The Crystal Structure of the Tetragonal Modification

of YbOOH

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A tetragonal modification of ytterbium oxide hydroxide, YbOOH, was prepared using hydrothermal techniques. The crystal structure was investigated using Patterson and Fourier functions and was refined to a conventional R value of 9.5 %. The space group is $P42_1m$ with $a = 5.465$ Å and $c = 5.327$ Å. The ytterbium atom is seven coordinated with oxygen atoms, and the structure has weak hydrogen bonds.

Ytterbium oxide hydroxide, YbOOH, and some of the other rare earth oxide hydroxides can exist in a monoclinic and in a tetragonal modification. The two modifications were prepared by hydrothermal methods. The monoclinic form [1] was prepared at 440°C at a pressure of 460 atm, and the tetragonal form [2] was prepared at 800°C at a pressure of 50 kb. In the monoclinic modification, the metal atom is seven coordinated with oxygen atoms, and the structure is not hydrogen bonded.[3] The crystal structure of the tetragonal form is reported below.

EXPERIMENTAL

The preparation of the tetragonal modification of ytterbium oxide hydroxide is reported in Ref. 2. The powder pattern of YbOOH was obtained with a Guinier camera using $FeK\alpha_1$ radiation ($\lambda = 1.9359$ Å). No internal standard was used. The intensities of the powder lines were measured using a Joyce double beam recording microdensitometer. The powder pattern listed in Table 1 was indexed using a tetragonal unit cell with $a = 5.465$ and $c = 5.327$ Å.

A flat crystal shaped as a square plate with an edge length of 0.014 cm and a thickness of approximately 0.001 cm was investigated using precession methods, and the space group $P\bar{4}2_1m$ was found.[2] A total of 163 independent hkl reflections with $I > 2\sigma(I)$ were measured with a diffractometer of the Arndt-Phillips design using $MoK\alpha$ radiation made monochromatic by reflection from a graphite crystal and using a scintillation

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Table 1. X-Ray powder pattern of tetragonal YbOOH. $a = 5.465$ Å, $c = 5.327$ Å.

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
0 0 1	5.345	5.327	14
1 0 1	3.828	3.815	9
1 1 1	3.135	3.128	100
2 0 0	2.741	2.733	43
0 0 2	2.663	2.664	11
2 1 0	2.447	2.444	6
2 0 1	2.432	2.431	2
1 2 1	2.224	2.221	9
1 1 2	2.195	2.193	21
2 2 0	1.934	1.932	21
2 0 2	1.909	1.907	22
2 2 1	1.818	1.816	4
2 1 2	1.802	1.801	8
0 0 3	1.777	1.776	4
3 0 1	1.725	1.724	12
3 1 1	1.644	1.644	31
1 1 3	1.614	1.614	7
2 2 2	1.566	1.564	7
3 2 0	1.518	1.516	1
3 0 2	1.506	1.504	1
2 0 3	1.490	1.489	8
3 2 1	1.461	1.458	11
3 1 2	1.451	1.451	11
2 1 3	1.438	1.437	2

Table 2. Atomic coordinates and temperature factors with standard deviations. Diffractometer data, 163 reflections, $R = 9.5$ %.

Atom	x	y	z	B (Å²)
Yb	0.2194(4)	0.7194(4)	0.2000(5)	0.81(4)
O_1	0.50	0.00	0.10(1)	1(1)
O_2	0.00	0.00	0.00	2(1)
O_3	0.324(6)	0.824(6)	0.59(1)	1.1(8)

Table 3. Interatomic distances (Å) and bond angles (degrees) with standard deviations. The number after the angle identifier is the number of such angles at one oxygen atom.

Bond	Å	Å × 10⁻³	Angle	Degrees	
$Yb-O_1$	2.238	(21)	$Yb-O_1-Yb$ (4)	99.8	(1.4)
$Yb-O_1$	2.314	(58)	$Yb-O_1-Yb$ (1)	94.2	(3.2)
$Yb-O_2$	2.219	(3)	$Yb-O_1-Yb$ (1)	151.2	(4.4)
$Yb-O_3$	2.228	(59)	$Yb-O_2-Yb$ (4)	103.4	(0.1)
$Yb-O_3$	2.446	(46)	$Yb-O_2-Yb$ (2)	122.6	(0.1)
			$Yb-O_3-Yb$ (2)	129.2	(2.3)
			$Yb-O_3-Yb$ (1)	87.7	(1.6)

Table 4. Observed and calculated structure factors (10 × absolute scale) and the calculated phase angles at the end of the refinement.

h k l	Fobs	Fcal	Phase	h k l	Fobs	Fcal	Phase	h k l	Fobs	Fcal	Phase	h k l	Fobs	Fcal	Phase	h k l	Fobs	Fcal	Phase
0 0 1	602	766	0	0 4 6	199	208	0	1 3 5	172	202	1	2 3 3	559	572	49	3 4 1	596	589	244
0 0 2	1236	1435	180	0 5 1	1167	967	90	1 3 6	165	772	-86	2 3 4	718	692	101	3 4 2	707	716	-30
0 0 3	1109	1426	180	0 5 2	592	543	90	1 4 0	1087	1015	0	2 3 5	289	344	181	3 4 3	624	625	25
0 0 4	321	441	0	0 5 3	591	564	270	1 4 1	431	450	22	2 3 6	302	485	258	3 4 4	456	420	118
0 0 5	1145	1416	0	0 5 4	948	881	270	1 4 2	828	867	174	2 4 0	880	919	180	3 4 5	666	542	180
0 0 6	257	290	0	0 6 0	378	367	180	1 4 3	783	781	192	2 4 1	414	418	126	3 5 0	623	575	0
0 0 7	591	728	180	0 6 1	120	147	180	1 4 4	311	340	-31	2 4 2	840	868	19	3 5 1	559	564	-78
0 1 1	403	431	90	0 6 2	428	414	0	1 4 5	804	674	-1	2 4 3	765	766	-19	3 5 2	498	497	219
0 1 3	143	221	270	0 6 3	374	353	0	1 4 6	212	261	29	2 4 4	358	354	225	3 5 3	466	456	140
0 1 4	271	369	270	0 6 4	164	149	180	1 5 0	279	255	180	2 4 5	786	676	181	3 6 0	827	785	0
0 1 6	179	225	90	0 7 1	1019	898	270	1 5 1	701	755	94	2 4 6	165	287	134	3 6 1	320	299	36
0 1 7	137	112	90	0 7 2	644	556	270	1 5 2	413	423	67	2 5 0	317	324	0	3 6 2	648	618	167
0 2 0	1973	1859	180	0 7 3	734	476	90	1 5 3	372	397	-63	2 5 1	965	968	87	3 6 3	635	591	198
0 2 1	329	335	180	1 1 0	159	148	180	1 5 4	626	594	270	2 5 2	596	590	110	3 7 0	572	468	180
0 2 2	1541	1427	0	1 1 1	1917	1751	89	1 5 5	90	122	176	2 5 3	497	488	247	3 7 1	266	220	134
0 2 3	1177	1304	0	1 1 2	1279	1258	86	1 6 0	1151	1013	180	2 5 4	784	732	-86	4 4 1	618	586	-65
0 2 4	358	398	180	1 1 3	1044	1125	-84	1 6 1	396	344	195	2 5 5	272	216	2	4 4 2	592	595	220
0 2 5	964	1230	180	1 1 4	1064	1349	-87	1 6 2	806	799	-7	2 6 0	424	437	0	4 4 3	562	567	141
0 2 6	253	289	180	1 1 6	757	1001	87	1 6 3	737	733	3	2 6 1	420	398	-60	4 4 4	504	439	70
0 2 7	507	653	0	1 1 7	472	550	85	1 6 4	300	264	172	2 6 2	363	377	216	4 4 5	475	440	2
0 3 1	1153	982	270	1 2 0	627	657	180	1 7 0	215	164	0	2 6 3	373	358	145	4 5 0	518	471	180
0 3 2	534	512	270	1 2 1	548	572	231	1 7 1	236	228	-78	2 6 4	390	300	68	4 5 1	617	587	260
0 3 3	367	355	90	1 2 2	631	671	-21	1 7 2	163	158	212	2 7 0	233	114	180	4 5 2	489	464	-47
0 3 4	775	749	90	1 2 3	547	531	9	2 2 0	1862	1807	0	2 7 1	873	765	-90	4 5 3	489	475	50
0 3 6	443	519	270	1 2 4	315	319	132	2 2 1	647	646	-18	2 7 2	525	449	-84	4 5 4	602	505	100
0 4 0	1333	1262	0	1 2 5	327	420	181	2 2 2	1116	1146	191	3 3 0	591	589	180	4 6 0	256	249	180
0 4 1	510	474	0	1 2 6	178	232	227	2 2 3	1049	1085	170	3 3 1	1026	1040	93	4 6 1	596	550	94
0 4 2	850	829	180	1 2 7	247	291	-13	2 2 4	356	385	23	3 3 2	704	700	61	4 6 2	455	412	57
0 4 3	772	788	180	1 3 0	256	259	0	2 2 5	767	1039	1	3 3 3	631	660	-58	5 5 0	751	679	180
0 4 4	286	284	0	1 3 1	1339	1408	-90	2 2 6	189	277	-28	3 3 4	837	795	268	5 5 1	360	340	123
0 4 5	856	742	0	1 3 2	827	859	264	2 3 0	545	542	180	3 3 5	254	311	180	5 5 2	588	524	22
				1 3 3	720	770	95	2 3 1	866	854	258	3 3 6	338	596	91				
				1 3 4	1088	1048	86	2 3 2	563	563	-42	3 4 0	826	804	180				

counter in conjunction with a pulse height analyzer. Lorentz-polarization corrections were applied and absorption correction was made using Wells' method.[4]

The IR spectrum of the compound was recorded over the frequency range 4000 to 400 cm⁻¹ on a Perkin-Elmer 521 spectrophotometer using a pellet of a mixture of 2 mg YbOOH and 200 mg of CsI. The spectrum had an absorption band at 3380 cm⁻¹.

STRUCTURE DETERMINATION

The space group is $P\bar{4}2_1m$ (No. 113).[2] A three dimensional Patterson function gave the position (0.22,0.72,0.20) for the ytterbium atom. A three dimensional difference Fourier map phased on this assumption gave positions of oxygen atoms at (0.5,0,0.082), (0,0,0), and (0.32,0.82,0.59). The refinement proceeded by the methods of least squares (G403),[5] using isotropic temperature factors, giving an *R*-value of 9.5 %.

CRYSTAL DATA

The compound has four formula units in the unit cell. The crystal system is tetragonal with $a = 5.465$ Å and $c = 5.327$ Å, and the space group is $P\bar{4}2_1m$. The density calculated for four formula units in the cell is 8.47 g/cm³. The absorption coefficient for Mo-radiation is 610 cm⁻¹. The structure factors for the oxygen atoms were calculated using atomic scattering factors from Vol. III of *International Tables of X-Ray Crystallography*. The structure factors for the ytterbium atoms were calculated from a table of X-ray scattering factors computed from numerical Hartree-Fock wave functions by Cromer and Mann.[6] The atomic scattering factors were approximated by Bassi[7] polynomials. Atomic coordinates and temperature factors are listed in Table 2, and inter-
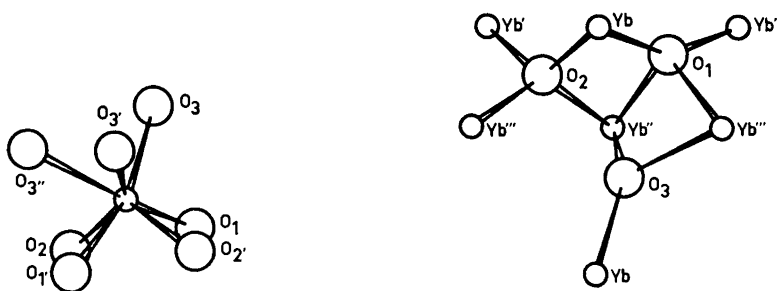
Fig. 1. YbO$_7$ coordination polyhedron.   Fig. 2. Coordination of the oxygen atoms
                                            with the ytterbium atoms.

atomic distances and bond angles in Table 3. A list of observed and calculated structure factors is shown in Table 4. Fig. 1 is a drawing of the YbO$_7$ coordination polyhedron, Fig. 2 shows the coordination of the oxygen atoms with the metal atoms, and Figs. 3 and 4 are projections of the structure. Fig. 5 is a projection of the O$_1$ coordination polyhedron on the (2,2,0) plane.

DISCUSSION

The tetragonal modification of ytterbium oxide hydroxide is a high pressure form of the compound with a density 5 % greater than that of the monoclinic form. The structure comprises YbO$_7$ polyhedra of the same type as the polyhedra found in the monoclinic modification of the rare earth oxide hydroxides,[3] but the polyhedra are, however, deformed in comparison with those. The polyhedra are packed in layers parallel to the (110) plane, and polyhedra with the same z coordinate of the ytterbium atoms are held together by corner sharing by the oxygen atoms O$_1$ and O$_2$, respectively. Polyhedra with the ytterbium atoms at the height $z = 0.20$ are held together with polyhedra with the ytterbium atoms at the height $z = -0.20$ by corner sharing by the oxygen atoms O$_3$. The oxygen atom O$_1$ is coordinated to four ytterbium atoms in a rather deformed tetrahedron which may be described also as a deformed octahedron with two *cis* positions unoccupied (Figs. 2 and 5). The oxygen atom O$_2$ is coordinated by four ytterbium atoms in a slightly deformed tetrahedron (Fig. 2), and the oxygen atom O$_3$ is coordinated with three ytterbium atoms giving a coordination polyhedron shaped as a flat triangular pyramide.

The three-coordinated oxygen atom O$_3$ has longer distances to ytterbium (average 2.373 Å) than O$_1$ (average 2.276 Å) and O$_2$ (average 2.219 Å); therefore there can be little doubt that this is the hydroxyl oxygen atom. Consideration of the geometry around O$_3$ suggests that the hydrogen atom could be at (0.22,0.72,0.70), pointing towards an O$_1$-atom 3.01 Å away from O$_3$, and thus forming a very weak hydrogen bond. The standard deviation of this distance is 0.07 Å and a distance two to three standard deviations smaller than 3.01 Å could be regarded as an O – O distance in a very weak hydrogen
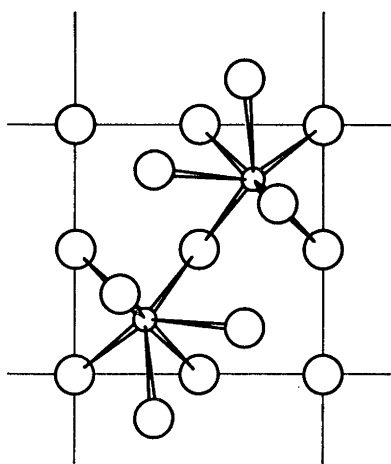
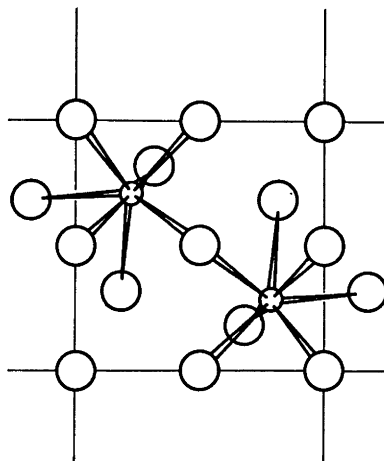Fig. 3. Projection along [001] of YbO_7 coordination polyhedra. Metal atoms are at $z = 0.200$.

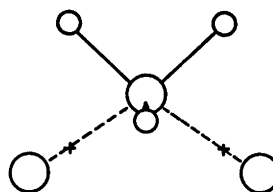Fig. 4. Projection along [001] of YbO_7 coordination polyhedra. Metal atoms are at $z = 0.800$.

Fig. 5. Projection of the O_1-coordination polyhedron on the (2,2,0) plane.

bond. The deformed octahedron around O_1 is therefore completed. Unfortunately, a difference Fourier map showed too much false detail to test this assumption.

The monoclinic modification of the rare earth oxide hydroxides is not hydrogen bonded, as all the oxygen atoms are sp^3 hybridised and the metal atoms are seven coordinated.[8] The presence of the oxygen atom O_1 in the tetragonal modification with an electron density distribution deviating from that found for sp^3 hybridised oxygen atoms makes the presence of weak hydrogen bonds possible. The absorption band at 3380 cm^{-1} in the IR spectrum also indicates the structure to contain weak hydrogen bonds. The tetragonal modification has a denser packing of the atoms than that of the monoclinic modification, and both forms have the same coordination of the metal atoms.

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