Zeitschrift für Kristallographie 164, 67–77 (1983)

Re-examination of "$P2_1/a$ coesite"

Satoshi Sasaki, Hwai-Kuo Chen, Charles T. Prewitt,
and Yoshiharu Nakajima[1]

Department of Earth and Space Sciences, State University of New York,
Stony Brook, New York 11794, U.S.A.

Received: September 14, 1982

Coesite / Twin / $P2_1/a$ coesite / X-ray / TEM / SiO_2

Abstract. Kirfel, Will, and Arndt (1979) reported a quenchable new phase of SiO_2, synthesized in aqueous solution at 44–49 kbar and 610 °C, having the space group $P2_1/a$ and a crystal structure closely related to coesite. However, single-crystal X-ray and TEM studies have revealed that their observations could be the result of (100)-twinning of $C2/c$ coesite. Therefore, a distinct $P2_1/a$ phase probably does not exist. The evidence is: (1) The intensity distributions in the diffraction patterns of the (100)-twinned $C2/c$ coesite are similar to those calculated using the reported $P2_1/a$ structure. (2) The least-squares refinements using the (100)-twinned model yielded results similar to those reported for the $P2_1/a$ phase. (3) The cell dimensions reported for the $P2_1/a$ phase, when transformed to a $C2/c$ cell, are not significantly different from those reported by other authors for normal coesite. (4) The $P2_1/a$ phase cannot be distinguished from normal coesite on the basis of the calculated powder diffraction patterns. (5) Syntheses under a wide range of conditions have produced only $C2/c$ coesite crystals.

Introduction

Coesite, a high-pressure polymorph of SiO_2, was first synthesized by Coes (1953) and was discovered subsequently as a mineral at Meteor Crater, Arizona (Chao, Shoemaker, and Madsen, 1960). Through single crystal X-ray studies (Ramsdell, 1955; Zoltai and Buerger, 1959; Araki and Zoltai, 1969; Gibbs, Prewitt, and Baldwin, 1977; Levien and Prewitt, 1981), the

---

[1] *Present address:* Central Research Lab., Sharp Corporation, 2613-1 Ichinomoto, Tenri, Nara 632, Japan

space group of coesite has been determined to be $C2/c$ with a framework crystal structure related to that of the feldspars. Kirfel, Will, and Arndt (1979), however, reported a quenchable new phase of "coesite"[2] synthesized in aqueous solution at 44–49 kbar and 610 °C, having the space group $P2_1/a$ and a unit cell with a volume 1% smaller than for the conventional coesite cell. Their report also included a crystal structure refinement that showed the new structure to have essentially the same linkage of SiO_4 tetrahedra as in coesite, but with different Si–O distances and different Si–O–Si angles. At the time that the Kirfel et al. paper appeared, we had just completed a study of coesite at high pressure in this laboratory (Levien and Prewitt, 1981) without noticing any indication of a primitive cell. This was of concern to us because we felt that we might have missed seeing diffraction spots indicating a primitive cell or that a phase change might have taken place at high pressure without being detected. Furthermore, we were intrigued because the proposed new structure did not contain the unusual 180° Si–O–Si bond angles that have been controversial (Liebau, 1961), and because the small differences in cell volume indicated that a displacive phase transition should take place at high pressure. Therefore, because of the implications of this discovery on other coesite research, we decided to try to duplicate the experiments of Kirfel et al. (1979) in order to confirm the new structure and to explore its relationship to the known $C2/c$ structure of coesite. A preliminary communication has been reported in abstract form (Chen, Sasaki, Prewitt, and Nakajima, 1981).

Experimental

Coesite crystals were synthesized using a girdle solid-media, high-pressure apparatus equipped with an internal graphite heater. Powdered crystals of quartz and silicic acid, $SiO_2 \cdot nH_2O$, in the ratio of 1 : 1 (wt%) were used as starting materials in a Pt capsule containing about 20 wt% H_2O. The open ends of the capsule were crimped tight, welded shut, and cold-pressed with the aid of a pellet press; the final volume of the capsule was about 35 mm^3. The seal of the capsule was perfect and the water in the capsule was maintained during runs. The capsule was enclosed by pyrophyllite inside a graphite heater that was, in turn, enclosed by polycrystalline NaCl and an outer container of pyrophyllite.

Several high-pressure experiments were performed using the following procedure: (1) the sample was raised to a desired pressure at room temperature and then heated for 2 h at a desired temperature; (2) the sample

---

[2] According to mineralogical practice, one should not assign a mineral name to a phase not found in nature. However, because no generally accepted scheme has been adopted for labeling the SiO_2 polymorphs, we refer to this proposed phase as "$P2_1/a$ coesite"

was then either directly quenched or cooled isobarically to about 200° C and quenched; (3) the pressure was released. In this study, cell pressure and temperature in the girdle were estimated from the P–T calibration curves of Liebermann, Ringwood, Mayson, and Major (1975), based on ram load versus pressure and electric power versus temperature. For the synthesis, similar experimental conditions to those reported by Kirfel et al. (1979) were chosen; the P–T conditions were within the range of 40–52 kbar and 400–650° C.

The crystals synthesized are transparent and pseudo-hexagonal, lath- or cube-like in shape, and the maximum size is about 0.35 mm. Crystals having dimensions from 0.1–0.3 mm were selected using the polarizing microscope; they were optically free of cracks. The space group of each crystal was determined with the precession method (Zr-filtered Mo*Kα* radiation) and, partly, with the Weissenberg method (Ni-filtered Cu*Kα*). Intensity data for all possible reflections up to $2\theta = 40°$ were collected for both single and twinned crystals with a Picker four-circle diffractometer using graphite monochromatized Mo*Kα* radiation ($\lambda = 0.71069$ Å). The experimental conditions for data collection were as follows: $\omega - 2\theta$ technique in the bisecting mode; scan speed 1.5 (°/min) in 2θ, scan width $2 + 0.7 \tan\theta$ (°) in 2θ. The cell dimensions obtained from single crystal diffractometry (Mo$K\alpha_1$ radiation) are compared with the previous determinations in Table 1.

Samples were also prepared for observation by transmission electron microscopy (TEM) by making doubly-polished, oriented thin sections using

Table 1. Comparison of cell parameters: $P2_1/a$ vs. $C2/c$ coesite

	$P2_1/a$	$C2/c$			
	Kirfel et al. (1979)	This study		Gibbs et al. (1977)	Araki and Zoltai (1969)
		single crystal	(100) twinned		
$C2/c$ orientation					
a (Å)	7.098	7.137(2)	7.131(3)	7.135(1)	7.173(4)
b (Å)	12.334	12.370(1)	12.370(2)	12.372(1)	12.328(6)
c (Å)	7.148	7.174(1)	7.171(2)	7.174(1)	7.175(4)
β (°)	120.10	120.33(1)	120.28(2)	120.36(1)	120.0
V (Å^3)	541.3(2)	546.6(2)	546.3(3)	546.4(3)	549.5
$P2_1/a$ orientation					
a (Å)	7.148(2)	7.174(2)	7.171(3)		
b (Å)	12.334(3)	12.370(1)	12.370(2)		
c (Å)	7.112(2)	7.119(1)	7.121(1)		
β (°)	120.30(2)	120.09(1)	120.14(2)		
V (Å^3)	541.3(2)	546.6(2)	546.3(2)		

the ion-thinning technique. After carbon coating they were studied in a JEOL 200CX transmission electron microscope operating at 200 KV and equipped with a ±45° double-tilt, side entry goniometric stage.

Analysis of diffraction patterns

In spite of the monoclinic distribution of intensity, the cell of coesite has strong pseudosymmetry: $a^* \cong 2b^* \cong c^*$, $\beta^* \cong 60°$. Therefore, there is a possibility that, in certain different orientations, a reciprocal lattice net for one member of a twin can coincide with that of another member. All of the crystals produced in our experiment belong to space group $C2/c$; however, some are single and some are twinned. Two types of twins in coesite were described by Ramsdell (1955): (021) and (100). Examples of both types were found in our synthesized crystals. A zero-level precession photograph of the plane composed of the $[\bar{2}21]^*$ and b^* axes could be mistaken for the $h0l$ plane; for a crystal in this orientation and twinned on (021), analysis of the diffraction pattern would indicate space group $C2$, but with a slightly different unit cell from $C2/c$ coesite. Because the upper-layer precession photographs of twinned crystals in this orientation mimic the C lattice type, they can be clearly distinguished from those of so-called "$P2_1/a$ coesite".

In the single-crystal X-ray and TEM studies on the crystals synthesized in our experiments, we also found that some were twinned on (100) and that the observed intensity distributions in the diffraction patterns of the twinned

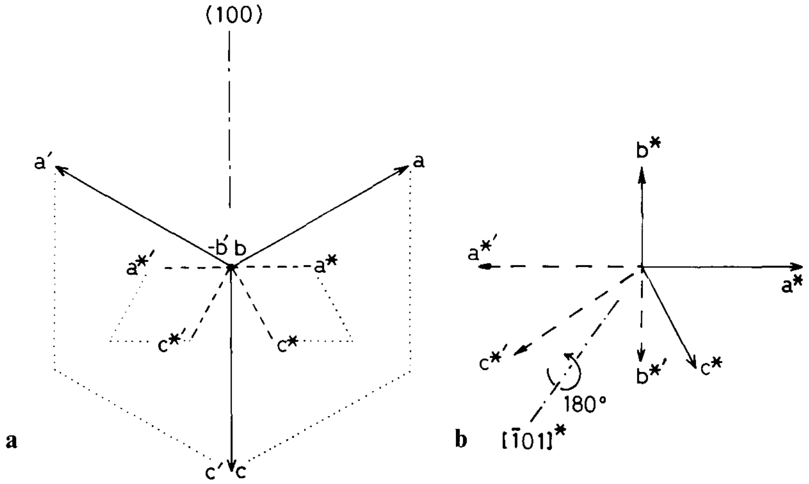

Fig. 1. Schematic diagrams on (100) twinning which show (**a**) the relationship between the real and reciprocal lattices and (**b**) the reciprocal axes from each member of the twin

crystals were similar to those calculated using the reported $P2_1/a$ structure. Precession photographs of crystals twinned on (100) have the following characteristics: The zero-level photographs show patterns similar to $h0l$ of $C2/c$ coesite with systematic absences of $h = 2n$ and $l = 2n$ on $(h0l)$, whereas there are no systematic absences on hkl (inidicating a primitive lattice). As shown in a schematic diagram of Figure 1, the (100) twin plane corresponds to, in reciprocal space, an operation of a 180° rotation along $[\bar{1}01]^*$, which is perpendicular to the $hk0$ plane. The hkl's from each member of the twin are related by:

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \begin{pmatrix} -1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Because it appears that the (100)-twinned coesite can produce a diffraction pattern consistent with "$P2_1/a$ coesite", the detailed characteristics of the relevant diffraction patterns are described in the following section.

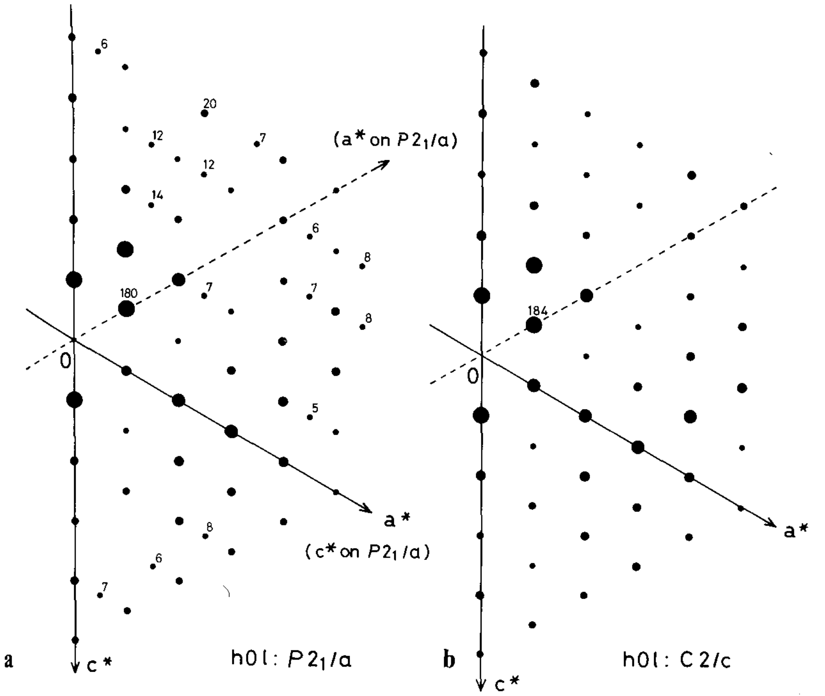

Fig. 2. Schematic diffraction patterns on $(h0l)$ of (**a**) the $P2_1/a$ and (**b**) the (100)-twinned $C2/c$ phase

Comparison between $P2_1/a$ and the (100)-twinned $C2/c$ coesites

Cell parameters

Because Kirfel et al. (1979) represented the $P2_1/a$ phase using a different orientation from normal $C2/c$ coesite (see Fig. 2 of their paper), a transformation of crystal axes was made in order to compare our result to theirs; the cell dimensions after the transformation are given in Table 1. Although their reported $P2_1/a$ cell is 1 % smaller in volume than the cell for normal coesite, the axial ratios between the two are close: 0.576 : 1 : 0.580 for the (100)-twinned one; 0.575 : 1 : 0.580 for the $P2_1/a$ phase.

Intensity distribution on single-crystal photographs

Figures 2, 3, and 4 show schematic distributions of the calculated structure factors on $h0l$, $h1l$, and $h2l$ for both the $P2_1/a$ phase and the (100)-twinned model, respectively. As shown in these figures, the intensity distribution for

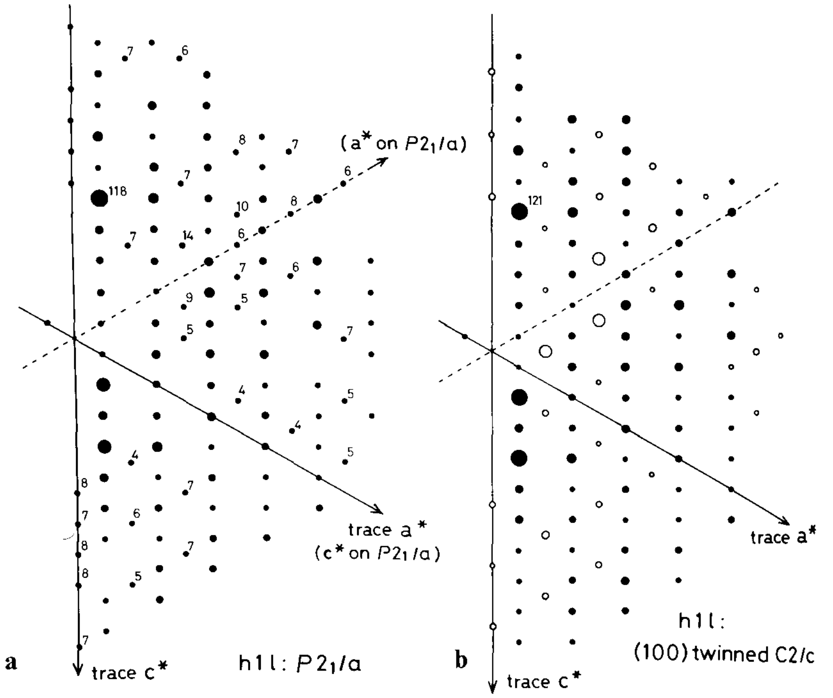

Fig. 3. Schematic diffraction patterns on ($h1l$) of (**a**) primitive and (**b**) normal coesites. The open circles show the unoverlapped forbidden reflections of $C2/c$ caused by (100) twinning

$P2_1/a$ is very close to that of a single crystal of $C2/c$ coesite (see solid circles in Figures 2b, 3b, and 4b and compare with the corresponding spots of the respective $P2_1/a$ patterns). Even in comparing the forbidden reflections of the C lattice, the appearance of the $h+k=2n+1$ reflections on hkl of the $P2_1/a$ pattern closely resembles that of the (100)-twinned model (see open circles in Figs. 3b and 4b). For example, in the $h2l$ pattern of Figure 4, most of the extra spots diffracted by the second part of the twinned $C2/c$ crystal, shown in open circles, are comparable to the corresponding spots of the $P2_1/a$ phase. The first level patterns also resemble each other (see Fig. 3). Precession photographs of the $h1l$ and $h2l$ reciprocal lattice levels are also shown in Figure 5. Using TEM photographs and a comparison of the X-ray intensities, the precession photographs can be explained as from a $C2/c$ coesite crystal associated with a small fraction of (100)-twinning. The chief difference between the two is that only a few reflections on $h0l$ such as -306 and -504 are distinctive because, on the $h0l$ plane of the twinned crystal, reflections for $h=2n+1$ and $l=2n+1$ are missing. Because the observed

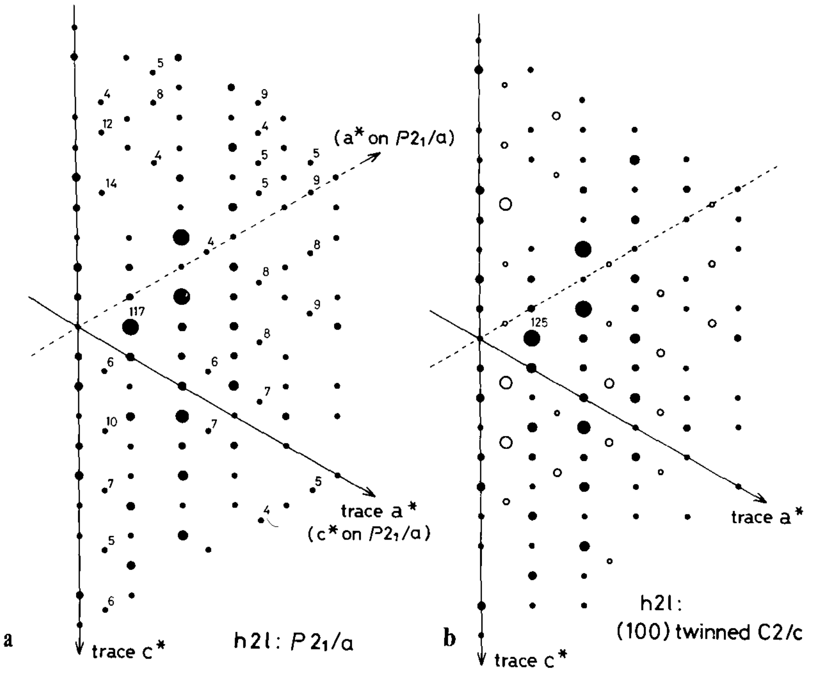

Fig. 4. Schematic diffraction patterns on ($h2l$) of (**a**) primitive and (**b**) normal coesites. The open circles show the unoverlapped reflections caused by (100) twinning

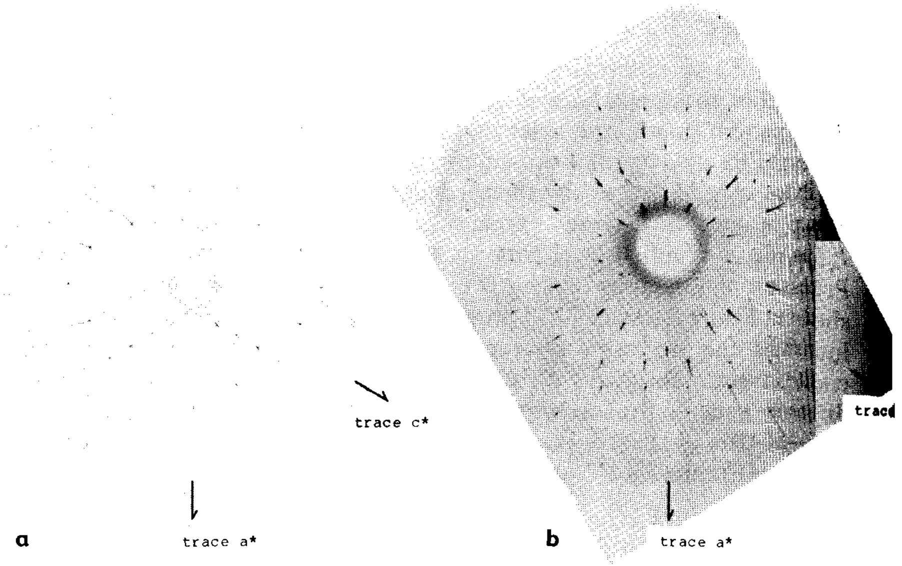

Fig. 5. Precession photographs of the (100)-twinned coesite, showing (**a**) (*h*1*l*) and (**b**) (*h*2*l*) reflections; Mo$K\alpha$, $\mu = 25°$. The a^* and c^* axes of the main crystal are indicated

structure factors for $P2_1/a$ were not available, we used calculated values; therefore, strict coincidence in the intensity distributions of the two are not expected. However, the similarities lead us to conclude that the $P2_1/a$ phase and the (100)-twinned $C2/c$ phases are nearly indistinguishable on the basis of diffraction patterns.

Powder diffraction patterns

We have calculated powder diffraction patterns based on the atomic parameters reported for both $C2/c$ (Gibbs et al., 1977) and the $P2_1/a$ phase (Kirfel et al., 1979). The reflections for the primitive lattice have almost the same d values as those of the C lattice. It is clear that the two coesite phases cannot be distinguished in powder diffraction patterns, although Kirfel et al. (1979) implied that these two phases could be distinguished on X-ray powder patterns even though no such patterns were reported in their paper.

Comparison of crystal structures

If Kirfel et al. (1979) worked with twinned crystals, it should be possible to duplicate the results of their "$P2_1/a$" coesite refinement by using the structure factors derived from the (100)-twinning of normal coesite. The structure factors in the tables of $C2/c$ coesite (Gibbs et al., 1977), up to $\sin\theta/\lambda = 0.807$, were used both for the standard refinement of $C2/c$ and for making the (100)-twinned model. The size of this data set is chosen as same as that used by Kirfel et al. (1979). Based on the 1092 independent reflections with $F_{\mathrm{obs}} \geq 3\,\sigma_F$, the scale and isotropic extinction factors (Becker and Coppens, 1974), atomic coordinates, and isotropic temperature factors for the $C2/c$ structure were determined by least-squares refinement using the program, RADY, a modified version of RADIEL (Coppens et al., 1979). The calculations converged to $R = 4.8\,\%$ for the $C2/c$ phase.

In order to obtain the structure factors for the (100)-twinned model, the volume ratio of the two parts of the twin was first estimated as 1 : 0.016 using 37 unoverlapped reflections on $h1l$ and $h2l$ such as 121, 123, $12\bar{5}$ and $41\bar{3}$. Of a

Table 2. Atomic fractional coordinates and isotropic thermal parameters: (100)-twinned model ($C2/c$ coesite) vs. "$P2_1/a$ coesite"

Atom	x	y	z	B^a (Å^2)
$C2/c$ phase [(100) twinned model]				
Si(1)	0.3256(6)	0.3575(5)	0.3905(7)	0.05(6)
Si(2)	0.6928(8)	0.3595(6)	0.1100(8)	0.80(8)
Si(3)	0.7804(8)	0.4037(5)	0.7376(8)	0.44(7)
Si(4)	0.2124(8)	0.4124(5)	0.7505(8)	0.39(7)
O(1)	0.2312(16)	0.2501(10)	0.2533(18)	0.09(12)
O(2)	−0.0148(19)	0.3660(7)	0.7520(19)	0.36(12)
O(3)	0.2385(14)	0.3535(11)	0.5627(15)	−0.17(13)
O(4)	0.5876(19)	0.3740(12)	0.5209(20)	0.56(18)
O(5)	0.7923(16)	0.4621(9)	0.2632(15)	−0.21(12)
O(6)	0.2238(29)	0.4610(17)	0.2239(31)	2.00(31)
O(7)	0.4362(20)	0.3734(14)	0.0123(21)	0.79(19)
O(8)	0.7818(31)	0.3541(21)	0.0567(32)	2.52(33)
$P2_1/a$ phase^b				
Si(1)	0.3224(1)	0.3585(1)	0.3910(1)	0.63
Si(2)	0.6864(1)	0.3582(1)	0.1106(1)	0.58
Si(3)	0.7874(1)	0.4086(1)	0.7432(1)	1.09
Si(4)	0.2190(1)	0.4074(1)	0.7562(1)	0.32
O(1)	0.2498(17)	0.2513(3)	0.2486(20)	1.00
O(2)	0.0039(7)	0.3662(1)	0.7520(9)	0.88
O(3)	0.2351(3)	0.3548(2)	0.5609(3)	0.94
O(4)	0.5791(3)	0.3726(2)	0.5144(3)	0.92
O(5)	0.7865(3)	0.4648(1)	0.2681(3)	0.82
O(6)	0.2083(4)	0.4581(2)	0.2334(4)	1.46
O(7)	0.4275(3)	0.3738(2)	−0.0184(3)	0.99
O(8)	0.7700(4)	0.3530(2)	−0.0597(4)	2.03

[a] Equivalent isotropic temperature factor for $P2_1/a$ phase

[b] Kirfel et al. (1979)

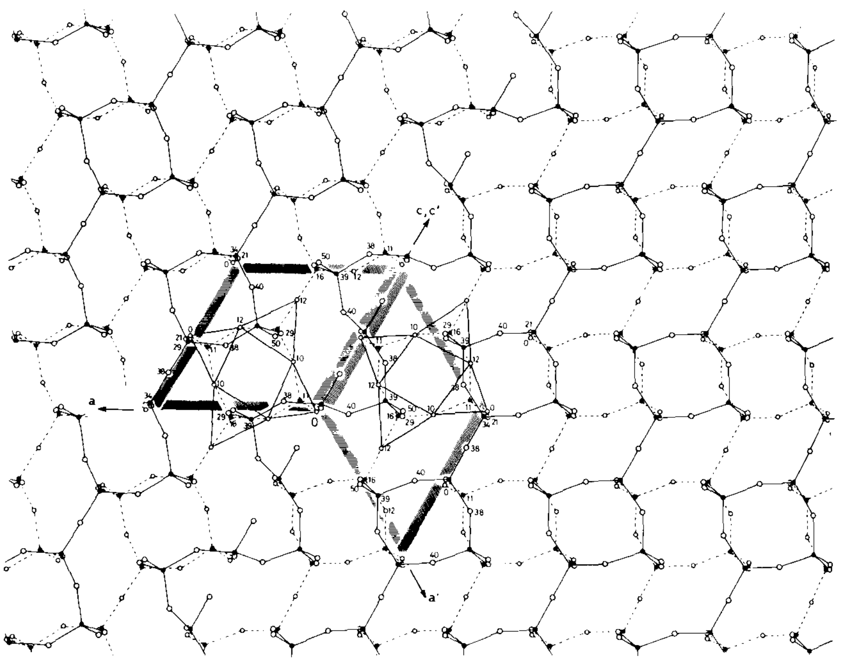

Fig. 6. Twinning of coesite on (100). Si and O atoms are shown by solid and open circles, respectively. Numbers denote the height along the y-axis in units of $n/100$

total of 1400 reflections created in this way (omitting some of unobserveds), 1044 reflections ($F_{\text{obs}} \geq 3\,\sigma_F$) were used for refinement based on the atomic coordinates of the $P2_1/a$ phase. The least-squares calculations converged with $R = 12.8\,\%$ when isotropic temperature factors were used [Kirfel et al. (1979) reported $R = 4.7\,\%$ and $9.6\,\%$ with anisotropic temperature factors for 1390 and 2327 reflections, respectively]; two of twelve independent atoms had negative temperature factors. The atomic coordinates and isotropic temperature factors are given in Table 2, in comparison with those of the $P2_1/a$ phase reported by Kirfel et al. (1979). The maximum deviation of the atomic coordinates between the two are 0.019, 0.005, and 0.009 for x, y, and z, respectively. The small deviations do not allow clear distinction between the $P2_1/a$ structure and the (100)-twinned model. Kirfel et al. (1979) reported large equivalent isotropic temperature factors for the O(6) and O(8) atoms, 1.46 and 2.03 (Å^2), respectively. The respective B values of 2.00 and 2.52 (Å^2) in this calculation give further support to the twin model.

A schematic diagram on the (010) projection of the probable (100)-twinning of $C2/c$ coesite is shown in Figure 6. In this figure, the four-membered rings of silicon tetrahedra parallel to (010) that correspond to those of Figure 5 in Kirfel et al. (1979), may be connected smoothly across the twin boundary. There is only a very small discrepancy at the twin boundary, especially for the lower level drawn in dotted lines. This may explain the common incidence of twinning in coesite.

Conclusions

The above discussion is based on the data calculated from the atomic coordinates of the $P2_1/a$ phase reported by Kirfel et al. (1979). Considering the fact that we were unable to synthesize a $P2_1/a$ phase and that the diffraction pattern for our twinned model closely approximates that calculated with the coordinates from the Kirfel et al. paper, we now believe that "$P2_1/a$ coesite" probably does not exist.

Acknowledgements. The authors are grateful to Prof. R. Liebermann and Dr. J. Bass of our Department for help with the syntheses of the coesite crystals used in our experiments. Also, we wish to thank Mr. K. Baldwin for his useful suggestions and Mr. H. Belsky for a critical reading of the manuscript. This project was supported by NSF Grants EAR81-20950 and EAR82-13513.

References

Araki, T., Zoltai, T.: Refinement of a coesite structure. Z. Kristallogr. **129**, 381–387 (1969)
Becker, P. J., Coppens, P.: Extinction within the limit of validity of the Darwin transfer equations. I. General formalisms for primary and secondary extinction and their application. Acta Crystallogr. **A30**, 129–147 (1974)
Chao, E. C. T., Shoemaker, E. M., Madsen, B. M.: First natural occurrence of coesite. Science, **132**, 220–222 (1960)
Chen, H., Sasaki, S., Prewitt, C. T., Nakajima, Y.: Does $P2_1/a$ coesite exist? Geol. Soc. America 94th Annual Meeting at Cincinnati (abstract), 426 (1981)
Coes, L.: A new dense crystalline silica. Science, **118**, 131–132 (1953)
Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J., Yang, Y. W.: Net atomic charges and molecular dipole moments from spherical-atom X-ray refinements, and the relation between atomic charge and shape. Acta Crystallogr. **A35**, 63–72 (1979)
Gibbs, G. V., Prewitt, C. T., Baldwin, K. J.: A study of the structural chemistry of coesite. Z. Kristallogr. **145**, 108–123 (1977)
Kirfel, A., Will, G., Arndt, J.: A new phase of coesite SiO_2. Z. Kristallogr. **149**, 315–326 (1979)
Liebau, F.: Untersuchungen über die Grösse des Si–O–Si-Valenzwinkels. Acta Crystallogr. **14**, 1103–1109 (1961)
Liebermann, R. C., Ringwood, A. E., Mayson, D. J., Major, A.: Hot-pressing of polycrystalline aggregates at very high pressure for ultrasonic measurements. Proc. 4th Internat. Confer. on High Pressure, Kyoto 1974, Ed. by J. Osugi, Physico-chemical Society of Japan, Kyoto 495–502 (1975)
Levien, L., Prewitt, C. T.: High-pressure crystal structure and compressibility of coesite. Am. Mineral. **66**, 324–333 (1981)
Ramsdell, L. S.: The crystallography of "coesite". Am. Mineral. **40**, 975–982 (1955)
Zoltai, T., Buerger, M. J.: The crystal structure of coesite, the dense, high-pressure form of silica. Z. Kristallogr. **111**, 129–141 (1959)