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Silicates M_3SiO_5. II. Relationships between Sr_3SiO_5, Cd_3SiO_5 and Ca_3SiO_5

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Despite differences in unit cells and symmetries, Sr_3SiO_5 and Ca_3SiO_5 are based on similar structural units. A possible structure for Cd_3SiO_5 is deduced.

Introduction

The polymorphism of Ca_3SiO_5 has long interested workers studying Portland cement, and many studies have been made of both the pure compound and its solid solutions (*e.g.* Jeffery, 1952; Yamaguchi & Miyabe, 1960; Yannaquis, Regourd, Mazières & Guinier, 1962; Woermann, Hahn & Eysel, 1963). Nurse (1952) prepared Sr_3SiO_5 to see if it were analogous; because of the dissimilarity of the powder patterns he concluded that it was not. Dent Glasser & Glasser (1964) prepared Cd_3SiO_5, and showed that its structure was probably a variant of that of Ca_3SiO_5.

The studies on Sr_3SiO_5 described in the preceding article established the principal features of its structure. During the unit-cell determination, a relationship was noted between its unit cell and that of Cd_3SiO_5, and by implication with that of Ca_3SiO_5 also. Examination of models of the proposed structure of Sr_3SiO_5 and of the pseudo-structure of Ca_3SiO_5 (Jeffery, 1952) showed that the relationships in cell dimensions originated from structural similarities, despite the differences in symmetry. Study of the structural units from which the two substances are built enables a plausible structure to be deduced for Cd_3SiO_5; it also suggests that the polymorphism of Ca_3SiO_5 might be explained in terms of variations in the stacking of these units.

Unit-cell relationships

Table 1 compares the unit cells or pseudo-cells of the three compounds. The relationship between the pseudo-cells of Ca_3SiO_5 and Cd_3SiO_5 is immediately obvious. The relationship of the pseudo-rhombohedral cell to the tetragonal cell of Sr_3SiO_5 was noticed during an attempt to determine the true cell of Cd_3SiO_5. The trigonal (pseudo-rhombohedral) cell is outlined on the left of Fig. 1: shaded circles represent pseudo-lattice points. Because only poor crystals were available the true symmetry of the compound was not determined, but all the true lattice points can be accounted for in terms of the primitive cell outlined by dotted lines in the centre of the diagram: a_p, b_p and c_p represent the axes of this cell.

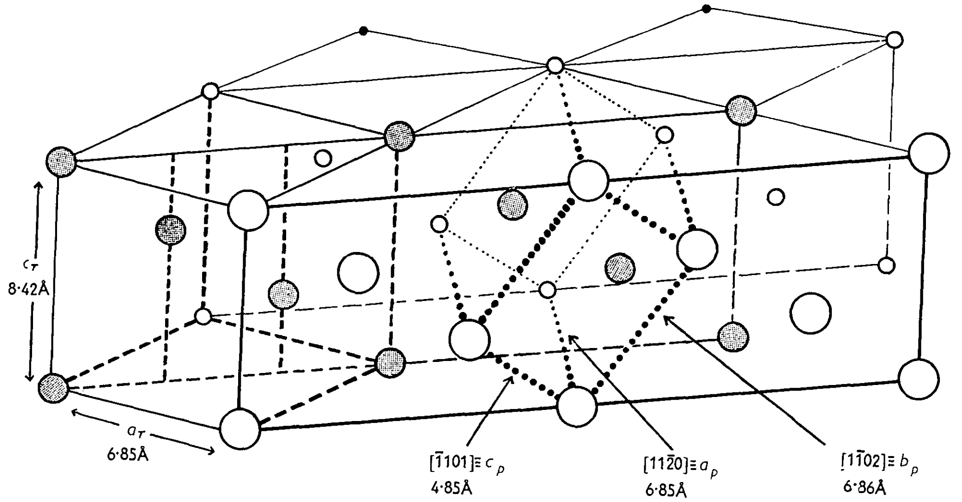


Fig. 1. The crystal lattice of Cd_3SiO_5. Open circles are true lattice points; shaded circles are pseudo-lattice points. The trigonal pseudo-cell (axes a_T and c_T) is outlined on the left; it is compound (rhombohedral). The front of the diagram is cut off along (trigonal) $11\bar{2}0$, so as to display the lattice points at $\frac{1}{3}$, $\frac{2}{3}$, $\frac{2}{3}$. A true, primitive cell (axes a_p, b_p and c_p) is outlined by dotted lines; it is approximately tetragonal in shape, but its true symmetry is unknown. $[\bar{1}101]$, $[11\bar{2}0]$ and $[1\bar{1}02]$ are directions in the trigonal lattice.

Table 1. *Comparison of unit cells or pseudo-cells*

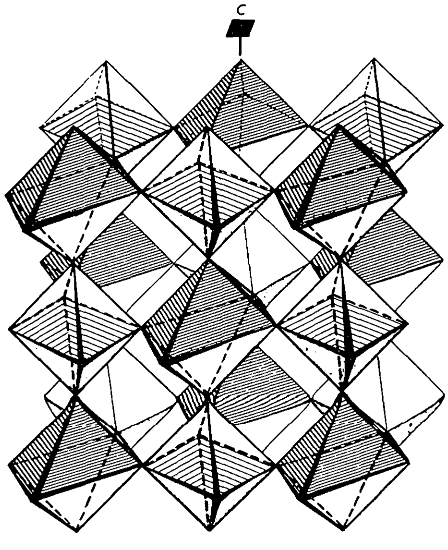
Ca_3SiO_5	Cd_3SiO_5		Sr_3SiO_5
Pseudo-rhombohedral cell*	Pseudo-rhombohedral cell*	Orthogonal cell	Tetragonal cell
a 7·07 Å	a 6·85 Å	a 6·85 Å	a 6·93
c 25·09 (3 × 8·36)	c 8·42	b 6·86	
		c 4·85	c 10·72 (2 × 5·36)

* Trigonal axes.

This primitive cell is orthogonal, or nearly so, with $a_p \simeq b_p$: if c_p be doubled it is very similar in shape to the tetragonal unit cell of Sr_3SiO_5.

Such a relationship seemed rather far-fetched, but on the chance that it might be significant, a model of Ca_3SiO_5 was built, based on Jeffery's (1952) coordinates for the pseudo-structure, and compared with a model of the proposed structure for Sr_3SiO_5 to see whether there was any underlying structural similarity. It was found that there was. Both structures are built of M^{2+} ions (M = Ca, Sr or Cd), O^{2-} ions and isolated SiO_4^{4-} tetrahedra. In both structures, all the O^{2-} ions are surrounded by regular octahedra of M^{2+} ions; the difference between them lies in the way in which these units are linked to each other and to the SiO_4^{4-} tetrahedra. This is illustrated by Fig. 2, in which the units are shown as solid octahedra with M^{2+} ions at the corners surrounding central O^{2-} ions. (*These octahedra should not be confused with the conventional representation of the coordination polyhedron of a metal ion.*)

Fig. 2(*a*) shows the arrangement in Sr_3SiO_5. The octahedra all have one fourfold axis parallel to c, and they share corners; that is each Sr^{2+} ion is bonded to two oxygen atoms, and these two oxygen atoms have only one Sr^{2+} ion in common. The coordination



(*a*)

Fig. 2. (*a*) The arrangement of Sr^{2+} and O^{2-} ions in Sr_3SiO_5. Six Sr^{2+} ions at the corners of each octahedron surround a central O^{2-} ion. Shaded faces lie roughly parallel to faces of $SiO_4{}^{4-}$ tetrahedra. The direction of tetragonal c is indicated.

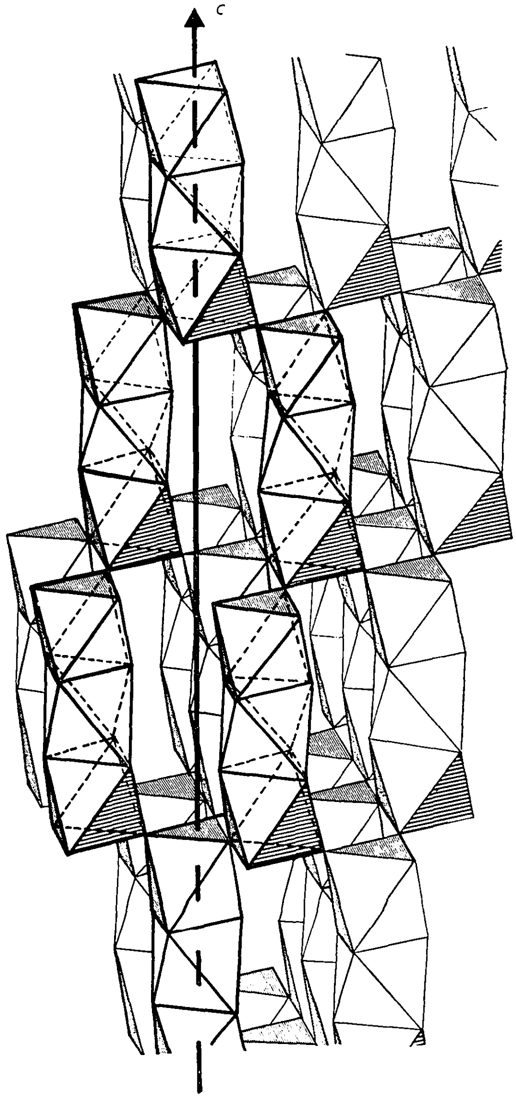
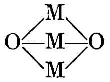


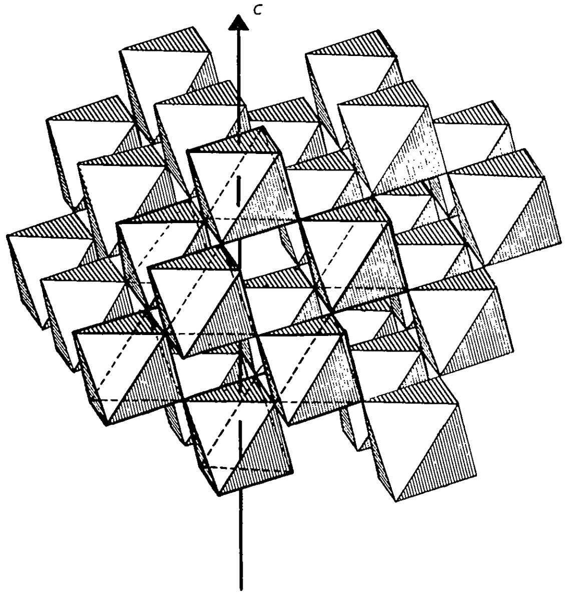
Fig. 2. (*b*) The arrangement of Ca^{2+} and O^{2-} ions in Ca_3SiO_5. Ca^{2+} ions lie at the corners of the octahedra which share faces as well as corners. Shaded faces lie roughly parallel to faces of $SiO_4{}^{4-}$ tetrahedra. The direction of trigonal c is indicated.

of the Sr^{2+} ion is completed with oxygen atoms belonging to SiO_4^{4-} tetrahedra. These are not shown; the tetrahedra are arranged with their faces very roughly parallel to those faces of the octahedra which are shaded.

Fig. 2(*b*) shows the arrangement in Ca_3SiO_5. The octahedra all have one threefold axis parallel to *c*; groups of three share faces, forming short columns parallel to *c*. These columns contain the grouping



which is not found in Sr_3SiO_5. The topmost octahedron of each column shares corners with three octahedra at the bottom of columns in the layer above (Fig. 2(*b*)): if this arrangement is repeated regularly, rhombohedral symmetry is produced. It is suggested that the lower symmetries observed in Ca_3SiO_5 and its solid solutions are produced by slight changes in the stacking arrangement, or the introduction of columns of octahedra of different length. In the case of solid solutions, such modifications might well be produced by the introduction of small quantities of cations having different coordination requirements.



(c)

Fig. 2. (*c*) A possible arrangement of Cd^{2+} and O^{2-} ions in Cd_3SiO_5. Cd^{2+} ions lie at the corners of the octahedra. Shaded faces have no significance other than artistic. The direction of trigonal *c* is indicated.

Fig. 2(*c*) shows a possible arrangement of the octahedra in Cd_3SiO_5, deduced by analogy with Ca_3SiO_5 and Sr_3SiO_5. Comparison of this arrangement with that in Fig. 2(*a*) shows how arrangements with rhombohedral or tetragonal symmetry can be derived by distortion of the same basic structure. The arrangement shown in Fig. 2(*c*) is cubic; the pseudo-rhombohedral symmetry appropriate to Cd_3SiO_5 is produced by the arrangement of the SiO_4^{4-} tetrahedra, with their threefold axes parallel to *c*, and probably also by some distortion of the octahedra about this axis. (The structure derived in this way is idealized, since the true symmetry is probably lower than rhombohedral). The arrangement in Fig. 2(*a*), on the other hand, is derived from the cubic arrangement in Fig. 2(*c*) by slight rotations of the octahedra about one of the fourfold axes, reducing the symmetry to tetragonal; each of the isolated SiO_4^{4-} tetrahedra has a fourfold inversion axis parallel to tetragonal *c*.

The relationship between these three structures is an interesting example of a structure type occurring with different unit cells and symmetries: it is to be hoped that more compounds of this type can be prepared.

References

Dent Glasser, L. S. & Glasser, F. P. (1964). *Inorg. Chem.* **3**, 1228.

Jeffery, J. W. (1952). *Acta Cryst.* **5**, 26.

Nurse, R. W. (1952). *J. Appl. Chem.* **2**, 244.

Woermann, E., Hahn, Th. & Eysel, W. (1963). *Zement-Kalk-Gips*, **16**, 370.

Yamaguchi, G. & Miyabe, H. (1960). *J. Amer. Ceram. Soc.* **43**, 219.

Yannaquis, N., Regourd, M., Mazières, C. & Guinier, A. (1962). *Bull. Soc. franç. Minér. Crist.* **85**, 271.