

The crystal structure of monoclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$:
a case of monoclinic structure
closely simulating orthorhombic symmetry

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(Received 9 April 1973)

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Eine metastabile monokline Modifikation von der Zusammensetzung des Anorthits, $\text{CaAl}_2\text{Si}_2\text{O}_8$, wurde synthetisch dargestellt. Die Kristalle sind meist submikroskopisch verzwilligt. Die Raumgruppe der Substanz ist $P2_1$. Ihre Gitterkonstanten sind $a = 8,228(1)$, $b = 8,621(1)$, $c = 4,827(1)$, $\beta = 90,00(5)$; $Z = 2$. Die Struktur wurde nach der Minimumfunktions-Methode bestimmt aus den mit einem automatischen Diffraktometer gemessenen Intensitäten. Es ist eine Gerüststruktur mit Ringen aus vier Tetraedern wie beim Feldspat. Die Ca-Atome sind statistisch auf zwei Punktlagen verteilt mit den Besetzungswahrscheinlichkeiten 0,403(1) und 0,564(5). Die Struktur weist eine betonte Pseudosymmetrie nach $Pmnm$ auf. Die Abweichungen davon lassen sich in erster Linie durch die nahezu vollständige Ordnung der Al- und Si-Verteilung erklären. Die mittleren T–O–T-Winkel an den zwei- und dreifach-kooordinierten O-Atomen sind in der monoklinen Struktur kleiner als beim Anorthit. Als Grund für die Verzwilligung werden Fehler bei der Al- und Si-Anlagerung während des Wachstums vermutet.

Es spricht nichts für die Annahme, daß die monokline Phase verschieden vom „rhombischen $\text{CaAl}_2\text{Si}_2\text{O}_8$ “ von DAVIS und TUTTLE ist.

Abstract

A monoclinic metastable phase of anorthite composition, $\text{CaAl}_2\text{Si}_2\text{O}_8$, has been synthesized as an artificial product. Crystals are twinned mostly on a sub-microscopic scale. In the cell whose dimensions are $a = 8.228(1)$, $b = 8.621(1)$, $c = 4.827(1)$ Å, $\beta = 90.00(5)^\circ$, there are two formula units. The space group is $P2_1$. The structure has been worked out with the minimum-function method based upon intensities measured on an automated diffractometer. Final atomic

coordinates give an R of 0.06 with isotropic thermal parameters. The structure is a framework in which there can be recognized rings of four tetrahedra like the ones of feldspar. The calcium atoms are statistically distributed in two point positions with the occupancies of 0.403(4) and 0.564(5) respectively. The structure has a pronounced pseudosymmetry of $Pmnm$. The deviation from this higher symmetry is primarily explained by nearly complete order in the Si and Al sites in the framework. A comparison of this structure with that of anorthite has revealed that the mean T–O–T angles at two- and three-coordinated oxygen atoms are smaller than the corresponding angles of anorthite. A mechanism of twinning is suggested in terms of mistakes in the Si and Al placements which may occur in the process of crystal growth.

There is no evidence that the synthetic "orthorhombic $\text{CaAl}_2\text{Si}_2\text{O}_8$ ", described by DAVIS and TUTTLE (1952), is distinct from the present monoclinic phase.

Introduction

Three polymorphic forms are known for $\text{CaAl}_2\text{Si}_2\text{O}_8$. They are hexagonal, orthorhombic and triclinic. Among them the triclinic form, which is called anorthite, occurs in nature as one of the common rock-forming silicates. On the other hand, the hexagonal and orthorhombic forms are metastable and known only as artificial products (DAVIS and TUTTLE, 1952). Of these metastable phase, the crystal structure of the hexagonal form has been worked out by TAKÉUCHI and DONNAY (1959); it consists of sheets similar to those of hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$ (Iro, 1950; TAKÉUCHI, 1958).

In a series of investigations on growing feldspar crystals, one of the present authors (J. Iro) obtained a new metastable phase of the anorthite composition $\text{CaAl}_2\text{Si}_2\text{O}_8$. The crystals of this phase are monoclinic but close to orthorhombic. The following account presents the results of our investigation carried out in the hope that the elucidation of the metastable structure might throw light on the structural features characteristic of metastable phases of silicates in general.

Material

The metastable phase of anorthite composition was obtained during the investigation which was undertaken to establish a high-temperature solvent method for growing crystalline phases in the feldspar group. The crystals of the metastable phase were formed by rapid cooling of a melt caused by an accidental burning-up of the heating element of the furnace. The rapid cooling occurred at an undeterminable rate from the soaking temperature of 1400°C to 1000°C . From the temperature of 1000°C , the melt was cooled down to 750°C at the rate of 4°C per hour. The final crystalline product of this particular run mostly consists

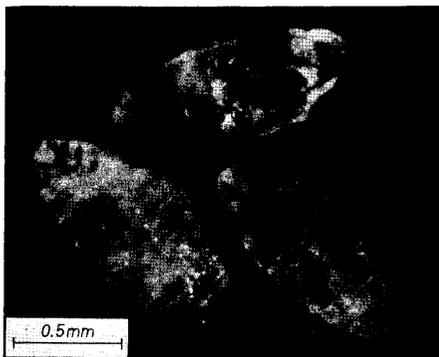


Fig. 1. Crystals of monoclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$

of triclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) having crystal sizes of up to 3 mm in length, and fine mullite, in addition to crystals of the metastable phase. A small amount of corundum and cristobalite were also identified in it. In the product we have further found, to date, one crystal of hexagonal $\text{CaAl}_2\text{Si}_2\text{O}_8$ whose a axis, unlike that of the previously reported hexagonal form (DAVIS and TUTTLE, 1952; TAKÉUCHI and DONNAY, 1959) is doubled, tentative measurement giving a periodicity of 10.2 Å. The mode of assemblage of these crystalline phases clearly indicates that the crystallization took place under nonequilibrium conditions. On heating at 1300°C for two hours, the crystals of this metastable phase are transformed into the triclinic form.

The crystals of the metastable phase are shown in Fig. 1; they are elongated parallel to the c axis, and have well developed (100) faces. They are colorless and transparent. Aggregates of fine cristobalite are often observed as inclusions. Two representative results of microprobe analyses carried out by Dr. DAVID WALKER, Harvard University, are compared below with the ideal composition of anorthite:

	1	2	Anorthite
SiO_2	44.4%	48.1%	43.2%
Al_2O_3	35.6	31.8	36.7
CaO	19.9	18.0	20.1
Na_2O	0.1	0.1	—
	100.0	98.0	100.0

The first result yields the formula $\text{Ca}_{0.99}\text{Na}_{0.01}\text{Al}_{1.94}\text{Si}_{2.05}\text{O}_8$, and the second $\text{Ca}_{0.9}\text{Na}_{0.01}\text{Al}_{1.75}\text{Si}_{2.24}\text{O}_8$; the latter has been given as an extreme example showing deviation from the anorthite composition. In addition to the microprobe analyses, we carried out a wet chemical analysis of hand-picked bulk specimens with the result as follows: SiO_2 48.4%, Al_2O_3 33.3%, CaO 17.9%, and Na_2O 0.1%, total 99.7%. Since it was not possible to separate cristobalite inclusions completely, the higher value in the SiO_2 component is attributable to cristobalite. If therefore this value for the silica component is reduced so that the resulting value gives a value of 43.2% like that for the anorthite composition, the contents for the remaining components are calculated to be: Al_2O_3 36.8%, CaO 19.9%, Na_2O 0.1%. The chemical composition of this material thus essentially corresponds to the anorthite composition, $\text{CaAl}_2\text{Si}_2\text{O}_8$. The above result of microprobe analyses, however, might suggest that the composition may not necessarily be homogeneous in a crystal but variable from the anorthite composition to $\text{Ca}_{0.9}\text{Al}_{1.8}\text{Si}_{2.2}\text{O}_8$.

Lattice constants and space group

The single-crystal diffraction patterns show monoclinic diffraction symmetry, but are markedly close to orthorhombic. The lattice constants determined with a four-circle diffractometer ($\text{MoK}\alpha$, $\lambda = 0.70926$ Å) at 18°C are:

$$a = 8.228(1) \text{ \AA}, b = 8.621(1) \text{ \AA}, c = 4.827(1) \text{ \AA}, \beta = 90.00(5)^\circ.$$

The unit cell contains two molecules of $\text{CaAl}_2\text{Si}_2\text{O}_8$, giving a calculated specific gravity of 2.69 g/cm³. This value is compared below with those of other modifications of $\text{CaAl}_2\text{Si}_2\text{O}_8$.

Specific gravity	Hexagonal	Monoclinic	Anorthite
Calculated	2.77 ^a g/cm ³ 2.78 ^b	2.69; g/cm ³ 2.66 ^{c*}	2.76 ₂ g/cm ³
Observed	2.74 ^a	2.69(1) ^e 2.70 ^a	2.76 ^d

^a DAVIS and TUTTLE (1952), ^b TAKÉUCHI and DONNAY (1959), ^c Calculated by the present authors based upon the cell volume given by WAINWRIGHT and STARKEY (1971) for an An_{100} specimen, ^d DEER, HOWIE and ZUSSMAN (1963), ^e Present study. * The value for $\text{Ca}_{0.9}\text{Al}_{1.8}\text{Si}_{2.2}\text{O}_8$.

As observed in the above table, the specific gravity of the present material gives the smallest value among the known polymorphic forms of $\text{CaAl}_2\text{Si}_2\text{O}_8$.

The observed value of 2.70 given in this table for the monoclinic modification is the one reported by DAVIS and TUTTLE (1952) for a metastable phase of $\text{CaAl}_2\text{Si}_2\text{O}_8$ which they called "orthorhombic $\text{CaAl}_2\text{Si}_2\text{O}_8$ ". Their lattice constants are near to those of the monoclinic phase: $a = 8.224(6)$, $b = 8.606(6)$, $c = 4.836(5)$ Å. In addition, the powder-diffraction patterns of the "orthorhombic" phase and the present phase are identical, suggesting that the "orthorhombic" phase is identical with the present monoclinic phase. The confusion undoubtedly arose from the fact that DAVIS and TUTTLE (1952) obtained the crystal data for their material only from its powder pattern.

The crystals of monoclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$ are weakly piezoelectric, so that they must be acentric. The $0k0$ and $h00$ reflections are missing on precession and Weissenberg photographs if k and h are odd. Since the diffraction symmetry is monoclinic, the extinction rule for $0k0$ leads to the acentric space group $P2_1$ as most probable one. The missing spectra for $h00$ reflections can then be considered as structural extinctions. Indeed a counter-diffractometer measurement has revealed very weak intensity for the 900 reflection which is slightly above background level.

Analysis

Analysis using a twinned crystal

Until we came across a crystal fragment which exhibited monoclinic diffraction symmetry, all crystal fragments had given orthorhombic diffraction symmetry. Their lattice constants are identical, within errors of experiment, with those given above. The extinction rule of spectra is consistent with that of the space group $P2_12_12$. Since these crystallographic data are parallel with those of "orthorhombic $\text{CaAl}_2\text{Si}_2\text{O}_8$ ", we were naturally misled to assume that the crystals were orthorhombic and identical with "orthorhombic $\text{CaAl}_2\text{Si}_2\text{O}_8$ ".

In order to carry out the structure analysis, all reflections within one octant of reciprocal space up to $\sin \theta \leq 0.70$ were measured with monochromatized $\text{MoK}\alpha$ radiation on a four-circle diffractometer. At this early stage of analysis, we became aware of the fact that the space group $P2_12_12$ is not probable for the structure under consideration for two reasons. First, in the intensity distribution observed in x-ray photographs, it is observed that the intensities of $hk0$ and $h0l$ are very

weak if $h+k$ and $h+l$ respectively are odd. It follows that, if these weak reflections are left out, the remaining reflections lead to space group $Pmnn$ or $P2nn$. This situation suggests that the structure of the present material may be regarded as a derivative of a structure which has either a space group $Pmnn$ or $P2nn$.

In that event, the space group of this material should be, according to the theory of derivative crystal structures (BUERGER, 1947), one of the subgroups of $Pmnn$ or $P2nn$. A difficulty then arose that neither $Pmnn$ nor $P2nn$ have subgroup $P2_12_12$. Though the space group $Pmnn$ does contain a dihedral subgroup of $P2_12_1$, it is obviously different from $P2_12_12$. However, comparing these two dihedral groups, we immediately notice that they have a common monoclinic subgroup $P2_1$ whose unique axis is parallel to the b axis of the present material. The above consideration leads to a view that the true symmetry of this material would be $P2_1$, and its structure would be a derivative of a structure having a space group $Pmnn$.

We now explain the second reason which eliminates space group $P2_12_12$. Since the unit cell of this material is small, and the structure would presumably be built on a framework consisting of oxygen tetrahedra around Si and Al atoms, it is not difficult to construct possible structural models. Preliminary calculations of structure factors, however, soon disclosed that none of the models explained the intensities of $0kl$ and $h0l$ reflections satisfactorily, though they gave rough agreement between F_o and F_c for $hk0$ reflections with $h+k = 2n$ (n , an integer). This situation was such that it could not be improved by any means so long as there are twofold axes parallel to the c axis, suggesting that $P2_12_12$ is not probable. We therefore decided to assume the space group $P2_1$. It was thought that the $P2_1$ structure would produce a diffraction pattern which is close enough to orthorhombic symmetry.

The first attempts to derive an approximate structure were made by examining the Patterson function. Because of the strong pseudosymmetry of $Pmnn$, the distribution of peaks in the Patterson function should bear the geometrical relation characteristic of the vector sets arisen from point sets having space group $Pmnn$. Utilizing this geometrical relation, we were indeed successful in interpreting the Patterson function to form a minimum function $M_2(xyz)$ (Fig. 2). It is to be noted that $M_2(xyz)$ thus obtained is a multiple of a possible true solution and its inverse image because the crystal is acentric.

Noting that the c -axis projection would probably be close to centrosymmetrical because of the pseudosymmetry, then, to confirm the

above result, we applied the symbolic-addition procedure to the reflections of the $hk0$ zone. Out of 78 $hk0$ reflections with $h+k=2n$, 34 reflections have $|E|$ values bigger than 1.0. Among them the signs of E 's for 31 reflections were determined and they were used to form an E map. As shown in Fig. 3, the resulting E map gave the distribution of peaks which is essentially consistent with that in the c -axis projection of $M_2(xyz)$.

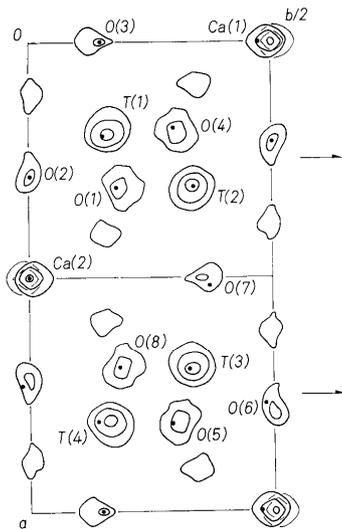


Fig. 2

Fig. 2. $M_2(xyz)$. Final atomic locations are indicated. The origin is taken at $-\frac{1}{4}, 0, -\frac{1}{4}$ of the conventional cell of $P2_1$.

Fig. 3. Two-dimensional E map based upon $hk0$ reflections. Since the space group $Pmnn$ was assumed, this projection has a plane symmetry cm . Final atomic locations are indicated by dots. The origin is taken at $-\frac{1}{4}, 0, -\frac{1}{4}$ of the conventional cell of $P2_1$.

Based upon $M_2(xyz)$, we can readily derive a framework structure having $P2_1$ symmetry. As will be observed in Fig. 2, there are in $M_2(xyz)$ two possible twofold positions, Ca(1) and Ca(2), for calcium atoms. Since the unit cell contains only two calcium atoms, we placed

the calcium atoms in the Ca(1) site. Structure-factor calculations based upon this initial set of atomic coordinates gave a residual $R = 0.25$. The atomic coordinates were then refined to $R = 0.16$ with the full-matrix least-squares program, ORFLS, written for IBM 7090 computer by BUSING, MARTIN and LEVY (1962) and modified by IITAKA for HITAC 5020 E. A difference Fourier synthesis computed at this stage indicated that calcium atoms should also be located in the Ca(2) site. This implies that two calcium atoms in the unit cell are statistically distributed over two sets of twofold locations. In the subsequent least-squares calculations applying thermal parameters, we therefore refined the occupancy parameters for the sites Ca(1) and Ca(2). The value of R was then reduced to 0.12.

A difficulty again arose in that this value of R could not be reduced any further. Though the agreement between F_o and F_c is in general fairly good, that for the particular set of weak $hk0$ reflections having $h+k \neq 2n$ is thoroughly unacceptable. To explain this difficulty, we finally decided to assume that the crystal fragment under investigation was a twin of the $P2_1$ structure formed on a submicroscopic scale. Since the symmetry of the $P2_1$ structure is close to $Pmnn$, the occurrence of such a twinning is highly likely. A similar example has been reported for the so-called hexagonal modification of $\text{BaAl}_2\text{Si}_2\text{O}_8$. This form is apparently hexagonal (Iro, 1950), but the hexagonal symmetry is actually the result of a submicroscopic twinning of an orthorhombic structure (TAKÉUCHI, 1958).

True structure

In the meantime we happened to find a tiny crystal fragment which does exhibit monoclinic diffraction symmetry. It was then proved that the crystal fragment on which we had been working was indeed a twin. The shape of the new crystal is roughly that of parallelepiped with dimensions $0.10 \times 0.10 \times 0.15$ mm. The lattice constants given previously are those of this crystal. A new set of 2303 intensities was therefore measured on a four-circle diffractometer using $\text{MoK}\alpha$ radiation for all reflections having $\sin \theta \leq 0.6$. Intensities of symmetrically equivalent reflections were averaged, and a total of 1157 reflections was collected. Of these, 955 reflections which have values bigger than $2\sigma(I)$ were used for the following refinements. Correction for transmission was not made.

Structure-factor calculations based upon the $P2_1$ structure, which gave an $R = 0.12$ for the previous set of F_o 's obtained from the twinned

crystal, gives for this new set of F_o 's a value of 0.08. Successive least-squares refinement applying isotropic temperature factors reduced it to 0.06. For these computations, an empirical weighting factor was used of the form: $w_i = 1/(a + 1/F_{\text{obs}} + c/F_{\text{obs}}^2)$ (CRUICKSHANK, 1965). The values of a and c which minimized the variation of $(F_o - F_c)$ with F_{obs} were 5.4 and 0.028 respectively. It is now concluded that the monoclinic modification of the anorthite composition has been established. The final atomic parameters which give $R = 0.06$ are listed in Table 1.

Discussion

General features of structure

The c -axis and a -axis projections of the crystal structure (Fig. 4 and Fig. 5) show that the structure is built on a framework which is composed of tetrahedral groups around silicon and aluminium sharing every corner with neighbouring groups. The links of the framework consist of rings of four tetrahedra whose configuration is closely similar to that of the rings found by TAYLOR (1933) in feldspars. The linkage of the rings, however, is different from that in the feldspar structure. As will be observed (Fig. 4 and Fig. 5) the tetrahedra divide themselves into two groups; small and large tetrahedra alternate in every direction

Table 1. Fractional atomic coordinates, isotropic thermal parameters and their standard deviations (in parentheses)

The sites Ca(1) and Ca(2) are occupied by calcium atoms with the occupancies of 0.403(4) and 0.564(5) respectively

	x	y	z	B
Ca(1)	0.7470(5)	0.4738(4)	0.8642(9)	0.48(5) Å ²
Ca(2)	0.2498(4)	0	0.3440(8)	1.42(5)
T(1)	0.9503(2)	0.1498(6)	0.8945(4)	0.25(3)
T(2)	0.0650(3)	0.3360(6)	0.3976(5)	0.70(3)
T(3)	0.4454(3)	0.3276(6)	0.3952(5)	0.45(4)
T(4)	0.5676(3)	0.1373(6)	0.8941(5)	0.62(3)
O(1)	0.0609(8)	0.1819(10)	0.1737(15)	1.05(10)
O(2)	0.0380(7)	0.0021(9)	0.7381(12)	0.88(9)
O(3)	0.7614(8)	0.1378(11)	0.0021(14)	1.47(10)
O(4)	0.9540(7)	0.2974(9)	0.6863(12)	0.50(8)
O(5)	0.5619(7)	0.2930(9)	0.6604(13)	0.60(8)
O(6)	0.5254(7)	0.4807(10)	0.2486(13)	1.30(11)
O(7)	0.2664(6)	0.3714(9)	0.4789(10)	0.81(8)
O(8)	0.4408(7)	0.1762(9)	0.1895(14)	1.11(10)

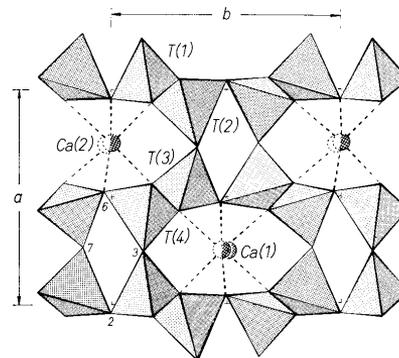


Fig. 4. The c -axis projection of the crystal structure of monoclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$

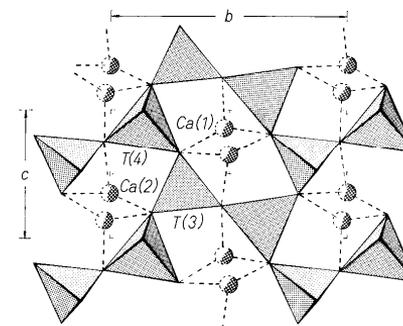


Fig. 5. Projection on (100) of a slab bounded by $x = 1/4$ and $x = 3/4$

so that each oxygen atom is shared by one small and one large one. The difference is more conspicuous if we look at the T—O bond lengths which are given in Table 2. The significant differences in the mean T—O bond lengths suggest that the small tetrahedra T(1) and T(3) are mainly occupied by silicon, and large tetrahedra T(2) and T(4) by aluminium atoms. These bond lengths are to be compared with those of anorthite (MEGAW, KEMPSTER and RADOSLOVICH, 1962; WAINWRIGHT and STARKEY, 1971). The mean T—O bond lengths in anorthite are 1.614 Å for small tetrahedra, and 1.749 Å for large tetrahedra, indicating that the ordering of Si and Al in anorthite is essentially

Table 2. T(i)—O(n) bond lengths, T(i)—O(n)—T(j) angles, and mean Ca—O(n) distances

Errors in bond lengths and distances are in the range from $\pm 0.005 \text{ \AA}$ to $\pm 0.009 \text{ \AA}$, and that in angles $\pm 0.5^\circ$

<i>i</i>	<i>n</i>	Bond length	Bond angle	<i>j</i>	<Ca—O(<i>n</i>)>
1	1	1.651 Å	131.1°	2	2.383 Å
	2	1.647	125.4	2'	2.602
	4	1.641	132.5	2''	2.434
	3	1.643	143.3	4	
Mean		1.641	133.1		
2	1	1.713	131.1	1	2.383
	4	1.700	132.2	1'	2.434
	2''	1.789	125.4	1''	2.602
	7	1.730	142.8	3	
Mean		1.733	135.4		
3	8	1.641	128.0	4	2.328
	6	1.637	129.5	4''	2.655
	5	1.628	131.3	4'	2.378
	7	1.574	142.8	2	
Mean		1.620	132.9		
4	8	1.799	128.0	3	2.328
	5	1.754	131.5	3'	2.378
	6'	1.699	129.5	3''	2.655
	3	1.678	143.3	1	
Mean		1.733	133.1		

perfect. Though the Si,Al order in monoclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$ is undoubtedly of high degree, it is not as complete as that of anorthite. This fact may be attributed to higher growth rate of this material.

Since T—O—T angles and neighbouring cations affect the T—O bond lengths (CRUICKSHANK, 1961; PANT and CRUICKSHANK, 1968; BROWN, GIBBS and RIBBE, 1969), the angles at O and the mean lengths between O and neighbouring Ca atoms are listed together so that we can easily inspect these correlations. Among four independent tetrahedra, the tetrahedron T(3), which is substantially occupied by silicium atoms, does show a beautiful correlation between T—O lengths and angles at O. With increasing angles at O, the T—O lengths of the tetrahedron decrease linearly. However, it seems difficult to find similar evidence for other individual tetrahedra.

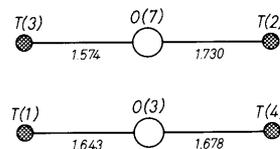


Fig. 6. Bond lengths (Å) between two-coordinated oxygen and T atoms

The oxygen atoms in this structure are grouped into two categories; those coordinated by one Si and one Al atoms, and those coordinated by one Si, one Al and one Ca atoms. Inspection of Table 2 reveals that there is a marked difference between angles at two-coordinated oxygen atoms and those at three-coordinated oxygen atoms. The mean value of the angles at two-coordinated O's is 143.1° , while that at three-coordinated O's 129.7° . This means that the residual charges at the oxygen atoms of Si—O—Al links are, like those in anorthite (MEGAW, KEMPSTER and RADOSLOVICH, 1962), related to increasing angles at O atoms, accordingly to shortening T—O bond lengths. It appears, however, that such a balance in an Si—O—Al link in our structure has been achieved not by shortening both the Si—O and Al—O bonds but by shortening only either one of them. This situation is shown in Fig. 6. In the T(3)—O(7)—T(2) link, the T(3)—O(7) bond length of 1.574 Å is the shortest one among T—O lengths of Si-rich tetrahedra, while the T(2)—O(7) length is essentially identical to the average T—O bond length in the Al-rich tetrahedra. On the contrary, the T(1)—O(3) bond length of 1.643 Å in the T(1)—O(3)—T(4) link is longer than the average T—O bond length of Si-rich tetrahedra, while the T(4)—O(3) bond length of 1.678 Å is the shortest T—O bond in the Al-rich tetrahedra. Edge lengths and angles at T of each tetrahedron are listed in Table 3.

Two calcium atoms in the unit cell are statistically distributed over two twofold positions, Ca(1) and Ca(2) respectively, with occupancies of 0.403 ± 0.004 and 0.564 ± 0.005 . The difference between these two values is highly significant. In fact, this difference in the calcium contents between the Ca(1) and Ca(2) positions is responsible for the observed intensity of 001 reflection. Each position has six near oxygen neighbours. The shape of the polyhedra formed by these oxygen atoms is close to that of a trigonal prism. The Ca(1) site has seventh oxygen neighbour at the distance of $2.975 \pm 0.009 \text{ \AA}$, and the Ca(2) site at the distance of $3.271 \pm 0.008 \text{ \AA}$. The closest approach of the Ca(1) and

Table 3. O(p)—O(q) distances and O(p)—T(i)—O(q) angles

<i>i</i>	<i>p</i>	<i>q</i>	Distances	Angles
1	2	1	2.621(10) Å	105.3(4)°
		4	2.651(11)	108.3(4)
	2	3	2.860(9)	120.8(5)
		4	2.704(9)	111.4(5)
	1	3	2.629(9)	105.9(4)
4	3	2.595(9)	105.2(4)	
Mean			2.677	
2	4	1	2.810(9)	110.8(4)
		7	2.832(8)	111.3(3)
	4	2	2.706(9)	101.7(4)
		7	2.775(9)	107.4(4)
	1	2	2.910(11)	112.4(4)
	7	2	2.940(8)	113.3(4)
	Mean			2.829
3	7	8	2.617(9)	108.9(9)
		5	2.672(9)	113.1(3)
	7	6	2.582(9)	107.1(4)
		5	2.680(9)	110.2(5)
	8	6	2.732(12)	112.9(4)
	5	6	2.583(10)	104.6(4)
Mean			2.644	
4	8	6	2.720(10)	102.0(4)
		3	2.809(9)	107.7(3)
	8	5	2.922(9)	110.6(4)
		3	2.978(9)	123.8(5)
	6	5	2.822(11)	109.6(4)
	3	5	2.685(9)	102.9(4)
Mean			2.823	

Ca(2) positions is 1.031 ± 0.003 Å. It is obviously unlikely that the Ca atoms occupy simultaneously such a pair of two positions having the short distance. If therefore we exclude that possibility, we find that the effective shortest distance between calcium atoms is 3.832 ± 0.003 Å, which is shorter than the shortest Ca—Ca distance of 3.880 Å found in anorthite (MEGAW, KEMPSTER and RADOSLOVICH, 1962). It is interesting to note that the shortest Ca—Ca distance in hexagonal $\text{CaAl}_2\text{Si}_2\text{O}_8$ has, in contrast with the above values, a large value of 5.10 Å (TAKÉUCHI and DONNAY, 1959). The Ca—O bond lengths are listed in Table 4.

Table 4. Individual Ca—O bond lengths

Ca(1)—O(4)	2.440(8) Å	Ca(2)—O(1)	2.357(8) Å
O(5)	2.392(8)	O(2)	2.581(7)
O(6)	2.603(7)	O(4'')	2.427(7)
O(2'')	2.623(7)	O(5'')	2.364(8)
O(8'')	2.346(9)	O(6')	2.706(7)
O(1'')	2.399(9)	O(8)	2.310(8)
Mean	2.467		2.458

Table 5. Distortions of O(p)—T(i)—O(q) angles

Deviation from the tetrahedral angle is given for each bond angle. The angles are classified into three categories according to the topological differences of edges subtending angles (see text)

<i>i</i>	<i>p</i>	<i>q</i>	Distortions		
			T _A	T _B	T _C
1	2	1		− 4.2°	
		4			− 1.2°
	2	3	+ 11.3°		
		4			+ 1.9
	1	3			− 3.6
4	3		− 4.3		
2	4	1			+ 1.3
		7			+ 1.8
	4	2		− 7.8	
		7		− 2.1	
	1	2			+ 2.9
7	2	+ 3.8			
3	7	8		− 0.6	
		5			+ 3.6
	7	6	− 2.4		
		5			+ 0.7
	8	6			+ 3.4
5	6		− 4.9		
4	8	6		− 7.5	
		3			− 1.8
	8	5			+ 1.1
		3	+ 14.3		
	6	5			+ 0.1
3	5		− 6.6		
Mean			+ 6.8	− 4.8	+ 0.9

As will be observed in Table 6, the coordination polyhedra about Ca atoms in hexagonal and monoclinic modifications have higher symmetry than those of anorthite. Since metastable structures like the present one are those in which assemblages of atoms at higher temperature have been trapped in place by rapid cooling, this symmetry relationship among coordination polyhedra would be nothing but an indication that assemblages of atoms stable at higher temperature tend to be of higher symmetry.

Distortion of tetrahedra, and T—O—T angles

In Table 3, which shows bond angles at T atoms, it is observed that the angles range from 101.7° to 123.8°. In anorthite, the angles are in the range from 96.3° to 121.3° (MEGAW, KEMPSTER and RADOSLOVICH, 1962). On these angles, we carried out the following statistics: the range of angles from 95° to 125° was divided into ten groups with an equal interval of 3° and, with respect to total number, the percentage in the number of angles which fall in each group was evaluated. The results are compared with those for anorthite (Fig. 7). It is to be

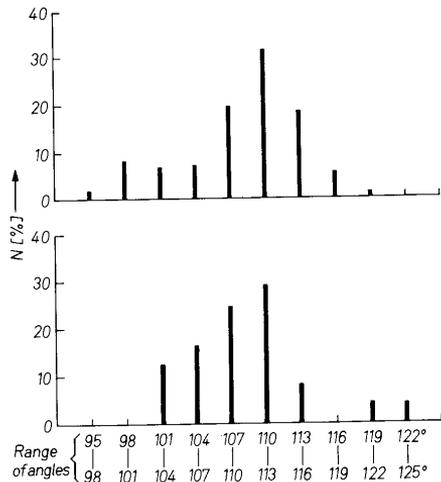


Fig. 7. Frequency (percent) in the number of O—T—O angles (in degrees) in anorthite (upper), and in monoclinic CaAl₂Si₂O₈ (lower)

noted that the percentage in the number of angles exceeding 120° in our structure is significantly larger than that of anorthite. Examination of our structure shows that the angles which give such a large positive distortion from the tetrahedral angle are those between T—O bonds whose terminal oxygen atoms participate in forming quadrilaterals, like 2-3-6-7, in the four-membered rings (Fig. 4).

Bond angles at T in our structure are then classified into three categories, T_A, T_B, and T_C, respectively according to the following topological differences of edges subtending angles: (i) those which form the quadrilateral in a four-membered ring of tetrahedra, (ii) those which participate in forming, in the *c*-axis projection, an eight-sided polygon around Ca atoms, and (iii) those which do not fall in the above categories. The deviations of angles from the tetrahedral angle which MEGAW, KEMPSTER and RADOSLOVICH (1962) called bond-angle strains, are evaluated for angles in each category and listed in Table 5. The bond-angle strains thus classified bring out a marked feature: those of the angles in the category T_A show mostly positive strain, giving a large positive mean value of +6.8; those for T_B are all negative, giving a negative mean value of -4.8; while, the mean value of the bond strains for T_C is essentially zero. The negative bond-angle strains of angles in the category T_B suggest that the O—O edges subtending the angles tend to shrink in order to shield the tetrahedral cations from the electrostatic field of the neighbouring Ca atoms.

As will be observed in Table 5, and also in Fig. 4, each tetrahedron has at least two O—O edges close to Ca atoms, giving rise to shortening these edges. It naturally follows that some other edges must be lengthened in order to maintain proper T—O bond lengths in the tetrahedron. The observed bond-angle strains seem to suggest that such a lengthening of O—O edges tend to occur preferably to those which participate in forming quadrilaterals in the four-membered rings.

For the known polymorphic forms of CaAl₂Si₂O₈, we next compare the mean T—O bond lengths and T—O—T angles (Table 6). It is observed in this table that the mean T—O lengths are essentially identical. On the other hand, some differences are observed among mean T—O—T angles. The mean angle at oxygen atoms coordinated to only two T atoms in the monoclinic modification is significantly smaller than that of anorthite by about 5°. The corresponding angle in the hexagonal modification has an extreme value of 180°. That at oxygen atoms coordinated to two T atoms and one Ca atom in the monoclinic modification is again smaller than that of anorthite, though the difference

Table 6. Comparison of the structure with those of other forms of $\text{CaAl}_2\text{Si}_2\text{O}_8$

	Coordination number of oxygen atom	Hexagonal	Monoclinic	Triclinic (anorthite)
T—O—T angle (mean)	2	180°	143.1°	148.5°
	3	119	129.7	131.9°
	4	—	—	136.9°
T—O length (mena)		1.68	1.682	1.682 Å
Ca—O length (mena)		2.39	2.463	2.498 Å
Polyhedra about Ca, with point symmetry		trigonal antiprism	trigonal prism	hexahedron or heptahedron relating to trigonal prism
		$\bar{3}m$	m (approximately)	1

is small and may not be significant. For the case of hexagonal modification, this angle is even smaller; the value is only 119°.

This situation may therefore be summarized as follows: the T—O—T angles at oxygen atoms in the metastable modifications of $\text{CaAl}_2\text{Si}_2\text{O}_8$ tend to be smaller than those of anorthite, with the exception of the 180° angles in the hexagonal modification. Since, in general, a decrease in the T—O—T angles in a structure produce the effect of an increasing Madelung potential of the structure, as has been shown by TAKÉUCHI and SADANAGA (1966) for the structure of xanthophyllite, the above trend in T—O—T angles might be related, though speculatively, to the metastability of the monoclinic and hexagonal modifications.

Pseudosymmetry

One of the remarkable features of the structure is its strong $Pm\bar{3}n$ ($P \frac{2}{m} \frac{2}{n} \frac{2}{n}$) pseudosymmetry. As has been discussed, the structure has failed to attain this higher symmetry owing to its nearly complete Si,Al order. If, therefore, silicon and aluminium atoms were distributed at random over the tetrahedral sites, all tetrahedra in the structure would become equal in size, and the structure would have space group

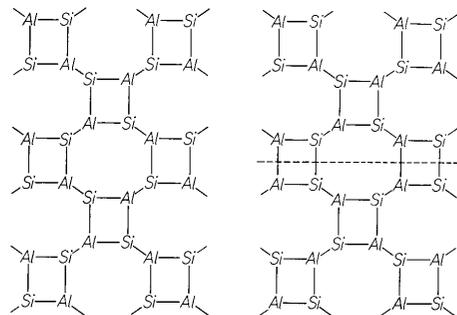


Fig. 8. Mechanism of twinning. Left: Schematic projection of the framework on (001). Right: Schematic representation of twinning on (100) viewed along the c axis. The broken line shows the twin boundary

$Pm\bar{3}n$. The Si,Al order necessarily suppresses twofold screw axes along the c axis of the space group $Pm\bar{3}n$, twofold axes along the a axis, and n glides parallel to the (001) plane. Specifically, however, the n glides parallel to the (010) plane are not necessarily affected by the Si,Al order (Fig. 4). This set of glides is missing in the $P2_1$ structure only because of a very slight distortion of the structure, not the result of tetrahedral occupancy. This is the reason why reflections are weak for $h0l$ spectra with $h+l=2n$, and why odd-ordered reflections of $h00$ spectra are almost all missing. The occurrence of odd-ordered reflections of $00l$ spectra is, as previously mentioned, mainly due to the difference in the site contents between the Ca(1) and Ca(2) sites. This difference has no influence on the $h00$ spectra because Ca atoms have, when projected on the a axis, a marked pseudoperiodicity of $a/2$.

We finally consider the possible mechanism of twinning. Any symmetry elements of $Pm\bar{3}n$, other than the 2_1 along the b axis, can act as twin elements. If any one of these elements is used to form a twin, it is readily shown that the regular alteration of small and large tetrahedra in the $P2_1$ structure is necessarily disturbed at its twin boundary, producing links of tetrahedra of the same size. This geometrical consideration therefore leads to the view that, physically, the formation of twins is closely related to mistakes in the alternating arrangement of silicon and aluminium tetrahedra which would occur in the process of crystal growth. The formation of twins based upon this mechanism is schematically shown in Fig. 8.

We are grateful to Prof. GABRIELLE DONNAY, McGill University, for critical reading of the manuscript, commenting and suggestions. We wish to thank Prof. R. SADANAGA for his interest in this work. We are indebted to Prof. Y. SAITO, Dr. F. MARUMO, Institute for Solid State Physics, and Prof. Y. IITAKA, Pharmaceutical Department, University of Tokyo, for their help in collecting counter-intensity data, and to Dr. D. WALKER, Harvard University, for microprobe analyses. The computations were performed at the Computer Centre of the University of Tokyo.

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