# The Structure of a Quaternary Phase Ca$_{20}$Al$_{32-2v}$Mg$_v$Si$_v$O$_{68}$

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## Abstract

The crystal structure of a quaternary phase $Q$, Ca$_{20}$Al$_{32-2v}$Mg$_v$Si$_v$O$_{68}$, has been determined by X-ray analysis. The compound crystallizes in the ortho-rhombic space group *Pmmn* with $a = 27 \cdot 638$ (3), $b = 10 \cdot 799$ (2), $c = 5 \cdot 123$ (1) Å. Owing to the isoelec-tronic nature of the ions Mg$^{2+}$, Al$^{3+}$ and Si$^{4+}$, block-diagonal least-squares refinement of atomic positional coordinates and anisotropic temperature parameters has resulted in an $R$ of $0 \cdot 085$ for com-positions with $v = 2$, 3 and 4. Crystal-chemical considerations have been applied for the indirect determination of $v$, based on comparison of the observed and calculated interatomic distances within $M$O$_4$ tetrahedra ($M$ = Mg/Al, Si/Al, or Al); $v$ acquired a value between 2 and 3. The structure contains twelve AlO$_4$, twelve (Mg,Al)O$_4$ and eight (Al,Si)O$_4$ tetrahedra with mean $M$–O distances of $1 \cdot 76$, $1 \cdot 79$ and $1 \cdot 71$ Å respectively. AlO$_4$ and (Al,Si)O$_4$ tetrahedra are linked through corners to form a network of five-membered rings, similar to those found in gehlenite and in 5CaO.3Al$_2$O$_3$. These differ in the propagation of the five-membered rings of $M$O$_4$ tetrahedra. While in $Q$, $M$O$_4$ tetrahedra are connected into infinite strips of five-membered rings in the **b** direction separated by chains of (Mg,Al)O$_4$ tetrahedra, the five-membered rings in the last two compounds extend into infinite networks. Twelve Ca$^{2+}$ ions in $Q$ are coordinated by eight O$^{2-}$, and eight Ca$^{2+}$ by six O$^{2-}$ anions. The structural formula is $^{VIII}$Ca$_{12}$$^{IV}$Ca$_8$$^{IV}$Al$_{32-2v}$$^{IV}$Si$_v$-$^{IV}$O$_{68}$. The epitaxial overgrowth of 3CaO.2Al$_2$O$_3$.-MgO on $Q$ is discussed.

## Introduction

The system CaO–Al$_2$O$_3$–MgO–SiO$_2$ is one of the most intensively and thoroughly studied quaternary oxide systems because of its importance to silicate tech-nology and geology. The phase relationships presented in previous studies disagree particularly as to the existence, composition and stability of a quaternary compound $Q$. Parker & Ryder (1954) suggested that $Q$

had the composition $C_6A_4MS$ (in the shorthand notation $C$ = CaO, $A$ = Al$_2$O$_3$, $S$ = SiO$_2$, $M$ = MgO). Biggar (1971) apparently accepted this formula. However, Glasser & Marr (1975) believed that the composition $C_6A_4MS$ consisted of two separate com-pounds: one was $Q$, to which they assigned the formula $C_{22}A_{13}M_3S_4$, and the other, $R$, had the composition $C_{21}A_{14}M_7S$. Majumdar (1966) obtained crystallo-graphic data for $Q$ and verified the anticipated composition. The molar mass of $Q$ corresponding to his crystal data turned out to be significantly lower than that of the formula $C_6A_4MS$. This important con-clusion escaped notice in successive work dedicated to the quaternary phase $Q$. Thus, the formula Ca$_{35}$-Mg$_4$Al$_4$(Al$_2$O$_7$)$_8$(AlO$_4$)$_{13}$(SiO$_4$)$_5$ proposed by Midgley (1968) seems to have an unacceptably high molar mass. Moreover, the formula contains insufficient O atoms to balance the positive charge of the cations (Glasser & Marr, 1975). Aruja (1957) discussed the pronounced crystallographic similarity of $Q$ both to gehlenite ($C_2AS$) and to $C_5A_3$.

The purpose of this work is to give reliable chemical and structural characteristics of $Q$.

## Experimental

$Q$ was synthetized from standardized precursors [normalized aqueous solutions of Ca(NO$_3$)$_2$, Al(NO$_3$)$_3$, Mg(NO$_3$)$_2$, and sol.SiO$_2$, prepared from analytical grade CaCO$_3$, Al$_2$O$_3$, MgO and SiO$_2$]. The stoichio-metric mixtures were first dried at 373 K, then the temperature was slowly increased to 1000 K to decompose the nitrates. Afterwards, the samples were cooled, homogenized in an agate mortar and com-pressed to cylindrical pellets. These were heated for 4 h at 1550 K. The compositions of ignited systems were varied in order to find the stoichiometry which gave the purest phase $Q$ with a minimum amount of accom-panying phases. The composition was checked by X-ray phase analysis with a Philips 1540 powder diffractometer [Cu $K\alpha$ radiation, $\lambda = 1 \cdot 54178$ Å, scanning rate 1° ($2\theta$) min$^{-1}$]. Several compositions

within the concentration limits (20–22)CaO.(12–14)-$Al_2O_3$.(2–4)MgO.(2–4)$SiO_2$ gave a single phase. If we write the general formula as $Ca_xAl_uMg_vSi_w$-$O_{x+(3/2)u+v+w}$ (I), the probable composition of $Q$ should occur in limits: $x = 20$–22, $u = 24$–28, $v = 2$–4, $w = 2$–4.

Single crystals of $Q$ were prepared in two ways: first, by slow cooling of systems from the liquidus temperature above 1650 K (crystallization from the melt) and, secondly, by annealing the composition for 600 h at 1550 K (single-crystal formation by direct solid-state reaction at subsolidus temperature). All heating experiments were performed with compositions within the above concentration limits. Although these compositions did not differ greatly from each other, they developed traces of different accompanying phases: $CA$, $C_{12}A_7$, $C_2S$, $C_2AS$, $MA$, MgO. These accompanying phases never grew as single crystals, but were present as microcrystalline admixtures. However, the single crystals of $Q$ from different syntheses always showed identical lattice parameters, suggesting that $Q$ forms only very limited solid solutions with accompanying phases. Glasser & Marr (1975) reached a similar conclusion.

Crystals available for X-ray analysis were of rather poor quality. The best crystal which could be used for data collection had a regular form (0·10, 0·15, 0·25 mm) and gave excellent sharp diffraction patterns. Several very weak extra spots (four reflections in the $hk0$ zone) could be detected on Weissenberg films. They probably arose from a subparallel twinning of a small part of the accompanying phase, $X$, epitaxially grown on the basic $Q$-phase substrate. Preliminary Weissenberg photographs revealed that the crystals of both compounds, $Q$ and $X$, are orthorhombic.

## Crystal data

Cell dimensions of $Q$ were obtained by least squares from 15 reflections determined on a Syntex $P2_1$ automated four-circle diffractometer with a graphite monochromator and Mo $K\alpha$ radiation at 293 K. These were $a = 27\cdot638$ (3), $b = 10\cdot799$ (2), $c = 5\cdot123$ (1) Å, $V = 1529\cdot025$ Å$^3$, in fair agreement with the data of Majumdar (1966).

From the Weissenberg photographs, the approximate lattice parameters of the accompanying phase $X$ and its orientation relative to $Q$ could be established: $a_X$ $\sim 16\cdot6$, $b_X \sim 10\cdot8$, $c_X \sim 5\cdot12$ Å; $\mathbf{a}_X = \mathbf{a}_Q$, $\mathbf{b}_X = \mathbf{b}_Q$, $\mathbf{c}_X = \mathbf{c}_Q$. The lattice parameters of $X$ may be compared with the values for $Ca_3Al_4MgO_{10}$ ($C_3A_2M$) (Majumdar, 1966): $a_{C_3A_2M} = 16\cdot77$, $b_{C_3A_2M} = 10\cdot72$, $c_{C_3A_2M} = 5\cdot13$ Å.

Though the phase $X$ represents only an extremely small part of the single crystal investigated, the identification of $X$ with $C_3A_2M$ allows some important

conclusions to be drawn about the reaction mechanism in the synthesis of $Q$ and about a close structural relationship between both phases. On the other hand, the expected interference of some reflections of the two compounds might, at least in the case of weak reflections, spoil the agreement between observed and calculated structure factors.

Three possible space groups were assigned to the crystal structure of $Q$ by Majumdar (1966): $P2_12_12$, $Pmm2$ or $Pmmn$. According to the systematic absences of reflections $hk0$ with $h + k = 2n + 1$ (640 reflections were checked), the true space group is unambiguously $Pmmn$.

$D_m$ was determined by flotation in a mixture of Clerici's solution and $H_2O$ at 298 K as 2·983 (0·015) Mg m$^{-3}$. The molar mass corresponding to this value and to the cell volume is 2747·3 ± 13·8 g mol$^{-1}$. This experimental molar mass may be used for comparison with the assumed formula to prove its correctness. The equation for the calculation of the molar mass is:

$$\text{Molar mass} = 56\cdot079x + 50\cdot981u + 40\cdot311v$$
$$+ 60\cdot084w = 2747\cdot3 \text{ g mol}^{-1}. \quad (1)$$

Further limitations for the selection of a formula for $Q$ can be inferred from the space-group requirements. The multiplicity of any equivalent position of the space group $Pmmn$ is $2n$, where $n = 1, 2$ or 4. Therefore, any formula requiring, for example, odd numbers of O atoms in the unit cell should be incorrect, provided no vacant positions occur. The number, $A$, of O atoms in the cell is defined by

$$A = x + \tfrac{3}{2}u + v + 2w. \quad (2)$$

We also suppose that $Ca^{2+}$ ions do not create solid solutions with $Al^{3+}$, $Mg^{2+}$ or $Si^{4+}$ ions. For this reason, the Ca atoms should occupy independent positions having even multiplicities. However, the $Al^{3+}$ and $Mg^{2+}$, as well as $Al^{3+}$ and $Si^{4+}$, ions are likely to occur statistically in common equivalent positions. In this case, we can leave out formulae in which the sum $B$ of Al, Mg and Si atoms in the unit cell,

$$B = u + v + w, \quad (3)$$

would be an odd number.

Direct methods give the possibility of developing a self-consistent solution of this problem by X-ray structure analysis. The number of main peaks in the $E$ map corresponding to the Ca atoms is 20 ($x = 20$); the number of second-highest peaks which can be attributed to the $B$ ions is 32. The value $B = 32$ establishes that

$$v = w, \quad (4)$$

which means that an equivalent substitution of ($Mg^{2+}$ + $Si^{4+}$) for $2Al^{3+}$ takes place. The values $A$ (O), $u$ (Al) and $v$ (Mg or Si) follow from solution of (1)–(4). While the number of O atoms, $A$, is found to be fixed with $A =$

68, the values of $u$ and $v$ are acceptable with variable ratios of Al, Mg and Si, at a constant sum $B = 32$. The value of $v$, compatible with the requirements of phase analysis (Kaprálik & Hanic, 1980), is limited within the interval $\varepsilon \langle 2 \cdot 5, v, 3 \cdot 5 \rangle$. Thus, the composition of $Q$ is defined through the formula $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$ (II). Both previously proposed formulae for $Q$ [$C_{24}A_{16}M_4S_4$ (Parker & Ryder, 1954) and $C_{22}A_{13}M_3S_4$ (Glasser & Marr, 1975)] show unacceptably high molar masses and calculated densities.

The number of electrons, $Z_o$, in the unit cell is constant irrespective of the value $v$ ($Z_o = 1360$). This also means that evaluation of normalized structure factors, $E_{hkl}$, gives much the same results irrespective of which formula (II) was employed for the scaling.

In connection with the epitaxial growth of $C_3A_2M$ on $Q$, it may be noted that $D_x$ of $C_3A_2M$ (2·986 Mg m$^{-3}$) is practically identical with that of $Q$.

Intensities for $Q$ were recorded on a Syntex $P2_1$ four-circle diffractometer by the $\theta$–$2\theta$ scan technique with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda_{MoK\alpha} = 0.71069$ Å) to a $2\theta$ maximum of 60°. The scan speed was variable, according to the peak intensity. The background was measured on both sides of the scanning range by stationary counting for half the scan time. The intensities of two standard reflections were measured every 100 reflections.

The net intensity, $I$ (relative to a constant scan rate of 1° min$^{-1}$), and its e.s.d., $\sigma(I)$, were evaluated from:

$$I = \left( T - \frac{B}{R} \right) W, \qquad (5)$$

$$\sigma(I) = \left( T + \frac{P}{R^2} \right)^{1/2} W. \qquad (6)$$

$T$ is the total scan count, $B$ the total background count given by the sum of left $B_1$ and right $B_2$ background counts, $R$ the background count to scan time ratio, and $W$ the scan speed. 2349 measured intensities were reduced to 1218 observed intensities [$I > 1 \cdot 96\sigma(I)$] with $INTER$ based on the $XTL$ system (Langer, 1977). No absorption or extinction corrections were made ($\mu = 2 \cdot 24$ mm$^{-1}$). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

## Structure determination and refinement

The structure was solved by direct methods with *TANFOR* (Drew & Larson, 1968). The $E$ Fourier synthesis computed with the sign combination having the highest figures of merit correctly revealed the peaks of all cations and the majority of the O atoms. Two successive cycles of Fourier syntheses calculated with *DRF* (Zalkin, 1970) served to find the positions of all atoms and to refine them. The formula $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$ was unambiguously verified. The atomic

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

| | Ca(1) | Ca(2) | Ca(3) | Ca(4) | Al(1) |
|---|---|---|---|---|---|
| $x$ | 0.0686 (1) | 0.8127 (1) | 0.2500 | 0.1249 (1) | 0.8974 (2) |
| $y$ | 0.9219 (2) | 0.2500 | 0.0884 (3) | 0.2500 | 0.2500 |
| $z$ | 0.3136 (4) | 0.6802 (7) | 0.2795 (6) | 0.2773 (7) | 0.2399 (9) |

| | Al(2) | MA(1) | MA(2) | SA(1) | SA(2) |
|---|---|---|---|---|---|
| $x$ | 0.8492 (1) | 0.9543 (1) | 0.0161 (2) | 0.2500 | 0.1943 (2) |
| $y$ | 0.9964 (3) | 0.8989 (3) | 0.2500 | 0.8929 (4) | 0.2500 |
| $z$ | 0.1975 (6) | 0.1256 (6) | 0.3719 (9) | 0.8434 (9) | 0.7376 (9) |

| | O(1) | O(2) | O(3) | O(4) | O(5) |
|---|---|---|---|---|---|
| $x$ | 0.9568 (3) | 0.8976 (3) | 0.8688 (2) | 0.7993 (3) | 0.8347 (3) |
| $y$ | 0.8800 (6) | 0.9463 (6) | 0.1205 (7) | 0.0383 (7) | 0.8741 (7) |
| $z$ | 0.4740 (15) | 0.9952 (14) | 0.3857 (12) | 0.0105 (13) | 0.4092 (13) |

| | O(6) | O(7) | O(8) | O(9) | O(10) |
|---|---|---|---|---|---|
| $x$ | 0.0379 (4) | 0.0000 | 0.8971 (4) | 0.1952 (4) | 0.2500 |
| $y$ | 0.2500 | 0.0000 | 0.2500 | 0.2500 | 0.8899 (10) |
| $z$ | 0.0365 (21) | 0.0000 | 0.9018 (20) | 0.0661 (21) | 0.5158 (20) |

| | O(11) | O(12) | O(13) |
|---|---|---|---|
| $x$ | 0.9541 (4) | 0.2500 | 0.2500 |
| $y$ | 0.2500 | 0.2500 | 0.7500 |
| $z$ | 0.4063 (19) | 0.5994 (30) | 0.9898 (30) |

arrangement derived from the Fourier syntheses was used as a starting set in the block-diagonal least-squares refinement with the anisotropic thermal parameters. The refinement was based on the observed reflections with NRC programs (Ahmed, Hall, Pippy & Huber, 1966).

Three models were refined, with $v = 4$, 3 and 2. The occupation of equivalent positions by the Al, Mg and Si atoms was deduced from interatomic distances within $MO_4$ tetrahedra and from the assumed formula as explained below. All three models converged, due to the isoelectronic nature of Mg$^{2+}$, Al$^{3+}$ and Si$^{4+}$, with $R = 0.085$, and weighted $R_w = 0.059$.* In the final cycles the largest shift in any parameter was <10% of its e.s.d. The final positional parameters of corresponding atoms in all three models differed by less than one e.s.d. Table 1 presents the coordinates corresponding to the model in which $v$ is assumed to be 3 ($Ca_{20}Al_{26}Mg_3Si_3O_{68}$).

## Description of the structure and discussion

Bond lengths and angles are presented in Tables 2 and 3. The results were calculated by the NRC programs (Ahmed *et al.*, 1966). Even though the bond lengths and angles in Tables 2 and 3 relate to the model $Ca_{20}Al_{26}Mg_3Si_3O_{68}$, they also represent results for $Ca_{20}Al_{24}Mg_4Si_4O_{68}$ and $Ca_{20}Al_{28}Mg_2Si_2O_{68}$ within

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Table 2. *Bond lengths* (Å) *in* $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$, *with e.s.d.'s in parentheses*

Ca(1)–O$_6$

| | |
|---|---|
| Ca(1)–O(1) | 2·500 (8) |
| Ca(1)–O(2) | 2·325 (7) |
| Ca(1)–O(3) | 2·362 (7) |
| Ca(1)–O(7) | 2·624 (2) |
| Ca(1)–O(8) | 2·359 (7) |
| Ca(1)–O(11) | 2·428 (7) |
| ⟨Ca(1)–O⟩ | 2·433 |

Ca(2)–O$_8$

| | |
|---|---|
| 2× Ca(2)–O(3) | 2·577 (7) |
| 2× Ca(2)–O(4) | 2·869 (8) |
| Ca(2)–O(8) | 2·595 (11) |
| 2× Ca(2)–O(10) | 2·508 (8) |
| Ca(2)–O(13) | 2·420 (11) |
| ⟨Ca(2)–O⟩ | 2·615 |

Ca(3)–O$_8$

| | |
|---|---|
| 2× Ca(3)–O(4) | 2·436 (8) |
| 2× Ca(3)–O(5) | 2·862 (7) |
| 2× Ca(3)–O(9) | 2·557 (8) |
| Ca(3)–O(10) | 2·462 (11) |
| Ca(3)–O(12) | 2·394 (11) |
| ⟨Ca(3)–O⟩ | 2·571 |

Ca(4)–O$_8$

| | |
|---|---|
| 2× Ca(4)–O(1) | 2·949 (9) |
| 2× Ca(4)–O(2) | 2·614 (7) |
| 2× Ca(4)–O(5) | 2·370 (8) |
| Ca(4)–O(6) | 2·702 (11) |
| Ca(4)–O(9) | 2·222 (11) |
| ⟨Ca(4)–O⟩ | 2·599 |

Al(1)–O$_4$

| | |
|---|---|
| 2× Al(1)–O(3) | 1·772 (7) |
| Al(1)–O(8) | 1·732 (11) |
| Al(1)–O(11) | 1·783 (11) |
| ⟨Al(1)–O⟩ | 1·765 |

Al(2)–O$_4$

| | |
|---|---|
| Al(2)–O(2) | 1·775 (8) |
| Al(2)–O(3) | 1·736 (7) |
| Al(2)–O(4) | 1·740 (8) |
| Al(2)–O(5) | 1·756 (8) |
| ⟨Al(2)–O⟩ | 1·752 |

MA(1)–O$_4$

| | |
|---|---|
| MA(1)–O(1) | 1·798 (8) |
| MA(1)–O(2) | 1·780 (8) |
| MA(1)–O(6) | 1·822 (6) |
| MA(1)–O(7) | 1·788 (3) |
| ⟨MA(1)–O⟩ | 1·797 |

MA(2)–O$_4$

| | |
|---|---|
| 2× MA(2)–O(1) | 1·777 (8) |
| MA(2)–O(6) | 1·822 (12) |
| MA(2)–O(11) | 1·723 (11) |
| ⟨MA(2)–O⟩ | 1·775 |

SA(1)–O$_4$

| | |
|---|---|
| 2× SA(1)–O(4) | 1·722 (7) |
| SA(1)–O(10) | 1·678 (11) |
| SA(1)–O(13) | 1·716 (8) |
| ⟨SA(1)–O⟩ | 1·710 |

SA(2)–O$_4$

| | |
|---|---|
| 2× SA(2)–O(5) | 1·733 (8) |
| SA(2)–O(9) | 1·683 (12) |
| SA(2)–O(12) | 1·694 (8) |
| ⟨SA(2)–O⟩ | 1·711 |

are 1·95, 1·77 and 1·64 Å, respectively, for $r(^{IV}O^2) = 1·38$ Å. We can well suppose that twelve tetrahedra around Al(1) and Al(2) are occupied only by the Al atoms. Si and Al atoms enter into eight $MO_4$ tetrahedra



Fig. 1. The structure of $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$ projected on (001).

Table 3. *Bond angles* (°) *in* $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$ *with e.s.d.'s in parentheses*

| $O_i$–Ca(1)–$O_j$ | | $O_i$–Ca(3)–$O_j$ | |
|---|---|---|---|
| O(1)–Ca(1)–O(2) | 83·4 (0·3) | O(4)–Ca(3)–O(5) | 87·8 (0·2) |
| O(1)–Ca(1)–O(3) | 95·0 (0·3) | O(4)–Ca(3)–O(9) | 78·0 (0·3) |
| O(1)–Ca(1)–O(7) | 77·8 (0·2) | O(4)–Ca(3)–O(10) | 79·1 (0·3) |
| O(1)–Ca(1)–O(8) | 171·7 (0·3) | O(4)–Ca(3)–O(12) | 145·8 (0·3) |
| O(1)–Ca(1)–O(11) | 109·0 (0·3) | O(5)–Ca(3)–O(9) | 69·9 (0·2) |
| O(2)–Ca(1)–O(3) | 105·5 (0·2) | O(5)–Ca(3)–O(10) | 81·3 (0·3) |
| O(2)–Ca(1)–O(7) | 71·2 (0·2) | O(5)–Ca(3)–O(12) | 61·0 (0·3) |
| O(2)–Ca(1)–O(8) | 90·1 (0·3) | O(9)–Ca(3)–O(10) | 143·6 (0·3) |
| O(2)–Ca(1)–O(11) | 166·9 (0·3) | O(9)–Ca(3)–O(12) | 78·2 (0·3) |
| O(3)–Ca(1)–O(7) | 172·3 (0·2) | O(10)–Ca(3)–O(12) | 107·3 (0·3) |
| O(3)–Ca(1)–O(8) | 81·8 (0·3) | | |
| O(3)–Ca(1)–O(11) | 69·9 (0·3) | $O_i$–Ca(4)–$O_j$ | |
| O(7)–Ca(1)–O(8) | 104·9 (0·2) | O(1)–Ca(4)–O(2) | 70·3 (0·2) |
| O(7)–Ca(1)–O(11) | 114·9 (0·2) | O(1)–Ca(4)–O(5) | 78·4 (0·2) |
| O(8)–Ca(1)–O(11) | 77·2 (0·3) | O(1)–Ca(4)–O(6) | 61·0 (0·3) |
| | | O(1)–Ca(4)–O(9) | 151·6 (0·3) |
| $O_i$–Ca(2)–$O_j$ | | O(2)–Ca(4)–O(5) | 90·9 (0·2) |
| O(3)–Ca(2)–O(4) | 89·5 (0·2) | O(2)–Ca(4)–O(6) | 62·9 (0·3) |
| O(3)–Ca(2)–O(8) | 73·4 (0·2) | O(2)–Ca(4)–O(9) | 87·0 (0·3) |
| O(3) ·Ca(2)–O(10) | 81·6 (0·3) | O(5)–Ca(4)–O(6) | 136·7 (0·3) |
| O(3)–Ca(2)–O(13) | 147·1 (0·3) | O(5)–Ca(4)–O(9) | 85·4 (0·3) |
| O(4)–Ca(2)–O(8) | 81·8 (0·2) | O(6)–Ca(4)–O(9) | 123·7 (0·3) |
| O(4)–Ca(2)–O(10) | 70·6 (0·3) | | |
| O(4)–Ca(2)–O(13) | 59·7 (0·3) | $O_i$–Al(1)–$O_j$ | |
| O(8)–Ca(2)–O(10) | 142·8 (0·3) | 2× O(3)–Al(1)–O(8) | 114·8 (0·4) |
| O(8)–Ca(2)–O(13) | 109·8 (0·3) | 2× O(3)–Al(1)–O(11) | 101·0 (0·4) |
| O(10)–Ca(2)–O(13) | 77·6 (0·3) | O(8)–Al(1)–O(11) | 118·9 (0·4) |
| | | O(3)–Al(1)–O(3)' | 104·3 (0·4) |
| $O_i$–Al(2)–$O_j$ | | | |
| O(2)–Al(2)–O(3) | 109·0 (0·4) | $O_i$–SA(1)–$O_j$ | |
| O(2)–Al(2)–O(4) | 110·8 (0·4) | O(4)–SA(1)–O(4)' | 104·5 (0·4) |
| O(2)–Al(2)–O(5) | 107·7 (0·4) | 2× O(4)–SA(1)–O(10) | 116·3 (0·4) |
| O(3)–Al(2)–O(4) | 110·6 (0·4) | 2× O(4)–SA(1)–O(13) | 101·4 (0·4) |
| O(3)–Al(2)–O(5) | 108·0 (0·4) | O(10)–SA(1)–O(13) | 114·8 (0·5) |
| O(4)–Al(2)–O(5) | 110·7 (0·4) | | |
| | | $O_i$–SA(2)–$O_j$ | |
| $O_i$–MA(1)–$O_j$ | | O(5)–SA(2)–O(5)' | 101·2 (0·4) |
| O(1)–MA(1)–O(2) | 116·0 (0·4) | 2× O(5)–SA(2)–O(9) | 116·1 (0·4) |
| O(1)–MA(1)–O(6) | 110·4 (0·4) | 2× O(5)–SA(2)–O(12) | 103·8 (0·4) |
| O(1)–MA(1)–O(7) | 113·6 (0·3) | O(9)–SA(2)–O(12) | 113·9 (0·5) |
| O(2)–MA(1)–O(6) | 100·7 (0·4) | | |
| O(2)–MA(1)–O(7) | 108·2 (0·3) | | |
| O(6)–MA(1)–O(7) | 107·0 (0·3) | | |
| | | | |
| $O_i$–MA(2)–$O_j$ | | | |
| O(1)–MA(2)–O(1)' | 104·4 (0·4) | | |
| 2× O(1)–MA(2)–O(6) | 106·2 (0·4) | | |
| 2× O(1)–MA(2)–O(11) | 112·0 (0·4) | | |
| O(6)–MA(2)–O(11) | 115·3 (0·4) | | |

e.s.d.'s. The atomic arrangement may be seen in Fig. 1. The structure consists of alternating twisted sheets of distorted $AlO_4$, $(Al,Mg)O_4$ and $(Al,Si)O_4$ tetrahedra and layers of $Ca^{2+}$ ions oriented perpendicular to [001]. As $Mg^{2+}$, $Al^{3+}$ and $Si^{4+}$ are isoelectronic, the expected heights of the electron density maxima are approximately the same. Substitution of Mg for Al, or Si for Al can be more precisely suggested from the interatomic distances within tetrahedra, since the ionic radii of $Mg^{2+}$, $Al^{3+}$ and $Si^{4+}$ ions differ significantly: $r(^{IV}Mg^{2+}) = 0·57$, $r(^{IV}Al^{3+}) = 0·39$, $r(^{IV}Si^{4+}) = 0·26$ Å (Shannon, 1976). The unit cell of $Q$ contains 32 $MO_4$ tetrahedra. Four tetrahedra around Al(1) and eight around Al(2) give average distances of 1·765 and 1·752 Å respectively. Four tetrahedra $SA(1)O_4$ give an average $M$–O distance of 1·710 Å; within four $SA(2)O_4$ it is 1·711 Å. Eight $MA(1)O_4$ tetrahedra show an average $M$–O distance of 1·797 Å; four $MA(2)$ tetrahedra give an average value of 1·775 Å. E.s.d.'s of single bonds lie between 0·004 and 0·012 Å. The expected distances in $MgO_4$, $AlO_4$ and $SiO_4$ tetrahedra

around $SA(1)$ and $SA(2)$ central atoms. Twelve $MO_4$ tetrahedra around the $MA(1)$ and $MA(2)$ atoms contain Mg and Al atoms.

The $M$—O distances within $MO_4$ tetrahedra vary according to the degree of substitution of Mg for Al, or Si for Al controlled by the composition $Ca_{20}Al_{32-2v}$-$Mg_vSi_vO_{68}$. The ratios Mg to Al, and Si to Al within $MO_4$ tetrahedra are given as $Mg_{v/12}Al_{(12-v)/12}$ (III) or $Si_{v/8}Al_{(8-v)/8}$ (IV). Depending on $v$, the interatomic distances $M$—O vary as:

$$(Al-O)_{calc} = 0.39 + 1.38 = 1.77 \text{ Å} \tag{7}$$

$$(Mg,Al-O)_{calc} = \frac{1.95v}{12} + \frac{1.77(12-v)}{12}$$
$$= (1.77 + 0.015v) \text{ Å} \tag{8}$$

$$(Si,Al-O)_{calc} = \frac{1.64v}{8} + \frac{1.77(8-v)}{8}$$
$$= (1.77 - 0.016v) \text{ Å}. \tag{9}$$

Fig. 2 shows the dependence of the function

$$\sum_{i=1}^{32} [(M_i-O)_{calc} - (M_i - O)_{obs}]^2 \tag{10}$$

on $v$. All 32 $MO_4$ tetrahedra are included in summation (10). The function shows a minimum between $v = 2$ and 3. The conclusions of the crystallographic investigation agree well with the results of phase-equilibria research in the system $CaO-Al_2O_3-MgO-SiO_2$ (Kaprálik & Hanic, 1980).

$MO_4$ tetrahedra show the following arrangement: $AlO_4$ and $(Al,Si)O_4$ tetrahedra are linked through corners to form a network of five-membered rings. A

comparison of Figs. 3 and 4 with Fig. 1 shows that, in general, the arrangement of tetrahedra is essentially the same as that found in gehlenite, $Ca_2Al_2SiO_7$ ($C_2AS$): $P\bar{4}2_1m$, $a = 7.717$, $c = 5.086$ Å (Louisnathan, 1970), and in $Ca_5Al_6O_{14}$ ($C_5A_3$): $Cmc2_1$, $a = 11.253$, $b = 10.996$, $c = 10.290$ Å (Vincent & Jeffery, 1978). The difference between the structure of $Q$ on the one hand and $C_2AS$ and $C_5A_3$ on the other is in the extension of the five-membered rings. While in $C_2AS$ and $C_5A_3$, the $MO_4$ tetrahedra condense into infinite networks of five-membered rings, in $Q$ they extend infinitely in only one direction [010]. These chains of five-membered rings are separated by chains of $(Al,Mg)O_4$ tetrahedra. The $(Al,Mg)O_4$ chains are linked through common O—O edges and O vertices into layers perpendicular to [100]. The diffusion of Mg into the structure of $Q$ probably takes place along these layers. They are also of importance in twinning between $Q$ and $C_3A_2M$, as shown in Fig. 5 which portrays the overgrowth of the $C_3A_2M$ structure on $Q$, consistent with the cell dimensions and the twinning condition.

Some typical $M$—O—$M'$ bond angles appear in the five-membered rings (Fig. 6). The largest angles are $SA(1)$—$O(4)$—$SA(1)'$ and $SA(2)$—$O(12)$—$SA(2)'$ (128.2 and 130.6° respectively), in which O atoms link



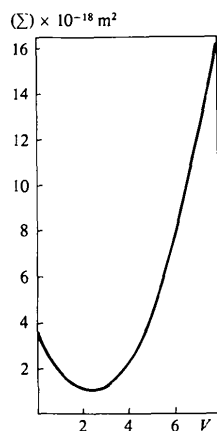Fig. 3. The structure of gehlenite projected on (001) (after Louisnathan, 1970).
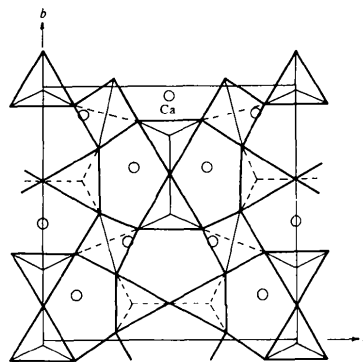


Fig. 2. Dependence of the function $\sum_{i=1}^{32}[(M_i - O)_{calc} - (M_i - O)_{obs}]^2$ on $v$ for $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$.



Fig. 4. The structure of $5CaO.3Al_2O_3$ projected on (001) (after Vincent & Jeffery, 1978).

Fig. 5. Twinning between $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$ and the proposed structure of $3CaO.2Al_2O_3.MgO$ $(C_3A_2M)$.



Fig. 6. Some typical $M-O-M'$ bond angles (°) in $Ca_{20}Al_{32-2v}$ $Mg_vSi_vO_{68}$ (e.s.d.'s are 0·3–0·5°).

Table 4. *Packing of atoms in* $Ca_{20}Al_{32-2v}Mg_vSi_vO_{68}$ *(Q)*, $Ca_2Al_2SiO_7$ *($C_2AS$), and* $Ca_5Al_6O_{14}$ *($C_5A_3$)*

($\varphi$ = the space-filling factor, $V$ = the unit-cell volume).

| Structural formula | $^{VIII}Ca_{12}{}^{VI}Ca_8$- $^{VI}M_{32}{}^{IV}O_{68}$ | $^{VIII}Ca_2{}^{IV}Al_2$- $^{IV}Si^{IV}O_7$ | $^{VI}Ca_5{}^{IV}Al_6{}^{IV}O_{14}$ |
|---|---|---|---|
| $\varphi$ | 0·563 | 0·590 | 0·556 |
| $\sum (M + Ca)/\sum MO_4$ | 1·625 | 1·667 | 1·833 |
| $\sum Ca/\sum MO_4$ | 0·625 | 0·666 | 0·834 |
| $\sum MO_4/\sum Ca$ | 1·600 | 1·500 | 1·200 |
| $\sum (M + Ca)/\sum O$ | 0·765 | 0·713 | 0·785 |
| $V/\sum O$ (Å³) | 22·486 | 21·634 | 22·675 |
| $D_m$ (Mg m⁻³) | 2·983 | 3·001 | 3·066 |
| $\langle Ca-O \rangle$ (Å) | 2·530 | 2·563 | 2·424 |
| $\varphi \sum (M + Ca)/\sum O$ | 0·431 | 0·421 | 0·436 |

distance $\langle Ca-O \rangle$ decreases in the expected order: 2·563 in $C_2AS$, 2·530 in $Q$ and 2·424 Å in $C_5A_3$. The space-filling factor $\varphi$, defined as the fraction of the unit-cell volume occupied by the ions, shows the same tendency: $\varphi_{C_2AS} = 0·590$, $\varphi_Q = 0·563$, $\varphi_{C_5A_3} = 0·556$. The number of cations per O atom, $\sum (M + Ca)/\sum O$, is inversely proportional to $\varphi$ in such a way that the product remains approximately constant: 0·421, 0·431 and 0·436, respectively.

The number of cations per $MO_4$ tetrahedron (Table 4), as well as the number of Ca per $MO_4$ are comparable in $Q$ and $C_2AS$ but they differ significantly from that in $C_5A_3$. This jump in cation content may be a reason for the doubling of $c$ in $C_5A_3$.

Accumulation of Mg and Al, as well as Si and Al, in separate layers and strips supports a suggestion that creation of the $Q$ phase in the system $CaO-Al_2O_3-MgO-SiO_2$ takes place in the subsolidus domain through a diffusion process which is rather slow.

All calculations were performed in the Computing Centre of Bratislava University on a Siemens 4004/150 computer. We are obliged to Dr Soldanova for her assistance in the intensity measurements.

central atoms partially occupied by Si atoms. All other $M-O-M'$ angles fluctuate between 114·8 and 123·9°, with an average of 119°.

Layers of Ca atoms lie approximately perpendicular to [001]. Four equivalent Ca(2), Ca(3) and Ca(4) atoms are coordinated by eight O atoms, the average Ca—O distances being 2·615, 2·571 and 2·599 Å respectively. Eight Ca(1) atoms are coordinated by six O atoms with an average Ca—O distance of 2·433 Å. The expected theoretical distances $^{VIII}Ca-^{IV}O$ and $^{VI}Ca-^{IV}O$ are 2·50 and 2·38 Å (Shannon, 1976). The corresponding distances differ by 0·1 and 0·05 Å, respectively, from those observed. The reason for this small elongation is not clear. There is a certain amount of electrostatic repulsion in the structure due to some short Ca—$M$ contacts: Ca(3)—$SA$(1) = 3·074, Ca(1)—Al(1) = 3·092, Ca(1)—$MA$(1) = 3·034 Å, which may contribute to this elongation.

Comparing coordination around Ca, we find the highest coordination number in gehlenite ($C_2AS$) (eight O atoms) and the lowest in $C_5A_3$ (six O atoms). $Q$ has both six and eight coordination. The observed average

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# Neutron Diffraction Studies of Polyiodides.
# I. Potassium Triiodide Monohydrate

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## Abstract

The crystal structure of $KI_3.H_2O$ has been determined directly from neutron diffraction data giving $R_{F^2} = 0.027$. This compound crystallizes in the monoclinic space group $Pc$ with $a = 4.629$ (1), $b = 10.047$ (3), $c = 9.662$ (3) Å, $\beta = 116.51$ (1)°, $Z = 2$. The linear $I_3^-$ ions are arranged in planes in a mutually perpendicular manner and are found to be very nearly symmetric [I—I = 2.925 (3), 2.935 (3) Å]. The $K^+$ ion and the water molecule are between the iodine planes, each water molecule being coordinated to two $K^+$ ions.

## Introduction

The $I_3^-$ ion is of interest because its structure is malleable to its crystal environment and, because of this, it has received considerable theoretical treatment (Brown & Nunn, 1966; Wiebenga & Kracht, 1969; Gabes & Nijman-Meester, 1973). Several structures containing the $I_3^-$ ion have been determined, usually containing a large cation or a cation solvated with organic molecules (see Table 4, in which are listed structural details of $I_3^-$ salts but excluding the linearly extended polyhalides found in channel inclusion complexes and $I_3^-$ units which form part of higher polyiodides). In order to investigate further the effect of the crystal environment on the structures of poly-

iodides, this study of the polyiodides of hydrated cations was commenced. This report represents the first structural determination of a polyiodide of a simple hydrated cation, which in the past has proved to be difficult by conventional X-ray diffraction because of the poor stability of such compounds to X-radiation. However, because it was possible to grow large crystals the stability problem was overcome by the use of neutron diffraction.

An account of the preparation of $KI_3.H_2O$ was first published by Johnson (1877) and the macroscopic crystallography was described by Wells, Weeler & Penfield (1892). An initial X-ray examination was carried out by Clark & Duane (1923) and the structure has provided the basis for a doctoral thesis (Finney, 1973).

## Preparation and mounting of the crystal

$KI_3.H_2O$ was prepared by dissolving a mixture of analytical grade KI and $I_2$ in the proportion 31:60 in a minimum of water to produce a saturated solution on the solubility arc of $KI_3.H_2O$ as indicated by the ternary phase diagram of Briggs, Clack, Ballard & Sassaman (1940). Slow evaporation over sulphuric acid at room temperature produced a crystal 3.8 × 4.6 × 5.5 mm. The composition of the crystals was checked by analysis ($I_2 = 58.00\%$; $KI_3.H_2O$ requires $I_2 = 57.99\%$).