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LETTER

Structure and twinning of single-crystal $MgSiO_3$ garnet synthesized at 17 GPa and 1800 °C

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ABSTRACT

Single crystals of $MgSiO_3$ garnet have been synthesized at 17 GPa and 1800 °C in a uniaxial split-sphere anvil device, and the structure has been determined by refinement of single-crystal X-ray diffraction data. This garnet is tetragonal with unit-cell parameters $a = 11.501(1)$ Å, $c = 11.480(2)$ Å, $V_{cell} = 1518.6(4)$ Å^3. The space group is $I4_1/a$, and all crystals display pervasive twinning by reflection on (110), making the apparent Laue symmetry close to $4/mmm$. Two Mg positions are coordinated by eight anions with average Mg–O bond lengths of 2.284 and 2.279 Å. Mg and Si are at least partially ordered over the octahedral sites with mean Si–O = 1.807 Å and mean Mg–O = 1.998 Å. The three tetrahedral sites are all occupied by Si with mean bond lengths of 1.622, 1.652, and 1.641 Å.

INTRODUCTION

Garnet phases, rich in a $MgSiO_3$ component, probably account for a significant fraction of the Earth's upper mantle above the 670-km discontinuity (e.g., Ito and Takahashi, 1987). Although most garnets, including those on most of the pyrope-enstatite join, have cubic symmetry (e.g., Ringwood, 1967; Akaogi and Akimoto, 1977; Liu, 1977), $MgSiO_3$-rich garnets are reported to display tetragonal symmetry (e.g., Kato and Kumazawa, 1985). Noncubic distortions of the garnet structure arise from cation ordering on the octahedrally coordinated sites within the structure. Takéuchi et al. (1982) studied optically anisotropic grandites and showed that partial Al,Fe ordering reduced the symmetries of various crystals from cubic to either orthorhombic (*Fddd*) or triclinic ($I\bar{1}$). Garnets having different sized octahedral cations appear to favor the $I4_1/a$ space group, especially for ABO_3 compositions in which the octahedral sites are occupied by equal numbers of A and B cations. High-pressure syntheses have resulted in the identification of such tetragonal garnet phases for $CaGeO_3$, $CdGeO_3$ (Prewitt and Sleight, 1969), and $MnSiO_3$ (Fujino et al., 1986), in which the octahedral cations are completely ordered. If cation ordering and associated symmetry reduction does occur for $MgSiO_3$ garnet, then it has important consequences for the thermodynamic properties of mantle garnets. In particular, the configurational entropy of an ordered $MgSiO_3$ garnet would be reduced relative to a disordered cubic phase, with an associated reduction in the enthalpy. We present the results of the first single-crystal X-ray diffraction study of $MgSiO_3$ garnet. These results confirm the reported tetragonal symmetry and indicate that the Mg and Si cations are almost completely ordered among octahedral sites.

EXPERIMENTAL DETAILS

The $MgSiO_3$ garnet was synthesized in a 2000-ton uniaxial split-sphere apparatus (USSA-2000) at approximately 17 GPa and 1700 °C in a 7-mm MgO octahedral cell assembly (Remsberg et al., 1988). Runs of 10-min duration using enstatite-glass starting material plus PbO flux resulted in polycrystalline aggregates of optically anisotropic crystals.

Transmission electron microscopy and electron diffraction were performed on ion-milled specimens with a Phillips 420 ST microscope operated at 120 keV. Although good thin areas were not obtained from milling the 30- to 40-μm-diameter crystals, it was still possible to determine the structural details of twinning present in the $MgSiO_3$ garnet. Two distinct types of twinning were observed. The first type occurred as pervasive, micrometer-scale domains with irregular shape and curved boundaries (Fig. 1a). These twins exhibited good contrast in dark-field micrographs obtained by imaging diffracted beams with $h \neq k$, especially those such as 240 and 260 that were shown by structure refinement to have substantially different structure factors for the *hkl* and *khl*

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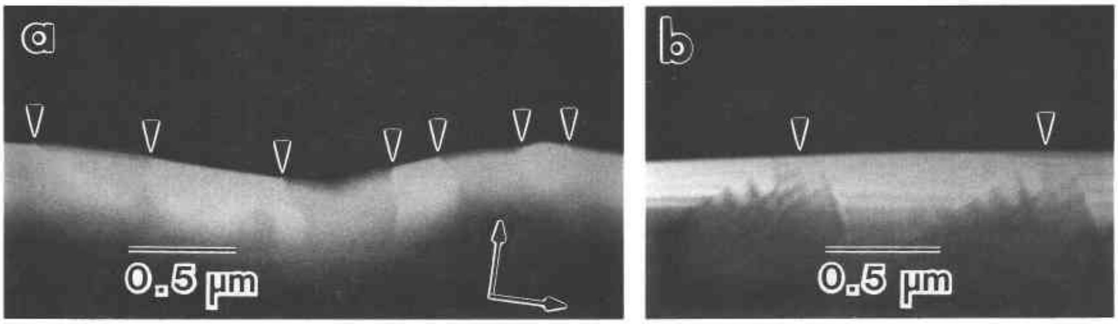

Fig. 1. (**a**) Dark-field TEM image ($g = 240$) showing light and dark merohedral twin domains in MgSiO$_3$ garnet. Arrows indicate the points at which twin boundaries intersect the specimen edge. (**b**) Dark-field image ($g = 440$) of two pseudomerohedral twin lamellae, tilted with respect to the electron beam and indicated by arrows. (The orientation of both parts is the same; crystallographic axes represented by arrows are not labeled, because axial orientation varies from domain to domain.)

pair. However, these twins were effectively invisible for beams with indices *hhl* or *h*0*l*. Convergent-beam electron-diffraction (CBED) patterns obtained from adjacent twin domains showed no observable differences in lattice orientation. These observations are consistent with perfectly merohedral twinning based on a twin law involving 2-fold rotation parallel to [110], which can also be described as reflection on {110}.

The second type of twinning occurred as irregularly spaced planar lamellae (Fig. 1b) having composition planes {110}. These twins exhibited at least weak contrast in bright- and dark-field images obtained with all classes of diffracted beams active, and CBED patterns from the lamellae and adjacent host indicated small differences in lattice orientation. These observations are consistent with pseudomerohedral twinning based on a twin law involving 3-fold rotation about [111], i.e., they involve switching the *c* axis with one of the *a* axes.

Twinning analogous to that of synthetic MgSiO$_3$ garnet occurs in other pseudocubic tetragonal structures. Leucite, for example, exhibits the same twin laws, having both merohedral twins with curved boundaries and pseudomerohedral twins with planar interfaces parallel to {110}, the orientation for which there is zero lattice misfit. Indeed, the imaging methods for this study of tetragonal garnet were identical to those used in studies of twinning in leucite (Rüscher et al., 1987; Heaney and Veblen, 1988). Unlike leucite, however, the difference between the lengths of *a* and *c* in the garnet is very small, and no consistent pattern of spot splitting could be observed in selected-area electron-diffraction patterns taken across pseudomerohedral twin boundaries.

A "single" crystal with approximate dimensions 30 × 40 × 60 μm was examined with a Rigaku AFC-5 goniometer equipped with a rotating-anode generator operated at 50 kV and 180 mA. Graphite-monochromatized MoKα_1 radiation ($\lambda = 0.7093$ Å) was used. Diffraction peaks were reasonably sharp, although other crystals examined exhibited distinct peak splitting. We concluded that crystals with split peaks possessed the coarse lamellar twinning observed by TEM, while single peaks were indicative of the presence of only the merohedral twins. Unit-cell parameters (Table 1) were determined from the positions of 24 centered reflections in the range $40 < 2\theta < 50°$.

Initial investigations showed that those reflections with $h + k + l$ odd were systematically absent from the diffraction pattern. All remaining reflections in one hemisphere of reciprocal space to $\sin \theta/\lambda = 0.71$, with $0 < h < 16$ and $-16 < k,l < 16$, were collected with continuous ω-scans in a constant precision mode. Three reflections were monitored as intensity and orientation standards every 150 reflections during the data collection, and these showed no systematic variation with time. Data reduction also indicated that reflections with h,k odd in $hk0$ and $l \neq 4n$ in $00l$ were absent, and the space group was therefore uniquely determined to be $I4_1/a$. The 4512 symmetry-allowed reflections that were measured were corrected for Lp effects and absorption (transmission coefficients ranged from 93 to 97%) and were re-

TABLE 1. Crystal data for MgSiO$_3$ garnet

a (Å)	11.501(1)	Space group $I4_1/a$
c (Å)	11.480(2)	Z = 32
V (Å^3)	1518.6(4)	$\rho_{calc} = 3.51$
R (obs. reflns.)	4.3	
Rw	4.6	$\lambda = 0.7093$ Å
G_{fit}	1.30	$2\theta_{max} = 60°$
N_{par}	39	$\mu_l = 11.65$ cm^{-1}
$N_{obs}I > 3\sigma_I$	373	

Note: Numbers in parentheses are the estimated standard deviations (1σ) in the last decimal place quoted. This convention applies to all subsequent tables.

TABLE 2. Positional and thermal parameters from refinement of MgSiO$_3$ garnet

Site*	Atom	x	y	z	B_{iso}
D1	Mg	0.1253(4)	0.0112(4)	0.2587(3)	1.33(8)
D2	Mg	0.0000	0.2500	0.6258(6)	1.54(9)
Oc1**	0.80(6)Mg 0.20(6)Si	0.0000	0.0000	0.5000	0.22(3)†
Oc2**	0.20(6)Mg 0.80(6)Si	0.0000	0.0000	0.0000	0.22(3)†
T1	Si	0.0000	0.2500	0.3750	1.03(12)
T2	Si	0.0000	0.2500	0.8750	0.37(10)
T3	Si	0.1249(3)	0.0065(3)	0.7544(3)	0.53(5)
O(1)	O	0.0282(6)	0.0550(6)	0.6633(6)	0.88(12)
O(2)	O	0.0380(6)	−0.0471(6)	0.8562(6)	1.31(14)
O(3)	O	0.2195(7)	0.1023(6)	0.8021(6)	1.28(14)
O(4)	O	0.2150(6)	−0.0894(6)	0.7000(6)	0.99(12)
O(5)	O	−0.0588(6)	0.1617(6)	0.4680(6)	0.89(12)
O(6)	O	−0.1040(6)	0.2080(6)	0.7851(6)	1.01(12)

* Origin of atomic coordinates shifted by ½,0,0 relative to standard origin at Wyckoff position 8*c*, in conformity with previous descriptions of tetragonal garnets.

** Total occupancies of each of these two sites constrained to be unity, and total $^{[6]}$Mg = total$^{[6]}$Si = 1.0

† Constrained equal.

duced to structure factors with the program of Burnham (1966). These were then averaged in Laue group $4/m$ with $R_{int} = 8.3\%$ (3.0% for observed reflections) to give 1100 symmetry-independent reflections, of which 373 with $I > 3\sigma_I$ were treated as observed and were included in the refinements.

Refinements were carried out with RFINE88, a development version of RFINE4 (Finger and Prince, 1975). A weight of $w = \sigma^{-2}(F_o)$ was assigned to each observed reflection, where $\sigma(F_o)$ is the error derived from counting statistics, and the function minimized was $\Sigma\ w(|F_o| - |F_c|)^2$. Atomic coordinates of $MnSiO_3$ tetragonal garnet (Fujino et al., 1986) were used as a starting model, and complex scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Refinement without a twin correction converged to $R \approx 14\%$. The resultant structure exhibited abnormal thermal parameters, and difference-Fourier maps showed considerable residual density at positions related by a tetrad axis to atoms in the structure. Addition of a {110} twin fraction, which refined to 0.48(1), allowed the refinement to proceed, although it was found necessary to constrain the temperature factors of the two octahedral sites to be equal in order to reduce correlations with the occupancies. Final agreement indices are reported in Table 1, atomic coordinates and temperature factors are listed in Table 2, observed and calculated structure factors in Table 3,[1] and bond lengths in Table 4.

TABLE 4. Bond lengths in $MgSiO_3$ garnet

D1–O(1)	2.121(8)		D2–O(1)	2.307(7)	[2]
–O(2)	2.333(8)		–O(2)	2.385(7)	[2]
–O(3)	2.266(8)		–O(5)	2.184(8)	[2]
–O(3)′	2.433(8)		–O(6)	2.239(9)	[2]
–O(4)	2.153(8)		Mean	2.279	
–O(4)′	2.250(8)				
–O(5)	2.132(8)				
–O(6)	2.582(8)				
Mean	2.284				
Oc1–O(1)	2.004(7)	[2]	Oc2–O(2)	1.792(7)	[2]
–O(4)	1.976(7)	[2]	–O(3)	1.836(7)	[2]
–O(5)	2.012(7)	[2]	–O(6)	1.793(7)	[2]
Mean	1.998		Mean	1.807	
Q.E.	1.004			1.000	
T1–O(5)	1.622(7)	[4]	T3–O(1)	1.623(7)	
Q.E.	1.021		–O(2)	1.657(8)	
T2–O(6)	1.652(7)	[4]	–O(3)	1.642(8)	
Q.E.	1.007		–O(4)	1.638(8)	
			Mean	1.641	
			Q.E.	1.015	

Note: Q.E. is the quadratic elongation as defined by Robinson et al. (1971).

DISCUSSION

All previous diffraction studies of $MgSiO_3$ garnet used powder methods. Kato and Kumazawa (1985) reported a unit cell with $a = 11.491$ and $c = 11.406$ Å, which are about 1% smaller than those we have measured here (Table 1) and also represent a larger distortion from cubic-lattice geometry [$c/a = 0.9926$ against our value of $c/a = 0.9982(2)$]. This discrepancy may have arisen from the difficulty of measuring accurate peak positions because of overlap of "split peaks" or from different values used for the X-ray wavelengths, or it may reflect real differences between samples. Indeed Kato and Kumazawa (1985) reported contamination by Al_2O_3, H_2O, and unspecified components from the pressure medium.

The pervasive twinning and relatively poor quality of the $MgSiO_3$ garnet crystals limit our analysis. Our data and refinement are sufficient, however, to demonstrate major structural features. The lattice symmetry is tetragonal body-centered, and the apparent Laue symmetry is $4/mmm$. The observation by TEM of pervasive twinning by reflection on {110} explains why this symmetry is too high and in conflict with the observed systematic absences that uniquely identify the space group as $I4_1/a$. As an additional check on this conclusion, we attempted a refinement of a structure with the only possible space group for garnet with $4/mmm$ Laue symmetry, $I4_1/acd$. This space group does not allow Mg,Si ordering on the octahedral sites, and the refinement converged to an R of 23%. Refinement was also attempted in the $Fddd$ space group (Takéuchi et al., 1982), which allows the same octahedral ordering pattern as $I4_1/a$. After removal of certain reflections that violate $Fddd$ symmetry, the refinement converged to $R \approx 14\%$, with all of the Oc1–O and Oc2–O bond lengths in the range 1.88 to 1.93 Å. This unreasonable absence of cation ordering, combined with the high R value and the presence of symmetry-violating reflections, allows us to reject the $Fddd$ model for $MgSiO_3$ garnet. The correct symmetry for $MgSiO_3$ garnet is thus $I4_1/a$.

Refined site occupancies, constrained to an overall chemistry of $MgSiO_3$, suggest that there is only partial order between the Oc1 and Oc2 sites (Table 2). This result must be treated with extreme caution, however, because the scattering factors of Mg and Si are very similar, and the refinement would only converge after the twin fraction (which was refined in previous cycles) was fixed and the temperature factors of the two octahedral sites were constrained to be equal. The mean M–O bond lengths of the two octahedral sites may therefore give a better indication of the distribution of Mg and Si between them. The Oc1 site is considerably smaller than that normally associated with Mg in octahedral coordination, 2.05 to 2.15 Å being the normal range although there are structures reported with mean $^{[6]}$Mg–O distances as short as 1.987 Å (Smyth and Bish, 1988). The mean bond lengths reported for Si in octahedral coordination range from 1.757 Å in stishovite (Hill et al., 1983) to 1.811 Å found in $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ pyroxene (Angel et al., 1988). The value for the Oc2 site, 1.807 Å, falls within this range, although it is marginally greater than that reported for the octahedral Si in $MnSiO_3$ garnet (1.795 Å, Fujino et al., 1986). The bond lengths thus suggest that although there might be slight octrahedral Mg,Si disorder, it is probably not as great as that given by the refined occupancies reported in Table 2.

Other structural features of $MgSiO_3$ garnet are similar

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[1] A copy of Table 3 may be ordered as Document AM-89-403 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

to those of other garnets. The mean tetrahedral bond lengths fall within the range reported for silicate garnets (see, for example, Smyth and Bish, 1988, or Novak and Gibbs, 1971) and are identical within experimental error to those in $MnSiO_3$ garnet (Fujino et al., 1986). The larger, eight-coordinated Mg sites in $MgSiO_3$ garnet are more distorted than that in pyrope, as allowed by the lower symmetry. The spread of bond lengths (Table 4) is therefore greater, but the mean values are almost identical to that found in pyrope (2.270 Å, Novak and Gibbs, 1971).

In conclusion, the noncubic symmetry of $MgSiO_3$ garnet results from the almost complete ordering of Mg and Si cations on the octahedral sites within the structure. Deviations from cubic symmetry, whether measured by c/a or by the deviation of atom coordinates from the values required by the high symmetry of the cubic structure, are smaller than those found in other tetragonal garnets, because the difference in size between Mg and Si is less than for any of these previously reported phases. We do not believe, however, that either of the twin laws found in this material have arisen from an inversion on quenching from a high-symmetry phase, as this would not only require Mg and Si to be disordered over the octahedral sites in the high-symmetry phase, but also would require these cations to become ordered during the very rapid quench (of the order of 1 s) from run conditions. The twinning therefore arises because of cation ordering during growth of the garnet phase. This interpretation also is consistent with the irregular distribution of the relatively coarse pseudomerohedral twin lamellae. Both the merohedral and pseudomerohedral twinning are presumably common in $MgSiO_3$ garnet, because neither type gives rise to lattice strain. Twinning in natural majorite garnets is now under investigation.

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