CALCIUM FLUOROSILICATES: THE $\text{Ca}_{6-0.5x}\text{Si}_2\text{O}_{10-x}\text{F}_x$ PHASE

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(Communicated by M. Regourd)
(Received Jan. 21, 1985)

ABSTRACT

The identity of $\text{Ca}_{6-0.5x}\text{Si}_2\text{O}_{10-x}\text{F}_x$ with other germanate and silicate phases reported in the literature is confirmed by X-ray methods. The crystals exhibit superstructure which is interpreted as arising from ordering of Ca vacancies in the [203] direction. Its crystallochemical relationships with other fluorosilicate and germanates is discussed.

Introduction

Although the role of minor constituents in the cement clinkering process has been the subject of numerous investigations, their role is still incompletely understood. The behaviour of constituents capable of acting as fluxes or mineralizers during burning is of particular interest. Fluorine, as F^- , is such a constituent. At clinkering temperatures it depresses solidus temperatures and reduces melt viscosity, thereby facilitating mass transport through the melt phase. The fate of an additive during cooling is of importance, too. Ideally, it should not greatly alter the balance between calcium silicates, aluminates, etc. and ultimately become camouflaged by dilute solid solution in the clinker phases. However, fluorine is known to enhance greatly the thermodynamic stability of C_{12}A_7 by forming solid solutions extending to the $\text{C}_{11}\text{A}_7\cdot\text{CaF}_2$ composition. Moreover, it may condition the formation of other phases not normally present in clinker. These are potential drawbacks to using fluorine: the supernumerary phase or phases are rich in Ca, Al and Si but have reduced cementitious potential relative to C_3S and C_2S .

We recently described a fluorosilicate phase in this class: $\text{Ca}_{6-0.5x}\text{Si}_2\text{O}_{10-x}\text{F}_x$ (1). Its composition and structure have several features relevant to clinkering reactions. First, it is compositionally similar to C_3S to which it bears a pronounced structural similarity.

Second, its structure bears an interesting relationship to that of C_3S . In its cell (hexagonal, $\text{P6}_3/\text{mmc}$, $a = 7.099$, $c = 5.687\text{\AA}$) oxide ions occupy the row 0,0,z (two O per cell translation along c), and the SiO_4 tetrahedra are confined to the 1/3, 2/3, z and 2/3, 1/3, z rows (1 SiO_4 per row

per cell translation along a). In the rhombohedral C_3S_2 (or alite) structure these rows are all alike and are occupied by sets of 3 oxide ions and 3 SiO_4 groups which alternate regularly e.g. $O.O.O.SiO_4.SiO_4.SiO_4$. Finally, the structure we proposed for the fluorosilicate had an unusual feature not hitherto encountered amongst crystalline calcium silicates: it had a variable Ca/Si ratio, the value of which was controlled by the F/O ratio. This variable Ca/Si ratio was achieved by omission of Ca.

Unknown to us, as well as to each other, several groups were at that time determining the crystal structures of phases either isostructural with $Ca_{6-0.5x}Si_2O_{10-x}F_x$ or of new hettotypes. Nishi and Takeuchi determined the crystal structure of the isomorphous $Ca_{3-x}(GeO_4)(O_{1-2x}F_{2x})$ phase (2), in the course of which confirming that charge balance was maintained by the omission of calcium. They studied a crystal having $x \approx 0.275$ in which $9.2 \pm 0.6\%$ of the Ca sites were found to be vacant. Breuer and Eisel also determined the structures of several Cd-Pb silicates and germanates having closely related structures and provided a summary of available synthesis and crystallochemical data on phases of the type $M_3(TO_4)(O,F)$. (3,4)

The present paper has been stimulated by the need to determine the relationship between $Ca_{6-0.5x}Si_2O_{10-x}F_x$ and Tanaka's fluorosilicate phase, $Ca_{12}Si_4O_{19}F_2$ (5), and to report details of the superstructure of $Ca_{6-0.5x}Si_2O_{10-x}F_x$ and its origin.

Identity of Tanaka's Phase and $Ca_{6-0.5x}Si_2O_{10-x}F_x$.

The identity of the phase reported by Tanaka (5) as having the composition $Ca_{12}Si_4O_{19}F_2$ with that which we described as $Ca_{6-0.5x}Si_2O_{10-x}F_x$ has been confirmed. Doubts about their identity arose because of irreconcilable differences in chemical formulae as well as differences in unit cell dimensions, although the powder patterns of the two phases are similar and the syntheses of both phases occurred under similar conditions. The identity has been established on the following basis. The atomic coordinates of $Ca_{6-0.5x}Si_2O_{10-x}F_x$ taken from reference (1) with $x = 1.0$ were used to calculate a powder pattern giving d spacings and peak intensities; the symmetry data were taken from International Tables (6). The calculated pattern thus obtained is given in Table 1; all d spacings from infinity to 1.09 for $CuK\alpha$ are listed. The calculated values agree well with those in (1) except for a few weaker reflections (e.g. 003) which ought to be systematically absent and which must arise from an impurity phase, probably β - C_2S . The single crystal used for intensity data is known to consist of a single phase, whereas the absolute phase purity of sintered bulk powder preparations is difficult to establish. Aside from these residual differences between calculated and observed patterns, which can be explained, both patterns are identical and, moreover, are essentially identical with that reported in (5). Thus, both phases are considered to be identical. However, differences in chemical formulae cannot be reconciled. Doubling the formula obtained from the structure in (1) and setting $x = 1.0$ and gives $Ca_{11}Si_4O_{18}F_2$ or, if the cation vacancies are included, $Ca_{11}\square Si_4O_{18}F_2$. This is the closest match which can be obtained while also observing the restriction that the doubled unit cell cannot contain more than 20 O or F atoms. Thus Tanaka's formula, indicating 21 O and F per doubled cell, cannot be correct.

Electron Diffraction Studies

Electron diffraction photographs obtained from single crystals confirm the existence of the hexagonal main cell first determined by X-ray diffraction. However, by electron diffraction, a complex pattern

TABLE 1

Calculated Powder X Ray Data For
 $\text{Ca}_{6-0.5x}\text{Si}_2\text{O}_{10-x}\text{F}_x$ ($x \sim 0.5$)

d spacing Å	h k l	I	d spacing Å	h k l	I
6.148	010	10	1.392	033	1
4.175	011	4	1.385	014	<1
3.550	110	2	1.369	231	1
3.074	020	49	1.352	042	4
2.843	002	38	1.342	140	<1
2.704	021	100	1.320	114	<1
2.581	012	1	1.306	141	2
2.324	120	3	1.290	024	2
2.219	112	9	1.264	232	1
2.151	121	7	1.213	142	1
2.087	022	32	1.213	124	<1
1.928	031	12	1.202	051	<1
1.812	013	2	1.194	043	7
1.799	122	2	1.183	330	<1
1.775	220	37	1.168	034	<1
1.663	032	4	1.162	240	2
1.633	131	1	1.138	241	11
1.614	023	29	1.132	233	1
1.537	040	2	1.129	052	<1
1.506	222	17	1.118	015	<1
1.484	041	13	1.110	224	8
1.469	123	<1	1.104	150	<1
1.462	132	<1	1.095	143	<1
1.422	004	3	1.092	332	<1
1.410	230	1	1.092	134	<1

Calculated for $\text{CuK}\alpha$ (weighted mean)
 2θ limits : $0 \sim 90^\circ$. Hexagonal cell.

of superstructure reflections is also observed. Figure 1, traced from the photographs (the superstructure reflections are rather weak) shows graphically the pattern of superstructure reflections and their relationship to the main reflections in both reciprocal and real lattices. This pattern of superstructure reflections is closely related to that obtained in (2), except that the superstructure reflections are effectively doubled, probably as a consequence of twinning in the germanate.

A series of photographs taken at different tilts revealing successive recognizable sections of the reciprocal lattice show that rows of superlattice reflections are commensurate with the main structure, passing through the main reflections in the $[203]^*$ direction. A Delaunay reduction gives the true cell as triclinic, $a = 23.839$, $b = 7.105$, $c = 16.755$ Å; $\alpha = 90^\circ$, $\beta = 117.3^\circ$, $\gamma = 98.56^\circ$.

It is suggested that the real structure departs from the ideal structure by the omission of cations, with concomitant substitution of O^{2-} by F^- . The superstructure reflections manifest themselves in the $[203]^*$ direction because of cation omission; indeed, the dominant contribution to the 203 reflection set arises from Ca - the calculated F_c values being

Fig. 1 - (left) drawing of the appearance of the e.d. photograph showing superstructure.

(right) relation of real unit cell to subcell.

Ca, 53.33; O_1 , 13.23; O_2 , 6.24 and Si, 12.76: oxygens O_1 and O_2 belong to the apex and basal portions of SiO_4 tetrahedra, respectively.² The oxygen not bonded to Si (O_3) makes zero contribution to the intensity. Moreover, this interpretation is supported by the arrangement of Ca in the structure, which can be viewed as consisting of sheets parallel to (203). Since $d_{203} \approx 1.675$ Å, the cation omission must occur every tenth layer, thereby generating the 16.75 Å c -axis repeat.

Discussion

The level of fluorine substitution, and hence the value of x in the formula of the title phase has not been fixed conclusively in this study. Several lines of evidence can, however, be introduced. Bulk analysis for F are relatively inconclusive, because of the difficulty of ascertaining the phase purity of preparations. But CORA analyses on individual crystals disclose that they have a mean Ca/Si ratio of 2.99, with $\sigma = 0.245$. The relatively large standard deviation means that not too much significance can be attached to the microanalyses: one standard deviation gives positive x values lying between 0 and 1.04. The higher value lies quite close to the fluorine contents reported by Tanaka (5) and, for the fluorogermanate, by Nishi and Takeuchi (2). We therefore conclude that a composition close to $Ca_{5.48} \square_{0.52} Si_2 O_{8.98} F_{1.02}$ or, in round numbers, $Ca_{5.5} \square_{0.5} Si_2 O_9 F$ would satisfy our analyses and be reasonably consistent with other determinations.

The departure from cation stoichiometry of this phase might be expected to have consequences in terms of its reactivity towards water. Although it has a rather high C/S ratio as well as a Ca vacancy population approaching 1 in 12, it reacts only slowly with water. We conclude that the relationship between reactivity and defect content of calcium silicates is not readily understood intuitively; it may well be that local electrostatic balance considerations are more important in determining reactivity, especially of anions, than the cation-defect distribution and balance.

The discovery and characterization of $Ca_{6-0.5x} Si_2 O_{10-x} F_x$ phase, as well as of other phases closely related in structure, suggests additional possibilities for creating new material structures amongst calcium silicates.

One such phase, in which SiO_4 is partially replaced by SO_4^{2-} , will be described by us in the near future (6). This and other new phases in this family may or may not have useful properties. However, they are characteristically more stable at lower temperatures than C_3S and their synthesis, characterization and determination of their properties assume new importance in understanding the sequence of chemical reactions occurring in the cooler zones of cement kilns as well as the chemical balance which might be obtained in mineralized, low-energy cements characteristically obtained by low temperature firings.

Acknowledgement

This work was made possible by a grant to M. Pérez Méndez from C.S.I.C., Spain, and a grant to J. Fayos from The Royal Society. J. Fayos also wishes to acknowledge the Instituto Rocasolano for leave of absence and M. Pérez Méndez to Instituto E. Torroja for her leave of absence.

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