

## Crystal growth and structures of mixed-anion silicates-germanates: $\text{Ca}_5[(\text{Ge,Si})_2\text{O}_7][(\text{Ge,Si})\text{O}_4]$ and $\text{Na}_2\text{Ca}_6[\text{Si}_2\text{O}_7][\text{SiO}_4]_2$

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### ABSTRACT

Hydrothermal experiments on  $\text{Ca}_2\text{ZnGe}_{1.5}\text{Si}_{0.5}\text{O}_7$  with the addition of NaOH at 973 K and 2 kbar produced  $\text{Ca}_5\text{Ge}_{2.23}\text{Si}_{0.77}\text{O}_{11}$  single crystals,  $a = 10.912(1)$ ,  $b = 8.695(2)$ ,  $c = 11.000(1)$  Å,  $\beta = 96.87(1)^\circ$ , space group  $C2/m$ . The structure was determined from X-ray single-crystal data ( $R = 3.3\%$ ,  $R_w = 4.9\%$ ) and consists of  $(\text{Ge,Si})_2\text{O}_7$  dimers and isolated  $(\text{Ge,Si})\text{O}_4$  tetrahedra. Ca is six-coordinated with octahedral and prismatic coordination. A corresponding phase was grown from a  $\text{SiO}_2$ -free starting product.

Fe-FeO buffered hydrothermal experiments on  $\text{Ca}_2\text{Fe}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_7$  with the addition of NaOH at 973 K and 2 kbar yielded single crystals of  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$ ,  $a = 5.525(1)$ ,  $b = 17.413(5)$ ,  $c = 14.489(2)$  Å,  $\beta = 90.57(1)^\circ$ , space group  $P2_1/c$ . Structure refinements ( $R = 2.5\%$ ,  $R_w = 3.3\%$ ) disclose two isolated  $\text{SiO}_4$  tetrahedra and one  $\text{Si}_2\text{O}_7$  dimer. Two metal sites are occupied by both Na and Ca. The remaining Na and Ca are ordered on one Na site and five Ca positions. Na and Ca are in strongly distorted six- and sevenfold coordination.

### INTRODUCTION

During a study of melilite-related compounds in the system  $\text{CaO-MeO-GeO}_2\text{-SiO}_2$  ( $\text{Me}^{2+} = \text{Zn, Fe, Mg}$ ), several new phases were synthesized by hydrothermal methods. Melilite-related compounds with tetrahedral sheet structure have previously been described by Armbruster et al. (1990). In order to obtain sufficiently large single crystals for subsequent X-ray structure analysis, NaOH was added as a solvent to the starting products in hydrothermal experiments. In many cases the addition of NaOH improved vapor transport within the inert metal capsules and led to larger crystals. However, in other cases NaOH did not remain in the fluid but was incorporated into additional coarse crystalline phases. This paper describes the growth and crystal structures of accidentally synthesized compounds that formed only by the addition of NaOH.

### EXPERIMENTAL PROCEDURE

#### Crystal growth and identification

( $\text{CaO-ZnO-GeO}_2\text{-SiO}_2\text{-NaOH}$ ). The starting material was a polycrystalline powder of composition  $\text{Ca}_2\text{-ZnGe}_{1.5}\text{Si}_{0.5}\text{O}_7$ . The powder was prepared from homogenized mixtures of  $\text{Ca}(\text{OH})_2$ , ZnO,  $\text{SiO}_2$ , and  $\text{GeO}_2$ , which were dried and subsequently sintered at 1463 K. Portions thereof were used for conventional hydrothermal experiments in Au capsules at 973 K and 2 kbar using 30% NaOH solution as solvent. After four days the batch was found to contain equidimensional crystals with monoclinic morphology up to 0.3 mm in their maximum di-

mension and fine crystalline products that were not further analyzed. When single-crystal experiments described below indicated that a new phase (phase 1) had been synthesized, the hydrothermal experiments were repeated using a  $\text{SiO}_2$ -free starting product ( $\text{Ca}_2\text{ZnGe}_2\text{O}_7$ ) at 913 K and 2 kbar with the NaOH solvent. A phase with corresponding morphology and cell dimensions as obtained from the  $\text{SiO}_2$ -containing sample was analyzed. In addition to this phase, transparent, platy crystals with pronounced monoclinic morphology (phase 2) and fine crystalline products were observed.

An equidimensional transparent crystal of phase 1 with maximum dimensions between 0.10 and 0.15 mm was selected from the  $\text{SiO}_2$ -containing hydrothermal batch for space-group and cell-parameter determination using a precession camera ( $\text{MoK}\alpha$  X-radiation), yielding space group  $Cm$ ,  $C2$  or  $C2/m$  with  $a = 10.9$ ,  $b = 8.7$ ,  $c = 11.0$  Å,  $\beta = 97^\circ$ . A platy crystal  $0.3 \times 0.4 \times 0.1$  of phase 2 mm was selected. Surprisingly, precession photographs indicated orthorhombic symmetry with  $a = 7.2$ ,  $b = 5.6$ ,  $c = 5.3$  Å and space group  $Pmn2_1$ , despite monoclinic morphology. A subsequent search in the Inorganic Crystal Structure Database (Bergerhoff et al., 1983) for compounds with space group  $Pmn2_1$ , cell volumes between 200 and 220 Å<sup>3</sup>, and similar cell dimensions yielded the compound  $\text{Na}_2\text{CoGeO}_4$  (Wintenberger, 1970). A search for a corresponding Zn analogue was successful on the basis of space group  $Pn$  with  $a = 7.27$ ,  $b = 5.60$ ,  $c = 5.33$ ,  $\beta = 90.0^\circ$  (Kuz'min et al., 1968). The monoclinic space group  $Pn$  possesses the same systematic extinctions as  $Pmn2_1$ . Thus there is no doubt that phase 2 is  $\text{Na}_2\text{ZnGeO}_4$ .

TABLE 1. Cell dimensions of synthesized single crystals

Compound	$\theta$ range MoK $\alpha$	No. of reflec- tions	$a$ (Å)	$b$ (Å) $\beta^\circ$	$c$ (Å)
Ca <sub>5</sub> Ge <sub>2,23</sub> Si <sub>0,77</sub> O <sub>11</sub>	20–25	20	10.912(1)	8.695(2) 96.87(1)	11.000(1)
Ca <sub>3</sub> Ge <sub>3</sub> O <sub>11</sub>	7–11	12	10.935(2)	8.707(2) 96.86(2)	11.050(4)
Na <sub>2</sub> ZnGeO <sub>4</sub>	23–25	20	7.165(1)	5.574(1) 90.08(2)	5.323(2)
Na <sub>2</sub> Ca <sub>6</sub> Si <sub>4</sub> O <sub>15</sub>	16–23	24	5.525(1)	17.413(5) 90.57(1)	14.489(2)

TABLE 2. Data measurement and refined parameters

	Ca <sub>5</sub> Ge <sub>2,23</sub> Si <sub>0,77</sub> O <sub>11</sub>	Na <sub>2</sub> Ca <sub>6</sub> Si <sub>4</sub> O <sub>15</sub>
Space group	<i>C2/m</i>	<i>P2<sub>1</sub>/c</i>
Scan mode	$\omega$	$\omega$
$\theta$ limit in deg.	30	30
Absorption corr.	Empirical	Empirical
Extinction corr.	Applied	Applied
Accepted refl.	1229	2834
No. of variables	105	247
$R$ [%]	3.3	2.5
$R_w$ [%]	4.9	3.3

Note:  $R = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum |F_{\text{obs}}|}$   
 $R_w = \left( \frac{\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum w |F_{\text{obs}}|^2} \right)^{1/2}$

This compound formed because of the addition of NaOH as a solvent in the hydrothermal experiments. These relations also explain why no Ca<sub>7</sub>ZnGe<sub>2</sub>O<sub>7</sub> phase was formed under these conditions.

(CaO-FeO-MgO-SiO<sub>2</sub>-NaOH). Hydrothermal experiments with Ca(OH)<sub>2</sub>, MgO, SiO<sub>2</sub>, and Fe-oxalate corresponding to the bulk composition Ca<sub>2</sub>Fe<sub>0,8</sub>Mg<sub>0,2</sub>Si<sub>2</sub>O<sub>7</sub> were performed for 12 h at 973 K and 2 kbar with 30% NaOH solution as the solvent and  $f_{\text{O}_2}$  defined by the Fe-FeO buffer. The experimental products contained platy, colorless, transparent crystals (phase 3) up to 0.5 mm in their maximum dimensions embedded in fine crystalline powder. Precession photographs of the platy single crystals yielded monoclinic symmetry with cell parameters  $a = 5.25$ ,  $b = 17.41$ ,  $c = 14.50$  Å,  $\beta = 91^\circ$  and space group *P2<sub>1</sub>/c*. Cell dimensions and symmetry could not be attributed to a known phase. Six months after synthesis, the crystal, which was mounted on a glass fiber and stored at room temperature with about 40% humidity, had transformed to clusters of fine fibers.

All synthesized single crystals were transferred to an Enraf Nonius CAD4 single-crystal diffractometer (graphite-monochromated MoK $\alpha$  X-radiation) for refinement of cell dimensions (Table 1).

### Single-crystal data measurement

Single crystals of phase 1 [Ca<sub>5</sub>(GeSi)<sub>3</sub>O<sub>11</sub>] and phase 3 (Na<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub>) were selected for data measurement using a CAD4 diffractometer (graphite monochromated MoK $\alpha$  X-radiation). Experimental details pertaining to data collection and refinement are given in Table 2. An empirical absorption correction was applied using the  $\psi$ -scan technique. Data reduction, including background and Lorentz-polarization corrections, was carried out with the SDP program system (Enraf Nonius, 1983). The structures were solved by direct methods and subsequent Fourier analyses using the program SHELXS-86 (Sheldrick, 1986). The program SHELX76 (Sheldrick, 1976) was used for structure refinement. Neutral-atom scattering factors and real as well as imaginary anomalous dispersion corrections were used. Structure factors with a cutoff  $F_{\text{obs}} > 6 \sigma (F_{\text{obs}})$  were weighted by the factor  $1/\sigma^2$ .

## RESULTS

### Phase 1 [Ca<sub>5</sub>(Ge,Si)<sub>3</sub>O<sub>11</sub>]

The direct method solution and subsequent difference-Fourier maps indicated on the basis of peak heights and interatomic distances that this phase does not contain Zn. In the final refinement cycle, the scale factor, the isotropic extinction parameter, atomic positions, anisotropic displacement parameters for all atoms, and populations for the tetrahedral sites Ge1, Ge2, and Ge3, allowing for solid solution of Ge and Si, were refined. The refined composition of the crystal is Ca<sub>5</sub>(Ge<sub>2,23</sub>Si<sub>0,77</sub>)O<sub>11</sub>. The Ge/Si ratio in the original mixture was 3/1; thus the refined ratio 2.9/1 reflects the starting composition. Observed and calculated structure factors are listed in Table 3.<sup>1</sup> Final atomic coordinates and displacement parameters are given in Tables 4 and 5.

The new compound can be described as a mixed anion structure with Ge1 and Ge2 building (Ge,Si)<sub>2</sub>O<sub>7</sub> dimers and isolated (Ge,Si)<sub>4</sub> groups formed by Ge3. There are only slight differences in Ge site preference for the sites Ge1, Ge2, and Ge3. The lowest Ge concentration (69%) is found in the (Ge,Si)<sub>4</sub> tetrahedron. The Ge,Si distribution can also be derived from the mean tetrahedral distances. Ge1 and Ge2 have mean (Ge,Si)-O distances of 1.729 Å and 1.727 Å, respectively, whereas in Ge3 the (Ge,Si)-O distance is slightly shorter, with the value 1.717 Å. Ge1 and Ge2 are linked by O5 with a Ge1-O5-Ge2 angle of 130.3(3)°. Ca shows two types of sixfold coordination by O with mean Ca-O distances  $\langle d(\text{Ca-O}) \rangle$  between 2.40 and 2.43 Å. Ca1, Ca3, and Ca4 possess a trigonal prismatic coordination, whereas Ca2 has a trigonal antiprismatic environment that can also be described as a distorted octahedron. Individual interatomic distances and tetrahedral angles are given in Table 6. Figure 1 shows that cations are assembled in layers perpendicular to the  $b$  axis. The first sheet at  $y = 0$  is formed by all tetrahedra and Ca1, and the second by Ca2, Ca3, and

<sup>1</sup> To obtain a copy of Tables 3 and 7, order Document AM-90-437 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

**TABLE 4.** Final atomic coordinates and  $B_{\text{eq}}$  values for  $\text{Ca}_5(\text{Ge}_{2.23}\text{Si}_{0.77})\text{O}_{11}$ 

Atom	x	y	z	$B_{\text{eq}}$ [Å <sup>2</sup> ]
Ge1 0.73(1) Ge 0.27 Si	0.5606(1)	0	0.2709(1)	0.66(1)
Ge2 0.81(1) Ge 0.19 Si	-0.1894(1)	0	0.4631(1)	0.55(1)
Ge3 0.69(1) Ge 0.31 Si	-0.2053(1)	0	0.0177(1)	0.59(1)
Ca1	-0.0162(1)	0	0.2497(1)	1.14(3)
Ca2	0.2701(1)	0.1876(1)	0.2436(1)	0.91(2)
Ca3	0	0.2890(2)	0	1.48(3)
Ca4	1/2	0.1768(2)	1/2	1.75(2)
O1	0.4187(4)	0	0.3234(4)	0.92(8)
O2	-0.1464(3)	0.1540(4)	0.1035(3)	0.92(5)
O3	-0.1299(3)	0.1546(4)	0.3925(3)	0.87(5)
O4	-0.1430(5)	0	-0.1205(5)	1.19(8)
O5	0.6490(4)	0	0.4208(4)	0.96(8)
O6	0.1648(4)	0	0.3813(4)	1.07(9)
O7	-0.1406(5)	1/2	0.0267(6)	1.9(1)
O8	0.5889(3)	-0.1719(5)	0.2070(3)	1.86(7)

Note: Standard deviations in parentheses.  $B_{\text{eq}} = 8/3\pi^2 \sum_i (U_i a_i^* a_i^* a_i^*)$ .  $\sigma(B_{\text{eq}})$ : Schomaker and Marsh (1983).

**TABLE 6.** Interatomic distances [Å] and selected angles [°] for  $\text{Ca}_5(\text{Ge}_{2.23}\text{Si}_{0.77})\text{O}_{11}$ 

Ca1-O2	2.419(3)*	Ca2-O1	2.392(3)
-O3	2.506(4)*	-O2	2.332(4)
-O4	2.372(6)	-O3	2.308(3)
-O6	2.305(4)	-O4	2.443(3)
		-O6	2.587(4)
		-O8	2.318(4)
Ca3-O2	2.379(4)*	Ca4-O1	2.552(4)*
-O7	2.432(4)*	-O3	2.271(4)*
-O8	2.390(3)*	-O5	2.471(4)*
Ge1-O1	1.716(5)	O1-Ge1-O5	95.6(2)
-O5	1.808(4)	O1-Ge1-O8	110.9(1)*
-O8	1.696(4)*	O5-Ge1-O8	105.9(1)*
		O8-Ge1-O8	123.6(2)
Ge2-O3	1.718(4)*	O3-Ge2-O3	103.0(2)
-O5	1.769(4)	O3-Ge2-O5	107.4(1)*
-O6	1.701(5)	O3-Ge2-O6	115.6(1)*
		O5-Ge2-O6	107.3(2)
Ge3-O2	1.718(3)*	O4-Ge3-O7	103.1(3)
-O4	1.738(6)	O4-Ge3-O2	108.7(2)*
-O7	1.694(6)	O7-Ge3-O2	116.9(2)*
		O2-Ge3-O2	102.4(2)

Note: Standard deviations in parentheses.

\* Distances and angles occur twice.

Ca4 at  $y = 0.18-0.32$ . At  $y = 1/2$ , the first layer is repeated but shifted  $1/2$  along  $a$ .

### Phase 3 ( $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$ )

The solution by direct methods and subsequent difference-Fourier analyses indicated that this compound does not contain significant Mg or Fe, although these cations were present in the mixture used for synthesis. Of the eight available metal positions, each with distances of about 2.4 Å to neighboring O atoms, three sites showed significantly lower peak heights in difference-Fourier maps, presumably owing to the presence of Na. In addition, assumption of occupancy only by Ca on all eight sites would result in an excess of positive charge relative to the observed 15 O positions. Population factors were therefore refined for the three metal sites having low electron densities, allowing for Ca and Na. The population of one site (Na3) refined to 100% Na. The populations of

the other two sites (Na1 and Na2) refined to 37% and 68% Na, respectively, resulting in a total of 2.05(2) Na per formula unit. Thus the composition of the new compound is  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$ . At this stage of the refinement, two O sites associated with mixed (Na,Ca) positions displayed strongly anisotropic displacement parameters along  $a$ . To model this anisotropy, which seemed to be static (space-averaged owing to Na,Ca disorder) rather than dynamic (time-averaged) in nature, the sites O11 and O15 were split into two positions (O11a, O11b, and O15a, O15b, respectively), for which isotropic displacement parameters were refined. Observed and calculated structure factors are summarized in Table 7. Final atomic positions and displacement parameters are given in Tables 8 and 9.

The structure belongs to the group of mixed anion silicates comprising two individual tetrahedra (Si1 and Si2) and one  $\text{Si}_2\text{O}_7$  dimer formed by Si3 and Si4 (Fig. 2). The two insular tetrahedra are undistorted with fairly uniform

**TABLE 5.** Anisotropic displacement parameters for  $\text{Ca}_5(\text{Ge}_{2.23}\text{Si}_{0.77})\text{O}_{11}$ 

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ge1	0.0045(4)	0.0125(4)	0.0081(4)	0.00000	0.0001(3)	0.00000
Ge2	0.0094(4)	0.0059(4)	0.0068(4)	0.00000	-0.0009(3)	0.00000
Ge3	0.0044(4)	0.0079(4)	0.0083(4)	0.00000	-0.0002(2)	0.00000
Ca1	0.0060(6)	0.0292(8)	0.0077(6)	0.00000	-0.0008(4)	0.00000
Ca2	0.0092(4)	0.0073(4)	0.0167(5)	-0.0020(3)	-0.0043(3)	0.0010(3)
Ca3	0.0161(7)	0.0298(8)	0.0113(7)	0.00000	0.0050(5)	0.00000
Ca4	0.0212(7)	0.0208(7)	0.0233(8)	0.00000	-0.0023(6)	0.00000
O1	0.005(2)	0.016(2)	0.014(2)	0.00000	0.001(2)	0.00000
O2	0.010(1)	0.012(2)	0.012(2)	-0.002(1)	-0.001(1)	-0.002(1)
O3	0.011(1)	0.008(1)	0.014(2)	-0.002(1)	0.000(1)	0.003(1)
O4	0.017(2)	0.016(2)	0.014(2)	0.00000	0.007(2)	0.00000
O5	0.010(2)	0.018(2)	0.009(2)	0.00000	0.000(2)	0.00000
O6	0.004(2)	0.023(3)	0.012(2)	0.00000	-0.002(2)	0.00000
O7	0.013(2)	0.012(2)	0.050(4)	0.00000	0.007(2)	0.00000
O8	0.016(2)	0.032(2)	0.020(2)	0.011(2)	-0.008(1)	-0.012(2)

Note: Standard deviations in parentheses. The displacement parameters are of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

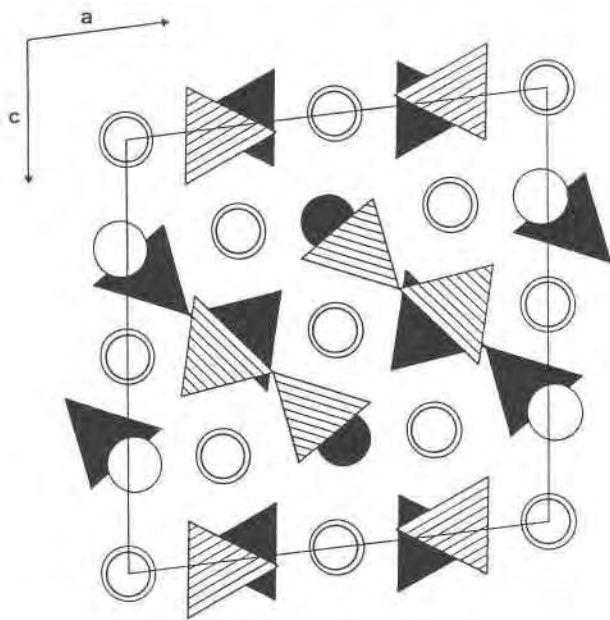


Fig. 1. Structure of  $\text{Ca}_5(\text{Ge,Si})_3\text{O}_{11}$  projected along the  $b$  axis. Circles represent Ca positions: open circles at  $y = 0, 1$ ; double circles at  $y = 0.18-0.32$ ; solid circles at  $y = 1/2$ . Hatched tetrahedra are at  $y = 0, 1$ ; solid tetrahedra at  $y = 1/2$ .

Si-O distances and O-Si-O angles (Table 10). The Si3 and Si4 tetrahedra forming the dimer are slightly more distorted; their longest Si-O distance is to the bridging O1. The Si3-O1-Si4 angle is  $130.4(1)$ . Pure Ca sites have very distorted coordinations with six or seven nearest neighbors. Two interpretations are possible for the coordination of Na1 (37% Na). If the site O15a is occupied, Na has six nearest neighbors with uneven distances ranging between 2.3 and 2.9 Å (Table 10). If the site O15b is occupied, the number of neighbors reduces to five with distances between 2.3 and 2.5 Å. Na2 (68% Na) is seven-coordinated with no significant difference in the mean (Ca,Na)-O distance, depending on whether O11a or O11b is occupied. Na3 (100% Na) has very distorted octahedral coordination.

## DISCUSSION

### $\text{Ca}_5(\text{Ge}_{2.23}\text{Si}_{0.77})\text{O}_{11}$

The following reaction is assumed for the formation of the observed coarse crystalline phases under hydrothermal conditions:  $5 \text{Ca}_2\text{Zn}(\text{Ge,Si})_2\text{O}_7 + 6 \text{NaOH} \rightarrow 3 \text{Na}_2\text{Zn}(\text{Ge,Si})\text{O}_4 + 3 \text{H}_2\text{O} + 2 \text{Ca}_5(\text{Ge,Si})_3\text{O}_{11} + \text{Zn}_2(\text{Ge,Si})\text{O}_3$ .  $\text{Ca}_5(\text{Ge,Si})_3\text{O}_{11}$  possesses stoichiometry analogous to  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ . The latter crystallizes in space group  $P\bar{6}$  and has attracted considerable interest because it is both ferroelectric and optically active (Newnham et al., 1973). In contrast,  $\text{Ca}_5(\text{Ge,Si})_3\text{O}_{11}$  has a centric structure, and thus no special physical effects can be expected. A similarity between both structures exists in the com-

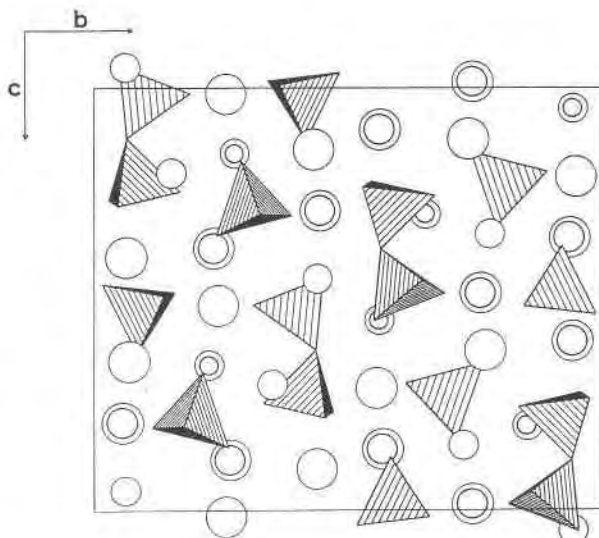


Fig. 2. Structure of  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$  projected along the  $a$  axis. Large circles represent Ca sites, small circles Na positions. Circles with double outlines are at  $x = 0.2-0.3$ , those with single outlines at  $x = 0.7-0.8$ . Tetrahedra are at corresponding heights.

mon occurrence of  $\text{GeO}_4$  and  $\text{Ge}_2\text{O}_7$  groups. Engel (1972) studied ganomalite-type compounds and described the compositions  $\text{Pb}_3\text{Ca}_2\text{Si}_3\text{O}_{11}$  and  $\text{Pb}_3\text{Ca}_2\text{Ge}_3\text{O}_{11}$  with the same structure as  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ . The limited substitution of two Pb by two Ca can be understood on the basis of available coordination polyhedra in the ganomalite structure. In  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ , Pb in two sites forms triangular  $\text{PbO}_3$  pyramids with Pb-O distances of 2.23 and 2.41 Å, respectively. The next nearest O neighbors have Pb-O  $\approx 3$  Å (Newnham et al., 1973). Thus these positions are highly unfavorable for cations like Ca.  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  possesses four additional crystallographically distinct Pb sites that are six-coordinated (three triangular prisms and one pentagonal pyramid).

Eulenberger et al. (1962) investigated compounds in the system  $\text{CaO-GeO}_2$  and established the existence of the following phases:  $\text{Ca}_3\text{GeO}_5$ ,  $\text{Ca}_2\text{GeO}_4$ ,  $\text{CaGeO}_3$ ,  $\text{CaGe}_2\text{O}_5$ , and  $\text{CaGe}_4\text{O}_9$ . Recent studies by Nishi and Takéuchi (1984, 1985) indicated that polytypes exist for the orthogermanate  $\text{Ca}_3\text{GeO}_5$  with two-, nine-, and 24-layer structures. An olivine and a  $\text{K}_2\text{NiF}_4$  type structure is observed for  $\text{Ca}_2\text{GeO}_4$  (Reid and Ringwood, 1970).  $\text{CaGeO}_3$  is known to transform from the wollastonite type structure through a garnet-like structure to the perovskite structure at more than 65 kbar and 1173 K (Sasaki et al., 1983).  $\text{CaGe}_2\text{O}_5$  is an orthogermanate with two modifications (Aust et al., 1976). A structure analogous to that of titanite has been described by Nevsky et al. (1979a). In addition, the structures of the compounds  $\text{Ca}_2\text{Ge}_4\text{O}_{16}$  (Nevsky et al., 1979b) with  $\text{GeO}_4$  insular tetrahedra and  $\text{Ge}_4\text{O}_{12}$  rings,  $\text{Ca}_3\text{Ge-chondrodite}$ ,  $\text{Ca}_3(\text{GeO}_4)_2(\text{OH})_2$  (Nevsky et al., 1978b), and  $\text{Ca}_4\text{Ge}_3\text{O}_{10} \cdot \text{H}_2\text{O}$  with  $\text{Ge}_3\text{O}_{10}$  trimers (Nevsky et al., 1978a) have been inves-

**TABLE 8.** Final atomic positional parameters and  $B_{\text{eq}}$  values for  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$

Atom	x	y	z	$B_{\text{eq}}$ [Å <sup>2</sup> ]
Na1 0.63(1)Ca 0.37 Na	0.7174(1)	0.43889(4)	0.4516(1)	1.23(1)
Na2 0.32(1)Ca 0.68 Na	0.2481(2)	0.2755(1)	0.1549(1)	1.50(2)
Na3	0.2274(2)	0.6503(1)	0.2985(1)	1.57(2)
Ca1	0.2446(1)	0.74221(3)	0.98536(4)	0.747(8)
Ca2	0.1948(1)	0.56255(3)	0.09917(4)	0.853(8)
Ca3	0.7049(1)	0.73337(3)	0.12063(4)	0.881(9)
Ca4	0.2888(1)	0.56823(4)	0.85372(3)	0.99(1)
Ca5	0.2538(1)	0.44438(3)	0.29060(4)	0.700(6)
Si1	0.7302(1)	0.59724(4)	0.98371(5)	0.50(1)
Si2	0.2044(1)	0.80792(4)	0.21690(5)	0.64(1)
Si3	0.7257(1)	0.57795(4)	0.2677(1)	0.50(1)
Si4	0.7812(1)	0.61555(4)	0.4710(1)	0.61(1)
O1	0.6865(3)	0.5639(1)	0.3805(1)	0.94(3)
O2	0.4700(3)	0.6346(1)	0.0073(1)	1.00(3)
O3	0.4800(3)	0.5464(1)	0.2202(1)	0.85(3)
O4	-0.0622(3)	0.6581(1)	0.0163(1)	1.04(3)
O5	0.2598(4)	0.4171(1)	0.1272(1)	1.17(4)
O6	0.0556(3)	0.8563(1)	0.9557(1)	1.22(3)
O7	0.2902(4)	0.7382(1)	0.1509(1)	1.30(3)
O8	-0.0437(3)	0.5287(1)	0.2342(1)	1.08(3)
O9	0.3571(4)	0.6132(1)	0.6975(1)	1.18(3)
O10	0.2245(3)	0.4832(1)	0.9643(1)	1.00(3)
O11a 0.52(5)O	0.217(3)	0.7118(3)	0.8282(3)	0.8(1)*
O11b 0.48(5)O	0.282(3)	0.7111(3)	0.8259(4)	0.9(1)*
O12	0.6014(4)	0.8128(1)	0.9865(2)	1.73(4)
O13	0.9175(3)	0.8248(1)	0.2009(1)	1.19(3)
O14	0.7703(4)	0.6680(1)	0.2539(1)	1.36(4)
O15a 0.38(4)O	0.199(3)	0.4506(3)	0.4493(4)	0.5(2)*
O15b 0.62(4)O	0.268(2)	0.4492(2)	0.4495(3)	1.1(1)*

Note: Anisotropic parameters used for other atoms for which the isotropic equivalent thermal parameters are listed, defined as  $B_{\text{eq}} = 8/3 \pi^2 \sum_i [U_{ij} a_i^* a_j^* a_i \cdot a_j]$ .  $\sigma(B_{\text{eq}})$ : Schomaker and Marsh (1983). Standard deviations in parentheses.

\*Isotropic temperature factor.

tigated. Thus the new structure of  $\text{Ca}_6\text{Ge}_3\text{O}_{11}$  is the only phase in the system  $\text{CaO-GeO}_2$  that is known to possess  $\text{Ge}_2\text{O}_7$  dimers.

$\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$

Under Fe-FeO buffered hydrothermal conditions (2 kbar, 973 K) the following hypothetical reaction is proposed for the formation of the new compound in the system  $\text{CaO-Na}_2\text{O-SiO}_2$ :  $3 \text{Ca}_2(\text{Mg,Fe})\text{Si}_2\text{O}_7 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15} + (\text{Mg,Fe})_2\text{SiO}_4 + (\text{Mg,Fe})\text{SiO}_3 + \text{H}_2\text{O}$ . That this structure has not been found before may be related to the instability of  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$  at room temperature with medium humidity.

A search for structurally characterized compounds in the system  $\text{Na}_2\text{O-CaO-SiO}_2$  with and without  $\text{H}_2\text{O}$  yielded a list of structures found in the Inorganic Crystal Structure Database in January, 1989 (Bergerhoff et al., 1983), which is given in Table 11. None of these structures displays  $\text{Si}_2\text{O}_7$  dimers. A search for the fragment  $\text{Si}_4\text{O}_{15}$  led to the structure of  $\text{Na}_2\text{Ba}_6[\text{Si}_2\text{O}_7][\text{SiO}_4]_2$  with space group  $P2_1/a$  (first setting),  $a = 11.528(4)$ ,  $b = 9.508(6)$ ,  $c = 7.856(2)$  Å,  $\gamma = 107.63(2)^\circ$  (Tamazyan et al., 1987), which shows stoichiometry analogous to our Na,Ca-silicate. Both structures have the  $\text{Si}_2\text{O}_7$  dimer, two  $\text{SiO}_4$  groups, and a sheetlike arrangement of Ba,Na or Ca,Na. However, based on the cell dimensions, the Ba and the Ca compound show no similarities. In  $\text{Na}_2\text{Ba}_6\text{Si}_4\text{O}_{15}$ , Ba occupies nine- and ten-coordinated O polyhedra with mean Ba-O distances of about 2.9 Å, and Na has fairly regular octahedral coordination with a mean Na-O distance of about 2.4 Å. Because of the distinct size difference between Na

**TABLE 9.** Anisotropic displacement parameters for  $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Na1	0.0216(4)	0.0115(4)	0.0135(4)	0.0015(3)	-0.0053(3)	0.0001(3)
Na2	0.0295(6)	0.0122(5)	0.0154(5)	0.0022(4)	0.0052(4)	0.0034(4)
Na3	0.0220(6)	0.0154(6)	0.0224(6)	0.0002(5)	0.0036(5)	-0.0061(5)
Ca1	0.0089(2)	0.0083(2)	0.0112(3)	0.0006(2)	0.0008(2)	0.0008(2)
Ca2	0.0098(2)	0.0146(3)	0.0080(2)	0.0004(2)	0.0001(2)	0.0026(2)
Ca3	0.0129(2)	0.0103(3)	0.0103(3)	0.0000(2)	0.0008(2)	0.0001(2)
Ca4	0.0155(3)	0.0122(3)	0.0099(3)	-0.0014(2)	-0.0003(2)	0.0024(2)
Ca5	0.0098(2)	0.0089(2)	0.0079(2)	0.0004(2)	0.0006(2)	0.0012(2)
Si1	0.0066(3)	0.0064(3)	0.0061(3)	0.0002(3)	0.0000(2)	0.0003(3)
Si2	0.0105(3)	0.0086(3)	0.0054(3)	0.0000(3)	0.0001(3)	-0.0006(3)
Si3	0.0066(3)	0.0063(3)	0.0060(3)	-0.0006(3)	0.0003(2)	0.0004(2)
Si4	0.0092(3)	0.0069(3)	0.0070(3)	0.0002(3)	0.0003(3)	-0.0007(3)
O1	0.017(1)	0.0128(9)	0.0057(9)	-0.0052(8)	0.0012(7)	-0.0010(7)
O2	0.0072(8)	0.0117(9)	0.019(1)	0.0032(7)	0.0037(8)	0.0016(8)
O3	0.0083(8)	0.0135(9)	0.0106(9)	-0.0018(7)	-0.0019(7)	0.0014(7)
O4	0.0097(9)	0.0125(9)	0.017(1)	-0.0029(7)	-0.0009(7)	-0.0038(8)
O5	0.024(1)	0.013(1)	0.0072(9)	0.0001(8)	0.0008(8)	-0.0007(7)
O6	0.013(1)	0.016(1)	0.018(1)	0.0042(8)	-0.0006(8)	0.0003(8)
O7	0.019(1)	0.018(1)	0.012(1)	0.0045(8)	0.0014(8)	-0.0055(8)
O8	0.0098(9)	0.019(1)	0.012(1)	0.0055(8)	0.0013(7)	0.0020(8)
O9	0.016(1)	0.016(1)	0.013(1)	0.0083(8)	0.0009(8)	-0.0004(8)
O10	0.0151(9)	0.0099(9)	0.013(1)	0.0018(8)	-0.0006(8)	0.0028(8)
O12	0.020(1)	0.021(1)	0.024(1)	-0.0112(9)	-0.0041(9)	0.0094(9)
O13	0.0113(9)	0.0110(9)	0.023(1)	0.0010(8)	-0.0011(8)	-0.0003(8)
O14	0.029(1)	0.0088(9)	0.014(1)	-0.0050(8)	-0.0019(9)	0.0021(8)

Note: Standard deviations in parentheses. The displacement parameters are of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

**TABLE 10.** Interatomic distances [Å] and selected angles [°] for Na<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub>

Na1-O1	2.413(2)	Na2-O2	2.699(3)	Na3-O3	2.566(2)
-O6	2.326(2)	-O4	2.915(2)	-O6	2.473(2)
-O9	2.375(2)	-O11a	2.59(1)	-O7	2.265(2)
-O15a	2.67(2)	-O11b	2.96(1)	-O8	2.743(2)
-O15b	3.05(1)	-O11a	2.97(2)	-O11a	2.440(6)
-O15a	2.420(4)	-O11b	2.62(2)	-O11b	2.466(6)
-O15b	2.49(1)	-O13	2.445(2)	-O14	2.605(3)
-O15a	2.87(2)	-O14	2.915(2)		
-O15b	2.443(6)				
Ca1-O2	2.270(2)	Ca2-O2	2.388(2)	Ca3-O2	2.701(2)
-O4	2.288(2)	-O3	2.362(2)	-O4	2.387(2)
-O6	2.283(2)	-O4	2.489(2)	-O7	2.339(2)
-O7	2.410(2)	-O5	2.589(2)	-O12	2.448(3)
-O11a	2.342(5)	-O8	2.441(2)	-O13	2.289(2)
-O11b	2.385(6)	-O10	2.609(2)	-O14	2.268(2)
-O12	2.323(2)	-O10	2.400(2)		
Ca4-O2	2.692(2)	Ca5-O3	2.405(2)		
-O3	2.605(2)	-O5	2.415(2)		
-O5	2.520(2)	-O8	2.345(2)		
-O8	2.504(2)	-O9	2.377(2)		
-O9	2.428(2)	-O13	2.291(2)		
-O10	2.213(2)	-O15a	2.325(6)		
-O11a	2.558(6)	-O15b	2.304(4)		
-O11b	2.521(5)				
Si1-O2	1.618(2)	O4-Si1-O5	110.8(1)	O5-Si1-O10	108.8(1)
-O4	1.629(2)	O4-Si1-O2	107.5(1)	O2-Si1-O10	112.7(1)
-O5	1.628(2)	O4-Si1-O10	109.0(1)		
-O10	1.608(2)	O5-Si1-O2	108.0(1)		
Si2-O7	1.619(2)	O7-Si2-O9	111.9(1)	O9-Si2-O11b	101.6(6)
-O9	1.638(2)	O7-Si2-O11a	114.3(3)	O9-Si2-O13	109.1(1)
-O11a	1.650(4)	O7-Si2-O11b	109.7(3)	O13-Si2-O11a	102.0(5)
-O11b	1.666(6)	O7-Si2-O13	110.0(1)	O13-Si2-O11b	114.4(6)
-O13	1.627(2)	O9-Si2-O11a	109.0(3)		
Si3-O1	1.669(2)	O1-Si3-O3	104.6(1)	O3-Si3-O14	114.2(1)
-O3	1.612(2)	O1-Si3-O14	106.7(1)	O8-Si3-O14	111.1(1)
-O8	1.614(2)	O1-Si3-O8	109.1(1)		
-O14	1.601(2)	O3-Si3-O8	110.8(1)		
Si4-O1	1.669(2)	O1-Si4-O12	109.7(1)	O12-Si4-O15a	119.0(5)
-O6	1.661(2)	O1-Si4-O6	110.1(1)	O12-Si4-O15b	109.2(4)
-O12	1.613(2)	O1-Si4-O15a	101.2(3)	O6-Si4-O15a	104.8(2)
-O15a	1.633(6)	O1-Si4-O15b	97.5(2)	O6-Si4-O15b	118.0(5)
-O15b	1.636(5)	O6-Si4-O12	111.4(1)		

Note: Standard deviations in parentheses.

and Ba, both cations occupy separate positions, whereas in Na<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub>, Na and Ca share two sites. The differences in size and shape of Ca and Ba coordination polyhedra lead to different arrangements in both structures.

**TABLE 11.** Crystal structures in the system CaO-Na<sub>2</sub>O-SiO<sub>2</sub>-(H<sub>2</sub>O)

Space group	Composition	SiO <sub>4</sub> units	Reference
<i>P2<sub>1</sub>3</i>	Na <sub>2</sub> CaSiO <sub>4</sub>	insular	Barth and Posnjak, 1932
<i>C2/c</i>	Na <sub>2</sub> Ca <sub>2</sub> Si <sub>2</sub> O <sub>10</sub>	trimers	Treushnikov et al., 1971
			Kuznetsova et al., 1980
<i>P3<sub>1</sub>21</i>	Na <sub>4</sub> Ca <sub>4</sub> Si <sub>6</sub> O <sub>18</sub>	cyclo-6	Fischer and Tillmanns, 1987
			Ohsato et al., 1986
<i>R3̄m</i>	Na <sub>4</sub> Ca <sub>4</sub> Si <sub>6</sub> O <sub>18</sub>	cyclo-6	Fischer and Tillmanns, 1987
<i>R3̄m</i>	Na <sub>4</sub> Ca <sub>2</sub> Si <sub>6</sub> O <sub>18</sub>	cyclo-6	Ohsato et al., 1985
<i>Pa3̄</i>	Na <sub>4</sub> CaSi <sub>6</sub> O <sub>18</sub>	cyclo-12	Fischer and Tillmanns, 1984
<i>P1̄</i>	Na <sub>2</sub> Ca <sub>2</sub> Si <sub>6</sub> O <sub>18</sub>	chains	Ihara et al., 1984
<i>C222<sub>1</sub></i>	NaCaHSiO <sub>4</sub>	insular	Lyutin et al., 1972
<i>P2<sub>1</sub>/m</i>		insular	Kazak et al., 1974
<i>P2<sub>1</sub></i>		insular	Cooksley and Taylor, 1974
<i>P1̄</i>	NaCa <sub>2</sub> HSi <sub>3</sub> O <sub>9</sub>	chains	Prewitt, 1967

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