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Neutron Diffraction Study of YOOD

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Hydrothermal methods were used to prepare yttrium oxide deuteroxide, YOOD. The compound is monoclinic with two formula units in the cell. The space group is $P2_1/m$ with $a = 5.95$ Å, $b = 3.65$ Å, $c = 4.30$ Å, and $\beta = 109.1°$. The position of the deuterium atom in the structure was determined from neutron diffraction powder data. The structure is not hydrogen bonded.

Yttrium oxide hydroxide, YOOH, is monoclinic, with space group $P2_1/m$.[1,2] Each yttrium atom is coordinated with seven oxygen atoms. One set of oxygen atoms is interpreted as O^{2-} ions which are coordinated with four yttrium atoms. The average Y—O distance in this coordination is 2.27 ± 0.03 Å. Another set of oxygen atoms is interpreted as OH^- ions which are coordinated with three yttrium atoms. In this coordination the average Y—O distance is 2.41 ± 0.03 Å. The average O^{2-}—OH^- distance is 3.01 ± 0.03 Å.[1] Using the radii 1.40 Å (Pauling [3]) for O^{2-} and 1.53 Å (Wells [4]) for OH^- the radii sum is obtained as 2.93 Å. The OH^- ion is either free or is a partner in a weak hydrogen bond. The same indication is obtained from the infra-red spectrum of YOOH.[2,5] In order to determine the position of the hydrogen atom in the structure it was decided to study the structure of yttrium oxide deuteroxide, YOOD, by a neutron diffraction investigation.

EXPERIMENTAL

A powder sample of YOOD was prepared by hydrothermal methods. Yttrium trideuteroxide was precipitated from a solution of $Y(NO_3)_3$ in D_2O (99.7 %) with a solution of NaOD in D_2O. The NaOD solution was prepared by dissolving sodium metal in D_2O. The precipitate was treated with a 0.1 m NaOD solution in a pressure bomb of 99 ml, lined with pure gold. The temperature of the pressure bomb was 470°C. The pressure

was measured as 700 atm. All manipulations on compounds containing deuterium were performed in a glove-box under dry, oxygen-free nitrogen.

The X-ray powder pattern of YOOD was obtained with a Guinier camera using Cu$K\alpha_1$ radiation. All lines in the powder pattern were indexed using the unit cell of YOOH, $a = 5.95$ Å, $b = 3.65$ Å, $c = 4.30$ Å, $\beta = 109.1°$.[1]

Neutron diffraction powder patterns of YOOD were obtained by a neutron diffractometer at the Swedish Research Council's Laboratory, Studsvik, using 1.07 Å neutrons. The sample was kept in a cylindrical aluminium container of 20 mm diameter. From the recorded powder patterns the intensities were obtained by measuring the areas under the peaks. The intensities were corrected for the contribution of the aluminium reflection 200 from the container. Six consecutive powder patterns were recorded, and the intensities used in the structure calculation are obtained as an average of the six measurements. Peaks with a height above the background less than half of the intensity of the background were not used in the calculations. Eight peaks were used in the calculation of the structure. Due to serious overlapping only three of them corresponded to single reflections.

STRUCTURE DETERMINATION AND CRYSTAL DATA

In the structure of YOOD the yttrium atom and the oxygen atoms are in the special positions (x, 0.75, z). The coordinates of the atoms obtained from the X-ray investigation[1] are given in Table 1. Assuming an O—D distance of 1.0 Å and a D—D distance of 2.4 Å, which is the van der Waals diameter of a hydrogen atom, the possible coordinates (0.42, 0.75, 0.82) or (0.63, 0.75, 1.00) for the deuterium atom are obtained. The first case gives a rather unusual coordination of the oxygen atom in the OD-group, the second case gives a more likely coordination. The relative intensity values were computed for the two trial structures. Table 2 gives the intensities I_a and I_b calculated for the trial structures with the deuterium coordinates (0.42, 0.75, 0.82) and (0.63, 0.75, 1.00), respectively, and the observed intensities. A comparison showed that the structure with the deuterium atom at (0.63, 0.75, 1.00) was basically correct.

Table 1. Atomic coordinates and temperature factors.

Atom	x	σx	y	z	σz	B (Å²)	σB (Å²)
Y	0.1898	0.0004	0.75	0.3314	0.0006	0.3	0.1
O	0.065	0.004	0.75	0.770	0.005	0.8	0.8
O	0.566	0.004	0.75	0.755	0.006	1.0	0.8
D	0.643	0.007	0.75	0.989	0.007	5	1

The number of parameters in the structure is 13, namely, one scale factor, the isotropic temperature factors, and the x and z parameter of the four atoms. To limit the number of parameters to be varied in the structure calculation, only four parameters were used, the scale factor, the isotropic temperature factor, and the x and z parameters of the deuterium atom. The isotropic temperature factors for the yttrium atom and for the oxygen atoms were calculated from the anisotropic vibration parameters reported in Ref. 1,

and the temperature factor for the deuterium atom was chosen as 4.5. The structure was refined by using an iterative procedure. Using the calculated structure factors for the trial structure and the 8 observed intensities, a set of 16 structure factors was determined. These structure factors were used in a programme written by Danielsen.[6] The nuclear scattering amplitudes for yttrium,[7] oxygen, and deuterium [8] were 0.788, 0.577, and 0.65, respectively. The x and z parameters of the deuterium atom were allowed to move 0.05 Å and the isotropic temperature factor was allowed to move 0.1 (Å)^2. After one shift in the x and z parameters, a new set of 16 structure factors was obtained. This first iteration was followed by four others. At this stage a conventional R-value ($R = \sum||F_o|-k|F_c||/\sum|F_o|$) of 5.4 % was obtained. From the last

Table 2. Observed and calculated intensities.

$2\theta_c$	hkl	I_a	I_b	I_o	I_c	
20.1°	110	567	40	68	42	
21.4°	101	104	304	350	312	
22.7°	011	718	480	503	96	554
23.0°	11$\bar{1}$				458	
27.4°	111				63	
27.8°	210	622	1959	1862	978	1880
28.0°	21$\bar{1}$				711	
28.8°	10$\bar{2}$				148	
30.5°	002				122	
30.7°	201	463	230	319	43	328
31.3°	20$\bar{2}$				163	
33.6°	11$\bar{2}$	586	562	582	36	558
34.1°	020				522	
35.1°	012	856	252	360	148	328
35.2°	211				180	
42.2°	$\bar{4}$01			267	283	

Table 3. Interatomic distances l (Å) and bond angles v.

	l	σl		v	σv
O_1-Y_1'	2.24	0.03	$Y_1-O_1-Y_1'$	144.1°	1.0°
O_1-Y_3	2.32	0.02	$Y_1-O_1-Y_3$	102.6°	0.7°
O_1-Y_1	2.28	0.02	$Y_3-O_1-Y_3'$	103.7°	0.7°
			$Y_3-O_1-Y_1'$	99.5°	0.7°
O_2-Y_1	2.38	0.02	$Y_1-O_2-D_1$	144.1°	1.0°
O_2-Y_2	2.44	0.02	$Y_1-O_2-Y_2$	109.9°	0.7°
O_2-D_1	0.96	0.04	$Y_2-O_2-Y_2'$	97.1°	0.7°
			$Y_2-O_2-D_1$	93.2°	1.0°
D_1-D_2	2.52	0.05			
O_2-O_3	3.06	0.03			
D_1-O_3	2.50	0.03	$D_1-O_2-O_3$	46.6°	1.0°

set of calculated structure factors a set of calculated intensities I_c, ($I_c = jF^2 \exp(-2B \sin^2\theta/\lambda^2)/\sin\theta \sin 2\theta$, Bacon [8]) was obtained (Table 2). An R'-value ($R' = \sum_i |\sum_g I_o - \sum_g I_c| / \sum_i \sum_g I_o$, where $\sum_g$ is a sum over a group of reflections which are not accurately resolved into individual reflections, and $\sum_i$ is a sum over i independent measurements) of 4.9 % was obtained from these intensities. Table 1 gives atomic coordinates and temperature factors with their standard deviations obtained from the last structure factor calculation. Table 3 gives some interatomic distances and bond angles.

DISCUSSION

The position and temperature factor of the deuterium atom has not been determined with a high precision, caused by the limited amount of data. The O—D distance of 0.96 ± 0.04 Å has a length which is within the interval between the O—H distance of 0.936 ± 0.003 Å found in calcium hydroxide,[9] which is a structure without any hydrogen bonds, and the O—H distance of 0.990 ± 0.004 Å found in diaspore,[10] which is a structure with hydrogen bonds. The D—D distance of 2.52 Å corresponds to the van der Waals distance between hydrogen atoms. Fig. 1 shows some bond angles and interatomic distances in the structure. The bond angles of the oxygen atom O_1, the O^{2-} ion, are similar to the bond angles of the oxygen atom O_2, belonging to the OD^- group (See Table 3).

The distance between the oxygen atom in the OD group and the O^{2-} ion belonging to the same coordination polyhedron is 3.07 ± 0.02 Å.[1] The deuterium atom is not on the line of centres between the two oxygen atoms, but instead, the O—D bond makes an angle of 46.6° ± 0.9° with this line. Smaller bond lengths and angles are often found in structures with hydrogen bonds.[10]

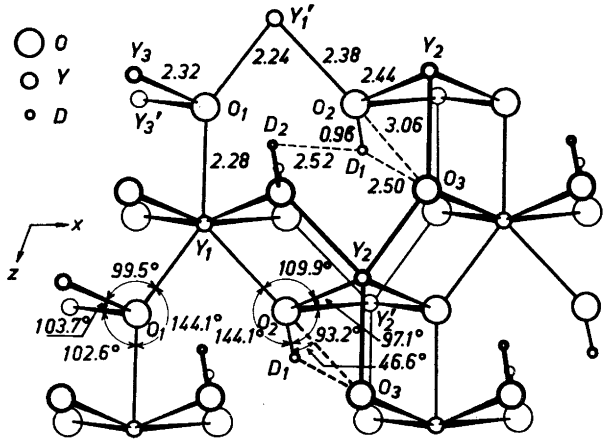

Fig. 1. Some bond angles and interatomic distances in YOOD. The atoms drawn with light, intermediate, and heavy lines are located on mirror planes with $z = \frac{1}{4}$, $z = \frac{3}{4}$, and $z = \frac{5}{4}$, respectively.

The O—D distance of 2.50 Å with a standard deviation of 0.03 Å is possibly not significantly smaller than the O—D distance of 2.6 Å derived from the sum of the van der Waals' radii of D (1.2 Å) and O (1.4 Å).[3] From this, it is concluded that the O—D group is free and is not participating in hydrogen bonding.

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