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Silicates M_3SiO_5 . I. Sr_3SiO_5

By L. S. DENT GLASSER AND F. P. GLASSER

Chemistry Department, University of Aberdeen, Scotland

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Single crystal X-ray studies show that Sr_3SiO_5 is tetragonal, $P4/ncc$, $a=6.934$, $c=10.72$ Å, $Z=4$. An approximate structure is deduced from symmetry and packing considerations.

Introduction

Tristrontium silicate, Sr_3SiO_5 , was first prepared by Nurse (1952) who published preparative details and optical and X-ray powder data, and very kindly provided us with some single crystals for the present X-ray study. We were especially interested in finding out whether Sr_3SiO_5 belongs to the same class of structure as Ca_3SiO_5 (Jeffery, 1952) and Cd_3SiO_5 (Dent Glasser & Glasser, 1964).

Experimental

Rotation and Weissenberg photographs of single crystals showed that the unit cell is tetragonal, with $a \approx 6.85$, $b \approx 10.62$ Å. Systematic absences were found in $hk0$ for $h+k$ odd, in $0kl$ for l odd, and in hhl for l odd. The space group is therefore No. 130, $P4/ncc$. There is in addition a pronounced systematic weakness among hkl reflexions with $h+k+l$ odd, implying that the structure is approximately body centred.

Powder data

The powder data (Table 1) were indexed by direct comparison of powder photographs and single-crystal rotation photographs taken on the same camera. The observed d -values are mainly taken from Nurse (1952). Three of his lines (3.512, 2.804, 2.737 Å, all very weak) cannot be indexed. These are missing from the pattern recorded by Dear (1957). They evidently do not belong to Sr_3SiO_5 . The cell parameters obtained from single-crystal measurements were adjusted slightly to improve the fit of d_c with d_o : the adjusted unit cell has $a=6.934$, $c=10.72$ Å.

Cell contents

The density of Sr_3SiO_5 was measured by toluene displacement as 4.72, giving $Z=3.95$. If it is assumed that $Z=4$, $D_x=4.78$. The agreement is satisfactory: furthermore, in the space group $P4/ncc$, all positions have a multiplicity of four or some multiple of four. The calculated cell contents therefore agree with the space group requirements.

Structure

From a knowledge of the space group and density, the structure may be deduced as follows. The unit cell contains 12 strontium, 4 silicon and twenty oxygen atoms. Because there are only four silicon atoms these must be placed in one of the three fourfold positions. One of these $(0, \frac{1}{2}, z)$ lies on the fourfold axis, and can therefore be eliminated because in this position it would be impossible to arrange four oxygen atoms tetrahedrally about it. Both the remaining positions, $0, 0, 0 (\bar{4})$ and $0, 0, \frac{1}{4} (222)$, permit a tetrahedral arrangement of oxygen about the silicon, and a possible structure can be deduced starting from either. The structure based on silicon at $0, 0, \frac{1}{4}$ was found, however, to lead to very odd coordination for the strontium atoms, and consideration of the relative intensities of some simple reflexions served to eliminate this possibility. Only the structure based on Si at $0, 0, 0 (\bar{4})$ will be discussed.

Sixteen oxygen atoms (O_I) in the general position x, y, z will form tetrahedra about the silicon atoms: these tetrahedra have one twofold axis parallel to c . The remaining four oxygen atoms (O_{II}) must lie on one of the fourfold special positions. $0, 0, 0$ is already occupied by Si; there is not sufficient room to place

Table 1. Powder data for Sr_3SiO_5

Values of d_o are from Nurse (1952) except for the four lines marked *. These are not recorded by Nurse, but are visible on the powder photograph used in the present work for direct comparison with single crystal photographs. This photograph was taken on a small (6 cm) diameter camera, and these four values are therefore less accurate than the rest. Reflexions in parentheses probably do not belong to Sr_3SiO_5 (see text)

d_o	I	hkl	d_c
3.595	1	112	3.62
[3.512	1]	—	—
2.967	4	211	2.98
2.903	10	202	2.91
[2.804	1]	—	—
[2.737	1]	—	—
2.675	4	{ 004	2.68
		{ 122	2.68
2.444	5	220	2.45
2.337	8	213	2.34
2.187	5	310	2.19
*2.04	1	214	2.03
1.891	2(broad)	321	1.893
1.808	6	224	1.809
1.763	3	215	1.764
*1.736	<1	400	1.733
1.696	3	314	1.697
1.678	1	116	1.679
1.660	5	411	1.661
*1.633	<1	330	1.635
1.589	5	206	1.588
1.562	3	332	1.563
1.550	2	420	1.550
1.522	4	413	1.522
1.489	2	422	1.489
1.456	2	404	1.456
*1.425	<1	{ 325	1.432
		{ 414	1.425
		{ 431	1.376
1.375	2	217	1.374
1.343	3	424	1.342
1.326	3	415	1.324
1.321	1	512	1.318
1.246	1	406	1.244
1.226	1	440	1.226
1.207	2	336	1.206

an oxygen atom at $0, 0, \frac{1}{4}$, so the remaining oxygen atoms must lie on $0, \frac{1}{2}, z$.

The twelve strontium atoms cannot lie on three fourfold positions for reasons similar to those applied in the previous sentence to the placing of O_{II} . They must therefore lie on one fourfold position (Sr_{II} ; $0, \frac{1}{2}, z$) and one eightfold position. Considerations of permissible bond lengths restrict the choice of eightfold position to $x, x, \frac{1}{4}$ (Sr_I).

A structure based on these positions, with parameters adjusted to give reasonable bond distances, is shown in Fig. 1. A list of the parameters is given in Table 2; bond distances are given in Table 3. Examination of Fig. 1 shows that the structure deviates from being body-centred only in a small rotation of the

Table 2. Parameters of the atoms

8 Sr_I	in $x, x, \frac{1}{4}$; $x=0.181$
4 Sr_{II}	in $0, \frac{1}{2}, z$; $z=0.0$
4 Si	in $0, 0, 0$
16 O_I	in x, y, z ; $x=0.169, y=-0.092, z=0.088$
4 O_{II}	in $0, \frac{1}{2}, z$; $z=0.250$

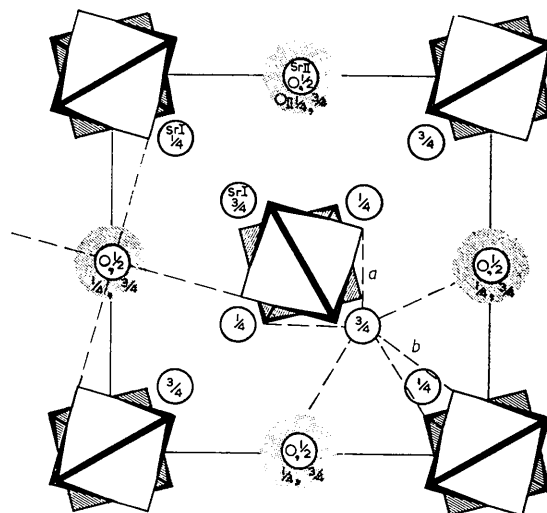


Fig. 1. The structure of Sr_3SiO_5 viewed along the c axis. Open tetrahedra represent SiO_4 groups with Si at height 0 or 1; shaded ones have Si at height $\frac{1}{4}$. Small open circles represent strontium, large shaded circles oxygen atoms; heights are marked on the appropriate circles.

Table 3. Bond distances

Si— O_I	1.63 Å
Sr_I — O_I	(a) 2.57
	(b) 2.57
Sr_I — O_{II}	2.54
Sr_{II} — O_I	2.56
Sr_{II} — O_{II}	2.68

SiO_4 tetrahedra about the c axis. Probably Sr_{II} & O_{II} do not lie exactly at $z=0$ and $z=\frac{1}{4}$ respectively, which would cause a further slight departure from body-centring. Such changes must be small however; details must await a full structure determination.

The coordination of the strontium atoms in this structure is roughly octahedral. It is interesting that the distortion of the Sr_{II} octahedron, with five of the six oxygen atoms crowded into one hemisphere, is of a similar type to that found for the Ca octahedra in Ca_3SiO_5 .

Contrary to earlier statements appearing in the literature, single-crystal studies have established that a definite structural relation exists between Sr_3SiO_5 and Ca_3SiO_5 . Cd_3SiO_5 also has a similar structure. These relationships are discussed in the following article.

Note added in proof.—Dr M. Mansmann (private communication) has pointed out that the proposed structure resembles that of Cs_3CoCl_5 .

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