Structure of Sodium Calcium Germanate Na₂CaGe₂O₆

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Abstract. $Na_2CaGe_2O_6$, $M_r = 490.9$, rhombohedral, $R\bar{3}m$, $a = 10.788$ (2), $c = 13.460$ (2) Å (hexagonal setting), $V = 1356.6$ Å^3, $Z = 9$, $D_x = 3.60$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 113.5$ cm^{-1}, $F(000) = 1386$, $T = 298$ K, $R = 0.051$, $wR = 0.055$ for 708 observed reflections. The structure has a six-membered ring of GeO_4 tetrahedra and contains pseudocubic subcells with an edge length of 3.8 Å. These basic features are similar to those of the silicate analogue $Na_2CaSi_2O_6$. The details of both structures are, however, different. All the O atoms, for example, have statistical distributions near two-fold axes and mirror planes, while the silicate analogue has only one set of O atoms having a statistical distribution. In addition, all of the metal sites have disordered distributions, while some of them are ordered in the silicate analogue.

Introduction. In the ternary system Na_2O–CaO–SiO_2, the compound $Na_2Ca_2Si_3O_9$ having the rhombohedral lattice ($a = 7.41$ Å, $\alpha = 89.7°$) was found by means of Debye–Scherrer photography (Köppen & Padurow, 1958). Later, the same compound was studied by means of a Weissenberg camera and, as a result, the crystal was assigned a trigonal space group, $P3_121$ or $P3_221$ (Glasser & Mileson, 1968). Maki & Sugimura (1968) studied solid solutions of the Na_2O–CaO–SiO_2 system and found a clear phase boundary between the compounds $Na_2Ca_2Si_3O_9$ and $Na_2CaSi_2O_6$. Their results were confirmed by Moir & Glasser (1974). Recently, the single crystals of both phases were synthesized and their structures clarified (Ohsato, Maki & Takéuchi, 1985; Ohsato, Takéuchi & Maki, 1986). According to their results, there are some interesting phenomena; for example, the order–disorder of Ca/Na atoms and the splittings of some O and metal atoms. Recently, Fischer & Tillmanns (1983) studied the crystal structures of two minerals, both having chemical formulae close to $Na_2Ca_2Si_3O_9$. One was combeite from Zaire having the space group $R\bar{3}m$ and the other was an unknown mineral from Eifel having the space group $P3_1$ or $P3_2$. They concluded that these two minerals probably correspond to the high- (Zaire combeite) and low- (unknown mineral from Eifel) temperature modifications of synthetic $Na_2Ca_2Si_3O_9$ (Maki & Sugimura, 1968), respectively.

We are now studying silicates and their germanate analogues in order to find the common rules or the fundamental principles among these many polymorphs. Therefore, we studied the Na_2O–CaO–GeO_2 system and we succeeded in synthesizing three kinds of single crystals: $Na_{3.70}Ca_{1.15}Ge_3O_9$ having a 12-membered ring (Nishi & Takéuchi, 1988), $Na_2CaGe_2O_6$ having a six-membered ring and $Na_{2.50}Ca_{1.75}Ge_3O_9$ having a deformed six-membered ring (Nishi & Takéuchi, 1987). In addition, we succeeded in making the transition from the low-temperature form of $Na_{2.50}Ca_{1.75}Ge_3O_9$ to the high-temperature one at 723 K (Nishi, Fuess & Kratz, 1989). The present paper reports the crystal structure of $Na_2CaGe_2O_6$ in comparison with that of the silicate analogue $Na_2CaSi_2O_6$ (Ohsato *et al.*, 1985).

Experimental. Single crystals were synthesized from Na_2CO_3, $CaCO_3$ and GeO_2 mixtures at 1500 K. The molecular ratio was 1:1:2 for the starting material and the result of the least-squares refinement of the structure showed that the estimated chemical composition was $Na_2CaGe_2O_6$. The crystal used for the structure analysis was ground approximately to a sphere with diameter 0.13 mm. The cell dimensions were obtained by least-squares refinement of $\sin(2\theta)$ for 15 reflections in the range $29 \le 2\theta \le 35°$. A Syntex $P2_1$ single-crystal diffractometer was used for intensity measurements; ω–2θ scan, graphite-monochromatized Mo $K\alpha$ radiation. The reflections revealed the crystal to have rhombohedral symmetry and we adopted the hexagonal axes notation. We collected a quarter of the whole reciprocal space up to $2\theta = 90°$ in order to obtain high-quality intensity data. The intensities of symmetrically equivalent reflections were averaged and 708 independent

Table 1. *Atomic parameters for* $Na_2CaGe_2O_6$ *(values of positional parameters are* $\times 10^4$*)*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	y	B_{eq} (Å²)
Ge	1·0	1504·0 (0·5)	−1504·0 (0·5)	5669·8 (0·5)	1·22
M(1)	0·35 (1) Ca, 0·65 (1) Na	0	0	2473 (3)	1·93
M(2)	0·10 (2) Ca, 0·90 (2) Na	5000	0	0	4·03
M(3)	0·39 (1) Ca, 0·61 (1) Na	5000	0	5000	2·38
M(4)	0·84 (2) Ca, 0·16 (2) Na	0	0	0	2·41
O(1)	0·5	2783 (11)	235 (12)	5267 (7)	3·0 (2)
O(2)	0·5	826 (7)	−1451 (7)	6799 (5)	2·0 (1)
O(3)	0·5	2697 (9)	−2129 (9)	5525 (6)	2·7 (2)

reflections with $F_o > 3\sigma(|F_o|)$ were used for the refinement. Index ranges $0 \le h \le 17$, $0 \le k \le 8$, $0 \le l \le 26$, three standard reflections ($02\bar{2}$, 404 and $\bar{6}60$), intensity variation 4·0%; Lorentz, polarization and absorption corrections (transmission coefficients: max. 0·39, min. 0·32). Ordinary anisotropic refinement was used; $\Sigma w(\Delta F)^2$ minimized, $R = 0·051$, $wR = 0·055$, $w = 1/\sigma^2(|F_o|)$, $S = 1·0$, mean $(\Delta/\sigma) = 0·1$, max. $(\Delta/\sigma) = 0·3$, isotropic extinction correction applied [$g_{iso} = 1·05$ (5) $\times 10^{-4}$]; max., min. heights in final $\Delta\rho$ map 1·0, $-0·7$ e Å^{-3}; neutral scattering factors with correction for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974). Calculations 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.* The structure basically includes subcells (1/8 structure of the true rhombohedral cell) having the shape of a cube of side 3·8 Å, similar to related compounds such as the silicate analogue $Na_2CaSi_2O_6$ (Ohsato *et al.*, 1985) and $Na_{3·70}Ca_{1·15}Ge_3O_9$ (Nishi & Takéuchi, 1988). The distinct six-membered ring, which is similar to that of the silicate analogue $Na_2CaSi_2O_6$ (Ohsato *et al.*, 1985) and that of the high- and low-temperature forms of $Na_{2·5}Ca_{1·75}Ge_3O_9$ (Nishi *et al.*, 1989), is found in this structure (Fig.1). When we performed least-squares refinements in space group $R\bar{3}m$, all the O atoms behaved abnormally. Their thermal parameters diverged and some of the Ge—O bond lengths were abnormally short or long ($\sim 1·5$ Å, $\sim 1·9$ Å). We therefore gave perfect positional freedom to them in spite of their special positions. As a result, the R value decreased significantly and the above-mentioned abnormal situations were corrected. It was thus decided that the space group was $R3m$, and

Fig. 1. The arrangement of six-membered rings in the unit cell. The hatched tetrahedra are at $z \approx 1/6$, the dotted ones at $z \approx -1/6$ and those without patterns at $x \approx -1/2$. All the O atoms are drawn at the average positions of each split half.

all the O atoms had statistical distributions close to the special positions.

With regard to the metal sites, all are statistically distributed over the $M(1)$–$M(4)$ sites (Table 1), while some have ordered distributions in $Na_2CaSi_2O_6$ (Ohsato *et al.*, 1985). Although there was some vacancy at the $M(2)$ site of $Na_2CaSi_2O_6$ (Ohsato *et al.*, 1985), the corresponding site in the present structure is not significantly vacant. At first, we allocated only an Na atom to the $M(2)$ site and refined its population factor. This value exceeded 1·0, suggesting that the $M(2)$ site is statistically occupied by Na and Ca atoms. After this step, refinements of the population factor of each atom were executed and we obtained reasonable values (Table 1). Finally, it became clear that the $M(2)$ site had no vacancy because the electron number of this site (derived in terms of the population factor of Na, as mentioned before) was almost the same as the electron number derived from our disordered result [90 (2)% Na and 10 (2)% Ca in Table 1]. This vacancy is said to play an important role in the transition in $Na_2Ca_2Si_3O_9$ (Ohsato *et al.*, 1985) whose structure is similar to the present structure.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52474 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
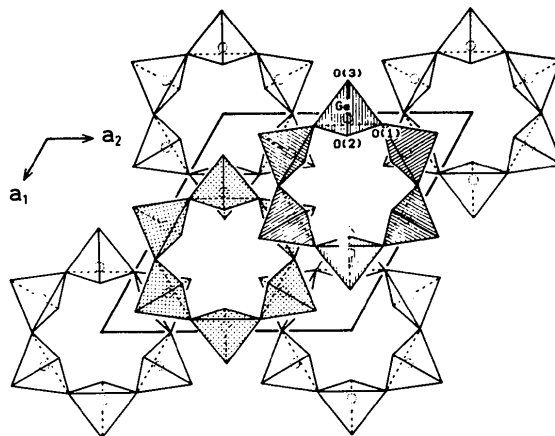
Table 2. Ge—O and (Ca/Na)—O bond lengths (Å);
occupancy of all the bonds is 0·5

Ge—O(2,2^i)	1·701 (8)
O(3,3^i)	1·736 (11)
O(1,1^i)	1·769 (9)
O(1^{ii},1^{iii})	1·787 (9)
Average	1·748
Total CN	4·0
$M(1)$—O(2^{ii},2^{iii},2^{iv},2^v,2^{vi},2^{vii})	2·365 (6)
O(3^{viii},3^{ix},3^x,3^{xi},3^{xii},3^{xiii})	2·504 (8)
Average	2·435
Total CN	6·0
$M(2)$—O(1^{xiv},1^{xv},1^{xvi},1^{xvii})	2·317 (9)
O(2^{viii},2^{xviii},2^{xix},2^{xx})	2·434 (7)
O(2^{xiv},2^{xv},2^{xvi},2^{xvii})	3·092 (7)
O(1^{xxi},1^{xxii},1^{xxiii},1^{xxiv})	3·157 (9)
Average	2·750
Total CN	8·0
$M(3)$—O(2^{xxi},2^{xxiii},2^{xxv},2^{xxvi})	2·314 (7)
O(3,3^{iii},3^{xxvii},3^{xxviii})	2·498 (8)
O(1,1^{iii},1^{xxvii},1^{xxviii})	2·553 (9)
O(3^i,3^v,v^{xxix},3^{xxx})	3·090 (8)
Average	2·614
Total CN	8·0
$M(4)$—O(3^{viii},3^{ix},3^x,3^{xii},3^{xiii}, 3^{xiv},3^{xvii},3^{xix},3^{xxxi},3^{xxxii},3^{xxxiii},3^{xxxiv})	2·326 (7)
Total CN	6·0

Symmetry codes: none x,y,z; (i) $-y,-x,z$; (ii) $y,y-x,1-z$; (iii) $x-y,-y,1-z$; (iv) $-x,-y,1-z$; (v) $x-y,x,1-z$; (vi) $y,x,1-z$; (vii) $-x,y-x,1-z$; (viii) $-x+1/3,-y-1/3,-z+2/3$; (ix) $y+1/3,y-x+2/3,-z+2/3$; (x) $x-y-2/3,x-1/3,-z+2/3$; (xi) $y+1/3,x-1/3,-z+2/3$; (xii) $-x+1/3,y-x+2/3,-z+2/3$; (xiii) $x-y-2/3,-y-1/3,-z+2/3$; (xiv) $y-x+2/3,-x+1/3,z-2/3$; (xv) $x-y+1/3,x-1/3,-z+2/3$; (xvi) $-y+2/3,-x+1/3,z-2/3$; (xvii) $y+1/3,x-1/3,-z+2/3$; (xviii) $x+2/3,y+1/3,z-2/3$; (xix) $y-x+2/3,y+1/3,z-2/3$; (xx) $x-y+1/3,-y-1/3,-z+2/3$; (xxi) $-y+1/3,x-y-1/3,z-1/3$; (xxii) $y+2/3,y-x+1/3,-z+1/3$; (xxiii) $x+1/3,x-y-1/3,z-1/3$; (xxiv) $-x+2/3,y-x+1/3,-z+1/3$; (xxv) $y+2/3,y-x+1/3,-z+4/3$; (xxvi) $-x+2/3,y-x+1/3,-z+4/3$; (xxvii) $-x+1,-y,-z+1$; (xxviii) $y-x+1,y,z$; (xxix) $y-x+1,-x,z$; (xxx) $y+1,x,1-z$; (xxxi) $x-1/3,y+1/3,z-2/3$; (xxxii) $-y-1/3,x-y-2/3,z-2/3$; (xxxiii) $-y-1/3,-x+1/3,z-2/3$; (xxxiv) $x-1/3,x-y-2/3,z-2/3$.

Ge—O and (Ca/Na)—O bond lengths are given in Table 2. For the evaluation of the mean (Ca/Na)—O bond length for each polyhedron, each (Ca/Na)—O bond length was weighted by its bond occupancy. The coordination number of each (Ca/Na) atom was counted by summing the occupancy of each (Ca/Na)—O bond. Each polyhedron is shown in Fig. 2. By comparing the MO_x polyhedra with one another, it can be seen that $M(4)O_x$ is the smallest and $M(2)O_x$ the largest (Table 2). This is reasonable because the former polyhedron includes the largest number of Ca atoms and the latter the smallest.
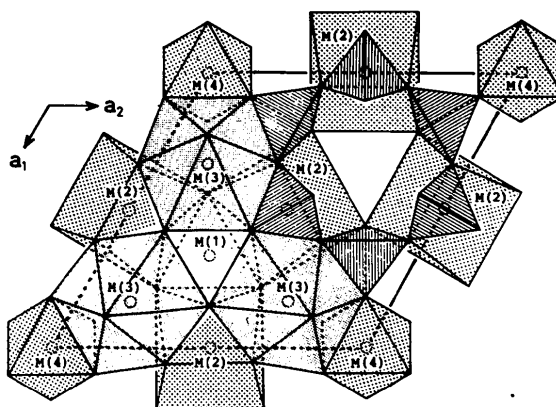

Fig. 2. The linkage of polyhedra and tetrahedra about cation sites. The hatched tetrahedra are at $z \simeq 1/6$, $M(3)$ polyhedra at $z = 1/2$, $M(1)$ polyhedron at $z \simeq 1/4$ and both of $M(2)$ and $M(4)$ at $z = 0$. All the O atoms are drawn as Fig. 1.

The split distances of O(1), O(2) and O(3) atoms are 0·84 (1), 0·674 (8) and 0·613 (9) Å, respectively. The split distance of O(1) of the present structure is larger than that in the $Na_2CaSi_2O_6$ structure (Ohsato et al., 1985). In addition, O(2) and O(3) atoms of the latter structure are not split. In order to clarify these differences and to understand the mechanism of the transition in the Na_2O–CaO–GeO_2 series, we tried and succeeded in observing the transition of $Na_{2.5}Ca_{1.75}Ge_3O_9$ at a high temperature. The results will be reported in the near future.

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