

## Cubic Structure of Sodium Calcium Germanate $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$

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**Abstract.**  $M_r = 492.9$ , cubic,  $Pa3$ ,  $a = 15.626(3) \text{ \AA}$ ,  $V = 3815.4 \text{ \AA}^3$ ,  $Z = 16$ ,  $D_x = 3.43 \text{ g cm}^{-3}$ ,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 106.8 \text{ cm}^{-1}$ ,  $F(000) = 3707.2$ ,  $T = 298 \text{ K}$ ,  $R = 0.059$ ,  $wR = 0.064$  for 1238 observed reflections. The structure of  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$ , which was found in a flux melt, is characterized by having a 12-membered ring of  $\text{GeO}_4$  tetrahedra and contains pseudocubic subcells with an edge length of  $3.9 \text{ \AA}$ . The ring is more corrugated than those of  $\text{K}_4\text{SrGe}_3\text{O}_9$  and the silicate analogue  $\text{Na}_4\text{CaSi}_3\text{O}_9$ , mainly owing to the difference in effective charge of the cations located around the centres of the rings. The trend is observed that the Ge–O bond length shortens with increase of Ge–O–Ge bond angle, giving in a Ge–O versus Ge–O–Ge diagram a slope which is much steeper than those for the silicate and aluminate tetrahedra.

**Introduction.** Silicates and their germanate analogues are not necessarily isotypic. Thus, for example, tricalcium germanates exhibit various polytypic structures which are not found for the silicate analogues (Nishi & Takéuchi, 1985; Takéuchi & Nishi, 1986). Even in isotypic cases, details of the configurational features of the anionic radicals or polyhedra about cations may differ significantly, mainly owing to the difference in size between Si and Ge.

As part of a project studying germanate analogues of silicates, we have succeeded in synthesizing single crystals of three new phases of sodium calcium germanates:  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$ ,  $\text{Na}_{3.0}\text{Ca}_{1.5}\text{Ge}_3\text{O}_9$  and  $\text{Na}_{2.50}\text{Ca}_{1.75}\text{Ge}_3\text{O}_9$  (Nishi & Takéuchi, 1987). The present paper reports the crystal structure of  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$  which has 12-membered rings of  $\text{GeO}_4$  tetrahedra; these are compared with those in  $\text{K}_4\text{SrGe}_3\text{O}_9$  (Baumgartner & Völlenkne, 1977) and the silicate analogue  $\text{Na}_4\text{CaSi}_3\text{O}_9$  (Fischer & Tillmanns, 1984).

**Experimental.** Single crystals of Na Ca germanates were synthesized from  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and  $\text{GeO}_2$  mixtures at 1500 K. Crystals showing cubic symmetry were found in the products. According to the result of

the present structure analysis, the estimated chemical composition is  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$ . The crystal was ground to a sphere with diameter  $0.16 \text{ mm}$ . The cell dimensions were obtained by least-squares refinement of  $\sin(2\theta)$  for 15 reflections in the range  $26^\circ \leq 2\theta \leq 33^\circ$ . A Syntex  $P2_1$  single-crystal diffractometer was used for intensity measurement;  $\omega$ – $2\theta$  scan, graphite-monochromatized  $\text{Mo } K\alpha$  radiation. Among the 1690 reflections collected up to  $2\theta = 70^\circ$ , 1238 reflections with  $F_o > 4\sigma(|F_o|)$  were used for the refinement. The index ranges are  $0 \leq h \leq 17$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 24$  and  $hkl$  reflections revealed the crystal to have space group  $Pa3$  ( $k = 2n$  for  $0kl$ ,  $l = 2n$  for  $h0l$  and  $h = 2n$  for  $hk0$ ). Three standard reflections ( $hkl$ ; 440, 404 and 044), intensity variation 3.0% (of  $I$  value); Lorentz, polarization and absorption corrections (transmission coefficients: max. 0.38, min. 0.32). Ordinary anisotropic refinement was used;  $\sum w(\Delta F)^2$  minimized,  $R = 0.059$ ,  $wR = 0.064$ ,  $w = 1/\sigma^2(|F_o|)$ ,  $S = 1.1$ , mean  $(\Delta/\sigma) < 0.1$ , isotropic extinction correction applied [ $g_{\text{iso}} = 0.48(3) \times 10^{-4}$ ], max., min. height in final  $\Delta\rho$  map 1.2,  $-0.8 \text{ e \AA}^{-3}$ , neutral scattering factors with correction for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974). The calculations were performed on a HITAC M280H computer of the University of Tokyo with the use of the least-squares program *LINUS* (Coppens & Hamilton, 1970).

**Discussion.** The final atomic parameters are given in Table 1.\* Ge–O and Ca–O bond lengths are given in Table 2. The basic structure is similar to those of  $\text{K}_4\text{SrGe}_3\text{O}_9$  and  $\text{Na}_4\text{CaSi}_3\text{O}_9$  (Baumgartner & Völlenkne, 1977; Fischer & Tillmanns, 1984); *i.e.* their structures consist of 64 subcells each having the shape of a cube with edge length  $3.9 \text{ \AA}$ . The Ge (or Si) atoms

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51131 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters for  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$  (values of positional parameters are multiplied by  $10^4$ )
$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

| Occupancy | x                        | y            | z            | $B_{\text{eq}}(\text{\AA}^2)$ |      |
|-----------|--------------------------|--------------|--------------|-------------------------------|------|
| Ge(1)     | 1-0                      | 4822.5 (8)   | 2092.5 (8)   | 2310.5 (7)                    | 0.75 |
| Ge(2)     | 1-0                      | 4713.4 (7)   | 56.0 (7)     | 2470.4 (8)                    | 0.64 |
| M(1)      | 0.92 (2) Ca, 0.08 (2) Na | 1182.6 (1.4) | 1182.6 (1.4) | 1182.6 (1.4)                  | 1.00 |
| M(2)      | 0.85 (2) Ca, 0.15 (2) Na | 3599.1 (1.5) | 3599.1 (1.5) | 3599.1 (1.5)                  | 0.96 |
| M(3)      | 0.22 (2) Ca, 0.78 (2) Na | 2410 (3)     | 2410 (3)     | 2410 (3)                      | 2.51 |
| M(4)      | 1-0 Na                   | 0            | 0            | 0                             | 1.30 |
| M(5)      | 0.41 (3) Na, 0.59 vacant | 5000         | 5000         | 5000                          | 0.78 |
| M(6)      | 0.10 (1) Ca, 0.90 (1) Na | 3950 (4)     | 1345 (5)     | 4002 (4)                      | 3.13 |
| M(7)      | 1-0 Na                   | 893 (6)      | 3455 (5)     | 1342 (5)                      | 3.90 |
| O(1)      |                          | 2304 (6)     | 2905 (6)     | 3918 (6)                      | 1.37 |
| O(2)      |                          | 3156 (8)     | 4834 (7)     | 4308 (7)                      | 2.36 |
| O(3)      |                          | 1033 (5)     | 1864 (5)     | 4752 (7)                      | 1.37 |
| O(4)      |                          | 794 (6)      | 2110 (6)     | 2193 (7)                      | 1.71 |
| O(5)      |                          | 113 (6)      | 207 (6)      | 1518 (6)                      | 1.75 |
| O(6)      |                          | 2716 (6)     | 1358 (5)     | 4775 (7)                      | 1.83 |

Table 2. Ge—O and Ca—O bond lengths ( $\text{\AA}$ ) for  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$ 

|   |            |  |            |
|---|------------|--|------------|
| Ge(1)—O(4 <sup>h</sup> )                                  | 1.713 (9)  | M(4)—O(5 <sup>h</sup> , 5 <sup>i</sup> , 5 <sup>ii</sup> , 5 <sup>iii</sup> )                                | 2.400 (9)  |
| O(1 <sup>h</sup> )  | 1.724 (9)  | M(5)—O(2 <sup>h</sup> , 2 <sup>i</sup> , 2 <sup>ii</sup> , 2 <sup>iii</sup> )                                | 3.089 (12) |
| O(6 <sup>h</sup> )  | 1.780 (9)  | O(3 <sup>h</sup> , 3 <sup>ii</sup> , 3 <sup>iii</sup> , 3 <sup>iv</sup> , 3 <sup>v</sup> , 3 <sup>vi</sup> ) | 3.353 (9)  |
| O(3 <sup>h</sup> )  | 1.800 (8)  |  | Ave. 3.221 |
| Ave. 1.754  |            |  |            |
| Ge(2)—O(2 <sup>h</sup> )                                  | 1.680 (11) | M(6)—O(6)  | 2.275 (12) |
| O(5 <sup>h</sup> )  | 1.716 (9)  | O(1 <sup>h</sup> )   | 2.278 (11) |
| O(6 <sup>h</sup> )  | 1.773 (9)  | O(5 <sup>h</sup> , <sup>ii</sup> )   | 2.418 (12) |
| O(3 <sup>h</sup> )  | 1.798 (9)  | O(5 <sup>h</sup> )   | 2.669 (12) |
| Ave. 1.742  |            | O(5 <sup>h</sup> , <sup>iii</sup> )  | 3.044 (12) |
|   |            | O(2 <sup>h</sup> )   | 3.164 (14) |
| M(1)—O(4 <sup>h</sup> , 4 <sup>i</sup> , 4 <sup>j</sup> ) | 2.317 (10) | O(6 <sup>h</sup> )   | 3.207 (13) |
| O(5 <sup>h</sup> , 5 <sup>i</sup> , 5 <sup>j</sup> )      | 2.322 (10) |  | Ave. 2.722 |
| Ave. 2.320  |            |  |            |
| M(2)—O(2 <sup>h</sup> , 2 <sup>i</sup> )                  | 2.330 (11) | M(7)—O(2 <sup>h</sup> )  | 2.265 (14) |
| O(1 <sup>h</sup> , 1 <sup>i</sup> , 1 <sup>j</sup> )      | 2.349 (9)  | O(4)   | 2.379 (13) |
| Ave. 2.340  |            | O(3 <sup>h</sup> )   | 2.543 (13) |
|   |            | O(3 <sup>h</sup> )   | 2.579 (13) |
| M(3)—O(1 <sup>h</sup> , 1 <sup>i</sup> , 1 <sup>j</sup> ) | 2.486 (11) | O(4 <sup>h</sup> )   | 2.960 (13) |
| O(4 <sup>h</sup> , 4 <sup>i</sup> , 4 <sup>j</sup> )      | 2.568 (10) | O(6 <sup>h</sup> )   | 3.066 (13) |
| Ave. 2.527  |            | O(2 <sup>h</sup> )   | 3.119 (14) |
|   |            |  | Ave. 2.702 |

Symmetry code: none  $x, y, z$ ; (i)  $x + \frac{1}{2}, y, -z + \frac{1}{2}$ ; (ii)  $z, x, y$ ; (iii)  $-y + 1, z - \frac{1}{2}, -x + \frac{1}{2}$ ; (iv)  $-y + \frac{1}{2}, z - \frac{1}{2}, x$ ; (v)  $y, z, x$ ; (vi)  $-x, -y, -z$ ; (vii)  $-z, -x, -y$ ; (viii)  $-y, -z, -x$ ; (ix)  $-x + 1, -y + 1, -z + 1$ ; (x)  $-z + 1, -x + 1, -y + 1$ ; (xi)  $-y + 1, -z + 1, -x + 1$ ; (xii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (xiii)  $-x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (xiv)  $-z + 1, x + \frac{1}{2}, -y + \frac{1}{2}$ ; (xv)  $z, -x + \frac{1}{2}, y + \frac{1}{2}$ ; (xvi)  $-y + \frac{1}{2}, -z + 1, x + \frac{1}{2}$ ; (xvii)  $y + \frac{1}{2}, z, -x + \frac{1}{2}$ ; (xviii)  $-z + \frac{1}{2}, -x, y + \frac{1}{2}$ ; (xix)  $y - \frac{1}{2}, z, -x + \frac{1}{2}$ ; (xx)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (xxi)  $z - \frac{1}{2}, x, -y + \frac{1}{2}$ .

are located around some of the corners of each subcell, while the cations such as Na and Ca (or K and Sr) are around the remaining corners and at the body-centred position. As a result of these unusual Ge-atom locations, this arrangement can be regarded as a linkage of a significant number of  $\text{GeO}_4$  tetrahedra. In fact, the present structure has a 12-membered ring of  $\text{GeO}_4$  tetrahedra (Fig. 1) and it has a configuration which is not expanded but highly contracted towards the  $\bar{3}$  rotoinversion axis of the ring. The presence of subcell structures and these unusual locations of the cations are similar to the situation found in the structure of tricalcium aluminates  $\text{Ca}_3\text{Al}_2\text{O}_6$  (Takeuchi, Nishi & Maki, 1980), except that the ring of  $\text{AlO}_4$  tetrahedra is six-membered. The arrangement of the present rings in the unit cell is shown in Fig. 2. Although the configuration of the ring is very similar to those found

in  $\text{K}_4\text{SrGe}_3\text{O}_9$  (Baumgartner & Völlenklee, 1977) and the silicate analogue  $\text{Na}_4\text{CaSi}_3\text{O}_9$  (Fischer & Tillmanns, 1984), our ring is more corrugated.

The two independent Ge—O—Ge angles in our structure in fact take considerably different values, 125.4 and 131.4°, whereas those in  $\text{K}_4\text{SrGe}_3\text{O}_9$  are 136.2 and 136.9° and almost the same. Such a difference may be accounted for by the difference in effective ionic charge of the cations occupying the atomic site M(5) (Table 1), at the centre of the ring; this site is fully occupied by the K atom in  $\text{K}_4\text{SrGe}_3\text{O}_9$ , while it is only 41% occupied by Na in the present structure, the site being 59% vacant (Table 1).

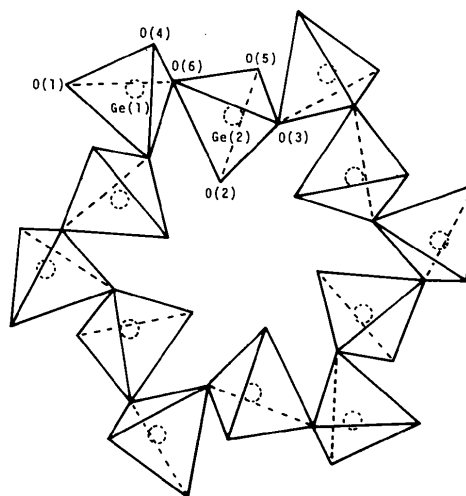


Fig. 1. The configuration of the 12-membered ring of  $\text{GeO}_4$  tetrahedra viewed down  $[111]$  in the polyhedron representation. Broken circles indicate the Ge atoms.

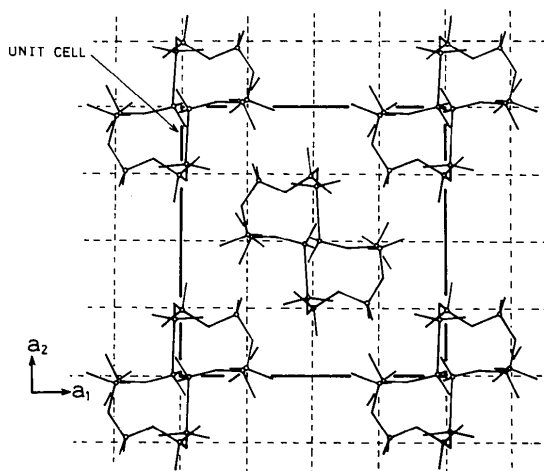


Fig. 2. The arrangement of 12-membered rings in the unit cell. Only those at the level  $z = \frac{1}{2}$  (the height of the centre of the ring is regarded as that of the ring) are shown; those at  $z = 0$  are omitted. Each ring is in the wire-frame representation. Broken lines represent the subcells.

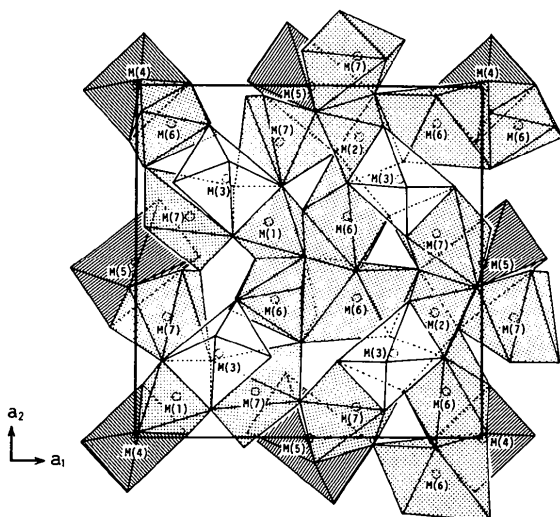


Fig. 3. The linkage of polyhedra about the cation sites; those in a slab bounded by  $z=0$  and  $z=\frac{1}{4}$  are shown. The hatched polyhedra are at  $z=0$ , the dotted ones at  $z=\frac{1}{4}$  and those without patterns at  $z=\frac{1}{2}$ .

Regarding the silicate analogue (Fischer & Tillmanns, 1984), we find that the corresponding angles are  $164.6$  and  $173.3^\circ$ . The difference between this set of values and that of our structure may be rationalized by the differences in size of the rings and of the cation occupying the centres of the rings.

It is notable that the Ge—O bond length varies significantly according to the Ge—O—Ge angle; a plot of Ge—O versus Ge—O—Ge defines a slope as in the cases of Si—O (Brown, Gibbs & Ribbe, 1969) and Al—O (Takéuchi, Nishi & Maki, 1980). The slope of the regression line for  $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$  (this study),  $\text{Na}_{3.0}\text{Ca}_{1.5}\text{Ge}_3\text{O}_9$  and  $\text{Na}_{2.50}\text{Ca}_{1.75}\text{Ge}_3\text{O}_9$  [ $-0.0026 \text{ \AA deg}^{-1}$  (Nishi & Takéuchi, 1987)] is found to be much

steeper than those for silicates [ $-0.0007 \text{ \AA deg}^{-1}$  (Brown, Gibbs & Ribbe, 1969)] and aluminates [ $-0.0006 \text{ \AA deg}^{-1}$  (Takéuchi, Nishi & Maki, 1980)]. We have only calculated the slope for germanates having ring structures, but the slope only changed slightly (approximately  $-0.0020 \text{ \AA deg}^{-1}$ ) even if some germanates having other structures were included. It would be desirable to refine the slope using more structural data for germanates in order to discuss in detail the difference in bonding character among these T—O bonds.

Fig. 3 illustrates the linkage of the metal polyhedra, including the octahedra about M(5). The polyhedral sheets consisting of the M(1), M(2), M(6) and M(7) cations can be observed and the displacement vector has the horizontal component  $a/2$  and the vertical component  $a/4$ .

In addition to this phase, we have derived the crystal structures of two Na Ca germanates having six-membered rings (Nishi & Takéuchi, 1987). The results will be published elsewhere.

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## Polymorphism of Nickel Sulfate Hexahydrate

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**Abstract.**  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $M_r = 262.85$ ; data collections with Mo K $\alpha$  radiation,  $\lambda = 0.7093 \text{ \AA}$ , room temperature. Monoclinic polymorph:  $C2/c$ ,  $a = 9.880$  (3),  $b = 7.228$  (2),  $c = 24.130$  (3)  $\text{\AA}$ ,  $\beta = 98.38$  (2) $^\circ$ ,  $V = 1704.7$  (6)  $\text{\AA}^3$ ,  $Z = 8$ ,  $D_x = 2.05 \text{ g cm}^{-3}$ ,  $\mu = 25.54 \text{ cm}^{-1}$ ,  $F(000) = 1088$ ,  $R = 0.031$  ( $wR = 0.038$ )

for 2176 observed reflections. Tetragonal polymorph:  $P4_2,2$ ,  $a = 6.780$  (1),  $c = 18.285$  (2)  $\text{\AA}$ ,  $V = 840.5$  (3)  $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 2.07 \text{ g cm}^{-3}$ ,  $\mu = 25.81 \text{ cm}^{-1}$ ,  $F(000) = 544$ ,  $R = 0.045$  ( $wR = 0.050$ ) for 2102 observed reflections. The structure of the tetragonal polymorph originally determined (without H