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ON THE PREPARATION OF SINGLE CRYSTALS OF $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ AND THE CONFIRMATION OF ITS CRYSTAL STRUCTURE

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ABSTRACT

Single crystals of $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2(C_{11}A_7{\cdot}CaF_2)$ of 40–120 μm in size were prepared by a flux evaporation method. The crystals were colorless trigonal tristetrahedrons with a refractive index of 1.601. By the method of single crystal X-ray diffraction it has been confirmed that the $C_{11}A_7{\cdot}CaF_2$ is cubic, with a = 11.981Å, space group $I\bar{4}3d$, Z = 2 and $D_X = 2.720$ g cm^{-3}. The calcium atom is coordinated either to six oxygen atoms in an irregular $[CaO_6]$ coordination with 2.380Å, 2.401Å and 2.502Å for Ca-O distances or to six oxygen atoms and one fluorine atom in an asymmetric arrangement with 2.816Å for F-Ca distance. The aluminum atoms are coordinated to four oxygen atoms forming two different AlO_4 tetrahedra: (1) the $[Al(1)O(2)_4]$, with symmetry $\bar{4}$ and Al(1)–O(2) distance = 1.745Å; and (2) the $[Al(2)O_4]$ composed of one Al(2) atom, one O(1) atom and three O(2) atoms, with symmetry 3, Al(2)–O(1) distance = 1.740Å and Al(2)–O(2) distance = 1.757Å. Neighboring AlO_4 tetrahedra are connected with each other by sharing oxygen atoms resulting in a three dimensional $[AlO_4]$ network-the basic framework of the crystal structure of $C_{11}A_7{\cdot}CaF_2$. © *1997 Elsevier Science Ltd*

Introduction

It is well known that the utilization of a composite mineralizer composed of fluorspar and gypsum possesses energy-saving advantages and can improve the quality of cement clinker, especially clinker produced in shaft kilns. Sometimes, though, fluoride-bearing cement sets abnormally; a fact which has been observed in both laboratories and plants. Consequently, the application of said cement has been subject to various problems (1–3). Many researchers attributed the reason for the cement's abnormal setting (flash or retarded setting) to: (a) the amount and crystal size of the $C_{11}A_7{\cdot}CaF_2$ phase; and (b) the variation in hydration activity

TABLE 1
Coordinates of Atoms in the Crystal of $C_{11}A_7{\cdot}CaF_2$ (After Ref. 6)

Atom	x	y	z	B	Occupancy factor
Ca (1)	0.10824	0	1/4	0.90	0.744
Ca (2)	0.06738	0	1/4	0.90	0.254
Al (1)	3/8	0	1/4	0.37	
Al (2)	0.98089	0.98089	0.98089	0.33	
O (1)	0.06977	0.06977	0.06977	0.79	
O (2)	0.19091	0.28616	0.09919	0.94	
F	7/8	0	1/4	1.29	0.238

of alite in the clinker. Because it is different from C_3A in hydration properties and plays an important role in the setting and hardening of fluoride-bearing cement, $C_{11}A_7{\cdot}CaF_2$ has attracted much attention. Many studies on its formation and stability at high temperatures as well as its setting and hydration behaviors under different conditions have been done in recent years (1–5).

The crystal structure of $C_{11}A_7{\cdot}CaF_2$ was revealed by Williams (6,7), who based his observations on powder X-ray diffraction data (Table 1). For purposes of comparison, the coordinates of atoms of $C_{12}A_7$, one of the phases closely related to $C_{11}A_7{\cdot}CaF_2$, are also presented in Table 2 (8). Table 1 shows that in the unit cell of $C_{11}A_7{\cdot}CaF_2$ there exist two kinds of calcium atoms: Ca(1) and Ca(2), but from the coordinates of which it can be found that their interatomic distance is only 0.489Å, less than the radius of Ca^{2+} ion (R_{Ca2+} = 1.00Å). From the standpoint of crystallography, it is evident that the Ca sites were somewhat inappropriately determined in this solution. Based on the data shown in Table 1, we tried to analyze the bonding in $C_{11}A_7{\cdot}CaF_2$ crystal utilizing a quantum chemistry method but ultimately failed. As we have learned through the method of single crystal X-ray diffraction, it is possible to obtain a more exact solution to crystal structure. Thus, single crystal studies will be required to improve on the structure reported by Williams. Using an ordinary crystal growth method will be very difficult to prepare single crystals of $C_{11}A_7{\cdot}CaF_2$ with a size larger than 50 μm. This difficulty is because a significant amount of fluorine in $C_{11}A_7{\cdot}CaF_2$ will be released when the heating temperature rises above 1200°C. Feng and Liao et al. found single crystals of $C_4A_3\bar{S}$, $11CaO{\cdot}7Al_2O_3{\cdot}CaCl_2$ and $3CaO{\cdot}3Al_2O_3{\cdot}SrSO_4$ greater than 100 μm in size could be obtained at temperatures below 1100°C by a flux evaporation method in which $PbCl_2$ was used as a flux (9,10).

TABLE 2
Coordinates of Atoms in the Crystal of $C_{12}A_7$ (After Ref. 8)

Atom	Wyckoff equipoint symbols	x	y	z
Ca	24d	0.1397	0	1/4
Al (1)	16c	0.0187	0.0187	0.0187
Al (2)	12b	7/8	0	1/4
O (1)	48e	0.1510	−0.0370	0.0570
O (2)	16c	−0.0641	−0.0641	−0.0641
O (3)	24d	−0.3370	0	1/4

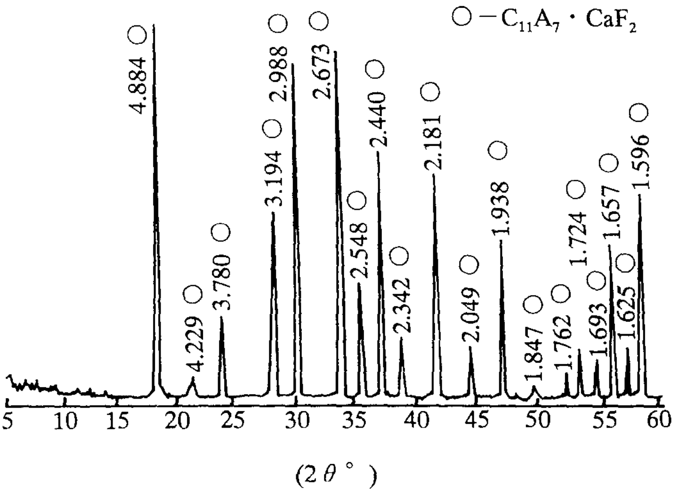


FIG. 1.

Powder X-ray diffraction pattern (Cu Kα 1 radiation, spacings in Å) of the product.

Experimental

Preparation of the Single Crystals of $C_{11}A_7 \cdot CaF_2$. Analytically pure $CaCO_3$, Al_2O_3 and CaF_2, oven dried at 105°C for 2 hours, were ground to pass through a 60 μm sieve. Considering a volatilization loss of 8.01% CaF_2 during the whole growth process of the crystals (5,11,12), a homogeneous mixture of the above agents with a molar ratio of $CaCO_3 : Al_2O_3 : CaF_2 = 11.00 : 7.00 : 1.08$ was fired at 1250°C for 2 hours in a silicon-carbide furnace and then quenched to room temperature in the air of R.H. less than 5%. By comparison to PDF-25-394, the product was proved to be $C_{11}A_7 \cdot CaF_2$.

In this study $PbCl_2$ was also used as a flux. The mixture of $PbCl_2$ and $C_{11}A_7 \cdot CaF_2$ at a weight ratio of 30 : 1 was placed in a Pt crucible and fired at 650°C for 2 hours, 850°C for 24 hours, 980°C for 30 hours and 1050°C for 10 hours sequentially under an oxidizing atmosphere. The final product contains 43.83% CaO, 50.91% Al_2O_3 and 5.26% CaF_2($C_{11\,02}A_{7\,04}C_{0\,95}$, C = CaO, A = Al_2O_3, C = CaF_2). Fig. 1 shows that the crystalline

TABLE 3

Experimental Powder X-ray Diffraction Pattern of the Final Product (2θ : 5–60°)

d(Å)	h k l	I	d(Å)	h k l	I	d(Å)	h k l	I
4.884	2 1 1	100	2.440	4 2 2	44	1.724	4 4 4	8
4.229	2 2 0	4	2.342	5 1 0	10	1.693	7 1 0	6
3.780	3 1 0	14	2.181	5 2 1	38	1.657	6 4 0	26
3.194	3 2 1	33	2.049	5 3 0	6	1.625	5 5 2	10
2.988	4 0 0	37	1.938	5 3 2	20	1.596	6 4 2	30
2.673	4 2 0	75	1.847	5 4 1	3			
2.548	3 3 2	13	1.762	6 3 1	4			

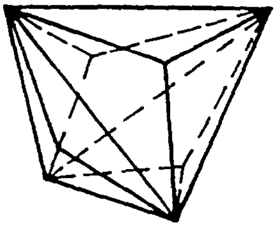


FIG. 2.
The form of the single crystal of $C_{11}A_7{\cdot}CaF_2$-trigonal tristetrahedron.

phase in it is only $C_{11}A_7{\cdot}CaF_2$, the observed d-I data of which are given in Table 3. Table 3 shows that the final product produces a pattern close to the calculated pattern PDF-25-394 in the range of 5–60° (2θ, Cu $K\alpha_1$ radiation). Microscopic observation proved that there were large numbers of colorless trigonal tristetrahedrons (Fig. 2) in the product. Their sizes ranged from 40 μm to 120 μm, and they had a refractive index of 1.601. The crystals of $C_{11}A_7{\cdot}CaF_2$ contained in industrial fluoride-bearing clinkers always appear in the form of rounded grains or dendrites (13). The difference of morphology between the single crystal of $C_{11}A_7{\cdot}CaF_2$ and the $C_{11}A_7{\cdot}CaF_2$ crystals in fluoride-bearing clinker may be possibly due to the great differences that exist between their growth conditions. During the sintering process of clinker, $C_{11}A_7{\cdot}CaF_2$ crystals can only grow in a much limited space for a short time.

Determination of the Crystal Structure of $C_{11}A_7{\cdot}CaF_2$. The single crystal of $C_{11}A_7{\cdot}CaF_2$ under examination was a well-grown trigonal tristetrahedron of about 0.07 × 0.07 × 0.07 mm^3; its elemental composition is shown in Table 4. The intensity data were collected by a RASA-5RP Four-circle single-crystal diffractometer under the following conditions:

Monochromator : graphite, Radiation : $MoK\alpha_1$(0.70926Å), Temperature : 25°C,
Voltage : 50kV, Current : 130mA, Scanning mode : $2\theta/\omega$,
Scanning rate : 4°/min, Scanning width : $\Delta\omega = 1.0 + 0.5tg\theta$,
Scanning range : $2\theta = 0\text{–}75°$, h = 0–20, k = 0–0, 1 = 0–20

The unit cell parameters were obtained by using 20 strong reflections. 2529 original reflections were collected, among which there were 1944 reflections possessing $F > \sigma(F)$. All of the collected data were corrected for LP factor and T factor. By using SHELX 76 program the symmetry equivalent reflections in the original were combined and averaged. 286 symmetry independent reflections were accepted in the final structure solution after rejecting the reflections with $F < 5\sigma(F)$ and $\sin\theta/\lambda > 0.8$. The crystal data and calculated X-ray diffraction pattern (40 reflections) of the single crystal of $C_{11}A_7{\cdot}CaF_2$ are shown in Table 5 and Table 6 respectively.

TABLE 4
Elemental Composition of the Single Crystal of $C_{11}A_7{\cdot}CaF_2$ Under Examination (by EPMA)

Atom	O	F	Si	Al	Cl	Pb	Fe	Ca
Observed (%)	50.85	3.10	0.03	24.41	2.16	0.22	0.02	19.21
Calculated (%)	53.30	3.30	0.00	23.40	0.00	0.00	0.00	20.00

TABLE 5

Crystal Data for the Single Crystal of $C_{11}A_7{\cdot}CaF_2$ (Figure in the Bracket is Error)

Molecu. weight	1408.68	Unit cell parameters	a = b = c = 11 981(2) Å $\alpha = \beta = \gamma = 90°$	D_x	2.72 g cm^{-3}
Crystal system	Cubic	Observed diffractions	h + k + l = 2n, 0kl : k + l = 2n, hhl : 2h + l = 4n, h00 . h = 4n	D_m	2.69 g cm^{-3}
Space group	I$\bar{4}$3d	Linear absorp. coefficient	21.43 cm^{-1}		
Z	2	Cell volume	1719.80 $Å^3$		

Results and Analysis

Heating Sequence Adopted in the Experiment. When a flux evaporation method is used, the size and purity of the product are closely related to the adopted heating sequence. Generally speaking, the heating sequence is mainly dependent on both the flux and the characteristics of the single crystals to be synthesized. Because (a) the melting point and boiling point of $PbCl_2$ (under standard atmosphere) are 498°C and 954°C respectively; and (b) the fluorine in $C_{11}A_7{\cdot}CaF_2$ will be released at a relatively high rate when the heating temperature is over 1200°C (11,12), the following heating processes were specially adopted in this experiment. Firstly, the mixture of $PbCl_2$ and $C_{11}A_7{\cdot}CaF_2$ was heated at 650°C for 2 hours in order to completely melt the $PbCl_2$ and, subsequently, dissolve $C_{11}A_7{\cdot}CaF_2$ in the molten $PbCl_2$. Secondly, the mixture was heated at 850°C (below the boiling point of $PbCl_2$) for 24 hours so as to slowly evaporate $PbCl_2$ and to keep the solution from being quickly supersaturated with $C_{11}A_7{\cdot}CaF_2$. Thirdly and finally, it was heated at 980°C (over the boiling point of $PbCl_2$) for 30 hours and then at 1050°C for 10 hours in order to evaporate any possible remains of $PbCl_2$. The heating time adopted at the above stages was determined on a trial basis.

TABLE 6

Calculated X-ray Diffraction Pattern of the Single Crystal of $C_{11}A_7{\cdot}CaF_2$

d(Å)	h k l	I	d(Å)	h k l	I	d(Å)	h k l	I
4.8910	2 1 1	100	1.7665	6 3 1	4	1.2772	6 6 4	3
4.2360	2 2 0	3	1.7293	4 4 4	9	1.2629	8 5 1	1
3.7887	3 1 0	6	1.6944	7 1 0	3	1.2357	9 3 2	2
3.2021	3 2 1	13	1.6615	6 4 0	22	1.2103	9 4 1	2
2.9952	4 0 0	28	1.6304	5 5 2	4	1.1863	7 7 2	1
2.6790	4 2 0	85	1.6010	6 4 2	23	1.1748	10 2 0	2
2.5544	3 3 2	4	1.5216	6 5 1	2	1.1423	7 6 5	3
2.4456	4 2 2	37	1.4976	8 0 0	4	1.1124	10 4 0	4
2.3497	5 1 0	8	1.4748	7 4 1	5	1.1029	9 6 1	1
2.1874	5 2 1	33	1.3928	7 4 3	4	1.0937	10 4 2	3
2.1180	4 4 0	1	1.3566	7 5 2	2			
2.0547	5 3 0	3	1.3395	8 4 0	4			
1.9436	5 3 2	22	1.3231	9 1 0	1			
1.8944	6 2 0	1	1.3072	8 4 2	7			
1.8487	5 4 1	2	1.2919	9 2 1	1			

TABLE 7
Coordinates, Occupancy Factor and Isotropic Thermal Vibration Parameter (U_{11}) of Atoms in the Single Crystal of $C_{11}A_7 \cdot CaF_2$ (Figures in Brackets are Errors)

Atom	Wyckoff equipoint symbols	X/A	Y/B	Z/C	Occupancy factor	Isotropic thermal vibration parameter
Ca	24d	0.1104 (1)	0	0.2500	1.0	0.0086 (5)
Al (1)	24d	0.3750 (2)	0	0.2500	1.0	0.09 (1)
Al (2)	16c	0.2324 (1)	0.2324 (1)	0.2324 (1)	1.0	0.04 (1)
O (1)	16c	0.0661 (1)	0.0661 (1)	0.0661 (1)	1.0	0.019 (3)
O (2)	48e	0.1955 (2)	0.2852 (1)	0.1004 (2)	1.0	0.014 (2)
F	48e	0.2500	0.1250	0.5000	0.333	0.024 (4)

Coordinates of Atoms in the Single Crystal of $C_{11}A_7 \cdot CaF_2$. Using the 286 symmetry independent reflections with $F > 5\sigma$ (F), the coordinates and isotropic thermal vibration parameters of 6 sets of atoms (1 set of Ca, 2 sets of Al, 2 sets of O and 1 set of F) were finally obtained after multiple-cycles by the least squares method (Table 7). The coordinates of Al and Ca atoms were determined by using the direct method proposed by Gilmore (14). The coordinates of O and F atoms were deduced from the result of successive differential calculation of electron density and the knowledge of crystal chemistry. The final deviation factor R and R_w are all equal to 0.090, thus showing that the precision of this solution can meet the requirement of accuracy defined in the solution of crystal structure (<0.100).

The unit cell of $C_{11}A_7 \cdot CaF_2$ crystal is composed of the following 120 atoms: 24 Ca, 12 Al(1), 16 Al(2), 48 O(2), 16 O(1) and 4 F. The coordinates of all the atoms in the unit cell of $C_{11}A_7 \cdot CaF_2$ crystal can be easily deduced from Table 7 and (15).

The projection drawing of the structure of $C_{11}A_7 \cdot CaF_2$ on (001) plane is shown in Fig. 3. This figure, when applying methods of quantum chemistry, will greatly assist in selecting the appropriate calculation model for analyzing its bond structure and bond formation (5). The data of bond distances and bond angles for the single crystal of $C_{11}A_7 \cdot CaF_2$ are shown in Table 8 and Table 9 respectively.

Description of the Crystal Structure of $C_{11}A_7 \cdot CaF_2$. Fig. 4 is an axonometric drawing of the structure of $C_{11}A_7 \cdot CaF_2$ in the range of x = −0.2a–1.2a, y = −0.2a–1.2a, z = −0.2a–0.4a. Fig. 5 shows the distribution of AlO_4 tetrahedra in the same range. There are two different $[AlO_4]$ in the structure of $C_{11}A_7 \cdot CaF_2$, i.e. the $[Al(1)O_4]$ with symmetry $\bar{4}$ (Fig. 6) and the $[Al(2)O_4]$ with symmetry 3 (Fig. 7). The former is a fairly regular tetrahetron composed of one Al(1) atom and four O(2) atoms, with Al–O distance = 1.745Å(4 equivalent bonds); the latter, extended along its triad axis, is made up of one Al(2) atom, three O(2) atoms and one O(1) atom, with Al(2)–O(2) distance = 1.757 (3 equivalent bonds) and Al(2)–O(1) distance = 1.740Å. From Fig. 4 and Fig. 5 it can be found that: (a) neighboring two $[AlO_4]$ are connected by one shared O atom; (b) an $[AlO_4]$ ring is formed by every $8[AlO_4]$; (c) the $[AlO_4]$ rings are further linked up by sharing O atoms resulting in a three dimensional $[AlO_4]$ network—the basic framework of the structure of $C_{11}A_7 \cdot CaF_2$; (d) each of the four corners of every $[AlO_4]$ is shared between neighboring AlO_4 tetrahetra; and (e) Ca and F atoms fill in the large cavity surrounded by the 8 AlO_4 tetrahedra.

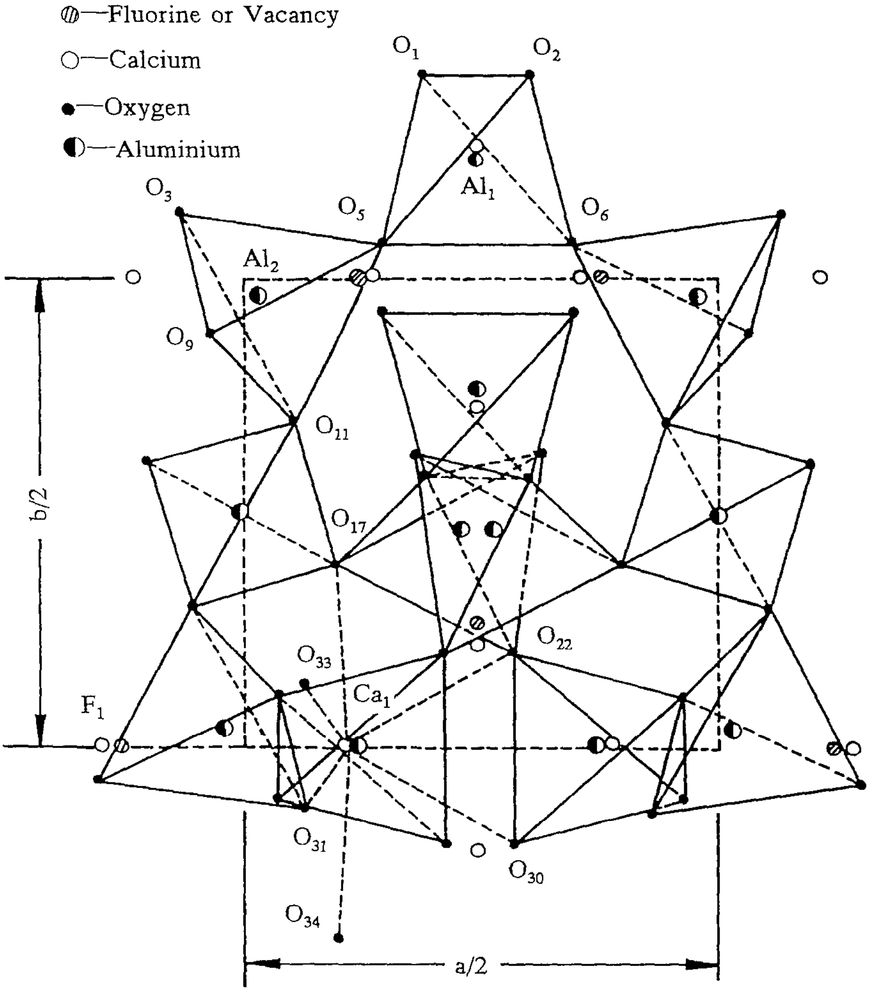


FIG. 3.
Projection drawing of the crystal structure of $C_{11}A_7{\cdot}CaF_2$ on (001) plane along C axis.

TABLE 8
Data of Bond Distances for the Single Crystal of $C_{11}A_7{\cdot}CaF_2$ (Å)

Ca—O(F)	Bond Distance	Al—O	Bond Distance
Ca—O(1)	2.401 (Ca_1—:O_{31}, O_{33})	Al(1)—O(2)	1.745 (Al_1—:O_1, O_2, O_5, O_6)
Ca—O(2)	2.380 (Ca_1—:O_{17}, O_{34})	Al(2)—O(1)	1.740 (Al_2—:O_3)
	2.502 (Ca_1—:O_{22}, O_{30})	Al(2)—O(2)	1.757 (Al_2—:O_5, O_9, O_{11})
Ca—F	2.816 (Ca_1—:F_1)		

TABLE 9
Data of Bond Angle for the Single Crystal of $C_{11}A_7 \cdot CaF_2$ (Degree)*

A_1	CA	A_2	Angle	A_1	CA	A_2	Angle	A_1	CA	A_2	Angle
O_{33}	$-Ca_1$	$-O_{31}$	54.76	O_{17}	$-Ca_1$	$-O_{34}$	174.65	O_1	$-Al_1$	$-O_5$	112.33
		$-O_{17}$	80.03			$-O_{22}$	67.19			$-O_6$	112.33
		$-O_{34}$	98.78			$-O_{30}$	117.76	O_2	$-Al_1$	$-O_5$	112.33
		$-O_{22}$	77.50			$-F_1$	87.33			$-O_6$	112.33
		$-O_{30}$	125.60	O_{34}	$-Ca_1$	$-O_{22}$	117.76	O_5	$-Al_1$	φO_6	103.90
		$-F_1$	77.38			$-O_{30}$	67.19	O_3	$-Al_2$	$-O_5$	117.18
O_{31}	$-Ca_1$	$-O_{17}$	98.78			$-F_1$	87.33			$-O_9$	117.18
		$-O_{34}$	80.03	O_{22}	$-Ca_1$	$-O_{30}$	66.40			$-O_{11}$	117.18
		$-O_{22}$	125.60			$-F_1$	146.80	O_5	$-Al_2$	$-O_9$	100.78
		$-O_{30}$	77.50	O_{30}	$-Ca_1$	$-F_1$	146.80			$-O_{11}$	100.78
		$-F_1$	77.38	O_1	$-Al_1$	$-O_2$	103.90	O_9	$-Al_2$	$-O_{11}$	100.78

*A_1-atom 1, A_2-atom 2, CA-central atom

In $C_{11}A_7 \cdot CaF_2$ crystals, there are four F atoms. They distribute statistically between the following 12 sites: (−1/8,0,1/4), (5/8,0,3/4), (1/4,7/8,0), (3/4,5/8,0), (0,1,4,7/8), (0,3/4,5/8), (3/8,1/2,3/4), (1/8,1/2,1/4), (3/4,3/8,1/2), (1/4,1/8,1/2), (1/2,3/4,3/8) and (1/2,1/4,1/8). The unoccupied eight sites are retained as vacancies.

One Ca atom is connected to 2 O(1) and 4 O(2) atoms forming an irregular CaO_6 octahedron, with Ca–O(1) distance = 2.401Å, Ca–O(2) distance = 2.380Å and 2.502Å. On the other hand, one Ca atom can also be coordinated to six O atoms and one F atom in some sites resulting in a deformed polyhedron (coordination number = 7), with a Ca F distance of 2.816Å (Table 8). The ratio between the number of Ca atoms with coordination number 6 and that with coordination number 7 is 5 : 1. $[Al(1)O_4]$, $[Al(2)O_4]$ and $[CaO_6]$ are joined by sharing O atoms (Fig. 3). It should be noted that the Ca-F bond distance is quite long for the ionic interactions occurring in such a strong bond. It was observed that the Ca-Cl distance in

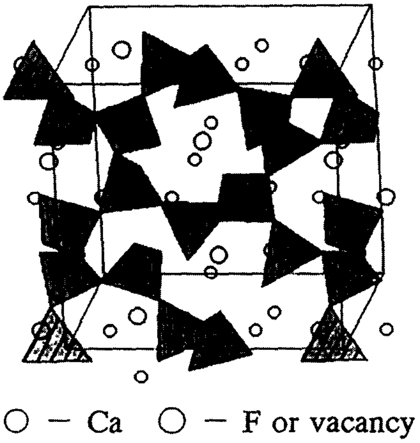


FIG. 4.
Axonometric chart of the crystal structure of $C_{11}A_7 \cdot CaF_2$.

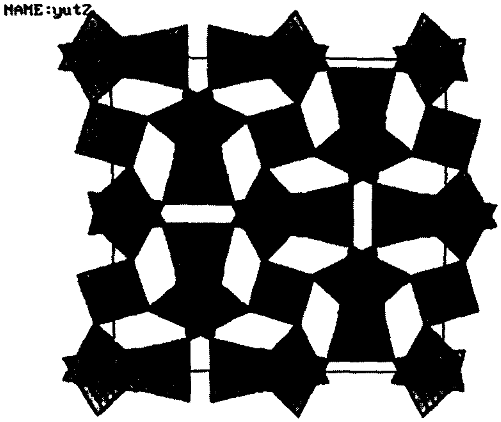
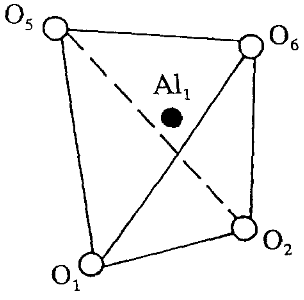


FIG. 5.
Schematic distribution of AlO_4 tetrahedra and the formation of AlO_4 framework.

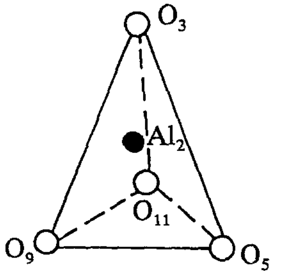
$C_{11}A_7 \cdot CaCl_2$ is about 2.73Å(6), which is also greater than the Ca-Cl distance (2.483Å) in $CaCl_2$ (16). Due to the limitation of experimental conditions and the authors' poor understanding of crystal chemistry, a clear explanation for the puzzling Ca-F distance can not be given in this study.

Table 2 shows that there is only one kind of site for calcium atoms in the structure of $C_{12}A_7$ as determined by Bartl (8), which happens to be the same as that in the structure of $C_{11}A_7 \cdot CaF_2$ as observed in this study. Studies on $C_{12}A_7$ shows its crystal structure to be built from Ca^{2+} ions, an incomplete framework of corner-sharing AlO_4 tetrahedra and empirical composition $Al_7O_{16}{}^{11-}$, and one O^{2-} ion per formula unit distributed statistically between 12 sites (17). The form of the AlO_4 framework of $C_{12}A_7$ is the same as that of $C_{11}A_7 \cdot CaF_2$ (18). However, compared to $C_{12}A_7$, there are four extra F atoms in the unit cell of $C_{11}A_7 \cdot CaF_2$. The F atoms fill in the large cavities surrounded by AlO_4 tetrahedra and coordinate with Ca and O atoms to form a pseudo-octahedron, which reduces the internal potential of $C_{11}A_7 \cdot CaF_2$ and stabilizes the structure of $C_{11}A_7 \cdot CaF_2$. Besides this lattice stabilization, the presence of



$Al_1 - Al(1)$, O_1, O_2, O_5, $O_6 - O(2)$

FIG. 6.
AlO_4 tetrahedron with symmetry $\bar{4}$.



$Al_2 - Al(2)$, O_5, O_9, $O_{11} - O(2)$, $O_3 - O(1)$

FIG. 7.
AlO_4 tetrahedron extended along its triad axis, with symmetry 3.

the extra F atoms in the structure also has a strengthening effect on the Al-O bonds by modifying the net charges around Al and O atoms. Li (18) found the Mulliken ionic bond orders of the Al(1)-O and Al(2)-O of $C_{11}A_7 \cdot CaF_2$ are 0.1610 and 0.0490, while those of the Al(1)-O and Al(2)-O of $C_{12}A_7$ are only 0.0351 and 0.0257. Therefore, the crystal structure of $C_{11}A_7 \cdot CaF_2$ is more stable than that of $C_{12}A_7$. In other words, the hydration activity of $C_{11}A_7 \cdot CaF_2$ is poorer than that of $C_{12}A_7$ (5,18).

Comparison of the XRD Pattern of $C_{11}A_7 \cdot CaF_2$ Obtained in This Study With Those of Before. There are two patterns of $C_{11}A_7 \cdot CaF_2$ in the Powder Diffraction File, i.e. PDF-25-394 and PDF-36-678. The former is often used to identify the $C_{11}A_7 \cdot CaF_2$ that exists in fluoride-bearing cement clinker (1–5) because it gives more perfect data than the latter does. Table 3 shows that in the range of 5–60° (2θ, Cu $K\alpha_1$ radiation), the powder X-ray diffraction pattern of $C_{11}A_7 \cdot CaF_2$ observed in this study is very close to the calculated pattern PDF-25-394 reported by Williams. Yet, by using single crystal X-ray diffraction, a more detailed pattern, as shown in Table 6, has been obtained. In the new pattern some missing distances in PDF 25-394, such as d = 2.1180Å, 1.8944Å, 1.3231Å, 1.2357Å, 1.1863Å, 1.1748Å and 1.1029Å, have been presented. If possible, the authors will submit the experimental and calculated patterns of $C_{11}A_7 \cdot CaF_2$ obtained in this study to the ICDD for inclusion in the PDF.

Conclusions

1. Single crystals of $C_{11}A_7 \cdot CaF_2$ measuring 40–120 μm suitable for single crystal study could be prepared by a fluxevaporation method in which $PbCl_2$ was used as a flux. The single crystal of $C_{11}A_7 \cdot CaF_2$ is cubic, with a = 11.981Å, space group $I\bar{4}3d$, Z = 2, n = 1.601, and $D_X = 2.720$ g cm^{-3}.
2. The calcium atom of $C_{11}A_7 \cdot CaF_2$ is coordinated either to six oxygen atoms in an irregular $[CaO_6]$ coordination or to six oxygen atoms and one fluorine atom resulting in a pseudo-octahedron with a coordination number of 7. The aluminum atom is bonded to four oxygen atoms forming two different Al-O tetrahedra. Every 8 $[AlO_4]$ form a $[AlO_4]$ ring. Furthermore, the rings join each other resulting in a three dimensional $[AlO_4]$ framework in the crystal of $C_{11}A_7 \cdot CaF_2$.

3. Fluorine atoms only occupy 1/3 of the available sites in the structure of $C_{11}A_7{\cdot}CaF_2$; the unoccupied 2/3 sites are retained as vacancies.
4. The distorted and irregular coordination of atoms; the presence of large cavities and vacancies in the structure; and the random distribution of fluorine atoms make $C_{11}A_7{\cdot}CaF_2$ have high internal potential as well as be active when it is exposed to water. But compared to $C_{12}A_7$, $C_{11}A_7{\cdot}CaF_2$ is more stable in crystal structure and slower in hydration due to the presence of fluorine atoms in its structure.

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