MINERALOGICAL JOURNAL, VOL. 4, NO. 2, PP. 115-130, AUG., 1963

X-RAY STUDY OF TRIDYMITE (1)

ON TRIDYMITE M AND TRIDYMITE S

MITSUO SATO

Geological and Mineralogical Institute, Faculty of Science, Tokyo University of Education

ABSTRACT

Tridymite was synthesized under various conditions with respect to starting materials and mineralizers in room pressures. Some of them, in its X-ray powder diffraction data, show the features of tridymite M and tridymite S, which were confirmed by Hill and Roy in sythetic tridymite under the hydrothermal condition, and the others are grouped into the intermediate between M and S. As the rusults of examination of their X-ray powder reflections and their D. T. A. curves, detailed criteria for grouping the tridymites by X-ray means in the present experiments were given along with the suggestions that these differences are due to the distortion of the structure at high-low inversion.

Introduction

Hill and Roy (1958) indicated for the first time that tridymites synthesized in H_2O-SiO_2 and D_2O-SiO_2 systems can be grouped into two types, *i. e.*, tridymite M and tridymite S, by their characteristic reflections of X-rays. In the course of study of tridymite crystallized from the dry melt, the writer also found that X-ray powder patterns of tridymites slightly differ one another with different starting materials and mineralizer. Some of them agree with tridymite M and tridymite S, and the others with the intermediate between them. In this paper, the grouping into two types are reexamined with the X-ray powder patterns and the D. T. A. curves, and some considerations on the origin of their differences are given.

Synthesis of tridymite and X-ray powder patterns

Synthesis of tridymite

As already reported by many investigators, tridymite is easily crystallized above 867°C from the mixture of SiO_2 and mineralizers such as Na_2WO_4, Na_2CO_3, KCl, etc.

In this experiment, pegmatite quartz from Naegi, Gifu, Japan, and silica gel (1) and (2) for chromatographic use were employed as starting materials, and Na_2WO_4, NaCl and Na_2CO_3 as mineralizers. The chemical composition other than the main SiO_2 constituent of the starting materials was determined as follows:

	Residue after treated with HF	Spectrographic analysis
Quartz	0.1%	Mg, Fe, Al
Silica gel (1)	1.3%	Mg, Ca, Fe, Al
Silica gel (2)	0.2%	Not examined

The starting materials and mineralizers were mixed in an agate motar, put into a platinum cruicible, and heated by a Mecker burner under room pressure. The products were crushed, washed with hot water and air dried. The kinds of starting materials and mineralizers etc. are listed in Table 1.

Table 1. Synthesis of tridymite.

Starting material	Mineralizer	Ratio of mixing	Time	Fig.
quartz	Na_2WO_4	1 : 1	24 hrs.	1-A
,,	NaCl	1 : 0. 5	,	1-B
,,	Na_2CO_3	1 : 0. 1	,,	1-C
silica gel (1)	Na_2WO_4	1 : 1	,,	2-A
,,	NaCl	1 : 0. 5	,,	2-B
,,	Na_2CO_3	1 : 0. 1	,,	2-C
,, (2)	Na_2WO_4	1 : 1	,,	3-A
,,	NaCl	1 : 0. 5	,,	3-B
,,	Na_2CO_3	1 : 0. 1	,,	3-C

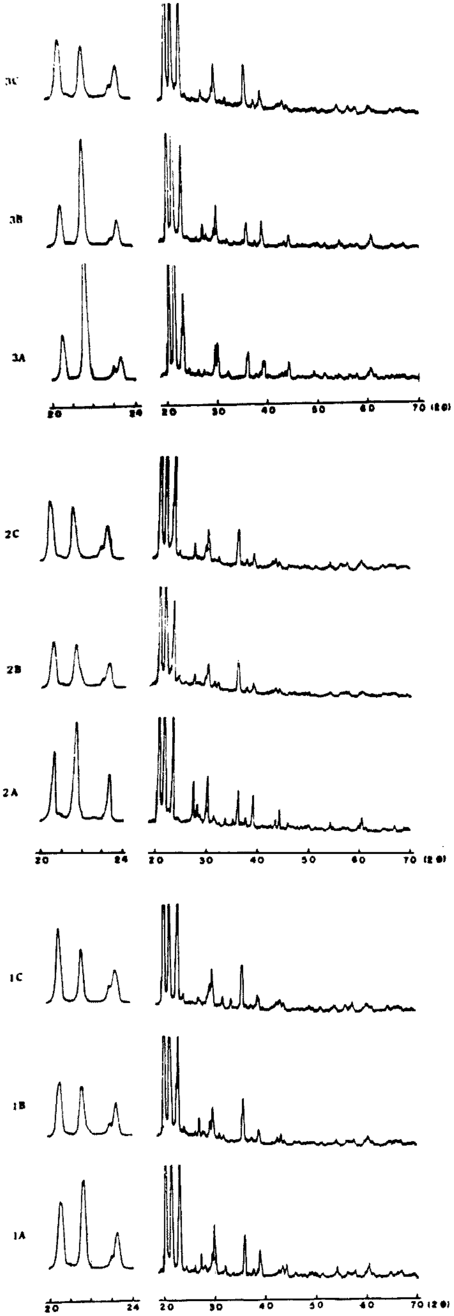

Fig. 1-3. X-ray powder patterns of tridymite synthesized with various starting materials and mineralizer.

Fig. 3-C	silica gel(2)	Na_2CO_3
Fig. 3-B	,,	NaCl
Fig. 3-A	,,	Na_2WO_4
Fig. 2-C	silica gel(1)	Na_2CO_3
Fig. 2-B	,,	NaCl
Fig. 2-A	,,	Na_2WO_4
Fig. 1-C	quartz	Na_2CO_3
Fig. 1-B	,,	NaCl
Fig. 1-A	,,	Na_2WO_4

Operation conditions:

Ni filtered copper radiation, 35 KV, 15 mA; Scanning speed, 2°/min.; scale factor, 32: multiplier, 1; time constant, 4; divergence slit, 1°; receiving slit, 0.4°.

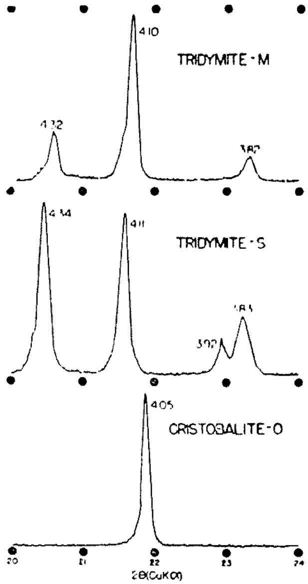

Fig. 4. Characteristic X-ray reflections of tridymites M and S, and cristobalite given by Hill & Roy (1958).

X-ray powder patterns

X-ray powder patterns of synthesized tridymites are shown in Figs. 1–3. So far as the reflections from 20° to 24° in $2\theta(\mathrm{Cu}K\alpha)$ are concerned, which were used for the grouping by Hill & Roy (Fig. 4), the following types are recognized: Type S (Figs. 1B, 1C, 2B, 2C, 3C), Type M (Fig. 2A) and the intermediate (Figs. 1A, 3A, 3B).

But taking the reflections up to 70° in $2\theta(\mathrm{Cu}K\alpha)$ into account, they can be also grouped as follows (Numbers in parentheses are in 2θ):

Type (1); Conspicuous doublets of 3.86 & 3.81A (23.0° & 23.3°), 3.01 & 2.97A (29.6° & 30.0°), 2.50 & 2.49A (35.9° & 36.0°) etc. (Figs. 1C, 3A)

Type (2); A strong reflection of 3.25A (27.4°) and no doublet (Fig. 2A)

Type (3); Doublets of type (1) associated with a reflection of type (2) (Figs. 1A, 1B, 2B, 2C, 3B, 3C).

The inconsistency of these two classifications is mainly resulted from taking or not 4.1A reflection (21.7° in 2θ) into account. This reflection is omitted in the latter classification. The reasons are presented in the following.

Structure of high tridymite

Some natural and synthetic tridymites were heated at 500°C, and their X-ray powder reflections were recorded at the temperature. The powder reflections are shown in comparison with those of the low form (Fig. 5).

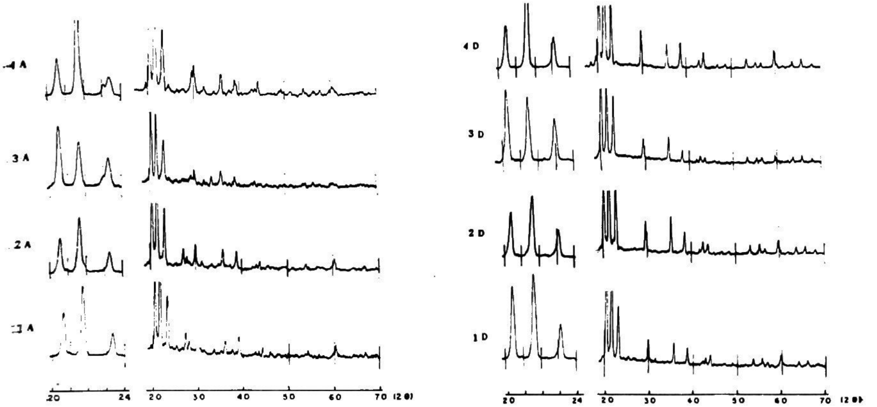

Fig. 5. X-ray powder patterns of low and high tridymite.

low	(room temp.)	high (500°C)	type
4-A	(synthetic)	4-D	intermediate
3-A	(,,)	3-D	S
2-A	(natural)	2-D	M
1-A	(synthetic)	1-D	M

(grouping with reference to Fig. 4)

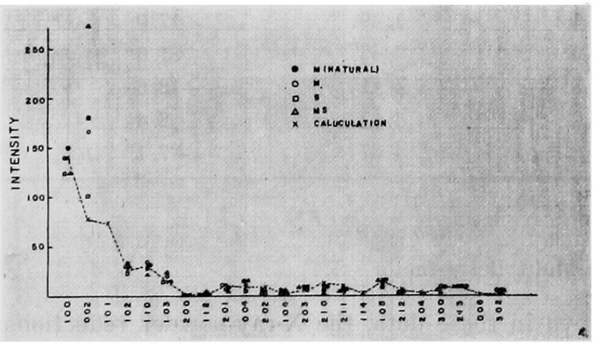

Fig. 6. The comparison of the observed and calculated intensities of powder reflections of the high form.

Types M and S correspond to those in Fig. 5, and type MS to the intermediate in the same figure (Not the MS defined in later section in the text!). The abscissa shows the indicies of reflections.

Table 2. The calculated values of spacings, structure factors and relative intensities of powder reflections of high tridymite based upon the structure model proposed by Gibbs.

$h\ k\ l$	d (Å)	F	I_{rel}
1 0 0	4.36	−43.8	140
0 0 · 2	4.11	59.5	78
1 0 · 1	3.85	−25.6	74
1 0 · 2	2.98	−20.4	27
1 1 · 0	2.51	37.2	31
1 0 · 3	2.31	−19.2	14
2 0 · 0	2.18	7.0	1
1 1 · 2	2.14	6.3	1
2 0 · 1	2.11	19.8	12
0 0 · 4	2.05	40.9	8
2 0 · 2	1.93	18.8	8
1 0 · 4	1.86	−14.4	4
2 0 · 3	1.70	19.1	6
2 1 · 0	1.65	−28.3	13
2 1 1	1.61	−17.2	10
1 1 · 4	1.59	−2.2	3
1 0 · 5	1.54	−32.6	15
2 1 · 2	1.53	−15.3	6
2 0 · 4	1.49	17.0	3
3 0 · 0	1.45	31.6	6
2 1 · 3	1.41	−18.6	8
3 0 · 2	1.37	8.4	1
0 0 · 6	1.37	−7.1	0.1

$$I_{\mathrm{rel}} \cong j\frac{1+\cos^2\theta}{2} \quad \frac{1}{2\sin^2\theta\cos\theta} \cdot F^2$$

j: Multiplicity factor

As shown in these data, the X-ray powder reflections become at this temperature to have a unique feature lacking the differences which are used for grouping of types M and S in the low form. Good agreement except for $00 \cdot l$ reflections was obtained between the observed and calculated intensities (Table 2 and Fig. 6), the calculation being based upon the structure proposed by Gibbs (1927).

as follows : symmetry, hexagonal ; cell dimensions, $a=5.03$A, $c=8.22$A ; space group, $P6_3/mmc$; atomic coordinates :—

Si in (f) $\pm(1/3, 2/3, u;\ 2/3, 1/3, u+\frac{1}{2})$, $u=7/16$,
O in (c) $\pm(1/3, 2/3, 1/4)$
O in (g) 1/2, 0, 1/2 ; 0, 1/2, 1/2 ; 1/2, 1/2, 0 ; 1/2, 0, 0 ;
0, 1/2, 0 ; 1/2, 1/2, 1/2.

Since good agreement between observed and calculated intensities was obtained in general and no other reflection was observed than those expected, the assumed structure is to be considered as a correct one. However, together with the fact that the observed intensities of $00{\cdot}l$ reflections are stronger than the calculated (particularly so with the specimens produced with the aid of Na_2WO_4), upon close examination $10{\cdot}l$ reflections also indicate discrepancies (Fig. 7). It is, therefore, suspected the presence of certain perferred orientation of crystallites in the specimens, and if so, the observed intensity of a $10{\cdot}l$ reflection should be the more enhanced, the larger the number of l. Fig. 7, in fact, well supports this expectation. Tridymite has

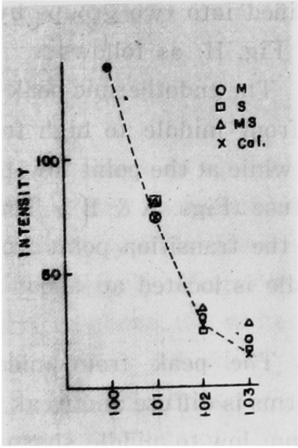

Fig. 7. The comparison of the calculated intensities of $10{\cdot}l$ reflections with the observed.

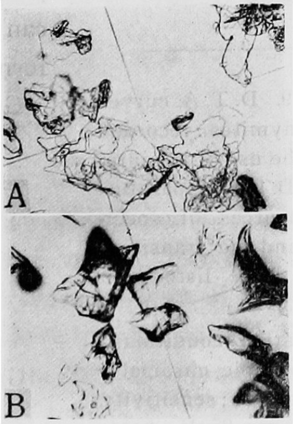

Fig. 8. Synthetic tridymite crystals.
A, from Na_2WO_4 ;
B, from Na_2CO_3 and NaCl.

its indistinct cleavage parallel to (1 1·0) and a parting to (0 0·1). In the present case, however, it seems that the flat crystal plates parallel to (0 0·1), not parting flakes, are responsible for the effect. As shown in Fig. 8, euhedral platy crystals are predominant in the samples synthesized using Na_2WO_4, while the other samples using Na_2CO_3 and NaCl are composed mostly of dendrites.

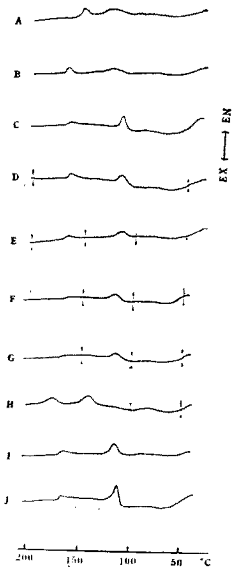

Fig. 9. D. T. A. curves of tridymites recorded with the use of an automatic D.T.A. apparatus. The sources of specimens and the transition points are listed in Table 3.

Operation conditions: thermocouple, chromel—alumel wires; sensitivity of amperes, 25uV; heatting rate, 2.5°C/min.; chart speed, 5 mm/min.; standard sample, alumina; heating in room air.

Differential thermal analysis

In Fig. 9 is shown the D. T. A. curves of tridymite from the various sources. Actually they were recorded up to 700°C, but no change of patterns could be detected above 200°C. Two endothermic peakes correspond to the transition points from low to middle and middle to high forms. The sources of specimens and the transition points are listed in Table 3. The curves can be classified into two groups by their form (except Fig. H) as follows:

Group (a); The endothermic peak at the point from middle to high forms is sharp, while at the point low to middle diffuse (Figs. A & B). The peak due to the transition point from low to middle is located at about 125°C, and

Group (b); The peak from middle to high forms is diffuse and weak, while that from low to middle sharp (Figs. C, D, E, F, G, I, J). The peak from low to middle is at about 115°C.

The comparison of the D. T. A. curves

Table 3. Sources and transition points of tridymites.

	Source of tridymite	Transition points		Corresponding X-ray powder patterns
A	natural, in opaline silica	128°C	155°C	Fig. 12-B
B	synthetic, silica gel (1), Na_2WO_4	125	168	12-A, 2-A
C	synthetic, quartz, Na_2WO_4	115	165	1-A
D	synthetic, silica gel (2), Na_2WO_4	115	165	3-A
E	synthetic, quartz, NaCl	113	165	1-B
F	synthetic, quartz, Na_2CO_3	118	162	1-C
G	synthetic, silica gel (2), Na_2CO_3	116	167	3-C
H	synthetic, quartz, Na_2WO_4, Al_2O_3 (1%)	143	177	11-B
I	synthetic, quartz, Na_2SO_4	115	165	
J	synthetic, from silica brick	112	167	

with the X-ray powder patterns reveals that the specimens belonging to group (a) are of type (2) and group (b) of type (1) and (3).

Classification of low tridymite

The difference in intensity of the 4.1A reflection was adopted by Hill and Roy as one of the important criteria for discriminating type M from type S. However, since it is quite probable that the intensity is largely affected by the preferred orientation of crystallites as described above, the writer proposes here for this purpose the use of X-ray powder reflections up to 70° in $2\theta(\mathrm{Cu}K\alpha)$ and a set of characteristic reflections for each type as follows:

Type S; Doublets of 3.86 & 3.81A, 3.01 & 2.97A, 2.50 & 2.49A, 2.31 & 2.29A are remarkable. The reflection of 3.25A is very weak.

Type M; Doublet does not appear. The reflection of 3.25A is very remarkable.

Type MS; Doublets of type S are associated with the reflection of type M.

Typical powder patterns of types M, S and MS are shown in Fig. 10. X-ray powder data of types M and S corresponding to Fig. 10-A and Fig. 10-B respectively are given in Table 4. Tridymite M and

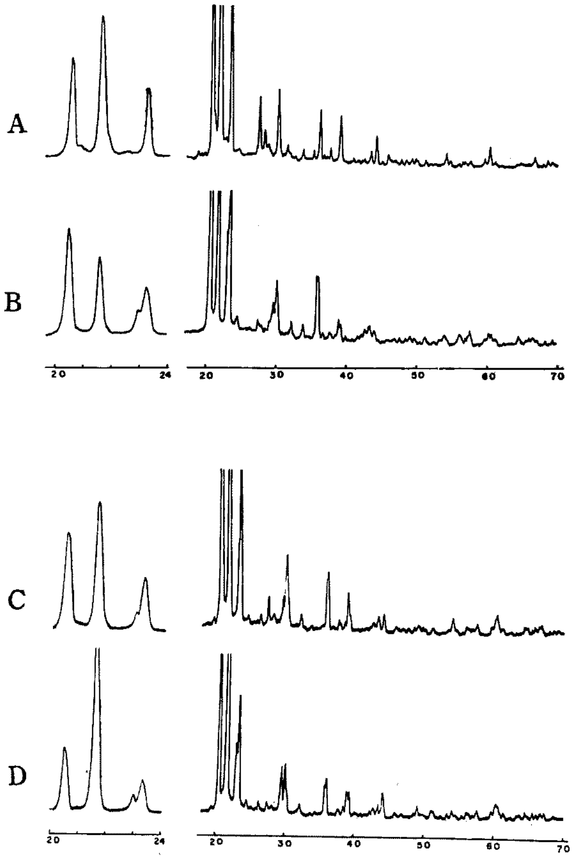

Fig. 10. Typical powder patterns of tridymites M, S and MS according to the classification newly proposed by the writer.

A, type M; B, type S; C, type MS; D, type S.

tridymite S illustrated in Figs. 5-1, 5-2, 5-3 are consistent with the newly defined type M and type S, but the intermediate in Fig. 5-4 should be looked upon as belonging to type S.

Table 4. X-ray powder data of tridymites M and S.

Type M			Type S		
2θ (Cu$K\alpha$)	d	I	2θ (Cu$K\alpha$)	d	I
20.60	4.311	132	20.50	4.332	246
20.86	4.258	6			
21.70	4.095	200	21.68	4.099	173
			23.03	3.862	50
23.33	3.813	100	23.33	3.813	100
24.35	3.654	2	24.35	3.655	8
25.70	3.466	2			
27.48	3.246	30	27.45	3.249	5
27.80	3.209	<1	27.86	3.202	3
28.14	3.171	12			
28.55	3.126	3			
28.75	3.105	2			
			29.06	3.073	4
29.22	3.056	<1			
29.55	3.023	<1	29.60	3.018	28
30.11	2.968	32	30.06	2.973	42
31.48	2.842	4			
31.79	2.815	2			
32.21	2.779	2	32.20	2.780	10
32.61	2.746	2			
33.64	2.664	5	33.85	2.648	8
34.51	2.599	2	34.30	2.614	1
35.28	2.544	3			
			35.90	2.501	30
36.14	2.485	26	36.00	2.495	30
36.78	2.443	2	36.80	2.442	3
37.23	2.415	2			
37.73	2.384	7	37.78	2.381	5
38.41	2.344	2	38.40	2.344	<1
39.09	2.304	26	38.97	2.311	18

Table 4. (cont.)

Type M			Type S		
2θ (Cu$K\alpha$)	d	I	2θ (Cu$K\alpha$)	d	I
			39.25	2.295	6
			39.95	2.257	2
40.34	2.235	1	40.20	2.243	<1
41.02	2.200	2	41.17	2.193	<1
			41.77	2.162	2
42.27	2.138	2	42.27	2.138	5
42.57	2.123	2	42.65	2.120	6
43.49	2.081	8	43.27	2.091	15
44.26	2.046	16	44.07	2.055	6
			44.52	2.035	<1
45.01	2.014	<1			
45.95	1.975	6	45.47	1.995	<1
46.41	1.956	2	46.20	1.965	<1
46.91	1.937	2	46.85	1.939	<1
47.83	1.902	2	47.62	1.910	2
48.61	1.873	<1	48.45	1.879	4
49.36	1.846	2	49.17	1.853	4
49.81	1.830	3	49.75	1.833	3
50.16	1.818	3			
51.36	1.779	2	51.27	1.782	7
51.83	1.764	1			
52.43	1.745	2	52.47	1.744	3
52.83	1.733	2			
53.68	1.707	10	53.47	1.714	4
54.29	1.690	3	54.10	1.695	12
54.82	1.674	3	54.52	1.683	2
			55.40	1.658	<1
56.72	1.623	3	56.22	1.636	10
57.02	1.614	3	57.10	1.613	2
57.77	1.596	4	57.62	1.600	15
58.32	1.582	1			
59.85	1.545	6	59.80	1.546	2
59.89	1.544	5			
60.53	1.530	12	60.32	1.534	14

Table 4. (cont.)

Type M			Type S		
2θ(Cu$K\alpha$)	d	I	2θ(Cu$K\alpha$)	d	I
61.30	1.512	2	61.07	1.517	7
			62.47	1.487	<1
63.43	1.466	1	63.30	1.469	<1
64.58	1.443	3	64.60	1.443	6
65.00	1.434	4			
66.03	1.415	3	65.90	1.417	4
66.73	1.401	2	66.62	1.404	6
66.98	1.397	6			
67.13	1.394	1	67.20	1.393	4
67.75	1.383	1			
68.20	1.375	2	68.37	1.372	<1
68.83	1.364	2			
69.43	1.354	2	69.23	1.357	2
69.68	1.349	2			
69.98	1.344	<1			

The problem of tridymite M and tridymite S

Hill and Roy (1958) insisted that tridymite M and tridymite S are related to each other by a sluggish reconstructive monotropic transformation; the M phase may be transformed to the S phase by prolonged heat treatment. Structurally they are related by polytypism, tridymite S having a structure of 20H, though the structure of tridymite M has not been known. Flörke (1961) explained their difference as due to the difference in stacking disorder between cristobalite and tridymite layers and the strong reflection of 4.1A peculiar to type M as due to the cristobalite layers. X-ray and thermal data certainly indicate the existence of two types, but it is questionable whether the difference is due to polytypism or stacking disorder. Although in the present study, the writer could not deduce the final conclusion concerning the nature of types M and S, the following facts will be worth recording here.

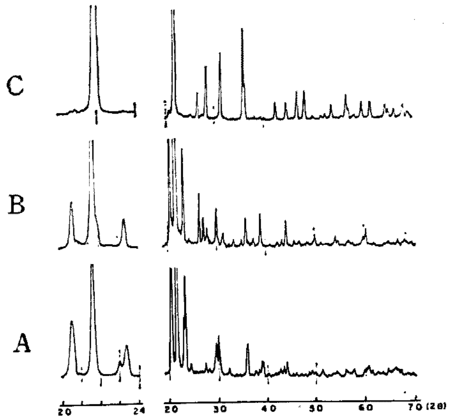

Fig. 11. X-ray powder patterns of synthetic tridymites.

C, quartz : Na_2WO_4 : Al_2O_3=1 : 1 : 0.02 (weight ratio);
B, „ „ „ =1 : 1 : 0.01;
A, „ „ „ =1 : 1 : 0.00.
Heating by a Mecker burner for 24 hours.

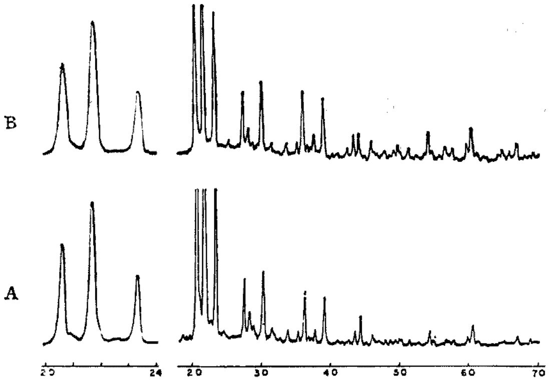

Fig. 12. X-ray powder patterns of natural and synthetic tridymites of type M.

B, natural in opaline silica;
A, synthetic, from silica gel(1) and Na_2WO_4.

(1) Type M can easily be synthesized from the mixture of silica gel (1) including impurity of 1.3% and Na_2WO_4 (Fig. 2-A). This fact can be also confirmed with Figs. 11 and 12. Fig. 11 shows that Al_2O_4 of 1% is effective for the formation of type M (Fig. 11-B), whereas without Al_2O_3, type S is formed (Fig. 11-A) and at the presence of Al_2O_3 of 2%, only cristobalite appears (Fig. 11-C). Fig. 12-B is of natural tridymite in opaline silica showing type M (Sato 1962). Its chemical composition is: SiO_2, 96.89; TiO_2, 0.86; Al_2O_3, 0.71; Fe_2O_3, tr.; FeO, none; MnO, none; MgO, none; CaO, none; Na_2O, 0.72; K_2O, 0.16; $H_2O(+)$, 0.12; $H_2O(-)$, 0.08; P_2O_5, tr.; total, 99.54%. Small amounts of impurities may be considered as responsible for the formation of type M.

(2) The differences of X-ray powder diffraction data found between type M and type S almost vanish for the high form (Fig. 5). Although slight variations are still confirmed among the reflections of the high form, they can well be explained to be due to the preferred orientation of crystal flakes.

(3) As well known, energy difference at the low to high inversion is very small (Mosemann & Pitzer 1941). This can also be confirmed by means of D. T. A. It is probably impossible for either polytypic change or stacking disorder to occur during the course of this transition.

In the light of these data, it is suggested that occurrence of M, S and other types may be mainly due to the difference in slight structural distortion at the high-low inversion, for which the amount and kind of impurities seem to be responsible.

Acknowledgement

The writer wishes to express his sincere gratitude to Prof. T. Sudo for his valuable suggestions and helpful guidance. His thanks are also due to Dr. N. Araki, Research Laboratory, Nihon Plate Glass Co. for his critical discussions and kind assistance.

REFERENCES

Flörke, O. W. (1961). *Ber. Deut. Ker. Gessel.*, **38**, 89.

Gibbs, R. E. (1927). *Proc. Roy. Soc. London*, **113**, 351.

Hill, V. G. & Roy, R. (1958). *Trans. Brit. Cer. Soc.* **57**, 496.

Mosemann, M. A. & Pitzer, K. S. (1941). *Jour. Am. Chem. Soc.*, **63**, 2348.

Sato, M. (1962). *Miner. Jour.*, **3**, 296.

Manuscript received 8 July 1963.