Acta Cryst. (1997). C**53**, 831–833

Dicalcium Sodium Fluoride Silicate

Ö. Andaç, F. P. Glasser and R. A. Howie

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB9 2UE, Scotland

(*Received 23 December 1994; accepted 13 January 1997*)

Abstract

The title compound, $Ca_2NaF(SiO_4)$, can be regarded as the sodium-rich end member of a series of solid-solution compounds related to tricalcium silicate (Ca_3SiO_5 or $Ca_2SiO_4.CaO$). The chemical formula of the series may be represented as $Ca_2SiO_4.(CaO)_{1-x}.(NaF)_x$ and the title compound has x close to 1. The structure of the title compound is closely related to that of tricalcium silicate and other related compounds.

Comment

Dicalcium sodium fluoride silicate was first reported by Brosset (1945), who examined needle-shaped crystals and reported the Laue symmetry as C_{2h}–$2/m$ with approximate unit-cell dimensions $a = 20.6$, $b = 21.1$, $c = 7.55$ Å; a possible space group was C_{2h}^5–$P2/c$. Funk & Thilo (1955) confirmed its synthesis and noted its structural similarity, as judged from powder data, to $LiCa_2SiO_4F$ and Ca_3SiO_5. Balmer & Silverman (1971*a*,*b*) reviewed the literature and gave improved powder X-ray diffraction data for $M$$Ca_2SiO_4F$ (M = Li, Na and K). In the present paper, $Ca_{3-x}Na_xSiO_4O_{1-x}F_x$ was prepared with $x = 1$ and its crystal structure determined.

While investigating ranges of composition of compounds of the type discussed above, a preparation was selected which produced the member of the series with x close to 1 (from the conditions of the preparation and subsequent electron-microscope elemental analysis) and yielded crystals suitable for structure analysis. While the X-ray structure analysis determines the positions and connectivity of the constituent atoms well enough, it is less satisfactory in establishing the chemical composition of the material due to the similar scattering power of O and F. The structure analysis revealed the following: (i) treating the atom designated as F in Table 1 as O rather than F resulted in unrealistic (non-positive definite) anisotropic displacement parameters for Si; (ii) treating both Ca sites in Table 1 as equivalent (Na and Ca disordered over all 12 sites), rather than the eightfold Ca1 site as Ca and the fourfold Ca2 site as Na, improved R from about 0.073 to 0.066. In the final stages, refining site-occupancy factors for Na and Ca in these sites but with common fractional coordinates and anisotropic displacement parameters improved R still further to the final value of 0.047.

The result of the X-ray analysis can be reconciled with the presumed formula, $Ca_2NaF(SiO_4)$, of the compound on the following basis. The structure, shown in Fig. 2, contains equal numbers of isolated $[SiO_4]^{2-}$ and F^- anions. Na and Ca in the approximate ratio 1:2 are distributed over the cation sites Ca1 and Ca2 as shown in Table 1. Whereas the eightfold Ca1 site is occupied by 0.57 (2) Ca and 0.43 (2) Na, the fourfold Ca2 site is occupied by 0.78 (2) Ca and 0.22 (2) Na, *i.e.* Ca preferentially occupies the fourfold Ca2 site. These occupancy factors correspond to a total Na:Ca ratio of 1.09:1.91, which is Na-rich compared with the idealized formula and thus requires that there be vacancies at the F site. However, further refinement has failed to confirm this and it is concluded that this site is fully occupied by F and that the Na:Ca ratio is not real. Indeed, the difference between the observed and ideal Na:Ca ratios is comparable in magnitude with the s.u. of the former. Each O atom is coordinated by three Na/Ca atoms in addition to Si in a very distorted tetrahedral arrangement. F, on the other hand, is surrounded by six Na/Ca atoms in a comparatively regular octahedron. Each Na/Ca site is surrounded by four O atoms and two F atoms in a rather less regular octahedron (see Table 2).

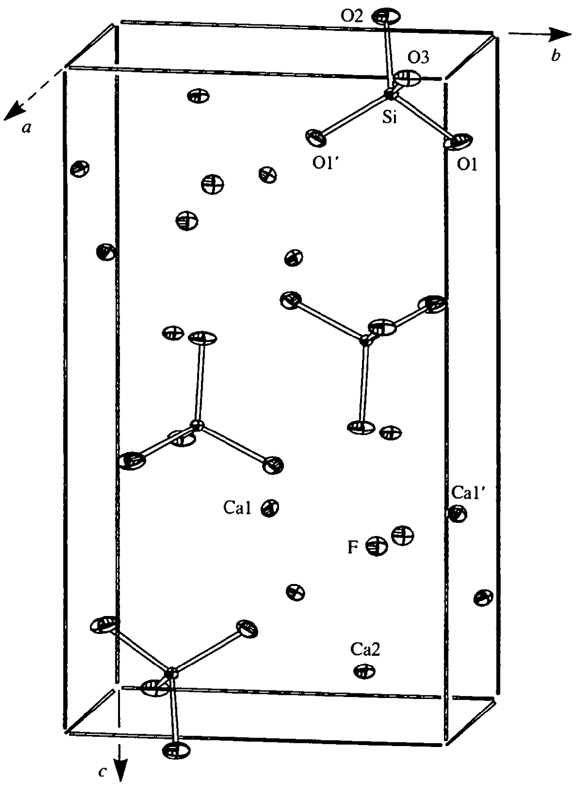

Fig. 1. Representative atoms of $Ca_2NaF(SiO_4)$ showing 40% probability ellipsoids. The unit-cell edges orientation and representative atoms are labelled.

A striking feature of this orthorhombic structure is its approximation to hexagonal symmetry, which introduces the possibility of comparing it with that of tricalcium silicate (C_3S) and related compounds. In particular, Perez-Mendez, Howie & Glasser (1984) described a highly disordered hexagonal structure for a material designated as 'phase *A*' in the series $Ca_{(6-0.5x)}Si_2O_{(10-x)}F_x$ and noted its possible structural relationship to C_3S and other compounds in a manner mentioned previously by Dent Glasser (1965). The possibility of a relationship between the structure described here and that of phase *A* becomes more obvious when the latter is formulated as $Ca_2SiO_4.Ca_{(1-y)}O_{(1-2y)}F_{2y}$ (y being one half of x, as given above). This formulation implies that the substitution of F into the structure of C_3S is accompanied by the creation of cation (Ca) vacancies for charge balance rather than the introduction of interstitial F. The structural relationship, if correct, also suggests that the hexagonal symmetry assumed for phase *A* is incorrect and an artefact of the very small poor-quality crystals available at the time, possibly aggravated by twinning.

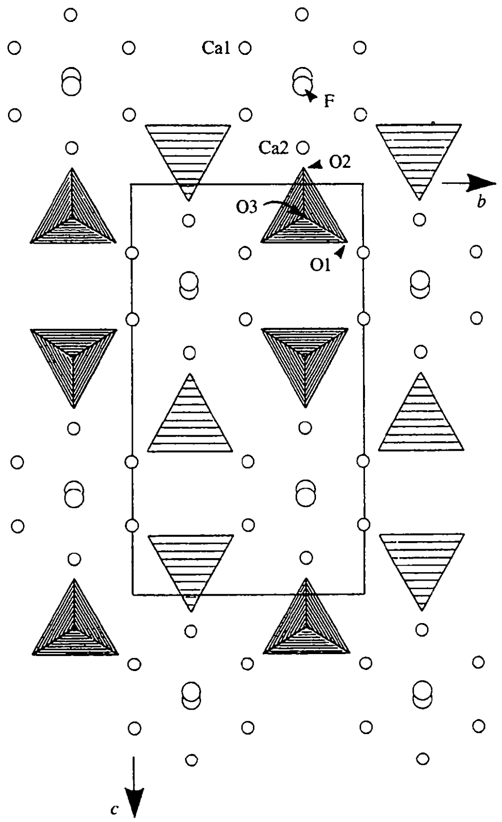

Fig. 2. (100) projection of the structure of $Ca_2NaF(SiO_4)$. F and Ca are large and small circles, respectively. SiO_4 are shown as tetrahedra. The directions of **b** and **c** (**a** down into the page) are indicated, as are Ca, O and F of the asymmetric unit. Si lies at the centroid of the labelled tetrahedron.

Experimental

Polycrystalline $Ca_2NaF(SiO_4)$ was prepared using freshly decarbonated 'AnalaR' $CaCO_3$, SiO_2 and NaF. These were reacted in an electrically heated muffle furnace at 1073 K for a total of 24 h with six intergrindings. Single crystals were prepared by mixing 20% NaF (*w*/*w*) with 80% $Ca_2NaF(SiO_4)$ (*w*/*w*) and heating at 1293 K for 16 h. The composition partially melts and $Ca_2NaF(SiO_4)$ crystallizes upon partial evaporation of the flux components. A suitable crystal was selected using a petrographic microscope.

Crystal data

$Ca_2NaF(SiO_4)$
$M_r = 214.23$
Orthorhombic
Pnma
$a = 5.335\ (3)$ Å
$b = 7.144\ (4)$ Å
$c = 12.438\ (4)$ Å
$V = 474.1\ (4)$ Å^3
$Z = 4$
$D_x = 3.000$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 7.5–13.8°$
$\mu = 2.63$ mm^{-1}
$T = 298$ K
Tabular
0.3 × 0.14 × 0.1 mm
Colourless

Data collection

Nicolet *P*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
859 measured reflections
697 independent reflections
574 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.004$

$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 17$
2 standard reflections every 50 reflections intensity decay: 1.72 and 1.51%

Refinement

Refinement on *F*
$R = 0.047$
$wR = 0.060$
$S = 0.81$
574 reflections
52 parameters
$w = 1/[\sigma^2(F) + 0.007575F^2]$
$(\Delta/\sigma)_{\rm max} = 0.04$

$\Delta\rho_{\rm max} = 0.75$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.85$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ca1†	0.7584 (2)	0.5035 (2)	−0.3298 (1)	0.0181 (4)
Na1‡	0.7584 (2)	0.5035 (2)	−0.3298 (1)	0.0181 (4)
Ca2§	0.7326 (2)	3/4	−0.0894 (1)	0.0150 (5)
Na2¶	0.7326 (2)	3/4	−0.0894 (1)	0.0150 (5)
Si	0.2009 (3)	3/4	0.0821 (1)	0.0073 (4)
O1	0.2934 (7)	0.9365 (5)	0.1456 (2)	0.0326 (10)
O2	0.3002 (8)	3/4	−0.0418 (3)	0.0215 (12)
O3	−0.1069 (8)	3/4	0.0804 (3)	0.0195 (11)
F	0.0004 (5)	3/4	−0.2403 (3)	0.0168 (9)

† Occupancy = 0.57 (2). ‡ Occupancy = 0.43 (2). § Occupancy = 0.78 (2). ¶ Occupancy = 0.22 (2).

Table 2. *Selected distances (Å) and angles (°) with s.u. values in parentheses for* Ca$_2$NaF(SiO$_4$)

Ca—*X* [*X* = O (× 4) or F (× 2)]

	Ca1	Ca2
Minimum	2.276 (3)	2.278 (4)
Maximum	2.458 (4)	2.454 (3)
Mean† (of 6)	2.39 (6)	2.36 (5)

X—Ca—*X* (*X* = O or F) – large angles (L)‡

	X—Ca1—*X*	*X*—Ca2—*X*
Minimum	138.3 (1)	141.7 (1)
Maximum	169.0 (1)	171.8 (1)
Mean (of 3)	150 (13)	152 (13)

X—Ca—*X* (*X* = O or F) – small angles (S)§

	X—Ca1—*X*	*X*—Ca2—*X*
Minimum	67.0 (1)	67.6 (1)
Maximum	124.0 (1)	120.6 (1)
Mean (of 12)	89 (17)	88 (16)

F—Ca distances and Ca—F—Ca angles

	F—Ca	Ca—F—Ca (L)	Ca—F—Ca (S)
Minimum	2.359 (3)	173.0 (1)	82.8 (1)
Maximum	2.454 (3)	174.1 (1)	94.5 (1)
Mean (of 6, 3, 12)	2.42 (4)	173.7 (5)	90 (4)

Silicate anion

	Si—O	O—Si—O
Minimum	1.625 (4)	108.1 (2)
Maximum	1.643 (5)	111.2 (2)
Mean (of 4, 6)	1.631 (7)	109.4 (14)

† The s.u. values associated with the mean values are calculated on the basis of *n* observations, where *n* is as stated. ‡ *X*—*Y*—*Z* angles at *Y* involving diagonally opposite *X* and *Y*. § *X*—*Y*—*Z* angles at *Y* where *X* and *Z* are adjacent.

Data collection used 2θ scan rates of 5.33 ($I_p > 150$) to 58.6° min^{-1} ($I_p > 2500$), where I_p is the prescan intensity. Scan widths were 2.4 to 2.8° 2θ. Refinement was by full-matrix least-squares techniques. All atoms were refined anisotropically. Ca1 and Ca2 sites were interpreted in a chemical sense as disordered Na and Ca in the ratio 1:2; they were initially refined as Ca but were later treated as Na/Ca atom pairs with common coordinates and anisotropic displacement parameters but independent site-occupancy factors summing to unity for each site. F was treated as fluorine. All computations were performed on the SUN SPARCserver (UNIX operating system) of the Computing Centre of the University of Aberdeen.

Data collection: Nicolet *P*3 software. Cell refinement: Nicolet *P*3 software. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *STRUPLO*82 (Fischer, 1982).

Ömer Andaç acknowledges financial support and leave of absence to pursue postgraduate work from Ondokuz Mayis Universitesi.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1103). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 833-836

Room-Temperature Form of Manganese Hexafluorosilicate Hexahydrate: a New Model with Submicroscopic Twinning

Akira Torii,[a] Kazuhide Ogawa,[b] Hatsue Tamura[b] and Kenji Osaki[c]

[a]*Higashitoyonaka High School, Toyonaka, Osaka 560, Japan,* [b]*Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan, and* [c]*Nampei-dai 5-9-6, Takatsuki, Osaka 569-11, Japan*

(*Received 22 May 1996; accepted 13 December 1996*)

Abstract

A new model of MnSiF$_6$.6H$_2$O is presented which reproduces the 'weak' $h0l$ reflections not explained with the 'antiphase domain' model by Chevrier [*Acta Cryst.* (1991), **B47**, 224–228]. Good agreement for the 'weak' reflections was obtained by assuming a sort of submicroscopic twinning. The average distances are Mn—O 2.15, Si—F 1.69 and O···F 2.78 Å.

Comment

In the preceding report (Kodera, Torii, Osaki & Watanabe, 1972), the title compound was assigned the space group $P\bar{3}m1$, based on the observed Laue symmetry and extinction rules obtained from Weissenberg and precession photographs. In a later study, however, it became clear that a reasonable structure consisting of the known polyhedra Mn(H$_2$O)$_6^{2+}$ and SiF$_6^{2-}$ could not be constructed with this space group. It was then assumed that the true space group was $P\bar{3}$ and that the apparent symmetry plane must have been introduced by some kind of