V-110 ON THE CRYSTAL STRUCTURE OF $11CaO \cdot 7Al_2O_3 \cdot CaF_2$

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1. INTRODUCTION

Sometimes fluoroaluminate cement is used in shotcrete engineering in which $11CaO \cdot 7Al_2O_3 \cdot CaF_2$ ($C_{11}A_7 \cdot CaF_2$ for short) is one of its main constituent and plays an important role in the rapid setting and hardening of cement. But the crystal structure and characteristics of $C_{11}A_7 \cdot CaF_2$ and the relation between them have not been profoundly studied yet. Here single crystals of $C_{11}A_7 \cdot CaF_2$ were prepared and by four-cycles single crystal diffractometry method its structure information has been obtained in more detail and accurately.

2. EXPERIMENTAL

2.1 Growth of $C_{11}A_7 \cdot CaF_2$ Single Crystals

Flux evaporation method, using $PbCl_2$ as flux, was selected for growing $C_{11}A_7 \cdot CaF_2$ single crystals. The mix of $PbCl_2$ and $C_{11}A_7 \cdot CaF_2$ by weight ratio of 20－30:1 was held in a Pt crucible and kept at oxidizing atomsphere of 650℃ for 2hr, 850℃ for 24hr, 980℃for 30hr and 1050℃ for 10hr in sequence. Most of the final product were grains of 40－120 μm in size. Further investigations on them by XRD, chemical analysis and EPMA showed they were $C_{11}A_7 \cdot CaF_2$ crystals of trigonal tristetrahedron practically. The exact outer shape of them is shown in Fig. 1 schematically.

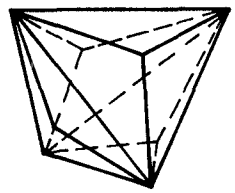


Fig. 1 $C_{11}A_7 \cdot CaF_2$ single crystal—trigonal tristetrahedron

2.2 Determination of the Structure of $C_{11}A_7 \cdot CaF_2$ Single Crystal

One trigonal tristetrahedron grain of $C_{11}A_7 \cdot CaF_2$ crystal of 70×70×70 μm was selected out for structure analysis. The conditions of intensity data collection are as followings:
Monochromator: graphite,
Radiation: MoK α_1(0.70926 Å),
Temp.: 25℃,
Voltage: 50kV,
Current: 130mA,
Scanning mode: $2\theta/\omega$,
Scanning rate: 4°/min,
Scanning width: $\triangle\omega = 1.0 + 0.5 \mathrm{tg}\theta$,
Linear absorp. cofficient: 21.43 cm^{-1}
Scanning range:
$2\theta = 0 - 75°$, h=0－20, k=0－20, l=0－20

Table 1 and Table 2 exhibit the crystallographic parameters.

Table 1 Crystallographic Parameters of $C_{11}A_7 \cdot CaF_2$

Mole. Weight	1408.68
Crystal System	Cubic System
Cell Parameters	a=b=c=11.981(2) Å $\alpha = \beta = \gamma = 90°$
Diffraction Conditions	h+k+l=2n, 0kl: k+l=2n, hhl: 2h+l=4n, h00: h=4n
Space Group	$I\bar{4}3d$
Z Value	2
$D_{calc.}$	2.72 g/cm^3
$D_{obs.}$	2.69 g/cm^3
Set Parameters	-0.0459427 -0.0611095 0.0334730 -0.0662817 0.0507801 0.0018598 -0.0217556 -0.0255642 -0.0763772
Cell Volume	1719.80 Å^3

Table 2 Final Coordinates, Occupancy Factors(K) and Isotropic Thermovibration Parameters(U_{11}) of Atoms

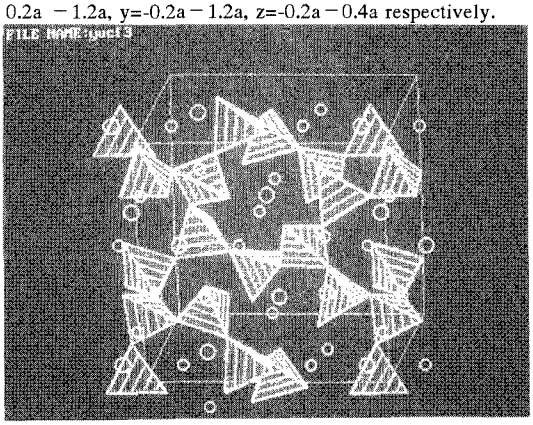
Atom	X/A	Y/B	Z/C	K	U_{11}
Ca(1)	0.1104	0	1/4	0.50	0.0086 (5)
Al(1)	0.3750	0	1/4	0.25	0.09(1)
Al(2)	0.2324	0.2324	0.2324	0.33(1)	0.04(1)
O(1)	0.0661	0.0661	0.0661	0.33(1)	0.019 (3)
O(2)	0.1955	0.2852	0.1004	1.00	0.014 (2)
F(1)	1/4	1/8	1/2	0.08(1)	0.024 (4)

The determination of coordinates of Al and Ca atoms

was by using direct method (MITHRIL) [1] and that of O and F atoms was by successive differential calcaulation of electronics density. By using 286 independent data of diffraction intensity the coordinates, occupancy factors(K) and isotropic thermovibration parameters of 6 sets of atoms(1 set of Ca , 2 sets 0f Al , 2 sets of O and 1 set of F atoms) were multiply modified by the least square method. The final structure deviation factors R and R_w are all equal to 0.090, which are within the accuracy defined in crystal structure analysis. One cell of $C_{11}A_7 \cdot CaF_2$ crystal contains 120 atoms which are 24 Ca(1), 12 Al(1), 16 Al(2), 48 O(2), 16 O(1) and 1 F(1). From Table 2 and [2] the coordinates of all atoms in a cell of $C_{11}A_7 \cdot CaF_2$ crystal can be deduced out easily.

3. RESULTS AND ANALYSIS

Fig. 2 and Fig.3 are the axonometric chart of the crystal structure and the schematic distribution of $[AlO_4]$ tetrahedra 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 respectively.



○—Ca, ○—F or hole

Fig. 2 Axonometric chart of the crystal structure of $C_{11}A_7 \cdot CaF_2$

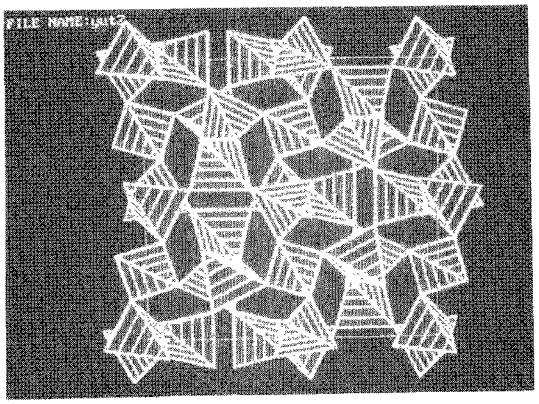


Fig. 3 Schematic picture of the distribution of $[AlO_4]$ tetrahedra in the crystal structure of $C_{11}A_7 \cdot CaF_2$

Table 3 shows its main bond distances.

Table 3 Main Bond Distances(Å)

Ca_1 —O_{31}	2.401	Al_1 —O_1	1.745
—O_{33}	2.401	—O_2	1.745
—O_{17}	2.380	—O_5	1.745
—O_{22}	2.502	—O_6	1.745
—O_{30}	2.502	Al_2—O_3	1.740
—O_{34}	2.380	—O_5	1.757
—F_1	2.816	—O_9	1.757
		—O_{11}	1.757

There are two kinds of $[AlO_4]$ tetrahedra in $C_{11}A_7 \cdot CaF_2$ structure, i.e., an approximate regular $[AlO_4]$ tetrahedron(symmetry 4) and a slightly distorted $[AlO_4]$ tetrahedron(symmetry 3). The former is composed of a Al(1) atom and 4 O(2) atoms and the latter is formed by atoms of 3 O(2), 1 O(1) and 1 Al(2). They are connected by one shared O(2) atom. Every 8 $[AlO_4]$ tetrahedra form a ring and then the rings connect each other by sharing one O atom , which make up of a three dimensional network. One calcium atom and 2 O(1), 4 O(2) atoms(coordination number=6), or together with one fluorine atom(coordination number=7) in some positions, produce a deformed octahedral coordination. Structure holes are also found in $C_{11}A_7 \cdot CaF_2$ structure.

4. CONCLUSION

(1) By flux evaporation method $C_{11}A_7 \cdot CaF_2$ single crystals of 40$-$120 μ m in size were prepared, and its crystallographic parameters have been obtained in more detail.

(2) In $C_{11}A_7 \cdot CaF_2$ calcium atoms are coordinated either to six oxygens in a very asymmetric manner or to six oxygens and one fluorine in an arrangement similar to distorted octahedral coordination. Aluminium atoms coordinated to four oxygens in an arrangement of $[AlO_4]$ tetrahedron which form a three dimensional network in the structure.

(3) From its distorted structure and the irregular coordination of atoms we can understand, more or less, the reason for its high hydration activity.

REFERENCES

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2. Theo Hahn. "International Tables for Crysta - llography" , Vol. A(Space $-$ Group Symmetry), D. Reidel Publishing Company, Holland, U. S. A., pp.659 $-$ 661, 1983.