The Crystal Structure of Barium Tellurite Monohydrate, BaTeO₃.H₂O

BaTeO$_3$.H$_2$O

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Single crystals of barium tellurite monohydrate BaTeO$_3$.H$_2$O were prepared by hydrothermal methods at 300°C. The crystals are monoclinic $P2_1/a$, with $a = 8.58$, $b = 7.53$, $c = 7.70$ Å, $\beta = 106.03°$. The structure was solved by means of the Patterson function, using three dimensional X-ray data, collected on an automatic diffractometer. After least squares refinement the R value is 0.039 for 1097 reflections. The structure contains TeO$_3$ pyramids with Te$-$O distances of 1.854 Å. The water molecule is loosely coordinated to a tellurium atom, the Te$-$O distance being 3.33 Å. One other oxygen atom has a second tellurium atom as a neighbour at a distance of 3.03 Å.

A $4s^2$ electron configuration may be assigned to gaseous atoms or ions: Zn⁰, Ga$^{1+}\cdots$Kr^{8+} and a $5s^2$ configuration to the corresponding elements Cd⁰, In$^{1+}\cdots$Xe^{8+}. On the basis of this description we could expect the formation of compounds of the following types:

(1) "Ionic" compounds with structures dominated by geometrical and electrostatic packing considerations,
(2) "Covalent" compounds using sp^3-orbitals on the central atom,
(3) "Crystal-field stabilized" compounds of various geometries.

Clear cut distinctions between the three alternatives are not easily found. Some compounds, *e.g.* CsGe(II)Cl$_3$[1] and CsSn(II)Cl$_3$[2], exhibit phase transformations which may be described as transformations from type (2) to type (1) and one particular element may form compounds of various types. Tetravalent tellurium may be described as predominantly ionic in the compound (NH$_4$)$_2$TeCl$_6$[3] which is isostructural with (NH$_4$)$_2$PtCl$_6$. TeO$_2$[4] might be quoted as an example of a "crystal-field stabilized" geometry and we expected that compounds of the type MTeO$_3$ where M is a bivalent metal would form pyramidal ions using $5sp^3$ orbitals.

BaTeO$_3$ as prepared by the usual wet method and at atmospheric pressure from TeO$_2$ and Ba(OH)$_2$ contains water of crystallization and is microcrystal-

line. In a series of hydrothermal preparations of tellurium compounds Christensen and Sørensen [5] prepared crystals of $BaTeO_3.H_2O$ big enough for an X-ray investigation and kindly supplied us with specimens for X-ray analysis.

EXPERIMENTAL

A solution of 1.23 mmol of $Ba(OH)_2.8H_2O$ in 50 ml water was mixed with 1.25 mmol of tellurium-dioxide and heated to 300°C in a 100 ml autoclave for 24 h. The crystals are tiny, flat needles; the one used for the X-ray work is $0.025 \times 0.1 \times 0.6$ mm³. The needle axis is a. Unit cell and space group were determined by means of rotation, Weissenberg and precession photographs taken with $CuK\alpha$ and $MoK\alpha$ radiation ($\lambda_{Cu} = 1.5418$ Å, $\lambda_{Mo} = 0.7107$ Å). The intensities were collected on an automatic diffractometer of the Arndt-Phillips design using $MoK\alpha$ radiation from a graphite monochromator. The monochromator device is described in Ref. 6. Higher order contamination was reduced by means of pulse height discrimination. About 1500 pairs of symmetry related reflections ($I > 2\sigma(I)$) were used after the ones near the rotation axis of the reciprocal lattice had been left out. Absorption corrections were calculated using a modified version of a program by Wells.[7]

The three-dimensional Patterson function gave one solution for the heavy atoms, and a Fourier map calculated with tellurium at both sites showed four atoms of which three were coordinated to one heavy atom, thus indicating that this was the tellurium atom. The fourth small peak filled a hole in the structure and from chemical considerations it was decided that it was a water molecule. Refinement including isotropic temperature factor parameters by the method of least squares using the block diagonal approximation gave a value of $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.06. Further refinement including anisotropic temperature factor parameters, anomalous dispersion effects ($\Delta f'_{Ba} = -0.50$, $\Delta f'_{Te} = -0.40$; $\Delta f''_{Te} = 2.00$),[8] and an isotropic extinction parameter led to a final R-value of 0.039. The two hydrogen atoms have not been found.

Table 1. Final atomic parameters.

Coordinates in fractions of the cell edges, standard deviations $\times 10^4$ in parentheses.

Atom	x		y		z	
Ba	.3323	(1)	.8491	(1)	.1175	(2)
Te	.0042	(1)	.1868	(1)	.2888	(1)
O_1	−.0470	(8)	.3159	(8)	.0749	(9)
O_2	.2029	(8)	.0986	(10)	.2808	(10)
O_3	−.1348	(7)	−.0024	(9)	.2026	(9)
O_4	.1381	(8)	.6053	(12)	.3582	(10)

Mean square amplitudes of vibration, $u_{ij} \times 10^4$, with standard deviations in parentheses.

	u_{11}		u_{12}		u_{13}		u_{12}		u_{13}		u_{23}	
Ba	337	(5)	324	(5)	375	(5)	− 1	(4)	80	(4)	5	(4)
Te	120	(3)	130	(3)	88	(3)	1	(2)	25	(2)	− 9	(2)
O_1	255	(33)	99	(28)	84	(31)	− 1	(25)	34	(27)	+47	(24)
O_2	149	(30)	287	(38)	202	(36)	40	(27)	40	(27)	− 30	(29)
O_3	128	(28)	176	(31)	205	(34)	−69	(24)	54	(26)	−16	(26)
O_4	142	(31)	579	(54)	163	(36)	122	(32)	48	(28)	−56	(34)

CRYSTAL DATA

$BaTeO_3.H_2O$

Crystal system: monoclinic, b unique;

$a = 8.58 \pm 0.02$ Å, $b = 7.53 \pm 0.02$ Å, $c = 7.70 \pm 0.02$ Å;

$\beta = 106.03° \pm 0.2°$;

$V = 478$ Å^3, $Z = 4$; $d_{calc} = 4.6$ g/cm^3

Systematic absences: $h0l$ for h odd

$0k0$ for k odd

Space group: $P2_1/a$ (C_{2h}^5, No. 14).

Final atomic parameters are given in Table 1, some interatomic distances and angles in Table 2, and a list of observed and calculated structure factors in Table 3. The structure is depicted in Figs. 1 – 3.

Table 2. Interatomic distances and angles, standard deviations in parentheses.

	l Å			l Å	
$Te-O_1$	1.858	(6)	$Ba-O_1$	2.780	(6)
$Te-O_2$	1.847	(7)	$Ba-O_1'$	2.781	(6)
$Te-O_3$	1.859	(6)	$Ba-O_1''$	2.675	(8)
$Te-O_2$	3.035	(7)	$Ba-O_2$	2.667	(8)
$Te-O_4$	3.332	(9)	$Ba-O_3$	2.688	(7)
O_2-O_4	2.738	(10)	$Ba-O_3'$	2.823	(6)
O_3-O_4	2.665	(11)	$Ba-O_4$	2.786	(6)

Angle	Degrees	Angle	Degrees
O_1-Te-O_2	98.81 (32)	O_2-Te-O_2'	168.55 (27)
O_1-Te-O_3	96.49 (28)	O_2-Te-O_4	93.66 (26)
O_2-Te-O_3	102.66 (30)	O_3-Te-O_2	86.68 (24)
O_1-Te-O_2'	73.26 (27)	O_3-Te-O_4	159.62 (22)
O_1-Te-O_4	68.66 (22)	$O_2'-Te-O_4$	75.87 (18)

Fig. 1. 001 Projection of the $BaTeO_3.H_2O$ structure. Hydrogen bonds shown as dotted lines.

Table 3. Observed and calculated structure factors.
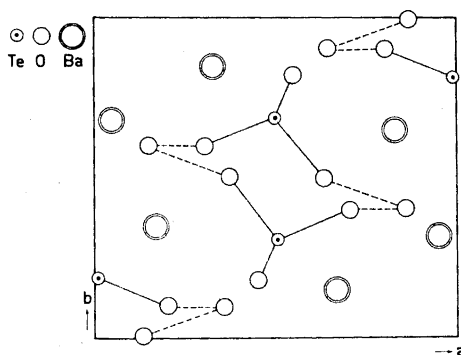
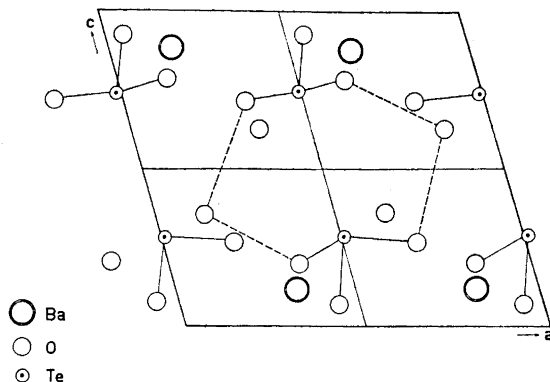*Fig. 2.* 010 Projection of the $BaTeO_3.H_2O$ structure. Hydrogen bonds shown as dotted lines.
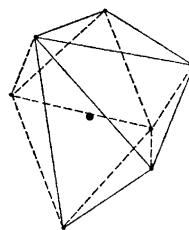
Fig. 3. The barium-oxygen polyhedron in $BaTeO_3.H_2O$.

DISCUSSION

$BaTeO_3.H_2O$ contains discrete, pyramidal TeO_3^{2-} ions, with a mean $Te-O$ distance of 1.855 Å. This indicates some double bond character since the expected value of a $Te-O$ single bond is 1.98 Å. The angles in the pyramid are smaller than the tetrahedral angle. Like many other elements of similar outer electron configuration ($4s^2$ or $5s^2$) Te shows some tendency to coordinate more atoms approximating an octahedral arrangement ("crystal-field stabilization"). One oxygen atom is 3.03 Å from a tellurium atom and the water molecule is 3.35 Å away. The sixth position of the octahedron is unoccupied.

Barium is surrounded by seven oxygen atoms in an irregular arrangement. All oxygen atoms have coordination number 4. Most of the angles around oxygen are close to the tetrahedral value, but some of the ones between weak bonds deviate from this ideal value. The hydrogen atoms of the water molecule were not found. As this oxygen atom has distances of 2.74 Å and 2.67 Å to two other oxygen atoms weak hydrogen bonding is indicated. The water molecule is driven off at elevated temperatures. A phase transition involving a rearrangement of the TeO_3^{2-} ions alone is not observed.

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