Discussion. Metal atoms occupy invariant positions (Table 1) and interatomic distances and bond angles are shown in Table 2. In this compound the Zn–S distance is shorter than that in ZnS (2·342 Å) (*International Tables for X-ray Crystallography,* 1968) and the Ti–S distances are longer than those in $Ti_{1+x}S_2$ (2·43 Å) (Tronc & Moret, 1981).

For the structure refinement neglecting diffuse reflections, the statistical occupation of Ti(2) and Zn at the positions in Table 1 gave the best fitting between observed and calculated structure factors. However, the distribution of real atoms in the Ti(2) and Zn positions can be different from unit cell to unit cell, and it is expected that Zn and Ti(2) atoms do not simultaneously coexist at the nearest positions. If one takes account of the existence of diffuse reflections (*e.g.* 200, 420, *etc.*), more detailed features of the structure will be clarified.

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Structure of $Na_2CaSi_2O_6$

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Abstract. $Na_6Ca_3[Si_6O_{18}]$, $M_r = 714{\cdot}6$, trigonal, $R\bar{3}m$, $a_R = 7{\cdot}488$ Å, $\alpha = 89{\cdot}04°$, $Z = 1$, $a_H = 10{\cdot}500$ (2), $c_H = 13{\cdot}184$ (1) Å, $V_H = 1258{\cdot}9$ (3) Å^3, $Z = 3$, $D_m = 2{\cdot}82$, $D_x = 2{\cdot}827$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}63$ mm^{-1}, $F(000) = 1062{\cdot}0$, $T = 293$ K, final $R = 0{\cdot}042$ for 1158 reflections. The basic structure consists of puckered six-membered rings (with point-group symmetry $\bar{3}m$) of silicate tetrahedra: $[Si_6O_{18}]^{12-}$. The rings are stacked in the fashion of cubic close packing and held together by Na^+ and Ca^{2+} ions located at four distinct positions. Each bridging O atom of the ring is split into a pair of sites off the twofold axis. Vacancies resulting from the replacement of 2Na by Ca occur exclusively at a specific Na position with ten near O atoms.

Introduction. The occurrence of $Na_2CaSi_2O_6$ in the ternary system Na_2O–CaO–SiO_2 was first described by Maki & Sugimura (1968) and later confirmed by Moir & Glasser (1974). It forms continuous solid solutions with the high-temperature form of $Na_2Ca_2Si_3O_9$ by the replacement of 2Na with Ca. Maki & Ohsato (1973) studied the crystal structure of $Na_2CaSi_2O_6$, showing that it consists of puckered six-membered rings of silicate tetrahedra. Details of the cation distribution, however, remained unknown. In a recent paper, Fischer & Tillmanns (1983) reported the structure of combeite (Sahama & Hytönen, 1957) which may be regarded as a Ca-rich natural analogue of $Na_2CaSi_2O_6$. We have determined the crystal structure of synthetic $Na_2CaSi_2O_6$. Compared to their result, our structure provides, as described in the present paper, more detailed features characteristic of the structure type.

Experimental. Single crystals with composition close to $Na_2CaSi_2O_6$ were grown by slowly cooling a melt of $Na_4CaSi_3O_9$. Details of the chemical composition were provided by the site-occupancy refinement. D_m measured by flotation method. Crystal was ground to the shape of a sphere with a radius r of 0·130 mm by the method of Bond (1951). Rigaku AFC5 single-crystal diffractometer, ω–2θ scan, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters refined by the least-squares method using 25 reflections in the range $81° < 2\theta < 86°$. 2576 reflections collected, 1283 unique ($R_{\rm int} = 0{\cdot}025$), 1158 with $F_o > 3\sigma(|F_o|)$. $2\theta < 90°$. $0 < h < 18$, $0 < k < 18$, $0 < l < 26$. 3 standard reflections with no significant variation. Lorentz and polarization correction. Absorption ignored because of the small μr, 0·212. The ideal unit-cell formula

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (*origin at* $\bar{3}m$)

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Position	Occupancy	x	y	z	B_{eq}(Å^2)
O(1)	18 (*g*)		0·2533 (6)	0·0131 (6)	0·5147 (3)	2·81 (15)
O(2)	18 (*h*)		0·1161 (1)	−0·1161 (1)	0·6734 (2)	2·68 (1)
O(3)	18 (*h*)		0·2373 (1)	−0·2373 (1)	0·5510 (2)	2·62 (2)
Si	18 (*h*)		0·1502 (1)	−0·1502 (1)	0·5636 (1)	0·58 (1)
M(1)	6 (*c*)	70·5%Na 29·5%Ca	0	0	0·2485 (1)	1·04 (3)
M(2)	9 (*e*)	97·2%Na 2·8% †	$\frac{1}{2}$	0	0	2·69 (12)
M(3)	9 (*d*)	50·1%Na 49·9%Ca	$\frac{1}{2}$	0	$\frac{1}{2}$	1·34 (10)
M(4)	3 (*a*)	100·0%Ca	0	0	0	0·81 (2)

† Vacancy.

$Na_{18}Ca_9Si_{18}O_{54}$ was employed at the outset of the analysis. The initial atomic parameters were those derived from the Patterson synthesis by Maki & Ohsato (1973). Distribution of Na and Ca was revealed from the difference Fourier map. Full-matrix least-squares refinement on F with unit weight, anisotropic thermal parameters, and occupancies for Na and Ca atoms. We split the O(1) site into a pair of sites, because of a large B_{eq} (4·56 Å^2) and split peaks on the difference Fourier map. The B_{eq} value then reduced to 2·7 Å^2, comparable with those for the other O atoms. The Na to Ca ratio was varied assuming full occupancies for O and Si sites and neutrality of the crystal. The refinement indicated that about 2·8% of the $M(2)$ site was vacant, resulting in the chemical composition $Na_{17.49}Ca_{9.25}Si_{18}O_{54}$. Final $R = 0{\cdot}0420$, $wR = 0{\cdot}0536$ for 43 variables and 1158 reflections. $\Delta\rho = \pm 0{\cdot}7$ e Å^{-3}. $(\Delta/\sigma)_{max} = 0{\cdot}11$ [U_{22} and U_{13} of $M(3)$], otherwise $\Delta/\sigma < 0{\cdot}01$. No correction for secondary extinction. Atomic scattering factors for O^{2-} provided by Tokonami (1965) and for other atoms from *International Tables for X-ray Crystallography* (1974). HITAC M280H computer of the University of Tokyo using the *RADY* least-squares program (Martin & Levy, 1962).

Discussion. The final atomic parameters and B_{eq} values are listed in Table 1.* The structure consists of the puckered six-membered ring $[Si_6O_{18}]^{12-}$ as shown in Fig. 1. These rings are stacked in the fashion of cubic close packing (Fig. 2) and held together by Na and Ca which are located at the four distinct positions denoted $M(1)$, $M(2)$, $M(3)$ and $M(4)$. The configuration of the six-membered ring is closely similar to that of the six-membered ring $[Al_6O_{18}]^{18-}$ found in the $Ca_3Al_2O_6$–Na_2O solid-solution series (Mondal & Jeffery, 1975; Takéuchi, Nishi & Maki, 1980).

Like other structures of this chemical series, the hexagonal cell of the present structure in fact consists of 24 pseudocubic subcells with a cell edge of 3·74 Å. Three of them are each occupied by the silicate ring with Si nearly at six corners of the subcell and with $M(1)$ occupied statistically by Na and Ca at the remaining two corners. The other alkali and alkaline-earth ions in the structure are located approximately at the body-centered sites of the remaining 21 subcells including two positions with nine atoms, $M(2)$ and $M(3)$, and a position with three atoms, $M(4)$. Details of the atomic occupancies are listed in Table 1. The $M(2)$ and $M(3)$ coordination numbers are ten and eight, respectively, and those of $M(1)$ and $M(4)$ are both six.

It is notable that vacancies occur exclusively at the $M(2)$ site located between a pair of silicate tetrahedra of the rings separated by $c/3$ (Fig. 2). The relatively large value of B_{eq} for this site (Table 1) is probably related to the existence of the vacancies. If in the solid solution $Na_2CaSi_2O_6$–$Na_2Ca_2Si_3O_9$ the chemical composition is shifted towards the Ca-rich composition, the vacancies at $M(2)$ would be increased. While, if the replacement of Ca by 2Na proceeds beyond the composition $Na_{18}Ca_9Si_{18}O_{54}$ and reaches $Na_{19.2}Ca_{8.4}Si_{18}O_{54}$ (Moir & Glasser, 1974), the excess Na would go to the centers of the six-membered rings by analogy with the case of the $Ca_3Al_2O_6$–Na_2O series (Takéuchi *et al.*, 1980).

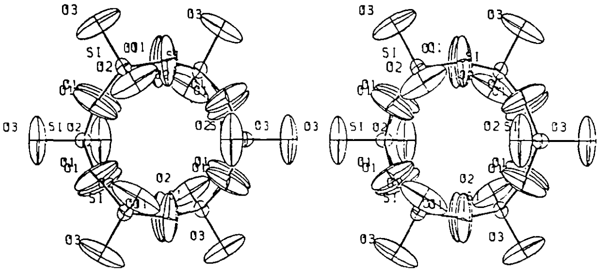

Fig. 1. Stereoscopic drawing of the $[Si_6O_{18}]^{12-}$ six-membered ring made with the *ORTEP* program (Johnson, 1965).

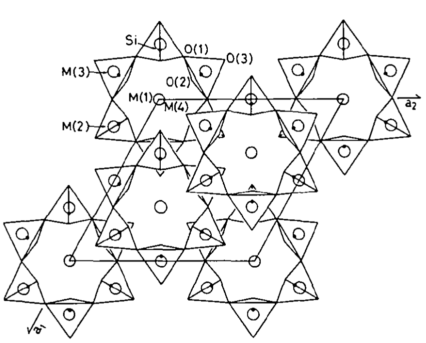

Fig. 2. Projection of the structure along the c axis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42324 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

These centers correspond to the body-centered sites of the three above-mentioned subcells occupied by the silicate rings. It has been found that the vacancies play an important role during transition in $Na_2Ca_2Si_3O_9$ as will be reported later (Ohsato, Takéuchi & Maki, 1985).

The bond lengths and angles are listed in Table 2. For calculating the bond lengths involving the split O(1), an average of the paired sets of the atomic coordinates was used. The three independent Si—O bonds of each SiO_4 tetrahedron have the length usually observed in silicates. The bridging Si—O(1) bonds are significantly longer than the nonbridging Si—O(2) and Si—O(3) bonds. The separation of the split O(1) sites is 0·45 Å. The distances from Si to the split sites are almost the same (1·635 Å).

Table 2. *Selected bond lengths* (Å) *and angles* (°)

The O(1) coordinates used for the calculation are the mean values of a pair of O(1).

Si site		
Si —O(1)	1·619 (1) ×2	
Si —O(2)	1·575 (2)	
Si —O(3)	1·592 (1)	
Average	1·601 (1)	
O(1) —O(1^{ii})	2·590 (4)	106·3 (2)
O(1) —O(2)	2·630 (3)	110·9 (1) ×2
O(1) —O(3)	2·535 (3)	104·3 (2) ×2
O(2) —O(3)	2·732 (2)	119·2 (1)
Average	2·609 (3)	
M(1) site		
M(1) —O(2^{i})	2·349 (2) ×3	
M(1) —O(3^{vi})	2·473 (2) ×3	
Average	2·411 (2)	
O(2^{i}) —O(2^{ii})	3·657 (2)	102·2 (1) ×3
O(2^{i}) —O(3^{viii})	3·400 (3)	89·6 (1) ×6
O(3^{vi}) —O(3^{viii})	3·025 (2)	75·4 (1) ×3
Average	3·370 (2)	
M(2) site		
M(2) —O(1^{iv})	2·670 (4) ×4	
M(2) —O(2^{vi})	2·693 (2) ×4	
M(2) —O(3^{iv})	3·144 (2) ×2	
Average	2·774 (3)	
O(1^{iv}) —O(1^{v})	2·590 (7)	58·0 (1) ×2
O(1^{iv}) —O(2^{vi})	2·630 (4)	58·7 (1) ×4
O(1^{iv}) —O(2^{vii})	3·517 (5)	82·0 (1) ×4
O(1^{iv}) —O(3^{iv})	2·535 (7)	50·9 (1) ×4
O(2^{vi}) —O(2^{viii})	3·657 (2)	85·5 (1) ×2
O(2^{vi}) —O(2^{vii})	3·955 (1)	94·5 (1) ×2
O(2^{vii}) —O(3^{iv})	3·400 (3)	70·8 (1) ×4
Average	3·124 (4)	
M(3) site		
M(3) —O(1)	2·660 (6) ×2	
M(3) —O(2^{iv})	2·301 (2) ×2	
M(3) —O(3)	2·720 (2) ×4	
Average	2·600 (3)	
O(1) —O(2^{iv})	3·517 (5)	90·0 (1) ×4
O(1) —O(3)	2·535 (3)	56·2 (1) ×4
O(2^{iv}) —O(3)	3·400 (3)	84·8 (1) ×4
O(2^{iv}) —O(3^{i})	3·718 (2)	95·2 (1) ×4
O(3) —O(3^{iii})	3·025 (2)	67·6 (1) ×2
Average	3·263 (3)	
M(4) site		
M(4) —O(3^{vi})	2·319 (2) ×6	
O(3^{vi}) —O(3^{viii})	3·025 (2)	81·4 (1) ×6
O(3^{vi}) —O(3^{vii})	3·515 (3)	98·6 (1) ×6
Average	3·270 (3)	

Symmetry operations: (i) $-x, -y, -z$; (ii) $y, -x+y, -z$; (iii) $-x+y, -x, z$; (iv) $\frac{1}{3}-y, \frac{2}{3}+x-y, \frac{2}{3}+z$; (v) $\frac{1}{3}+x, \frac{2}{3}+x-y, \frac{2}{3}+z$; (vi) $\frac{1}{3}-x, \frac{2}{3}-y, \frac{2}{3}-z$; (vii) $\frac{2}{3}-x+y, \frac{1}{3}-x, \frac{1}{3}+z$; (viii) $\frac{1}{3}+x-y, \frac{2}{3}+x, \frac{2}{3}-z$.

Now, the structure of combeite reported by Fischer & Tillmanns (1983) is closely similar to the present structure. The chemical composition $Na_{15}Ca_{12}Si_{18}O_{54}$ of their structure, however, does not give neutrality of crystal charge, nor does it agree with the formula $Na_{14.4}Ca_9Si_{18}O_{54}$ which they obtained by electron-probe microanalysis. This situation arose because they did not refine the atomic occupancies but simply assumed a mode of atomic distribution; so far as the mode of cation distribution is concerned, their structure is not fully consistent with our result. Thus, for example, the two distinct Ca sites in their structure show considerably different values of B_{eq}, one being 2·01 and the other 0·54 Å^2. The Ca(1) site which shows the former value corresponds to our $M(3)$, which, according to our analysis, contains Na and Ca in nearly the same amounts and shows $B_{\text{eq}} = 1{\cdot}3$ Å^2 (Table 1). It is expected that the existence of vacancies at the Na(2) site corresponding to our $M(2)$ would be more significant than in the present case, as the Ca/Na ratios of their chemical formulae are higher than that of our structure. The existence of such vacancies is one of the major features characteristic of the structure, as mentioned above.

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