CRYSTAL STRUCTURE OF THE CEMENT PHASE

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1970

SovietRxiv

Abstract

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UDC 548.736.6

CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF THE CEMENT PHASE

$Y = Ca_6[Si_2O_7][SiO_4](OH)_2$

The phase $Y = 6CaO \cdot 3SiO_2 \cdot H_2O \equiv C_6S_3H$ occupies a prominent place among calcium hydrosilicates ([1–3]). Its constant occurrence among the hydration products of cement clinker, its indifference to the composition and stoichiometry of the initial charge (phase Y arises under hydrothermal treatment of mixtures both from the silicates β-C_2S, γ-C_2S, $C_2SH(A)$, and from more elementary mixtures $CaO + SiO_2$, CaO+ quartz, $Ca(OH)_2 + SiO_2$, $CaCO_3$+ quartz, etc.), and its stability over a wide range of temperatures (up to 800°) and pressures (up to 2000 atm.) make phase Y one of the most stable products of hydration of Ca silicates, and thus often force one to represent differently the course of reactions in low-temperature hydrothermal synthesis, as well as in the processes of hydration and hardening of cement minerals. Nevertheless, up to now the structure of phase Y has not been deciphered.

For our X-ray structural analysis, colorless single-crystal fragments of size 0.1–0.2 mm were selected. The translations of the chosen triclinic cell, given by B. N. Delone ([4]), are the shortest and agree with those established earlier in ([2]): $a = 6.85$, $b = 6.95$, $c = 12.90$ Å; $\alpha = 90°45' \pm 15'$; $\beta = 97°20' \pm 20'$; $\gamma = 98°15' \pm 15'$; $Z = 2Ca_6Si_3O_{12} \cdot H_2O$. The three-dimensional Patterson function $P(uvw)$ was constructed from ~ 1800 nonzero reflections* $0kl$–$4kl$, $h0l$. The large number–18 medium atoms (12 Ca cations and 6 Si of similar scattering power) in the cell against a background of 26 light O atoms–caused numerous superpositions and overlaps of interatomic vectors Ca–Ca, Ca–Si, Ca–O and Si–Si and made their direct interpretation impossible.

It proved possible to extract the basic (point) system (b.s.) from the vector one with the aid of the "multiple peaks" method recently introduced into our X-ray structural practice ([6,7]). At the octahedron stage, first 10 points of the b.s. out of 18 were fixed, and then the remaining 8. However, the positions of these 18 points of the b.s. did not appear to be connected by a center of symmetry, and therefore (to avoid bias; cf. ([8])) the further solution of the structure was carried out within the acentric group $P1$**.

Fig. 1. Structure of phase Y. A three-membered wall of Ca polyhedra

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The discrepancy coefficient at this stage was 0.43. On the very first electron-density map $\rho(xyz)$, a regular alternation of maxima with periodicity $\sim b/2$ and $\sim c/6$ and $a/2$ was striking. This lattice substantially complicated both the identification of the points of the b.s. and the further solution. Although the 12 Ca atoms and 6 Si account for more than 60% of the scattering power of the cell, the R-factor did not fall below 0.40. The inclusion of the much lighter O atoms (with obligatory checking by $P(uvw)$—a process analogous to that described in ([6,7])) made it possible, in several cycles of syntheses of $\rho(xyz)$, to exclude false peaks, and within the group—

* MoK_α radiation, $\max \sin\theta/\lambda = 1.2$ Å^{-1}; intensities were estimated on the $\sqrt[4]{2}$ blackening scale; absorption was not taken into account because of the isometry of the sufficiently small specimen ($\sim 0.1\times0.15\times0.1$ mm), and also because there were no atoms in the cell that stood out in their scattering power. The latter excluded reservations in the statistical analysis of intensities ([5]), and according to its results the most probable was the Fedorov group $P\bar{1}$.

** It was subsequently found that two points of the identified b.s.— "foreign" ones—do not correspond to atoms, and precisely they violated centrosymmetry.

the group $P1$ to reduce R_{hkl} to 0.21 without introducing a thermal correction (1800 reflections; $\sin\theta/\lambda \leq 1.2$ Å^{-1}).

At this stage we nevertheless returned to the centrosymmetric variant. Least-squares refinement led to a decrease of R_{hkl} from the initial 0.25 to 0.128 with B_{hkl}—an isotropic thermal correction of 0.17 Å^2 (the corresponding R_{hkl} and B_{hkl} are 0.128 and 0.17 Å^2). In the absence of any clear advantage of one of the variants, it is natural to stop at the centrosymmetric one, and for it the final atomic coordinates are given in Table 1.

Three independent Si atoms are localized in tetrahedra. The distances Si_1-O = 1.63–1.65 Å with tetrahedral edges $O-O$ = 2.61–2.75 Å; Si_2-O =

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= 1.63–1.65 Å, with $O-O$ = 2.61–2.77 Å, and Si_3-O = 1.59–1.65 Å, with $O-O$ = 2.54–2.75 Å.

Of the six crystallographically independent Ca cations, three are surrounded by an octahedron: Ca_2-O = 2.32–2.52 Å, Ca_3-O = 2.28–2.51 Å, and Ca_5-O = 2.29–2.64 Å; moreover, for Ca_3 and Ca_5 one may single out one

Table 1

Fig. 2

Figure 2: Fig. 2

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Ca_1	0.082	0.194	0.103	O_3	0.615	0.184	0.806
Ca_2	0.192	0.206	0.489	O_4	0.747	0.153	0.174
Ca_3	0.315	0.191	0.876	O_5	0.988	0.149	0.910
Ca_4	0.560	0.034	0.321	O_6-(OH)	0.229	0.165	0.300
Ca_5	0.894	0.463	0.291	O_7	0.850	0.130	0.486
Ca_6	0.595	0.477	0.703	O_8-(OH)	0.192	0.210	0.685
Si_1	0.618	0.291	0.098	O_9	0.530	0.215	0.565
Si_2	0.809	0.285	0.885	O_{10}	0.743	0.336	0.999
Si_3	0.715	0.299	0.509	O_{11}	0.643	0.368	0.393
O_1	0.614	0.490	0.166	O_{12}	0.836	0.482	0.581
O_2	0.394	0.188	0.053	O_{13}	0.112	0.510	0.170

elongated distance (2.51 and 2.64 Å) among 2.28–2.43 Å, while for the Ca_2 cation there are two ($\sim$ 2.50 Å) against the background of four 2.32–2.38 Å. The three remaining Ca are located in seven-vertex polyhedra that are quite ordinary for large cations: a trigonal prism plus a half-octahedron. In them, too, one of the ligands is farther from the nucleus than the others: $Ca_6 - O$ = 2.31–2.48 and 2.61 Å,

Ca_4—O = 2.31—2.57 and 2.72 Å, Ca_1—O = 2.31—2.63 and 2.84 Å. The latter distance exceeds the average Ca_1—O (= 2.45 Å) by more than 15%, and subsequently (in describing the structure) the Ca_1 polyhedron was taken to be an octahedron.

In the structure of this more complex cement silicate, one may first of all distinguish a parallel (001) wall made up of Ca polyhedra (Fig. 1). In contrast to the walls described earlier in calcium silicates and in those of still larger cations ((8–10) and others), the wall is not continuous but trellis-like: in it, infinite chains parallel to the b axis, consisting of Ca semioctahedra (Ca_4 and Ca_6), are connected by discrete octahedra (Ca_5). In the windows there are OH^{1-} groups, whose role is discussed below.

Fig. 2. Phase Y projection xz. Highlighted: **A** –infinite ribbons of Ca octahedra; –against the background of the Ca motif, bonds of orthotetrahedra [SiO_4] and diorthogroups [Si_2O_7]

Along the c axis the cell is cut by two such walls, connected to one another by inversion centers. The latter are located in the gaps between the walls, and this permits the gaps to have different widths, as was recently found and seemed

unexpected in tilleyite [10]. In phase Y, one gap is twice as wide as the other, and in these gaps are placed the groups that bind the walls: groups of four Ca octahedra (Ca_1 and Ca_3) in the wide gaps and pairs (Ca_2) in the narrow ones. Through the windows in the walls (and through the mediation of the OH groups), the quadruplets and pairs are connected into continuous ribbons and, thus, the entire frame—

each of the six types of Ca polyhedra is a three-dimensional trellis with compartments—channels of two different cross sections.

Along the a axis (Fig. 2) the ribbons are joined to one another by island silicate radicals: pairs of octahedra by two orthogroups $[SiO_4]$, and foursomes by two diorthogroups $[Si_2O_7]$. In the empty octahedron between two orthogroups there is a center of symmetry, and in exactly the same way an empty centrosymmetric octahedron links the right tetrahedron of one diorthogroup with the left tetrahedron of another. Other centers of symmetry are located on the common edges of the group of two octahedra and of the central pair in the foursome. The origin of the cell has been chosen at the latter center.

Phase Y is the first Ca silicate and, together with epidote, zoisite, and $K_2Mn_2Zn_4[SiO_4]_2[Si_2O_7]$ (11), one of the few silicates in whose structures ortho- and diorthosilicate groups coexist.

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Received
29 X 1969

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Note: Figure translations are in progress. See original paper for figures.