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HIGH PRESSURE TRANSFORMATIONS IN $MnSiO_3$

SYUN-ITI AKIMOTO AND YASUHIKO SYONO,[1] *Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan.*

ABSTRACT

Stability relations of $MnSiO_3$ have been studied over the temperature range 780 to 1400°C at pressures up to 130 kbar with the aid of the tetrahedral press and the Bridgman anvil with internal heating system. Four polymorphs have been identified and designated as I to IV in the order of increasing pressure. The atmospheric-pressure phase, $MnSiO_3$ I with a rhodonite structure transformed to $MnSiO_3$ II with a pyroxmangite structure. An equilibrium phase boundary between I and II was determined as $P(\text{kbar}) = 10 + 0.026\ T(°\text{C})$. $MnSiO_3$ II pyroxmangite transformed to $MnSiO_3$ III with a monoclinic pyroxene structure on the boundary curve represented approximately as $P(\text{kbar}) = 19 + 0.057\ T(°\text{C})$. $MnSiO_3$ III clinopyroxene further transformed to $MnSiO_3$ IV with a distorted garnet structure at pressures above 125 kbar. The density increase in the course of the high-pressure transformations was calculated at zero pressure as 0.5% for the I–II, as 1.3% for the II–III, and as 13.1% for the III–IV transformation.

INTRODUCTION

The known crystal structures of pyroxenes and pyroxenoids may be characterized in terms of approximate closest packing of oxygen atoms, with Si filling tetrahedral interstices and larger cations, *e. g.* Ca, Mn, Fe, Zn, Co, Mg, occupying octahedral sites (Liebau, 1962; Prewitt and Peacor, 1964; Syono *et al.*, 1971). Although in all these structures the SiO_4 coordination tetrahedra each share two vertices to form continuous single chains, an essential difference between pyroxenes and various pyroxenoids is the length of the repeat unit along the silicate chains: in pyroxenes the chain repeats after every two tetrahedra; in wollastonite ($CaSiO_3$) and bustamite ($CaMnSi_2O_6$) after every three (Buerger and Prewitt, 1961; Peacor and Buerger, 1963); in rhodonite ($Mn_4CaSi_5O_{15}$) after every five (Peacor and Niizeki, 1963); in pyroxmangite ($[Mn, Fe, Ca, Mg]SiO_3$) and pyroxferroite ($Ca_{0.15}Fe_{0.85}SiO_3$) after every seven (Liebau, 1959; Lindsley and Burham, 1970); and in ferrosilite III after nine (Burnham, 1966).

The atmospheric-pressure phase of $MnSiO_3$ is known to have a rhodonite structure, one of the pyroxenoid structures (Glasser, 1958; Liebau *et al.*, 1958). Ringwood and Major (1967) made a reconnaissance study on the high-pressure transformations of $MnSiO_3$ using $MnSiO_3$ glass and natural and synthetic rhodonite as starting ma-

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[1] Present address: Research Institute for Iron, Steel, and Other Metals, Tohoko University, Sendai 980, Japan.

terials. They found an unidentified polymorph of $MnSiO_3$ at pressures between 30 and 60 kbar and observed the transformation to a pyroxene type polymorph at pressures between 60 and 90 kbar. At pressures above 120 kbar they reported the synthesis of a high-pressure phase of $MnSiO_3$ which apparently had the garnet structure.

It is the purpose of the present paper to investigate the detailed stability relations in $MnSiO_3$ at high pressures and high temperatures, which lead to a better understanding of the crystal chemical relations between pyroxenoids and pyroxenes. It is also intended to identify the crystal structure of Ringwood and Major's unknown phase and to refine the cell data on the pyroxene and garnet phase of $MnSiO_3$, since we can prepare better crystals of these phases.

EXPERIMENTAL PROCEDURE

The atmospheric-pressure phase of $MnSiO_3$ was prepared by mixing intimately MnO and SiO_2 in the required proportions, pressing the mixture into a tablet, and firing at 1220°C for more than 10 hours under a controlled atmosphere. The control of the partial pressure of oxygen was made by the mixed gas technique using CO_2–H_2 system with mixing ratio of CO_2 to H_2, P_{CO_2}/P_{H_2} of 3/1. Structure analysis carried out by Tokonami and Morimoto using single crystals grown at the above condition revealed that the $MnSiO_3$ thus obtained had a rhodonite structure with triclinic symmetry. Cell data were determined by means of a four-circle single crystal diffractometer as $a = 7.616\ (3)$ Å, $b = 11.851\ (5)$ Å, $c = 6.707\ (2)$ Å, $\alpha = 92°33'(6')$, $\beta = 94°21'(6')$, $\gamma = 105°40'(6')$, cell volume $V = 580.0$ Å^3, number of formula unit per cell $(Z) = 10$ and calculated density $(D_x) = 3.75$ g/cm^3.

High-pressure and high-temperature experiments were made with the aid of a tetrahedral press up to 100 kbar and 1400°C, using specimens prepared as described above as starting materials. Three different sizes of cemented tungsten carbide anvils with 25 mm, 15 mm, and 9 mm edge length were used, depending upon maximum pressure desired. Powder samples of the starting materials were directly embedded in the tubular graphite furnace which was placed diagonally with the axis of the cylinder between opposite edges of the baked pyrophyllite tetrahedron. The pressure values in the runs were calibrated at room temperature on the basis of the pressure scale recommended at the Symposium on the Accurate Characterization of the High-Pressure Environment, U. S. National Bureau of Standards, October, 1968: Bi I–II, 25.5 kbar; Tl II–III, 36.7 kbar; Ba I–II, 55 kbar; Bi III–V, 77 kbar; Sn I–II, 100 kbar. The run temperatures were measured in the central part of the samples with a *Pt/Pt*-13 percent Rh thermocouple. No correction was made for the effect of pressure on the *e.m.f.* of the thermocouple, since this effect is not quantitatively known for this thermocouple in the range of temperatures and pressures employed.

In the runs for pressures exceeding 110 kbar, a Bridgman anvil type of high-pressure apparatus with internal heating system (Nishikawa and Akimoto, 1971) was used. The Bridgman anvils used in the present study are 26 mm in diameter at the truncated face. Pressure values in the Bridgman anvil were calibrated at room temperature against Drickamer's revised pressure scale (Drickamer, 1970). Ba II–III and Pb I–II transition pressures were tentatively fixed as 120 and 130 kbar respectively. The validity of this method of pressure calibration for high-temperature use was guaranteed through the study of the coesite-stishovite phase transformation (Nishikawa and Akimoto, 1971).

Phase relations of $MnSiO_3$ at high-pressures and high-temperatures were determined by means of the usual quenching method. After pressure was applied to the samples, the temperature was brought to the desired value and held for the desired interval of time. Then the sample was quenched by switching off the power to the furnace under the working pressure. After releasing the pressure slowly, the phases present in the central part of the quenched samples were examined by the X-ray diffraction technique. Unit cell dimensions of some high-pressure phases of $MnSiO_3$ were determined by a least-squares refinement of the powder data which were collected by X-ray diffractometer with scanning speed of $0.5°(2\theta)$ per minute. 2θ angles were calibrated with pure silicon standard. $CuK\alpha_1$ radiation was used throughout.

RESULTS AND DISCUSSION

Equilibrium data at various pressure-temperature-time conditions are summarized in Table 1. Diagrams showing the phases present and their stability field are given in Figure 1. $MnSiO_3$ I with the rhodonite structure became unstable beyond about 30–43 kbar and transformed to a high-pressure polymorph of $MnSiO_3$ II. Structure analysis carried out by Tokonami and Morimoto using a single crystal grown at 74 kbar and 1320°C revealed that $MnSiO_3$ II was assigned to be a pyroxmangite structure with triclinic symmetry. Cell data determined by them are $a = 6.721(2)$ Å, $b = 7.603(3)$ Å, $c = 17.455(6)$ Å, $\alpha = 113°10'(6')$, $\beta = 82°16'(6')$, $\gamma = 94°08'(6')$, cell volume $V = 808.0$ Å^3, number of formula unit per cell $(Z) = 14$, and calculated density $(D_x) = 3.77$ g/cm^3. A more comprehensive report on the structure of $MnSiO_3$ II will be published elsewhere. The X-ray powder diffraction pattern of $MnSiO_3$ II includes all the strong reflections reported by Ringwood and Major (1967) on their samples synthesized at pressures between 30 and 60 kbar and 700°C. This suggests that the new phase reported by Ringwood and Major is successfully identified as pyroxmangite. Experimental runs using $MnSiO_3$ II as starting material proved that the transformation between $MnSiO_3$ I and II was completely reversible. An equilibrium phase boundary was determined as P (kbar) $= 10 + 0.026\ T$ (°C).

$MnSiO_3$ II transformed to $MnSiO_3$ III above about 70–95 kbar. This transformation is accompanied by the remarkable color change from light pink of $MnSiO_3$ II to light lilac of $MnSiO_3$ III. The X-ray diffraction lines of $MnSiO_3$ III could all be indexed on the basis of a monoclinic pyroxene structure. The unit cell parameters and both the observed and calculated d-spacings are listed in Table 2. Structure analysis by Tokonami and Morimoto using a single crystal grown at

100 kbar and 1200°C for 25 minutes established that $MnSiO_3$ III was assigned to be the monoclinic pyroxene structure with space group of $P\,2_1/c$. Reverse reactions using $MnSiO_3$ III as starting material yielded a successful result. The $MnSiO_3$ II–III transformation curve was tentatively fitted by the linear relation $P(\text{kbar}) = 19 + 0.057\,T(°\text{C})$. Ringwood and Major (1967) also reported the synthesis of $MnSiO_3$ pyroxene in the similar pressure range to the present study. Although they presumed an orthopyroxene for $MnSiO_3$ III, only a clinopyroxene form was found to be stable in a relatively wide region in the pressure-temperature diagram.

In the run using the Bridgman anvil type of high-pressure apparatus, it was found that $MnSiO_3$ III further transformed to another

Table 1. Results of runs on the high-pressure and high-temperature phase transformations in $MnSiO_3$

Run no.#	Pressure, kbar	Temperature, °C	Time, min	Phases present
19	20	1030	70	rhodonite
22	30	830	100	rhodonite
28	30	970	60	rhodonite
21	30	1040	75	rhodonite
31	32	1100	60	rhodonite
29	35	1300	40	rhodonite
25	37	880	70	pyroxmangite
26*	38	1190	60	pyroxmangite + rhodonite
20	39	1040	75	pyroxmangite
32	42	1100	62	pyroxmangite
23	42	1300	25	rhodonite
27*	42	1400	30	rhodonite
30	45	1200	55	pyroxmangite
24	48	1300	25	pyroxmangite
13	66	860	70	pyroxmangite
18**	68	940	85	pyroxmangite + clinopyroxene
12	72	900	67	clinopyroxene + trace pyroxmangite
2	72	1240	30	pyroxmangite
9	74	1320	15	pyroxmangite
3	76	850	42	clinopyroxene
4	76	1030	30	pyroxmangite
1	76	1230	30	pyroxmangite
5	76	1270	20	pyroxmangite
17**	79	1170	50	pyroxmangite
10	82	950	45	clinopyroxene
11	82	1200	25	pyroxmangite
15	88	1090	40	clinopyroxene
16**	88	1320	30	pyroxmangite
14	97	1290	20	clinopyroxene
6	98	1000	21	clinopyroxene
8	100	1140	30	clinopyroxene
7	100	1200	25	clinopyroxene
33	115	920	63	clinopyroxene
34	117	800	100	clinopyroxene
35	119	780	20	clinopyroxene
36	119	1000	50	clinopyroxene
37	126	800	80	garnet + clinopyroxene
38	126	1000	40	garnet
39	130	800	95	garnet + trace clinopyroxene

* Starting material : $MnSiO_3$ II pyroxmangite

** Starting material : $MnSiO_3$ III clinopyroxene

\# Unless otherwise stated, starting materials are $MnSiO_3$ I rhodonite.

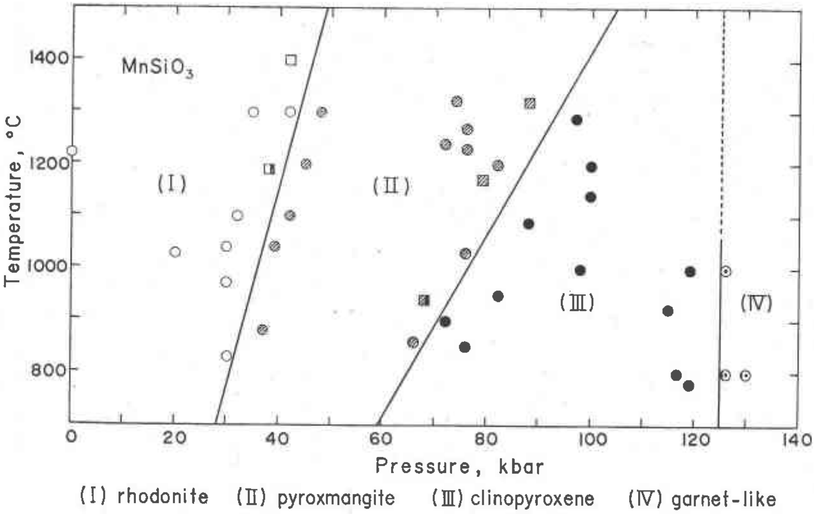

FIG. 1. Synthesis diagram for the high-pressure and high-temperature transformations of $MnSiO_3$. Starting materials are $MnSiO_3$ I, rhodonite, except for reverse reaction runs indicated by squares.

high-pressure phase $MnSiO_3$ IV at around 125 kbar. Complete transformation was attained at 126 kbar and at 1000°C. $MnSiO_3$ IV showed the powder X-ray diffraction pattern similar to garnet. Present results are quite consistent with the preliminary report by Ringwood and Major (1967). Considerable splitting of diffraction lines of garnet was observed in the X-ray powder pattern of $MnSiO_3$ IV. This suggests that $MnSiO_3$ IV is analogous to the $CaGeO_3$ and $CdGeO_3$ garnet-like phase, of which structure was first suggested by Ringwood and Major (1967) and analysed in detail by Prewitt and Sleight (1969). In Table 3 both observed and calculated d-spacings of $MnSiO_3$ IV are given on the basis of the tetragonal unit cell which was established by Prewitt and Sleight (1969) for $CdGeO_3$ and $CaGeO_3$ with garnet-like structure. It is seen that the reflections of the powder X-ray diffraction pattern can be successfully indexed on the basis of this unit cell. The unit cell dimensions of the tetragonal lattice are determined to be $a = 11.769(3)$ Å, $c = 11.624(3)$ Å and cell volume $V = 1610(1)$ Å^3. As was suggested by Ringwood and Major (1967) the tetragonal distorsion of $MnSiO_3$ IV is most probably due to the ordering of Mn^{2+} and Si^{4+} ions into distinct crystallographic sites: Mn^{2+} ions occupy the dodecahedral and octahedral sites, and Si^{4+} ions the octahedral and tetrahedral sites.

Table 2. Powder data for clinopyroxene $MnSiO_3$

h k l	d_{obs}	d_{calc}	Intensity
1 1 0	6.563 A	6.557 A	30
2 0 0	4.687	4.685	50
1 1 $\bar{1}$	3.626	3.627	10
2 2 0	3.280	3.278	70
2 2 1	3.075	3.071	70
3 1 0	2.9572	2.9567	100
1 3 1	2.6315	2.6312	40
0 0 2	2.5159	2.5162	30
2 2 $\bar{1}$	2.5081	2.5074	40
1 1 $\bar{2}$	2.1943	2.1941	40
3 3 1	2.1877	2.1872	50
4 2 1	2.1508	2.1508	10
4 0 2	2.0666	2.0668	20
-	1.9993	-	10
-	1.8451	-	10
2 2 $\bar{2}$	1.8131	1.8136	30
1 5 0	1.8014	1.8015	30
4 2 $\bar{1}$	1.7615	1.7615	10
5 3 1	1.6556	1.6557	30
6 0 0	1.5615	1.5616	30
-	1.5196	-	10
-	1.4820	-	10

Monoclinic, a = 9.864(2) Å
b = 9.179(2) Å
c = 5.298(1) Å
β = 71°47'(1')
V = 455.6(2) $Å^3$
Z = 8, ρ_{calc} = 3.82 g/cm^3

Note : Interplanar d-spacings were determined directly from diffraction chart using Cu $K\alpha_1$ radiation. Intensity was estimated from diffraction chart.

Using cell dimensions of high-pressure polymorphs of $MnSiO_3$, the density increase in the course of the high-pressure transformations of $MnSiO_3$ was calculated at zero-pressure as 0.5 percent for the I–II transformation, as 1.3 percent for the II–III transformation, and as 13.1 percent for the III–IV transformation. The total density increase from the rhodonite to garnet-like structure amounts to 15.2 percent. The small density change in the transformation of $MnSiO_3$ I–II–III, and the large density change in the transformation of III–IV can be explained by the fact that the former is accompanied by no change in the primary coordination number of cations, whereas the latter is accompanied by a partial increase in the coordination number both in Mn^{2+} $(6 \rightarrow 8)$ and in Si^{4+} $(4 \rightarrow 6)$, on account of the formation of the distorted garnet.

Systematic change in a certain repeat unit of the crystal structure is often found in the pressure-induced phase transformations without any change in the coordination number of constituent atoms. A typical example is seen in the olivine-spinel transformation, in which the stacking unit of oxygen layer changes from hexagonal close-packed type to a cubic close-packed one. It is also found in the high-pressure transformations of the hexagonal perovskite-like compounds of ABX_3 that the repetition of the stacking of AX_3 layers occurs along the hexagonal c-axis (or cubic [111] axis) after every second, ninth, fourth, sixth, and third layer with increasing pressure (Syono *et al.*, 1969). The pyroxenoid-pyroxene transformation established in the present study is likely to add one more case to the list of examples of the high-pressure transformation where the mode of stacking changes regularly. The detailed structure analyses for $MnSiO_3$ I, II, and III, which are now being carried out by Morimoto and Tokonami, confirm that the repetition of silicate chains occurs after every five tetrahedra in the rhodonite form, after every seven tetrahedra in the pyroxmangite form and after every two tetrahedra in the clinopyroxene form of $MnSiO_3$ (Morimoto, private communication, 1971).

The structures of ionic compounds are largely governed by the radius ratios of constituent ions. It is well known that the number of repeats in the chain pattern of pyroxenoids and pyroxene increases with decreasing average size of the octahedral cation. There is a sidestep after an infinite repetition of two tetrahedra unit in the pyroxene structure. When $MnSiO_3$ is subjected to high-pressure, the Mn^{2+}/Si^{4+} ionic radius ratio is expected to become smaller since the larger Mn^{2+} ions tend to contract relatively more than the small Si^{4+} ions. Hence it may be reasonable to presume that the high-pressure phase of $MnSiO_3$ is turned into the pyroxenoid and pyroxene corresponding

Table 3. Powder data for garnet-like $MnSiO_3$

h k l	d_{obs}	d_{calc}	Intensity
2 1 1	4.800 A	4.795 A	10
3 2 1	3.141	3.143	<10
3 1 2	3.129	3.134	<10
2 1 3	3.118	3.120	<10
4 0 0	2.9425	2.9422	60
0 0 4	2.9060	2.9060	30
4 2 0	2.6315	2.6316	100
4 0 2	2.6255	2.6250	100
2 0 4	2.6048	2.6056	50
3 2 3	2.4959	2.4963	10
4 2 2	2.3963	2.3973	30
2 2 4	2.3834	2.3824	15
-	2.3063	-	<10
5 2 1	2.1493	2.1478	20
5 1 2	2.1454	2.1451	20
2 1 5	2.1261	2.1266	10
-	1.9053	-	10
-	1.8908	-	10
4 4 4	1.6911	1.6916	10
6 4 0	1.6318	1.6320	20
6 0 4	1.6255	1.6258	20
4 0 6	1.6181	1.6180	20
6 4 2	1.5712	1.5713	30
6 2 4	1.5673	1.5671	30
4 2 6	1.5604	1.5601	30

Tetragonal, a = 11.769(3) Å
c = 11.624(3) Å
V = 1610(1) Å^3
Z = 32, ρ_{calc} = 4.32 g/cm^3

Note : Interplanar d-spacings were determined directly from diffraction chart using Cu $K\alpha_1$ radiation. Intensity was estimated from diffraction chart.

to the smaller average size of the octahedral cation. These considerations may explain the rhodonite-pyroxmangite-clinopyroxene transformation of $MnSiO_3$ found in this study.

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