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The Crystal Structure of $Ba_2SnO_2(OH)_4 \cdot 10H_2O$

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The crystal structure of $Ba_2SnO_2(OH)_4 \cdot 10H_2O$ has been determined from three-dimensional X-ray diffractometer data. The symmetry is triclinic, space group $P\bar{1}$, with $a=8.771(3)$ Å, $b=8.816(4)$ Å, $c=6.175(2)$ Å, $\alpha=91.33(3)°$, $\beta=67.70(3)°$, $\gamma=116.16(3)°$ and $Z=1$. Full-matrix least-squares refinement based on 3069 non-zero reflections yielded a final R value of 4.9 %.

The tin atom is octahedrally coordinated to six oxygen atoms. The barium atoms are nine-coordinated. The tin oxygen octahedra and the barium atoms together with eight of the nine coordinated oxygen atoms form layers, while the remaining oxygen atoms lie in interposed layers. The different types of layer are held together by Ba – O and O···H – O bonds. Within the layers of oxygen atoms there are hydrogen bonds only. The Sn – O (or – OH) bond distances range from 2.041(4) to 2.068(5) Å while the Ba – O bond distances range from 2.756(5) to 2.912(5) Å.

In order to study the effect of the lone pair of electrons in Sn(II), a number of crystal structures[1-3] have been determined. It is, however, also of interest to study the same element without the lone pair *i.e.* Sn (IV) but with the same type of environment. An investigation of the crystal structure of $Ba_2SnO_2(OH)_4 \cdot 10H_2O$ was therefore undertaken.

EXPERIMENTAL

The barium stannate(IV) crystals were prepared together with barium stannate(II) crystals according to Ref. 4. No special precautions were taken to prevent oxidation of Sn(II) to Sn(IV). Stannate crystals containing both Sn(II) and Sn(IV) were obtained. At least two different compounds with approximately the same crystal form have been identified. A prism-shaped crystal with dimensions 0.18 mm × 0.04 mm × 0.32 mm was selected.

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Three-dimensional X-ray data were collected with a SYNTEX single crystal diffractometer (Mo$K\alpha$ radiation). No separate measurement of background was made during the data collection. A profile analysis based on the Larsen-Lehmann method[5] was instead applied to the 96-step profile collected for each reflection. 3069 independent reflections with $F_o^2 > 3\sigma(F_o^2)$ were considered observed and were used in the subsequent calculations.

One set of Weissenberg equi-inclination photographs was also taken, together with a rotation photograph around [001], using Cu$K\alpha$ radiation.

UNIT CELL AND SPACE GROUP

The crystals of $Ba_2SnO_2(OH)_4 \cdot 10H_2O$ are triclinic. The cell parameter calculations were based on sin $^2\theta$ values for twelve reflections and gave the following results:

$a=8.771(3)$ Å, $b=8.816(4)$ Å, $c=6.175(2)$ Å, $\alpha=91.33(3)°$, $\beta=67.70(3)°$, $\gamma=116.16(3)°$, $V=390.5(3)$ Å^3, $\mu_{MoK\alpha}=68.0$ cm^{-1}.

There were no systematically absent reflections which supports the triclinic system and the space group $P\bar{1}$ (No. 2).[6] The small standard deviations and the low R-value show that the symmetry ought not be lowered to the space group $P1$ (No. 1). (No. 1). For $Z=1$ a calculated density of 2.86 g/cm^3 is obtained.

STRUCTURE DETERMINATION

The intensity values were corrected for Lorentz and polarization effects (SYN).[7] A correction for absorption effects (DATAPH)[7] was performed when an approximate structure had been derived.

Table 1. Fractional coordinates and isotropic thermal parameters (standard deviations within parentheses).

Atom	x	Y	z	U(Å^2)
Ba	0.3040(1)	0.0378(1)	0.3470(1)	
Sn	0.0000	0.0000	0.0000	
O1	0.7358(6)	0.8332(6)	0.0265(8)	0.0195(7)
O2	0.8927(6)	0.1465(5)	0.1971(8)	0.0168(7)
O3	0.9528(6)	0.8754(6)	0.3151(8)	0.0175(7)
O4	0.6746(7)	0.1770(6)	0.0035(9)	0.0222(8)
O5	0.4660(10)	0.4094(9)	0.2847(13)	0.0388(13)
O6	0.4466(7)	0.8150(7)	0.4148(9)	0.0248(8)
O7	0.1965(9)	0.4772(8)	0.1163(12)	0.0366(13)
O8	0.8661(9)	0.5098(9)	0.3043(12)	0.0355(12)

Table 2. Anisotropic thermal parameters (standard deviations within parantheses). The temperature coefficient is exp $[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	0.0126(2)	0.0219(2)	0.0111(2)	0.0095(1)	−0.0046(1)	−0.0030(1)
Sn	0.0111(2)	0.0162(2)	0.0100(2)	0.0076(2)	−0.0039(1)	−0.0028(1)

The barium and tin parameters were evaluated from a Patterson synthesis (DRF).[7] Subsequent electron density calculations (DRF)[7] and successive cycles of block-diagonal least-squares refinement (BLOCK)[7] revealed the oxygen atoms. Atomic scattering factors for Ba, Sn and O were taken from Ref. 8. A correction for extinction was included (LINUS).[7] The final value of the isotropic extinction parameter was $g=0.29(3)\times10^4$. Anisotropic thermal parameters for the barium and tin atoms were also included. The R value converged to 4.9 % and R_w to 7.3 %. A weighting scheme according to Cruickshank[9] was used in the refinement ($w=(30.0+F_o+0.01F_o^2+0.00F_o^3)^{-1}$). No attempts were made to locate the hydrogen atoms.

A three-dimensional F_o-F_c Fourier synthesis calculated after the refinement showed some spurious maxima and minima in the vicinity of the heavy atoms. These peaks can probably be attributed to termination effects. Final positional parameters and temperature factors are given with

Table 3. Selected interatomic distances (Å) and angles (°) with their standard deviations in parentheses. Atoms in the unit cell above or below, in the z direction, are marked with an asterisk.

Ba−O1*	2.795(5)	Ba−O4*	2.850(5)
Ba−O2	2.756(5)	Ba−O5	2.905(7)
Ba−O3*	2.809(4)	Ba−O6	2.863(5)
Ba−O3	2.853(5)	Ba−O6′	2.912(5)
Ba−O4	2.818(5)		
Sn−O1	2.068(5)	O1−Sn−O1*	180.0
Sn−O2	2.041(4)	O1−Sn−O2	88.7(2)
Sn−O3	2.061(4)	O1−Sn−O3*	87.8(2)
		O2−Sn−O3	87.2(2)

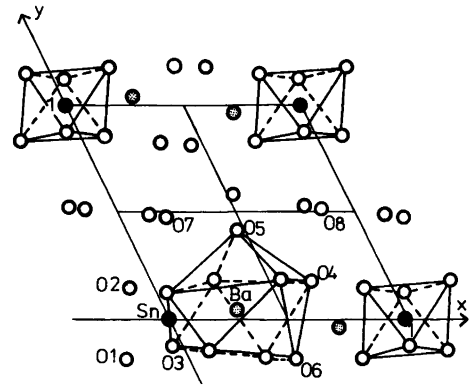

Fig. 1. Projection of the structure of $Ba_2SnO_2(OH)_4\cdot10H_2O$ on the xy plane. Coordination polyhedra for the Ba and Sn atoms are indicated. Dot-filled circles represent barium. Filled circles correspond to tin atoms and unfilled circles to oxygen.

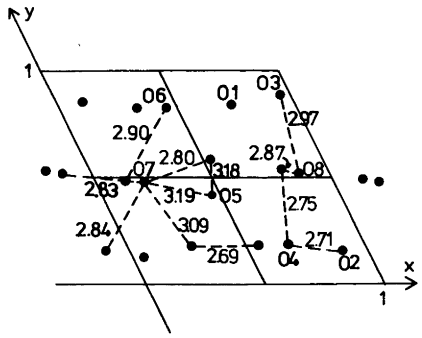

Fig. 2. Projection of the oxygen atoms in the structure of $Ba_2SnO_2(OH)_4 \cdot 10H_2O$ on the xy plane. Short O – O distances are indicated.

their standard deviations in Tables 1 and 2. Selected interatomic distances and angles and their standard deviations were calculated (DISTAN)[7] and the results are given in Table 3. A list of F_o and F_c is available on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure contains two different types of layer parallel to [001] (see Fig. 1). One type consists of Sn and Ba atoms and 10 oxygen atoms coordinated to these. The other type is composed of the remaining water oxygen atoms. The atoms O1, O2 and O3 are bonded to both Sn and Ba. The other oxygen atoms are water oxygen atoms, one formula unit thus containing 10 H_2O. The Sn atoms are sixfold coordinated which means that the initial ion was $Sn(OH)_6^{2-}$. The correct formula must be $Ba_2SnO_2(OH)_4 \cdot 10H_2O$. From Table 3 it is seen that the O2 atoms are most strongly bonded to both Sn and Ba. Probably the O2 atom therefore corresponds to an O^{2-} ion. The $SnO_2(OH)_4^{4-}$ group has a somewhat distorted octahedral configuration (see Fig. 1), the distortion of angles being within limits known from other structures.[10] The remaining Sn – O (or – OH) distances are 2.06 – 2.07 Å, which are normal[11,12] for Sn(IV) – O.

The Ba^{2+} ions are ninefold coordinated. Eight of the oxygen atoms form a square antiprism which is distorted through the ninth oxygen atom (O5 outside one of the square faces (see Fig. 1). The Ba – O distances vary from 2.76 to 2.91 Å which is in good agreement with values published earlier.[13]

According to the formula of the compound there are 24 hydrogen atoms in the unit cell. Examination of short O – O distances shows that the different layers are held together by hydrogen bonds as well as Ba – O5 bonds. Within the oxygen layers there are no other bonding possibilities than these hydrogen bonds. As in indicated in Fig. 2, there are several hydrogen bond distances[14] between oxygen atoms.

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