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The Crystal Structure of an Ordered Sodium Tin Germanium Oxide Hydroxide

F. KREBS LARSEN, A. NØRLUND CHRISTENSEN and S. E. RASMUSSEN

Department of Inorganic Chemistry, Aarhus University, Aarhus C, Denmark

A sodium tin germanium oxide hydroxide was prepared by hydrothermal synthesis. The composition of the compound is $Na_8Sn_4Ge_{10}O_{30}(OH)_4$ in agreement with chemical analysis, infrared spectra, and crystal structure analysis. The structure has been determined using automatically collected counter data. The compound is monoclinic with $a = 6.95_6$ Å, $b = 5.36_2$ Å, $c = 20.79_0$ Å, $\beta = 106.21°$ and space group $P2/c$. Germanium atoms are tetrahedrally coordinated and tin atoms are octahedrally coordinated.

Hydrothermal synthesis with mixtures of germanium oxide and tin oxide can yield a variety of phases, often as mixtures. One of the phases is $Na_4Ge_9O_{20}$, another phase contains both tin and germanium but is otherwise as yet of undetermined composition; a third phase is the compound described in this paper.

By trial and error methods it was possible to obtain crystals of a good quality of this phase. The formula of the compound is $Na_2Sn_{0.85}Ge_{2.15}O_7$ according to chemical analysis.

A crystal structure analysis was undertaken in order to determine whether there was a statistical distribution of the germanium and of the tin atoms in the structure.

EXPERIMENTAL

Chemistry. The compound $Na_8Sn_4Ge_{10}O_{30}(OH)_4$ was prepared using hydrothermal technique. A pressure bomb of 20 ml volume lined with pure silver was used. When a mixture of 300 mg GeO_2 and 100 mg SnO_2 was treated with 5 ml of a 1 M NaOH solution at 470°C, 500 atm, the compound was formed within 60 h. It proved difficult to prepare the compound as a pure phase as it often was formed together with $Na_4Ge_9O_{20}$ and a Sn-Ge-containing phase of as yet unknown composition.

In the compound $Na_8Sn_4Ge_{10}O_{30}(OH)_4$, sodium was determined by flame photometry with solutions of NaCl as standards. Tin and germanium were determined using X-ray fluorescence technique with standards prepared from mixtures of SnO_2, GeO_2, and NaF. (Found: Na 8.8; Sn 23.3; Ge 36.8. Calc. for $Na_8Sn_4Ge_{10}O_{30}(OH)_4$: Na 9.5; Sn 24.6; Ge 37.6).

X-Ray technique. Unit cell and space group were determined from Weissenberg, precession and retigraph films using Cu- and Mo-radiation. Lattice constants were determined from the photographic data and were confirmed by diffractometer measurements. A Guinier powder photograph was indexed on the basis of the unit cell found from single crystal data.

A crystal with dimensions 0.3 × 0.10 × 0.12 mm³ was selected under the polarizing microscope for intensity measurements. The crystal was mounted along the longest edge which is along the symmetry axis. Three-dimensional data were measured with a linear diffractometer designed by Arndt and Phillips [1] and manufactured by Hilger and Watts. Mo-radiation was employed. Balanced filters SrO, ZrO_2 in conjunction with a pulse height analyzer ensured simulation of a monochromatic Mo$K\alpha$ beam. No absorption correction was applied.

The intensities measured were symmetry related in pairs. 1643 of 2175 independent reflexions showed intensities greater than twice their standard deviation. This was estimated as the square root of the total number of counts in an intensity measurement.

The data were processed using a GIER computer with an ALGOL program [2] which evaluated intensities, calculated averages, Lp corrections and standard deviations.

STRUCTURE DETERMINATION

The compound belongs to the monoclinic system. Reflexions *h0l* are missing for $l = 2n + 1$. No piezoelectric effects were detected using the Giebe-Scheibe method.

A test for a centre of symmetry was made according to the method of Howells, Phillips and Rogers [3] (Fig. 1). The result points towards existence of hypercentrosymmetry or some sort of bi-parallelity. On the basis of the absence of piezoelectricity and on the statistical test the space group $P2/c$ was assumed.

A Wilson plot is shown in Fig. 2. The function $\Phi(\sin\theta/\lambda) = \sqrt{\langle U^2\rangle/\langle I_{obs}\rangle}$ is shown in Fig. 3. Unitary structure factors were computed as $U = \Phi F_{obs}$ using a polynomial approximation for Φ.

The root mean square of the unitary structure factors is 0.2. Inequalities were therefore likely to be useful and were applied to the *h0l* data. The first Harker-Kasper inequality yielded the signs of (8,0,8), (2,0,12), and (6,0,16). The arbitrary signs + were given to (1,0,6) and $(\bar{3},0,8)$ to fix the origin of the projection. Using the signs obtained the inquality: $(|U_h| + |U_{h'}|)^2 \leq \{1 + s(h)s(h')s(h + h')|U_{h+h'}|\}\{1 + s(h)s(h')s(h-h')|U_{h-h'}|\}$ was applied. The notation is that of Woolfson.[4]

Two sign symbols α and β were given to (4,0,4) and (6,0,8). The first inequality is nearly fulfilled for determining the sign of (4,0,4) as positive and using this assumption the conclusion was reached that β also was positive.

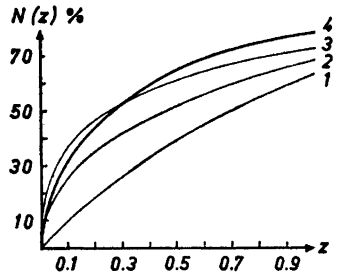

Fig. 1. Test for centre of symmetry according to Ref. 3. Curve $1({}_1N(z))$, $2({}_{\bar{1}}N(z))$ and $3({}_2N(z))$ are theoretically computed curves for acentric, centric and hypercentric distributions respectively. Curve 4 is the experimentally found curve for $Na_8Sn_4Ge_{10}O_{30}(OH)_4$.

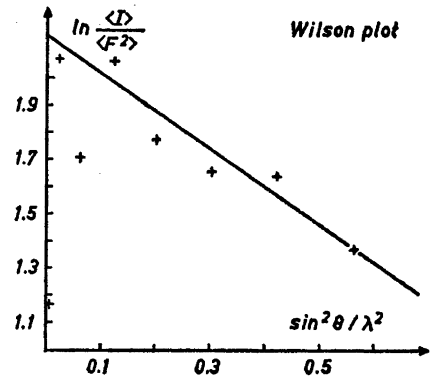

Fig. 2. Wilson plot for $Na_8Sn_4Ge_{10}O_{30}(OH)_4$.

In all 62 signs were determined on this basis. Using these as basic set 24 other signs were determined using the sign relation: $s(U_h) \approx s(\sum U_{h'} U_{h+h'})$. With 86 signs determined the signs of all unitary structure factors larger than 0.20 were determined. All these signs were later found to be correct.

A Fourier projection (Fig. 4) was calculated using the signs found. Two interpretations were tried: One assuming that the highest peaks belonged to statistically distributed (Ge, Sn) atoms gave a conventional R-value of 53.5 %. The other interpretation which assumed that the highest peak showed a tin atom and the next highest peaks showed germanium atoms gave an R-value of 36.6 %.

The Fourier map was interpreted assuming tetrahedral coordination around germanium and octahedral coordination around tin. The structure was refined assuming that the asymmetric unit contained $Na_2SnGe_{2.5}O_8$.

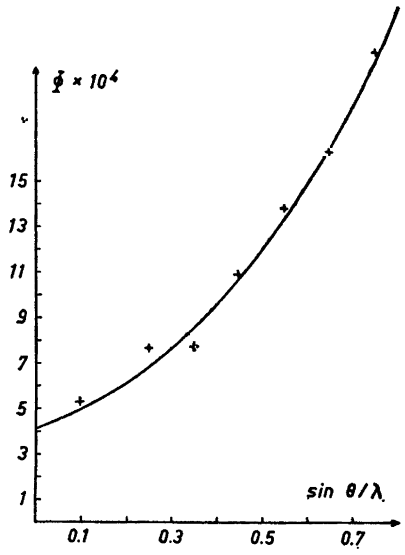

Fig. 3. The function $\Phi = \sqrt{\langle U^2 \rangle / \langle I_{obs} \rangle}$ plotted as a function of $\sin \theta/\lambda$.

Fig. 4. Fourier projection on (010) using 86 reflexions with signs determined from inequalities and sign relationships. Contours at equal, arbitrary intervals.

Refinement with these atoms using the method of Bhuiya and Stanley [5] gave an R-value of 6.3 % at convergence. The program used employs isotropic temperature factors. It was written in ALGOL by Danielsen.[6]

A difference Fourier map based on this refinement revealed a residual electron density of 3 e/Å^2 at the centre of symmetry at (0.5,0,0). Insertion of an oxygen atom at this point lowered the R-value to 4.9 % at convergence of the new refinement. The principle of balanced valencies leads to the formula $Na_2SnGe_{2.5}O_{7.5}(OH)$ for an asymmetric unit. The presence of a hydroxyl group was confirmed by the existence of an absorption band at 3440 cm^{-1}. The loss of weight by ignition at 940°C was 2.5 %. The sample so treated had a powder pattern, which was different from that of the investigated compound.

Distinction between centres of symmetry and twofold axes is of no consequence in the $h0l$ projection. Because of the halving of the c-axis in this projection the reflexions (1,0,6) and ($\bar{3}$,0,8) can be considered as belonging to different parity groups, but in three dimensions only one sign, say ($\bar{3}$,0,8) has been chosen. As tetrahedral grouping around the germanium atoms was assumed, the germanium atom which is in a special position had to be placed in a twofold axis rather than on an centre of symmetry. With this assumption the signs of the $00l$ reflexions could be considered known. Signs of two reflexions could be chosen for the $0kl$ projection. The signs of (0,3,13) and (0,4,3) were both chosen as positive.

The first Harker-Kasper inequality determined one sign: (0,4,0) as positive. The inequality:

$$U^2_{o,k,l} \leq 1/4(1 - U_{o,2k,o})(1 - U_{o,o,2l})$$

for l odd yielded two signs when used in conjunction with the signs of the $00l$ reflexions which were taken from the refined $h0l$ data.

Further sign determination was carried out using the coincidence method of Grant, Howells, and Rogers,[7] and the method of structure invariants of Woolfson.[5] Signs of 55 $0kl$ structure factors were determined. All of them proved later to be correct. A Fourier projection based on these 55 signs was

calculated. It was readily interpreted and was refined to an R-value of 7.8 % using isotropic temperature factors.

At that stage a computer program written by Lehmann [8] became available to us for evaluating the sign of a structure factor U_h from $\sum U_{h'}U_{h+h'}$. Previously found signs of 168 $h0l$ and $0kl$ structure factors were used as basic set. After two iterations 985 signs were determined. Of these 44 (4.5 %) were later proved to be incorrect.

A three dimensional Fourier map was calculated using these 985 structure factors. It did show a few false details, *e.g.* two spurious atoms of electron density as sodium on $0,y,0.25$, but it was otherwise consistent with the results from the two projections. The spurious peaks were proved to be false by the refinement.

A least squares analysis was carried out with a program written by Danielsen.[9] It uses the diagonal approximation and employs isotropic temperature factors. Convergence was reached at an R-value of 5.8 %. Additional refinement was carried out on the IBM 7090 of NEUCC using a full matrix least squares program written by Gantzel, Sparks, Long and Trueblood.[10] The program employs anisotropic temperature factors. Convergence was reached at

Table 1. X-Ray powder pattern of $Na_8Sn_4Ge_{10}O_{30}(OH)_4$. $a = 6.95_6$ Å, $b = 5.36_2$ Å, $c = 20.79_0$ Å, $\beta = 106.21°$.

$h\ k\ l$	d_{obs}	d_{calc}	I
0 0 2	10.0	9.98	m
1 0 $\bar{0}$	6.72	6.68	m
1 0 $\bar{2}$	6.46	6.45	w
0 1 0	5.38	5.36	vw
0 1 1	5.21	5.18	vw
0 0 4	5.02	4.99	m
1 0 2	4.96	4.95	vw
0 1 $\bar{2}$	4.73	4.72	vw
1 1 $\bar{1}$	4.24	4.24	s
0 1 3	4.19	4.18	vw
1 1 $\bar{2}$	4.14	4.12	vw
1 1 $\bar{3}$	3.86	3.86	s
0 1 4	3.66	3.65	w
1 1 2	3.64	3.64	w
1 1 $\bar{4}$	3.53	3.52	m
2 0 $\bar{2}$	3.47	3.47	vw
1 0 $\bar{6}$	3.39	3.38	vw
2 0 0	3.34	3.34	s
1 1 3	3.30	3.29	vw
2 0 $\bar{4}$	3.21	3.22	w
1 1 $\bar{5}$	3.18	3.18	s
2 0 2	2.930	2.931	w
2 1 $\bar{1}$	2.902	2.904	vs
2 1 $\bar{3}$	2.863	2.864	w
2 1 0	2.835	2.835	w
2 1 $\bar{4}$	2.764	2.762	w
2 1 1	2.714	2.719	m
1 0 6	2.700	2.693	s
0 2 0	2.682	2.681	m

$R = 5.3$ % using 1599 reflexions. A final difference Fourier map showed fluctuations between $\pm$ 0.5 e/Å^3.

CRYSTAL DATA

Crystal system: monoclinic, $a = 6.95_6$ Å, $b = 5.36_2$ Å, $c = 20.79_0$ Å, $\beta = 106.21°$, space group $P2/c$ (No. 13). The indexing of the powder photograph is given in Table 1. The coordinates and their estimated standard deviations are given in Table 2. Thermal parameters are given in Table 3. Table 4 gives interatomic distances and their standard deviations, and Table 5 gives observed and calculated structure factors. The atomic scattering factors used were taken from *Intern. Tables*, Vol. III.

Table 2. Coordinates in fractions of cell edges and their standard deviations.

	x/a	$\sigma\, x/a$	y/b	$\sigma\, y/b$	z/c	$\sigma\, z/c$
Ge(3)	0		0.50481	0.00030	0.25000	
O(15)	0.50000		0.30114	0.00253	0.25000	
Na(1)	0.25489	0.00086	0.00499	0.00095	0.20994	0.00028
Na(2)	0.38975	0.00084	0.24537	0.00087	0.02761	0.00030
Ge(4)	0.18472	0.00019	0.71552	0.00021	0.07642	0.00007
Ge(5)	0.34728	0.00020	0.75232	0.00020	0.36566	0.00007
Sn(6)	0.11435	0.00012	0.24076	0.00013	0.41075	0.00004
O(7)	0.34545	0.00128	0.06029	0.00143	0.38766	0.00043
O(8)	0.03144	0.00117	0.31945	0.00136	0.18536	0.00144
O(9)	0.11673	0.00134	0.39955	0.00160	0.06307	0.00047
O(10)	0.30880	0.00132	0.53812	0.00144	0.42403	0.00042
O(11)	0.41011	0.00138	0.70545	0.00179	0.14493	0.00046
O(12)	0.20322	0.00130	0.70616	0.00167	0.28182	0.00042
O(13)	0.25426	0.00135	0.83896	0.00150	0.00873	0.00041
O(14)	0.03376	0.00132	0.90629	0.00149	0.10753	0.00047

Table 3. Thermal parameters and their standard deviations in Å^2 $\times$ 10^4. The form of the temperature factor used was: $\exp-(b_{11}h^2+\ldots+b_{23}kl)$ with $b_{11} = 2\pi^2a^{*2}u_{11}$, $b_{23} = 4\pi^2b^*c^*u_{23}$.

	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
Ge(3)	63	8	115	7	54	8	0		−18	6	0	
O(15)	394	97	135	59	682	115	0		−59	83	0	
Na(1)	213	28	200	23	155	26	18	22	−40	21	32	22
Na(2)	155	29	192	24	195	30	7	21	30	23	44	21
Ge(4)	53	6	89	5	75	6	4	42	− 1	45	7	43
Ge(5)	56	6	85	5	82	6	− 4	42	−11	46	− 8	42
Sn(6)	46	4	68	3	62	4	0	26	− 5	29	3	26
O(7)	114	42	104	33	125	41	−44	32	33	33	−48	32
O(8)	169	44	76	31	124	43	−28	33	−30	35	−63	33
O(9)	73	42	218	37	213	48	−12	34	40	36	25	37
O(10)	132	44	113	34	108	40	−29	33	46	33	−18	32
O(11)	80	43	407	48	71	41	−15	39	14	33	40	38
O(12)	53	41	313	43	32	39	−41	35	−58	31	−44	34
O(13)	136	43	141	34	50	39	−33	33	−39	32	−34	31
O(14)	127	44	110	34	232	49	70	33	85	37	63	35

Table 4. Interatomic distances and bond angles in $Na_8Sn_4Ge_{10}O_{30}(OH)_4$. Standard deviations in parentheses.

	Distances in Å		Angles in degrees
Ge(3)—O(8)	1.734 (0.009)	O(8) —Ge(3)—O(8)	110.04 (0.41)
Ge(3)—O(12)	1.755 (0.009)	O(8) —Ge(3)—O(12)	112.47 (0.44)
		O(8) —Ge(3)—O(12)	108.85 (0.39)
		O(12)—Ge(3)—O(12)	104.06 (0.41)
Ge(4)—O(9)	1.760 (0.009)	O(9) —Ge(4)—O(11)	103.43 (0.41)
Ge(4)—O(11)	1.801 (0.008)	O(9) —Ge(4)—O(13)	111.19 (0.44)
Ge(4)—O(13)	1.741 (0.010)	O(9) —Ge(4)—O(14)	117.86 (0.45)
Ge(4)—O(14)	1.717 (0.010)	O(11)—Ge(4)—O(13)	105.88 (0.44)
		O(11)—Ge(4)—O(14)	102.06 (0.43)
		O(13)—Ge(4)—O(14)	114.52 (0.42)
Ge(5)—O(7)	1.714 (0.008)	O(7) —Ge(5)—O(10)	115.75 (0.43)
Ge(5)—O(10)	1.745 (0.009)	O(7) —Ge(5)—O(11)	104.29 (0.44)
Ge(5)—O(11)	1.780 (0.010)	O(7) —Ge(5)—O(12)	110.69 (0.39)
Ge(5)—O(12)	1.769 (0.008)	O(10)—Ge(5)—O(11)	109.14 (0.43)
		O(10)—Ge(5)—O(12)	116.01 (0.40)
		O(11)—Ge(5)—O(12)	98.88 (0.43)
Sn(6)—O(7)	2.045 (0.009)	O(7) —Sn(6)—O(9)	176.31 (0.36)
Sn(6)—O(8)	2.017 (0.008)	O(7) —Sn(6)—O(10)	82.41 (0.34)
Sn(6)—O(9)	2.023 (0.010)	O(7) —Sn(6)—O(13)	87.03 (0.36)
Sn(6)—O(10)	2.059 (0.008)	O(7) —Sn(6)—O(14)	85.98 (0.35)
Sn(6)—O(13)	2.043 (0.008)	O(8) —Sn(6)—O(9)	87.76 (0.38)
Sn(6)—O(14)	2.050 (0.008)	O(8) —Sn(6)—O(10)	95.78 (0.33)
		O(8) —Sn(6)—O(13)	178.35 (0.41)
		O(8) —Sn(6)—O(14)	84.93 (0.34)
Na(1)—O(8)	2.253 (0.010)	O(9) —Sn(6)—O(10)	100.34 (0.36)
Na(1)—O(11)	2.527 (0.012)	O(9) —Sn(6)—O(13)	90.74 (0.37)
Na(1)—O(12)	2.287 (0.011)	O(9) —Sn(6)—O(14)	91.27 (0.37)
Na(1)—O(14)	2.313 (0.010)	O(10)—Sn(6)—O(13)	85.19 (0.33)
Na(1)—O(15)	2.309 (0.011)	O(10)—Sn(6)—O(14)	168.38 (0.38)
		O(13)—Sn(6)—O(14)	94.40 (0.34)
Na(2)—O(7)	2.381 (0.009)		
Na(2)—O(9)	2.370 (0.012)		
Na(2)—O(10)	2.587 (0.010)		
Na(2)—O(10)	2.372 (0.010)		
Na(2)—O(13)	2.363 (0.009)		
Na(2)—O(13)	2.820 (0.012)		
O—O distances within GeO_4 tetrahedra			
O(11)—O(12)	2.696 (0.012)		
O(11)—O(14)	2.735 (0.013)		
O(7) —O(11)	2.759 (0.014)		
O(12)—O(12)	2.767 (0.012)		
O(9) —O(11)	2.795 (0.012)		
O—O distances within SnO_6 octahedra			
O(7) —O(10)	2.704 (0.011)		
O(8) —O(14)	2.746 (0.012)		
O(10)—O(13)	2.776 (0.012)		
O(7) —O(14)	2.792 (0.013)		
O(8) —O(9)	2.800 (0.015)		

Table 5. Observed and calculated structure factors.

h	k	l	Fobs	Fcalc
-8	0	2	912	984
-8	0	4	258	238
-8	0	6	826	-842
-8	0	8	309	305
-8	0	10	483	482
-8	0	12	253	267
-8	0	14	440	-432
-8	0	18	412	-439
-7	0	2	660	683
-7	0	4	1616	1712
-7	0	6	582	-614
-7	0	8	1528	-1554
-7	0	10	1240	-1274
-7	0	12	1155	1177
-7	0	14	418	455
-7	0	18	264	-301
-7	0	22	572	-589
-7	0	24	210	209
-6	0	2	623	640
-6	0	4	846	910
-6	0	6	350	-352
-6	0	8	608	-640
-6	0	10	1955	-2027
-6	0	12	740	726
-6	0	14	1442	1490
-6	0	16	1446	1498
-6	0	18	876	-855
-6	0	20	1089	-1107
-6	0	22	623	-619
-5	0	2	799	781
-5	0	4	558	582
-5	0	6	587	-623
-5	0	10	210	-215
-5	0	14	181	-169
-5	0	16	1130	1168
-5	0	18	196	-242
-5	0	20	907	-921
-5	0	22	884	-931
-5	0	24	650	655
-5	0	26	674	646
-4	0	4	871	889
-4	0	6	1224	1245
-4	0	8	502	528
-4	0	10	165	162
-4	0	12	430	461
-4	0	14	961	-971
-4	0	16	282	-314
-4	0	18	496	477
-4	0	20	1114	1107
-4	0	22	575	-603
-3	0	2	2117	-2276
-3	0	4	948	-939
-3	0	6	1858	1981
-3	0	10	479	-445
-3	0	12	1646	-1734
-3	0	14	1579	-1641
-3	0	16	385	374
-3	0	18	253	253
-3	0	20	1041	1126
-3	0	22	240	208
-3	0	24	795	-807
-3	0	26	1349	-1439
-2	0	2	414	-385
-2	0	6	686	-712
-2	0	8	1411	1516
-2	0	10	249	-264
-2	0	12	928	-900
-2	0	16	496	495
-2	0	18	1266	1330
-2	0	20	1250	1318
-2	0	22	338	-312
-2	0	24	594	-647
-2	0	26	853	-916
-1	0	2	877	-917
-1	0	4	212	217
-1	0	6	683	-699
-1	0	8	493	-543
-1	0	10	440	438
-1	0	12	1730	1850
-1	0	14	515	-539
-1	0	16	179	-176
-1	0	20	1308	-1366
-1	0	24	458	-430
-1	0	26	436	-481
0	0	2	900	899
0	0	4	1769	-1863
0	0	8	283	322
0	0	10	732	668
0	0	12	1319	1405
0	0	14	1063	1102
0	0	18	1902	-2046
0	0	20	365	-359
0	0	22	566	598
0	0	24	822	883
0	0	26	511	-497
1	0	0	1638	1695
1	0	2	1259	1146
1	0	4	138	-101
1	0	8	1546	-1489
1	0	10	1574	1574
1	0	12	2045	2041
1	0	14	435	-420
1	0	16	454	-451
1	0	18	970	-976
1	0	20	572	-570
1	0	24	1455	1564
1	0	26	330	294
2	0	0	649	-661
2	0	2	1385	-1320
2	0	4	813	801
2	0	6	563	512
2	0	8	177	-149
2	0	10	888	-895
2	0	12	1585	1643
2	0	16	174	-156
2	0	18	1321	-1397
2	0	20	353	340
2	0	24	377	401
3	0	0	244	226
3	0	4	785	788
3	0	6	1056	1059
3	0	8	531	497
3	0	10	1696	-1713
3	0	12	1034	-1022
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-5	3	20	372	-375
-5	3	21	694	680
-5	3	22	324	-315
-4	3	1	529	-504
-4	3	2	195	-178

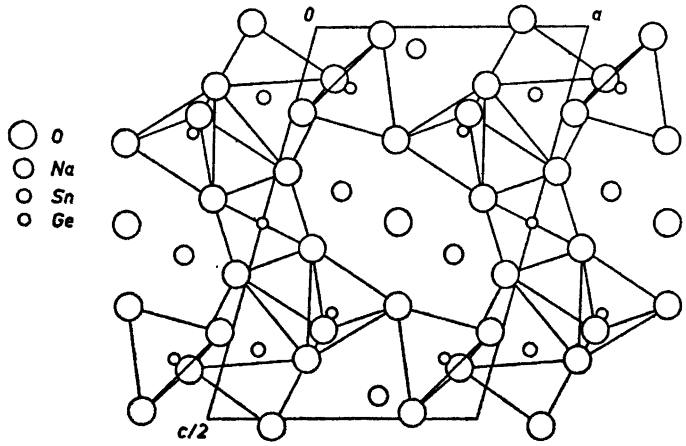

Fig. 5. Projection of the structure on (010) showing linking of tetrahedra (Ge) and octahedra (Sn). The oxygen atom O_{15} which is bound to sodium only stands out clearly in the center of the figure.

DISCUSSION

The X-ray structure analysis appears to yield a more accurate chemical formula than that of the chemical analysis. Especially the analysis for sodium appears erroneous whereas the Ge/Sn ratio seems quite accurately determined.

The compound has not been described in the literature as a mineral. However, it may be pertinent to draw attention to the fact that tin and germanium both are found in comparatively large amounts in forest litter and in the ashes of certain coals (Goldschmidt).[11]

The structure is shown in projection in Fig. 5. The germanium atoms are tetrahedrally coordinated. Strings of germanium tetrahedra run approximately along [401] Ge(3)—Ge(5)—Ge(4). The tetrahedra share corners at the oxygen atoms O(11) and O(12). Corner sharing is also used in connecting germanium tetrahedra with tin octahedra. The oxygen atoms O(7), O(8), O(9), O(10), O(13), and O(14) are thus bonded both to germanium and tin. One oxygen atom, O(15), which is located on a twofold axis is only coordinated to the sodium atoms Na(1).

Ten germanium-oxygen distances were measured. The average Ge—O distance ($\bar{y}$) is 1.752 Å. The distances Ge(4)—O(11) and Ge(5)—O(11) are the two longest of the set with a mean ($\bar{y}_1$) of 1.791 Å. The mean of the eight other Ge—O distances is 1.742 Å ($\bar{y}_2$). Since some of the oxygen atoms are bound to two germanium atoms the Ge—O distances are not strictly independent, but we have nevertheless found the following statistical considerations helpful. An analysis of variance was carried out to test the significance level of the difference between $\bar{y}_1$ and y_2. The notation of Hamilton [12] is used in the statistical considerations. The within-classes sum of squares was computed

as $S_w = \sum_{i=1}^{2} \sum_{j=1}^{2,8} (y_{ij}-\bar{y}_i)^2 = 0.00282$ Å^2. The between-classes sum of squares $S_b = \sum_{i=1}^{2} m_i (\bar{y}_i-\bar{y}) = 0.00384$ Å^2. The quotient $\frac{S_b/1}{S_w/8} = 10.9$, and $F_{1,8,0.025} = 7.57$. The null hypothesis that the two means are equal can be rejected at the 2.5 % significance level. By combining chemical and statistical considerations we propose that O(11) is the oxygen atom of a hydroxyl group. A multiple comparison of the Ge—O distances was also carried out. By grouping the distances according to size the following three means were calculated: $\mu_1 = 1.791$ Å (Ge—OH), (two values), $\mu_2 = 1.722$ Å, (three values), $\mu_3 = 1.754$ Å, (five values). The contrasts $\theta_1 = \mu_1-\mu_2$, $\theta_2 = \mu_1-\mu_3$, $\theta_3 = \mu_2-\mu_3$ were considered. The following 95 % confidence statements were computed: $0.038 < \theta_1 < 0.10$, $0.009 < \theta_2 < 0.065$, $0.007 < \theta_3 < 0.057$. Thus it is possible at this level of confidence to reject the hypothesis that $\mu_2 = \mu_3$.

The assumption that O(11) represents a hydroxyl group is reasonable from naive valence considerations. The grouping of the other Ge—O distances in two sets is, however, difficult to interpret from such considerations, and it lacks support from other evidence.

Smith and Isaacs [13] quote the following values for Ge—O distances in the quartz modifikation of GeO_2: 1.737 Å, $\sigma = 0.003$ Å, and 1.741 Å, $\sigma = 0.002$ Å. Ingri and Lundgren [14] find the value 1.740 Å for the Ge—O distance of tetrahedrally coordinated germanium in $Na_4Ge_9O_{20}$. These values compare favourably with the mean value which we compute for eight Ge—O distances: $y_2 = 1.742$ Å, $\sigma = 0.007$ Å.

The oxygen-tin distances appear to be divided in two groups: Sn—O(8) and Sn—O(9) are almost equal with a mean of 2.020 Å. The other four distances give the mean 2.049 Å. The average over all six distances is 2.040 Å. An analysis of variance gives a within classes sum of squares $S_w = 0.00017$ Å^2 and a between classes sum of squares $S_b = 0.00112$ Å^2. The quotient $\frac{S_b/1}{S_w/4} = 26.4$ as compared with $F_{1,4,0.01} = 21.2$. Thus we can reject at the 1 % level the assumption that the two means are equal.

Distorted octahedra occur in perovskites containing tin, and the distortion reported here is in accordance with general trends in the stereochemistry of tin.

The coordination around the sodium atoms bears a close resemblance to the sodium-oxygen configuration in $Na_4Ge_9O_{20}$.[15] The sodium atom Na(1) has four nearest oxygen neighbours at a mean distance of 2.291 Å, $\sigma = 0.015$ Å. The next nearest neighbour is the alleged hydroxyl oxygen O(11), at 2.527 Å. The sodium atom Na(2) has four oxygen atoms as nearest neighbours at a mean distance of 2.371 Å, $\sigma = 0.004$ Å. A fifth neighbour is O(10) at 2.587 Å and a sixth atom at 2.820 Å has a weak link with Na(2). The two sets of Na—O distances, 2.29 Å and 2.37 Å, illustrate the uncertainty of the application of ionic radii, packing considerations etc. The oxygen-oxygen distances are given in Table 4. There is little evidence for the existence of a definite hydrogen bond. The alleged hydroxyl frequency at 3440 cm^{-1} is also an indication of only a low degree of hydrogen bonding.

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