Discussion. The final atomic parameters are listed in Table 1,* bond lengths and angles in Table 2. As shown in Fig. 1, the structure projected along |001| shows a pseudohexagonal arrangement of tetrahedral ions, $MnBr_4$ and one kind of $N(CH_3)_4$ at $z \sim 1/4$ and $3/4$; another kind of $N(CH_3)_4$ takes positions at the vacant places at $z \simeq 0$ and $1/2$. The distortion of $MnBr_4$ is relatively small. For $N(CH_3)_4$ ions C—N(1)—C angles range from $96°$ to $119°$ with standard deviations about $3°$; the large distortion of tetrahedra is significant.

It is noticeable that values of the thermal parameters of Br and C atoms are unusually large. Large thermal parameters have been observed in many isomorphous materials (Wiesner *et al.*, 1967; Clay, Murray-Rust & Murray-Rust, 1975; Trouélan *et al.*, 1984). The present result strongly suggests the possibility of disordering of the constituent ions. The disordered-type model was studied by using a block-diagonal-matrix least-squares program, where each ion occupies two mirror-symmetry-related positions with equal probability. However, no definite result without any assumptions has been obtained.

A study at low temperature is now in progress to study the structural changes accompanying the transition.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51633 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

CLAY, R., MURRAY-RUST, J. & MURRAY-RUST, P. (1975). *Acta Cryst.* B31, 289–290.
GESI, K. (1983). *J. Phys. Soc. Jpn*, 52, 2931–2935.
GESI, K. (1986). *Ferroelectrics*, 66, 269–286.
HASEBE, K., MASHIYAMA, H. & TANISAKI, S. (1985). *Jpn. J. Appl. Phys.* 24, *Suppl.* 24-2, 758–760.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
SAKURAI, T. & KOBAYASHI, K. (1979). *Rep. Inst. Phys. Chem. Res.* 55, 69.
SAWADA, S., SHIROISHI, Y., YAMAMOTO, A., TAKASHIGE, M. & MATSUO, M. (1978). *Phys. Lett.* 67A, 56–58.
TROUÉLAN, P., LEFEBVRE, J. & DEROLLEZ, P. (1984). *Acta Cryst.* C40, 386–389.
TROUÉLAN, P., LEFEBVRE, J. & DEROLLEZ, P. (1985). *Acta Cryst.* C41, 846–850.
WIESNER, J. R., SRIVASTAVA, R. C., KENNARD, C. H. L., DIVAIRA, M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* 23, 565–574.

Structures of Sodium Alumino-Germanate Sodalites [Na8(Al6Ge6O24)A2, A = Cl, Br, I]

BY MICHAEL E. FLEET

Department of Geology, University of Western Ontario, London, Ontario, Canada N6A 5B7

Abstract. $Na_8(Al_6Ge_6O_{24})Cl_2$, $M_r = 1236 \cdot 2$, cubic, $P\bar{4}3n$, $a = 9 \cdot 0438$ (7) Å, $V = 739 \cdot 7$ Å³, $Z = 1$, $D_x = 2 \cdot 775$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0 \cdot 71069$ Å, $\mu = 69 \cdot 50$ cm⁻¹, $F(000) = 584$, room temperature, final $R = 0 \cdot 013$ for 111 unique reflections. $Na_8(Al_6Ge_6O_{24})Br_2$, $M_r = 1325 \cdot 1$, $a = 9 \cdot 0949$ (7) Å, $V = 752 \cdot 3$ Å³, $D_x = 2 \cdot 925$ g cm⁻³, $\mu = 94 \cdot 71$ cm⁻¹, $F(000) = 620$, final $R = 0 \cdot 019$ for 453 unique reflections. $Na_8(Al_6Ge_6O_{24})I_2$, $M_r = 1419 \cdot 1$, $a = 9 \cdot 1755$ (10) Å, $V = 772 \cdot 5$ Å³, $D_x = 3 \cdot 050$ g cm⁻³, $\mu = 85 \cdot 04$ cm⁻¹, $F(000) = 656$, final $R = 0 \cdot 016$ for 461 unique reflections. The Na_8Br_2- and Na_8I_2-sodalite have completely ordered (Al,Ge)O_4 tetrahedral frameworks, but the Na_8Cl_2-sodalite, which was synthesized at the highest temperature investigated (1048 K), has incipient (12%) Al,Ge disorder. There is distortion of the (Al,Ge)O_4 tetrahedra with halide substitution, and the collapse of the alumino-germanate framework to accommodate the interframework ions is not controlled exclusively by simple rotation of the tetrahedral groups.

Introduction. Sodalite $|Na_8(Al_6Si_6O_{24})Cl_2$ (Pauling, 1930)| has a cuboctahedral framework of (Al,Si)O_4 tetrahedral (*T*) units linked into six-membered rings parallel to {111} and four-membered rings parallel to {100} (Fig. 1). The framework cavity is large enough to accommodate ClNa₄ tetrahedral groups. The six-membered rings form continuous channels that allow diffusion of interframework ions (Barrer & Vaughan, 1971). Sodalite *sensu stricto* is a clathrosil framework silicate (Liebau, 1985) but the sodalite cage is used as a building unit in many zeolite structures (Meier, 1968).

The sodalite structure allows a wide range of atomic substitution (*e.g.* Merlino, 1984; Hassan & Grundy, 1984): for the structural formula $C_8(T1_6T2_6O_{24})A_2$, $C = Li^+, Na^+, K^+, Fe^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+}; T1 = Al^{3+}$, $Ga^{3+}, Be^{2+}; T2 = Si^{4+}, Ge^{4+}, Al^{3+}$; and $A = F^-, Cl^-$, $Br^-, I^-, OH^-, S^{2-}, SO_4^{2-}$.

As noted by Pauling (1930), the sodalite framework is partially collapsed by rotation of the TO_4 tetrahedra (*cf.* Hassan & Grundy, 1984) to accommodate the interframework (or cavity) ions. The maximum symmetry of sodalite-type structures, with disordered $T1,T2$ tetrahedral cations, is $I\bar{4}3m$. In sodalite itself and most other sodalite-type phases with $C_8(T1_6T2_6O_{24})A_2$ stoichiometry, the $T1,T2$ tetrahedral cations are ordered and the symmetry is reduced to $P\bar{4}3n$.

$Na_8(Al_6Ge_6O_{24})Cl_2$ and $Na_8(Ga_6Si_6O_{24})Cl_2$ have been synthesized in powdered form by McLaughlan & Marshall (1970). Here, I report the synthesis and refinement of $Na_8(Al_6Ge_6O_{24})Cl_2$, $Na_8(Al_6Ge_6O_{24})Br_2$, and $Na_8(Al_6Ge_6O_{24})I_2$.

Experimental. Sodium alumino-germanate sodalite crystals were prepared by hydrothermal synthesis, by reaction of NaAlGeO$_4$ |beryllonite phase (Klaska, 1974; Barbier & Fleet, 1987)|, sodium halide (analytical grade) and distilled–deionized water (in the weight proportion 0·025:0·025:0·01 g) in sealed gold capsules. NaAlGeO$_4$ was prepared from pure Na_2CO_3, Al_2O_3 and GeO_2, melted at 1473 K (12 h) and crystallized at 1073 K (45 h). $Na_8(Al_6Ge_6O_{24})Cl_2$ was heated at 1048 K, 0·22 GPa for about one day and quenched in air. $Na_8(Al_6Ge_6O_{24})Br_2$ was heated at 1048 K, 0·18 GPa for one day, 948 K, 0·15 GPa for nine days, and 773 K, 0·08 GPa for five days. $Na_8(Al_6Ge_6O_{24})I_2$ was heated at 1038 K, 0·18 GPa for about one day, and 933 K, 0·14 GPa for nine days. The products consisted of a few dodecahedral crystals of

Fig. 1. Structure of $Na_8(Al_6Ge_6O_{24})I_2$.

sodalite phase (up to 0·3 to 0·5 mm in diameter) in a fine-grained matrix. Runs for the chloride and iodide sodalites also gave minor amounts of NaAlGeO$_4$ (beryllonite phase).

$Na_8(Al_6Ge_6O_{24})Cl_2$. The crystal was dodecahedral, with approximate dimensions 0·09 × 0·12 × 0·12 mm and a calculated volume of 0·95 × 10^{-3} mm^3. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ X-radiation. 20 reflections in 2θ range 48·1–56·2° for cell parameter. Data collected by θ–2θ scan; scan angle $(2\theta) = 2\cdot4°$, with dispersion correction. 2619 hkl reflections allowed by space group $P\bar{4}3n$ out to $2\theta = 80°$ measured; $0 \le h \le 16$, $0 \le k \le 16$, $0 \le l \le 16$. Standard reflections $2\bar{2}0$, $2\bar{2}\bar{2}$, $2\bar{2}\bar{2}$; $R_{int} = 0\cdot01$, no significant variation in intensity. Background, Lorentz, polarization and absorption corrections applied; transmission factors (by Gaussian integration with a 12 × 12 × 12 grid) varied from 0·526 for 14,6,5 to 0·608 for 001. 442 unique reflections. The crystal was subsequently found to be twinned ({111} twin plane) and therefore the data list was reduced to 111 unique reflections independent of the twin operation. 57 reflections considered unobserved on the basis of $I < 3\sigma(I)$ $\{\sigma(I) = [I_m + 0\cdot002^2(I_m - B)^2 + 0\cdot005^2(I - I_m)^2]^{1/2}$, I_m, measured intensity and B, background$\}$.

Structure refinement proceeded from the parameters for $Na_8(Al_6Si_6O_{24})Cl_2$ (Hassan & Grundy, 1984). $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2$; weak reflections $||F_o| < (|F_o|_{max}/20)|$ were given a low weight ($\sigma = 1000$). Refinement using all reflections out to $2\theta = 80°$ and 17 variable parameters converged to $R = 0\cdot013$, $wR = 0\cdot009$, $S = 0\cdot0338$, $(\Delta/\sigma)_{max} = <1 \times 10^{-9}$, $\rho = -0\cdot1$ (at 0·4,0,0) to 0·1 e Å^{-3} (at 0·45,0,0). The isotropic extinction parameter for type I extinction (g; Coppens & Hamilton, 1970) is 0·68 (10) × 10^{-4}. The crystal showed incipient tetrahedral cation disorder, the refined Ge-site occupancies being 0·938 Ge, 0·062 (1) Al. Scattering factors for neutral atomic species and f', f'' taken from Tables 2.2B and 2.3.1 of *International Tables for X-ray Crystallography* (1974), respectively. Computations carried out with *DATAP77* and *LINEX77* (State University of New York at Buffalo).

$Na_8(Al_6Ge_6O_{24})Br_2$. The crystal was dodecahedral, with approximate dimensions 0·14 × 0·14 × 0·15 mm and a calculated volume of 2·90 × 10^{-3} mm^3. 20 reflections in 2θ range 47·8–55·8° for cell parameter. 2682 hkl reflections measured. Transmission factors varied from 0·267 for 011 to 0·386 for 5,10,12. 453 unique reflections: 184 considered unobserved. Refinement converged to $R = 0\cdot019$, $wR = 0\cdot016$, $S = 0\cdot118$, $(\Delta/\sigma)_{max} = 3 \times 10^{-8}$, $\rho = -0\cdot5$ (at 0,$\frac{1}{4}$,0) to 0·6 e Å^{-3} (at Br); $g = 0\cdot89$ (2) × 10^{-4}.

$Na_8(Al_6Ge_6O_{24})I_2$. The crystal was dodecahedral, with approximate dimensions 0·13 × 0·14 × 0·15 mm and a calculated volume of 2·14 × 10^{-3} mm^3. 20
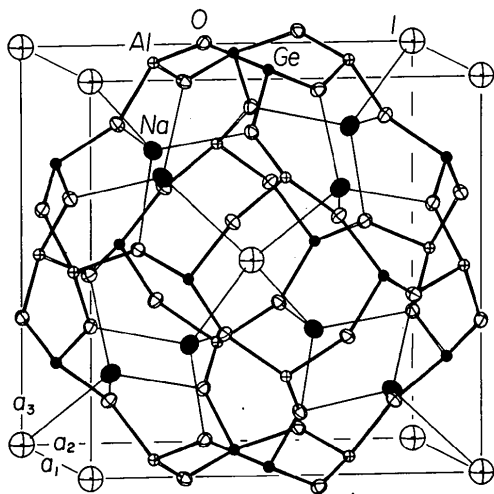
reflections in 2θ range $47 \cdot 4 - 55 \cdot 3°$ for cell parameter. 2724 hkl reflections measured. Transmission factors varied from $0 \cdot 351$ for 011 to $0 \cdot 422$ for 12,11,0. 461 unique reflections: 207 considered unobserved. Refinement converged to $R = 0 \cdot 016$, $wR = 0 \cdot 014$, $S = 0 \cdot 100$, $(\Delta/\sigma)_{max} = 5 \times 10^{-7}$, $\rho = -0 \cdot 4$ (near I) to $0 \cdot 6 \, e \, Å^{-3}$ (at I); $g = 0 \cdot 60 \, (1) \times 10^{-4}$.

Discussion. Positional parameters are given in Table 1, and selected interatomic distances and bond angles in Table 2.*

The unit-cell parameter of $Na_8(Al_6Ge_6O_{24})Cl_2$ is comparable to the value of McLaughlan & Marshall |(1970), $a = 9 \cdot 037$ (3) Å|. Neither gallo-silicate nor gallo-germanate sodalites were successfully synthesized in any form using the present hydrothermal procedure with annealing temperatures as low as 773 K. The experimental products for gallo-silicate and gallo-germanate compositions were beryllonite-structure phase and sodium halide. Clearly, the sodium alumino-germanate sodalites have a greater range of temperature stability, which can be attributed to the smaller framework cage.

The AlO_4 and GeO_4 bond lengths and equivalent bond angles are very similar in each of the sodalite structures studied. The AlO_4 bond lengths and bond angles for the Na_8Cl_2-sodalite are comparable to those of natural sodium alumino-silicate sodalite |Table 2 of Hassan & Grundy (1984)|. The Ge—O distances are similar to the mean Ge—O distance in beryllonite-phase $NaAlGeO_4$ |1·746 Å (Klaska, 1974)|. The six-membered tetrahedral rings are puckered |by rotation of the (Al,Ge)O_4 tetrahedra| to allow three bridging O atoms in each ring to bond with sodium, which is then in fourfold (trigonal pyramidal) coordination, forming NaO_3A ($A = Cl$, Br, I) groups. As noted earlier, the halide ions at the centre of the framework cage (at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$) are in tetrahedral coordination with sodium, with $\overline{4}3$ point symmetry.

The Na_8Br_2- and Na_8I_2-sodalites have completely ordered tetrahedral frameworks: Al and Ge cations occupy alternate sites in both the six- and the four-membered (Al,Ge)O_4 tetrahedral rings (Fig. 1). The Na_8Cl_2-sodalite shows slight (12%) disorder. This may be attributable to the higher annealing temperature (1048 K) for this composition. Sodalites and zeolites with equal proportions of different $T1$ and $T2$ cations generally have ordered tetrahedral cation distributions, and reports of disordered structures may be attributable to poor structural resolution |$e.g.$ the assignment of $I\overline{4}3m$ symmetry for $Na_8(Al_6Si_6O_{24})I_2$ (Beagley, Hender-

* Tables of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51635 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters ($Å^2$) for sodium alumino-germanate sodalites*

$$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

Equipoint		x	y	z	B_{eq}
$Na_8(Al_6Ge_6O_{24})Cl_2$					
Na	8(e)	0·1729 (3)	x	x	1·33 (14)
Cl	2(a)	0	0	0	1·64 (18)
Al	6(d)	$\frac{1}{4}$	0	$\frac{1}{2}$	0·74 (3)
Ge	6(c)	$\frac{1}{4}$	$\frac{1}{2}$	0	0·53 (1)
O	24(i)	0·1424 (3)	0·1426 (3)	0·4278 (3)	1·08 (5)
$Na_8(Al_6Ge_6O_{24})Br_2$					
Na	8(e)	0·1813 (1)	x	x	1·39 (3)
Br	2(a)	0	0	0	2·11 (2)
Al	6(d)	$\frac{1}{4}$	0	$\frac{1}{2}$	0·54 (2)
Ge	6(c)	$\frac{1}{4}$	$\frac{1}{2}$	0	0·467 (8)
O	24(i)	0·1445 (2)	0·1451 (2)	0·4321 (2)	0·86 (3)
$Na_8(Al_6Ge_6O_{24})I_2$					
Na	8(e)	0·1933 (1)	x	x	1·56 (3)
I	2(a)	0	0	0	2·69 (2)
Al	6(d)	$\frac{1}{4}$	0	$\frac{1}{2}$	0·55 (2)
Ge	6(c)	$\frac{1}{4}$	$\frac{1}{2}$	0	0·471 (7)
O	24(i)	0·1460 (2)	0·1470 (2)	0·4386 (2)	0·94 (3)

Table 2. *Selected interatomic distances (Å) and bond angles (°) in sodium alumino-germanate sodalites* |$Na_8(Al_6Ge_6O_{24})A_2$, $A = Cl$, Br, I|

		$A = Cl$	$A = Br$	$A = I$
Al—O	(×4)	1·743 (3)	1·745 (2)	1·745 (2)
Ge—O	(×4)	1·740 (3)	1·737 (2)	1·734 (2)
Na—O	(×3)	2·337 (2)	2·329 (2)	2·331 (2)
Na—A	(×1)	2·709 (5)	2·856 (2)	3·072 (2)
O—Al—O	(×4)	108·18 (8)	107·61 (6)	107·39 (6)
O—Al—O	(×2)	112·09 (17)	113·27 (12)	113·73 (12)
O—Ge—O	(×4)	108·15 (8)	107·54 (6)	107·30 (6)
O—Ge—O	(×2)	112·14 (17)	113·40 (12)	113·91 (12)
Al—O—Ge		133·28 (16)	134·89 (11)	137·61 (11)
O—Na—O	(×3)	102·61 (15)	105·00 (8)	108·77 (6)
O—Na—A	(×3)	115·68 (14)	113·64 (7)	110·16 (6)

son & Taylor, 1982; Hassan & Grundy, 1984)| and domain structure. Ordered distributions of framework cations are certainly consistent with the relatively low-temperature stability of zeolite phases. Further study of the variation of Al,Ge disorder in alumino-germanate sodalites with temperature would be desirable, even though the progression to complete disorder might be interrupted by breakdown of the sodalite phases at high temperature. It is noteworthy that the good X-ray scattering resolution between Al and Ge facilitates the direct and relatively precise determination of the state of tetrahedral-cation order. In contrast, X-ray structure refinements of alumino-silicate sodalites give ordering information only indirectly, from differences in mean tetrahedral bond lengths.

The most significant factor effecting variation in the structure of the sodium alumino-germanate sodalites is spatial accommodation of the halide ion ($A = Cl$, Br, I). The structural parameters change systematically in proportion to the relative size of the halide ions ($e.g.$ the progressive increase in unit-cell parameter and change

in O—Na—O, O—Na—A bond angles, Tables 3, 2). The relationship between the atomic coordinates for the sodalite framework and the unit-cell edge has been systematized for alumino-silicate sodalites in the computer model of Beagley *et al.* (1982) and the geometrical model of Hassan & Grundy (1984). Following the early work of Taylor (1972), Nyman & Hyde (1981), Beagley *et al.* (1982) and others, Hassan & Grundy (1984) derived a simple and practical geometrical relationship between the unit-cell edge, rotation of the $(Al,Si)O_4$ tetrahedra about their $\bar{4}$ axis, and the O-atom coordinates. The model was calibrated with data from refinement of the structure of natural sodalite.

The present structural data provide independent confirmation of equations (7) of the Hassan & Grundy (1984) model. Calculated oxygen positional parameters (Table 3) are in excellent agreement with the refined experimental data (Table 1), although admittedly the agreement is facilitated by the close similarity of the AlO_4 and GeO_4 tetrahedral geometries and the calculated parameters are not completely independent of the refined ones.

A more stringent test of the Hassan & Grundy (1984) model is afforded by calibrating it for alumino-germanate sodalites with the refined experimental data for the Na_8Cl_2-sodalite, and then using these calibrated data to calculate structural parameters for the Na_8Br_2- and Na_8I_2-sodalites from knowledge of their unit-cell parameter. The derived equations are: $\cos \varphi_{Ge} = a/5\cdot774 - 0\cdot6742$, and $\cos \varphi_{Al} = a/5\cdot784 - 0\cdot6719$, corresponding to equations (5') of Hassan & Grundy (1984), and $x = \frac{1}{4} - 0\cdot9732/a$, $y = \frac{1}{4} - 0\cdot9716/a$, $z_{Al} = \frac{1}{2} - 1\cdot4460(\sin\varphi_{Al}/a)$, and $z_{Ge} = \frac{1}{2} - 1\cdot4435(\sin\varphi_{Ge}/a)$, corresponding to equations (7'). The calculated structural parameters for $Na_8(Al_6Ge_6O_{24})Br_2$ are: $\varphi_{Al} = 25\cdot8$, $\varphi_{Ge} = 25\cdot7°$, $x = 0\cdot1430$, $y = 0\cdot1432$, $z_{Al} = 0\cdot4309$, and $z_{Ge} = 0\cdot4311$; and for $Na_8(Al_6Ge_6O_{24})I_2$ are: $\varphi_{Al} = 23\cdot9$, $\varphi_{Ge} = 23\cdot8°$, $x = 0\cdot1439$, $y = 0\cdot1441$, $z_{Al} = 0\cdot4362$, and $z_{Ge} = 0\cdot4365$. The calculated oxygen parameters show only fair correspondence to the respective experimental values (Table 1). This is because the Hassan & Grundy model (with a single calibration structure) does not take into account distortion of the $(T1,T2)O_4$ tetrahedra with halide (and alkali metal) substitution.

Although TO_4 rotation is the dominant mechanism causing collapse of the sodalite framework, it alone cannot position the O atoms to satisfy all of the possible A—C and C—O bond lengths. Small adjustments in $T2$—O—$T1$ and O—T—O bond angles are also necessary. In the sodium alumino-germanate sodalites, distortion of the $(Al,Ge)O_4$ tetrahedra with halide substitution (in the sequence Cl, Br, I) is apparent by progressive decrease of the Ge—O distance and progressive increase of the bond-angle distortion from the ideal tetrahedral value ($109\cdot47°$, Table 2). The

Table 3. *Calculated structural parameters for sodium alumino-germanate sodalites* $|Na_8(Al_6Ge_6O_{24})A_2$, A $= Cl$, Br, $I|$ $|cf.$ *Hassan & Grundy* (1984), *equations* (5), (7)|

	$A = Cl$	$A = Br$	$A = I$
a (Å)	9·0438	9·0949	9·1755
Al—O (Å)	1·743	1·745	1·745
$E_{Al}{}^1$ (Å)	2·892	2·914	2·923
Ge—O (Å)	1·740	1·737	1·734
$E_{Ge}{}^1$ (Å)	2·887	2·904	2·907
$\varphi_{Al}{}^2$ (°)	26·9	25·0	22·7
$\varphi_{Ge}{}^2$ (°)	26·9	25·2	22·7
x^3	0·1424	0·1444	0·1461
y^3	0·1426	0·1452	0·1469
$z_{Al}{}^3$	0·4276	0·4323	0·4385
$z_{Ge}{}^3$	0·4279	0·4319	0·4387

Notes: (1) long $(Al,Ge)O_4$ edges; (2) rotation of $(Al,Ge)O_4$ tetrahedra from ideal structure; (3) oxygen coordinates (*cf.* Table 1).

$(Al,Ge)O_4$ tetrahedra are compressed in the direction of the $\bar{4}$ axis: the O—(Al,Ge)—O angles enclosed by the four-membered $(Al,Ge)O_4$ rings are greater than the ideal tetrahedral value, and the angles enclosed by the six-membered rings are correspondingly smaller than the ideal value. This distortion results because the O atoms are pulled toward the Na atoms, which are located immediately below (or above) the plane of the six-membered rings (Fig. 1), and away from the four-membered rings. Furthermore, the magnitude of the O—(Al,Ge)—O bond-angle distortion varies with halide substitution, because the latter changes the direction and bond strength of the O—Na bond (see below).

Thus, halide substitution in the sequence Cl, Br, I results in the expected expansion and straightening of the alumino-germanate framework cage to accommodate progressively larger halide ions. This is effected very largely by decrease in the angle of rotation of the $(Al,Ge)O_4$ tetrahedra. However, the O—(Al,Ge)—O bond angles in the four-membered rings also increase (Table 2) as does the Al—O—Ge bond angle (although, of course, this increase is partly accounted for by the decrease in the angle of rotation), and the Ge—O distance decreases.

The sodium—halide bond lengths in the three alumino-germanate structures are similar to the bond lengths in the corresponding rock-salt-type structures, when allowance is made for the difference in coordination number; the bond-length ratios (sodalite/rock salt) being 0·961, 0·956, and 0·949 for $A = Cl$, Br, and I, respectively, compared with an average correction factor of 0·94 for change in coordination from octahedral to tetrahedral (*e.g.* Megaw, 1973). The O—Na—O and O—Na—A bond angles within the NaO_3A ($A = Cl$, Br, I) groups vary markedly with halide substitution, and converge toward the ideal tetrahedral bond angle in the Na_8I_2-sodalite. Increase in size of the halide ion moves the Na atom closer to

the plane of the three O atoms. Clearly, spatial accommodation of the sodium-halide pair is much more important than the precise direction of bonds within the NaO_3A groups. The Na atom has a marked anisotropy of thermal motion in the direction of the sodium—halide bond which may be related to the rather large thermal vibration of the halide ion. The oxygen thermal motion is markedly anisotropic normal to the plane of the Al—O,Ge—O bond plane, as expected.

References

BARBIER, J. & FLEET, M. E. (1987). *J. Solid State Chem.* **71**, 361–370.

BARRER, R. M. & VAUGHAN, D. E. W. (1971). *J. Phys. Chem. Solids*, **32**, 731–743.

BEAGLEY, B., HENDERSON, C. M. B. & TAYLOR, D. (1982). *Mineral. Mag.* **46**, 459–464.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

HASSAN, I. & GRUNDY, H. D. (1984). *Acta Cryst.* B**40**, 6–13.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KLASKA, K.-H. (1974). *Strukturuntersuchungen an Tridymitabkommlingen (Beryllonitreihe, Trinephelin)*, p. 103. Dissertation, Univ. of Hamburg, Federal Republic of Germany.

LIEBAU, F. (1985). In *Structural Chemistry of Silicates*. Berlin: Springer-Verlag.

MCLAUGHLAN, S. D. & MARSHALL, D. J. (1970). *Phys. Lett. A*, **32**, 343–344.

MEGAW, H. D. (1973). *Crystal Structures*. Philadelphia: W. B. Saunders.

MEIER, W. M. (1968). *Zeolite Structures*. In *Molecular Sieves*, pp. 10–27. London: Society of Chemistry for Industry.

MERLINO, S. (1984). *Feldspathoids: Their average and real structures*. In *Feldspars and Feldspathoids*, NATO ASI Ser. C, Vol. 137, pp. 435–470. Dordrecht: Reidel.

NYMAN, H. & HYDE, B. G. (1981). *Acta Cryst.* A**37**, 11–17.

PAULING, L. (1930). *Z. Kristallogr.* **74**, 213–225.

TAYLOR, D. (1972). *Mineral. Mag.* **38**, 593–604.

Structure of Tin Hafnium Sulfide and Lead Hafnium Sulfide

BY G. A. WIEGERS,* A. MEETSMA, R. J. HAANGE AND J. L. DE BOER

Laboratory of Inorganic Chemistry, Materials Science Centre of the University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Abstract. $SnHfS_3$, $M_r = 393 \cdot 36$, orthorhombic, *Pnma*, $a = 9 \cdot 139$ (1), $b = 3 \cdot 694$ (1), $c = 13 \cdot 875$ (4) Å, $V = 468 \cdot 4$ (2) Å^3, $Z = 4$, $D_x = 5 \cdot 578$ g cm^{-3}, $\lambda(Mo\ K\bar{\alpha}) = 0 \cdot 71073$ Å, $\mu = 284 \cdot 1$ cm^{-1}, $F(000) = 680$, $T = 298$ K, $R_F = 0 \cdot 036$ for 1301 observed reflections with $I \geq 2 \cdot 5\sigma(I)$. $PbHfS_3$, $M_r = 481 \cdot 88$, orthorhombic, *Pnma*, $a = 8 \cdot 988$ (2), $b = 3 \cdot 739$ (1), $c = 13 \cdot 924$ (2) Å, $V = 467 \cdot 9$ (2) Å^3, $Z = 4$, $D_x = 6 \cdot 840$ g cm^{-3}, $\lambda(Mo\ K\bar{\alpha}) = 0 \cdot 71073$ Å, $\mu = 593 \cdot 0$ cm^{-1}, $F(000) = 808$, $T = 298$ K, $R_F = 0 \cdot 036$ for 1343 observed reflections with $I \geq 2 \cdot 5\sigma(I)$. The compounds are isostructural with $PbZrS_3$ with modified NH_4CdCl_3 structure. There are columns running along the *b* axis of double edge-sharing octahedra $(Hf_2S_6)_\infty$; these columns are linked by Sn or Pb with coordinations typical for Sn^{2+} and Pb^{2+} with lone-pair s^2 electrons.

Introduction. Structures of the ternary sulfides ABS_3 (A = Pb; B = Zr, Hf) have been studied using powder methods by Sterzel & Horn (1970), Yamaoka & Okai

(1970) and Lelieveld & IJdo (1978). The latter authors concluded from a neutron powder diffraction refinement of $PbZrS_3$ that the compound, and probably also $PbHfS_3$, is isostructural with $PbSnS_3$ and Sn_2S_3. The structures are strongly related to the NH_4CdCl_3 structure (*Strukturbericht*, type E 24). In a study of the ternary sulfides with the assumed composition ABS_3 (A = Sn, Pb; B = Nb, Ta) we found that single crystals could be obtained by vapour transport using chlorine as transport agent. We found this method also suitable for compounds $PbHfS_3$ and $SnHfS_3$, the latter being a new compound. Structure determinations using single crystals are reported.

Experimental. Powder samples of $SnHfS_3$ and $PbHfS_3$ were obtained by heating the elements in evacuated quartz ampoules. An intimate mixture of the elements was first slowly heated to about 673 K for two days during which the binary sulfides are probably formed. The ampoules were then heated at 1023 K for ten days. In this way the reaction of the metals with quartz from the wall was avoided. $PbHfS_3$ was then heated for three

---

* Author to who correspondence should be addressed.