●Ni(1)   ●Ni(2)   ⊘Sn(1)   ○Sn(2)

Fig. 1. The crystal structure of Ni$_3$Sn$_4$. In the upper part of the drawing atoms at $y = 0$ are connected by thick lines, and atoms at $y = \frac{1}{2}$ are not connected. The positions of the large voids are marked with asterisks. In the lower part of the figure the coordination polyhedra of the Ni atoms and the void position are shown. In the sketches of the near-neighbor environments of the Sn atoms only atoms closer than 3·25 Å are connected to the central atoms.

d^2sp^3 hybrid) to the six Ge neighbors. It is, however, not possible to rationalize the whole structure of CoGe (or Ni$_3$Sn$_4$) with classical two-electron bonds.

References

Bhan, S. & Schubert, K. (1960). Z. Metallkd. 51, 327–339.
Braun, D. J. & Jeitschko, W. (1978). Acta Cryst. B34, 2069–2074.
Cromer, D. T. & Liberman, D. (1970). J. Chem. Phys. 53, 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). Acta Cryst. A24, 321–324.
Frank, F. C. & Kasper, J. S. (1958). Acta Cryst. 11, 184–190.
Jeitschko, W. & Jaberg, B. (1980a). Z. Anorg. Allg. Chem. 467, 95–104.
Jeitschko, W. & Jaberg, B. (1980b). J. Solid State Chem. 35, 312–317.
Kleshchinskii, L. I., Popov, Yu. V., Romanenko, V. N., Sobolev, V. V. & Sidorov, A. F. (1970). Izv. Akad. Nauk SSSR Neorg. Mater. 6, 1228–1231.
Michel, W. (1963). Ann. Phys. (Leipzig). 11, 321–353.
Nowotny, H. & Schubert, K. (1946). Z. Metallkd. 37, 23–31.
Sheldrick, G. M. (1976). SHELX 76. A program for crystal structure determination. Univ. of Cambridge, England.
Shoemaker, C. B. & Shoemaker, D. P. (1971). Monatsh. Chem. 102, 1643–1666.

Structure of Trirubidium Heptabromodimanganate

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Abstract. Rb$_3$Mn$_2$Br$_7$, tetragonal, $I4/mmm$, $a = 5·37$ (1), $c = 27·80$ (5) Å, $D_o = 3·80$, $D_x = 3·84$ Mg m^{-3}, $Z = 2$. The final R was 10·0% for 149 visually estimated reflexions. The structure is composed of discrete double-perovskite-type layers stacked parallel to (001), alternate layers being displaced $a/\sqrt{2}$ in the [110] direction. Mn and Rb(2) ions lie within the layers such that each Mn is octahedrally coordinated by Br ions and each Rb(2) ion is in contact with 12 Br ions. Br ions lying in the surface of a layer are linked to Rb(1) ions in the surface of the adjacent layer, each Rb(1) ion being coordinated by nine Br ions. The structure is isomorphous with that of Sr$_3$Ti$_2$O$_7$.

Introduction. A number of complex halides of composition $A_3B_2X_7$ have been reported as having a body-centred tetragonal cell containing two formula units with an axial ratio $c/a \sim 5$. Such structures are likely to be isomorphous with that of Sr$_3$Ti$_2$O$_7$ (Ruddlesden &

Popper, 1958) and this was confirmed for $Rb_3Mn_2Cl_7$ (Goodyear, Ali & Sutherland, 1978).

Single crystals of $Rb_3Mn_2Br_7$ were prepared by heating stoichiometric amounts of $RbBr$ and $MnBr_2$ in an evacuated sealed silica tube until molten and then cooling the sample to room temperature at the rate of 5 K h^{-1}. Because of the extremely hygroscopic nature of the material the crystal selected for X-ray examination was mounted in a sealed Lindemann-glass tube.

Unit-cell dimensions were determined from $\alpha_1 - \alpha_2$ doublet separations on a zero-layer a-axis Weissenberg photograph taken with Cu $K\alpha$ radiation (λ_{α_1} = 1·54051 Å). The axial ratio of 5·18 is the same as that found for $Rb_3Mn_2Cl_7$.

Intensity data were collected from equi-inclination Weissenberg photographs taken about a with Mo $K\alpha$ radiation. The intensities of 149 independent reflexions were measured visually on layer lines 0–4 from accurately timed film exposures. Systematic absences, $h + k + l = 2n + 1$, are consistent with the space group, $I4/mmm$, of $Rb_3Mn_2Cl_7$. The data were corrected for the Lorentz–polarization factor and for absorption by considering the crystal to be cylindrical in shape with a mean μr value of 1·1.

Isomorphism with $Rb_3Mn_2Cl_7$ would require the a parameter to be twice the Mn–Br bond length in an $MnBr_6$ octahedron. In the structure of $RbMnBr_3$ (Goodyear, Ali & Sutherland, 1980), the mean Mn–Br bond length is 2·68 Å, which is very nearly equal to $a/2$. It was thus assumed that the structures of $Rb_3Mn_2Br_7$ and $Rb_3Mn_2Cl_7$ were strictly isomorphous.

In the initial cycle of least-squares refinement, idealized positional parameters were assumed and an isotropic temperature factor of 2 Å^2 was assigned to each atom. After several cycles the residual, $R = \sum ||F_o| - |F_c||/\sum |F_o|$, reduced to 10·0%, and all atomic parameter shifts were $<0·05\sigma$. The calculated structure factors of 42 unobserved reflexions were all less than the minimum observable value. Atomic scattering factors for Rb^+, Mn^{2+} and Br^- were taken from *International Tables for X-ray Crystallography* (1974).

The weighting scheme used in the least-squares refinement was $w = 1/(2|F_{min}| + |F_o| + 2|F_o|^2/|F_{max}| + 5|F_o|^3/|F_{max}|^2)$.

The computer programs were written by Drs C. Morgan, H. H. Sutherland and M. J. Mottram.

Table 1. *Final atomic parameters* (*origin at centre* 4/*mmm*)

	Equipoint	x	y	z	B (Å^2)
Mn	4(e)	0	0	0·4021 (8)	1·42 (31)
Rb(1)	4(e)	0	0	0·1899 (6)	2·37 (25)
Rb(2)	2(a)	0	0	0	1·76 (31)
Br(1)	2(b)	0	0	$\frac{1}{2}$	1·60 (32)
Br(2)	4(e)	0	0	0·3091 (5)	1·59 (22)
Br(3)	8(g)	0	$\frac{1}{2}$	0·1002 (4)	1·86 (16)

Table 2. *Selected interatomic distances* (Å)

Mn–Br octahedron		Multiplicity		Location of atoms			
Mn–Br(1)	2·722 (23)	1		Mn	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2} - z$
Mn–Br(2^{ii})	2·585 (26)	1		Br(1)	$\frac{1}{2}$	$\frac{1}{2}$	0
Mn–Br(3^i)	2·686 (5)	4		Br(2^i)	0	0	z
Br(1)–Br(3^i)	3·869 (9)	4		Br(2^{ii})	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2} - z$
Br(2^{ii})–Br(3^i)	3·683 (13)	4		Br(3^i)	0	$\frac{1}{2}$	z
Br(3^i)–Br(3^{ii})	3·797 (7)	4		Br(3^{ii})	$\frac{1}{2}$	0	z
				Rb(1)	0	0	z
Rb–Br distances				Rb(2)	0	0	0
Rb(1)–Br(2^i)	3·314 (22)	1					
Rb(1)–Br(2^{ii})	3·797 (7)	4					
Rb(1)–Br(3^i)	3·664 (14)	4					
Rb(2)–Br(1)	3·797 (7)	4					
Rb(2)–Br(3^i)	3·869 (9)	8					

Final atomic parameters and some selected bond lengths are listed in Tables 1 and 2.*

Discussion. The Mn ions are octahedrally coordinated by Br ions. Each octahedron shares four Br(3) vertices and one Br(1) vertex with neighbouring octahedra to form discrete slices of perovskite-type structure, of thickness twice the parameter of the perovskite subcell. These slices are stacked parallel to (001), alternate slices being displaced a distance $a/\sqrt{2}$ in the |110| direction. The c parameter accommodates two such slices with the base of the subcell coinciding with the (001) face of the tetragonal cell. The unshared Br(2) vertices of the $MnBr_6$ octahedra lie in the surfaces of the slices and are linked to Rb(1) ions lying in the surfaces of adjacent slices, giving Rb(1) the unusual coordination of nine. Because of the unsymmetrical nature of this coordination grouping, the Rb(1)–Br(2^i) separation is much shorter than the other Rb(1)–Br distances. The Rb(2) ions lie within the perovskite double layers and are coordinated by 12 Br ions at distances which are more regular.

Distortion of the $MnBr_6$ octahedron arises partly because of the uneven sharing of Br ions. The difference between the Mn–Br(1) and Mn–Br(2^{ii}) bond lengths can be assumed to be a consequence of the mutual repulsion along |001| of neighbouring Mn ions in the perovskite-type double layer. This was found to be the case for the Mn–Cl(1) and Mn–Cl(2^{ii}) bonds in the structure of $Rb_3Mn_2Cl_7$, where the repulsive interaction between the Mn ions also explained why the Cl(3^i)–Mn–Cl(2^{ii}) angle (91·5°) was somewhat greater than the Cl(3^i)–Mn–Cl(1) angle of 88·5°. In the present structure these angular distor-

tions of the octahedron are reversed, the Br(3^i)—Mn—Br(2^{ii}) and Br(3^i)—Mn—Br(1) angles being 88·6 (7) and 91·4 (6)° respectively, whilst the Br(3^i)—Mn—Br(3^{ii}) angle is 90·0 (3)°. This difference between the structures is probably due to the less favourable radius ratio for the close-packing of the Rb and halogen ions in the heptabromodimanganate. This in turn has led to a more uneven distribution of Rb—halogen separations and given Br(3) a somewhat greater z parameter than Cl(3) in the structure of $Rb_3Mn_2Cl_7$.

The mean Mn—Br and Br—Br lengths, 2·68 and 3·78 Å respectively, agree very well with the corresponding values (2·68 and 3·79 Å) in $RbMnBr_3$.

References

GOODYEAR, J., ALI, E. M. & SUTHERLAND, H. H. (1978). *Acta Cryst.* B34, 2617–2618.
GOODYEAR, J., ALI, E. M. & SUTHERLAND, H. H. (1980). *Acta Cryst.* B36, 671–672.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
RUDDLESDEN, S. N. & POPPER, P. (1958). *Acta Cryst.* 11, 54–55.

Cation-Site Location in a Natural Chabazite

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Abstract. (Ca,Sr) chabazite, $Ca_{1.4}Sr_{0.3}Al_{3.8}Si_{8.3}O_{24}.13H_2O$ from electron microprobe analysis, rhombohedral, $R\bar{3}m$, $a = 9.421$ (4) Å, $\alpha = 94.20$ (1)°, $U = 829$ Å^3, $Z = 1$, μ(Mo $K\alpha$) = 0·82 mm^{-1}; final $R = 0.071$ for 578 independent reflections. The location of three cation sites along the [111] direction and of water molecules in the zeolitic cage is discussed and compared with that previously attributed on the basis of a two-dimensional analysis.

Introduction. Chabazite is a natural zeolite of group 4, its framework being built up by double six-membered rings (D6R), linked by tilted four-membered rings (Fig. 1). The framework contains large ellipsoidal cavities of 6·7 × 10 Å, entered by eight-membered rings (Breck, 1974). The ion-exchange properties and the role played by exchangeable cations in molecule-sieving properties justify the interest for a structural study of chabazites (Mortier, Pluth & Smith, 1977*a,b*; Pluth, Smith & Mortier, 1977; Barrer, 1978). On the other hand only two-dimensional X-ray diffraction analyses have been reported for hydrated natural chabazites (Smith, Rinaldi & Dent Glasser, 1963; Smith, Knowles & Rinaldi, 1964). From these results it was suggested that cations occupy but one site at $x = 0.357$, $y = 0.494$, $z = 0.577$, so that the crystal should contain two calcium ions and 13 water molecules per unit cell.

To verify such an arrangement of cations and water molecules, we have undertaken the three-dimensional

X-ray analysis of a natural chabazite as the first step of a structural study of chabazites exchanged with transition-metal ions. The natural sample was from north-east Azerbaijan, Iran (Comin-Chiaramonti, Pongiluppi & Vezzalini, 1979). Wavelength dispersive microprobe analysis was carried out on eight single crystals of chabazite, using a fully automated ARLSEMQ instrument.

The mean chemical analysis and the atomic ratios evaluated for 24 O atoms are given in Table 1. The chemical analysis indicates that the chabazite is particularly rich in strontium.
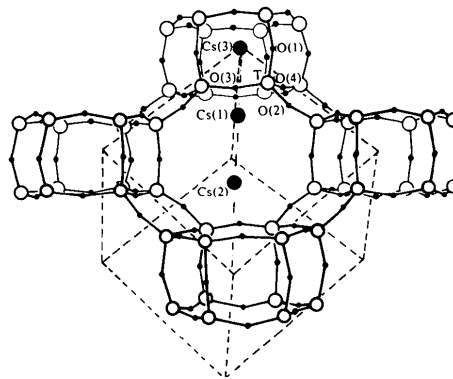

Fig. 1. A view of a model of the natural chabazite with the unit cell. The numbering scheme for the framework atoms and cationic sites is shown.