

## Trigonal sodium calcium germanate, $\text{Na}_{2.54}\text{Ca}_{1.73}\text{Ge}_3\text{O}_9$

Fumito Nishi

Saitama Institute of Technology, Fusaiji 1690, Okabe, Ohsato-gun, Saitama  
369-0293, Japan

Correspondence e-mail: nishi@sit.ac.jp

Received 17 May 2001

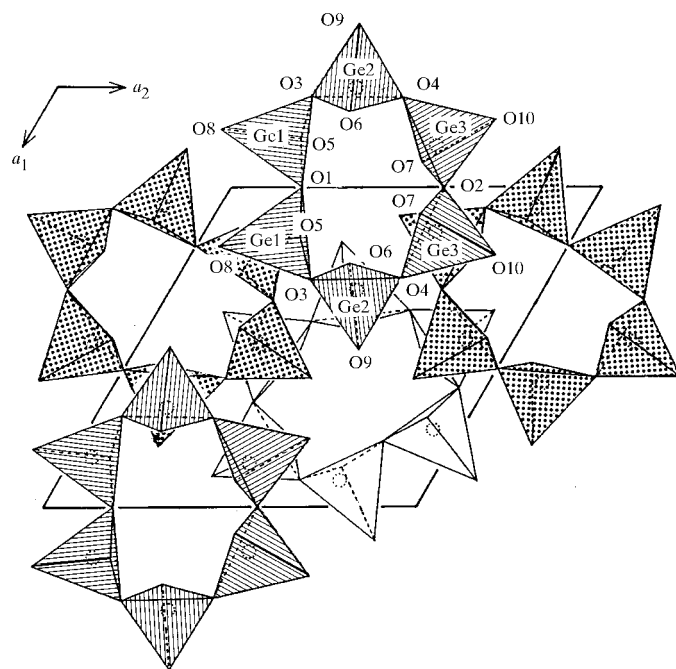
Accepted 2 August 2001

Single crystals of a new germanate,  $\text{Na}_{2.54}\text{Ca}_{1.73}\text{Ge}_3\text{O}_9$ , have been synthesized. The structure has a six-membered ring of  $\text{GeO}_4$  tetrahedra, which is similar to the rings of the silicate analogue  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ , and both structures contain pseudo-cubic subcells with an edge length of 3.8 Å. The details of the two compounds are slightly different, however. For example, two O atoms are statistically distributed about twofold axes in the title compound, while the silicate analogue has no such O-atom distributions. In addition, the title germanate has an extra partially populated metal site containing 54 (4)% Na, with no equivalent site in the silicate analogue.

### Comment

In the ternary system  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ , Koppen & Padurow (1958) identified the compound  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  as having a rhombohedral lattice ( $a = 7.41$  Å and  $\alpha = 89.7^\circ$ ) by means of Debye-Scherrer photography. Glasser & Mileson (1968) studied the same compound by means of a Weissenberg method and found that its structure had a trigonal space group, *i.e.*  $P3_121$  or  $P3_221$ . Maki & Sugimura (1968) studied solid solutions of the  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$  system and found a clear phase boundary between the compounds  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  (low-temperature modification) and  $\text{Na}_2\text{CaSi}_2\text{O}_6$  (high-temperature modification). Their results were confirmed by Moir & Glasser (1974). The crystal structures of two minerals, both having a composition close to  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ , were studied by Fischer & Tillmanns (1983). One was combeite from Zaire, with the space group  $R\bar{3}m$ , and the other was an unknown mineral from Eifel, with the space group  $P3_1$  or  $P3_2$ . They thought that this compound had two modifications, with the former probably corresponding to the quenched high-temperature modification and the latter corresponding to the low-temperature phase of Maki & Sugimura (1968). Single crystals of  $\text{Na}_2\text{CaSi}_2\text{O}_6$  (high-temperature modification) and  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  (low-temperature modification) were synthesized and studied in detail by Ohsato *et al.* in 1985 and 1986, respectively. These authors reported some interesting structural characteristics, such as disorder of the Na and Ca atoms, and splitting of the O and metal atoms.

The silicates and their germanate analogues are being investigated in our laboratory in order to find the common rules and principles among these compounds. The  $\text{Na}_2\text{O}-\text{CaO}-\text{GeO}_2$  system has been studied and three different types of single crystal have been synthesized. The first was  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$ , which has a 12-membered ring (Nishi & Takéuchi, 1988), while the second was  $\text{Na}_2\text{CaGe}_2\text{O}_6$ , which has a six-membered ring (Nishi & Takéuchi, 1990) analogous to  $\text{Na}_2\text{CaSi}_2\text{O}_6$  (high-temperature modification; Ohsato *et al.*, 1985). The crystal structure of the third compound,  $\text{Na}_{2.54}\text{Ca}_{1.73}\text{Ge}_3\text{O}_9$ , corresponding to  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  (low-temperature modification; Ohsato *et al.*, 1986), is the subject of the present paper.



**Figure 1**

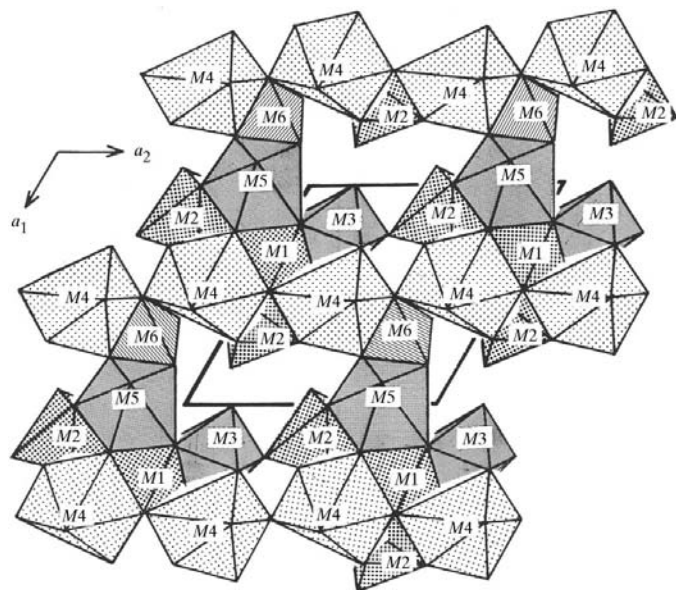
The arrangement of six-membered rings in the unit cell. The hatched tetrahedra are at  $z \approx \frac{2}{6}$ , the dotted tetrahedra at  $z \approx \frac{5}{6}$  and those without patterns at  $z \approx \frac{3}{6}$ . Atoms O1 and O2 are drawn at the average positions of each split half.

After the least-squares refinement, two O atoms (O1 and O2), which were located on twofold axes, showed abnormal atomic displacement parameters. In addition, the bond lengths between Ge and these O atoms were abnormal. Consequently, atoms O1 and O2 were assigned to general positions and split into two components about their twofold axes, with each component separated by 0.87 (2) and 0.93 (2) Å for O1 and O2, respectively.

The trigonal unit cell basically includes pseudo-cubic subcells with an edge length of 3.8 Å, similar to related compounds, such as  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$  (Nishi & Takeuchi, 1988),  $\text{Na}_2\text{CaGe}_2\text{O}_6$  (Nishi & Takéuchi, 1990), and the silicate analogues  $\text{Na}_2\text{CaSi}_2\text{O}_6$  (Ohsato *et al.*, 1985) and  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  (Ohsato *et al.*, 1986).

The six-membered ring of the title germanate, which is very similar to that of the silicate analogue  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  (Ohsato *et al.*, 1986), is a little deformed in comparison with the regular six-membered ring of  $\text{Na}_2\text{CaGe}_2\text{O}_6$  (Nishi & Takéuchi, 1990) and the silicate analogue  $\text{Na}_2\text{CaSi}_2\text{O}_6$  (Ohsato *et al.*, 1985). The arrangement of the six-membered rings is shown in Fig. 1.

The refined site occupancies of the disordered Na and Ca atoms over the sites  $M1$ – $M6$  are as follows:  $M1 = 0.56$  (2) Na +  $0.44$  (2) Ca,  $M2 = 0.93$  (2) Na +  $0.07$  (2) Ca,  $M3 = 0.54$  (4) Na,  $M4 = 0.72$  (2) Na +  $0.28$  (2) Ca,  $M5 = 0.12$  (4) Na +  $0.88$  (4) Ca and  $M6 = \text{Ca}$ . Thus, it can be seen that the site occupancies of the Na atoms range from 0% (site  $M6$ ) to 93 (2)% (site  $M2$ ). Judging from the average  $M$ –O distances for each  $M$  polyhedron (Table 1), we can conclude that the greater the Na-atom population of a given  $M$  site, the larger is the average value of the  $M$ –O distances involving that site. The average value of the  $M3$ –O distances is abnormally large, on account of the  $M3$  site vacancy [46 (4)%]. The  $M3$  site itself constitutes the fundamental difference between this germanate and the silicate analogue  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  (Ohsato *et al.*, 1986); the former has Na atoms with an occupancy of 54 (4)% in this site, but there is no equivalent populated site in the latter.



**Figure 2**  
The arrangement of polyhedra about the cation sites.  $M1$  polyhedra are at  $z \approx 0.09$ ,  $M2$  at  $z \approx 0.0$ ,  $M3$  at  $z = 0$ ,  $M4$  at  $z \approx 0.16$ ,  $M5$  at  $z = \frac{1}{6}$  and  $M6$  at  $z = 0$ . Atoms O1 and O2 are drawn as in Fig. 1. The refined site occupancies are given in the text.

The total numbers of Na and Ca atoms for the title germanate and  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$  (Ohsato *et al.*, 1986) are 4.27 (*i.e.*  $2.54 + 1.73$ ) and 4 (*i.e.*  $2 + 2$ ). Accordingly, this germanate requires extra sites to accommodate the excess Na atoms. The new  $M3$  site, located at one of the vertices of the pseudo-cubic subcells, plays precisely this role. In Fig. 2, the  $M1$ – $M6$  polyhedra are shown.

**Experimental**

Single crystals of sodium calcium germanate were synthesized from a mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and  $\text{GeO}_2$  at 1500 K. Electron microprobe analyses of the crystals showed the chemical formula to be  $\text{Na}_{2.54}\text{Ca}_{1.73}\text{Ge}_3\text{O}_9$ . The intensities of the reflections were measured at the X-ray laboratory of Nihon University, Japan.

*Crystal data*

$\text{Na}_{2.54}\text{Ca}_{1.73}\text{Ge}_3\text{O}_9$   
 $M_r = 489.5$   
Trigonal,  $P3_121$   
 $a = 10.780$  (2) Å  
 $c = 13.449$  (2) Å  
 $V = 1353.5$  (3) Å<sup>3</sup>  
 $Z = 6$   
 $D_x = 3.60$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 20 reflections  
 $\theta = 10.5$ – $20.5^\circ$   
 $\mu = 11.07$  mm<sup>-1</sup>  
 $T = 293$  K  
Sphere, colourless  
Radius: 0.14 mm

**Table 1**

Selected geometric parameters (Å, °).

$M1-O6^i$	2.31 (1)	$M4-O9^{ix}$	2.900 (9)
$M1-O5$	2.38 (1)	$M5-O5^{vii}$	2.27 (1)
$M1-O7$	2.39 (1)	$M5-O5^{ii}$	2.27 (1)
$M1-O9^{ii}$	2.41 (1)	$M5-O8^{xi}$	2.386 (8)
$M1-O8^{iii}$	2.520 (8)	$M5-O8^{xii}$	2.386 (8)
$M1-O10^{iv}$	2.73 (1)	$M5-O10$	2.52 (1)
$M2-O5$	2.41 (1)	$M5-O10^{xiii}$	2.52 (1)
$M2-O7^v$	2.39 (1)	$M5-O2$	2.92 (2)
$M2-O4$	2.60 (2)	$M5-O2^{xiii}$	2.92 (2)
$M2-O3$	2.64 (2)	$M6-O10^{iv}$	2.274 (9)
$M2-O2^{iv}$	2.24 (1)	$M6-O10^{xiv}$	2.274 (9)
$M2-O2^v$	3.16 (2)	$M6-O9^{ix}$	2.30 (1)
$M2-O6^{vi}$	2.915 (8)	$M6-O9^{ii}$	2.30 (1)
$M2-O4^{iv}$	2.85 (1)	$M6-O8^{iii}$	2.412 (8)
$M2-O7$	3.09 (2)	$M6-O8^x$	2.412 (8)
$M3-O6^{vii}$	2.44 (1)	Ge1–O8	1.721 (13)
$M3-O6^{viii}$	2.44 (1)	Ge1–O5	1.727 (11)
$M3-O1^{ix}$	2.57 (1)	Ge1–O3	1.725 (15)
$M3-O1^{ii}$	2.57 (1)	Ge1–O1	1.833 (16)
$M3-O3^{ix}$	2.79 (2)	Ge1–O1 <sup>xiii</sup>	1.719 (18)
$M3-O3^{ii}$	2.79 (2)	Ge2–O9	1.728 (10)
$M3-O8^{ix}$	3.115 (9)	Ge2–O6 <sup>xv</sup>	1.711 (10)
$M3-O8^{ii}$	3.115 (9)	Ge2–O3	1.734 (19)
$M4-O6$	2.33 (1)	Ge2–O4	1.762 (13)
$M4-O7^{iv}$	2.37 (1)	Ge3–O7	1.646 (10)
$M4-O4^{ix}$	2.43 (1)	Ge3–O2	1.809 (15)
$M4-O3^x$	2.51 (2)	Ge3–O2 <sup>xiii</sup>	1.694 (17)
$M4-O9^x$	2.70 (1)	Ge3–O10	1.729 (10)
$M4-O10^{ix}$	2.821 (8)	Ge3–O4	1.736 (13)
O1–Ge1–O1 <sup>xiii</sup>	28.0 (14)	O6 <sup>xv</sup> –Ge2–O3	105.5 (6)
O8–Ge1–O5	119.5 (6)	O6 <sup>xv</sup> –Ge2–O4	119.7 (6)
O8–Ge1–O3	107.9 (9)	O3–Ge2–O4	103.5 (8)
O8–Ge1–O1	108.4 (8)	O2–Ge3–O2 <sup>xiii</sup>	30.6 (12)
O8–Ge1–O1 <sup>xiii</sup>	116.7 (5)	O7–Ge3–O2	114.6 (6)
O5–Ge1–O3	100.9 (6)	O7–Ge3–O2 <sup>xiii</sup>	85.4 (5)
O5–Ge1–O1	122.9 (8)	O7–Ge3–O10	118.8 (5)
O5–Ge1–O1 <sup>xiii</sup>	98.9 (6)	O7–Ge3–O4	120.7 (7)
O3–Ge1–O1	91.4 (8)	O2–Ge3–O10	98.5 (7)
O3–Ge1–O1 <sup>xiii</sup>	111.7 (8)	O2 <sup>xiii</sup> –Ge3–O10	106.8 (5)
O9–Ge2–O6 <sup>xv</sup>	123.2 (6)	O2–Ge3–O4	95.1 (8)
O9–Ge2–O3	101.3 (7)	O2 <sup>xiii</sup> –Ge3–O4	119.7 (6)
O9–Ge2–O4	100.6 (5)	O4–Ge3–O10	104.5 (5)

Symmetry codes: (i)  $x - y, -y, \frac{2}{3} - z$ ; (ii)  $1 - x, y - x, \frac{4}{3} - z$ ; (iii)  $y - x, -x, z - \frac{1}{3}$ ; (iv)  $1 + y - x, 1 - x, z - \frac{1}{3}$ ; (v)  $1 - x, 1 + y - x, \frac{4}{3} - z$ ; (vi)  $1 + y - x, 1 - x, \frac{2}{3} + z$ ; (vii)  $1 - y, x - y, \frac{1}{3} + z$ ; (viii)  $1 - x, y - x, \frac{1}{3} - z$ ; (ix)  $1 - y, x - y, z - \frac{2}{3}$ ; (x)  $y, x, 1 - z$ ; (xi)  $1 + x, y, z$ ; (xii)  $1 + x - y, -y, \frac{2}{3} - z$ ; (xiii)  $x - y, -y, \frac{2}{3} - z$ ; (xiv)  $y, x - 1, 1 - z$ ; (xv)  $x, y, 1 + z$ .

*Data collection*

Rigaku AFC-5 diffractometer	2142 reflections with $I > 3\sigma(I)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.063$
Absorption correction: spherical	$\theta_{\text{max}} = 40^\circ$
( <i>International Tables for X-ray Crystallography</i> , 1959, Vol. 2, Table 5.3.6B)	$h = -16 \rightarrow 16$
$T_{\text{min}} = 0.114$ , $T_{\text{max}} = 0.158$	$k = 0 \rightarrow 19$
4377 measured reflections	$l = 0 \rightarrow 24$
3108 independent reflections	3 standard reflections every 150 reflections
	intensity decay: 1.1%

*Refinement*

Refinement on $F$	$(\Delta/\sigma)_{\text{max}} = 0.04$
$R = 0.062$	$\Delta\rho_{\text{max}} = 1.1 \text{ e } \text{\AA}^{-3}$
$wR = 0.068$	$\Delta\rho_{\text{min}} = -0.1 \text{ e } \text{\AA}^{-3}$
$S = 1.34$	Extinction correction: isotropic (Zachariasen, 1963)
2142 reflections	Extinction coefficient: $5.0(2) \times 10^{-5}$
117 parameters	
$w = 1/[\sigma^2(F) + 0.0001F^2]$	

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *ORFFE* (Busing *et al.*, 1964); program(s) used to refine

structure: *LINUS* (Coppens & Hamilton, 1970); molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1014). Services for accessing these data are described at the back of the journal.

## References

- Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.
- Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- Fischer, R. X. & Tillmanns, E. (1983). *Neues Jahrb. Mineral. Monatsh.* **2**, 49–59.
- Glasser, L. S. D. & Miles, J. S. (1968). *J. Am. Ceram. Soc.* **51**, 55–57.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Koppen, N. & Padurow, N. N. (1958). *Naturwissenschaften*, **45**, 622–625.
- Maki, I. & Sugimura, T. (1968). *Yogyo Kyokai Shi*, **76**, 144–148. (In Japanese.)
- Moir, G. K. & Glasser, F. P. (1974). *Phys. Chem. Glasses*, **15**, 6–11.
- Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software* and *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nishi, F. & Takeuchi, Y. (1988). *Acta Cryst.* **C44**, 1867–1869.
- Nishi, F. & Takeuchi, Y. (1990). *Acta Cryst.* **C46**, 544–546.
- Ohsato, H., Maki, I. & Takeuchi, Y. (1985). *Acta Cryst.* **C41**, 1575–1577.
- Ohsato, H., Takeuchi, Y. & Maki, I. (1986). *Acta Cryst.* **C42**, 934–937.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.