trigonal structure of $Pb(ReO_4)_2$ (Picard *et al.*, 1984), where all six bridges are of the *a*-type.

The layers form a three-dimensional structure *via* Ba—O(11) bonds and an extensive system of O···H—O bonds with the participation of the water molecules (*W*1–*W*4). *W*1, *W*2 and *W*3 are coordinated to Ba and, besides donating two protons each, they also accept one: *W*1 from *W*3, *W*2 from *W*4, and *W*3 from *W*2. The molecule *W*4 represents an interstitial water and is completely involved in hydrogen bonding both as donor and acceptor. The non-H tetrahedral neighbourhood of the water O atoms includes either Ba and three O atoms (*W*1, *W*2, *W*3) or four O atoms (*W*4), the O···O/Ba—O distances extending from 2.771 (11) [O(*W*1)···O(24)] to 2.953 (8) Å [Ba—O(*W*3)].

The presence of *W*4 in the structure together with the non-uniformity of the Ba—O bond valences which, according to the valence-matching principle (Brown, 1981), is a source of internal strength in the structure, may explain the observed instability of $Ba(ReO_4)_2.4H_2O$ crystals in air and their slow decomposition into a lower hydrate (Macíček, 1990). Our attempts to obtain crystals of the latter hydrate, suitable for X-ray analysis, gave promising results which would make it possible to examine their structure containing no 'redundant' water molecules.

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References

Aït Ali Slimane, Z., Silvestre, J.-P., Freundlich, W. & Rimsky, A. (1982). *Acta Cryst.* B38, 1070–1074.

Beintema, J. (1937). *Z. Kristallogr.* A97, 300–322.

Betz, T. & Hoppe, R. (1983). *Z. Anorg. Allg. Chem.* **500**, 23–30.

Brown, I. D. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 1–30. New York: Academic Press.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B41, 244–247.

Enraf–Nonius (1985). *Structure Determination Package. SDP/PDP V*3.0 *Users Guide.* Enraf–Nonius, Delft, The Netherlands.

Favas, M. C. & Kepert, D. L. (1981). *Prog. Inorg. Chem.* **28**, 309–367.

Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

Krebs, B. & Hasse, K.-D. (1976). *Acta Cryst.* B32, 1334–1337.

Kruger, G. J. & Reynhardt, E. C. (1978). *Acta Cryst.* B34, 259–261.

Lock, C. J. L. & Turner, G. (1975). *Acta Cryst.* B31, 1764–1765.

Macíček, J. (1990). *JCPDS Grant-in-Aid Report.* Bulgarian Academy of Sciences, Sofia, Bulgaria.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures form X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mashonkin, V. P., Ilyukhin, V. V. & Belov, N. V. (1974). *Dokl. Acad. Nauk SSSR*, **218**, 1086–1088.

Mashonkin, V. P., Ionov, V. M., Ilyukhin, V. V. & Belov, N. V. (1975). *Dokl. Acad. Nauk SSSR*, **222**, 1097–1099.

Mashonkin, V. P., Varfolomeyev, M. B. & Ilyukhin, V. V. (1977). *Koord. Khim.* **3**, 1248–1251.

Matveeva, R. G., Ilyukhin, V. V., Varfolomeyev, M. B. & Belov, N. V. (1980). *Dokl. Acad. Nauk SSSR*, **252**, 99–101.

Picard, J. P., Baud, G., Besse, J. P., Chevalier, R. & Gasperin, M. (1984). *J. Less-Common Met.* **96**, 171–176.

Picard, J. P., Besse, J. P., Chevalier, R. & Gasperin, M. (1987). *J. Solid State Chem.* **69**, 380–384.

Picard, J. P., Besse, J. P., Chevalier, R. & Gasperin, M. (1988). *J. Solid State Chem.* **75**, 205–206.

Smith, W. T. & Maxwell, G. E. (1951). *J. Am. Chem. Soc.* **73**, 658–660.

Varfolomeyev, M. B., Chupakhin, I. P. & Plyuschtev, V. E. (1969). *Kristallografiya*, **14**, 1065–1066.

Acta Cryst. (1992). C48, 603–607

Structure of $Rb_3D(SeO_4)_2$ at 25, 110 and 297 K

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Abstract. Trirubidium deuteriumbiselenate, $Rb_3D(SeO_4)_2$, M_r = 544.3, $A2/a$, $Z = 4$, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 22.4$ mm^{-1}, $F(000) = 976$. At T = 297 K, a = 10.4775 (6), b = 6.086 (1), c = 15.421 (1) Å, β = 102.919 (9)°, V = 958.1 (3) Å^3, D_x = 3.773 Mg m^{-3}; at T = 110 K, a = 10.4019 (7), b = 6.049 (1), c = 15.321 (1) Å, β = 102.827 (8)°, V = 939.9 (2) Å^3, D_x = 3.846 Mg m^{-3}; at T = 25 K, a =

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10.3827 (7), $b = 6.039$ (1), $c = 15.294$ (1) Å, $\beta = 102.816$ (8)°, $V = 935.0$ (2) Å^3, $D_x = 3.866$ Mg m^{-3}. $R(F^2) = 0.0808$ for 2514 unique reflections at 297 K, $R(F^2) = 0.0550$ for 2487 unique reflections at 110 K, and $R(F^2) = 0.0488$ for 2444 unique reflections at 25 K. The isotope effect in the bond distances and angles is not significant. The temperature effects on the structure are mainly noticeable in the Rb—O distances in the oxygen coordination polyhedra of Rb (0.015 Å/100 K on average). No space-group change was detected at 25 K; the possible nature of the low-temperature phase below the 92 K transition is discussed.

Introduction. $Rb_3D(SeO_4)_2$ is a member of the family of hydrogen-bonded crystals with the general formula $M_3H(XO_4)_2$ (M = K, Rb, Cs; X = S, Se). Since the discovery of successive phase transitions in $(NH_4)_3H(SO_4)_2$, $M_3H(XO_3)_2$-type crystals have been studied with much interest. At room temperature (RT) all the members are ferroelastic with space group $A2/a$ [except for $C2/m$ in $Cs_3H(SeO_4)_2$ and $Cs_3D(SeO_4)_2$]. They undergo a ferroelastic transition around 339–456 K to the same trigonal ($R\bar{3}m$) paraelastic and superionic phase (*cf.* for example, Baranov, Tregubchenko, Shuvalov & Shchagina, 1987). Some of the member crystals also exhibit another phase transition below RT. Our present interest lies in the region below RT. The interesting characteristics of the $M_3H(XO_4)_2$-type crystals from our viewpoint are their (*a*) isomorphism, (*b*) low transition temperature, (*c*) dramatic isotope effects and (*d*) 'zero-dimensional' hydrogen-bond network [isolated hydrogen-bonded dimers $H(XO_4)_2^{3-}$] (Ichikawa, Gustafsson, Motida, Olovsson & Gesi, 1990; Ichikawa, Motida, Gustafsson & Olovsson, 1990; Ichikawa, Gustafsson & Olovsson, 1991). The first characteristic makes the $M_3H(XO_4)_2$-type crystals suitable for systematic studies on the relationship between the structure and phase transition. In particular, an interesting point is that the undeuterated crystals $K_3H(SO_4)_2$, $Rb_3H(SO_4)_2$ and $Rb_3H(SeO_4)_2$ do not exhibit any phase transition down to 4.2 K, *i.e.* the transition is induced by deuteration (Gesi, 1980, 1981). $Rb_3H(SeO_4)_2$ seems the most suitable crystal among them for drawing decisive conclusions concerning the proton position if we assume that the hydrogen-bond length is a good measure of this position: this compound has the longest crystallographically symmetric hydrogen bond of 2.514 (7) Å (Makarova, Verin & Shchagina, 1986) and the protons in $Rb_3H(SeO_4)_2$ are most probably disordered.

Preceding results on the lattice constants of $Rb_3H(SeO_4)_2$ demonstrated the puzzling nature of the protonated compound, *i.e.* it does not exhibit any transition although the proton is almost certainly disordered (Ichikawa, Gustafsson, Motida, Olovsson & Gesi, 1990); the lattice constants of $Rb_3D(SeO_4)_2$ indicated that those changes around the low-temperature (LT) transition are very small ($\sim 10^{-4}$) (Ichikawa, Motida, Gustafsson & Olovsson, 1990). As we expect more clear changes in bond lengths and angles *etc.* at the transition than in the lattice constants, the X-ray structure of $Rb_3D(SeO_4)_2$ has been investigated at 297 and 110 K (above the LT transition around 92 K) and at 25 K (below the transition).

Experimental. A prismatic crystal of dimensions 0.175 × 0.090 × 0.088 mm with a ferroelastic single domain and six faces was used, which is the same specimen used by Ichikawa, Motida, Gustasson & Olovsson (1990). The data were collected with Mo $K\alpha$ radiation (0.71073 Å, $\mu = 224$ cm^{-1}) on a Huber automatic 4-circle X-ray diffractometer with a closed-cycle helium refrigerator (Samson, Goldish & Dick, 1980). The temperature was measured by silicon sensors installed in the cold-station extender (T_A) and in the φ shaft of the diffractometer (T_B). The temperature at the specimen (T_s) was calibrated against the transition temperatures of KH_2PO_4 (123 K) and $KMnF_3$ (81 K and 187 K). (No calibration was made below 81 K, but T_s at 25 K is less uncertain since $T_A < T_B \simeq T_s$ and T_B is close to T_A in this range.) The stability of T_B during the measurement was within 1 K. The accuracy of T_s is estimated to be within 2 K.

The data collection was carried out in the order 295, 25 and 110 K. The lattice parameters are those determined for the same crystal by Ichikawa, Motida, Gustafsson & Olovsson (1990) [21 reflections (23–28° in 2θ) at 297 K, 30 (24–30°) at 110 K and 20 (25–30°) at 25 K]. Intensity measurements were carried out for one unique set in the ω-scan mode. The step width was 0.010° with a minimum number of 80 steps plus the $\alpha_1 - \alpha_2$ splitting. The measuring time varied from 0.5 to 2.0 s step^{-1} in the range $2 < 2\theta < 75°$ for $-17 \le h \le 17$, $0 \le k \le 10$, $-26 \le l \le 0$ (maximum $\sin\theta/\lambda = 0.8565$ Å^{-1}). Five standard reflections monitored every 3 h were used to check the stability of the measurements. The intensities and standard deviations were corrected by the method of McCandlish, Stout & Andrews (1975). The data set was corrected for the background effect (Lehmann & Larsen, 1974) and Lorentz, polarization and absorption effects (the last-named by numerical integration, transmission factors 0.0253–0.2427 at 297 K, 0.0254–0.2440 at 110 K, 0.0255–0.2443 at 25 K). Experimental details are summarized in Table 1.

Examination of the diffraction symmetry and systematic absences above the LT transition showed the same space group $A2/a$ as $Rb_3H(SeO_4)_2$ (Makarova *et al.*, 1986; equivalent positions: x, y, z; $-x$,

Table 1. *Details of data collection and structure refinement*

	25 K	110 K	297 K
Data collection			
Total number of reflections	2514	2557	2683
Number of unique reflections	2444	2487	2514
$wR_{\rm int}$ ($= \sum w\lvert I - \langle I\rangle\rvert/\sum w\lvert I\rvert$)	0.039	0.044	0.052
Intensity fluctuation of test reflections: min. and max. value of correction factor	1.0	0.983–1.0	0.903–1.0
Final least-squares refinement			
Function minimized		$\sum w(F_o^2 - F_c^2)^2$	
Weight		$1/\sigma^2(F^2)$	
Number of parameters	62	62	62
Isotropic secondary-extinction parameter	0.70 (2) × 10^4	0.45 (1) × 10^4	0.78 (3) × 10^4
Maximum value of correction factor and indices of reflections (included in the refinements)	1.60 (040)	1.51 (040)	1.62 ($\bar{4}2\bar{2}$)
$R(F^2)$	0.0488	0.0550	0.0808
wR	0.0614	0.0717	0.0953
S	1.48	1.39	1.21
Maximum Δ/σ	0.02	0.02	0.04
Final $\Delta\rho$ map			
Maximum, minimum $\Delta\rho$ (e Å^{-3})	1.24, −1.06	1.19, −1.28	1.30, −1.17

Table 2. *Fractional coordinates* (× 10^5) *and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
297 K				
Rb(1)	25000	75184 (10)	0	2.11
Rb(2)	65183 (4)	73485 (7)	19502 (3)	2.66
Se	46198 (3)	22717 (7)	11627 (3)	1.67
O(1)	39868 (26)	1747 (46)	15624 (19)	2.69
O(2)	43994 (28)	17795 (54)	590 (18)	2.52
O(3)	61937 (24)	24196 (48)	15444 (20)	2.05
O(4)	38814 (27)	45293 (50)	12849 (19)	3.33
D	0	0	0	4.6 (19)
110 K				
Rb(1)	25000	75522 (7)	0	0.86
Rb(2)	65166 (3)	73589 (6)	19491 (2)	1.04
Se	46197 (3)	22824 (6)	11661 (2)	0.69
O(1)	39837 (21)	1608 (36)	15682 (15)	1.11
O(2)	43969 (21)	17830 (40)	523 (14)	1.12
O(3)	62070 (21)	24270 (37)	15493 (14)	0.81
O(4)	38781 (21)	45728 (38)	12956 (15)	1.47
D	0	0	0	14.8 (47)
25 K				
Rb(1)	25000	75623 (6)	0	0.48
Rb(2)	65153 (2)	73651 (5)	19498 (2)	0.61
Se	46186 (2)	22891 (5)	11671 (2)	0.41
O(1)	39804 (19)	1603 (33)	15677 (14)	0.75
O(2)	43947 (19)	17875 (35)	491 (14)	0.64
O(3)	62140 (17)	24359 (33)	15499 (13)	0.51
O(4)	38744 (19)	45866 (33)	13000 (14)	0.93
D	0	0	0	13.1 (43)

$-y, -z; \frac{1}{2}-x, y, -z; \frac{1}{2}+x, -y, z$). In order to check the possibility of cell doubling below the transition, a Q scan was performed at 25 K along the a^*, b^* and c^* axes from index 0 to 3; in the 2θ range 2–15.5° the data collection was also performed with a cell having all axes doubled. No evidence of cell doubling was found. Furthermore, the data collection at 25 K was performed with the inclusion of systematic absences above the transition. The examination of the systematic absences indicated no change; that is, the space group is $A2/a$ or Aa.

The refinement was commenced with the RT structure of $Rb_3H(SeO_4)_2$ (Makarova *et al.*, 1986); the space group $A2/a$ was assumed at all three temperatures. All atoms except D were refined with anisotropic displacement parameters, D with an isotropic one. All reflections measured were included in the refinement. A type I isotropic extinction parameter with Lorentzian distribution resulted in the best agreement between observed and calculated data for the three data sets. Eight (297 K), eight (110 K) and seven (25 K) reflections with strong extinction effects were omitted at the later stages of the refinement. The details of the refinements are given in Table 1. All calculations were performed using the program system described by Lundgren (1983); the structure was drawn with *ORTEP*II (Johnson, 1976). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Final positional and isotropic displacement parameters are given in Table 2.† Interatomic distances and angles are given in Table 3; a riding-model correction for thermal motion has also been made for SeO_4 and is given in Table 3. The projection of the structure along **b** is shown in Fig. 1.

Discussion. The structure of $Rb_3D(SeO_4)_2$ is built up of hydrogen-bonded SeO_4 dimers and oxygen polyhedra around Rb (Fig. 1). There are two kinds of Rb atoms: Rb(1) occupies a special position on a twofold axis, Rb(2) is in a general position. Both types of Rb atoms are surrounded by ten O atoms. The Rb(1)—O length is larger than the Rb(2)—O length by 0.031 Å, on average. The two SeO_4 ions in the hydrogen-bonded dimers are related by a centre of symmetry, with the H atom either at the centre of symmetry or at two disordered positions around this centre.

In an acid tetrahedron HXO_4, it is well known that the X—O(H) distance is longer than the other three X—O distances (*cf.* Baur, 1974; Ferraris & Ivaldi, 1984); ideally the X atom is shifted from the centre of the oxygen tetrahedron, while retaining site symmetry $3m$ (Ichikawa, 1987, 1988). This leads to three larger and three smaller O—X—O angles. As seen from Table 3, this general trend is also satisfied in $Rb_3D(SeO_4)_2$. It is noted that the thermal motion of O(2)(H) and O(3) is considerably anisotropic and disk shaped. This disk-shaped anisotropy is still kept at 25 K. A plausible reason might be disorder of SeO_4 groups (this could be a reason for R and wR values larger than 0.07 in the 297 K and 110 K data). Similar trends were also pointed out in $K_3H(SO_4)_2$

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† Lists of anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54720 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0220]

Table 3. *Bond distances* (Å) *and angles* (°)

Bond distances have not been corrected for thermal motion, except for Se—O distances where the riding-model corrected values are also given in the second row. The corresponding values for $Rb_3H(SeO_4)_2$ at 293 K by Makarova, Verin & Shchagina (1986) are also given for comparison. Superscripts on the atom labels denote equivalent positions: (i) $x, 1+y, z$; (ii) $1-x, -y, -z$; (iii) $1-x, 1-y, -z$; (iv) $1-x, \frac{1}{2}-y, \frac{1}{2}-z$; (v) $1-x, \frac{3}{2}-y, \frac{1}{2}-z$; (vi) $\frac{1}{2}+x, 1-y, z$; (vii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

	25 K	110 K	297 K	$Rb_3H(SeO_4)_2$ 293 K
Rb-atom coordination				
Rb(1)—O(1^{i}) (×2)	2.990 (2)	3.000 (2)	3.028 (3)	3.031 (4)
—O(2^{i}) (×2)	3.213 (2)	3.222 (2)	3.258 (3)	3.255 (4)
—O(2^{iii}) (×2)	3.265 (2)	3.271 (2)	3.298 (3)	3.292 (3)
—O(3^{iii}) (×2)	2.967 (2)	2.977 (2)	3.001 (3)	3.006 (3)
—O(4) (×2)	2.821 (2)	2.825 (2)	2.837 (3)	2.836 (5)
Average	3.051	3.059	3.084	3.086
Rb(2)—O(1^{i})	3.072 (2)	3.078 (2)	3.105 (3)	3.106 (3)
—O(1^{vi})	3.129 (2)	3.137 (2)	3.164 (3)	3.163 (3)
—O(1^{iv})	2.872 (2)	2.877 (2)	2.905 (3)	2.899 (4)
—O(2^{iii})	3.036 (2)	3.047 (2)	3.078 (3)	3.081 (3)
—O(3)	3.041 (2)	3.048 (2)	3.067 (3)	3.069 (4)
—O(3^{i})	3.125 (2)	3.129 (2)	3.152 (3)	3.153 (4)
—O(3^{vii})	2.903 (2)	2.912 (2)	2.941 (3)	2.943 (4)
—O(4)	3.180 (2)	3.187 (2)	3.219 (3)	3.217 (3)
—O(4^{vi})	3.075 (2)	3.081 (2)	3.102 (3)	3.098 (3)
—O(4^{v})	3.346 (2)	3.367 (2)	3.421 (3)	3.421 (4)
Average	3.078	3.086	3.115	3.115
SeO_4 ion				
Se—O(1)	1.627 (2)	1.626 (2)	1.622 (3)	1.625 (4)
	1.630	1.630	1.631	
—O(2)	1.701 (2)	1.697 (2)	1.692 (3)	1.692 (4)
	1.705	1.703	1.706	
—O(3)	1.632 (2)	1.627 (2)	1.625 (3)	1.621 (4)
	1.635	1.631	1.635	
—O(4)	1.623 (2)	1.619 (2)	1.608 (3)	1.616 (5)
	1.626	1.625	1.619	
Average	1.646	1.642	1.637	1.639
	1.649	1.647	1.648	
O(1)—O(2)	2.643 (3)	2.643 (3)	2.639 (4)	2.643 (5)
—O(3)	2.701 (3)	2.694 (3)	2.691 (4)	2.688 (6)
—O(4)	2.703 (3)	2.700 (3)	2.683 (4)	2.690 (6)
O(2)—O(3)	2.658 (3)	2.653 (3)	2.647 (4)	2.643 (6)
—O(4)	2.696 (3)	2.688 (3)	2.670 (4)	2.679 (6)
O(3)—O(4)	2.706 (3)	2.699 (3)	2.692 (4)	2.694 (7)
Average	2.685	2.680	2.670	2.673
O(1)—Se—O(2)	105.2 (1)	105.3 (1)	105.5 (2)	105.6 (3)
—Se—O(3)	111.9 (1)	111.8 (1)	112.0 (1)	111.8 (3)
—Se—O(4)	112.5 (1)	112.6 (1)	112.3 (2)	112.3 (3)
O(2)—Se—O(3)	105.8 (1)	105.9 (1)	105.9 (1)	105.8 (3)
—Se—O(4)	108.4 (1)	108.2 (1)	107.9 (2)	108.2 (3)
O(3)—Se—O(4)	112.5 (1)	112.5 (1)	112.7 (1)	112.7 (3)
Average	109.4	109.4	109.4	109.4
Hydrogen bond				
O(2)···O(2^{ii})	2.519 (4)	2.518 (5)	2.532 (6)	2.514 (7)

and $K_3D(SO_4)_2$ (Noda & Kasatani, 1991), although less pronounced.

A comparison between present results at 297 K and those at 293 K by Makarova *et al.* (1986) gives an isotope effect $\leq \sigma$ for most bond parameters, 1.3σ–1.7σ for four bond distances, and 2σ for the hydrogen-bond length. The isotope effect in the bond distances and angles is thus very small and consistent with the lattice-constant results (Ichikawa, Motida, Gustafsson & Olovsson, 1990). The isotope effect of the hydrogen-bond length, 0.018 (9) Å, could be real, but marginally significant.

Temperature changes in the structure are mainly noticeable in the Rb—O bond distances in the oxygen coordination polyhedra of Rb (0.015 Å/100 K on average). This may explain the temperature dependence of the lattice constants. The decrease in the hydrogen bond length *R* is smaller, 0.007 Å/100 K, comparable to the corresponding value 0.009 Å/100 K for $Cs_3D(SeO_4)_2$ (Ichikawa, Gustafsson & Olovsson, 1992). The constancy of the average *X*—O distance in XO_4 ions is well known (*cf.* Baur, 1974; Ichikawa, 1987, 1988). In the present compound there is an excellent agreement among the mean Se—O distances at the three temperatures after riding-model correction (Table 3). Each individual bond distance and angle in the SeO_4 group also remains almost unchanged with temperature except those involving O(2)(H) and O(4) (Table 3).

Unexpectedly the 25 K data could be satisfactorily refined with the same space group *A*2/*a* as above the transition. This literally means that the LT transition is a symmetry-invariant transition. This is rare and in clear contrast to $K_3D(SO_4)_2$ (Noda, Watanabe, Kasatani, Terauchi & Gesi, 1991) and $Cs_3D(SeO_4)_2$ (Ichikawa *et al.*, 1991, 1992) where breaking of the *A*- and *C*-base centering is clearly seen and the space group changes to $P2_1/a$ and $P2_1/m$, respectively. However, it is possible that the real space group is *Aa*, but that the deviations of the atomic positions from *A*2/*a* are too small to be detected in the refinements, at least for the non-deuterium atoms.

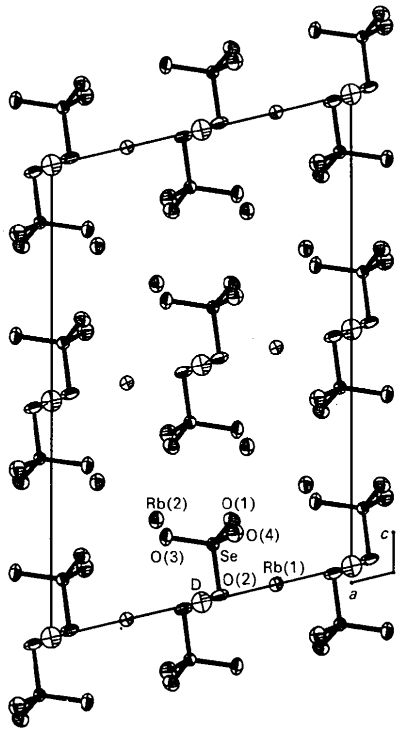

Fig. 1. The *b*-axis projection of the structure of $Rb_3D(SeO_4)_2$.

Since *Aa* is a polar space group we expect evidence for ferroelectricity in this case. However, the shape of the dielectric-constant curve (Gesi, 1981) is reminiscent of that of an antiferroelectric, being incompatible with the polar space group *Aa*. At present, neither a ferrorelectric nor an antiferroelectric hysteresis loop has been observed (Gesi, 1980). Thus it is still uncertain which is more plausible. Furthermore, an anomalously large *B* value for the D atom is noted at 110 and 25 K, although hardly significant. Thus we cannot exclude that the *A*-base centering is broken if we take the H atom into consideration, although X-ray data cannot detect the difference. Some additional work will be needed to clear up this point. Powder neutron analysis, which is now in progress, is expected to give more decisive information.

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References

BARANOV, A. I., TREGUBCHENKO, A. V., SHUVALOV, L. A. & SHCHAGINA, N. M. (1987). *Sov. Phys. Solid State*, **29**, 1448–1449.

BAUR, W. H. (1974). *Acta Cryst.* B**30**, 1195–1215.

FERRARIS, G. & IVALDI, G. (1984). *Acta Cryst.* B**40**, 1–6.

GESI, K. (1980). *J. Phys. Soc. Jpn*, **48**, 886–889.

GESI, K. (1981). *J. Phys. Soc. Jpn*, **50**, 3185–3186.

ICHIKAWA, M. (1987). *Acta Cryst.* B**43**, 23–28.

ICHIKAWA, M. (1988). *J. Mol. Struct.* **177**, 441–448.

ICHIKAWA, M., GUSTAFSSON, T., MOTIDA, K., OLOVSSON, I. & GESI, K. (1990). *Ferrolectrics*, **108**, 307–312.

ICHIKAWA, M., GUSTAFSSON T. & OLOVSSON, I. (1991). *Solid State Commun.* **78**, 547–551.

ICHIKAWA, M., GUSTAFSSON T. & OLOVSSON, I. (1992). *Acta Cryst.* Submitted.

ICHIKAWA, M., MOTIDA, K., GUSTAFSSON T. & OLOVSSON, I. (1990). *Solid State Commun.* **76**, 547–550.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

LUNDGREN, J.-O. (1983). *Crystallographic Computer Programs.* Report UUIC-B13-4-05. Institute of Chemistry, Univ. of Uppsala, Sweden.

MAKAROVA, I. P., VERIN, I. A. & SHCHAGINA, N. M. (1986). *Sov. Phys. Crystallogr.* **31**, 105–106.

MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* A**31**, 245–249.

NODA, Y. & KASATANI, H. (1991). *J. Phys. Soc. Jpn*, **60**, 13–16.

NODA, Y., WATANABE, Y., KASATANI, H., TERAUCHI, H. & GESI, K. (1991). *J. Phys. Soc. Jpn*, **60**, 1972–1977.

SAMSON, S., GOLDISH, E. & DICK, C. J. (1980). *J. Appl. Cryst.* **13**, 425–432.

Acta Cryst. (1992). C**48**, 607–610

Structure of $NaGaTi_5O_{12}$

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Abstract. $NaGaTi_5O_{12}$, $M_r = 524.11$, monoclinic, $C2/m$, $a = 15.221$ (2), $b = 3.7310$ (5), $c = 9.3273$ (9) Å, $\beta = 122.042$ (6)°, $V = 449.01$ (9) Å^3, $Z = 2$, $D_x = 3.88$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 72.7$ cm^{-1}, $F(000) = 496$, $T = 295$ K, final $R = 0.024$ for 1947 independent reflections. The structure consists basically of MO_6 (M = Ti, Ga) octahedra, which form a novel tunnel accommodating Na ions. Mean M—O distances in three nonequivalent octahedra are quite similar to each other (1.978–1.985 Å). Ga atoms are distributed at these three octahedral sites with occupancies of 10.6, 25.3 and 14.1%, respectively. Na atoms are located at the center of the tunnel and in a square-planar coordination of four O atoms. This compound is closely related to the sodium titanates, $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$.

Introduction. In the pseudo-ternary system A_2O–Ga_2O_3–TiO_2 (A: alkali metal), several compounds such as $Na_{1-x}Ti_xGa_{5-x}O_8$ ($x \simeq 0.3$) (Chandrashekhar, Bednowitz & La Placa, 1979), $K_xGa_{2+x}Ti_{2-x}O_7$ ($x \simeq 0.14$) (Watanabe, Sasaki, Kitami & Fujiki, 1987) and $K_{1-x}Ti_{2+x}Ga_{5-x}O_{12}$ ($x \simeq 0.2$) (Watanabe, Fujiki, Yoshikado & Ohachi, 1989) have been reported. These compounds, whose structures have one-dimensional tunnels containing alkali cations, are promising ionic conductors. From the crystallographic point of view, it is also interesting that

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