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Structure of Cesium Hydrogensulfate

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Abstract. CsHSO$_4$, monoclinic, $P2_1/m$, a = 7·3039 (9), b = 5·8099 (10), c = 5·4908 (8) Å, β = 101·51 (1)°, V = 228·31 (6) Å^3, Z = 2, D_c = 3·345 Mg m^{-3}. The structure was refined to R = 0·038 for 1442 observed reflexions. Hydrogen-bonded chains of SO$_4$ groups run along the b axis one-dimensionally.

Introduction. It is known that RbHSO$_4$ and NH$_4$HSO$_4$ undergo ferroelectric phase transitions (Pepinsky & Vedam, 1960; Pepinsky, Vedam, Hoshino & Okaya, 1958). It seems worthwhile to study what kind of structures of the AHSO$_4$ type (A = monovalent atoms or groups) exhibit ferroelectric activity. In the course of this work, we determined the crystal structure of CsHSO$_4$ at room temperature.

Colorless single crystals were grown by cooling an aqueous solution containing equimolar amounts of Cs$_2$SO$_4$ and H$_2$SO$_4$ from 333 K to room temperature. Cleavages are observed for the (100) plane. The crystals show a twin structure. An untwinned spherical specimen, 0·68 mm in diameter, was mounted on a Rigaku AFC-5 automatic four-circle diffractometer; graphite-monochromated Mo $K\alpha$ radiation was used. Measurements were made in the range $2\theta \leq 80°$ by the θ–2θ scanning method with a scan speed of 8° min^{-1} in 2θ. The data were corrected for background and Lp factors. An absorption correction was made in view of the considerable absorption effect (μr = 2·94). Three standard reflexions were monitored every 200 measurements and no significant variation was observed. 1601 independent reflexions were obtained; of these, 60 were omitted because of the extinction effect. Finally 1442 reflexions with values of $|F_o|$ greater than $3\sigma(|F_o|)$ were used for least-squares calculations. The space group is either $P2_1$ or $P2_1/m$ from the systematic extinctions. Since no piezoelectric signal was observed in the frequency range from 50 kHz to 12 MHz by the transmission-circuit method, we determined the space group to be uniquely $P2_1/m$. Consistent with this conclusion, no ferroelectric activity was observed by dielectric-hysteresis measurement at room temperature.

The positions of the Cs and S atoms were found from a three-dimensional Patterson map and those of the O atoms were found on a difference Fourier map phased with the heavy atoms. Since the average position of the H atom must be located at any of the special positions 2(a) to 2(e), we have identified the peak of the electron density near the 2(c) site as that of H. Refinement was carried out by using neutral scattering factors (*International Tables for X-ray Crystallography*, 1968). In the calculations equal weights were used throughout, the quantity minimized being $\sum||F_o| - |F_c||^2/\sum|F_o|^2$. In the final cycle all parameter shifts were far less than one tenth of their e.s.d.'s and R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ reached 0·038. Positional and thermal parameters are given in Table 1* and bond lengths and angles in Table 2. The structure is shown in Fig. 1.

Table 1. *Positional parameters and thermal parameters* [U_{eq} ($\times 10^2$) *for* Cs, S *and* O; U_{iso} ($\times 10^2$) *for* H] *with e.s.d.'s in parentheses*

The equivalent isotropic thermal parameters, U_{eq}, have been calculated from $U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3$.

	x	y	z	U_{eq} or U_{iso} (Å^2)
Cs	0·28805 (4)	0·25	0·98352 (6)	2·61 (1)
S	0·7543 (2)	0·25	0·5490 (2)	2·12 (3)
O(1)	0·6990 (7)	0·25	0·2814 (8)	3·5 (1)
O(2)	0·6076 (6)	0·25	0·6847 (10)	3·7 (1)
O(3)	0·8759 (5)	0·0434 (6)	0·6301 (6)	3·8 (1)
H	0·0	0·0	0·5	6·3 (42)

Table 2. *Atomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cs–O(1$^{\rm i}$)	3·119 (5)	O(1)–O(2$^{\rm ii}$)	3·211 (7)
–O(1$^{\rm iv}$)	3·259 (5)	–O(3)	2·406 (6)
–O(2)	3·110 (5)	O(2)–O(3)	2·367 (6)
S–O(1)	1·444 (5)	O(3)–O(3$^{\rm iii}$)	2·401 (7)
–O(2)	1·421 (5)	–O(3$^{\rm v}$)	2·572 (7)
–O(3)	1·507 (4)	–H$^{\rm vi}$	1·286 (4)
O(1)–O(2)	2·437 (7)		

O(1)–S–O(2)	116·5 (3)	O(2)–S–O(3)	107·9 (3)
O(1)–S–O(3)	109·2 (2)	O(3)–H$^{\rm vi}$–O(3$^{\rm v}$)	180·0

Symmetry code: (i) $x, y, 1 + z$; (ii) $x, y, -1 + z$; (iii) $x, \frac{1}{2} - y, z$; (iv) $1 - x, -y, 1 - z$; (v) $2 - x, -y, 1 - z$; (vi) $1 + x, y, z$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36135 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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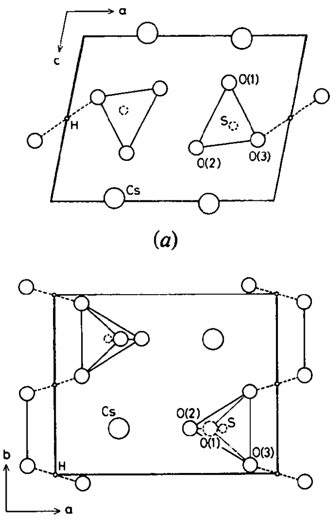

(a)

(b)

Fig. 1. (a) The b axis and (b) c axis views of the $CsHSO_4$ structure. The hydrogen bonds are drawn with broken lines.

Discussion. A map of residual electron density computed after the final refinement showed an irregular maximum of 1·6 e Å^{-3} near Cs, maxima of 0·7–1·3 e Å^{-3} near S, O(1), O(2) and O(3), and no peaks >0·6 e Å^{-3} in the remaining places.

As depicted in Fig. 1, Cs and SO_4 lie on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. The separate chains of hydrogen bonds run along the b axis one-dimensionally. This structure is not isomorphous with those of ferroelectric $RbHSO_4$ (Ashmore & Petch, 1975) and NH_4HSO_4 (Nelmes, 1972), or with the nonferroelectric $NaHSO_4$ and $KHSO_4$ (Sonneveld & Visser, 1978). It is interesting that the structure of $CsHSO_4$ resembles rather that of CsH_2PO_4 in the paraelectric phase (Matsunaga, Itoh & Nakamura, 1980) apart from the presence of an extra H in CsH_2PO_4, which combines O(1) and O($2^{\rm II}$).

As shown in Table 2, the shape of SO_4 is rather regular while the bond length S—O(3) is somewhat longer than S—O(1) and S—O(2). Remembering that O(3) and O($3^{\rm v}$) are linked by $H^{\rm vi}$, we can attribute the greater length of the S—O(3) bond to the formation of the hydrogen bond as in the case of other AHSO$_4$-type compounds (Sonneveld & Visser, 1978).

As mentioned above, the peak of H electron density is not located exactly at the 2(c) site of (0·0, 0·0, 0·5) but two peaks of height 0·6 e Å^{-3} are observed near the positions of (0·00, 0·05, 0·55) and (0·00, −0·05, 0·45). Although the peak height is the same as that of ripples on the Fourier map, this result implies that the structure has a disordered H atom. From this structure, it is expected that a phase transition which brings H atoms into an ordered state occurs below room temperature.

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An X-ray Diffraction Refinement of the Structure of Natural Natrolite

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Abstract. $Na_2Al_2Si_3O_{10}.2H_2O$, orthorhombic, $Fdd2$, a = 18·325 (5), b = 18·653 (5), c = 6·601 (5) Å, V = 2256 Å^3, Z = 8, D_c = 2·135, D_o = 2·15 Mg m^{-3}. The atomic positions have been determined from single-crystal X-ray diffraction data. The final R value for 400 independent observed reflections is 0·056. Si,Al is coordinated to four O atoms. The average Al—O and Si—O distances are 1·746 (2) and 1·619 (2) Å respectively. The average O—H distance is 1·044 (2) Å.

Introduction. Natrolite is one of the natural hydrated aluminosilicate zeolites. First reports of its crystal structure were presented by Pauling (1930), Taylor, Meek & Jackson (1933) and Meier (1960). According

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