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High Pressure and High Temperature Investigations in the System MgO–SiO_2–H_2O

KATSUHIRO YAMAMOTO
Water Research Laboratory, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464, Japan

AND

SYUN-ITI AKIMOTO
Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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The system MgO–SiO_2–H_2O was investigated at pressures between 40 and 95 kbar and at temperatures between 500 and 1400°C. The reaction products were examined by X-ray, optical and thermal analysis techniques and the density of phase A discovered by Ringwood and Major was also measured. It was found that phase A was hydrated and its chemical formula was $H_6Mg_7Si_2O_{14}$. When the Mg/Si ratio of the system is 2, phase A + clinoenstatite, and forsterite are stable at temperatures lower and higher than a boundary curve $T\,(°C) = 10P$ (kbar), respectively. When the Mg/Si ratio of the system is 3, phase A + phase D (which is completely different from the phases, A, B and C discovered by Ringwood and Major, and any other known phases of magnesium silicate) and phase D + brucite are stable at temperatures lower and higher than a boundary curve $T(°C) = 10P$ (kbar) + 200. Phase A has approximately an hexagonal symmetry and the space group and the lattice parameters are determined as $P6_3$ or $P6_3/m$ and $a = 7.866(2)$ Å and $c = 9.600(3)$ Å, respectively. The measured density is 2.96 ± 0.02 g/cm³. The optical observations show that phase A is biaxial positive crystal with refractive indices $\alpha = 1.638 \pm 0.001$, $\beta = 1.640 \pm 0.002$, and $\gamma = 1.649 \pm 0.001$. Some interpretation is given on the inconsistency between the symmetry determined by the X-ray diffraction and the optical observation. The new phase D belongs to the space group $P2_1/c$ with lattice parameters $a = 7.914(2)$ Å, $b = 4.752(1)$ Å, $c = 10.350(2)$ Å and $\beta = 108.71(5)°$ and is a biaxial crystal with refractive indices $\alpha = 1.630 \pm 0.002$, $\beta = 1.642 \pm 0.002$ and $\gamma = 1.658 \pm 0.001$.

Introduction

Previous studies (*1*, *2*) of the phase diagram in the system MgO–SiO_2–H_2O were mostly limited to the lower range of pressures up to about 30 kbar. Ringwood and Major (*3*) investigated this system at very high pressures between 100 and 180 kbar and at temperatures from 600 to 1100°C, using gels and oxide mixtures (silicic acid plus MgO) with compositions $x\mathrm{MgO}\cdot\mathrm{SiO_2}$, where $x = 1$, 2, 2.5, 3, 4 and 5, as starting materials. They discovered three new phases denoted A, B and C, and reported that the mean refractive indices of phases A and B were approximately 1.65 and between 1.71 and 1.77, respectively. They suspected that phases A, B and C were all hydrated and that MgO/SiO_2 ratios of phases A, B and C were in the vicinity of 3/2 or 2, between 2 and 3, and between 3 and 5, respectively. Although their reconnaissance investigations provided quite interesting high-pressure chemistry of hydrous silicates, highly non-uniform temperatures in their furnace and very short run-times gave rise to some uncertainty in their results because many phases were synthesized in a run and especially because they could not determine the reaction temperature.

The present experiments were carried out under the conditions of long run-times (30 to 300 min), uniform temperatures between 500 and 1400°C and uniform pressures between 35 and 95 kbar. The chemical formula, the crystal structure and the stability field of phase A were investigated.

It is noted that no study in the system MgO–SiO_2–H_2O has been carried out in the pressure and temperature range of these experiments. A new phase denoted phase D was also found, and its details are reported below.

Experimental Procedure

Mixtures of guaranteed grades of the reagents $Mg(OH)_2$, MgO and anhydrous SiO_2 were used as starting materials in these experiments. $Mg(OH)_2$ was used instead of $MgO + H_2O$ because of ease of treatment. The mixtures were labeled by (p, q) which denotes the composition, $p Mg(OH)_2 + (q-p) MgO + H_2O = p H_2O + q MgO + SiO_2$ (it is noted that q is the ratio Mg/Si), and divided into four groups according to the experimental aims.

Group I, (2, 2) and (3, 3), was studied to examine the stability field of phase A at high pressures and temperatures.

Group II, (1, 1), (3/2, 3/2), (1, 2), (5/2, 5/2), (2, 3), (1, 4), (11/2, 11/2), (3, 8) and (1, 10), was used to examine the stability field of phase A at 77 kbar, the pressure of Bi III–V transition point.

Group III, (3/2, 3/2), (7/4, 7/4), (2, 2), (9/4, 9/4), (5/2, 5/2), (3, 3), (13/4, 13/4), (7/2, 7/2) and (4, 4) was studied to determine the chemical formula of phase A.

Group IV, (13/4, 13/4), was studied to determine the structures of phase A and phase D using X-ray diffraction and optical method.

All values of p and q were determined from mixing ratios of $Mg(OH)_2$ and MgO to SiO_2 and it was confirmed on (13/4, 13/4) sample that the value of (p, q) was consistent with that fixed from wet chemical analysis.

A tetrahedral-anvil type of high-pressure apparatus was used for this study. Anvils with 30 mm edge and pyrophyllite tetrahedrons with 36 mm edge were used in the pressure range from 35 to 40 kbar. Anvils with 15 mm edge and tetrahedrons with 20 mm edge were used in the range from 50 to 80 kbar. Anvils with 9 mm edge and tetrahedrons with 15 mm edge were used in the range from 80 to 95 kbar. The pressure values were calibrated at the room temperature on the basis of the pressure scale recommended at the U.S. National Bureau of Standards Symposium, 1968, using resistance transitions of Bi I–II (25.5 kbar), Tl II–III (36.7 kbar), Bi III–V (77 kbar) and Sn I–II (100 kbar).

The desired temperature was obtained by cylindrical heaters of graphite of 5 mm in outer diameter, 4 mm in inner diameter and 10 mm in length, 4.2 mm in outer diameter, 3.2 mm in inner diameter and 6.5 mm in length, and 2.7 mm in outer diameter, 2.0 mm in inner diameter and 4 mm in length which were placed in the pyrophyllite tetrahedrons with 36, 20 and 15 mm edges, respectively.

In order to prevent the water loss during the run, the starting materials were sealed in Au or Pt tubes by means of dc carbon arc welding. The size of the tube was varied from 2.5 mm in outer diameter and 2.2 mm in inner diameter to 1.1 mm in outer diameter and 0.9 mm in inner diameter depending upon the size of the heater. This sealing procedure is also expected to be effective to make the pressure and temperature of samples uniform.

A furnace assembly is illustrated in Fig. 1. The tube was insulated electrically from the heater by a pair of disks and sleeves of pyrophyllite. The remaining space in the heater was filled with pyrophyllite powder. Temperatures were measured with Pt/Pt–13 %Rh thermocouple in contact with the tube. The effect of pressure on the emf of the thermocouple was ignored. In all of the Group II experiments, three Pt tubes, which contained mixtures of different compositions, were put into one heater. In the Group III cases, Au foil of 30 μm thickness was used instead of tube in order to obtain as much sample as possible. In these cases the temperature was estimated from the electric power of the heating element.

Intervals of run-time for Group I and Group II

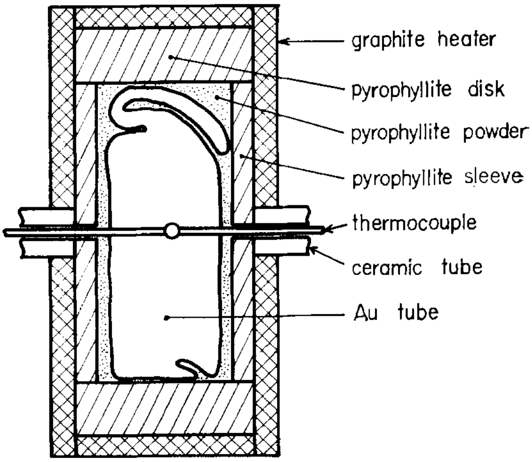

FIG. 1. Furnace assembly.

were 300, 120, 60 and 30 min at 500, 700, 900 and 1100°C, respectively. Run-time for Group III was 240 min at about 700°C. Time intervals for Group IV were 120, 90 and 60 min at 1000, 1100 and 1200°C.

Samples were quenched in the usual method under working pressure and examined by the X-ray diffraction technique after each run. In the study of Group III some samples were examined using a thermobalance, thermoflex 8002 type made by Rigaku Denki, in a self-generating atmosphere under a heating rate of 5°C/min. α-Al_2O_3 of the same mass as the samples was used as a reference material for the differential thermal analyses. Gas exhausted during the thermal analyses was examined by gas chromatography using N_2 as carrier gas. At each step observed in the thermographs, the structure of the samples was examined using an X-ray diffractometer.

The samples of Group IV were examined using not only a rotating camera of radius 35 mm and a Weissenberg camera of radius 28.7 mm (Cu*Kα* radiation was used in all the X-ray analyses) but also a petrographic microscope with a conoscope and an orthoscope. The refractive indices of phase

TABLE I

X-RAY DIFFRACTION DATA FOR PHASE *A*[a]

	Present work			Ringwood and Major (*3*)	
h k l	d_{obs} (Å)	d_{calc} (Å)	Intensity	d_{obs}	Intensity
1 0 0	6.86	6.81	3		
1 0 1	5.56	5.56	2		
0 0 2	4.78	4.80	6		
1 1 0 1 0 2	3.938	3.933 3.924	30	3.94	50
1 1 1	3.643	3.639	33	3.65	30
2 0 1	3.215	2.210	9		
1 1 2	3.043	3.042	4	2.99	20
1 0 3	2.895	2.896	14	2.90	10
2 0 2	2.780	2.778	61	2.79	70
2 1 0	2.576	2.575	2		
2 1 1 1 1 3	2.483	2.487 2.482	23		
0 0 4	2.397	2.400	8		
3 0 0 2 1 2	2.271	2.271 2.269	100	2.27	100
3 0 2 1 1 4	2.052	2.053 2.049	4		
2 1 3	2.006	2.006	38	2.01	40
2 2 1	1.9278	1.9265	3		
3 1 1 3 0 3	1.8531	1.8538 1.8519	5		
2 1 4	1.7552	1.7556	17	1.76	30
4 0 0	1.7019	1.7030	4		
2 2 3 2 0 5	1.6743	1.6754 1.6726	3		
3 0 4	1.6488	1.6495	5		
3 1 3	1.6271	1.6269	4		
2 1 5	1.5379	1.5392	28	1.54	40
4 0 3	1.5027	1.5034	4		
4 1 0 3 2 2	1.4869	1.4865 1.4860	41	1.49	80

[a] Hexagonal ($P6_3$ or $P6_3/m$) $a = 7.866 \pm 0.002$ Å; $c = 9.600 \pm 0.003$ Å; $V = 514.4 \pm 0.4$ Å^3.

A and phase D were determined by the usual Becke-line method.

The density of phase A was measured at temperatures ranging from 7 to 40°C by a floatation method using *s*-tetrabromoethane as a immersion medium (*4*). The density of *s*-tetrabromoethane was calibrated at 24°C by means of a pycnometer.

Experimental Results

The reaction products of these experiments; clinoenstatite, orthoenstatite, forsterite, coesite, periclase, brucite, phase A and new phase D; were distinguished using the X-ray diffractometer. It is established by the diffraction patterns shown in Table I that phase A in this experiment is the same as phase A denoted by Ringwood and Major (*3*). The existence of the new phase D, different from all of the magnesium silicates listed in ASTM cards and of phases B and C denoted by Ringwood and Major (*3*), was verified by the X-ray analysis of the single crystals and polycrystalline powder of this phase. Production of H_2O during the reaction could be detected by observing the welling-out of water from the tube when it was cut.

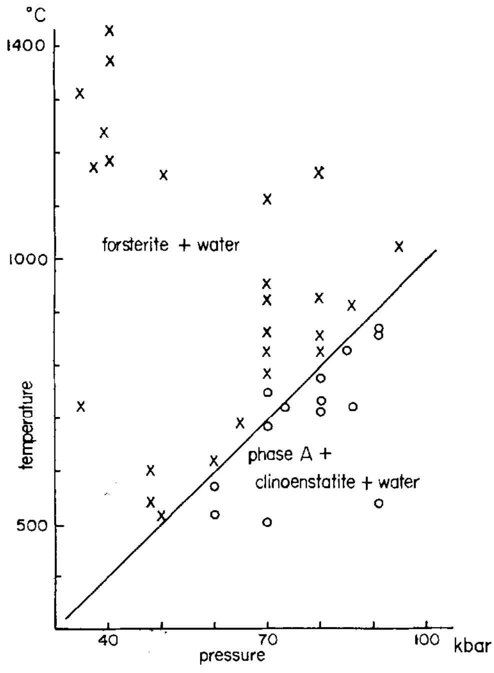

FIG. 2. High-pressure and high-temperature stability diagram for $2Mg(OH)_2 + SiO_2$.

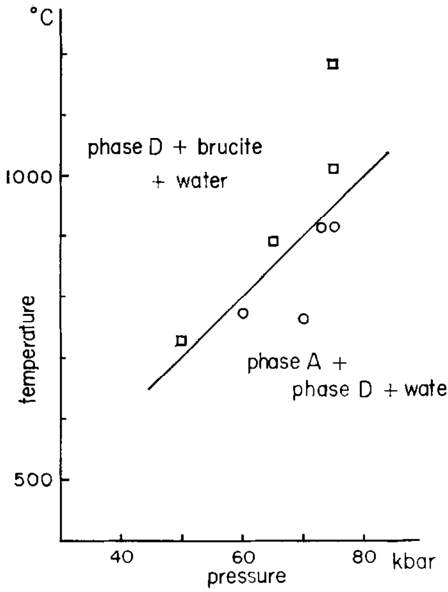

FIG. 3. High-pressure and high-temperature stability diagram for $3Mg(OH)_2 + SiO_2$.

Group I

Results for (2, 2) samples are summarized in Fig. 2 which is divided into two regions by an equilibrium line. In the lower region the fine powders of phase A and clinoenstatite were synthesized. In the upper region large crystals of forsterite were synthesized. From Fig. 2 the equilibrium line was determined as $T\,(°\mathrm{C}) = 10P$ (kbar).

Results for (3, 3) samples are shown in Fig. 3 which is divided into two regions by an equilibrium line similar to Fig. 2. In the upper region phase D and brucite were identified. In the lower region phase A and phase D were synthesized. For some samples, brucite and coesite remained unreacted in both regions. The equilibrium line in Fig. 3 is given by $T(°\mathrm{C}) = 10P(\mathrm{kbar}) + 200$.

Group II

Results for Group II at the pressure of Bi III–V transition point are summarized in Table II. At 725°C, phase A was synthesized for all q except 1. When $q \leqq 3$, clinoenstatite was identified, while when $q \geqq 4$, brucite and periclase remained unreacted. At 925°C, when $q \geqq 3$, phase A was synthesized. When $q = 5/2$ and 3, phase D was synthesized. At 1125°C, phase D was obtained when $q \geqq 3$. Some of the starting materials remained more or less unreacted, and

TABLE II

RESULTS OF RUNS IN pMg(OH)$_2$ + $(q-p)$MgO + SiO$_2$ AT 77 kbar[a]

Temp (C°):	725	925	1125
Run time (min):	120	60	30
Starting materials (p,q)			
(1, 1)	CE + W	CE + W	OE + Br + Coe + W
(3/2, 3/2)	A + CE + W	Fo + CE + W	Fo + OE + W
(1, 2)	A + CE + W	Fo + W	Fo + Br + W
(5/2, 5/2)	A + CE + W	D + W	Unknown + W
(2, 3)	A + CE + W	A + D + W	D + Br + W
(1, 4)	A + Pe + Br + Coe	A + Pe + Br + Coe	D + Pe + Br
(11/2, 11/2)	A + Br + W	A + Pe + Br	D + Pe + Br
(3, 8)	A + Pe + Br	A + Pe + Br	D + Pe + Br
(1, 10)	A + Pe	A + Pe + Coe	D + Pe + Br

[a] Abbreviations: A, phase A; D, phase D; Br, brucite; CE, clinoenstatite; Coe, coesite; Fo, forsterite; OE, orthoenstatite; Pe, periclase; W, water.

in some samples the formation of coesite was observed. Brucite in the samples reacted at 925 and 1125°C may be formed during quenching as suggested by Yamaoka, Fukunaga and Saito (*5*).

Group III

Group III was reacted at the pressure of the Bi III–V transition point and at a temperature of about 700°C. For p and $q \leqq 13/4$, phase A and clinoenstatite were synthesized. For p and $q = 4$, a small amount of brucite remained. In order to determine the Mg/Si ratio of phase A, which is necessary for fixing its chemical formula, the intensity ratios of the diffraction line (331) of clinoenstatite to that of d-spacing = 2.006 Å [hexagonal index is (213)] were measured and are shown in Table III. These diffraction lines were adopted because they had medium intensity and did not overlap in any of the diffraction lines of the other phase.

TABLE III

X-RAY DIFFRACTION INTENSITY RATIO, R, OF CLINOENSTATITE TO PHASE A ON THE SAMPLES SYNTHESIZED FROM pMg(OH)$_2$ + Si O$_2$ AT 77 kbar AND AT 700°C

	R = Clinoenstatite (3 3 1)/Phase A(2 1 3)	
$p = q$	Observation	Calculation (A = 0.15)[a]
5/4	2.0	2.7
3/2	1.1	1.2
7/4	0.70	0.70
2	0.45	0.45
9/4	0.25	0.25
3	0.08	0.08
13/4	0.05	0.03
7/2	0.0	0.0
4	0.0	0.0

[a] A is a proportional constant in Eq. (4).

The results of the thermal analysis are given in Table IV and the thermogram of (13/4, 13/4) samples is illustrated in Fig. 4, in which the differential thermal analysis curve is also shown. From Fig. 4 it can be seen that there are three stages I, II and III in the temperature range from 400 to 800°C. X-Ray analysis showed that any change of the structure did not take place in stage I. Forsterite, synthesized from (2, 2) mixture at 77 kbar and about 900°C, showed this stage I as well as phase A. Just before stage III, X-ray diffraction showed that forsterite and periclase were formed in slight amounts. After it, phase A disappeared while forsterite and periclase were synthesized. When the samples of phase A were heated again after heating up to the temperature just before stage III and cooling to room temperature, stage II was observed again. In the thermobalance experiments, stages II and III were not precisely distinguished. It was found by gas chromatography that CO$_2$ and H$_2$O were exhausted during stage I and during stages II

TABLE IV

RESULTS OF THERMAL ANALYSIS ON THE SAMPLES SYNTHESIZED FROM pMg(OH)$_2$ + SiO$_2$ AT 77 kbar AND AT 700°C

$p = q$	Mass of sample (mg)	Stage	Temp (°C)	Amount of endotherm	Exhausted gas	Loss of wt (mg)	Amount of hydration (wt %)	
							W_{obs}	W_{calc}
3/2	11.6	I	470–520	Undetectable	CO$_2$	0.3	4	4.2
		II, III	610–720	Large	H$_2$O	0.4		
2	22.7	I	425–497	A little	Not determined	0.27	7.0	6.8
		II	575–	Medium		0.64		
		III	680–726	Large		0.94		
3	17.4	I	470–510	Undetectable	CO$_2$	0.2	12	9.9
		II, III	580–720	Large	H$_2$O	2.1		
13/4	19.7	I	428–522	A little	Not determined	0.30	11.0	10.5
		II	574–	Medium		0.77		
		III	680–730	Large		1.39		
7/2	7.3	I	470–510	Undetectable	CO$_2$	0.2	12	10.9
		II, III	580–730	Large	H$_2$O	0.9		
Fo[a]	17.3		470–530	Undetectable	CO$_2$	0.2		
			650–690		H$_2$O	0.1		

[a] Fo, forsterite synthesized from 2Mg(OH)$_2$ + SiO$_2$ at 77 kbar and 900°C.

and III, respectively. These three reactions were endothermic.

Group IV

Phase A was synthesized from (13/4, 13/4) mixtures up to 1025°C and at 77 kbar. Phase D and forsterite were identified at 1125°C and at 1225°C, respectively.

The analysis of the single crystals of phase A by Weissenberg and rotating cameras showed that the space group was $P6_3$ or $P6_3/m$. In Table I, both observed and calculated d-spacings of phase A are given on the basis of this hexagonal lattice. It is seen that the reflections of the powder X-ray diffraction pattern can be successfully indexed. The unit cell dimensions were determined as $a = 7.866(2)$ Å and $c = 9.600(3)$ Å. More precise structure analysis was made difficult by

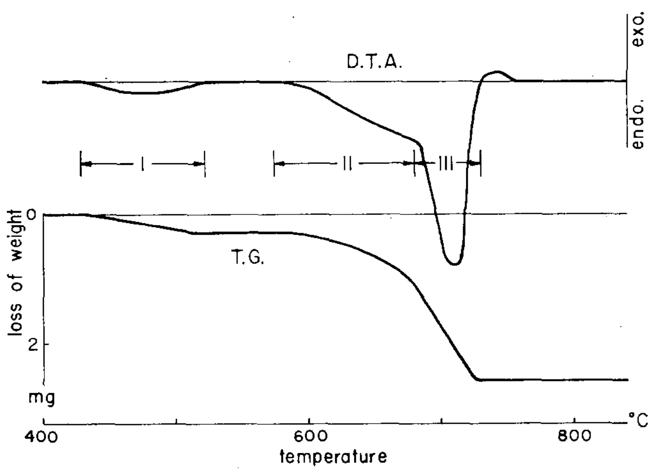

FIG. 4. Thermogram and differential thermal analysis curve for the sample synthesized from 13/4Mg(OH)$_2$ + SiO$_2$ at 77 kbar and at 700°C.

TABLE V

X-RAY DIFFRACTION DATA FOR PHASE D[a]

h k l	d_{obs}	d_{calc}	Intensity
1 0 0	7.49	7.50	15
$\bar{1}$ 0 2	4.89	4.88	40
1 1 0	4.02	4.01	15
2 0 0	3.752	3.748	25
1 0 2	3.608	3.607	30
$\bar{2}$ 0 2	3.586	3.583	20
1 1 1	3.508	3.509	25
0 1 2	3.415	3.412	20
$\bar{2}$ 1 1	3.037	3.037	40
$\bar{2}$ 1 2	2.862	2.861	10
$\bar{1}$ 1 3	2.781	2.778	40
0 1 3	2.695	2.693	45
2 1 1	2.641	2.641	50
$\bar{2}$ 1 3	2.527	2.526	65
0 0 4	2.453	2.451	15
$\bar{2}$ 0 4	2.445	2.441	15
1 1 3	2.349	2.345	50
0 2 1 $\bar{3}$ 1 1	2.303	2.309 2.302	45
2 1 2	2.283	2.282	60
$\bar{1}$ 1 4 $\bar{3}$ 1 2	2.273	2.272 2.272	100
1 2 1	2.162	2.161	20
$\bar{3}$ 0 4	2.121	2.123	8
3 1 1 $\bar{2}$ 2 1	2.037	2.037 2.036	15
0 1 5	1.8137	1.8125	6
$\bar{4}$ 1 1	1.8121	1.8121	5
2 2 2 $\bar{1}$ 2 4 $\bar{3}$ 2 2	1.7502	1.7545 1.7501 1.7499	80
3 2 0	1.7207	1.7218	5
0 2 4 $\bar{2}$ 2 4	1.7051	1.7060 1.7026	10
1 1 5	1.6537	1.6533	6
0 0 6	1.6348	1.6339	10
3 1 3 $\bar{3}$ 0 6	1.6292	1.6294 1.6273	20
4 0 2	1.5893	1.5886	4
$\bar{3}$ 2 4 $\bar{5}$ 0 2	1.5828	1.5830 1.5825	7
$\bar{5}$ 0 4	1.5127	1.5130	5
1 0 6 5 0 0	1.4492	1.4995 1.4995	40
$\bar{4}$ 0 6	1.4910	1.4910	30
$\bar{5}$ 1 3	1.4873	1.4875	20

[a] Monoclinic ($P2_1/c$) $a = 7.914 \pm 0.002$ Å; $b = 4.752 \pm 0.001$ Å; $c = 10.350 \pm 0.002$ Å; $\beta = 108.71 \pm 0.05°$; $V = 368.7 \pm 0.1$ Å^3.

the existence of the twinning on the (210) plane, which was proved by the following evidences; the Weissenberg photographs about *c*-axis showed as if phase A had the symmetry element of reflection in a mirror plane (210), while the intensities of the two Laue spots which were in the relation of the reflection were different and the difference depended upon samples.

It was found that phase D belonged to $P2_1/c$ of space group. On the basis of this monoclinic lattice, the powder chart of the X-ray diffraction of phase D was indexed in Table V, and the cell parameters were determined as $a = 7.914(2)$ Å, $b = 4.752(1)$ Å, $c = 10.350(2)$ Å, and $\beta = 108.71(5)°$.

Crystal forms of phase A were nearly hexagonal plates perpendicular to *c*-axis and needles parallel to *c*-axis. On the other hand the crystals of phase D showed various kind of forms. Polysynthetic twins were observed occasionally in both phases. The (210) twin of phase A could not be detected optically. Conoscopic figures showed that phase A was a biaxial positive crystal. The refractive indices were $\alpha = 1.638 \pm 0.001$, $\beta = 1.640 \pm 0.002$ and $\gamma = 1.649 \pm 0.001$. The fragments of phase A crushed in a mortar were rectangular and had a positive sign of elongation. Phase D was a biaxial positive crystal with $\alpha = 1.630 \pm 0.002$, $\beta = 1.642 \pm 0.002$ and $\gamma = 1.658 \pm 0.001$.

Crystals of phase A floated on *s*-tetrabromoethane at temperatures below 15°C and sank in at temperatures above 32°C. The density of *s*-tetrabromoethane was measured at 24°C as 2.955 g/cm^3, and thus the density of phase A was estimated to be 2.96 ± 0.02 g/cm^3 at room temperature.

Discussion and Conclusion

Thermal Analysis of Phase A

The exhaustion of CO_2 from the samples was found in forsterite as well as phase A, and it is known that the temperature of the decomposition of $MgCO_3$ is the same as that of stage I of Fig. 4 (*6*). From these facts it is plausible to consider that $MgCO_3$, which has been formed by the coupling of some amount of $Mg(OH)_2$ in the starting materials with CO_2 in air before the formation of phase A, still survives in the run products and decomposes in stage I with evolution of CO_2.

It is very difficult to find out the mechanism of the decomposition in stages II and III. However, it can be concluded that the water vapor formed in stages II and III influences the rate of decomposition of phase A, because the decomposition rates in stages II and III of the samples surrounded by moving N_2 gas are smaller than those of the samples surrounded by self-generated water vapor.

Structure of Phase A

There is inconsistency between the results obtained by the X-ray measurement and by the optical observation; Weissenberg photograph shows that phase A has a hexagonal symmetry, while conoscopic figure indicates that phase A belongs to a biaxial crystal. The following three explanations might be conceivable to account for this inconsistency: (a) Phase A has a hexagonal symmetry but a residual strain makes the optical symmetry lower. (b) Some atoms slightly dislocate from the positions of the 6_3 symmetry so that the axis symmetry is 2_1 or lower than 2_1. (c) Hydrogen atoms insensible to X-rays construct a super-lattice. Unfortunately, since every crystal examined by Weissenberg camera is twinning, it is impossible to detect the diffraction spots due to super-lattice or that due to lower symmetry than 6_3. However, it may safely be said that phase A is of hexagonal symmetry as an approximation.

Chemical Formula of Phase A

In this paragraph we determine L, M, N and S in the chemical formula of phase A, $H_LMg_MSi_NO_S$. Since the refractive index of phase A is very close to that of hydrated and nonhydrated magnesium silicates, we can assume that the arrangement of oxygen atoms of phase A is nearly close-packed and the volume per oxygen atom is approximately 18 Å^3 as in the typical magnesium silicates such as forsterite and enstatite. As the volume of a unit cell of phase A is 514.4 ± 0.4 Å^3, calculated from the lattice constants, the number of oxygen atoms per unit cell becomes 28. This value can be confirmed by the following method. Since phase A has an hexagonal symmetry, the oxygen atoms must form two-dimensional hexagonal close-packed sheets perpendicular to c-axis. Taking into account the lattice constants and the ionic radius of oxygen, a simple calculation shows that the number of sheets in the unit cell is 4.0 and the number of oxygen atoms in the sheet in the unit cell is nominally 7.3. Since the number n of oxygen atoms in the sheet in the unit cell must satisfy the geometrical condition

$$n = h^2 + k^2 + hk = 3, 4, 7, 9 \text{ and so on,}$$

where h and k are integers, n should be 7. Therefore, the number of oxygen atoms in the unit cell is 28 which coincides completely with the value calculated by the above method. As a result of these calculations we can determine $S = 28$ and prove that the assumptions of the symmetry and the stacking of oxygen atoms in phase A are correct.

From the chemical formula it can be found that the following equation must be satisfied,

$$L/2 + M + 2N = S = 28. \qquad (1)$$

The density D is obtained theoretically as follows,

$$D = (L + 24.3M + 28.1N + 448.0)/N_A V, \qquad (2)$$

where N_A and V are Avogadro's number and the volume of the unit cell. Substituting the measured density and the calculated volume of the unit cell to D and V in the above equation, we obtain

$$L + 24.3M + 28.1N = 496 \pm 6. \qquad (3)$$

In the experiment of Group III, when p and $q \leqq 13/4$, the reaction equation is as follows;

$$p\mathrm{Mg(OH)_2} + \mathrm{SiO} \rightarrow x(\mathrm{H}_L\mathrm{Mg}_M\mathrm{Si}_N\mathrm{O}_{28}) + y\mathrm{MgSiO_3} + z\mathrm{H_2O}$$

and x, y and z are given as functions of p by the following equations:

$$x = (p-1)/(M-N),$$
$$y = (M-Np)/(M-N),$$
$$z = p - [(p-1)L/2(M-N)].$$

The ratio R of diffraction intensity of (331) of clinoenstatite to that of (213) of phase A is expressed by

$$R = Ay/x = A(M-Np)/(p-1), \qquad (4)$$

where A is a constant. The amount of hydration of phase A must be equal to the amount of water exhausted in stages II and III of Fig. 4, W, then

$$W(\%) = 900L(p-1)/[(p-1)(L + 24.3M + 28.1N + 448.0) + 100.4(M-Np)]. \qquad (5)$$

The measured R and W for different values of p and q are shown in Tables III and IV. We can fix the values of L, M and N using these measured values. The calculation of Eqs. (1), (3), (4) and (5), gives $L = 12$, $M = 14$ and $N = 4$ as most reasonable value, and we can determine the chemical formula of phase A as $H_{12}Mg_{14}Si_4O_{28}$ or $H_6Mg_7Si_2O_{14}[\equiv 3Mg(OH)_2 \cdot 2Mg_2SiO_4]$. Using the values of L, M and N, we can also obtain the theoretical values of D, R, A and W from Eqs. (2), (4) and (5). The calculated density of phase A is 2.945 ± 0.003 g/cm^3 and the calculated A, R and W are shown in Tables III and IV.

Twinning in Phase A

The packing of oxygen atoms in phase A obtained in the last section suggests that the position of oxygen atoms has twofold symmetry axes; one is perpendicular to (210) plane and the other perpendicular to (140) plane. This might be a reason for the frequent observation of twinning on the (210) plane (or the (140) plane). This twin might also induce strain which explains two observed results that the crystals show an optical anomaly and have the approximately equal refractive indices α and β. Phase A also satisfies the other twinning condition that the ratio, $a^2 : c^2$, must approach a rational number (*7*) (in the case of phase A, $a^2 : c^2 = 2 : 3$) and polysynthetic twin are occasionally observed.

Phase D

The lattice constants and space group of phase D are very close to those of chondrodite $Mg(F,OH)_2 \cdot 2Mg_2SiO_4$ but their diffraction patterns and refractive indices are different from each other. From Table II it is inferred that the ratio of Mg/Si of phase D is around 5/2.

Comparison with the Study by Ringwood and Major (3)

If the equilibrium curve of Fig. 2 is permitted to be extrapolated beyond 100 kbar, the result obtained for (2, 2) mixtures is consistent with that obtained by Ringwood and Major for mixtures having a ratio of Mg/Si = 2. There is a difference between the two sets of experiments in the regions of $q \geqq 5/2$. In their study phase A was not synthesized in this region. This difference may be due to their having studied in the water-deficient region of the ternary system $MgO–SiO_2–H_2O$. Our experiments indicate, as shown in Table IV, that the amount of water required for the formation of phase A increases as increasing q. The water pressure in their study was thus too low for the formation of phase A.

The reasons why we could not find in our experiments phases B and C which were discovered by Ringwood and Major is attributed to the situation that these phases are unstable at 77 kbar or stable only at lower water pressure than in our experiments. The observation of phase D only in our experiments suggests that this phase is unstable at pressures higher than 100 kbar or stable only in an environment of sufficient water.

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