	<i>I</i> _{obs}
2 0 0	55.9	53.6
3 1 0	90.2	89.2
4 0 0	65.2	65.9
4 2 0	86.6	87.4
4 2 2	26.3	26.0
4 4 0	20.8	22.5
4 3 3 / 5 3 0	57.1	56.5
6 0 0 / 4 4 2	33.1	30.2
6 2 2	11.8	11.0
4 4 4	4.89	5.08
5 4 3 / 7 1 0 / 5 5 0	29.4	26.7
8 2 2 / 6 6 0	72.7	72.8
7 4 3 / 7 5 0 / 8 3 1	36.3	37.8
6 6 2	15.5	14.2
8 3 3 / 9 1 0	5.82	6.00
8 4 2	15.5	10.9
6 6 4	14.8	13.8
8 5 1 / 7 5 4 / 9 3 0	19.9	18.6

in all the deuterium atoms shifting onto one site (0, 0.06, 0.34). The other site was thus removed from the refinement and the occupancy of (0, 0.06, 0.34) site fixed at 1.0. The final refinement included a scale factor, two oxygen and two deuterium positional parameters, and three isotropic temperature factors and converged to give an R_1 of 3.9%. The final calculated and observed intensities are given in Table VI and the atom parameters in Table VII.

Discussion

The tilting of the TaO₆ octahedra at RT and 2 K is similar, however at low tempera-

TABLE VII
ATOMIC PARAMETERS FOR HTaO₃ AT 2 K

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Occ.
Ta	0.25	0.25	0.25	1.04(10)	1.0
O	0.0	0.1910(9)	0.2949(11)	1.53	3.0
D	0.0	0.051(3)	0.318(3)	3.0(6)	1.0

tures the distortion lowers the symmetry of the oxygen positions and results in one shorter O–O distance. Figures 1 and 2 show a portion of the yz plane for the room-temperature and 2 K structures, respectively. A distortion resulting in nonequivalent O–O distances in the small square has been observed in HNbO_3 , $\text{In}(\text{OH})_3$, and H_xReO_3 . The result of this distortion is to remove the equivalence of the two deuterium sites. The shortest O–O distance of 2.91 Å is sufficiently low for a weak hydrogen bond to occur between the two atoms and a deuterium site between this pair of atoms becomes the position of lowest energy. Hence the sole occupancy of this site at low temperature is readily interpretable on energetic grounds. Table VIII shows some important bond lengths and angles derived from both the room- and low-temperature data. For a defect compound such as DTaO_3 these refer to the contents of the average unit cell of the crystal.

The tilt of the TaO_6 octahedra of 16° is similar to that observed in HNbO_3 (15.98°) though considerably larger than the tilt in

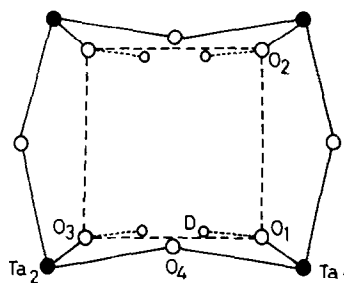


FIG. 2. The average deuterium distribution around $(0, 0, \frac{1}{2})$ at 2 K in HTaO_3 .

D_xWO_3 (11). This is probably due to the greater hydrogen content of these materials resulting in greater O–H—O interactions which tilt the octahedra. The degree of tilting in $\text{In}(\text{OH})_3$ of 22.8° is in accordance with this idea.

At room temperature the deuterium atoms are statistically attached to all the oxygen atoms as deuterioxy bonds ~ 1.10 Å long and displaced $\sim 15^\circ$ off the line to the neighboring oxygen atom. This deviation is slightly larger than found in D_xWO_3 , however fairly large deviations are observed for systems containing weak hydrogen bonds (9). The size of this deviation is in good agreement with values predicted by the work of Brown, of $\sim 16^\circ$, for the O–O distance under consideration. The displacement off the O–O line of deuterium at low temperature is only 9° and this lower value is to be expected as the result of a shortening of the O–O distance. The fairly long O–D bond length is similar to values found in other defect structures of this type and is probably due to relaxation of oxygen atoms from their average position whenever a deuterium atom is attached.

TABLE VIII

IMPORTANT BOND LENGTHS AND ANGLES

Bond distances (Å)		Bond angles (degrees)	
Room-temperature data			
O–D ₁	1.10	Ta ₁ –Ta ₂ –O ₄	16.0
O–D ₂	1.11	Ta ₁ –O ₄ –Ta ₂	148.0
Ta–Ta	3.811	O ₂ –O ₁ –D ₁	17.6
O ₁ –O ₂	3.083	O ₃ –O ₁ –D ₁	14.6
Ta–O	1.9825		
OD ₁ —O ₂	1.996		
OD ₂ —O ₃	2.005		
2 K Data			
O ₁ –D	1.08	Ta–Ta–O ₄	16.6
Ta–Ta	3.797	Ta–O ₂ –Ta	146.8
Ta–O	1.981	O ₃ –O ₁ –D	9.4
O ₁ –O ₂	3.116		
O ₁ –O ₃	2.901		
O ₁ D—O ₃	1.846		

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References

1. C. E. RICE AND J. L. JACKEL, *J. Solid State Chem.* **41**, 308 (1982).
2. R. J. CAVA, A. SANTORO, D. W. MURPHY, S. M. ZAHURAK, AND R. S. ROTH, *J. Solid State Chem.* **50**, 121 (1983).
3. J. PEBLER, D. REINEN, K. SCHMIDT, AND F. STEFFENS, *J. Solid State Chem.* **25**, 107 (1978).
4. S. J. HIBBLE, D. Phil. thesis, Oxford, 1984.
5. J. L. FOURQUET, M. F. RENOU, R. DE. PAPE, H. THEVENEAU, P. P. MAN, O. LUCAS, AND J. PANNETTIER, *Solid State Ionics* **9, 10**, 1011 (1983).
6. P. J. WISEMAN AND P. G. DICKENS, *J. Solid State Chem.* **6**, 374 (1973).
7. P. G. DICKENS AND M. T. WELLER, *J. Solid State Chem.* **48**, 407 (1983).
8. D. F. MULLICA, G. W. BEALL, W. O. MILLIGAN, J. D. KORP, AND I. BERNAL, *J. Inorg. Nucl. Chem.* **41**, 277 (1979).
9. I. D. BROWN, *Acta Crystallogr. Sect. A* **32**, 24 (1976).