**β-Mg$_2$SiO$_4$: Single-crystal X-ray diffraction study**

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**Abstract**

The crystal structure of β-Mg$_2$SiO$_4$ has been refined using a single crystal synthesized at 185 kbar and 2000°C, by means of X-ray diffraction data. Magnesium and silicon atoms are completely ordered on octahedral and tetrahedral sites, respectively. Octahedral distortions are smaller in MgO$_6$ octahedra and greater in the larger unoccupied octahedra, O$_6$. The density increase involved in the α→β→γ phase transformations is mainly attributed to the volume decrease of unoccupied octahedra. The distortions from regular octahedra and the octahedral volumes in the β-Mg$_2$SiO$_4$ structure are much smaller than those of α-Mg$_2$SiO$_4$ and the octahedral distortions and volumes of MgO$_6$ and O$_6$ will be further decreased in association with the β→γ phase transformation to the minimum degree observed in β-Mg$_2$SiO$_4$.

**Introduction**

The presence of a complex intermediate phase in the high pressure transformation of olivine(α)→spinel(γ) was first pointed out for compositions close to nearly iron-free (Mg,Fe)$_2$SiO$_4$ by Ringwood and Major (1966). This intermediate phase was confirmed to be a stable phase by Akimoto and Sato (1968) and Akimoto (1970) by analogy to new high-pressure polymorphs of Co$_2$SiO$_4$ and Mn$_2$GeO$_4$, which were subsequently designated as the “β-phase”. A number of phase equilibrium studies of Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ were subsequently initiated, because the phase transformations α→β→γ of this system are believed to directly involve the structure and constitution of the transition zone in the earth's mantle. For example, phase equilibria in the system MgO-FeO-SiO$_2$ and in pure Mg$_2$SiO$_4$ up to pressures around 200 kbar were reported by Akimoto (1972) and by Suito and Kawai (1979), respectively, and the post-spinel phases of Mg$_2$SiO$_4$ were studied by several investigators such as Kumazawa, Sawamoto, Ohtani and Masaki (1974), Liu (1976), Ito (1977) and others.

The crystal structure of the β-phase was determined by Morimoto, Akimoto, Koto and Tokonami (1969) for a single crystal of Mn$_2$GeO$_4$, and almost simultaneously by Moore and Smith (1970) for a powder specimen of (Mg$_{0.3}$Ni$_{0.5}$)$_2$SiO$_4$ synthesized by Ringwood and Major (1969). Following the determination of the crystal structures of the aforementioned compounds, those of β-Co$_2$SiO$_4$ and Ni$_2$Al$_2$SiO$_4$ III(β-phase) were also studied in detail by Morimoto, Tokonami, Watanabe and Koto (1974), and Ma and Sahl (1975), respectively.

Precise studies on the crystal structures of β- and γ-phases of Mg$_2$SiO$_4$ have not been carried out because of technical difficulties in obtaining single crystals large enough for single-crystal investigations, although its prime importance has been widely recognized in the investigation of mantle substances.

In this work, the crystal structure of pure β-Mg$_2$SiO$_4$ was refined using single crystal X-ray diffraction data. The crystal structure is described in detail in comparison with the α-phase of Mg$_2$SiO$_4$.

**Experimental**

Single crystals of β-Mg$_2$SiO$_4$ were synthesized from powdered α-Mg$_2$SiO$_4$ crystals at 2000°C and 185 kbar by means of a multi-anvil-type high pressure and high temperature apparatus. The run-time
was 60 minutes. The crystals obtained are around 100 μm in maximum size, colorless and transparent, and optically biaxial. The specimen studied in this experiment approximates a parallelepiped in shape and is 88 x 75 x 75 μm in size. X-ray photographs indicate systematic absence of reflections with h+k+l = 2n+1, and with h = 2n+1 for hk0, which is consistent with space group Imma. Cell dimensions were determined by the least-squares method using 73 reflections (28 Kα; λ = 0.70930, 28 Kα; λ = 0.71359 and 17 Kβ; λ = 0.63229Å reflections) which were measured on a four-circle diffractometer. The crystal data are summarized in Table 1.

MoKα radiation monochromated by pyrolytic graphite was used for intensity measurement. The intensities of 2545 reflections including crystallographically equivalent reflections within the range 0° < 2θ < 70° were obtained by the 2θ-θ scan technique on a four-circle (RIGAKU AFC-3) diffractometer. All the observed reflections were condensed to 675 unique reflections, of which 237 had high standard deviations (σFo > 1Fo) or zero intensity, where σFo is a standard deviation of each reflection obtained from counting statistics. Conventional polarization and Lorentz corrections were carried out in the process of the data collection. No absorption correction was applied because of the sufficiently small value of μ(0.05).

Refinement of the structure

The β-Mg2SiO4 structure refinement was initiated with the atomic coordinates of β-(Mg0.98Ni0.02)2SiO4 reported by Moore and Smith (1970). The space group, Imma, was assumed for the structure and was confirmed by structure refinement. The scattering factor curves of Mg, Si and O used for calculations are those of neutral atoms (International Tables for X-Ray Crystallography, Vol. IV(1974)). The 438 reflections with |Fo| > 3σFo were used in the structure refinement, applying the weight 1/σFo for each reflection.

Two modes of refinement were carried out in order to clarify the cation distributions on octahedral and tetrahedral sites. In the first mode, case (1), perfect ordering of cations was assumed (Mg and Si atoms on octahedral and tetrahedral sites, respectively) and only atomic coordinates and anisotropic temperature factors were refined. In the second mode, case (2), the starting distribution of 0.25Si + 0.75Mg and 0.50Si + 0.50Mg was assigned to octahedral and tetrahedral sites, respectively, and the occupancy factors together with coordinates were refined.

The value of R, roughly 0.15 for the initial atomic parameters, was reduced to 0.028 for both cases after about 10 cycles of refinement. The final atomic parameters thus obtained are given in Table 2 for both cases together with the initial ones reported by Moore and Smith (1970).

The choice of atomic scattering factors, whether for neutral or charged atoms, does not affect the results because the value of the difference between them, particularly in the range of sinθ/λ > 0.2, is quite small and more than 97% of the reflections used for the structure analysis lie in the above range.

Table 3 show bond distances and angles calculated with the results of case (1). All computations for the least-squares refinement of lattice constants and structure parameters, interatomic distances and angles, and crystal structure diagrams, were carried out using the program LCLSQ(Burnham, 1962), RFINE(Finger, 1972), UMBADTEA(Finger, 1968) and ORTEP-II (Johnson, 1971) at the Crystallographic Research Center, Institute for Protein Research, Osaka University (ACOS-700).

Results and Discussion

General features of the β-phase structure

The crystal structure of the β-phase, as shown by β-Mn2GeO4(Morimoto et al., 1969), is based on a slightly distorted cubic closest-packing of oxygen atoms. The a-axis of the β-phase is half the diagonal
of the spinel unit cell, the b-axis is associated with the other diagonal, and the c axis is in common with the third axis of spinel. There are 64 tetrahedral and 32 octahedral sites per unit cell, and one-eighth of the tetrahedral and one-half of the octahedral sites are occupied by cations in the β-phase as well as in the γ-phase structures. There are four crystallographically non-equivalent cations in the structure, of which one (T atom) is tetrahedrally and the others (M atoms) are octahedrally coordinated by oxygen atoms. The TO₄ tetrahedron shares a vertex with a neighboring tetrahedron to form the T₂O₆ group. The M(1)O₆ octahedron shares edges with adjacent M(2)O₆ octahedra and together they form a single octahedral chain, M(1)–M(2)–M(1)–M(2)–, which runs parallel to the b-axis. The M(3) octahedron shares an edge with the adjacent crystallographically equivalent M(3) octahedron to form a double chain running along the a-axis. The double chain of M(3) octahedra is crossed by M(1)–M(2)– single chains, and octahedra of these two chains share vertices. The perspective view of the structure of β-Mg₂SiO₄ is illustrated in Figure 1, in which Mg and Si correspond to M and T atoms in the above explanation.

**Cation distributions in β-Mg₂SiO₄**

Although the occupancy factors for Mg atoms on the octahedral sites exceed unity, this is in accord with negative values for the factors for Si atoms as shown in Table 2. Therefore the distributions of Mg atoms on their sites, cₐ's, may be numerically adjusted to 0.97Mg on M(1), 1.00Mg on M(2) and
1.00Mg on M(3) by introducing the relation $c_M = c_{Mg} + (14/12)c_{Si}$, where $c_{Mg}$ and $c_{Si}$ are the refined values of distribution of Mg and Si atoms on each site, and the numbers, 12 and 14, are the atomic numbers for Mg and Si. In the same manner, the distribution of the Si atom on the tetrahedral site numerically results in 1.00Si by introducing the relation $c_T = (12/14)c_{Mg} + c_{Si}$. Thus, the results of the refinement (case (2)) concerning the distribution of Mg and Si atoms, essentially demonstrated an ordered arrangement within the experimental error; that is, Mg and Si atoms are located on octahedral and tetrahedral sites, respectively. This conclusion is also supported by the fact that the refined atomic coordinates of the two cases (1) and (2) are completely consistent as shown in Table 2.

**Interatomic distances**

The increased density of Mg$_2$SiO$_4$ resulting from the $\alpha \rightarrow \beta$ phase transformation must be reflected in the change of the interatomic distances in the structure, since the oxygen coordination numbers around cations do not change before and after the phase transformation although the oxygen arrangement changes from hexagonal to cubic close-packing. Therefore, it is of interest to compare the interatomic distances of $\beta$-Mg$_2$SiO$_4$ with those of $\alpha$-Mg$_2$SiO$_4$. The interatomic distances for $\alpha$-Mg$_2$SiO$_4$ employed here for comparison were those determined at one atmosphere (Hazen, 1976) after the phase had been subjected to 50 kbar pressure.

The mean interatomic distances of the largest octahedron (Mg–O 2.090 and O–O 2.954Å) of three MgO$_6$ octahedra in $\beta$-Mg$_2$SiO$_4$ are comparable to those of the smaller one (mean Mg–O 2.091 and O–O 2.947Å) of two MgO$_6$ octahedra in $\alpha$-Mg$_2$SiO$_4$. On the average, MgO$_6$ octahedra are roughly 1 percent compressed in $\beta$-Mg$_2$SiO$_4$ in comparison with those of $\alpha$-Mg$_2$SiO$_4$. On the other hand, the SiO$_4$ tetrahedron is about 1.5 percent expanded in $\beta$-Mg$_2$SiO$_4$ in
comparison with that of α-Mg$_2$SiO$_4$ (mean values are Si–O 1.651 and O–O 2.693 Å for β-Mg$_2$SiO$_4$, and Si– O 1.628 and O–O 2.649 Å for α-Mg$_2$SiO$_4$). The values of the Si–O(2) distance and Si–O(2)–Si angle which are affected by strong Si–Si repulsive force are 1.706 Å and 122.2° (109.45° in an ideal closest packed structure), and they are comparable to those in β-Co$_2$SiO$_4$.

The calculated density increase for the α → β structural change of Mg$_2$SiO$_4$ is approximately 7 percent. Therefore, the compression of unoccupied octahedra □O$_6$ must be responsible for the density increase of the phase change in Mg$_2$SiO$_4$. There are three crystallographically independent □O$_6$ sites in the β-phase structure, and all of the mean values of O–O distances of □O$_6$ are much smaller than those of the MgO$_6$ octahedra. There are two □O$_6$ in the α-Mg$_2$SiO$_4$ structure and their mean values are larger than those of □O$_6$ in β-Mg$_2$SiO$_4$ (see Table 4). For each polyhedron, the deviation of each cation–oxygen or oxygen–oxygen distance from the mean value is greater in α-Mg$_2$SiO$_4$ than in the β-Mg$_2$SiO$_4$ structure. The magnitude of the above deviation serves as a measure of the distortion from the ideal close-packed structure. The relationship between the sizes and distortions of MO$_6$ and □O$_6$ octahedra in the α, β and γ-phase structures is discussed in detail in the next section.

Comparison between Mg$_2$SiO$_4$ and Co$_2$SiO$_4$

Co$_2$SiO$_4$ (Akimoto and Sato, 1968, Morimoto et al., 1974) also shows the α → β → γ phase transformations. The increase and/or decrease of the polyhedral interatomic distances in Mg$_2$SiO$_4$, before and after the α → β phase transformation, bear close resemblance to those in Co$_2$SiO$_4$; i.e., MO$_6$ octahedra are compressed and SiO$_4$ tetrahedron expanded in the β-phase in comparison with the α-phase.

Small structural differences between β-Mg$_2$SiO$_4$ and β-Co$_2$SiO$_4$ noted here are (1) the mean values of

Table 4. Mean values of O–O lengths and distortion factors, $s_{oo}$, of octahedra

<table>
<thead>
<tr>
<th>polyhedra</th>
<th>for O–O and $s_{oo}$</th>
<th>Co$_2$SiO$_4$</th>
<th>Mg$_2$SiO$_4$</th>
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<tbody>
<tr>
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<td>2.947Å</td>
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<tr>
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<td>3.015Å</td>
<td>2.998Å</td>
</tr>
<tr>
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<td></td>
<td>2.855Å</td>
<td>2.844Å</td>
</tr>
<tr>
<td>□O$_6$</td>
<td></td>
<td>3.078Å</td>
<td>3.053Å</td>
</tr>
<tr>
<td>O–O</td>
<td>□O$_6$</td>
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<td>$s_{oo}$</td>
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</table>

References: α, β and γ-Co$_2$SiO$_4$: Morimoto et al. (1974) α-Mg$_2$SiO$_4$: Hazen (1976)
Si–O of SiO₄ tetrahedra are slightly larger in β-Mg₂SiO₄ which is stable at higher pressure than β-Co₂SiO₄, and (2) M–O distances of β-Mg₂SiO₄ are slightly smaller than those of β-Co₂SiO₄, in accord with the difference between the ionic radii of Mg²⁺ and Co²⁺. As a result, the difference between O–O distances of SiO₄ tetrahedra and those of MO₆ octahedra is smaller in β-Mg₂SiO₄ than in β-Co₂SiO₄.

This means that the distortion from the regular oxygen close-packing is less in β-Mg₂SiO₄ than in β-Co₂SiO₄.

**Configurations of MO₆, □O₆ and SiO₄ polyhedra**

The polyhedral configurations of oxygen atoms of the β-phases are distinctly different in MO₆ (octahedra occupied by Mg or Co) and □O₆ (octahedra

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**Fig. 2.** The relationship between distortion and volume of octahedra MO₆ and □O₆ in α-, β-, γ-Co₂SiO₄ and α-, β-Mg₂SiO₄.
unoccupied by cations). The degree of distortion from the regular polyhedron of oxygen atoms can be represented by the distortion factor defined by $s_{oo} = \frac{\sigma^2}{\bar{x}^2}$ where $\sigma^2$ is the polyhedral O-O distance variance which is given by

$$\sigma^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{(n - 1)}.$$  

The $x_i$ is the length of the i-th O-O edge of each polyhedron and is the mean value of $n$ edge lengths. A greater value of $s_{oo}$ implies a larger distortion of the polyhedron. The value of $s_{oo}$ of each polyhedron is listed in Table 4, and it is plotted against the mean value of the O-O distance, $\bar{x}$ (Fig. 2).

The volume of the octahedron may be proportional to $\bar{x}^3$. In the $\beta$-phase, the MO$_6$ octahedra are greater in volume and less distorted than MO$_6$ octahedra, and both their volumes and distortion factors are distributed within a narrow range. On the other hand, the distortion factor of the MO$_6$ octahedron systematically varies depending on the octahedral volume. The larger octahedron shows the greater distortion, resulting in a wide distribution of distortion factors. In particular, the MO$_6$ octahedra which involve O(2) (i.e., the bridging oxygen of O$_3$-Si-O-Si-O$_3$) are more distorted than the others. However, the distortion factors of most of the octahedra in the $\beta$-phases are still smaller than those in the $\alpha$-phase. Volumes and distortion factors of octahedra in the $\alpha$-phase are arrayed to show expanded volumes and greater distortions without distinction between MO$_6$ and MO$_6$ octahedra. On the other hand, those of the octahedra in the $\gamma$-gamma phase are comparable to the minimum values of volumes and distortion factors of octahedra in the $\beta$-phase.

The distortion of the SiO$_4$ tetrahedron becomes less in the higher-pressure phase in accordance with the volume expansion.

**Conclusion**

Mg and Si atoms are completely ordered in the $\beta$-Mg$_2$SiO$_4$ structure. Mg atoms occupy octahedral sites and Si the tetrahedral site. The degree of distortion of MO$_6$ octahedra in the $\beta$-phase is much less than in the $\alpha$-phase, and the volumes are slightly compressed in the $\beta$-phase. On the other hand, the degree of distortion of MO$_6$ octahedra, which are unoccupied by cations, systematically decreases in accordance with the decrease in O-O distance. The increase of density through the $\alpha \to \beta$ phase transformation is mainly attributed to the volume decrease of MO$_6$ octahedra. The volumes of MO$_6$ octahedra in the $\gamma$-phase will be smaller than those in the $\beta$-phase and will approach the minimum limit of MO$_6$ volumes in the $\beta$-phase structure. Therefore, we conclude that the compression of unoccupied oxygen polyhedra plays an important role in the density increase of pressure-induced phase transformations without changes of coordination numbers. In particular, such a phenomenon takes place in association with the $\alpha \to \beta \to \gamma$ phase transformations in Mg$_2$SiO$_4$.

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