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X-RAY STUDY OF TRIDYMITE (3)
UNIT CELL DIMENSIONS AND PHASE TRANSITION OF TRIDYMITE, TYPE S

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ABSTRACT

Four phases named S1, S2, S3 and S4 in tridymite of type S were confirmed on the close examination of the change of X-ray powder reflections with increasing temperatures.

Unit cell dimensions are:

S1; monoclinic, $a=10.04$Å, $b=17.28$Å, $c=8.20$Å, $\beta=91.50°$,
S2; orthorhombic, $a=10.04$Å, $b=17.28$Å, $c=8.20$Å,
S3; domain structure,
and S4; hexagonal, $a=5.046\sim5.06$Å, $c=8.236\sim8.30$Å.

Their relations are as follows,

$$\text{S1} \xrightarrow[60\text{-}75°\text{C}]{} \text{S2} \xrightarrow[115°]{} \text{S3} \xrightarrow[250°\text{C}]{} \text{S4}.$$

Though the change of the patterns with decreasing temperatures is not thoroughly investigated, the transition is reversible.

Introduction

In the first paper, of this series (Sato, 1964), X-ray and D. T. A. criteria for tridymite, type S were presented. In this paper its unit cell dimensions and the phase transition between four phases found in the type are investigated with the aid of newly found triplets in their X-ray powder pattern.

X-ray powder reflections at room temperature

X-ray powder patterns of three specimens of tridymite, type S are shown in Fig. 1 and listed in Table 1-1. They are all synthetic,

* This specimen was kindly supplied by Nihon Plate Glass Company.

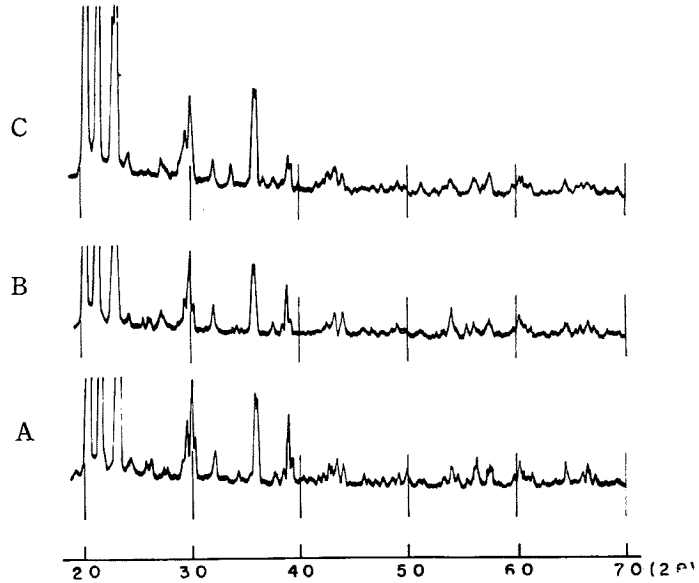

Fig. 1. Three X-ray powder patterns of tridymite, type S(SI).
C; Product from quartz and Na_2CO_3
B; Product from quartz and Na_2WO_4
A; Crystals developed on the surface of a silica brick

but of different sources. Specimen A (Fig. 1A) consists of dendritic crystals developed on the surface of a silica brick.* Specimen B (Fig. 1B) is derived from a mixture of pegmatite quartz and Na_2WO_4 through heating in an electrical furnance (about 1300°C) for 24 hours. Specimen C (Fig. 1C) is produced also from a mixture of pegmatite quartz and Na_2CO_3, but through heating by a Mecker burner (about 1000-1100°C) for 24 hours.

General features of these three patterns agree with one another. However, in details they vary a little from specimen to specimen. Especially, the doublets (3.018Å, 2.973Å; 2.311Å, 2.295Å) in specimen C, which were described in the first paper as the reflections characteristic of type S, are replaced by distinct triplets in specimen A and B (3.016Å, 2.975Å, 2.948Å; 2.340Å, 2.309Å, 2.291Å). During the course of the determination of unit cell dimensions of type S, how-

Table 1. Observed and calculated spacings of low tridymite, type S(SI).

Table 1-1						Table 1-2			
A		B		C		Calc.			
$d_{obs.}$	I	$d_{obs.}$	I	$d_{obs.}$	I	h	k	l	d
						2	2	0	4.339Å
4.332Å	180	4.328Å	180	4.332Å	246	$\bar{2}$	0	1	4.331
						0	4	0	4.320
4.234	2	4.236	4			2	0	1	4.231
4.107	170	4.107	200	4.099	173	0	0	2	4.099
3.860	20	3.867	40	3.862	50	$\bar{2}$	2	1	3.872
3.822	100	3.818	100	3.813	100	0	4	1	3.822
						2	2	1	3.800
		3.672	5			1	1	2	3.674
3.657	10	3.642	6	3.655	8				
3.453	4	3.461	3			$\bar{2}$	3	1	3.461
3.396	6	3.396	6			2	3	1	3.410
3.297	<1	3.297	1			3	1	0	3.285
3.261	2	3.250	6	3.249	5	1	5	0	3.268
3.210	3	3.215	3	3.202	3	$\bar{2}$	0	2	3.216
3.173	<1	3.171	1			$\bar{2}$	1	2	3.162
3.135	<1	3.126	<1			2	0	2	3.134
3.080	<1	3.087	<1	3.073	4	2	1	2	3.084
3.046	<1	3.049	<1			$\bar{1}$	5	1	3.044
3.016	14	3.017	9	3.018	28	$\bar{2}$	2	2	3.014
2.975	48	2.975	48	2.973	42	0	4	2	2.973
2.948	4	2.950	3			2	2	2	2.947
2.777	15	2.776	17	2.780	10	1	6	0	2.768
				2.648	8	3	4	0	2.645
2.611	4	2.609	4	2.614	1	$\bar{3}$	1	2	2.596
2.538	2	2.540	1			3	1	2	2.532
2.501	28	2.500	30	2.501	30	4	0	0	2.509
2.489	26	2.490	27	2.495	30	2	6	0	2.498
						4	1	0	2.483
				2.442	3	3	2	2	2.454
2.381	8	2.385	3	2.381	5	2	6	1	2.381
2.340	4	2.342	3	2.344	<1	$\bar{2}$	2	3	2.336
2.309	28	2.308	30	2.311	18	0	4	3	2.309

Table 1. (Cont.)

Table 1-1						Table 1-2			
A		B		C		Calc.			
2.291	2	2.294	3	2.295	6	2	2	3	2.289
				2.257	2	$\bar{1}$	4	3	2.261
2.238	3	2.238	3	2.243	<1	$\bar{3}$	4	2	2.244
2.202	1	2.205	2	2.193	1	3	4	2	2.202
				2.162	2	$\bar{4}$	0	2	2.165
2.137	1	2.137	5	2.138	5	2	6	2	2.122
2.117	9	2.117	7	2.120	6	4	0	2	2.115
2.088	12	2.086	15	2.091	15	0	8	1	2.089
						4	4	1	2.086
2.050	10	2.049	14	2.055	6	0	0	4	2.049
		2.031	<1	2.035	<1	0	1	4	2.035
				1.995	<1	5	1	0	1.994
		1.976	2	1.965	<1	$\bar{1}$	2	4	1.965
		1.943	2	1.939	<1	1	2	4	1.946
		1.905	2	1.910	2	$\bar{2}$	0	4	1.915
1.873	4	1.874	4	1.879	4	2	0	4	1.880
1.853	4	1.855	4	1.853	4	0	4	4	1.852
1.829	9	1.829	2	1.833	3	$\bar{4}$	2	3	1.830
1.783	5	1.783	6	1.782	7	4	2	3	1.785
						$\bar{5}$	2	2	1.782
				1.744	3	5	2	2	1.747
1.713	7	1.715	2	1.714	4	$\bar{4}$	4	3	1.718
1.695	14	1.695	25	1.695	12	0	8	3	1.694
				1.683	2	4	4	3	1.681
1.656	2	1.654	3	1.658	<1	3	8	2	1.651
1.636	15	1.635	15	1.636	10	4	8	0	1.637
						2	10	0	1.634
				1.613	2	0	2	5	1.611
1.600	14	1.600	20	1.600	15	2	10	1	1.600
1.549	4	1.546	3	1.546	2	$\bar{4}$	3	4	1.549
1.534	15	1.534	20	1.534	14	0	4	5	1.533
		1.530	<1			$\bar{4}$	8	2	1.529
1.519	9	1.517	2	1.517	7	$\bar{2}$	10	2	1.522
						2	10	2	1.513

Table 1. (Cont.)

Table 1-1						Table 1-2			
A		B		C		Calc.			
		1.510	3			4	3	4	1.512
						4	8	2	1.511
		1.488	<1	1.487	<1	$\bar{4}$	7	3	1.492
1.467	<1	1.467	2	1.469	<1	4	7	3	1.467
1.443	9	1.443	4	1.443	6	$\bar{3}$	10	2	1.443
1.439	<1	1.439	4			$\bar{3}$	7	4	1.438
1.435	<1	1.434	2			7	0	0	1.434
1.432	<1					3	10	2	1.432
1.415	<1	1.413	3	1.417	4	3	7	4	1.415
1.402	5	1.402	9	1.404	6				

ever, it was confirmed that these reflections should essentially be classified into triplets, though one of the components of a triplet may be too weak to be observed.

Phase transition

As previousely described in the first paper, two characteristic endothermic peaks at 115°C and 150°C in the D. T. A. curve of type S seem to correspond to two transition points between three forms, i. e., low to middle and middle to high. However, the change of X-ray powder reflections with increasing temperatures is not necessarily consistent with this expectation.

Fig. 2A is the pattern of specimen B at room temperature, 2B at 78°C, 2C at 116°C, 2D at 140°C, 2E at 160°C, 2F at 230°C, and 2G at 330°C. Fig. 3A, B, D and G are the details of Fig. 2A, B, D and G respectively. These patterns indicate that there are at least three transition points.

The first point, at 60–75°C, is characterized by the change of the triplets and doublets peculiar to type S (T in Fig. 2A and D in Fig. 3A respectively) into singlets. This transition point is not detected in the D. T. A. curve. The second point, at 115°C, is charac-

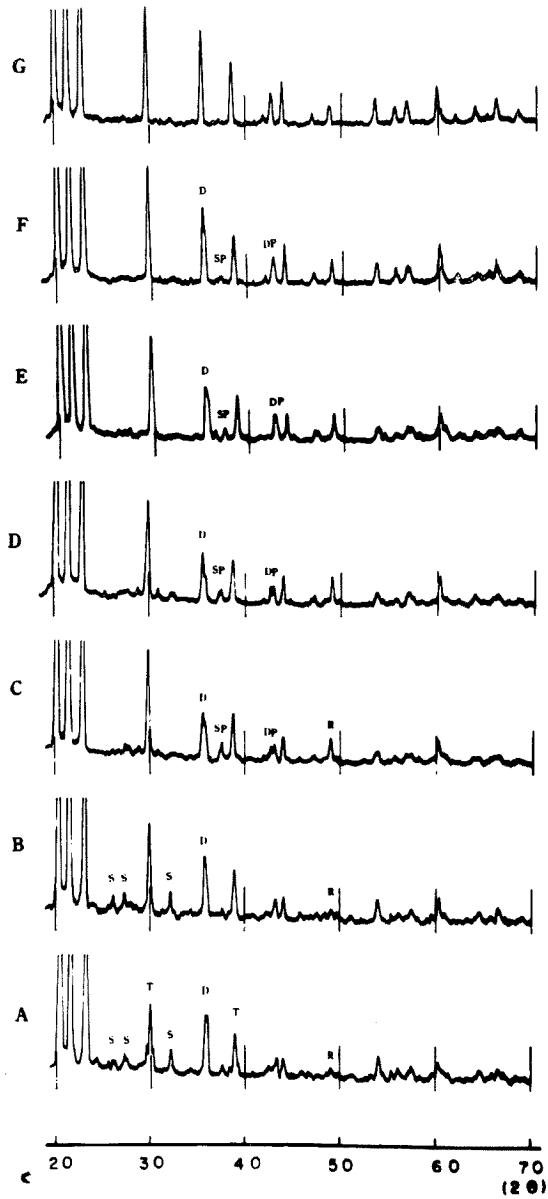

Fig. 2. Change of X-ray powder reflections with increasing tepmeratures.
A; at room temperature: B; at 78°C: C; at 116°C
D; at 140°C: E; at 160°C: F; at 230°C: G; at 330°C

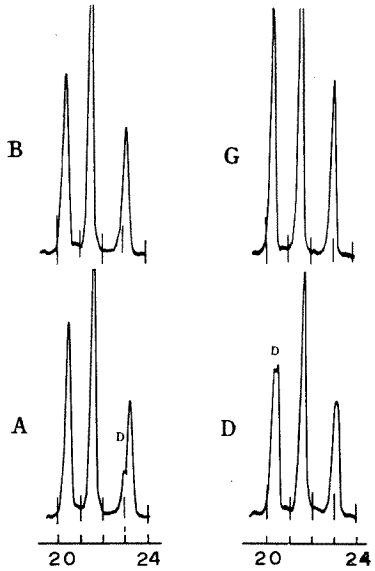

Fig. 3. Change of X-ray powder reflections with increasing temperatures.

A, B, D and G correspond to part of Fig. 2 A, B. D and G respectively.

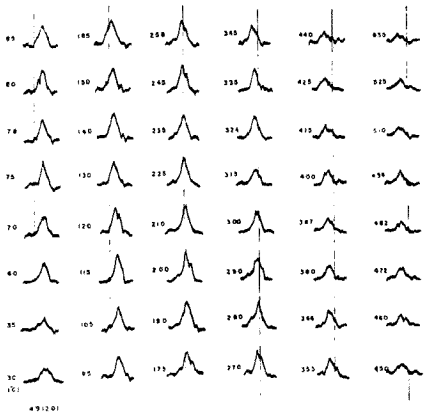

Fig. 4. Change of 1.855Å reflection with increasing temperatures.

terized by the disappearance of super-reflections (S in Fig. 2B) and the sudden increase of intensities of 2.39Å and 1.855Å lines (SP and R respectively in Fig. 2C). The details of the change of 1.855Å reflection through the transition are shown in Fig. 4. In addition, at this point two reflections of 4.33Å, and 2.09Å begin to spilit into doublets (4.364Å and 4.332Å, 2.109Å and 2.093Å) and at about 140°C maximum values of splitting are observed (DP in Fig. 2C and D in Fig. 3D respectively). This exactly corresponds to the first endothermic point confirmed in the D. T. A. curve. The third point, at about 250°C, is characterized by the change of the doublet, which has been remained through the transition, into a singlet. The detailed feature of this is traced in Fig. 5. Four names of S1, S2, S3 and S4 are proposed here for the four phases confirmed. Their mutual re-

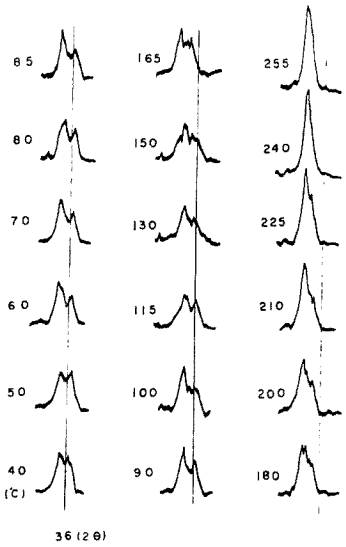

Fig. 5. Change of a doublet (2.50Å and 2.49Å) with increasing temperatures.

lations are as follows,

$$S1 \xrightarrow[60\text{-}75°C]{} S2 \xrightarrow[115°C]{} S3 \xrightarrow[250°C]{} S4.$$

Although the X-ray and D. T. A. criteria for type S proposed here are different from those by HILL and ROY (1958), the nomenclature is the same as adopted by them. The transition points with increasing temperatures are not exactly determined yet, but the transition is obviously reversible, the details of which will be discussed in near future. The X-ray data of four phases are listed in Table 2, in which very weak reflections are omitted.

Table 2. Observed and calculated spacings of four phases tridymite, type S. (Specimen B)

S1 a=10.04Å b=17.28Å c=8.20Å β=91.50°				S2 a=10.04Å b=17.28Å c=8.20Å				S3	S4 a=5.046Å c=8.236Å			
$d_{obs.}$	h	k	l	$d_{calc.}$	$d_{obs.}$	h	k	l	$d_{calc.}$	$d_{obs.}$	$d_{obs.}$	h	k	l	$d_{calc.}$
										4.364Å	4.370Å	1	0	0	4.370Å
4.328Å	2	2	0	4.339Å	4.332Å	2	2	0	4.341Å	4.332					
	0	4	0	4.320		0	4	0	4.320						
4.107	0	0	2	4.099	4.105	0	0	2	4.100	4.105	4.118	0	0	2	4.118
3.867	$\bar{2}$	2	1	3.872											
3.818	0	4	1	3.822	3.826	2	2	1	3.836	3.845	3.862	1	0	1	3.860
	2	2	1	3.800		0	4	1	3.822						
					3.401										
3.250	1	5	0	3.268	3.257	1	5	0	3.268						

Table 2. (Cont.)

S1 $a=10.04$Å $b=17.28$Å $c=8.20$Å $\beta=91.50°$				S2 $a=10.04$Å $b=17.28$Å $c=8.20$Å				S3	S4 $a=5.046$Å $c=8.236$Å			
$d_{obs.}$	h	k	l	$d_{calc.}$	$d_{obs.}$	h	k	l	$d_{calc.}$	$d_{obs.}$	$d_{obs.}$	h	k	l	$d_{calc.}$
3.016	$\bar{2}$	2	2	3.014											
2.975	0	4	2	2.973	2.976	2	2	2	2.981	2.985	2.995	1	0	2	2.997
						0	4	2	2.974						
2.950	2	2	2	2.947											
2.776	1	6	0	2.768	2.782	2	3	2	2.781						
2.500	4	0	0	2.509	2.506	4	0	0	2.510	2.513	2.523	1	1	0	2.523
2.490	2	6	0	2.498	2.493	2	6	0	2.498	2.495					
2.385	2	6	1	2.381	2.387	2	6	1	2.390	2.393					
2.342	$\bar{2}$	2	3	2.336											
2.308	0	4	3	2.309	2.311	2	2	3	2.313	2.313	2.325	1	0	3	2.325
						0	4	3	2.310						
2.294	2	2	3	2.289											
2.137	2	6	2	2.122	2.130	2	6	2	2.133	2.146	2.152	1	1	2	2.151
										2.109	2.114	2	0	1	2.112
2.086	0	8	1	2.089	2.090	4	4	1	2.098	2.093					
	4	4	1	2.086		0	8	1	2.089						
2.049	0	0	4	2.049	2.050	0	0	4	2.050	2.050	2.059	0	0	4	2.059
										1.922	1.930	2	0	2	1.930
1.855	0	4	4	1.852	1.853	2	2	4	1.854	1.853	1.863	1	0	4	1.863
						0	4	4	1.852						
1.695	0	8	3	1.694	1.697	0	8	3	1.695	1.702	1.710	2	0	3	1.710
1.654	3	8	2	1.651	1.658	3	8	2	1.660						
1.635	4	8	0	1.637	1.635	4	8	0	1.637		1.651	2	1	0	1.652
	2	10	0	1.634		2	10	0	1.634						
1.600	2	10	1	1.600	1.602	2	10	1	1.602	1.616	1.619	2	1	1	1.619
					1.550	1	11	0	1.552						
1.534	0	4	5	1.533	1.534	2	2	5	1.534	1.535	1.542	1	0	5	1.541
						0	4	5	1.533						
1.517	$\bar{2}$	10	2	1.522	1.518	2	10	2	1.518	1.517	1.531	2	1	2	1.533
	2	10	2	1.513											

Unit cell dimensions of four phases

The unit cell dimensions and other crystallographic features of these four phases were determined as follows:

S1; Trials showed that a monoclinic supercell, a=10.04Å, b=17.28Å, c=8.20Å, β=91.50Å sufficiently accounts for the observed characteristic triplets, doublets and other weak reflections. The result is shown in Table 1-2.

S2; An orthorhombic cell, a=10.04Å, b=17.28Å, c=8.20Å, derived from the S1 cell, most reasonably explains not only the change of triplets into singlets, but also other reflections.

S3; As shown in Table 2, newly appearing reflections in this phase correspond to the reflection of the S4 phase, some of them being produced by splitting of S2 reflections such as 4.33Å and 2.09Å lines. No remarkable change of basal reflections is noticed through the transition. These facts suggest that it is a domain structure consisting of the S2 and S4 phases and having the c axis in common.

S4; This can be easily confirmed to have a hexagonal cell, a=5.046Å, c=8.236Å, but the values increase continuously to a=5.06Å, c=8.30Å at 500°C.

The observed and calculated spacings of the four phases are listed in Table 2.

Summary

The above mentioned facts are summarized as follows:

1) The newly found triplets of the X-ray reflections (3.016Å, 2.975Å, 2.948Å; 2.340Å, 2.309Å 2.291Å) should be supplemented for the criteria of tridymite, type S(S1).

2) Four phases named S1, S2, S3 and S4 are confirmed on the close examination of the change of X-ray powder reflections with increasing temperatures. However, not all of these phases are indicated in the D. T. A. curve.

3) Unit cell dimensions of the four phases are determined from

their powder X-rays patterns:

S1; monoclinic, a=10.04Å, b=17.28Å, c=8.20Å, β=91.50°,

S2; orthorhombic, a=10.04Å, b=17.28Å, c=8.20Å,

S3; domain structure,

and S4; hexagonal a=5.046~5.06Å c=8.236~8.30Å.

Acknowledgement

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