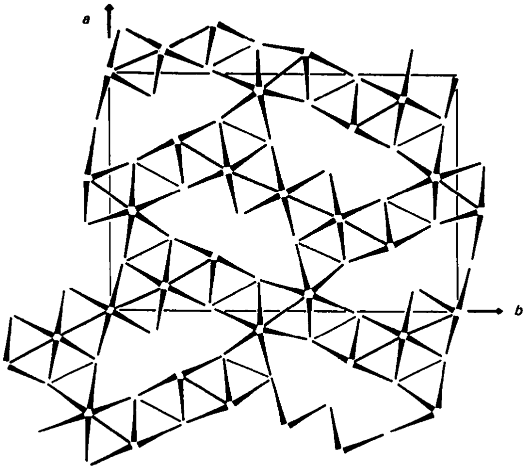

Fig. 2. Enchaînement des octaèdres dans $In_{18}Sn_7S_{34}$. Les plans équatoriaux perpendiculaires aux axes 0*x* 0*y* sont représentés par des traits continus: épais si les atomes qui les définissent sont en $z = 0$ et ± 1; fins si les atomes qui les définissent sont $z = \pm \frac{1}{2}$.

deux In(4) et deux In(5) est lié aux octaèdres des atomes In(1) et In(2) par mise en commun d'une arête. L'octaèdre autour de In(3) est lié par une arête à chacun des deux octaèdres formés par In(2) et par un sommet à l'octaèdre de In(1) (Fig. 1).

Cet ensemble d'octaèdres forme un réseau tridimensionnel dans lequel viennent s'insérer les atomes d'étain (Fig. 2).

L'environnement des sites d'étain Sn^{2+} peut être envisagé de deux façons. Si on ne considère que les distances Sn—S inférieures à 3,20 Å comme Jumas *et al.* (1980) dans $Sn_4Sb_6S_{13}$, les deux atomes d'étain ont des environnements différents. L'atome Sn(2) est entouré de sept atomes de soufre formant un prisme triangulaire monocapé. L'atome Sn(1) n'est, lui, entouré que par six atomes de soufre proches et irrégulièrement répartis. Cette disposition peut être considérée comme une manifestation de la paire électronique non liée dont l'influence se ferait sentir pour Sn(1) et non pour Sn(2). Mais le tableau des distances Sn—S est tel que nous préférons tenir compte de l'ensemble des atomes de soufre situés à une distance inférieure à 3,48 Å. Les atomes d'étain ont alors un environnement identique avec une moyenne des distances Sn—S de 3,07 Å dans les deux cas. Les atomes d'étain sont à l'intérieur d'un prisme triangulaire dicapé, les distances les plus longues correspondant à des liaisons faibles, ce qui est fréquent pour les coordinences élevées.

L'atome S(1) présente un facteur d'agitation thermique plus élevé que les autres (4,0 Å) dû à sa position particulière entre deux sites d'étain partiellement occupés.

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Structure of Rubidium Selenate at Room Temperature

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Abstract. Rb_2SeO_4, $M_r = 313{\cdot}89$, orthorhombic, *Pnam*, $a = 7{\cdot}961\,(2)$, $b = 10{\cdot}794\,(3)$, $c = 6{\cdot}161\,(1)$ Å, $V = 529{\cdot}42\,(36)$ Å^3, $Z = 4$, $D_x = 3{\cdot}94$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}710730$ Å, $\mu = 246{\cdot}9$ cm^{-1}, $F(000) = 560$, room temperature, final $R = 0{\cdot}039$ for 1184 independent reflections. A collection with the rigid-body vibration model gives an almost regular SeO_4 tetrahedron with an average bond length of 1·640 Å and bond angle of 109·7°. The SeO_4 is linked by the contact bonds of O(1)—Rb(1) and two O(3)—Rb(2). Compared with isomorphous ferroelectrics such as K_2SeO_4, $(NH_4)_2SO_4$ and $(NH_4)_2BeF_4$, relatively isotropic thermal motions of the SeO_4 tetrahedron are found.

Introduction. Recently, many substances having the β-K_2SO_4 structure such as $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$,

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K_2SeO_4, K_2ZnCl_4 have been studied extensively because of their peculiar ferroelectric behaviour and their successive structural phase transitions. The dielectric susceptibility along the ferroelectric axis shows very weak temperature dependence and obeys the Curie–Weiss law only in a narrow temperature region above T_c. The Curie–Weiss constants are 30 for K_2SeO_4, 15·6 for $(NH_4)_2SO_4$ and 16·4 for $(NH_4)_2BeF_4$. These values are smaller by about two or four orders of magnitudes than those of usual ferroelectrics (Strukov, Skomorokhova, Kopstik, Boiko & Izrailenko, 1973; Onodera, Cynshi & Shiozaki, 1985). The spontaneous polarization is very small: 0·62 μC cm^{-2} for $(NH_4)_2SO_4$, 0·22 μC cm^{-2} for $(NH_4)_2BeF_4$ and 0·14 μC cm^{-2} for K_2SeO_4 (Unruh, 1970; Hoshino, Vedam, Okaya & Pepinsky, 1958; Aiki, Hukuda, Koga & Kobayashi, 1970). The polar direction is along the *b* axis for $(NH_4)_2BeF_4$ whereas it is along the *c* axis for the others. Furthermore, most of them undergo incommensurate phase transitions (Iizumi, Axe, Shirane & Shimaoka, 1977; Iizumi & Gesi, 1977; Gesi & Iizumi, 1979). The modulation wave vectors in the incommensurate phase are $\sim 1/3a^*$ for K_2SeO_4, K_2ZnCl_4 and Rb_2ZnCl_4 and $\sim 1/2b^*$ for $(NH_4)_2BeF_4$.

Although there are some differences, the similarities mentioned above suggest that the phase transitions in these substances come from a certain common origin. It is of interest to study the crystal structures in A_2BX_4-type substances more widely and discuss why the similarities exist.

In this paper, we report the crystal structure of a new A_2BX_4-type crystal, Rb_2SeO_4. For this substance the lattice constants and the space group at room temperature were investigated (Gattow, 1962). However, the crystal structure and the dielectric properties have not yet been reported. In particular, the thermal motions of Rb atoms and SeO_4 tetrahedra are compared with isomorphous ferroelectric substances.

Experimental. Crystallization from aqueous equimolar solution of Rb_2CO_3 and H_2SeO_4 at 311 K by slow evaporation yielded single crystals which are colourless transparent plates. X-ray oscillation and Weissenberg photographs revealed no superlattice and no incommensurate reflections. A spherical single crystal, diameter 0·13 mm, was mounted on a Rigaku AFC-6B four-circle diffractometer with graphite-monochromated Mo *K*α radiation. The ω–2θ scan technique was adopted. Three standard reflections monitored after every 60 reflections showed no systematic changes. 2007 reflections, 1184 independent with $|F_o| > 3\sigma(|F_o|)$, were collected in the region $0 \le h \le 14$, $0 \le k \le 19$, $0 \le l \le 11$ $(0 < \sin\theta/\lambda < 0{\cdot}90\ \text{Å}^{-1})$. Lattice constants were obtained by the least-squares method for 17 reflections having $15 < \theta < 35°$. From the possible space groups, *Pnam* and $Pna2_1$, *Pnam* is adopted from the statistical distribution of the observed intensities. An absorption correction was made ($\mu r = 3{\cdot}21$ for Mo *K*α radiation). Max., min. absorption factor A^* 44·67, 16·68. Using the parameters of K_2SeO_4 (Kalman, Stephens & Cruickshank, 1970) as an initial set, refinements on $|F|$ were made by full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). The values of the atomic scattering factors and the anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). An isotropic secondary-extinction correction was taken into account, $g = 7{\cdot}0497 \times 10^{-4}$ (Coppens & Hamilton, 1970). The refinement converged to $R = 0{\cdot}039$ and $wR = 0{\cdot}037$, $w = 1/[\sigma^2(|F_o|) + (0{\cdot}001|F_o|)^2]$, and $S = 2{\cdot}66$, max. $\Delta/\sigma = 0{\cdot}57$. Final difference map revealed no unusual features with max. and min. values 2·5 and −1·6 e Å^{-3}.†

Table 1. *Fractional coordinates and isotropic thermal parameters* U_{eq}(Å$^2 \times 10^4$)

For Se, O atoms, corrected parameters of the rigid-body vibration analysis are given in the second row. U_{eq} is one third the trace of the diagonalized anisotropic thermal-parameter matrix.

	x	y	z	U_{eq}
Rb(1)	0·6729 (1)	0·4911 (1)	0·2500	241·7
Rb(2)	0·9904 (1)	0·7072 (1)	0·2500	223·0
Se	0·2296 (1)	0·4204 (1)	0·2500	140·0
	0·2296 (1)	0·4204 (1)	0·2500	
O(1)	0·0258 (7)	0·4179 (7)	0·2500	412·3
	0·0246 (7)	0·4178 (7)	0·2500	
O(2)	0·2995 (8)	0·5634 (5)	0·2500	290·7
	0·3000 (8)	0·5642 (5)	0·2500	
O(3)	0·2999 (6)	0·3511 (4)	0·0331 (7)	341·3
	0·3003 (6)	0·3508 (4)	0·0318 (7)	

Discussion. Atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s are listed in Table 1. The pseudo-hexagonal structure can be recognized easily from the projection along [100] as in the case of K_2SeO_4 (Kalman *et al.*, 1970). The ratio *b*/*c* is 1·752, which is close to $3^{1/2}$. The values of this ratio are 1·755, 1·765 and 1·744 for $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$ and K_2SeO_4, respectively, at room temperature. This is associated with pseudo-hexagonal symmetry (Makita, Sawada & Takagi, 1976; Sawada, Makita & Takagi, 1976).

The thermal parameters of the O atoms are large and highly anisotropic (Table 1). The average Se—O bond length is 1·631 Å, which is about 0·01 Å shorter than the mean length in other crystals (Gibbs, Chiari,

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43343 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for the* SeO_4 *group*

	Uncorrected	Corrected		Uncorrected	Corrected
Se—O(1)	1·623	1·632 (8)	O(3)—Se—O(2)	108·4	108·3 (3)
Se—O(2)	1·641	1·650 (6)	O(2)—Se—O(1)	110·8	110·8 (4)
Se—O(3)	1·630	1·639 (5)	O(3)—Se—O(3′)	110·1	110·2 (2)
Average	1·631	1·640 (6)	O(3)—Se—O(1)	109·6	109·6 (3)
			Average	109·7	109·7 (3)

Table 3. *The r.m.s. displacements and the r.m.s. amplitudes of* SeO_4, SO_4, *and* BeF_4 *at room temperature*

One of the principal axes is along **c** and the others are nearly along **a** and **b**.

R.m.s. displacement along the principal axes (Å)

	~*a* axis	~*b* axis	*c* axis
SeO_4 (Rb_2SeO_4)	0·116	0·129	0·126
SeO_4 (K_2SeO_4)	0·122	0·134	0·130
SO_4 [$(NH_4)_2SO_4$]	0·152	0·163	0·154
BeF_4 [$(NH_4)_2BeF_4$]	0·124	0·166	0·147

R.m.s. amplitude around the principal axes (°)

	~*a* axis	~*b* axis	*c* axis
SeO_4 (Rb_2SeO_4)	5·50	6·59	5·58
SeO_4 (K_2SeO_4)	5·26	7·33	6·58
SO_4 [$(NH_4)_2SO_4$]	6·32	7·43	7·87
BeF_4 [$(NH_4)_2BeF_4$]	7·53	6·54	7·89

Louisnathan & Cruickshank, 1976). Thus, rigid-body thermal analysis was carried out treating SeO_4 as a rigid body (Cruickshank, 1956). The corrected and uncorrected bond lengths are summarized in Table 2. The corrected average bond length is 1·640 Å which is almost equal to those in other crystals. The corrected average bond angle for O—Se—O is 109·7°. The shape of SeO_4 is a regular tetrahedron within the e.s.d.'s. Root-mean-square (r.m.s.) displacements and r.m.s. librational amplitudes of the rigid SeO_4 are compared with those in other crystals in Table 3 (Kalman *et al.*, 1970; Onodera & Shiozaki, 1981). The r.m.s. translational displacements and the r.m.s. librational amplitudes show that the thermal motions of SeO_4 in Rb_2SeO_4 are nearly isotropic compared with those of the others. The phase transition from the paraelectric phase to the incommensurate phase for K_2SeO_4 is caused by the soft mode which belongs to the $\sum_2$ optic branch (Iizumi, Axe, Shirane & Shimaoka, 1977). When Rb_2SeO_4 exhibits a similar phase transition, the transition temperature will be very low compared with that of K_2SeO_4. Indeed, it has no phase transition down to about 20 K.

Several differences in the two crystallographically independent Rb atoms are obvious. The Rb(1) ion is surrounded by 11 O atoms; there are only 9 O atoms near Rb(2). The interatomic distances between Rb and O are given in Fig. 1 (Å). The sum of their ionic radii is 2·88 Å [1·48 Å for Rb^+ and 1·40 Å for O^{2-} (Pauling, 1960)] or 3·08 Å [1·73 Å for Rb^+ and 1·35 Å for O^{2-} (Shannon & Prewitt, 1969)]. Short interatomic distances are observed between O and Rb: O(1)—Rb(1) = 2·811 Å, two O(3)—Rb(2) = 2·871 Å. The two O(2) atoms are weakly connected to the Rb(2) ions (2·905, 2·910 Å). The SeO_4 tetrahedron is linked by these contact bonds to the surrounding Rb ions. The average interatomic Rb(1)—O length is 3·24 Å and that of Rb(2) is 3·04 Å. Rb(1)—O(1) (3·74 Å) is quite long. If we exclude O(1), the average length of Rb(1)—O becomes 3·19 Å, which is closer to the sum of the two ionic radii. The r.m.s. displacements of Rb(1) are larger than those of Rb(2) as shown in Table 4. The r.m.s. displacements of Rb atoms are similar to those of K atoms in K_2SeO_4, but Rb atoms are more isotropic than K atoms.

It is interesting to study the possibility of the appearance of ferroelectricity and of structural phase transitions. The measurement is now under way and should be reported in the near future.

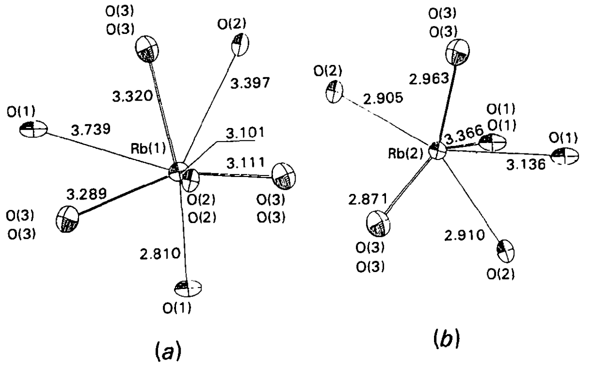

Fig. 1. Environment of Rb atoms viewed along the *c* axis; (*a*) around Rb(1) and (*b*) around Rb(2). Doubly labelled O atoms are above and below the mirror plane and overlap in this figure.

Table 4. *The r.m.s. displacements* (Å) *along the principal axes of* Rb, K, *and* N *atoms at room temperature*

The orientation of the principal axis is given in brackets in degrees as (θ_a, θ_b, θ_c); θ_a is the angle between the principal axis and the *a* axis.

Rb_2SeO_4			
Rb(1)	0·165 (80, 10, 90)	0·155 (90, 90, 0)	0·145 (10, 80, 90)
Rb(2)	0·164 (90, 90, 0)	0·144 (74, 16, 90)	0·135 (16, 74, 90)
K_2SeO_4			
K(1)	0·174 (77, 13, 90)	0·168 (90, 90, 0)	0·125 (13, 77, 90)
K(2)	0·162 (90, 90, 0)	0·141 (88, 2, 90)	0·166 (2, 88, 90)
$(NH_4)_2SO_4$			
N(1)	0·180 (67, 23, 90)	0·168 (90, 90, 0)	0·158 (23, 67, 90)
N(2)	0·183 (90, 90, 0)	0·181 (18, 72, 90)	0·167 (72, 18, 90)
$(NH_4)_2BeF_4$			
N(1)	0·185 (87, 3, 90)	0·172 (90, 90, 0)	0·154 (3, 87, 90)
N(2)	0·158 (49, 41, 90)	0·156 (90, 90, 0)	0·147 (41, 49, 90)

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Structure of Strontium Diselenite

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Abstract. $SrSe_2O_5$, $M_r = 325{\cdot}54$, triclinic, $P\bar{1}$, $a = 6{\cdot}916\,(1)$, $b = 6{\cdot}971\,(1)$, $c = 10{\cdot}875\,(2)$ Å, $\alpha = 85{\cdot}07\,(1)$, $\beta = 81{\cdot}46\,(1)$, $\gamma = 79{\cdot}56\,(1)°$, $V = 509{\cdot}0$ Å^3, $Z = 4$, $D_x = 4{\cdot}25$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}710688$ Å, $\mu = 24{\cdot}32$ mm^{-1}, $F(000) = 584$, room temperature, $R = 0{\cdot}035$ for 3753 observed reflections up to $\sin\theta/\lambda = 0{\cdot}81$ Å^{-1}. The mean Sr—O distance for the eight-coordinated Sr(1) atom (2·604 Å) is somewhat shorter than that for the nine-coordinated Sr(2) atom (2·661 Å). The two crystallographically different diselenite groups have Se—O bond lengths to the bridging O atoms ranging from 1·822 to 1·879 Å, others from 1·645 to 1·685 Å; the Se—O—Se angles are 120·7 and 122·5°.

Introduction. Crystal structures of compounds with the general formula $M^{2+}Se_2O_5$ have been determined for $M = $ Ca (Delage, Carpy & Goursolle, 1982), $M = $ Mn (Koskenlinna, Niinistö & Valkonen, 1976), $M = $ Cu (Meunier, Svensson & Carpy, 1976), and $M = $ Zn (Meunier & Bertaud, 1974). Other diselenite groups in inorganic crystal structures were found in $VO(Se_2O_5)$ (Meunier, Bertaud & Galy, 1974), $MnH(SeO_3)(Se_2O_5)$ (Koskenlinna & Valkonen, 1977*b*), $PrH_3(SeO_3)_2(Se_2O_5)$ (Koskenlinna & Valkonen, 1977*a*), $Y(NO_3)(Se_2O_5).3H_2O$ (Valkonen & Ylinen, 1979), $(NH_4)_2(Se_2O_5)$ (Chomnilpan, 1980), $Au_2(SeO_3)_2(Se_2O_5)$ (Jones, Schwarzmann, Sheldrick & Timpe, 1981), $Ca_2(HSeO_3)_2(Se_2O_5)$ (Valkonen, 1985), and $K_2Se_2O_5$ (Rider, Sarin, Bydanov & Vinogradova, 1985). During synthesis of the monazite-type strontium selenate $SrSeO_4$ (Effenberger & Pertlik, 1986), the new compound $SrSe_2O_5$ was obtained. In connection with studies on the chemical behaviour of selenites, the crystal structure of $SrSe_2O_5$ was determined.

Experimental. *Synthesis.* Crystals of $SrSe_2O_5$ were synthesized hydrothermally in a steel vessel lined with Teflon. 2 g of a mixture of $SrCO_3$ and H_2SeO_3 (molar ratio 1:2) were put into the vessel with ~6 ml capacity and 1 ml H_2O_2 (Perhydrol) was added. The vessel was filled up with H_2O to about 80 vol% and was heated for 48 h at 493 (5) K. After cooling to room temperature (~12 h), crystals of $SrSe_2O_5$ were observed. The title compound forms colourless and equidimensional crystals up to a diameter of 0·5 mm.

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