

## 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 *PI*, with  $a=5.77_3$  Å,  $b=11.61_5$  Å,  $c=5.54_0$  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.  $\text{GeO}_4$ -tetrahedra form strings along [001], by sharing corners. The strings are bonded together by  $\text{SnO}_6$ -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.<sup>1</sup> The structure of the second compound was reported by Larsen, Christensen and Rasmussen,<sup>2</sup> 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  $\text{GeO}_2$  and 25 mg  $\text{SnO}_2$  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  $0.17 \times 0.17 \times 0.04$  mm<sup>3</sup> was investigated by Weissenberg and precession methods using  $\text{CuK}\alpha$ -radiation. Weissenberg photographs were taken of *hk0* and *hk1*, and precession photographs were taken of *h0l* and *0kl*. 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  $P1$  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),<sup>3</sup> 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  $a = 5.77_8 \text{ \AA}$ ,  $b = 11.61_5 \text{ \AA}$ ,  $c = 5.54_0 \text{ \AA}$ ,  $\alpha = 107.62^\circ$ ,  $\beta = 75.75^\circ$ ,  $\lambda = 94.75^\circ$ . The calculated density is  $4.20 \text{ g/cm}^3$  and the absorption coefficient for Mo-radiation is  $130 \text{ cm}^{-1}$  ( $\lambda = 0.7107 \text{ \AA}$ ). The structure factors were calculated using the atomic scattering factors from Vol. III of *International Tables of X-ray Crystallography* approximated by Bassi polynomials.<sup>4</sup> 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	$x$	$\sigma x$	$y$	$\sigma y$	$z$	$\sigma z$
O <sub>1</sub>	0.1681	(17)	0.0535	(9)	0.3031	(19)
O <sub>2</sub>	0.6798	(15)	0.0364	(9)	0.2522	(19)
O <sub>3</sub>	0.4919	(16)	0.2098	(9)	0.0740	(21)
O <sub>4</sub>	0.4415	(15)	0.2321	(8)	0.6024	(19)
O <sub>5</sub>	0.0241	(17)	0.1687	(8)	0.9668	(20)
O <sub>6</sub>	0.2440	(17)	0.4028	(9)	0.0626	(18)
O <sub>7</sub>	0.7365	(16)	0.4398	(9)	0.2449	(20)
O <sub>8</sub>	0.9381	(18)	0.3612	(9)	0.6925	(23)
Na <sub>1</sub>	0.5830	(10)	0.4375	(5)	0.6710	(11)
Na <sub>2</sub>	0.8251	(10)	0.1509	(6)	0.6435	(12)
Ge <sub>1</sub>	0.2808	(2)	0.2501	(1)	0.9317	(3)
Ge <sub>2</sub>	0.4378	(2)	0.1251	(1)	0.3009	(3)
Sn <sub>1</sub>	0		0		0	
Sn <sub>2</sub>	0		0.5		0	
H <sub>1</sub>	0.697	(40)	0.360	(23)	0.191	(49)
H <sub>2</sub>	0.316	(32)	0.271	(18)	0.658	(39)

Table 1. Continued.

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

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

<sup>a</sup> The value was -83 in the final refinement.<sup>b</sup> Isotropic temperature factor coefficient  $B$  ( $\text{\AA}^2$ ) and  $\sigma B$  ( $\text{\AA}^2$ ).<sup>c</sup> The value was -0.9 in the final refinement.Table 2. Interatomic distances in  $\text{\AA}$  and bond angles in degrees in Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>4</sub>O<sub>12</sub>(OH)<sub>4</sub>. Standard deviations in parantheses.

Ge <sub>1</sub> -O <sub>3</sub> '	1.767 (12)	O <sub>4</sub> -Ge <sub>1</sub> -O <sub>5</sub> '	115.11 (46)
Ge <sub>1</sub> -O <sub>4</sub>	1.789 (9)	O <sub>4</sub> -Ge <sub>1</sub> -O <sub>3</sub> '	103.30 (50)
Ge <sub>1</sub> -O <sub>5</sub>	1.694 (9)	O <sub>4</sub> -Ge <sub>1</sub> -O <sub>5</sub> '	104.11 (43)
Ge <sub>1</sub> -O <sub>6</sub> '	1.710 (9)	O <sub>5</sub> -Ge <sub>1</sub> -O <sub>3</sub> '	112.64 (46)
		O <sub>5</sub> -Ge <sub>1</sub> -O <sub>6</sub> '	114.28 (46)
Ge <sub>2</sub> -O <sub>3</sub>	1.774 (12)	O <sub>3</sub> '-Ge <sub>1</sub> -O <sub>6</sub> '	106.33 (44)
Ge <sub>2</sub> -O <sub>4</sub>	1.758 (9)		
Ge <sub>2</sub> -O <sub>1</sub>	1.703 (9)	O <sub>1</sub> -Ge <sub>2</sub> -O <sub>3</sub>	116.64 (47)
Ge <sub>2</sub> -O <sub>2</sub>	1.725 (10)	O <sub>1</sub> -Ge <sub>2</sub> -O <sub>3</sub>	109.54 (52)
		O <sub>1</sub> -Ge <sub>2</sub> -O <sub>4</sub>	111.73 (40)
Sn <sub>1</sub> -O <sub>1</sub>	2.055 (11)	O <sub>2</sub> -Ge <sub>2</sub> -O <sub>3</sub>	110.85 (46)
Sn <sub>1</sub> -O <sub>2</sub>	2.013 (8)	O <sub>2</sub> -Ge <sub>2</sub> -O <sub>4</sub>	102.32 (47)
Sn <sub>1</sub> -O <sub>5</sub> '	2.013 (10)	O <sub>3</sub> -Ge <sub>2</sub> -O <sub>4</sub>	104.99 (47)
Sn <sub>2</sub> -O <sub>6</sub>	2.031 (11)	O <sub>5</sub> -Sn <sub>1</sub> -O <sub>1</sub> '	90.97 (35)
Sn <sub>2</sub> -O <sub>7</sub> '	2.007 (10)	O <sub>5</sub> -Sn <sub>1</sub> -O <sub>2</sub> '	90.91 (35)
Sn <sub>2</sub> -O <sub>8</sub> '	2.042 (10)	O <sub>1</sub> '-Sn <sub>1</sub> -O <sub>2</sub> '	90.50 (35)
Na <sub>1</sub> -O <sub>4</sub>	2.405 (11)	O <sub>6</sub> -Sn <sub>2</sub> -O <sub>7</sub> '	90.97 (35)
Na <sub>1</sub> -O <sub>6</sub> ''	2.320 (11)	O <sub>6</sub> -Sn <sub>2</sub> -O <sub>8</sub> '	92.15 (35)
Na <sub>1</sub> -O <sub>6</sub> '	2.648 (11)	O <sub>7</sub> '-Sn <sub>2</sub> -O <sub>8</sub> '	90.61 (35)
Na <sub>1</sub> -O <sub>7</sub> '	2.316 (13)		
Na <sub>1</sub> -O <sub>7</sub> ''	2.295 (12)		
Na <sub>1</sub> -O <sub>8</sub>	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)
$\text{Na}_2-\text{O}_8$	2.428	(12)
$\text{O}_7-\text{H}_1$	0.9	(2)
$\text{O}_4-\text{H}_2$	0.8	(2)

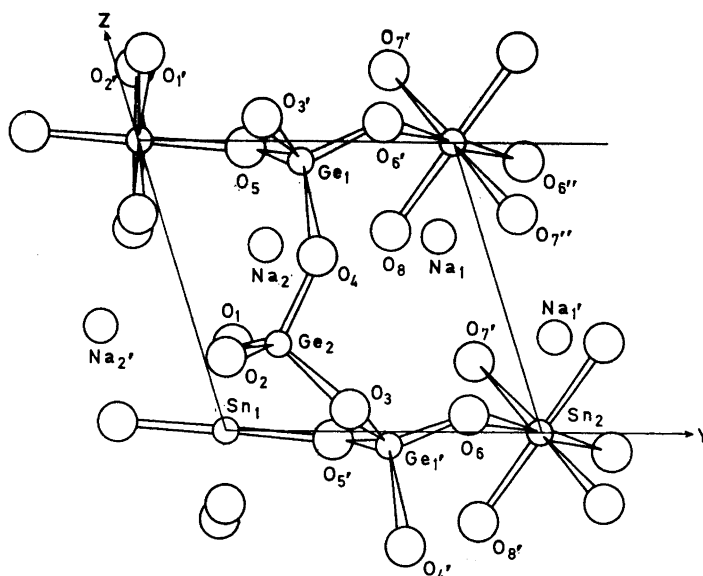


Fig. 1. Projection of a part of the structure along [100].

## 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 Ge—O distances were calculated. The mean distance was 1.730 Å,  $\sigma = 0.003$  Å in fair agreement with the average Ge—O distance of 1.737 Å,  $\sigma = 0.003$  Å, found by Smith and Isaacs<sup>5</sup> in the quartz modification of GeO<sub>2</sub>, and the average Ge—O distance of 1.741 Å,  $\sigma = 0.002$  Å, reported by Ingri and Lundgren<sup>1</sup> for the tetrahedrally coordinated germanium atoms in the Na<sub>4</sub>Ge<sub>3</sub>O<sub>20</sub> structure. The distances from Ge<sub>1</sub> to





$\text{O}_3'$  and  $\text{O}_4$  have a mean value of 1.776 Å,  $\sigma = 0.007$  Å, and the distances from  $\text{Ge}_1$  to  $\text{O}_5$  and  $\text{O}_6'$  have a mean value of 1.702 Å,  $\sigma = 0.006$  Å. The distances from  $\text{Ge}_2$  to  $\text{O}_3$  and  $\text{O}_4$  have a mean value of 1.763 Å,  $\sigma = 0.007$  Å, and the distances from  $\text{Ge}_2$  to  $\text{O}_1$  and  $\text{O}_2$  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,<sup>2</sup> 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  $\text{O}_3$  is only bonded to two germanium atoms, and the oxygen atom  $\text{O}_4$  is bonded to two germanium and two sodium atoms. From consideration of those distances it is assumed that  $\text{O}_3$  and  $\text{O}_4$  are oxygen atoms in  $\text{OH}^-$  ions. Before the last refinement cycle the hydrogen atoms  $\text{H}_1$  and  $\text{H}_2$  were inserted so that the distances were 1 Å to  $\text{O}_3$  and  $\text{O}_4$ , respectively. However, the hydrogen atom  $\text{H}_1$  moved close to  $\text{O}_7$  in the last cycle of refinement.

The Sn–O distances from  $\text{Sn}_1$  to  $\text{O}_1$ ,  $\text{O}_2$ , and  $\text{O}_5'$  can be divided in two groups.  $\text{Sn}_1$ – $\text{O}_1$  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  $\text{Sn}_2$  to  $\text{O}_6$ ,  $\text{O}_7'$  and  $\text{O}_8'$  can be divided in two groups.  $\text{Sn}_2$ – $\text{O}_7'$  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  $\text{SnO}_6$ -octahedra were also found in the  $\text{Na}_8\text{Sn}_4\text{Ge}_{10}\text{O}_{30}(\text{OH})_4$ -structure,<sup>2</sup> 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  $\text{O}_1$ ,  $\text{O}_2$ ,  $\text{O}_5$ , and  $\text{O}_6$  are bonded to sodium, germanium, and tin atoms, and the oxygen atoms  $\text{O}_7$  and  $\text{O}_8$  are only bonded to sodium and tin atoms.

The two sodium ions in the structure,  $\text{Na}_1$  and  $\text{Na}_2$ , 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  $\text{GeO}_3$ -chains held together by sodium and tin atoms.

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