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STRUCTURE REFINEMENT OF CALCIUM SULFOALUMINATE, $C_4A_3\bar{S}$ WITH EMPHASIS TO OXYGEN DEFICIENCY

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ABSTRACT

Structure refinement of synthetic calcium sulfoaluminate, $C_4A_3\bar{S}$ ($4Ca0.3A1_20_3.SO_3$) has been carried out by using a powder sample. XRD pattern included some extra diffraction peaks originating from superstructure of the sample. All peaks were indexed to be cubic by taking double cell of subcell. Cell parameter was 18.402Å. Assuming space group I23, atomic coordinates were determined with final R(F) value 0.077. Oxygen depletion was detected which would be responsible for the superstructure.

Introduction

Presence of calcium sulfoaluminate was found in the course of studying expansive cements by Klein(1) and its exact chemical composition was determined by Fukuda(2) to be $4Ca0.3A1_2 0_3.SO_3$. The crystal structure was studied by several authors(3–6). The structure is similar to the naturally occurring mineral, hauyne, $(Ca,Na)_{4-8}\,[A1_6SI_60_{24}]\,(SO_4)_{1-2}$. However, there are still some controversies on the space groups as well as the cause of superstructures. If $C_4\,A_3\,\bar{S}$ is isostructural with hauyne, the following space groups may be possible for subcell: $P\bar{4}3m$ (Barth(7)), $P\bar{4}3n$ (Machatschki(8), Halstead and Moore(3)), $I\bar{4}3m$ (Halstead and Moore (3), Kondo(4), Saalfeld and Depmeier(5), Xiuji and Guanglin(6)). According to Kondo(4) the former two space groups are implausible in view of extinction rules. According to Halstead and Moore(3), Saalfeld and Depmeier and Xiuji and Guanglin(6) space group $I4_132$ is applicable to supercell to explain the superstructure. In this paper crystal structure of $C_4A_3\bar{S}$, which is one of the main clinker minerals in calcium sulfoaluminate cements, will be studied to contribute to these arguments.

Experimental

Chemical reagents, $CaCO_3$, α - Al_2O_3 and $CaSO_4$ were weighed in a 10 g batch in stoichiometric proportion to form $C_4A_3\bar{S}$ and well mixed and ground for 10 h with ethanol in a small type

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*Present address; Astra-Japan Co., Ltd., 3-6-8 Kyutaro, Chuo-ku, Osaka 541, Japan laboratory pot mill made of alumina. The $CaSO_4$ was prepared from $CaSO_4 \cdot 2H_2O$ by calcination at 1000°C for 2 h beforehand. Then the ethanol was completely removed by drying in an oven at 70°C. The mixture was transferred to a platinum crucible to fire at 1300°C for 9 h. The product pulverized in an agate mortar was found to be single phase $C_4A_3\bar{S}$ by checking with XRD and a polarizing microscope.

Employing Mac Science MXP3 computer aided automatic powder X-ray diffractometer, XRD measurement for structure refinement was carried out by following conditions: 40KV and 20mA Ni-filtered CuK α radiation, 1° (DS), 0.15° (RS) and 1° (SS) slit system, 0.02° step width, and 12 s counting time at each step. Thus, intensities of discrete 16 peaks were collected (Tables 1 and 3). Peaks obtained were indexed by using computing system installed in the apparatus together with cell parameter determination. Laboratory made computer program was used to determine atomic coordinates and site occupancies of atoms to find minimum R(F) values by using conventionally accepted equation:

$$R(F)=(\Sigma \| Fobs| - |Fcalc \|)/\Sigma |Fobs|$$

where Fobs and Fcalc denote observed and calculated structure factors, respectively. Calculations were performed assuming the space group I23, applying peak height intensities to avoid frequent overlapping between subcell and supercell reflections. Atomic scattering factors used were those for CA^{2+}, Al^{3+}, S° and 0^{-} followed by International Tables for X-ray Crystallography(9).

Results and Discussion

Indexing XRD Peaks. Many extra peaks not assigned to subcell having 9.201Å cell edge were encountered, different from the data of Kondo(4) in which no extra reflections were observed. Results of indexing are tabulated in Table 1. When double cell of the subcell was taken into account, excellent indexing was achieved to assign all reflections to supercell having 18.402Å cell edge. Under the miscroscope it was obvious that the sample was entirely extinct and isotropic in crossed polar condition, quite different from the observation after Peixing(10) whose sample showed birefringence due to tetragonal distortion. Therefore, present sample should be cubic as postulated. Refractive index measured was 1.567 close to 1.569 of Halstead and Moore(3). As a consequence cell parameter 18.402Å was obtained for the supercell.

Determination of Atomic Coordinates. Starting from space group I23 Kondo(4) found $C_4A_3\bar{S}$ belongs to the space group $I\bar{4}3m$. Other workers Saalfeld and Depmeier(5), and Xiuji and Guanglin(6) also selected $I\bar{4}3m$ for subcell. In this paper calculation was primarily performed on subcell starting with I23 where Ca, Al, S, O(S) surrounding S, and O(A) surrounding Al are located 8c, 12e, 2a, 8c and 24f Wyckoff positions, respectively. Atomic coordinates determined by taking subcell are shown in Table 2 in comparison with the data obtained by Kondo(4). Calculation was ceased at the second decimal place for the coordinates, firstly because the peak height intensities were used that may be not so accurate as integrated intensities as usually accepted and secondly because calculation was performed on subcell that is not real cell. Without considering the depletion of oxygen atoms R(F) value became 0.122. However, R(F) value 0.077 was reached, when oxygen depletion was taken into consideration by reducing oxygen scattering factor gradually. Then, site occupanices 79% and 80% were reached for O(S)

TABLE 1

Summary of XRD Results for $C_4A_3\bar{S}$

Supercell			Subcell	Supercell			Subcell
HKL	d	I	hkl	HKL	d	I	hkl
411	4.345	2		910,833	2.038	2	
422	3.772	100	211	921,761,655	1.990	2	
440	3.261	8	220	664	1.964	2	332
530,433	3.164	2		844	1.882	2	422
532,611	2.997	2		941,853,770	1.863	1	
620	2.920	7	310	862,10 2 0	1.809	3	431,510
541	2.846	2		950,943	1.792	1	
444	2.661	35	222	952,765	1.757	<1	
710,550,543	2.610	1		10 4 2	1.684	1	521
721,633,552	2.512	2		11 1 0,873	1.669	2	
642	2.464	7	321	880	1.626	9	440
730	2.426	1		10 6 0,866	1.580	4	530,433
732,651	2.344	<1		12 0 0,884	1.534	2	600,442
800	2.308	4	400	12 2 2, 10 6 4	1.495	5	611,532
811,741	2.270	3		12 4 4	1.390	5	622
554,653	2.201	1		12 6 2	1.359	2	631
822,644	2.175	24	330,411	888	1.329	3	444
831,750	2.136	2		14 4 2,10 10 4 ,12 6 6	1.254	3	721,552 ,633
743,840	2.063	1	420				

and for O(A), respectively. Therefore, resulting data strongly support the oxygen defects occurring in $C_4A_3\bar{S}$ that may lead to the superstructure, when ordering of oxygen defects takes place, forming some triangular coordination of oxygen atoms. Other cause of the superstructure such as atomic displacements has been pointed out so far on this problem(11) as well as rotation of [SO_4] — tetrahedra(5). No depletion was observed on sulfur as well as other cations. To the contrary, however, considerable displacements of atomic positions were detected especially on O(S) atoms, contracting from 0.10(4) to 0.07, probably due to the depletion of some O(S) atoms, resulted. Although this contraction violates the ionic radius rule strongly, some compensation may take place due to the loosened structure occurring by the O(S) oxygen deficiency.

Careful measurements of the density of the sample by the paraffin medium method (see appendix) showed 2.53 g/cm^3 indicating 93% oxygen occupancy, higher than theoretically expected value of 2.38 g/cm^3 for present XRD results. If there is no oxygen depletion this value should be 2.60g/cm^3 theoretically. Halstead and Moore(3) measured the density being 2.61 g/cm^3 with kerosene medium. But their sample contained the other impurity phases in minor and was not single phase. Considering the inaccuracy of X-ray measurements due to relatively

TABLE 2

Atomic Coordinates Determined to $C_4A_3\bar{S}$

Atom	Position	x	y	z	Occupancy(%)
Ca	8c	0.19 [0.21]	0.19 [0.21]	0.19 [0.21]	100
Al	12e	0.26 [0.25]	1/2	0	100
O(A)	24f	0.57 [0.545]	0.16 [0.155]	0.17 [0.155]	80
S	2a	0	0	0	100
O(S)	8c	0.07 [0.10]	0.07 [0.10]	0.07 [0.10]	79

Space group I23 [I$\bar{4}$3m] ,Cubic,a_0=18.402Å for supercell,R(F)=0.077 [0.199] O(A) and O(S) denote oxygen atoms of [AlO_4] - and [SO_4] -tetrahedra, respectively. [ ] showing the results after Kondo(4).

low atomic scattering factors of oxygen, the density determined by XRD measurements is in the permitting range of agreement with the expected density. However, the cause of the oxygen defect is unexplainable at present. We have also found the same phenomena in synthetic hauynes containing sodium other than calcium (unpublished data).

There is no discrimination in X-ray selection rules between I23 and I$\bar{4}$3m. The only difference between them is primarily O(A) atomic coordinates and secondly on Al atomic coordinates(12). Atomic coordinates of I23 can be transformed to those of I$\bar{4}$3m, only shifting

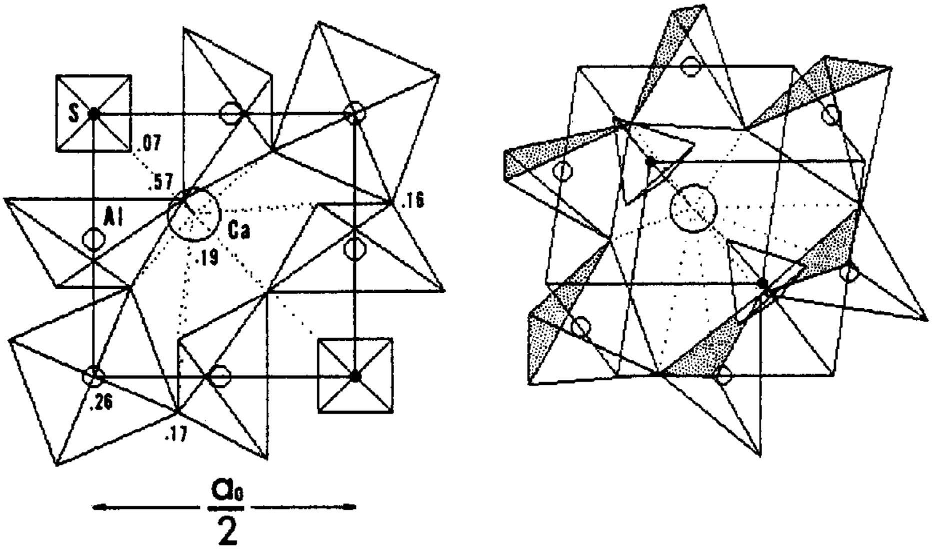

FIG. 1.
Crystal structure of $C_4A_3\bar{S}$ drawn to subcell. Right, (001) projection. Left, nearly (112) projection.

TABLE 3

Observed and Calculated Intensities and Structure Factors Normalized to 1000

No.	h k l	Icalc	Iobs	|ΔI|	Fcalc	Fobs	|ΔF|
1.	2 1 1	6315	5768	547	1174	1095	79
2.	2 2 0	418	467	49	499	514	15
3.	3 1 0	191	389	198	380	529	149
4.	2 2 2	1523	1750	227	1457	1523	66
5.	4 0 0	221	231	10	754	752	2
6.	4 2 0	117	111	6	448	427	21
7.	3 3 2	96	102	6	300	301	1
8.	4 2 2	136	125	11	376	352	24
9.	4 4 0	419	481	62	1117	1167	50
10.	6 2 0	55	36	19	467	370	97
11.	5 4 1	29	43	14	246	291	45
12.	6 2 2	224	236	12	700	700	0
13.	6 3 1	69	95	26	401	457	56
14.	4 4 4	105	112	7	876	882	6
15.	6 4 0	39	30	9	452	387	65
16.	6 4 2	43	24	19	353	253	100

x and y coordinates to common values for O(A) together with fixing x-parameter on 1/4 for Al. No exact 1/4 positions were reached in present results, even if atomic coordintes were calculated down to the third decimal place. The slight atomic displacements from $I\bar{4}3m$ positions to I23 ones may be attributed to the O(A) oxygen deficiency. This deficiency may give rise to some symmetrical effect to displace x-coordinate slightly from exact 1/4 positions for Al atoms together with slight difference between y and z coordinates for O(A) atoms themselves.

The crystal structure drawn from the present results is shown in Fig. 1 for subcell with space group I23. Accurate determination of oxygen deficiency is usually performed by the neutron diffraction technique. However, for a superconductor $YBa_2Cu_3O_{8-x}$ we showed the X-ray diffraction technique is also amenable to such determination in a certain high precision(13). The Rietveld technique which might have higher accuracy is now under way of consideration. Theoretical and observed intensities resulted are summarized in Table 3.

Conclusion

XRD structure refinements have been performed on $C_4A_3\bar{S}$, using powder sample. The following items have been reached as conclusions.

(1) $C_4A_3\bar{S}$ has a superstructure of cubic system. All reflections can be indexed by taking the double cell having 18.402Å cell edge.

(2) The space group I23 is more likely rather than $I\bar{4}3m$, judging from the atomic coordinates obtained.

(3) Oxygen deficiency has been detected which may be the cause of the superstructure of $C_4A_3\bar{S}$ as well as atomic displacements of oxygen and aluminum atoms from $I\bar{4}3m$ positions to I23 ones.

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Appendix

Generally the kerosene medium method using a pycnometer is accepted to determine the densities of powders. However, this method requires a great deal of skill and is a tedious work. The paraffin medium method using a sample bottle developed in our laboratory is very easy and accurate.

Prepare 10 ml sample bottles made of glass with flat bottom and some pieces of paraffin with recommending melting point around 60°C. Charge the objective sample powder (0.5–1 g) and paraffin (1–2 g) in a bottle and melt the paraffin in an oven at 110°C for 15 min. Stir the melt with a bar made of a paper clip to eliminate air bubbles while hot, especially the bottom corner. Repeat this melting and stirring for several times in 5 min intervals until no more bubbling. Don't wipe the stir bar. Place the bottle on a porcelain plate to cool for 30 min to create smooth meniscus surface. Hang the bottle on a hook of chemical balance with an electric wire as thin as 0.15 mm ⌀ and dip the bottle deep enough into the water in a 300 ml beaker. Neglecting a droplet of paraffin lost by adhering on the stir bar and the bouyancy of suspending wire, the density is calculated immediately in high accuracy (±0.02) from the following equation:

$$Dsp = Wsp/\{W - (W' + Wb/Db + Wp/Dp)\}$$

where Dsp, Db and Dp are the densities of the sample powder, bottle and paraffin, respectively. Wsp, Wb and Wp are the weights of sample powder, bottle and paraffin, respectively. W and W' are the overall weights of Wsp + Wb+ Wp measured in air and in water, respectively. The Db should be measured beforehand and the Dp should be determined separately by melting for the same duration with that of the sample. This technique is also applicable to samples containing combined water, only lowering the heating temperature around 80°C.