

The superstructure of meteoritic low tridymite solved by computer simulation

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Below 107°C meteoritic tridymite transforms reversibly to the low-tridymite structure, a superstructure with a cell volume six times the volume of the orthorhombic high-tridymite cell. Low tridymite is monoclinic, space group *Cc*, with cell dimensions: $a=18.524(4)$, $b=5.0032(15)$, $c=23.810(8)\text{\AA}$, $\beta=105.62(2)^\circ$. The crystal structure has been determined through computer modeling and refined using 1260 $\text{MoK}\alpha$ reflections ($R=0.069$). The asymmetric unit contains 12 Si atoms and 24 O atoms. The SiO_4 tetrahedra are regular within the margin of error (mean Si-O: 1.601\AA). Twenty-three of the 24 Si-O-Si angles fall in the range 142° to 159° , while one is linear (178.5°). The characteristic six-membered rings of the ideal tridymite structure are distorted into two different configurations: two-thirds have a ditrigonal shape (similar to the shape of the rings found in micas and in stuffed derivative structures of tridymite) while one-third have an oval shape (similar to those found in the low-cristobalite structure).

Introduction

In spite of its simple chemical formula, SiO_2 is structurally a remarkably complex material. At least ten polymorphs have been recognized, but the crystal structures of several of these are unknown or only incompletely known. One of the unknown SiO_2 structures is that of meteoritic low tridymite. Tridymite is the stable phase of SiO_2 at low pressure and temperatures between 867 and 1470°C (Boyd and England, 1960). Its stability field is rapidly reduced with increasing pressure. The atomic arrangement has not been studied with modern methods at equilibrium conditions, but it is thought to be closely similar to the ideal hexagonal high-tridymite structure (Gibbs, 1926). Due to the reconstructive nature of transformations to other polymorphs, tridymite tends to persist metastably upon rapid cooling. The crystal structure at 220° has been determined using a sample from the Steinbach meteorite (Dollase, 1967). This structure is orthorhombic, $C22_1$, with an atomic arrangement slightly distorted from the ideal hexagonal structure. Below about 107°C this tridymite under-

goes a reversible displacive transformation to the low-tridymite structure. The structural relaxation occurring at the transformation results in the formation of a superstructure with a cell volume six times the volume of the orthorhombic cell.

The meteoritic low tridymite is different from terrestrial low tridymite, which has the diffraction aspect F^{***} , orthorhombic (Gardner and Appleman, 1974). The structure of one such terrestrial tridymite has been solved by Konnerd and Appleman (1975) in a triclinic $F1$ cell.

To date no systematic method has been presented for the solution of superstructures, although many different techniques have been applied with varying degrees of success. Most of the methods employed the diffraction evidence itself, although this presents a problem, as superstructures are characterized by a small set of intense substructure peaks (containing primarily information on the average structure) and a larger set of much weaker superstructure reflections which contain information about the deviations between the various sub-cells comprising the true cell.

LOW TRIDYMITITE TABLE OF OBSERVED

H	K	L	FO/SE	FC
0	0	6	150.7659	147.5043
0	0	10	13.1744	14.5585
0	0	12	42.0177	38.1889
0	0	16	43.9495	47.0260
0	0	22	24.6725	25.5018
0	0	30	51.4700	49.4712
0	2	0	260.0447	271.8728
0	2	1	13.4125	14.3968
0	2	5	24.6687	18.4616
0	2	6	89.6147	90.1358
0	2	7	29.4393	28.0806
0	2	9	38.4464	37.2226
0	2	11	46.6966	45.2122
0	2	12	24.7508	26.5908
0	2	13	25.0130	25.5554
0	2	14	22.4586	20.8550
0	2	15	15.9003	16.9887
0	2	16	21.4509	26.8215
0	2	17	31.9014	31.2094
0	2	23	36.8254	42.1557
0	2	30	48.1432	47.7449
0	4	0	55.8450	66.5509
0	4	1	26.4011	26.3746
0	4	3	38.8912	62.8504
0	4	5	72.5293	73.7574
0	4	6	35.3358	42.1792
0	4	7	44.2899	42.0299
0	4	11	53.5356	63.1530
0	4	13	39.7064	35.4433
0	4	17	29.5965	30.3555
0	4	23	38.4754	38.1069
0	6	0	21.2169	23.8299
0	6	1	23.7034	16.8235
0	6	3	30.6952	27.4780
0	6	5	47.0925	43.2067
0	6	11	35.1491	32.9749
0	6	12	20.7903	26.7012
1	1	-32	27.7107	11.2958
1	1	-23	19.7223	14.1285
1	1	-22	21.0166	34.6566
1	1	-20	25.5106	28.0755
1	1	-18	25.6511	33.1605
1	1	-17	24.9081	24.5623
1	1	-16	135.9944	136.6237
1	1	-15	26.6106	30.6171
1	1	-13	21.7976	24.0802
1	1	-12	24.9296	24.6597
1	1	-11	17.5745	19.8915
1	1	-10	15.5128	19.2575
1	1	-9	40.2303	35.9189
1	1	-7	29.4623	27.3532
1	1	-5	44.6043	44.4965
1	1	-4	141.7740	136.4592
1	1	-3	29.0726	30.2727
1	1	-2	24.8820	22.4525
1	1	0	16.1340	16.0108
1	1	2	233.7010	230.0137
1	1	3	15.0340	14.7764
1	1	5	38.8132	36.7537
1	1	6	22.3414	24.0551
1	1	7	77.7701	80.5540

1	1	9	63.0955	62.9197
1	1	0	25.2487	25.0701
1	1	1	23.9298	25.8289
1	1	4	48.1158	49.0102
1	1	15	20.3509	20.2470
1	1	8	35.7253	35.0789
1	1	20	92.5311	94.4596
1	1	22	25.5368	18.7166
1	3	-23	30.6965	31.4744
1	3	-21	55.2904	55.0010
1	3	-19	27.3971	30.4283
1	3	-18	23.2581	20.5877
1	3	-16	59.0235	56.5739
1	3	-13	32.8225	24.0148
1	3	-12	32.5561	32.4497
1	3	-10	62.3008	55.6945
1	3	-9	31.0894	31.2626
1	3	-7	28.3049	29.2991
1	3	-5	46.1233	46.5345
1	3	-4	73.8626	77.9380
1	3	-3	35.2539	33.3414
1	3	-1	12.3337	9.5308
1	3	2	128.7400	131.0574
1	3	3	17.8627	18.0602
1	3	5	48.8273	50.4962
1	3	6	19.1460	18.7448
1	3	7	89.1037	88.9857
1	3	8	9.8997	7.8937
1	3	9	66.3171	65.4059
1	3	10	26.1654	26.4018
1	3	11	26.3384	21.9836
1	3	12	21.2414	17.0711
1	3	13	26.3749	23.0806
1	3	14	82.4357	81.5327
1	3	15	34.9134	34.7911
1	3	16	21.8438	22.3354
1	3	17	6.8434	15.9166
1	3	20	41.7446	41.1854
1	3	23	22.5175	16.6587
1	5	-23	36.1444	28.2644
1	5	-21	59.4287	60.7649
1	5	-19	25.5555	27.5356
1	5	-5	21.6604	29.4832
1	5	2	19.7473	28.0019
1	5	5	30.0710	32.4517
1	5	7	56.7833	58.7505
1	5	9	41.2779	38.1474
1	5	13	37.9992	33.6752
1	5	15	36.6118	32.6363
1	5	19	26.7416	24.7619
2	0	-28	24.5415	27.8171
2	0	-26	42.9437	44.0972
2	0	-20	16.6729	11.5572
2	0	-18	26.6106	28.1222
2	0	-16	33.8657	35.4287
2	0	-14	145.4389	145.7216
2	0	-12	44.2114	45.1345
2	0	-10	43.4780	42.3466
2	0	-8	104.9714	103.9033
2	0	-6	27.7631	27.6434
2	0	2	12.7291	10.7488
2	0	4	250.9929	245.4410
2	0	6	54.7666	55.3587
2	0	8	25.1701	22.5345
2	0	10	108.6725	103.7418
2	0	12	31.8228	31.9417
2	0	16	124.3182	119.2305

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	2	2	-8	36.5320	28.7738
	2	2	-7	44.1852	42.4466
	2	2	-6	20.1675	20.2347
	2	2	-5	23.9689	24.3514
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5	1 1	49.8313	51.5017
5	1 3	75.9032	77.0954
5	1 5	73.1793	72.1528
5	1 6	29.2560	32.6126
5	1 7	20.3574	21.7534
5	1 10	95.1419	90.2945
5	1 11	22.3152	24.2467
5	1 12	53.6141	51.9967
5	1 16	44.4315	42.3921
5	1 20	21.8700	16.0602
5	1 22	70.4942	73.7543
5	1 26	27.0257	28.6364
5	1 28	58.2744	59.6305
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5	3 -14	27.5844	31.8243
5	3 -13	31.3775	28.0820
5	3 -11	31.2905	29.1002

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5	3	-7	30.5585	30.2287
5	3	-6	52.7760	52.5957
5	3	-5	22.0935	24.3192
5	3	-4	24.6725	22.3401
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5	3	-2	67.2090	66.2196
5	3	-1	38.8945	36.8901
5	3	1	52.1462	54.8730
5	3	2	17.9936	18.3955
5	3	3	80.0415	81.3290
5	3	4	27.6624	25.8900
5	3	5	80.5915	80.0249
5	3	6	20.0104	18.2597
5	3	7	15.7551	24.2183
5	3	10	113.3546	115.7265
5	3	11	19.3818	15.9771
5	3	15	19.6699	14.7473
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5	5	-11	18.6393	17.0443
5	5	-3	36.9039	38.9258
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5	5	3	47.9044	53.2479
5	5	5	48.8997	48.9140
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12	2	-22	27.9464	25.2114
12	2	-21	17.8746	18.9876
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12	2	-7	35.5610	30.8233
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12	4	-26	31.8752	13.3128
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13	1	3	22.2628	20.5576
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2831

1260 REFLECTIONS