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Ammonium Deuterium Selenate and Rubidium Deuterium Selenate

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Abstract. The title compounds are orthorhombic, $P2_12_12_1$, $Z = 4$; $M_r = 231{\cdot}5$, $a = 12{\cdot}887$ (3), $b = 4{\cdot}599$ (6), $c = 7{\cdot}515$ (4) Å, $V = 445{\cdot}4$ Å^3, $D_c = 3{\cdot}451$ Mg m^{-3}, $\mu = 16{\cdot}33$ mm^{-1} and $M_r = 168{\cdot}0$, $a = 12{\cdot}847$ (3), $b = 4{\cdot}595$ (6), $c = 7{\cdot}503$ (4) Å, $V = 442{\cdot}9$ Å^3, $D_c = 2{\cdot}518$ Mg m^{-3}, $\mu = 8{\cdot}13$ mm^{-1} for $RbDSeO_4$ and ND_4DSeO_4, respectively. The structure of ND_4DSeO_4 was solved by the Patterson method and refined by full-matrix least squares to $R = 0{\cdot}041$ ($R_w = 0{\cdot}043$) for 1772 reflections with $|F| > \sigma(|F_o|)$. $RbDSeO_4$ is isomorphous with ND_4DSeO_4 and was refined to $R = 0{\cdot}061$ ($R_w = 0{\cdot}065$) for 1724 reflections. The SeO_4 tetrahedra are connected by O—D$\cdots$O bonds to form chains almost parallel to the b axis. The asymmetric nature of the O—D$\cdots$O bond and differences in the symmetry of the deuterated analogues explain the disappearance of the ferroelectric properties in highly deuterated selenates.

Introduction. NH_4HSeO_4 (AHSe) and $RbHSeO_4$ (RHSe) have been found by Czapla, Lis & Sobczyk (1979) to be ferroelectrics below the Curie points $T_c = 251{\cdot}3$ K and $T_c = 370{\cdot}5$ K, respectively. Recently, Gesi (1980) has reported the results of dielectric and DTA measurements performed in a wide temperature range on AHSe. Gesi (1980) found an additional anomaly in the plot of the temperature dependence of the dielectric constant measured along the c axis. This anomaly, at about $T_2 = 93$ K, corresponds to the first-order phase transition to another pyroelectric phase. High-temperature transitions were observed at 417 K in AHSe (Czapla, 1981) and at 447 K in RHSe (Suzuki, Osaka & Makita, 1979). The crystal structure of RHSe at room temperature has been determined from X-ray data by Waśkowska, Olejnik, Łukaszewicz & Głowiak (1978) and that at 388 K by Waśkowska, Olejnik, Łukaszewicz & Czapla (1980). Neutron diffraction results were reported by Rozière (1979). The crystal structure of AHSe at room temperature has been solved by Olejnik, Waśkowska & Łukaszewicz (1979) and independently by Aleksandrov, Kruglik, Misyul & Simonov (1980) and that of the ferroelectric phase by Kruglik, Misyul & Aleksandrov (1980). From these studies the following conclusions can be inferred: the triclinic ↔ monoclinic phase transition might occur due to the order–disorder displacements of protons in hydrogen bonds or due to the arrangement of dipole moments of SeO_4 tetrahedra linked into chains by hydrogen bonds.

In order to study whether the role of protons in hydrogen bonds is essential for the appearance of the spontaneous polarization in these crystals, deuterated ND_4DSeO_4 (ADSe) and $RbDSeO_4$ (RDSe) crystals were investigated by Czapla & Sobczyk (1980). It was observed that in partly deuterated samples, the transition point T_c is shifted towards higher temperatures. Crystals with a high level of deuteration [above 0·50 for AHSe (Czapla, Czupiński & Sobczyk, 1981) and 0·95 for RHSe (Czapla, 1981)] lose their ferroelectric properties and simultaneously change their symmetry to that of space group $P2_12_12_1$.

Because of the physical significance of this group of crystals, the structures of ADSe and RDSe at room temperature have been investigated.

Crystals of ADSe and RDSe were prepared as described previously (Czapla & Sobczyk, 1980; Czapla *et al.*, 1981). For the samples used in our experiment the degree of deuteration estimated from IR spectra reached 90 and 92% in ADSe and RDSe, respectively. ADSe was mounted in a Lindemann-glass capillary to prevent it from deliquescing, whereas the RDSe crystal, which was more stable in laboratory conditions, was covered with silicone grease. The cell parameters were obtained using the CAD-4 auto-indexing procedure from the setting angles of 15 reflections. The intensities were collected with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). During the data collection three standard reflections were measured regularly after every 60 reflections. A loss of about 12% in intensity was observed for RDSe due to slow decomposition of the crystal. Assuming

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Table 1. *Experimental conditions*

	$RbDSeO_4$	ND_4DSeO_4
Crystal dimensions	0·55 mm	0·38 mm
Systematic absences	$h00$: $h = 2n + 1$, $0k0$: $k = 2n + 1$, $00l$: $l = 2n + 1$	
θ_{max}	33°	
Scanning mode	ω–2θ	
Scan width	$\Delta\omega = (0{\cdot}75 + 0{\cdot}40 \tan\theta)°$	
Number of observable reflections	1924	1983
Number of reflections with $\lvert F\rvert > \sigma(\lvert F_o\rvert)$	1724	1722
Number of test reflections	3	
R	0·061	0·041
R_w	0·065	0·043
w	$(\sigma\lvert F_o\rvert)^{-2}$	

$\sigma(F_o) = [\sigma(I) + (0{\cdot}03I)]^{1/2}/2I^{1/2}$

that the intensities varied linearly with time, a scale correction was applied. Details of data collection are given in Table 1. The intensities were corrected for Lorentz, polarization and absorption effects (spherical crystals). For both crystals the final reflection data set consisted of the two subsets: $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ in order to correct scattering factors of Se and Rb for anomalous dispersion. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

ND_4DSeO_4. The structure was solved by Patterson and Fourier methods and refined using full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms. The deuterium atoms, belonging to the ND_4 group could not be identified on the final difference Fourier map, but the D atom involved in the O—D···O bond connecting the SeO_4 tetrahedra appeared in its expected position as a peak with the intensity of 0·7 e Å^{-3}. Atomic coordinates with isotropic temperature factors are listed in Table 2.* The anisotropic temperature factors U_{ij} do not show any unusual features.

Table 2. ND_4DSeO_4: *Atomic coordinates and thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$, for D atom B_{iso} is given.

	x	y	z	U_{eq} (Å^2 × 10^2)
Se	0·12557 (4)	0·2333 (1)	0·53950 (3)	2·03 (1)
N	0·1208 (3)	0·3252 (9)	0·0516 (5)	3·17 (1)
O(1)	0·2167 (3)	0·0837 (8)	0·4249 (4)	4·11 (2)
O(2)	0·0288 (3)	0·3419 (7)	0·4167 (4)	3·34 (2)
O(3)	0·1675 (2)	0·4855 (7)	0·6742 (4)	2·92 (2)
O(4)	0·0725 (2)	−0·0219 (7)	0·6793 (4)	2·83 (2)
D	0·102 (6)	−0·226 (9)	0·677 (7)	5·2 (1·5)

Table 3. $RbDSeO_4$: *Atomic coordinates and thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} (Å^2 × 10^2)
Se	0·12637 (3)	0·23157 (8)	0·54024 (5)	1·28 (1)
Rb	0·12224 (3)	0·31597 (9)	0·05116 (5)	2·32 (1)
O(1)	0·2173 (3)	0·0806 (9)	0·4309 (5)	3·62 (1)
O(2)	0·0313 (3)	0·3417 (9)	0·4202 (4)	2·67 (1)
O(3)	0·1696 (3)	0·4823 (8)	0·6730 (5)	2·51 (1)
O(4)	0·0745 (3)	−0·0236 (8)	0·6806 (3)	2·04 (1)
D	0·109 (6)	−0·225 (9)	0·678 (6)	6·8 (1·9)

$RbDSeO_4$. The starting parameters for the refinement were atomic positions obtained for ADSe and the refinement procedure was similar to that for ADSe. Final coordinates and U_{eq} values are given in Table 3.* Since the effect of anomalous scattering was included in the structure factor calculations the determination of the absolute configuration was possible. The refinement, repeated for the structures having the absolute configuration opposite to that given in Tables 2 and 3, converged with agreement factors $R(-) = 0{\cdot}051$, $R_w(-) = 0{\cdot}057$ and $R(-) = 0{\cdot}068$, $R_2(-) = 0{\cdot}074$ for ADSe and RDSe, respectively. Hamilton's R-factor ratio test indicated a high significance for the original coordinates (Hamilton, 1965).

All calculations were performed with the XRAY76 program system (Stewart, 1976).

Discussion. ADSe and RDSe are isomorphous. The main structural motif in the hydrogen analogues, consisting of a long chain, parallel to the b axis, of SeO_4 tetrahedra connected by hydrogen bonds, remains unchanged (Fig. 1). The configuration of SeO_4 tetrahedra in both deuterated compounds is given in Table 4. The deformation of these groups is very similar to

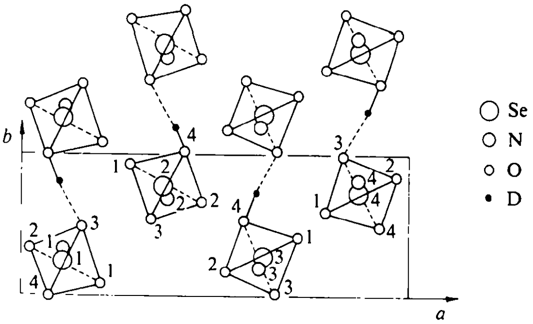

Fig. 1. Projection of the structure down the c axis.

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* Lists of structure factors, anisotropic thermal parameters and NH_4···O and Rb···O contact distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36729 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

Table 4. *Configuration of* SeO_4 *tetrahedra: bond distances* (Å) *and angles* (°)

	ND_4DSeO_4	$RbDSeO_4$
Se–O(1)	1·606 (4)	1·592 (4)
–O(2)	1·626 (3)	1·603 (3)
–O(3)	1·629 (3)	1·623 (4)
–O(4)	1·714 (3)	1·714 (3)
Mean	1·644 (7)	1·633 (7)
O(1)–Se–O(2)	112·7 (2)	114·1 (2)
O(1)– –O(3)	113·3 (2)	112·1 (2)
O(1)– –O(4)	108·9 (2)	107·8 (2)
O(2)– –O(3)	112·7 (2)	112·6 (2)
O(2)– –O(4)	104·6 (2)	105·3 (1)
O(3)– –O(4)	103·8 (2)	104·0 (2)

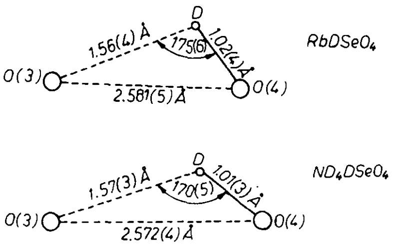

Fig. 2. Configuration of O—D···O bonds in ND_4DSeO_4 and $RbDSeO_4$.

that described for hydrogenselenates and is associated with the participation of O atoms in O—D···O bonds of lengths 2·572 (4) and 2·581 (5) Å for ADSe and RDSe, respectively. The configuration of O—D···O bonds is shown in Fig. 2. Unfortunately, it is impossible to say much about the arrangement of D atoms around the N atom. The ND_4 ion executes pronounced thermal motion. However, several of the N—O distances,* *e.g.* N—O(2), $-O(3^{I})$,† $-O(1^{III})$ and $-O(2^{V})$ equal to 2·984 (5), 2·987 (5), 2·966 (5) and 2·946 (5) Å respectively, suggest that these oxygens might be acceptors of N—O···O bonds.

Replacement of the hydrogen by deuterium changes the crystal symmetry and in consequence the physical properties. Comparing asymmetric units of the ferroelectric and paraelectric unit cells of RHSe and of the deuterated salt we can find the relationship between them as shown in Fig. 3. In the triclinic phase the asymmetric unit consists of three symmetrically inequivalent formula units which form three types of SeO_4 tetrahedra chains with three different hydrogen bonds. In chain II the hydrogen bond is shorter than in the other two. In the monoclinic phase chains I and III become equivalent. The twofold axis at the midpoint between the two tetrahedra forming chain II splits H(2) into two equivalent positions close to the center of the O···O distance. In the ferroelectric phase only one of these positions is occupied. The deuterated orthorhombic unit cell contains only one type of chain. The asymmetric potential well of the O—D···O bond prevents the order–disorder motion of the deuteron and causes T_c to vanish. Assuming that the appearance of spontaneous polarization in hydrogenselenates is connected with the proton motion in hydrogen bonds, we propose the following microscopic model for the phase transition: the ordering of protons in hydrogen bonds in the triclinic phase gives a resultant dipole moment ≠ 0; the polarization reversal may be caused by the proton transfer between the oxygens involved in the O—H···O bond. Symmetry restrictions in the monoclinic phase cause the dipole moments connected with the hydrogen bonds in chains I and III to cancel each other. The dipole moment of the hydrogen bond in chain II also disappears owing to the disordered motion of the protons of type H(2). From the X-ray data it is, however, impossible to characterize this motion and its change during the phase transition. This will be a subject of further studies.

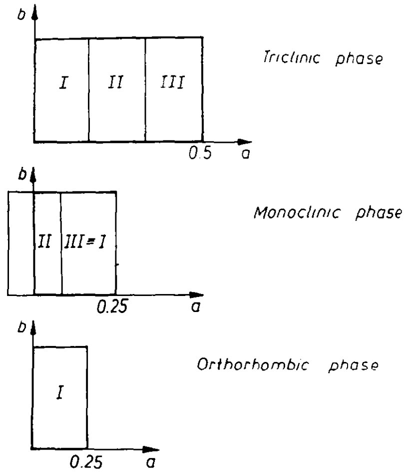

Fig. 3. Asymmetric units (heavy lines) in hydrogenselenates and in deuterated analogues. Each block represents one formula unit.

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* See deposition footnote.

† Symmetry code: (I) $x, y, z-1$; (III) $\frac{1}{2}-x, \bar{y}, z-\frac{1}{2}$; (V) $\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$.

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Crystal Growth and Structure of Diantimony(III) Zinc Oxide

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Abstract. $ZnSb_2O_4$, tetragonal, space group $P4_2/mbc$, $a = b = 8{\cdot}527\ (2)$, $c = 5{\cdot}942\ (2)$ Å, $U = 432{\cdot}1\ (2)$ Å^3, $Z = 4$, $D_c = 5{\cdot}73$ Mg m^{-3}. Single crystals have been grown using Sb_2O_3 as flux. The structure proposed by Stahl [*Ark. Kemi, Mineral. Geol.* (1943). **17**B (5), 1–7] from powder data has been confirmed and refined to $R = 0{\cdot}015$ for 168 independent reflections. It consists of chains of twisted and elongated ZnO_6 octahedra sharing opposite edges, these chains being linked by the Sb atoms, each with a pyramidal arrangement of three neighbouring O atoms.

Introduction. The crystal structure of $ZnSb_2O_4$ was studied by Stahl (1943) in a powdered sample. The atomic arrangement of Pb_3O_4 (space group $P4_2/mbc$) was assumed, Sb and Zn replacing Pb^{II} and Pb^{IV} respectively. The positions of the O atoms were fixed from the Zn—O distance, assumed to be 2·05 Å. The structure consists of ZnO_6 octahedra linked together by opposite edges, forming chains in the direction of the *c* axis, the chains being joined laterally by SbO_3 pyramids connected with each other (Wells, 1975). There are two Sb—O distances of 2·01 Å and one of 1·87 Å, and two O—Sb—O bond angles of 100·1° and one of 94·8°. More recently, single crystals of the isomorphous compound $MgSb_2O_4$ have been prepared from $MgCl_2.KCl$ flux by Giroux-Maraine & Pérez (1975), who have established the atomic positions and isotropic temperature factors, refining the structure in space group $P4_2/mbc$ to $R = 0{\cdot}042$. Simultaneously Fischer & Pertlik (1975) refined the structure of the mineral schafarzikite, $FeSb_2O_4$ with small amounts of Mn, in the same space group to $R = 0{\cdot}056$, with anisotropic temperature factors. As there are a good number of synthetic AB_2O_4 complex oxides isostructural with $ZnSb_2O_4$, the present paper reports the refinement of the structure of this compound using data from a synthetic crystal.

After several fruitless attempts, $ZnSb_2O_4$ crystals were grown from analytical-grade reagents by reaction of ZnO and a large excess of Sb_2O_3 in an evacuated and sealed quartz ampoule at 1023 K for 24 h, and then slowly decreasing the temperature to 873 K over a period of two days.

A colourless, approximately cubic crystal of 0·05 mm edge was examined at 291 K on a Nonius CAD-4F automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The unit-cell parameters were obtained by least-squares refinement of the setting angles of 24 reflections with $19° < 2\theta < 48°$.

Intensities were collected by ω–2θ scans, with scan rates varying from 1·8 to 6·7° (2θ) min^{-1} so that weaker reflections were measured more slowly. The scan width varied from 1·2° at low 2θ to 1·76° at higher angles. There was no appreciable drop in intensity of three standard reflections, checked every hour. 1566 reflections within half a sphere with 2° <

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