

On the crystal structure of pseudowollastonite (CaSiO₃)

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ABSTRACT

A single-crystal X-ray diffraction study of synthetic pseudowollastonite (CaSiO₃) shows that this crystal has monoclinic *C2/c* symmetry, with $a = 6.8394(5)$, $b = 11.8704(9)$, $c = 19.6313(7)$ Å, $\beta = 90.667(6)^\circ$, and $V = 1593.7(2)$ Å³. Basic features of the *C2/c* structure are similar to those previously determined with a *C1* symmetry but fewer sites exist for the monoclinic space group: five symmetrically nonequivalent Ca sites, three Si sites, and nine O sites.

INTRODUCTION

Pseudowollastonite is the high-temperature form of CaSiO₃ above ~1125 °C and commonly occurs in slags, cement, and ceramic materials. Jeffery and Heller (1953) made the first preliminary X-ray investigation of pseudowollastonite on the basis of oscillation, rotation, and Weissenberg photographs and found it to be triclinic with pseudo-planes of symmetry perpendicular to all three axes. The structure was thus considered as pseudo-orthorhombic or pseudo-hexagonal. In addition, Jeffery and Heller (1953) observed systematic absences that indicated a C-centered lattice. Unfortunately, the crystals examined by Jeffery and Heller (1953) were not good enough for them to proceed with a detailed structure determination. Following Liebau's (1960) suggestion that SrGeO₃ and SrSiO₃, as well as the low-temperature phase of BaSiO₃, were structural analogs of pseudowollastonite, Dornberger-Schiff (1962) and Hilmer (1963) discussed the symmetry and structure of pseudowollastonite based on the structural data obtained for SrGeO₃ to avoid the difficulties encountered in the sample preparation.

Yamanaka and Mori (1981) successfully grew large pseudowollastonite crystals by using CaCl₂ flux and found from X-ray precession photographs the presence of at least three polytypes of pseudowollastonite: a four-layer (dominant phase), six-layer, and a disordered structure. The six-layer polytype, which has pseudo-symmetry *C2/c*, was regarded to be probably isostructural to SrGeO₃ described by Dornberger-Schiff (1962) and Hilmer (1963). For the four-layer polytype, Yamanaka and Mori (1981) obtained a triclinic unit cell (parameters are given in Table 1) with systematic reflection absences corresponding to a C-centered lattice and a pseudo-*c*-glide plane perpendicular to the *b* axis, leading them to conclude that pseudowollastonite has pseudo-monoclinic *C2/c* symmetry. The structure was solved based on space group *C1*. Ingrin (1993) investigated polytypism in pseudowollastonite using transmission electron microscopy and observed the coexistence of two-, four-, and six-layer polytypes in the form of lamellae parallel

to (001). High-temperature properties of pseudowollastonite were studied by Richet et al. (1998) using powder X-ray diffraction and Raman spectroscopy up to its melting point. In this study, we re-determine the structure of a high-quality synthetic pseudowollastonite crystal. Our results show the symmetry of pseudowollastonite to be monoclinic *C2/c*, rather than triclinic, *C1*.

EXPERIMENTAL PROCEDURES

The pseudowollastonite sample was synthesized and kindly supplied by N. Boctor of the Geophysical Laboratory. A CaSiO₃ gel was prepared from stoichiometric amounts of puratronic CaCO₃ and tetraethyl orthosilicate. The dried gel was crystallized at 1400 °C for 5 d to ensure that no phases other than pseudowollastonite formed metastably. The crystalline pseudowollastonite was then melted at 1570 °C and quenched to room temperature. The homogeneous CaSiO₃ glass was crystallized at 1440 °C for 7 d and quickly quenched into liquid mercury. Optical and X-ray diffraction examination revealed no other phases but transparent pseudowollastonite. Most crystals have irregular shapes; the longest dimension of the largest crystal is greater than 1 mm. Microprobe analysis shows the stoichiometric composition of CaSiO₃ and absence of any impurities. Based on optical examination, four crystals were selected for precession photography; they all had unit-cell dimensions similar to those reported by Yamanaka and Mori (1981) and no diffuse streaks or other polytypes were observed. A nearly cube-shaped single-crystal fragment (0.10 × 0.10 × 0.09 mm) with exceptionally sharp peak profiles was placed on a Picker four-circle diffractometer equipped with a Mo X-ray tube ($\lambda = 0.71073$ Å, θ -filtered) for all X-ray diffraction measurements. Unit-cell parameters (Table 1) were determined by fitting the positions of 18 reflections with $20^\circ < 2\theta < 35^\circ$ following the procedure of King and Finger (1979) to eliminate the effect of any crystal offset errors and diffractometer aberrations from the measured setting angles.

X-ray diffraction intensity data from a hemisphere of reciprocal space with $0^\circ < 2\theta < 60^\circ$ were collected on the basis of the C-centered lattice using scans of 1° width in step in-

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TABLE 1. Unit-cell parameters and space groups for pseudowollastonite (CaSiO₃)

<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	(°)	(°)	(°)	<i>V</i> (Å ³)	S.G.	References
6.90	11.78	19.65	90	90.80	90	1597	triclinic	Jeffrey and Heller (1953)
6.853(3)	11.895(5)	19.674(13)	90.12(3)	90.55(3)	90.00(3)	1603.9	C $\bar{1}$	Yamanaka and Mori (1981)
6.829(1)	11.856(4)	19.618(3)	89.98(2)	90.68(2)	89.99(2)	1588.3	C $\bar{1}$	Matteson (1983)
6.83	11.85	20.58	90.00	90.70	90.00	1664.72	C $\bar{1}$	Taniguchi et al. (1995)
6.856(12)	11.901(8)	19.672(22)	90.06(9)	90.36(14)	89.93(14)	1605(4)	triclinic	Richet et al. (1998)
6.8391(4)	11.8711(8)	19.6318(11)	90.006(6)	90.670(5)	89.994(6)	1593.8(2)	C2/ <i>c</i>	This study (unconstrained)
6.8394(5)	11.8704(9)	19.6313(9)	90	90.667(6)	90	1593.7(2)	C2/ <i>c</i>	This study (constrained)

TABLE 2. Atomic positional coordinates and displacement factors for pseudowollastonite

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>11</i>	<i>22</i>	<i>33</i>	<i>12</i>	<i>13</i>	<i>23</i>
Ca1	0	0	0	0.00491(6)	0.00123(2)	0.00032(1)	0.00100(3)	0.00020(2)	0.00010(1)
Ca2	0	0.34259(3)	0.25	0.00437(6)	0.00093(2)	0.00030(1)	0	0.00025(2)	0
Ca3	0	0.32910(3)	0.75	0.00253(6)	0.00202(2)	0.00030(1)	0	-0.0001(2)	0
Ca4	0	0.00462(3)	0.75	0.00378(6)	0.00095(2)	0.00027(1)	0	0.00008(2)	0
Ca5	0.01127(3)	0.33571(2)	0.00047(1)	0.00310(4)	0.00123(2)	0.00028(1)	-0.00033(2)	0.00011(1)	-0.00005(1)
Si1	0.29298(4)	0.03898(2)	0.37507(1)	0.00260(6)	0.00076(2)	0.00018(1)	0.00019(2)	0.00007(1)	-0.00001(1)
Si2	0.09283(4)	0.17035(3)	0.12790(1)	0.00195(5)	0.00098(2)	0.00019(1)	-0.0001(2)	0.00007(1)	0.00001(1)
Si3	0.29798(4)	0.29716(3)	0.37784(2)	0.00260(6)	0.00077(2)	0.00019(1)	-0.00021(2)	0.00006(1)	-0.00001(1)
O1	0.34734(12)	0.34508(7)	0.45190(4)	0.00547(16)	0.00152(5)	0.00030(2)	-0.00061(7)	-0.0010(4)	-0.0015(2)
O2	0.15484(12)	0.48810(7)	0.19713(4)	0.00613(17)	0.00161(5)	0.00031(2)	-0.00066(8)	0.00022(4)	0.00020(2)
O3	0.19052(12)	0.17222(7)	0.20205(4)	0.00397(15)	0.00206(6)	0.00030(2)	0.00021(7)	-0.00026(4)	-0.00004(2)
O4	0.05651(11)	0.28096(7)	0.37492(4)	0.00277(15)	0.00100(5)	0.00063(2)	0.00004(7)	-0.00004(4)	-0.00005(3)
O5	0.20071(12)	0.17028(7)	0.05692(4)	0.00430(16)	0.00254(6)	0.00037(2)	0.00016(7)	0.00053(4)	0.00008(3)
O6	0.05217(12)	0.05793(7)	0.37380(4)	0.00285(15)	0.00098(5)	0.00066(2)	0.00002(7)	0.00000(4)	0.00002(2)
O7	0.35429(13)	0.35084(7)	0.30682(4)	0.00697(18)	0.00159(6)	0.00037(2)	-0.00083(8)	0.00036(5)	0.00021(3)
O8	0.15804(12)	0.48546(7)	0.05278(4)	0.00593(17)	0.00164(5)	0.00032(2)	-0.00067(8)	-0.00004(4)	-0.00023(2)
O9	0.38933(12)	0.16744(6)	0.37627(4)	0.00291(15)	0.00099(5)	0.00066(2)	-0.0002(7)	0.00007(4)	-0.00003(2)

TABLE 3. Selected interatomic distances (Å) in four-layer pseudowollastonite

Ca1-O1 ×2	2.311(1)	Si1-O2	1.585(1)
Ca1-O5 ×2	2.680(1)	Si1-O6	1.662(1)
Ca1-O6 ×2	2.600(1)	Si1-O8	1.585(1)
Ca1-O8 ×2	2.575(1)	Si1-O9	1.661(1)
Avg.	2.542	Avg.	1.623
Ca2-O2 ×2	2.282(1)	Si2-O3	1.595(1)
Ca2-O3 ×2	2.589(1)	Si2-O4	1.664(1)
Ca2-O4 ×2	2.584(1)	Si2-O5	1.584(1)
Ca2-O7 ×2	2.658(1)	Si2-O6	1.663(1)
Avg.	2.528	Avg.	1.627
Ca3-O2 ×2	2.633(1)	Si3-O1	1.594(1)
Ca3-O3 ×2	2.307(1)	Si3-O4	1.663(1)
Ca3-O7 ×2	2.613(1)	Si3-O7	1.585(1)
Ca3-O9 ×2	2.601(1)	Si3-O9	1.662(1)
Avg.	2.539	Avg.	1.626
Ca4-O2 ×2	2.569(1)		
Ca4-O3 ×2	2.649(1)		
Ca4-O6 ×2	2.562(1)		
Ca4-O7 ×2	2.282(1)		
Avg.	2.516		
Ca5-O1	2.637(1)		
Ca5-O1'	2.598(1)		
Ca5-O4	2.578(1)		
Ca5-O5	2.594(1)		
Ca5-O5'	2.282(1)		
Ca5-O8	2.280(1)		
Ca5-O8'	2.629(1)		
Ca5-O9	2.568(1)		
Avg.	2.521		

crements of 0.025° and 2s per step counting time. To check if any reflections violated the *C*-centered symmetry, a data set with 0° 2 30° was first collected in a 1s per step counting time based on the primitive lattice; no such reflections were detected. Digitized step data were integrated by the method of

Lehmann and Larsen (1974) with background manually reset when necessary. Corrections were made for Lorentz and polarization effects, and for X-ray absorption by the crystal ($\mu = 25.00 \text{ cm}^{-1}$). The total number of measured reflections was 4829. Examination of measured reflections indicated the possible space groups *Cc* and *C2/c*. After symmetry-equivalent reflections were averaged in Laue group *2/m* ($R_{\text{merge}} = 0.014$), there were 2067 reflections with $I > 2\sigma$, which were included in the structure determination and refinement.

Because the E-value statistics of the X-ray intensity data showed that the pseudowollastonite structure is probably centric, we began solution of the structure with space group *C2/c*. The structure was solved using program SHELX97 and refined with RFINE90. Procedures of structure refinements were similar to those described by Yang et al. (1997). The anisotropic refinement for all atoms converged after five cycles ($R_w = 0.018$ and $R = 0.018$) and resulted in featureless difference Fourier maps. A model based on the *Cc* symmetry was also attempted, but it did not improve the refinement statistics significantly. Thus, the *C2/c* symmetry was adopted for all refinements. Final atomic positional coordinates and displacement parameters are presented in Table 2 and selected interatomic distances in Table 3.

RESULTS AND DISCUSSION

The basic features of the pseudowollastonite structure determined in this study are similar to those reported by Yamanaka and Mori (1981) based on $C\bar{1}$ symmetry. It is characterized by four layers, each of which is composed of a layer of ternary (Si₃O₉) tetrahedral rings and a layer of distorted-bicapped Ca octahedra (Fig. 1). A distorted-bicapped octahedron is formed by eight O atoms, with six of them in an octahedral arrange-

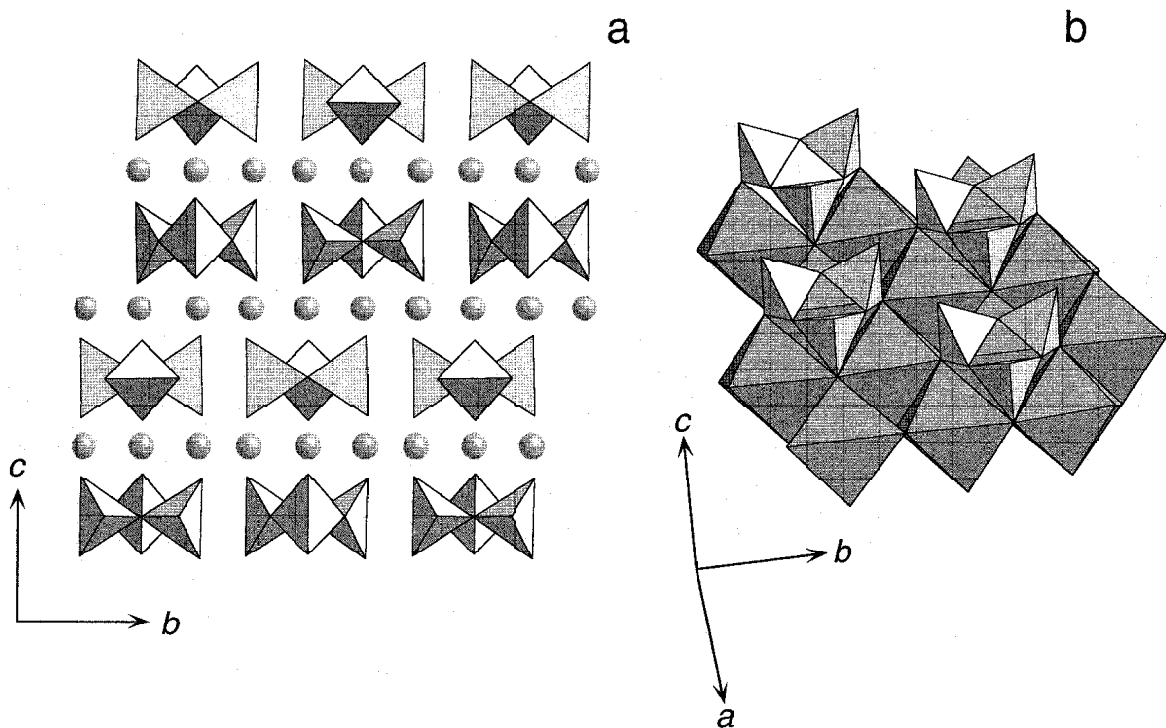


FIGURE 1. (a) The pseudowollastonite structure showing the layering feature of Ca atoms (shaded spheres) and Si_3O_9 ternary rings along the c axis. (b) A portion of the pseudowollastonite structure showing the arrangement of the Si_3O_9 ternary rings on the CaO_6 octahedral layers. The ternary rings are located at the void spaces defined by three octahedra.

ment plus two from bridging O atoms of the Si_3O_9 ternary rings, one above and one below the octahedron. The ternary rings are elongated along the stacking [001] direction, whereas the CaO_8 polyhedral layers are compressed in the same direction. However, our structural data and unit-cell parameters clearly point to monoclinic $C2/c$ symmetry, rather than triclinic $C\bar{1}$ symmetry, as suggested by Yamanaka and Mori (1981). Compared to the $C\bar{1}$ structure, which has seven crystallographically distinct Ca sites, six Si sites, and eighteen O sites, the $C2/c$ structure has only five symmetrically distinct Ca sites, three Si sites, and nine O sites. All SiO_4 and CaO_8 polyhedra in the $C2/c$ structure are slightly less distorted than those in the $C\bar{1}$ structure.

On the basis of a careful examination of X-ray diffraction data collected from a twinned pseudowollastonite crystal, Matteson (1983) noted that, in addition to the systematic absences that indicated the presence of the C -centered lattice and a c -glide plane normal to the b axis, all $I_{hkl} = I_{h\bar{k}l}$ (within one σ), and $I_{hkl} = I_{\bar{h}kl}$. Although structure refinements based on either monoclinic or triclinic symmetry were unsuccessful for the twinned crystal, Matteson (1983) proposed that pseudowollastonite could have crystallized in space group Cc or $C2/c$. Furthermore, Matteson (1983) re-examined X-ray intensity data obtained by Yamanaka and Mori (1981) and found that observed structure factors, as well as calculated ones, for any pairs of hkl and $\bar{h}kl$ reflections were equal within one σ . Accordingly, the pseudowollastonite crystal investigated by Yamanaka and Mori (1981) most likely possesses monoclinic symmetry, instead of triclinic symmetry (also see below).

All pseudowollastonite unit-cell parameters (Table 1) suggest a monoclinic unit cell given the experimental uncertainties. Although the unit-cell dimensions measured by Jeffery and Heller (1953) indicated a monoclinic cell, no reason was given why they claimed pseudowollastonite to be triclinic. Using the energy minimization technique, Taniguchi et al. (1995) simulated the structures and physical properties of pseudowollastonite and several other Ca-rich silicates. Interestingly, without any particular assumptions about the nature of the bonding or the interatomic forces, the unit-cell parameters (Table 1) and cation configurations they obtained all suggested monoclinic symmetry for pseudowollastonite. Also, the unit-cell dimensions reported by Richet et al. (1998) at 17 different temperatures between 305 and 1793 K appear to be monoclinic within the experimental errors, yet these were based on the structural data of Yamanaka and Mori (1981). Also noteworthy are the significant differences among reported unit-cell dimensions: the largest difference in unit-cell volumes amounts to 17 \AA^3 . Presumably, disordered stacking of various polytypes and twinning are responsible for these discrepancies, because such phenomena were observed in all previous studies (Jeffery and Heller 1953; Yamanaka and Mori 1981; Matteson 1983; Ingrin 1993; Richet et al. 1998). These structural defects may also account for the slight deviation of the β angle [$90.12(3)^\circ$] from 90° in the crystal examined by Yamanaka and Mori (1981).

Crystals synthesized by the method outlined in this letter showed only the four-layer pseudowollastonite polytype. Pseudowollastonite crystals crystallized by Ingrin (1993) from

glass annealed at 1350 °C for 50 h showed three (two-, four-, and six-layer) coexisting polytypes. It is likely that the higher annealing temperature (1440 °C), prolonged annealing time (168 vs. 50 h), and the fast quenching rate in our experiment are responsible for the preservation of a single "equilibrium" polytype of pseudowollastonite.

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