

## A Reinvestigation of the Crystal Structure of YOOH

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Preparation of yttrium oxide-hydroxide by hydrothermal methods was reported by Shafer and Roy,<sup>1</sup> and by Klevtsov, Klevtsova and Sheina.<sup>2</sup> The crystal structure of the compound was reported by Klevtsova and Klevtsov.<sup>3</sup> They reported a short yttrium-oxygen distance of 2.12 Å; this is much shorter than the Y—O distance calculated from Pauling's radii. Shafer and Roy<sup>1</sup> proposed that YOOH was isomorphous with the rare earth oxide-hydroxides. A reinvestigation of the crystal structure of YOOH was undertaken in order to determine the Y—O distances from counter diffractometer data.

Crystals of yttrium oxide-hydroxide were formed by treating freshly precipitated yttrium hydroxide at 450°C and 500 atm. with a 12 M sodium hydroxide solution in a pressure bomb of 20 ml volume, lined with pure silver. No piezoelectric effect was detected in YOOH. A needle-shaped crystal of dimensions 0.05 mm × 0.08 mm × 0.13 mm was investigated by Weissenberg methods. The needle axis proved to be [010]. The crystal was twinned along the {001} plane. The twinning was of the same type as in HoOOH.<sup>4</sup> Reflexions from each individual could be measured separately except for the (001) reflexions.

202 independent (*hkl*) reflexions were collected with an automatic diffractometer using Mo radiation and balanced filter techniques with a scintillation counter. No absorption correction was applied. The usual Lorentz-polarisation corrections were applied.

YOOH proved to be isostructural with HoOOH.<sup>4</sup> An *R*-value of 19.7 was obtained on inserting Y atoms only in the structure factor calculations using the coordinates of Ho in HoOOH. The Y contributions determine almost all the signs of the structure factors of the (*hkl*) reflexions and a difference Fourier was calculated for *y* = 0.25, 0.50, 0.75, and 1.00. This gave possible oxygen positions at (0.06, 0.75, 0.76) and (0.56, 0.75, 0.76).

Coordinates and anisotropic temperature factors were refined by the method of least squares. The anisotropic vibration parameters were expressed as the dimensionless coefficients *b*<sub>ij</sub> of the exponential, exp(−(*b*<sub>11</sub>*h*<sup>2</sup> + *b*<sub>12</sub>*hk* + ...)). The program used was written by Grønbaek<sup>5</sup> and employs the block diagonal approximation as described by Cruickshank.<sup>6</sup> The atomic scattering factor used for oxygen was from Vol. III of *International Tables for X-ray Crystallography*. Cromer's<sup>7</sup> values were used for yttrium. The interpolation formula of Bassi<sup>8</sup> was employed. The refinement yielded an *R*-value of 8.1%. A difference Fourier was calculated for *y* = 0.25, 0.50, 0.75, and 1.00, with the differences obtained from the last cycle of the refinement. This gave no peaks which could be interpreted as atoms.

The crystallographic data obtained are: Crystal system: monoclinic; *a* = 5.95 ± 0.01 Å, *b* = 3.65 ± 0.01 Å, *c* = 4.30 ± 0.01 Å, and β = 109.1 ± 0.1°. Space group: No. 11, *P*2<sub>1</sub>/*m*. Density calculated (for two formula units in the unit cell): 4.58 g/cm<sup>3</sup>. Density determined pycnometrically: 4.62 g/cm<sup>3</sup>. Absorption coefficient μ = 336 cm<sup>−1</sup> for MoKα-radiation.

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Table 1. Atomic coordinates and temperature factor coefficients.

Atom	<i>x</i>	<i>σx</i>	<i>y</i>	<i>z</i>	<i>σz</i>	
Y	0.1898	0.0004	0.75	0.3314	0.0006	
O <sub>1</sub>	0.065	0.004	0.75	0.770	0.005	
O <sub>2</sub>	0.566	0.004	0.75	0.755	0.006	
	<i>b</i> <sub>11</sub>	<i>σb</i> <sub>11</sub>	<i>b</i> <sub>22</sub>	<i>σb</i> <sub>22</sub>	<i>b</i> <sub>33</sub>	<i>σb</i> <sub>33</sub>
					<i>b</i> <sub>13</sub>	<i>σb</i> <sub>13</sub>

Y	−0.04	0.01	0.17	0.01	0.05	0.02	−0.10	0.01
O <sub>1</sub>	0.50	0.20	−0.19	0.10	0.17	0.17	0.23	0.15
O <sub>2</sub>	−0.09	0.13	0.20	0.15	0.48	0.23	0.14	0.14

Coordinates from Ref. 3 transformed to setting used in this work.

	<i>x</i>	<i>y</i>	<i>z</i>
Y	0.190	0.75	0.331
O <sub>1</sub>	0.047	0.75	0.771
O <sub>2</sub>	0.550	0.75	0.748

Table 2. Interatomic distances  $l$  and O—Y—O angles  $v$  in coordination polyhedra YO<sub>7</sub>.

	$l$	$\sigma l$
Y—O <sub>1</sub>	2.24	0.03 Å
Y—O <sub>2</sub>	2.38	0.02 Å
Y—O <sub>3</sub>	2.44	0.02 Å
Y—O <sub>5</sub>	2.28	0.02 Å
Y—O <sub>7</sub>	2.32	0.02 Å
O <sub>1</sub> —O <sub>2</sub>	3.00	0.04 Å
O <sub>1</sub> —O <sub>7</sub>	2.86	0.02 Å
O <sub>2</sub> —O <sub>3</sub>	2.77	0.03 Å
O <sub>3</sub> —O <sub>7</sub>	2.95	0.04 Å
O <sub>5</sub> —O <sub>3</sub>	3.07	0.02 Å
O <sub>5</sub> —O <sub>7</sub>	2.98	0.03 Å
O <sub>3</sub> —O <sub>4</sub>	3.66	0.01 Å
	$v$	$\sigma v$
O <sub>1</sub> —Y—O <sub>2</sub>	81.0°	0.9°
O <sub>1</sub> —Y—O <sub>5</sub>	143.8°	0.9°
O <sub>2</sub> —Y—O <sub>5</sub>	135.2°	1.0°
O <sub>1</sub> —Y—O <sub>7</sub>	77.4°	0.7°
O <sub>2</sub> —Y—O <sub>3</sub>	70.0°	0.6°
O <sub>7</sub> —Y—O <sub>5</sub>	80.5°	0.7°
O <sub>3</sub> —Y—O <sub>5</sub>	80.9°	0.7°
O <sub>5</sub> —Y—O <sub>6</sub>	103.7°	0.7°
O <sub>3</sub> —Y—O <sub>4</sub>	97.1°	0.7°

standard deviations. Table 2 gives interatomic distances. There are two sets of Y—O distances, one set with an average distance of  $2.27 \pm 0.03$  Å, and one with an average distance of  $2.41 \pm 0.03$  Å. These two distances are significantly different. The Y—O distance of 2.27 is comparable with the Y—O distances found in YO<sub>6</sub><sup>9</sup> and Y<sub>2</sub>O<sub>3</sub>,<sup>10</sup> and the distance of 2.41 Å is comparable with the distances found in Y(OH)<sub>3</sub>.<sup>11</sup> This indicates that O<sub>2</sub> of Table 1 is the hydroxyl oxygen. An ionic radius of 0.88 Å for the Y<sup>3+</sup> ion is calculated from these distances, using the radius 1.40 Å (Pauling) for O<sup>2-</sup> and 1.53 Å for OH<sup>-</sup>.

The present investigation confirms the results of Klevtsova and Klevtsov.<sup>3</sup> If the axes chosen here are transformed according to the following scheme  $a = c$ ,  $b = b$ ,  $c = -a - c$ , the unit cell parameters  $a = 4.30$  Å,  $b = 3.65$  Å,  $c = 6.09$  Å,  $\beta = 112.7^\circ$  are obtained for YOOH. These values are

close to those reported in Ref. 3:  $a = 4.28$  Å,  $b = 3.63$  Å,  $c = 6.05$  Å,  $\beta = 112.5^\circ$ . Transformation of atomic coordinates of YOOH<sup>3</sup> to the setting used in this investigation gives the coordinates shown in Table 2. The agreement between Y—O distances found in this investigation and those reported in Ref. 3 is good except for the distance 2.12 Å. This value could not be reproduced when the Y—O distances were computed with a GIER—ALGOL program<sup>12</sup> using the unit cell and atomic coordinates from Ref. 3 and it is probably a misprint. Instead the Y—O distance 2.28 Å was found.

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