

## Crystal structure and chemistry of MnSiO<sub>3</sub> tetragonal garnet

KIYOSHI FUJINO, HITOSHI MOMOI

Department of Earth Sciences, Faculty of Science, Ehime University,  
Bunkyo-cho, Matsuyama 790, Japan

HIROSHI SAWAMOTO

Department of Earth Sciences, Faculty of Science, Nagoya University,  
Nagoya 464, Japan

MINEO KUMAZAWA

Geophysical Institute, Faculty of Science, University of Tokyo,  
Hongo, Tokyo 113, Japan

### ABSTRACT

Single crystals of MnSiO<sub>3</sub> tetragonal garnet have been grown at 1500°C and about 12.0 GPa by means of an MA8-type high-pressure apparatus. The crystal-structure analysis using single-crystal X-ray intensity data reveals that (1) the space group is *I*4<sub>1</sub>/*a* with cell dimensions of *a* = 11.774(1) and *c* = 11.636(2) Å, (2) the Mn and Si atoms are fully ordered into different octahedral sites, and (3) the Si octahedron is very regular in shape with the mean Si–O distance of 1.795 Å. The structural comparison among four polymorphs of MnSiO<sub>3</sub> is also discussed.

### INTRODUCTION

The silicate garnets commonly occurring as rock-forming minerals have a cubic symmetry (space group, *Ia3d*). However, silicate garnets of the grossular-andradite series sometimes show optical birefringence. Recently Takéuchi et al. (1981) showed by single-crystal X-ray structure analyses that these birefringent garnets have an orthorhombic (*Fddd*) or triclinic (*I* $\bar{1}$ ) structure due to cation ordering in the octahedral positions.

Another type of noncubic garnet (*I*4<sub>1</sub>/*a*) is known in high-pressure phases of CdGeO<sub>3</sub> and CaGeO<sub>3</sub> (Ringwood and Major, 1967; Prewitt and Sleight, 1969). Ringwood and Major (1967) first suggested that the high-pressure phase of MnSiO<sub>3</sub> also had a noncubic garnet structure, just the same as those of CdGeO<sub>3</sub> and CaGeO<sub>3</sub>. Later Akimoto and Syono (1972) were successful in indexing the powder X-ray diffraction peaks of this noncubic phase of MnSiO<sub>3</sub> with a tetragonal unit-cell analogous to CdGeO<sub>3</sub>.

In the present study, we have grown single crystals of MnSiO<sub>3</sub> tetragonal garnet sufficiently large enough for single-crystal X-ray structure analysis for the first time and have carried out the X-ray structure analysis. This paper reports the detailed structure of this MnSiO<sub>3</sub> noncubic garnet and its crystal chemical properties in comparison with those of the other polymorphs of MnSiO<sub>3</sub>.

### EXPERIMENTAL PROCEDURE

#### High-pressure growth of single crystal

Akimoto and Syono (1972) reported the polymorphic phase transformations in MnSiO<sub>3</sub> with increasing pressure: rhodonite, pyroxmangite, clinopyroxene, and tetragonal garnet. The trans-

formation from clinopyroxene to tetragonal garnet was reported to take place at about 12.5 GPa at 1000°C.

In the present study, single crystals of MnSiO<sub>3</sub> tetragonal garnet have been grown from powdered MnSiO<sub>3</sub> rhodonite by means of an MA8-type high-pressure and high-temperature apparatus at Nagoya University. Our initial trial of growing single crystals was made at 1500°C and about 15.0 GPa and resulted in fine-grained powder. The pressures of trial runs were lowered gradually, and finally we could obtain single crystals as large as 100  $\mu$ m by 30-min runs at 1500°C and about 12.0 GPa, which is close to the phase boundary between the tetragonal garnet and the lower-pressure clinopyroxene. It is very important to keep the raw material at pressures and temperatures very close to the phase boundary for growing large single crystals by solid-state recrystallization. The synthesized single crystals were transparent, colorless to pale orange, and optically biaxial.

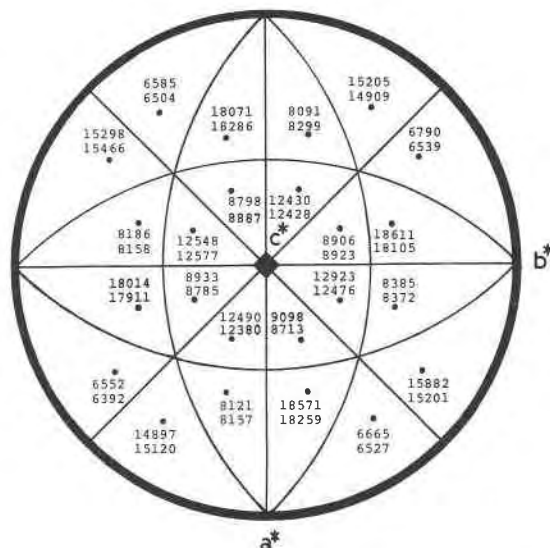
#### Refinement of the structure

Electron-microprobe analyses showed that the synthesized crystals have a homogeneous stoichiometric MnSiO<sub>3</sub> composition. A spherically ground crystal 79  $\mu$ m in diameter was prepared from one of the synthesized grains and was subjected to the single-crystal X-ray structure analysis. Preliminary precession photographs revealed the diffraction symmetry consistent with space group *I*4<sub>1</sub>/*a*. Intensity data were collected by Rigaku AFC-5 four-circle automated diffractometer set on the rotating anode X-ray generator (operating conditions: 160 mA, 50 kV), using the graphite-monochromatized MoK $\alpha$  radiation ( $\lambda$  = 0.71069 Å). The cell dimensions were determined by the least-squares method using 2 $\theta$  values of 25 reflections on the four-circle diffractometer. The crystal and intensity data are listed in Table 1.

In order to show the deviation of the diffraction symmetry from cubic symmetry, the intensity distribution of a set of 48 reflections of {246}—which should be equivalent for a cubic garnet—is illustrated in Figure 1. The diffraction intensities were

Table 1. Crystal and intensity data for MnSiO<sub>3</sub> tetragonal garnet

Space group	I4 <sub>1</sub> /a
Cell contents	32[MnSiO <sub>3</sub> ]
Cell dimensions	
a (Å)	11.774(1)
c (Å)	11.636(2)
v (Å <sup>3</sup> )	1613.1(3)
ρ <sub>calc</sub> (gcm <sup>-3</sup> )	4.32
Diameter of specimen	φ=79μm
μ(MoKα) (cm <sup>-1</sup> )	70.81
Scan type	ω-2θ
2θ <sub>max</sub>	80°
Number of reflections (measured)	2677
Number of reflections (used)	1206
R value	0.052
Weighted R value	0.050

Fig. 1. Intensity distribution of a set of 48 reflections of {246}, which should be equivalent for cubic garnet. The upper figures show the integrated intensities of the  $hkl$  ( $l > 0$ ) reflections and the lower figures those of the  $hkl$  ( $l < 0$ ).Table 2. Atomic coordinates and anisotropic thermal factors ( $\times 10^3$ ) for MnSiO<sub>3</sub> tetragonal garnet

Site	Equi-point	Symmetry	Atom	X	Y	Z	B <sub>eq</sub> *
D1	16f	1	Mn	0.1258(1)	0.0079(1)	0.2590(1)	0.57
D2	8e	2	Mn	0.0	0.25	0.6235(2)	0.58
Oc1	8c	$\bar{1}$	0.98(1)Mn +0.02(1)Si	0.0	0.0	0.5	0.41
Oc2	8d	$\bar{1}$	0.98(1)Si +0.02(1)Mn	0.0	0.0	0.0	0.41
T1	4a	$\bar{4}$	Si	0.0	0.25	0.375	0.48
T2	4b	$\bar{4}$	Si	0.0	0.25	0.875	0.30
T3	16f	1	Si	0.1262(2)	0.0143(1)	0.7597(2)	0.34
O(1)	16f	1	O	0.0302(4)	0.0617(4)	0.6730(4)	0.47
O(2)	16f	1	O	0.0465(4)	-0.0411(4)	0.8627(4)	0.42
O(3)	16f	1	O	0.2224(4)	0.1099(4)	0.8064(4)	0.50
O(4)	16f	1	O	0.2098(4)	-0.0796(4)	0.7039(4)	0.50
O(5)	16f	1	O	-0.0649(4)	0.1665(4)	0.4654(4)	0.48
O(6)	16f	1	O	-0.1034(4)	0.2152(4)	0.7858(4)	0.43
Site	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>	
D1	69(5)	98(5)	146(6)	-1(4)	16(4)	17(5)	
D2	133(9)	107(8)	74(6)	-20(7)	0	0	
Oc1	73(8)	83(8)	70(8)	-6(6)	-7(6)	-19(6)	
Oc2	44(14)	76(15)	102(17)	-2(10)	6(11)	-5(11)	
T1	102(13)	102(13)	57(20)	0	0	0	
T2	70(12)	70(12)	22(18)	0	0	0	
T3	60(9)	63(9)	63(9)	8(7)	6(8)	-22(8)	
O(1)	101(23)	96(23)	60(22)	4(18)	-26(18)	-9(17)	
O(2)	90(22)	76(21)	62(22)	11(17)	17(17)	-22(17)	
O(3)	87(22)	70(22)	115(22)	0(17)	2(18)	-4(18)	
O(4)	93(23)	77(22)	102(23)	-22(18)	22(19)	-22(18)	
O(5)	88(22)	130(24)	45(20)	-30(18)	36(18)	5(18)	
O(6)	55(21)	87(22)	90(23)	20(17)	3(18)	22(18)	

\* Equivalent isotropic thermal factor is calculated from anisotropic ones (Hamilton, 1959).

Anisotropic thermal factors are of the form:  $\exp\left\{-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij}\right\}$ .

The estimated standard deviations are indicated in parentheses.

Table 3. Interatomic distances, angles, and estimated standard errors for MnSiO<sub>3</sub> tetragonal garnet

D1 dodecahedron				Oc2 octahedron			
Mn-O(1)		2.161(5) Å		Si-O(2)	[x2]	1.757(4) Å	
-O(2)		2.505(4)		-O(3)	[x2]	1.805(4)	
-O(3)		2.400(5)		-O(6)	[x2]	1.823(4)	
-O(3)'		2.329(5)		mean		1.795	Angle at Si
-O(4)		2.207(5)		O(2) -O(3) d	[x2]	2.524(6)	90.2(2)°
-O(4)'		2.359(5)		O(2) -O(6) d	[x2]	2.554(6)	91.0(2)
-O(5)		2.166(4)		O(3) -O(6) d	[x2]	2.627(6)	92.8(2)
-O(6)		2.691(4)		O(2) -O(3)'	[x2]	2.514(6)	89.8(2)
mean		2.352	Angle at Mn	O(2) -O(6)'	[x2]	2.510(6)	89.0(2)
O(1) -O(2) t		2.524(6)	65.0(2)°	O(3)' -O(6)	[x2]	2.502(6)	87.2(2)
O(3)' -O(4) t		2.535(6)	67.9(2)				
O(1) -O(4)' o		3.033(6)	84.2(2)	T1 tetrahedron			
O(2) -O(3) o		2.524(6)	61.9(1)	Si-O(5)	[x4]	1.630(4)	Angle at Si
O(4) -O(5) o		2.890(6)	82.7(2)	O(5) -O(5)' d	[x2]	2.490(9)	99.6(3)
O(3)' -O(6) o		2.627(6)	62.6(1)	O(5) -O(5)''	[x4]	2.743(7)	114.6(2)
O(3) -O(4) d		2.769(6)	73.7(2)				
O(2) -O(5) d		2.856(6)	75.0(2)	T2 tetrahedron			
O(1) -O(6) d		2.732(6)	67.5(2)	Si-O(6)	[x4]	1.651(4)	Angle at Si
O(3)' -O(4)' d		2.769(6)	72.4(2)	O(6) -O(6)' d	[x2]	2.568(9)	102.1(3)
O(4)' -O(5)		2.799(6)	76.3(2)	O(6) -O(6)''	[x4]	2.758(8)	113.3(2)
O(3) -O(6)		2.904(6)	69.3(1)				
D2 dodecahedron				T3 tetrahedron			
Mn-O(1)	[x2]	2.318(4)		Si-O(1)		1.614(5)	
-O(2)	[x2]	2.524(4)		-O(2)		1.655(5)	
-O(5)	[x2]	2.221(5)		-O(3)		1.687(5)	
-O(6)	[x2]	2.284(5)		-O(4)		1.617(5)	
mean		2.337	Angle at Mn	mean		1.643	Angle at Si
O(5) -O(5)' t		2.490(9)	68.2(2)	O(1) -O(2) d		2.524(6)	101.1(2)
O(6) -O(6)' t		2.568(9)	68.4(2)	O(3) -O(4) d		2.535(6)	100.2(2)
O(1) -O(5) o	[x2]	2.935(6)	80.5(2)	O(1) -O(3)		2.802(6)	116.2(2)
O(2) -O(6) o	[x2]	2.554(6)	64.0(1)	O(1) -O(4)		2.714(6)	114.3(2)
O(1) -O(6) d	[x2]	2.732(6)	72.8(2)	O(2) -O(3)		2.806(6)	114.2(2)
O(2) -O(5) d	[x2]	2.856(6)	73.7(2)	O(2) -O(4)		2.704(6)	111.5(2)
O(1) -O(2)'	[x2]	2.776(6)	69.8(1)				
Oc1 octahedron							
Mn-O(1)	[x2]	2.170(4)					
-O(4)	[x2]	2.130(4)					
-O(5)	[x2]	2.142(5)					
mean		2.147	Angle at Mn				
O(1) -O(5) d	[x2]	2.935(6)	85.8(2)				
O(1) -O(4) d	[x2]	3.033(6)	89.7(2)				
O(4) -O(5) d	[x2]	2.890(6)	85.1(2)				
O(1) -O(5)'	[x2]	3.159(6)	94.2(2)				
O(1) -O(4)'	[x2]	3.048(6)	90.3(2)				
O(5) -O(4)'	[x2]	3.147(6)	94.9(2)				

t = edge shared by tetrahedron.  
o = edge shared by octahedron.  
d = edge shared by dodecahedron.  
Superscript prime or double prime distinguishes the equivalent anions in the same polyhedron.  
The estimated standard errors are indicated in parentheses.

corrected for Lorentz and polarization effects and absorption factors. The intensities greater than  $3\sigma(I_o)$  were used for structure refinement. The atomic scattering factors of the fully ionized atoms were used for refinements (Mn<sup>2+</sup> and Si<sup>4+</sup> from *International Tables for X-ray Crystallography*, volume III, 1962, and O<sup>2-</sup> from Tokonami, 1965). The anomalous dispersion terms were also included in the refinements. The full-matrix least-squares refinement was made by the program LINUS (Coppens and Hamilton, 1970) so as to minimize the residual factor

$$\sum_i (|F_o| - |F_c|)^2.$$

At the initial stage of the refinement, Mn and Si atoms were fixed to the different octahedral sites, respectively, and the po-

sitional and thermal parameters were refined using the atomic parameters for CdGeO<sub>3</sub> of Prewitt and Sleight (1969) as initial parameters. The isotropic extinction factor was also included in the refinement. At the final stage, the occupancy factors of the atoms at octahedral sites were also varied simultaneously with other parameters under the constraint of the given bulk composition. The final *R* value and weighted (unit weight) *R* value are 0.052 and 0.050, respectively, for 1206 independent reflections. Final atomic parameters are listed in Table 2. In Table 2, the origin of *I*A<sub>1</sub>/*a* is shifted by 1/2, 1/4, 1/8 from that given in *International Tables for X-ray Crystallography*, volume I (1952) to set the symmetry elements of *I*A<sub>1</sub>/*a* in a manner similar to those for *I*a3*d*. Interatomic distances, angles, and estimated standard errors were calculated with the program ORFFE of Busing et al.

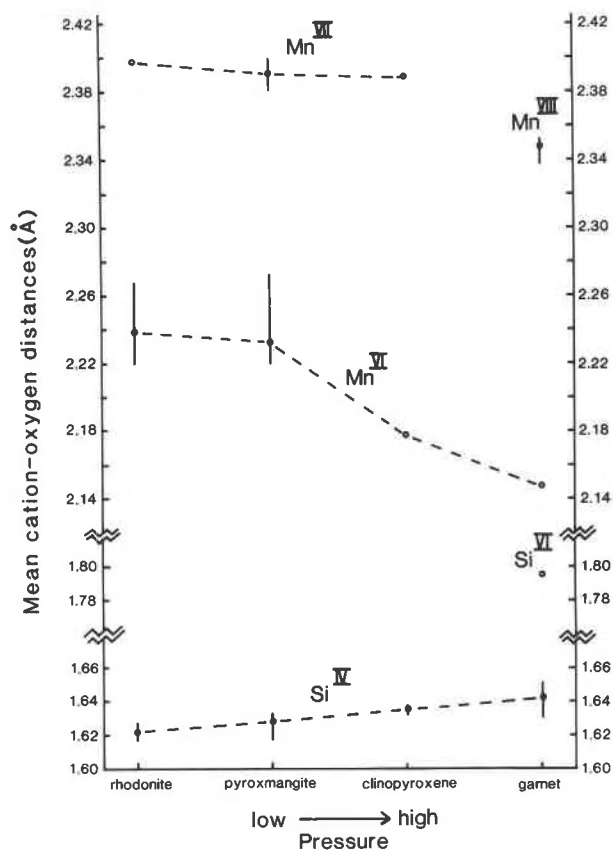


Fig. 2. Mean cation-oxygen distances of the different coordination-polyhedra of the four polymorphs of MnSiO<sub>3</sub>. The superscripts on Mn and Si refer to the coordination number of polyhedra. The filled circles and vertical bars indicate the mean value and range for polyhedra with the same coordination number, respectively.

(1964). The results are given in Table 3. The final observed and calculated structure factors are given in Table 4.<sup>1</sup>

## RESULTS AND DISCUSSION

The MnSiO<sub>3</sub> tetragonal garnet has seven different cation sites, namely, two dodecahedral (abbreviated as D1 and D2), two octahedral (Oc1 and Oc2), and three tetrahedral (T1, T2, and T3) sites. In the polymorphic transition from lower-pressure clinopyroxene to tetragonal garnet, the partial increase in the coordination number occurs both in Mn<sup>2+</sup> (6 → 8) and in Si<sup>4+</sup> (4 → 6). The numbers of Mn and Si atoms in octahedral sites in Table 2 indicate that the Mn and Si atoms are almost perfectly ordered into Oc1 and Oc2 sites, respectively. From this result combined with that of Takéuchi et al. (1981), it is inferred that the mode of cation ordering for the noncubic garnet structure depends on the difference in ionic radius between

the two kinds of octahedral cations. If the difference is small, as for Fe and Al in the grandite series, the *Fddd* or *I* $\bar{1}$  structure with partial ordering of octahedral cations is favored, whereas the *I4<sub>1</sub>/a* structure with perfect ordering is favored when the difference in ionic radii is large, as for Mn and Si in the present case.

The mean cation-oxygen distances in Table 3 are nearly equal to the predicted values on the basis of effective ionic radii of Shannon and Prewitt (1969), except for the Oc1 octahedron. The mean M-O distance of the Oc1 octahedron is 2.147 Å, whereas the predicted one is 2.21 Å. The same difference is also seen in CdGeO<sub>3</sub> (Prewitt and Sleight, 1969).

The Si octahedron is regular in shape: all the Si-O distances of the octahedron are between 1.76 and 1.82 Å, and the O-Si-O angles fall between 88.7° and 92.8°. Another characteristic of this Si octahedron is that the mean value (2.568 Å) of the shared O-O distances is larger than that (2.509 Å) of the unshared ones, as seen sometimes in the high-pressure phase, in contrast to the structural features seen commonly in the phases stable under atmospheric pressure.

The pressure-induced structural changes between MnSiO<sub>3</sub> polymorphs are a crystallochemically interesting problem. Figure 2 shows the variation of the mean cation-oxygen distances of the different coordination-polyhedra among four polymorphs of MnSiO<sub>3</sub> (Narita et al., 1977; Tokonami et al., 1979). The Mn polyhedra-octahedra in particular—are compressed with increasing pressure, whereas the Si tetrahedra expand. This fact seems to indicate that oxygen atoms tend to be packed in the more regular array with increasing pressure. This is the same tendency as observed in the structural changes in polymorphs of Co<sub>2</sub>SiO<sub>4</sub> (Morimoto et al., 1974) and Mg<sub>2</sub>SiO<sub>4</sub> (Horiuchi and Sawamoto, 1981).

Recently, MgSiO<sub>3</sub> was found to crystallize in garnet structure of noncubic type above 20 GPa and 1700°C (Sawamoto and Kozaki, 1984; Kato et al., 1984), and its stability field is being extensively investigated (Sawamoto and Kozaki, in prep.; Kato and Kumazawa, 1985). The noncubic MgSiO<sub>3</sub> garnet is probably isostructural with the MnSiO<sub>3</sub> tetragonal garnet described in this study. Therefore, the present structure analysis of MnSiO<sub>3</sub> garnet provides useful information on the crystallochemical characterization of possibly the major mineral in the deep upper mantle of the Earth.

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<sup>1</sup> To obtain a copy of Table 4, order Document AM-86-305 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit \$5.00 in advance for the microfiche.

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