

The Crystal Structure of $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$

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The crystal structure of $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$ was determined from three-dimensional Fourier functions and was refined to a conventional R -value of 5.4 %. The space group is $P\bar{1}$, with $a=5.77$ Å, $b=11.61$ Å, $c=5.54$ Å, $\alpha=107.62^\circ$, $\beta=75.75^\circ$, $\gamma=94.75^\circ$. The cell contains one formula unit. Germanium atoms were tetrahedrally coordinated with oxygen atoms and tin atoms are octahedrally coordinated with oxygen atoms. GeO_4 -tetrahedra form strings along [001], by sharing corners. The strings are bonded together by SnO_6 -octahedra.

Hydrothermal synthesis with mixtures of germanium(IV) oxide and tin(IV) oxide in a sodium hydroxide solution can yield the phases $\text{Na}_4\text{Ge}_9\text{O}_{20}$, $\text{Na}_8\text{Sn}_4\text{Ge}_{10}\text{O}_{30}(\text{OH})_4$, and $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$. The crystal structure of the first mentioned compound was determined by Ingri and Lundgren.¹ The structure of the second compound was reported by Larsen, Christensen and Rasmussen,² and the crystal structure of $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$ is given below.

EXPERIMENTAL

Chemistry. The compound $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$ was prepared hydrothermally in 20 ml pressure bombs lined with pure silver. In a typical experiment a mixture of 250 mg GeO_2 and 25 mg SnO_2 was treated with 5 ml of a 1 M NaOH solution at 450°C and 500 atm for 60 h. Microscopical investigation of the product proved it to consist of two phases. No chemical analysis was made.

X-Ray technique. The powder pattern of the product was obtained with a Guinier-de Wolff camera using $\text{CuK}\alpha$ -radiation ($\lambda=1.5418$ Å). One of the phases in the product was identified as $\text{Na}_8\text{Sn}_4\text{Ge}_{10}\text{O}_{30}(\text{OH})_4$ and the other as $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$. A crystal of dimensions $0.17 \times 0.17 \times 0.04$ mm³ was investigated by Weissenberg and precession methods using $\text{CuK}\alpha$ -radiation. Weissenberg photographs were taken of $h\bar{k}0$ and $h\bar{k}1$, and precession photographs were taken of $h\bar{0}l$ and $0\bar{k}l$. 1194 independent reflections with $I > 3 \sigma(I)$ were measured on a single crystal diffractometer with a scintillation counter using monochromatic $\text{MoK}\alpha$ -radiation ($\lambda=0.7107$ Å). The monochromator was a lithium fluoride crystal and the pulse height analyzer was set to include 99 % of the $\text{MoK}\alpha$ -peak thus excluding harmonics in the beam. The diffractometer was of equiinclination Weissenberg type manufactured by Supper and Pace.

Lorentz-polarisation corrections were applied and absorption correction was made.

STRUCTURE DETERMINATION

The space group $P\bar{1}$ or $P\bar{1}$ of the triclinic crystal was indicated from Weissenberg and precession photographs. The space group $P\bar{1}$ was assumed. One of the tin atoms was given the special position (0,0,0). A three-dimensional Fourier map based on this assumption showed the positions of all the heavy atoms. A new Fourier map based on structure factor signs calculated with all the heavy atoms gave the position of all sodium and oxygen atoms.

The refinement proceeded by the method of least squares, (Hazell),³ giving an R -value of 5.4 % at the end of the refinement. Anisotropic temperature factor coefficients were used. A final difference Fourier map showed the positions of the hydrogen atoms. With the hydrogen atoms inserted an R -value of 5.4 % was obtained.

CRYSTAL DATA

The formula of the compound is $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$ and the unit cell contains one formula unit. The crystal system is triclinic with $a = 5.77_8 \text{ \AA}$, $b = 11.61_5 \text{ \AA}$, $c = 5.54_0 \text{ \AA}$, $\alpha = 107.62^\circ$, $\beta = 75.75^\circ$, $\gamma = 94.75^\circ$. The calculated density is 4.20 g/cm^3 and the absorption coefficient for Mo-radiation is 130 cm^{-1} ($\lambda = 0.7107 \text{ \AA}$). The structure factors were calculated using the atomic scattering factors from Vol. III of *International Tables of X-ray Crystallography* approximated by Bassi polynomials.⁴ The atomic scattering factors for germanium and tin were corrected for dispersion, using the real part of the correction only.

Final atomic coordinates and temperature factor parameters are given in Table 1, and interatomic distances and bond angles in Table 2. Table 3 is a list of observed and calculated structure factors. Fig. 1 is a projection of a part of the structure along [100].

Table 1. Atomic coordinates and temperature factor coefficients. Diffractometer data, 1194 reflections, anisotropic refinement, $R = 5.4 \%$.

Atom	x	σx	y	σy	z	σz
O ₁	0.1681	(17)	0.0535	(9)	0.3031	(19)
O ₂	0.6798	(15)	0.0364	(9)	0.2522	(19)
O ₃	0.4919	(16)	0.2098	(9)	0.0740	(21)
O ₄	0.4415	(15)	0.2321	(8)	0.6024	(19)
O ₅	0.0241	(17)	0.1687	(8)	0.9668	(20)
O ₆	0.2440	(17)	0.4028	(9)	0.0626	(18)
O ₇	0.7365	(16)	0.4398	(9)	0.2449	(20)
O ₈	0.9381	(18)	0.3612	(9)	0.6925	(23)
Na ₁	0.5830	(10)	0.4375	(5)	0.6710	(11)
Na ₂	0.8251	(10)	0.1509	(6)	0.6435	(12)
Ge ₁	0.2808	(2)	0.2501	(1)	0.9317	(3)
Ge ₂	0.4378	(2)	0.1251	(1)	0.3009	(3)
Sn ₁	0		0		0	
Sn ₂	0		0.5		0	
H ₁	0.697	(40)	0.360	(23)	0.191	(49)
H ₂	0.316	(32)	0.271	(18)	0.658	(39)

Table 1. Continued.

Temperature factor coefficients with standard deviations ($\times 10^5$).

Atom	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
O ₁	1246	439	997	414	668	459	-743	332	3	349	-74	387
O ₂	151	386	1316	434	1062	442	-41	311	-360	326	335	397
O ₃	672	418	1071	428	1415	487	247	325	-10	354	429	409
O ₄	410	392	922	403	940	456	-3	311	-224	330	-255	387
O ₅	1552	477	456	381	1317	480	-63	328	-380	382	360	384
O ₆	1567	459	1257	427	0 ^a	395	41	342	-673	334	552	379
O ₇	559	423	1593	464	1388	488	-185	342	-749	357	168	421
O ₈	1174	457	1087	428	2374	577	-287	343	-459	403	521	443
Na ₁	1593	281	1601	269	953	268	-555	212	-597	217	527	245
Na ₂	1358	271	1573	264	1398	284	620	209	-437	216	234	246
Ge ₁	774	60	459	53	913	66	-54	45	-72	51	96	54
Ge ₂	739	60	529	55	825	65	57	44	61	49	108	54
Sn ₁	617	53	404	47	863	59	29	39	-9	44	165	48
Sn ₂	823	56	569	50	1240	63	112	41	-107	47	148	51
H ₁	1	5 ^b										
H ₂	0 ^c	4										

^a The value was -83 in the final refinement.^b Isotropic temperature factor coefficient B (\AA^2) and σB (\AA^2).^c The value was -0.9 in the final refinement.Table 2. Interatomic distances in \AA and bond angles in degrees in $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$. Standard deviations in parentheses.

Ge ₁ -O _{3'}	1.767 (12)	Ge ₄ -Ge ₁ -O _{5'}	115.11 (46)
Ge ₁ -O _{4'}	1.789 (9)	Ge ₄ -Ge ₁ -O ₃ '	103.30 (50)
Ge ₁ -O ₅ '	1.694 (9)	Ge ₄ -Ge ₁ -O ₈ '	104.11 (43)
Ge ₁ -O ₆ '	1.710 (9)	O ₅ -Ge ₁ -O ₃ '	112.64 (46)
Ge ₂ -O ₃	1.774 (12)	O ₅ -Ge ₁ -O ₆ '	114.28 (46)
Ge ₂ -O ₄	1.758 (9)	O ₈ '-Ge ₁ -O ₆ '	106.33 (44)
Ge ₂ -O ₁	1.703 (9)	O ₁ -Ge ₂ -O ₂	116.64 (47)
Ge ₂ -O ₂	1.725 (10)	O ₁ -Ge ₂ -O ₃	109.54 (52)
Sn ₁ -O ₁	2.055 (11)	O ₁ -Ge ₂ -O ₄	111.73 (40)
Sn ₁ -O ₂	2.013 (8)	O ₂ -Ge ₂ -O ₃	110.85 (46)
Sn ₁ -O ₅ '	2.013 (10)	O ₂ -Ge ₂ -O ₄	102.32 (47)
Sn ₂ -O ₆ '	2.031 (11)	O ₃ -Ge ₂ -O ₄	104.99 (47)
Sn ₂ -O ₇ '	2.007 (10)	O ₅ -Sn ₁ -O ₁ '	90.97 (35)
Sn ₂ -O ₈ '	2.042 (10)	O ₅ -Sn ₁ -O ₂ '	90.91 (35)
Na ₁ -O ₄	2.405 (11)	O ₆ -Sn ₂ -O ₇ '	90.97 (35)
Na ₁ -O ₆ ''	2.320 (11)	O ₆ -Sn ₂ -O ₈ '	92.15 (35)
Na ₁ -O ₆ '	2.648 (11)	O ₇ '-Sn ₂ -O ₈ '	90.61 (35)
Na ₁ -O ₇ '	2.316 (13)		
Na ₁ -O ₇ ''	2.295 (12)		
Na ₁ -O ₈	2.343 (13)		

Table 2. Continued.

$\text{Na}_2-\text{O}_1''$	2.483 (13)
$\text{Na}_2-\text{O}_2'$	2.478 (12)
$\text{Na}_2-\text{O}_3'$	2.614 (10)
$\text{Na}_2-\text{O}_4'$	2.565 (12)
$\text{Na}_2-\text{O}_5'$	2.307 (14)
$\text{Na}_2-\text{O}_6'$	2.428 (12)
O_7-H_1	0.9 (2)
O_4-H_2	0.8 (2)

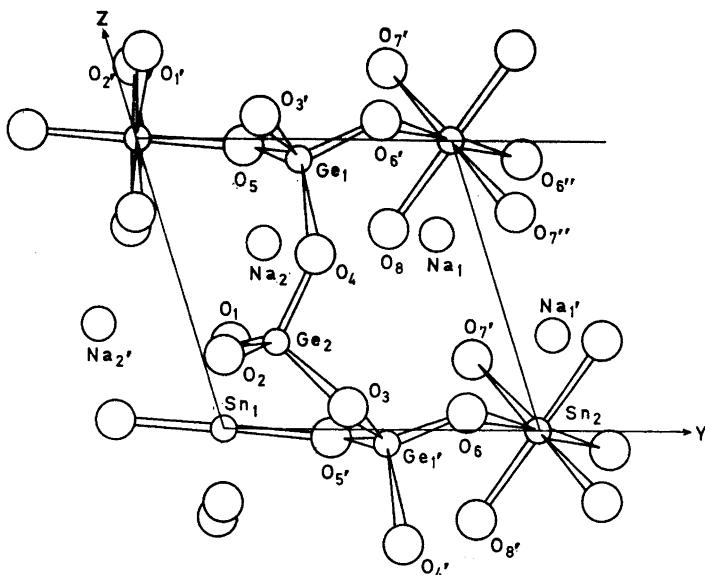


Fig. 1. Projection of a part of the structure along [100].

DISCUSSION

The X-ray structure analysis gave the chemical composition of the compound. The germanium atoms are tetrahedrally coordinated with oxygen atoms. The tetrahedra share corners and strings of germanium tetrahedra run along [001]. The tin atoms are octahedrally coordinated with oxygen atoms and corner sharing is used in connecting germanium tetrahedra with tin octahedra.

In the two germanium tetrahedra eight $\text{Ge}-\text{O}$ distances were calculated. The mean distance was 1.730 \AA , $\sigma = 0.003 \text{ \AA}$ in fair agreement with the average $\text{Ge}-\text{O}$ distance of 1.737 \AA , $\sigma = 0.003 \text{ \AA}$, found by Smith and Isaacs⁵ in the quartz modification of GeO_2 , and the average $\text{Ge}-\text{O}$ distance of 1.741 \AA , $\sigma = 0.002 \text{ \AA}$, reported by Ingri and Lundgren¹ for the tetrahedrally coordinated germanium atoms in the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ structure. The distances from Ge_1 to

Table 3. Observed and calculated structure factors.

h	k	l	F_O	F_C	1	7	0	417	424	-3	-6	1	276	267	-2	5	1	173	180	-1	-10	2	935	991
1	-15	0	199	-462	3	7	0	434	-448	-2	-6	1	885	897	-1	5	1	409	-403	0	-10	2	391	405
1	-14	0	199	209	6	7	0	511	-505	1	-6	1	1119	1177	0	5	1	414	-440	1	-10	2	174	163
2	-14	0	675	697	7	7	0	150	-161	-1	-6	1	133	82	1	5	1	817	-844	2	-10	2	636	649
2	-14	0	429	429	8	7	0	154	-157	2	-6	1	74	77	3	5	1	434	-450	3	-10	2	289	257
3	-13	0	307	314	1	8	0	256	258	4	-6	1	116	117	-5	6	1	183	-181	5	-10	2	141	172
4	-13	0	299	307	2	8	0	400	399	-5	-6	1	634	659	4	6	1	410	377	-4	-9	2	446	443
1	-12	0	553	584	3	8	0	560	556	-7	-5	1	201	-190	-3	6	1	269	264	-2	-9	2	136	130
3	-12	0	559	576	4	8	0	565	548	-6	-5	1	648	628	-2	6	1	1282	1358	-1	-9	2	237	244
4	-12	0	530	509	5	8	0	165	154	-5	-5	1	353	-361	1	6	1	545	-542	0	-8	2	600	-636
1	-11	0	154	174	6	7	0	242	242	-2	-5	1	576	576	0	6	1	483	507	1	-9	2	623	649
3	-11	0	524	541	1	9	0	762	-793	-1	-5	1	112	71	1	6	1	164	170	2	-9	2	158	-145
4	-11	0	398	-383	2	9	0	644	661	-1	-5	1	993	1035	2	6	1	1426	1447	3	-9	2	310	-311
1	-10	0	538	555	4	9	0	124	89	-2	-5	1	833	-819	3	6	1	499	479	6	-9	2	117	231
2	-10	0	571	601	5	9	0	256	-252	3	-5	1	108	-120	4	6	1	261	233	-6	-8	2	51	53
3	-10	0	554	577	6	9	0	120	115	-5	-5	1	377	359	5	6	1	531	-542	-8	-8	2	376	373
5	-10	0	694	689	7	9	0	477	477	-4	-4	1	486	477	6	6	1	246	315	-3	-8	2	724	748
6	-10	0	216	233	8	10	0	888	925	-6	-4	1	612	613	-5	7	1	248	247	-1	-8	2	363	380
1	-9	0	139	138	4	10	0	564	534	-4	-4	1	722	698	-4	7	1	649	-629	0	-8	2	557	600
2	-9	0	111	-101	5	10	0	232	241	-3	-4	1	389	380	-3	7	1	615	579	1	-8	2	1136	1186
3	-9	0	127	-105	6	10	0	532	505	-2	-4	1	819	802	-2	7	1	118	94	2	-8	2	260	-260
5	-9	0	345	329	0	11	0	277	274	-1	-4	1	107	106	-1	7	1	156	-156	3	-8	2	513	501
6	-9	0	509	491	1	11	0	406	400	-2	-4	1	908	949	1	8	1	184	-197	4	-8	2	668	650
1	-8	0	188	179	3	11	0	181	-201	3	-4	1	927	898	2	7	1	516	522	5	-8	2	429	472
2	-8	0	516	521	4	11	0	425	404	-4	-4	1	417	389	3	7	1	749	-760	-5	-7	2	288	-287
3	-8	0	507	510	5	11	0	108	-90	5	-5	1	712	710	4	7	1	568	545	-4	-7	2	586	571
4	-8	0	736	714	6	12	0	399	399	-7	-3	1	213	221	5	7	1	142	129	-3	-7	2	357	-347
5	-8	0	337	350	1	12	0	753	755	-6	-4	1	281	274	-5	6	1	240	240	0	-8	2	124	131
6	-8	0	143	163	2	14	0	553	541	-4	-4	1	216	268	6	8	1	258	325	0	-6	2	656	672
7	-8	0	497	493	4	12	0	491	479	-2	-3	1	171	-152	-3	8	1	858	827	3	-7	2	870	838
5	-7	0	152	-161	5	12	0	234	233	-1	-3	1	410	-405	-1	8	1	605	650	4	-7	2	444	-448
6	-7	0	220	226	6	13	0	177	-151	0	-3	1	757	806	0	8	1	636	670	-6	-6	2	256	253
1	-6	0	1020	1055	2	13	0	109	-84	-1	-3	1	804	811	1	8	1	457	469	5	-6	2	427	437
2	-6	0	1362	1361	3	13	0	311	311	-2	-3	1	639	-581	1	8	1	176	167	-4	-6	2	724	703
4	-6	0	446	445	4	14	0	290	-278	3	-3	1	410	407	3	8	1	349	316	-2	-6	2	1149	1159
5	-6	0	746	722	5	14	0	198	192	-4	-3	1	494	-469	4	8	1	867	799	-1	-6	2	529	514
1	-5	0	563	582	6	14	0	476	467	-5	-2	1	1051	1009	-1	9	1	189	178	2	-6	2	1158	1198
2	-5	0	232	231	7	14	0	282	289	-2	-3	1	451	461	-7	9	1	541	542	3	-6	2	465	466
3	-5	0	471	456	8	15	0	157	159	-2	-3	1	120	123	-1	10	1	571	574	4	-6	2	142	121
4	-5	0	504	514	9	15	0	424	425	-1	-2	1	685	682	0	9	1	156	-148	-5	-6	2	673	710
5	-5	0	192	-183	10	16	0	410	391	-1	-2	1	111	84	5	9	1	382	-352	-15	-5	2	152	151
7	-5	0	131	-149	11	16	0	347	-322	2	-2	1	1866	1956	6	9	1	291	327	-14	-5	2	178	-180
1	-4	0	863	931	12	15	1	298	282	3	-2	1	236	210	-5	10	1	477	463	-3	-5	2	103	-95
2	-4	0	117	112	13	15	1	183	-177	4	-2	1	425	401	-14	10	1	408	401	-2	-5	2	102	114
3	-4	0	1062	1012	14	15	1	199	195	-5	-2	1	574	577	5	7	1	459	456	-15	-5	2	908	-917
4	-4	0	575	573	15	16	1	220	-225	4	-1	1	706	663	-2	11	1	714	-714	-2	-5	2	465	449
6	-4	0	500	477	16	17	1	361	349	-5	-1	1	141	110	1	10	1	612	616	3	-5	2	407	-421
7	-4	0	307	320	17	14	1	672	669	-4	-1	1	707	-689	2	10	1	576	589	4	-5	2	105	107
1	-3	0	120	-142	18	14	1	216	-214	-3	-1	1	469	468	3	10	1	529	506	5	-5	2	431	458
2	-3	0	168	-172	19	14	1	450	456	-1	-1	1	478	443	5	10	1	464	495	-6	-4	2	222	230
3	-3	0	740	739	20	14	0	414	-412	1	-1	1	720	-721	2	12	1	474	439	-3	-4	2	398	-398
5	-3	0	556	546	21	15	0	450	450	-1	-1	1	154	-154	0	11	1	302	179	-4	-4	2	114	104
7	-3	0	247	-241	22	13	1	306	286	-2	-1	1	506	504	0	11	1	322	-303	-3	-4	2	181	1192
2	-2	0	252	251	23	13	1	161	-144	3	-1	1	576	556	-2	11	1	591	568	-2	-4	2	721	746
1	-2	0	1132	1185	24	13	1	220	-225	4	-1	1	706	663	8	11	1	716	-717	2	-4	2	519	505
3	-2	0	433	433	25	14	0	365	378	-6	-1	1	129	-146	4	12	1	316	303	-1	-3	2	231	233
6	-2	0	332	332	26	14	0	362	348	-5	-1	1	158	114	-3	13	1	330	-311	2	-3	2	284	-276
7	-1	0	174	158	27	11	1	522	-515	-1	-1	1	324	305	-3	12	1	419	419	5	-4	2	171	174
2	0	0	707	681	28	11	1	515	-512	1	-1	1	310	312	-5	13	1	344	324	-6	-2	2	286	310
3	0	0	649	619	29	11	1	424	-424	1	-1	1	158	-185	-2	14	1	621	-592	-5	-2	2	822	832
4	0	0	183	-183	30	12	1	424	-424	3	-1	1	740	723	-1	14	1	295	300	-4	-2	2	273	261
5	0	0	455	408	31	9	1	152	139	-3	-1	1	126	-103	-2	13	2	169	-162	-4	-1	2	287	-291
6	0	0	129	133	32	9	1	296	-275	-3	-1	1	334	-346	5	12	2	574	593	-3	-1	2	242	257
7	0	0	149	129	33	7	1	221	194	-2	-3	1	623	598	-1	14	2	215	200	-2	-1	2	131	118
3	0	0	561	521	34	-9	1	519	-510	4	-2	1	331	321	0	14	2	353	373	-1	-1	2	199	-202
4	0	0	196	198	35	-8	1	398	427	2	-3	1	377	-364	-3	12	2	704	710	-2	-2	2	474	466
5	0	0	91	74	36	-8	1	766	828	3	-3	1	142	-183	-2	12	2	363	385	-1	-2	2	369	393
6																								

Table 3. Continued.

-4	2	2	853	838	2	-12	3	309	291	0	2	3	871	902	-2	-7	4	611	-587	0	9	4	143	127
-5	2	2	150	-166	4	-12	3	724	675	2	2	3	1283	1309	-1	-7	4	150	182	2	9	4	222	-197
-2	2	2	120	127	5	-12	3	256	236	3	2	2	289	244	4	-7	4	569	496	3	9	4	154	-105
-1	2	2	425	438	-2	-11	3	285	283	-5	3	3	219	213	-6	-6	4	695	-352	-1	10	4	401	387
0	2	2	425	438	-2	-11	3	285	283	-5	3	3	219	213	-6	-6	4	370	352	-1	10	4	501	461
1	2	2	599	640	-1	-11	3	190	195	-4	3	3	396	-395	-4	-6	4	519	503	1	10	4	145	120
2	2	2	916	910	1	-11	3	279	282	-3	3	3	363	366	-3	-6	4	380	356	1	10	4	343	311
3	2	2	1162	1157	2	-11	3	355	-348	-1	3	3	147	155	-2	-6	4	166	139	2	10	4	274	248
4	2	2	272	272	5	-11	3	264	267	1	3	3	469	-502	-1	-6	4	986	924	3	10	4	556	487
5	2	2	928	941	-5	-10	3	272	268	3	3	3	151	162	-3	-6	4	788	701	-4	-7	5	206	196
6	2	2	118	189	-5	-10	3	647	625	3	3	3	447	442	-5	-6	4	607	565	-2	-5	5	85	667
-6	3	2	124	85	-4	-10	3	647	625	3	3	3	394	-363	-5	-6	4	153	122	-1	-5	5	823	855
-5	3	2	159	134	-2	-10	3	457	433	6	3	3	139	277	-3	-5	4	229	-222	-3	-3	5	307	311
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-3	3	2	322	322	-1	-10	3	458	436	-3	4	3	992	981	-1	-5	4	752	748	-4	-2	5	186	252
-2	3	2	612	615	-2	-10	3	409	374	-2	3	3	292	178	-3	-5	4	216	204	-3	-2	5	462	444
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0	3	2	128	-118	5	-10	3	325	300	0	4	3	237	251	5	5	4	211	211	0	-2	5	407	435
1	3	2	425	-456	6	-10	3	354	454	1	4	3	780	813	-4	-4	4	320	291	2	-2	5	375	418
2	3	2	477	479	-3	-9	3	313	-298	2	4	3	260	267	-3	-4	4	483	457	3	-2	5	398	321
3	3	2	332	-529	-2	-9	3	759	771	3	4	3	133	95	-2	-4	4	651	610	4	-2	5	714	587
4	3	2	202	-273	0	-9	3	303	-427	5	4	3	945	862	-1	-4	4	185	186	-1	-1	5	358	351
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-4	4	2	245	250	5	-9	3	510	458	-2	5	3	336	-341	-4	-3	4	529	499	6	-1	5	168	312
-3	4	2	791	792	6	-9	3	242	-299	-1	5	3	396	406	-3	-3	4	221	-227	7	-1	5	132	-169
-2	5	2	576	-576	7	-9	3	303	-337	0	5	3	143	193	-1	-3	4	252	-269	-4	0	5	140	137
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1	5	2	373	400	-2	-8	3	804	776	3	5	3	611	612	-2	-3	4	445	393	1	-1	5	388	415
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6	5	2	325	-324	4	-8	3	719	697	-2	6	3	400	404	-2	-4	4	546	516	1	1	5	279	318
-5	5	2	237	246	5	-8	3	611	794	-1	6	3	972	1007	1	-2	4	341	333	1	1	5	412	455
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-1	5	2	584	592	-6	-7	3	294	-305	1	6	3	509	494	2	-2	4	1081	971	3	1	5	281	223
0	5	2	341	412	-1	-7	3	239	-241	2	6	3	363	375	3	-2	4	768	649	-4	2	5	668	738
1	5	2	226	229	1	-7	3	831	-831	3	6	3	890	857	4	-2	4	172	141	-2	2	5	378	390
2	5	2	431	392	2	-7	3	123	145	-3	7	3	292	222	5	-2	4	185	160	1	2	5	349	344
3	5	2	553	-544	4	-7	3	253	224	2	7	3	446	456	-5	-1	4	255	273	1	2	5	335	332
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6	6	2	205	175	-5	-5	3	462	469	5	8	3	339	474	2	-2	4	424	407	5	2	5	161	270
-6	6	2	644	778	-3	-5	3	175	-175	-1	9	3	369	-371	5	0	4	136	198	0	4	5	614	600
-5	7	2	128	-128	0	-6	3	793	776	2	8	3	659	691	-3	-1	4	385	-324	0	3	5	175	-198
-4	7	2	197	-197	2	-5	3	645	644	1	9	3	461	474	-5	-1	4	146	-110	2	-4	5	553	493
-3	7	2	266	240	3	-5	3	607	-585	4	9	3	276	271	-1	-2	4	177	162	4	-5	5	348	378
0	7	2	552	-591	4	-5	3	158	131	-3	10	3	294	312	-3	-1	4	500	516	-3	5	5	148	199
1	7	2	765	784	6	-5	3	178	274	-2	10	3	278	275	-2	-1	4	311	-318	-2	-5	5	167	276
2	7	2	120	-161	6	-6	3	204	219	4	8	3	420	404	-1	-1	4	196	206	0	5	5	253	276
3	7	2	171	-158	5	-6	3	297	284	0	10	3	330	342	0	1	4	204	204	3	5	5	291	-262
4	8	2	449	-449	4	-5	3	355	353	-1	14	4	271	270	-2	-2	4	104	122	4	5	5	559	536
5	8	2	627	610	-3	-4	3	1114	1047	3	10	3	694	674	-3	-7	4	357	321	2	4	5	454	471
6	8	2	261	274	-2	-4	3	265	-314	4	10	3	348	340	-3	-6	4	197	175	-1	-6	5	442	500
0	8	2	313	325	2	-4	3	338	315	0	11	3	334	-329	4	1	4	535	442	1	6	5	166	145
1	8	2	498	516	3	-4	3	341	-367	-1	13	4	242	-444	-2	-3	4	182	-400	-2	-4	5	485	461
2	8	2	474	-474	3	-4	3	102	97	0	13	4	459	-444	-2	-3	4	312	297	-3	-3	5	324	373
3	9	2	239	447	4	-3	3	433	-410	1	13	4	247	242	-1	3	4	161	-161	-2	-3	6	194	-220
4	9	2	443	447	5	-3	3	567	632	-1	10	4	474	432	-2	-4	4	411	-416	3	-3	6	104	-113
5	10	2	115	-108	6	-2	3	272	297	4	13	4	212	-174	1	3	4	316	198	-3	-2	6	221	249
6	10	2	603	644	-6	-2	3	800	778	-5	12	4	228	228	2	-2	4	311	-377	-1	-2	6	374	415
7	10	2	443	456	-3	-2	3	178	-184	-2	12	4	236	-234	5	3	4	315	343	1	1	6	181	202
8	10	2	487	493	-2	-2	3	551	548	-1	12	4	222	218	-4	-4	4	370	375	1	-2	6	315	332
9	10	2	565	566	-1	-2	3	1086	1064	-1	12	4	779	770	-3	-4	4	347	334	3	-2	6	732	675
10	11	2	492	482	-2	-2	3	546	538	3	12	4	499	498	-2	-4	4	569	541	4	-2	6	124	231
11	11	2	358	-353	4	-2	3	141	-129	5	2	4	296	277	0	4	4	257	254	-5	1	6	251	-256
12	11	2	163	178	-5	-2	3	341	362	-1	11	4	314	-294	3	4	4	453	430	3	-1	6	264	

O_3' and O_4 have a mean value of 1.776 Å, $\sigma=0.007$ Å, and the distances from Ge_1 to O_5 and O_6' have a mean value of 1.702 Å, $\sigma=0.006$ Å. The distances from Ge_2 to O_3 and O_4 have a mean value of 1.763 Å, $\sigma=0.007$ Å, and the distances from Ge_2 to O_1 and O_2 have a mean value of 1.712 Å, $\sigma=0.007$ Å. This gives a mean value for the short Ge—O distances of 1.706 Å, $\sigma=0.005$ Å, and a mean value for the longer Ge—O distances of 1.774 Å, $\sigma=0.005$ Å. These distances are compared with the mean Ge—O distances in $\text{Na}_8\text{Sn}_4\text{Ge}_{10}\text{O}_{30}(\text{OH})_4$ given by Larsen, Christensen and Rasmussen,² a short Ge—O distance of 1.722 Å, $\sigma=0.005$ Å, a Ge—O distance of 1.754 Å, $\sigma=0.004$ Å, and a longer Ge—OH distance of 1.791 Å, $\sigma=0.006$ Å.

The oxygen atom O_3 is only bonded to two germanium atoms, and the oxygen atom O_4 is bonded to two germanium and two sodium atoms. From consideration of those distances it is assumed that O_3 and O_4 are oxygen atoms in OH^- ions. Before the last refinement cycle the hydrogen atoms H_1 and H_2 were inserted so that the distances were 1 Å to O_3 and O_4 , respectively. However, the hydrogen atom H_1 moved close to O_7 in the last cycle of refinement.

The Sn—O distances from Sn_1 to O_1 , O_2 , and O_5' can be divided in two groups. Sn_1 — O_1 is 2.055 Å, $\sigma=0.011$ Å, and the mean value of the two other distances is 2.013 Å, $\sigma=0.007$ Å. The hypothesis that the two sets of Sn—O distances are equal can be rejected at the 5 % significance level.

The Sn—O distances from Sn_2 to O_6 , O_7' and O_8' can be divided in two groups. Sn_2 — O_7' is 2.007 Å, $\sigma=0.010$ Å, and the mean value of the two other distances is 2.037 Å, $\sigma=0.007$ Å. The hypothesis that the two sets of Sn—O distances are equal can be rejected at the 5 % significance level. Distorted SnO_6 -octahedra were also found in the $\text{Na}_8\text{Sn}_4\text{Ge}_{10}\text{O}_{30}(\text{OH})_4$ -structure,² where Sn—O distances of 2.020 Å, $\sigma=0.006$ Å, and 2.049 Å, $\sigma=0.004$ Å, can be calculated. The oxygen atoms O_1 , O_2 , O_5 , and O_6 are bonded to sodium, germanium, and tin atoms, and the oxygen atoms O_7 and O_8 are only bonded to sodium and tin atoms.

The two sodium ions in the structure, Na_1 and Na_2 , are both coordinated with six oxygen atoms.

The crystal structure of $\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$ has points of resemblance with that of $\text{Na}_8\text{Sn}_4\text{Ge}_{10}\text{O}_{30}(\text{OH})_4$. Both have GeO_3 -chains held together by sodium and tin atoms.

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REFERENCES

1. Ingri, N. and Lundgren, G. *Acta Chem. Scand.* **17** (1963) 617.
2. Larsen, F. K., Christensen, A. N. and Rasmussen, S. E. *Acta Chem. Scand.* **21** (1967) 1281.
3. Hazell, R. G. G403, Least squares program, Department of Inorganic Chemistry, University of Aarhus.
4. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.
5. Smith, G. S. and Isaacs, P. B. *Acta Cryst.* **17** (1964) 842.

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