Rubidium Hydrogenselenate

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Abstract. $RbHSeO_4$, FW 229·4, triclinic, $P\bar{1}$; the crystal structure has been determined in the body-centred lattice cell $I\bar{1}$, $a = 19\cdot359$ (3), $b = 4\cdot619$ (3), $c = 7\cdot572$ (4) Å, $\alpha = 90\cdot60$ (5), $\beta = 89\cdot80$ (5), $\gamma = 90\cdot73$ (5)°, $V = 677$ Å^3, $Z = 6$, $\mu = 201$ cm^{-1}, λ(Mo $K\alpha$), $D_c = 3\cdot38$ g cm^{-3}. The structure was refined to an R value of 0·072 for 1654 reflections with $F > 3\cdot5\sigma(F_o)$. The asymmetric unit includes three independent molecules differing in the deformation of the SeO_4^{2-} tetrahedra. This deformation is connected with ferroelectric properties, which the title compound exhibits at room temperature.

Introduction. $RbHSeO_4$ (RHSe) was shown to be ferroelectric below 97·5 °C by Czapla, Sobczyk, Mróz & Waśkowska (1978). Above $t_c = 97\cdot5$ °C the crystal passes to a non-polar phase. The crystal structure of RHSe has not been investigated before, but we assumed it to be similar to the ferroelectric sulphates NH_4HSO_4 (Nelmes, 1971, 1972) and $RbHSO_4$ (Ashmore & Petch, 1975). NH_4HSO_4 (AHS) belongs to a small class of compounds which exhibit ferroelectric properties in a specified temperature range, between −3 and −119 °C (Pepinsky, Vedam, Hoshino & Okaya, 1958). $RbHSP_4$ (RHS) is ferroelectric below −15 °C (Pepinsky & Vedam, 1960). At room temperature both compounds are paraelectric and their symmetry may be described by the monoclinic space group $P2_1/c$ (Pepinsky *et al.*, 1958; Pepinsky & Vedam, 1960). It is, however, convenient to adopt a pseudoorthorhombic unit cell of space group $B2_1/a$. This cell contains sixteen formula units, two in each asymmetric unit. In the polar phase the symmetry of AHS and RHS is reduced to the space group Pc (*Ba*) with four independent formula units in the asymmetric unit. $RbHSeO_4$ appears to be a third ferroelectric compound belonging to the AHS family, although not strictly isomorphous.

Preliminary unit-cell parameters were found from Weissenberg photographs (rotation and zero-level), from which the pseudoorthorhombic symmetry was apparent. Only systematic absences for $h + k + l = 2n + 1$ were observed. Also all $h00$ reflections were weak except for $h = 3n$. In order to emphasize pseudo-symmetry and to allow an easy comparison with the structure of AHS and RHS a non-conventional, body-centred, triclinic cell with space group $I\bar{1}$ was chosen.

Final unit-cell dimensions and their standard deviations were obtained by the least-squares refinement of angular coordinates of 17 reflections measured on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. They agree very well with the precise lattice parameters of RHSe determined by the Bond method (Pietraszko, Waśkowska, Olejnik & Łukaszewicz, 1978). The crystal used for data collection was spherical ($r = 0\cdot01$ cm $\pm$ 5‰) and was covered with silicone grease to prevent deliquescence. The θ–2θ scan technique was employed for measurements of reflection intensities from one half of the reciprocal space (hemisphere $h \geq 0$, $\pm k$, $\pm l$) up to $2\theta \leq 55°$. The intensity of a standard reflection did not show any significant changes during the data collection. Intensities were corrected for Lp effects. Absorption correction for a sphere was introduced in the final stage of the refinement. Among 2005 measured reflections 1654 had structure factors $F > 3\cdot5\sigma(F_o)$. Structure factors were calculated with the neutral atomic scattering factors, taken from *International Tables for X-ray Crystallography* (1974). The structure was solved by the trial and error method. Strong reflections 300 and 600 indicated sixfold repetition of segments containing the $RbHSeO_4$ formula unit (Fig. 1) as compared with eight segments in AHS (Nelmes, 1974). Preliminary coordinates of Rb and Se atoms gave an R factor of about 0·20. Positions of the O atoms were revealed from difference Fourier syntheses. An arbitrary origin of the coordinate system was defined by fixing the x, y and z parameters for the Se(1) atom. After several cycles of full-matrix least-squares refinement with isotropic temperature factors, R dropped to 0·081. Introduction of anisotropic temperature factors reduced the R value to 0·072. No
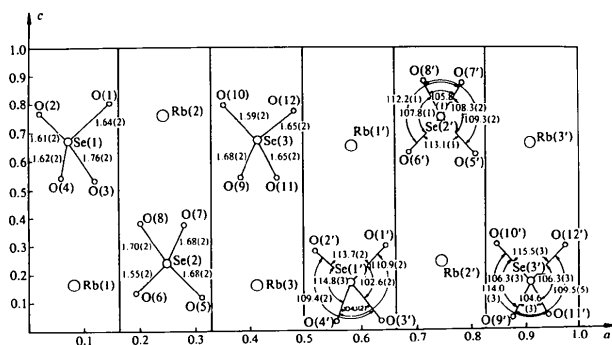
Fig. 1. Projection of the crystal structure down the b axis. The bond lengths (Å) and bond angles (°) are given with e.s.d.'s in parentheses.

attempts were made to locate the H atoms. The final list of parameters is given in Table 1.* Despite pseudo-repetition along the a direction, no pair of parameters in the correlation matrix has a correlation coefficient larger than 0·34. The thermal parameters do not show anomalies for any of the atoms. Calculations were performed on the NOVA 1200 computer with Syntex *XTL* structure determination programs except for the last few least-squares refinement cycles which were performed with the XRAY 70 program system (Stewart, Kundell & Baldwin, 1970).

Discussion. Although the crystal structure of RHSe appears to be non-isomorphous with AHS and RHS, there are similarities between them. The relations between the lattice cells of RHSe and AHS (pseudoorthorhombic setting) can be described as follows:

$$a_{RHSe} \simeq \tfrac{6}{8}a_{AHS}, \quad b_{RHSe} \simeq b_{AHS}, \quad c_{RHSe} \simeq \tfrac{1}{2}c_{AHS}.$$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33741 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters with e.s.d.'s in parentheses*

	x	y	z
Rb(1)	0·0840 (2)	0·7207 (8)	0·1585 (5)
Rb(2)	0·2495 (2)	0·3045 (10)	0·7583 (5)
Rb(3)	0·4151 (2)	0·8914 (8)	0·1601 (5)
Se(1)	0·0830*	0·8400*	0·6700*
Se(2)	0·2512 (2)	0·2992 (9)	0·2469 (4)
Se(3)	0·4175 (2)	0·7744 (6)	0·6701 (4)
O(1)	0·1476 (15)	0·7367 (57)	0·7924 (30)
O(2)	0·0213 (12)	0·9862 (54)	0·7806 (35)
O(3)	0·1218 (11)	0·1006 (47)	0·5328 (31)
O(4)	0·0589 (13)	0·5838 (43)	0·5347 (30)
O(5)	0·3171 (11)	0·4325 (47)	0·1262 (27)
O(6)	0·1895 (11)	0·1906 (47)	0·1325 (28)
O(7)	0·2818 (11)	0·0391 (42)	0·3773 (27)
O(8)	0·2217 (10)	0·5622 (45)	0·3857 (26)
O(9)	0·3842 (13)	0·5224 (46)	0·5326 (31)
O(10)	0·3555 (11)	0·8768 (50)	0·7942 (28)
O(11)	0·4482 (13)	0·0300 (47)	0·5388 (30)
O(12)	0·4848 (14)	0·6406 (60)	0·7734 (39)

* Fixed parameters.

The [010] projection of RHSe is shown in Fig. 1. Interatomic distances and bond angles in the selenate tetrahedra are also given. Though the mean Se—O distances in consecutive selenate ions (1·66, 1·65 and 1·64 ± 0·01 Å) are close to the values recorded in the other structure determinations, *e.g.* Gibbs, Chiari & Louisnathan (1976), Kálmán & Cruickshank (1970), there is considerable deviation from the ideal tetrahedral symmetry.

The distortion is evident for the Se(1)O$_4$ ion. The bond distance Se(1)—O(3), which is longer than the others, indicates the existence of a hydrogen bond of the O—H···O type between selenate ions displaced along the $\pm b$ axis. Although the deformation of the Se(2)O$_4$ and Se(3)O$_4$ tetrahedra does not give such clear information on the hydrogen bonds, their existence is implied by the short O—O distances involving

Table 2. *Rubidium—oxygen distances* (Å)

E.s.d.'s are given in parentheses. The first digit in the atom notation is the number of the equivalent position and the next three describe translations along the $\pm a$, $\pm b$ and $\pm c$ axes. Equivalent positions: (I) x,y,z; (II) $\tfrac{1}{2} + x, \tfrac{1}{2} + y, \tfrac{1}{2} + z$.

Rb(1)—O(1)$_{I,00-1}$	3·03 (3)	Rb(2)—O(1)$_{I,0-10}$	3·27 (3)	Rb(3)—O(2)$_{II,0-1-1}$	3·52 (4)
—O(2)$_{I,00-1}$	3·36 (3)	—O(1)$_{I,000}$	2·83 (3)	—O(2)$_{II,00-1}$	2·95 (3)
—O(3)$_{I,010}$	3·39 (3)	—O(3)$_{I,000}$	3·14 (3)	—O(4)$_{II,00-1}$	3·06 (2)
—O(4)$_{I,000}$	2·96 (3)	—O(5)$_{I,001}$	3·13 (3)	—O(5)$_{I,000}$	3·17 (3)
—O(6)$_{I,000}$	3·21 (3)	—O(6)$_{I,001}$	3·11 (3)	—O(5)$_{I,010}$	2·83 (3)
—O(6)$_{I,010}$	2·97 (2)	—O(7)$_{I,000}$	3·19 (3)	—O(7)$_{I,010}$	3·13 (3)
—O(8)$_{I,000}$	3·27 (3)	—O(8)$_{I,000}$	3·12 (3)	—O(9)$_{I,000}$	3·42 (4)
—O(11)$_{II,-10-1}$	2·91 (3)	—O(9)$_{I,000}$	3·27 (3)	—O(10)$_{I,00-1}$	3·00 (2)
—O(12)$_{II,-1-1-1}$	3·40 (3)	—O(10)$_{I,0-10}$	3·33 (3)	—O(11)$_{I,010}$	3·36 (4)
—O(12)$_{II,-10-1}$	2·87 (2)	—O(10)$_{I,000}$	2·88 (2)	—O(12)$_{I,00-1}$	3·42 (4)

O atoms of the SeO_4 tetrahedra translated along the b axis. The shortest O—O distances are as follows: $O(3)_{y+1} \cdots O(4)$ 2·556 (22), $O(7)_{y+1} \cdots O(8)$ 2·479 (21), $O(11)_{y+1} \cdots O(9)$ 2·605 (26) Å.

Assuming these O—O distances to be due to the hydrogen bonds, the crystal structure of RHSe can be described as consisting of SeO_4^{2-} chains similar to the SO_4^{2-} chains formed in AHS and RHS, although the mutual arrangement of the chains in RHSe is different.

The coordination polyhedra of the Rb ions are similar. Rb—O distances up to 3·5 Å are listed in Table 2. Assuming the radius of the coordination sphere of Rb to be equal to 3·5 Å, the coordination number of the Rb atom is 10.

The pseudosymmetry observed in RHSe in the ferroelectric phase points to the possible existence of an upper phase with higher symmetry, which might be treated as the starting phase (called the prototype) from which the ferroelectric phase can be derived by small displacements or deformations. Recent work performed in our laboratory showed that the symmetry of the high-temperature phase is monoclinic with space group $I2_1$, $\gamma = 90 \cdot 70$ (1)° (Pietraszko et al., 1978).

Detailed discussion of the spontaneous polarization and the phase-transition mechanism in RHSe will be given when the crystal structure of the paraelectric phase has been determined and more information on the ferroelectric properties of $RbHSeO_4$ is available.

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Non-Stoichiometric Sodium Iron(II) Titanium(IV) Oxide

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Abstract. $Na_{0.56}Fe_{0.28}Ti_{1.72}O_4$, orthorhombic, Pnma, $a = 9 \cdot 083$ (6), $b = 2 \cdot 954$ (1), $c = 10 \cdot 718$ (3) Å, $Z = 4$, $D_x = 4 \cdot 04$ g cm⁻³. The crystals were prepared by heating a mixture of Fe and TiO_2 in a $10 M$ NaOH solution sealed in a Au tube at 650°C and 1000 bar. After 7 d black prismatic crystals were obtained. The compound is isostructural with $CaFe_2O_4$, with mean M(1)—O, M(2)—O and Na—O distances of 2·00, 1·98 and 2·48 Å respectively.

Introduction. Oscillation and Weissenberg photographs showed the crystal to be orthorhombic. The systematic absences, $0kl$ with $k + l$ odd and $hk0$ with h odd, indicated the space group to be $Pn2_1a$ or Pnma; the structure refinement showed the latter to be correct. Cell dimensions were determined by the least-squares method from the 2θ values of 19 reflections.

A prismatic crystal with approximate dimensions $0 \cdot 04 \times 0 \cdot 30 \times 0 \cdot 04$ mm was used for intensity collection. Intensities were measured on a Philips automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by graphite up to $2\theta = 45°$, employing the ω–2θ scan technique. The scan speed was 4° min⁻¹ in ω and scanning was repeated twice when the total counts were less than 1000. The scan width was varied for each reflection according to the