

CRYSTALLOGRAPHY

CRYSTAL STRUCTURE OF CEMENT

PHASE Y = $\text{Ca}_6[\text{Si}_2\text{O}_7][\text{SiO}_4](\text{OH})_2$

R. M. Ganiev, V. V. Ilyukhin,
and Academician N. V. Belov

Institute of Crystallography, Academy of Sciences of the USSR, Moscow

Translated from Doklady Akademii Nauk SSSR, Vol. 190, No. 4,

pp. 831-834, February, 1970

Original article submitted October 29, 1969

The phase Y = $6\text{CaO} \cdot 3\text{SiO}_2 \cdot \text{H}_2\text{O} \equiv \text{C}_6\text{S}_3\text{H}$ occupies an important position in a number of calcium silicates [1-3]. Its unaltered appearance in the hydration products of cement clinker, its lack of dependence on the composition and stoichiometry of the basic mix [the phase Y arises during the hydrothermal treatment of mixes such as β - C_2S , γ - C_2S , $\text{C}_2\text{SH(A)}$ silicates, as well as from the reactions $\text{CaO} + \text{SiO}_2$, $\text{CaO} + \text{quartz}$, $\text{Ca(OH)}_2 + \text{SiO}_2$, $\text{CaO} + \text{quartz}$, $\text{Ca(OH)}_2 + \text{SiO}_2$, $\text{CaCO}_3 + \text{quartz}$, etc.], and its stability in a wide range of temperatures (up to 800°C) and pressures (up to 2000 atm) distinguishes the phase Y as one of the most stable products of hydration of Ca-silicates. By virtue of the above, the progress of the reaction, under conditions of low temperature hydrothermal synthesis and during the hydration and hardening of the cement minerals, should be represented in a different fashion. Nevertheless the phase Y structure has not been deciphered so far.

For our x-ray analysis uncrushed monocrystalline particles 0.1-0.2 mm size were chosen. The translations of the selected triclinical cells as shown by B. N. Delone [4] are the shortest and agree with those established earlier by L. Dent-Glasser et al. [2]. They are: $a = 6.85$, $b = 6.95$, $c = 12.90 \text{ \AA}$, $\alpha = 90^\circ 45' \pm 15'$, $\beta = 97^\circ 20' \pm 20'$, $\gamma = 98^\circ 15' \pm 15'$, $z = 2\text{Ca}_6\text{Si}_3\text{O}_{12} \cdot \text{H}_2\text{O}$. The three-dimensional Patterson function P (uvw) was constructed for 1800 nonzero reflections,¹ $0kl$, $-4kl$, $h0l$. A large number, i.e., 18 central atoms in the fundamental cell (12 Ca cations and 6 with a dispersive power close to Si) as against 26 light O atoms caused multiple superpositions and overlapping of interatom vectors Ca-Ca, Ca-Si, Ca-O and Si-Si, which rendered a direct interpretation impossible.

It was possible to separate the basic (point) system from the vectorial one with the help of the "multiple peak method" recently introduced into our x-ray structure practice [6, 7]. To begin with, 10 points out of a total of 18 were fixed on the basis of octahedra. Later, the remaining 8 were also fixed. However, the positions of these 18 points appeared to be unconnected to the center of symmetry and hence (for avoiding preconceived ideas, see Belov et al. [8]) further interpretation was conducted on the basis of the acentric group P1 .²

At this stage the deviation coefficient was 0.43. Prominently meeting the eye on the very first electron density chart ρ (xyz) was a regular sequence of maxima with a periodicity of $\sim b/2$ and $\sim c/6$ and $a/2$. This net considerably complicated both the identification of points on the basic system and the further interpretation. Though the 12 Ca atoms and 6 Si atoms account for more than 60 percent of the scattering power of the cell, the R-factor did not drop below 40%. Incorporation of lighter O atoms (with the necessary control on P (uvw) by a process analogous to the procedure described by Belov et al. and Kuzmin [6, 7]) facilitated the elimination of false peaks after several

¹MoK α source, $\max \sin \theta / \lambda = 1.2 \text{ \AA}^{-1}$; the intensity was evaluated on a $\sqrt{2}$ density scale; absorption was not taken into account in view of the sufficiently small sample size ($\sim 0.1 \times 0.15 \times 0.1 \text{ mm}$) and also the absence of atoms of exceptional scattering power in the cell. The latter made special stipulations in the statistical analysis of intensities [5] unnecessary and, as judged from the results, the Fedorov group PT was the most probable group.

²It was later discovered that two of the points of the basic system so fixed were "foreign points" i.e., did not correspond to atoms and thus violated the central symmetry.

TABLE 1

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	0.134	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	0.983	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	0.436
Ca ₆	0.595	0.477	0.703	O ₈ (OH)	0.192	0.210	0.685
Si ₁	0.613	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	0.363	0.393
O ₁	0.614	0.490	0.166	O ₁₂	0.836	0.482	0.581
O ₂	0.394	0.138	0.053	O ₁₃	0.112	0.510	0.170

synthesis cycles of $\rho(xyz)$. In the P1 group 1 R_{hkl} was lowered to 0.21 without making a thermal correction (1800 reflections $\sin \theta / \lambda \leq 1.2 \text{ \AA}^{-1}$).

At this stage we nevertheless reverted to the central symmetrical variant. A more precise idea about the polygon resulted in a reduction in $1R_{hkl}$ from an initial value of 0.25 to 0.128 when $1B_{hkl}$, the isotropic thermal correction, was $0.17 \text{ \AA}^2$ (the corresponding $1R_{hkl}$ and $1B_{hkl}$ values are 0.128 and $0.17 \text{ \AA}^2$ respectively). In the absence of any special apparent advantages in either of the variants attention was focussed on the central symmetrical system for which the final coordinates are presented in Table 1.

Three independent Si atoms are localized in the tetrahedra. The distances are: Si-O = 1.63-1.65 Å for tetrahedron edges O-O = 2.61-2.75 Å; Si₂O-O = 1.63-1.65 Å for O-O = 2.61-2.77 Å and Si₃-O = 1.59-1.65 Å for O-O = 2.54-2.75 Å.

Of the six crystallographically independent Ca cations three are octahedrally enclosed as follows: Ca₂-O = 2.32-2.52 Å, Ca₃-O = 2.28-2.51 Å, and

Ca₅-O = 2.29-2.64 Å; in this Ca₃ and Ca₅ have one longer distance (2.51 and 2.64 Å) as against 2.28 and 2.43 Å, while Ca₂ cations have two ($\sim 2.50 \text{ \AA}$) as against 2.32-2.38 Å for the rest. The remaining three Ca cations are located in a manner normal for large cations, in seven-vertex polyhedra - a triangular prism together with a half octahedron. Even here one of the points stands further away from the nucleus as compared to the rest: Ca₆-O = 2.31-2.63 and 2.84 Å. The last mentioned distance exceeds the average Ca₁-O (= 2.45 Å) by more than 15 percent and in further work the Ca₁ polyhedron was assumed to be an octahedron.

In the structure of this more complex cement silicate it is possible, in the first place, to distinguish a sheet of parallel Ca polyhedra (Fig. 1). In contrast to the calcium silicates and other heavier cations described earlier (Belov et al. [8, 10] and others) the face is not solid but trellised; in this the parallel b axes appear as continuous chains of Ca seven-vertex figures (Ca₄ and Ca₆) connected with discrete octahedra (Ca₅). Hydroxyl (OH⁻) groups are situated in the openings, about which more will be said later.

Intersecting along the C axis of the cell are two such faces which are connected to each other by centers of inversion. These centers are situated in the gaps between the faces and this permits the gaps to be of unequal width, as was unexpectedly discovered and demonstrated in the case of tundrite [10]. In phase Y one of the gaps is twice as wide as the other and groups of four Ca octahedra (Ca₁ and Ca₃) linking the faces are situated in the wider gaps, while the two other octahedra are in the narrow gaps. Through the openings in the faces (and through the OH groups) quartets and pairs are connected in a continuous strip and, therefore, the whole framework of six types of Ca polyhedra may be represented as a three-dimensional lattice with intercepting channels of two different cross-sections.

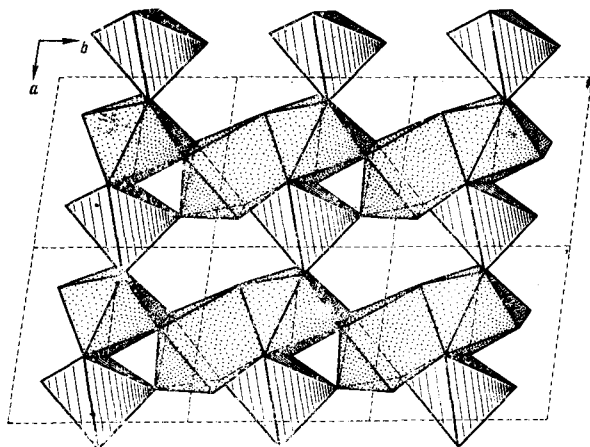


Fig. 1. The phase Y structure. Lattice faces of Ca polyhedra.

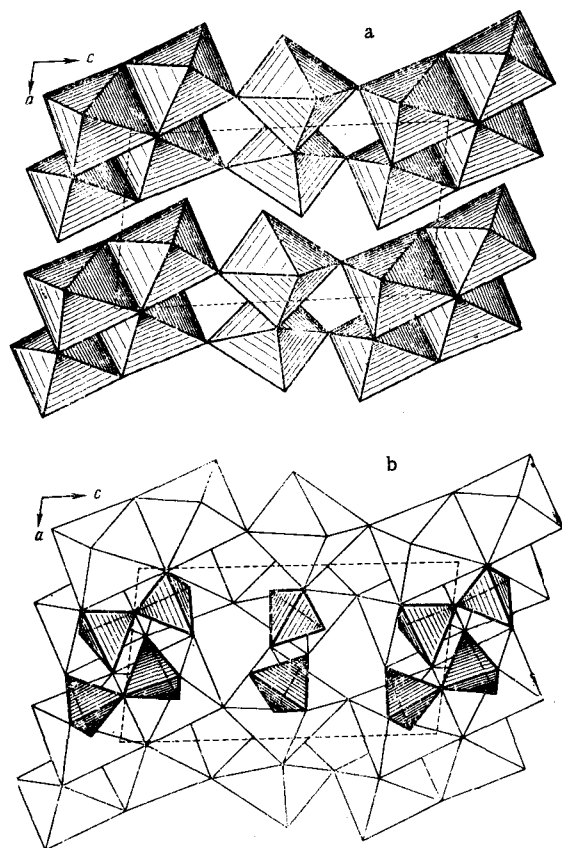


Fig. 2. xz projections for phase Y. Shown in the figure are: A) continuous strips of Ca octahedra; B) a bunch of SiO_4 orthotetrahedra and diorthogroups of Si_2O_7 on the background of a Ca motif.

Along the a axis (Fig. 2) the strips are connected to each other by silicon-oxygen radicals. Of these a pair of octahedrons is connected with two orthogroups SiO_4 while four others are connected by two diorthogroups Si_2O_7 . The center of symmetry is situated in the vacant octahedron between the two orthogroups, and precisely in the same manner the central symmetrical octahedron links

the right tetrahedron of one diorthogroup with the left tetrahedron of the other. Other centers of symmetry are located on the common edges of the group of two octahedra and the central pair in the other four. The origin of the cell is located at the last named center.

The phase Y is the first Ca silicate and along with epidote, tsoizite and $\text{K}_2\text{Mn}_4\text{Zn}_4[\text{SiO}_4]_2[\text{Si}_2\text{O}_7]$ it appears [11] to belong to a small group of silicates in which the structure is distinguished by ortho- and diorthosilicate groups.

LITERATURE CITED

1. L. Dent-Glasser and D. M. Roy, *Am. Mineral*, **44**, 447 (1959).
2. L. Dent-Glasser, H. Funk et al., *J. Appl. Chem.*, **11**, 5 (1961).
3. V. S. Bakshutov, R. M. Ganiev, V. A. Kuznetsov, V. V. Ilyukhin, and N. V. Belov, *Neorg. Materialy*, **4**, 2146 (1968).
4. V. Balashov, *Acta Crystallogr.*, **9**, 319 (1956).
5. E. R. Howells et al., *Acta Crystallogr.*, **3**, 210 (1950).
6. E. A. Kuzmin, V. V. Ilyukhin, and N. V. Belov, *Zh. Struk. Kh.*, **9**, 820 (1968).
7. E. A. Kuzmin, Dissertation, Moscow (1968).
8. R. F. Smirnova, I. M. Rumanova, and N. V. Belov, *Notes of the All-Union Mineralogical Society*, **84**, 159 (1955).
9. V. I. Simonov and N. V. Belov, *Kristallografiya*, **12**, 848 (1967) [*Sov. Phys.-Crystallogr.*, **12**, 740 (1968)].
10. N. G. Shumyatskaya, V. V. Ilyukhin, A. A. Voronkov, and N. V. Belov, *Dokl. Akad. Nauk*, **185**, 1289 (1969) [*Sov. Phys.-Dokl.*, **14**, 304 (1969)].
11. D. Yu. Pushcharovskii, E. A. Pobedinskaya, and N. V. Belov, *Dokl. Akad. Nauk*, **185**, 1045 (1969) [*Sov. Phys.-Dokl.*, **14**, 294 (1969)].