

Refinement of a coesite structure

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Auszug

Die Struktur wurde nach der Methode der kleinsten Quadrate bis zu dem Endwert $R = 7,6\%$ verfeinert. Die Intensitäten $I(hkl)$ wurden an dem gleichen synthetischen Material gemessen, das schon der ersten Strukturbestimmung¹ diente. Gegenüber den früheren Daten ergaben sich leichte Abweichungen bei den Atomparametern und etwas bedeutendere Differenzen bei den Größen der Wärmeschwingungen.

Abstract

Three-dimensional intensities were collected on a coesite crystal from the same synthetic material which was used for the original structure determination¹. The structure was refined with least-squares methods, giving a final R value of 7.6%, slightly different atomic positions and more significantly changed thermal data than originally obtained.

A crystal of coesite, measuring $0.16 \times 0.04 \times 0.16$ millimeters along the a , b and c axes respectively, from the same material made by L. COES² in 1953, used for the original structure determination¹, was selected for the refinement of its crystal structure. The crystal showed no sign of deterioration after 15 years of exposure to normal atmospheric pressure, although the diffraction spots in the precession photographs appeared to be more diffused than in the 1959 pictures.

A carefully prepared Debye-Scherrer powder pattern was measured and the lattice constants were refined with least-squares techniques. The refined data, in comparison with previously reported unit-cell

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¹ TIBOR ZOLTAI and M. J. BUERGER, The crystal structure of coesite, the dense, high-pressure form of silica. *Z. Kristallogr.* **111** (1959) 129–141.

² L. COES, JR., A new dense crystalline silica. *Science* **118** (1953) 131–132.

Table 1. Presently refined and previously reported unit-cell data of coesite

	Refined	RAMSDELL ³	ZOLTAI and BUERGER ¹	DACHILLE and ROY ⁴	SCLAR, GAR- RISON and SCHWARZ ⁵
<i>a</i>	7.173 Å ± 0.004	7.23 Å	7.17 Å	7.16 Å ± 0.01	7.14 Å ± 0.01
<i>b</i>	12.328 Å ± 0.006	12.52 Å	7.17 Å	12.39 Å	12.37 Å ± 0.01
<i>c</i>	7.175 Å ± 0.004	7.23 Å	12.38 Å	7.16 Å ± 0.01	7.14 Å ± 0.01
β or γ	120.00° ± 0.04	120°	120°	120°	120°

dimensions, are given in Table 1. The monoclinic second setting has been used in this work instead of the first setting given in the original paper¹, in order to yield to popular preference.

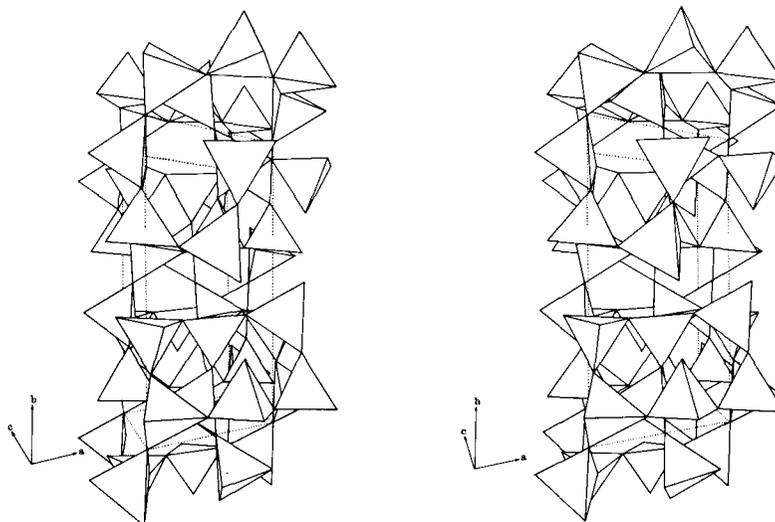


Fig. 1. Stereoscopic perspective drawing of the coesite structure

Three-dimensional intensities of 971 independent reflections were collected using MoK α radiation, Zr-Y balanced filters and an equi-inclination single-crystal diffractometer equipped with a scintillation

³ L. S. RAMSDELL, The crystallography of "coesite". *Amer. Mineral.* **40** (1955) 975–982.

⁴ F. DACHILLE and R. ROY, High-pressure region of the silica isotypes. *Z. Kristallogr.* **111** (1959) 451–461.

⁵ C. B. SCLAR, L. C. GARRISON and D. M. SCHWARZ, Optical crystallography of coesite. *Amer. Mineral.* **47** (1962) 1292–1302.

Table 2. *Atomic coordinates of the refined and the first coesite structure*
(the latter is converted to second monoclinic setting for the ease of comparison)

Atom	Refined coordinates			1959 values ¹		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	.3590	.3916	.4274	.3597	.3916	.4265
σ	.0003	.0001	.0003			
Si(2)	.4934	.1577	.4596	.4937	.1576	.4612
σ	.0004	.0001	.0004			
O(1)	0	0	0	0	0	0
σ	0	0	0			
O(2)	1/2	.1172	1/4	1/2	.1166	1/4
σ	0	.0005	0			
O(3)	.2670	.1238	.4418	.2694	.1256	.4405
σ	.0008	.0003	.0008			
O(4)	.1891	.3964	.1755	.1920	.3970	.1707
σ	.0008	.0004	.0008			
O(5)	.4807	.2882	.0212	.4877	.2888	.0274
σ	.0009	.0003	.0010			

counter. After correcting the intensities for Lorentz, polarization and absorption effects, a couple of cycles of least-squares refinement were calculated. The resulting isotropic temperature factors included several negative values and unreasonably high standard deviations for all parameters.

In order to improve the results, weights have been assigned to the reflections in accordance with the usual weighting schemes, and several cycles of refinement were run. No significant changes were obtained in the previous parameters. Fourier difference maps were also prepared. They turned out to be featureless, indicating no significant errors in the location of the atoms or in the values of thermal factors.

As the calculated density of this coesite (2.91 g/cm³) is about 3% lower than the experimentally observed value (3.01 g/cm³) the presence of impurities can be expected which may also be responsible for difficulties in the structure refinement. Under high magnification, carbonaceous inclusions and extensive block-structure features were observed in many crystals. The same specimens were also analyzed with the MAC 400 electron microprobe of the University

Table 3. Selected interatomic distances in the refined coesite structure

Atom	Pair	Distance	σ	Atom	Pair	Distance	σ	
Si(1) ^a	O(1) ^f	1.600 Å	.003 Å	O(2) ^a	O(3) ^a	2.645 Å**	.005 Å	
	O(3) ^g	1.607	.005		O(3) ^d	2.645	.005	
	O(4) ^a	1.598	.005		O(4) ^f	2.655**	.005	
	O(5) ^d	1.631	.005		O(4) ^g	2.655	.005	
Si(2) ^a	O(2) ^a	1.608	.003	O(3) ^a	O(5) ^d	2.633**	.007	
	O(3) ^a	1.619	.006		O(5) ^a	2.633	.007	
	O(4) ^f	1.625	.005		O(4) ^f	2.639**	.007	
	O(5) ^d	1.617	.005		O(4) ^g	2.615*	.006	
O(1) ^a	O(3) ^b	2.640*	.005	O(5) ^d	2.641**	.007		
	O(3) ^d	2.640	.005		O(5) ^f	2.625*	.008	
	O(4) ^f	2.614	.004	O(4) ^a	O(5) ^d	2.640*	.007	
	O(4) ^h	2.614*	.004		O(5) ^g	2.633**	.007	
	O(5) ^e	2.623	.004					
	O(5) ^g	2.623*	.004					

Mean tetrahedral distances: Si(1)—O = 1.609 Å; Si(2)—O = 1.618 Å;
 Si(1) tetrahedron: O—O = 2.626 Å;
 Si(2) tetrahedron: O—O = 2.641 Å.

Superscripts used in Tables 3 and 4:

^a	x	y	z	^e	$\frac{1}{2} + x$	$\frac{1}{2} + y$	z
^b	x	$-y$	$\frac{1}{2} + z$	^f	$\frac{1}{2} + x$	$\frac{1}{2} - y$	$\frac{1}{2} + z$
^c	$-x$	$-y$	$-z$	^g	$\frac{1}{2} - x$	$\frac{1}{2} - y$	$-z$
^d	$-x$	y	$\frac{1}{2} - z$	^h	$\frac{1}{2} - x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$

* O—O distances in Si(1) tetrahedron.

** O—O distances in Si(2) tetrahedron.

of Minnesota for the presence of foreign elements, such as Cu, Ag, P, Fe, Na and Cl. The results showed no detectable amounts of those elements.

In the succession of attempts to locate the cause of difficulties, the possibility of acentricity of the structure was tested next by an $N(Z)$ test⁶ and by running refinement cycles in a lower-symmetry space group after displacing the atoms from their positions in the centric space group. In the former case, the curves matched that of centric crystals and in the latter, further refinements resulted in

⁶ E. R. HOWELLS, D. C. PHILLIPS and D. ROGERS, The probability distribution of x-ray intensity. II. Experimental investigation and the x-ray detection of center of symmetry. *Acta Crystallogr.* **3** (1950) 210—214.

Table 4. Selected interatomic angles in the refined coesite structure

Atoms	Angle	σ
O(1) ^f —Si(1) ^a —O(3) ^g	111.0°	.2°
O(1) ^f O(4) ^a	109.8	.3
O(1) ^f O(5) ^d	108.7	.2
O(3) ^g O(4) ^a	109.4	.3
O(3) ^g O(5) ^d	108.3	.3
O(4) ^a O(5) ^d	109.7	.3
O(2) ^a —Si(2) ^a —O(3) ^a	110.1	.3
O(2) ^a O(4) ^f	110.4	.3
O(2) ^a O(5) ^d	109.5	.4
O(3) ^a O(4) ^f	108.9	.3
O(3) ^a O(5) ^d	109.4	.3
O(4) ^f O(5) ^d	108.7	.4
Si(1) ^f —O(1) ^a —Si(1) ^h	180.0	.0
Si(2) ^a —O(2) ^a —Si(2) ^d	143.8	.6
Si(1) ^g —O(3) ^a —Si(2) ^a	145.0	.4
Si(1) ^a —O(4) ^a —Si(2) ^f	150.4	.5
Si(1) ^d —O(5) ^a —Si(2) ^d	136.1	.5

Table 5. Isotropic and anisotropic temperature coefficients of coesite

Atom	Refined values							1959 values
	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Si(1)	.25	.00187	.00033	.00125	— .00013	.00050	— .00038	.813 Å ²
σ	.03	.00048	.00008	.00048	.00021	.00039	.00020	
Si(2)	.34	.00238	.00048	.00276	.00042	.00158	— .00002	.600
σ	.03	.00050	.00009	.00050	.00021	.00042	.00021	
O(1)	.73	.00132	.00074	.00523	— .00011	.00006	.00088	.856
σ	.14	.00185	.00032	.00245	.00075	.00183	.00068	
O(2)	.84	.00409	.00108	.00574	0	.00083	0	1.197
σ	.11	.00166	.00032	.00190		.00146		
O(3)	.76	.00434	.00128	.00402	.00079	.00110	— .00009	1.111
σ	.08	.00126	.00027	.00134	.00046	.00106	.00049	
O(4)	.85	.00680	.00170	.00204	— .00055	.00153	— .00029	1.381
σ	.08	.00136	.00024	.00124	.00056	.00104	.00055	
O(5)	.97	.00460	.00059	.01109	— .00008	.00331	— .00021	.656
σ	.09	.00142	.00024	.00170	.00053	.00132	.00054	

Table 6. *Thermal ellipsoids: root-mean-square displacements and orientations*

Atom	$\gamma-1$	$\gamma-2$	$\gamma-3$	$\phi(a)-1$	$\phi(a)-2$	$\phi(a)-3$
Si(1)	.032 ± .015 Å	.061 ± .008 Å	.068 ± .007 Å	90° ± 13°	121° ± 49°	149° ± 49°
Si(2)	.043 ± .012	.073 ± .007	.077 ± .007	134 ± 9	72 ± 50	49 ± 32
O(1)	.062 ± .025	.076 ± .024	.135 ± .018	80 ± 58	134 ± 15	134 ± 15
O(2)	.084 ± .019	.084 ± .014	.128 ± .015	48 ± 18	90 ± 0.4	138 ± 18
O(3)	.077 ± .015	.090 ± .014	.121 ± .011	51 ± 18	78 ± 33	139 ± 12
O(4)	.061 ± .019	.110 ± .011	.118 ± .011	95 ± 10	58 ± 26	32 ± 26
O(5)	.066 ± .014	.093 ± .015	.154 ± .010	97 ± 25	157 ± 12	111 ± 9

Atom	$\phi(b)-1$	$\phi(b)-2$	$\phi(b)-3$	$\phi(c)-1$	$\phi(c)-2$	$\phi(c)-3$
Si(1)	46° ± 12°	52° ± 29°	112° ± 34°	51° ± 11°	104° ± 36°	42° ± 21°
Si(2)	44 ± 9	65 ± 47	56 ± 37	64 ± 12	153 ± 23	83 ± 67
O(1)	143 ± 69	121 ± 76	72 ± 12	66 ± 14	95 ± 33	25 ± 13
O(2)	90 ± 0.5	180 ± 0	90 ± 0.1	72 ± 18	90 ± 0.1	18 ± 18
O(3)	122 ± 33	126 ± 34	127 ± 14	79 ± 39	141 ± 22	53 ± 17
O(4)	84 ± 14	32 ± 26	121 ± 26	26 ± 11	107 ± 16	108 ± 12
O(5)	173 ± 24	84 ± 24	87 ± 6	86 ± 7	82 ± 9	9 ± 8

$\gamma-1, \gamma-2, \gamma-3$ = displacement along principal axes,
 ϕ 's = angles between γ 's and the crystallographic axes.

divergent parameters. On the basis of these indications the presence of a center of symmetry has been assumed and the centric space group was used in subsequent studies.

Of the 971 independent reflections, an unusually high number, 414, had intensities either below or slightly above the limits of detection. In order to eliminate their effect on the calculations they were rejected, as an extreme measure of weighting. Similarly all reflections which had $(\sin \theta)/\lambda$ less than 0.280 and the 56 strongest reflections were rejected as they are likely to be significantly affected by extinction. The refinement with the remaining 466 reflections gave all definite and positive thermal ellipsoids and an R value of 7.9%. The coefficient for secondary-extinction correction was calculated at this stage ($C_0 = 1.473 \pm 0.258 \times 10^{-5}$) using ZACHARIANSEN'S technique⁷. All but 8 small-angle reflections [with $(\sin \theta)/\lambda < 0.162$], and all 56 strong reflections, were then returned to the files and were used in the next cycles. These 549 reflections gave a final R value of 7.6%.

⁷ W. H. ZACHARIANSEN, The secondary extinction correction. *Acta Crystallogr.* **16** (1963) 1139–1144.

The final atomic coordinates, interatomic distances and angles are given in Tables 2 through 4 with some corresponding data of the 1959 structure. The standard deviation of the atomic parameters in these tables is unusually high. However, this can be explained by the generally low peak-to-background intensity ratios and by the large number of unobservable peaks which are, in part, due to the small size of the crystal. The isotropic and anisotropic temperature factors are given in Tables 5 and 6 in the usual way of presentation.

Although this investigation has improved the model of the available coesite structure it is believed that an additional refinement on a different and less imperfect crystal should be undertaken.

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