Perovskite-type MgSiO₃: Single-crystal X-ray diffraction study

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Abstract

The crystal structure of orthorhombic perovskite-type MgSiO₃ has been refined by means of X-ray diffraction analysis using a single crystal synthesized at 27 GPa and 1830°C. In the structure, SiO₆ is close to an ideal octahedron in which the Si–O distances and O–Si–O angles are nearly equal; their values range from 1.783 to 1.801 Å and from 88.49 to 91.51°, respectively. On the other hand, the position of the Mg atom deviates from the center of the MgO₁₂ polyhedron. As a result, the Mg–O distances and O–Mg–O angles range widely from 2.014 to 3.120 Å and from 50.05 to 70.89°, respectively. As a result, rotation and tilting of cation octahedra govern the structure, as suggested in other orthorhombic perovskite-structure compounds.

Introduction

High-pressure modifications of magnesium silicates are significant endmembers of the mantle mineral assemblage, so detailed knowledge of their structures is of great importance, not only for high-pressure crystal chemistry, but also for understanding the state of the deep mantle. Therefore, much effort has been made to define the crystal structures of high-pressure magnesium silicates by means of X-ray single-crystal diffraction techniques; e.g., β-Mg₂SiO₄ (Horiuchi and Sawamoto, 1981), γ-Mg₂SiO₄ (Sasaki and Prewitt, 1982), ilmenite-type MgSiO₃ (Horiuchi et al., 1982), 2Mg₂SiO₄·3Mg(OH)₂ (phase A) (Horiuchi et al., 1979). On the basis of detailed ultrahigh-pressure phase relations in the system MgO-FeO-SiO₂ (Ito and Yamada, 1981; Ito et al., 1984), it was demonstrated that perovskite-type MgSiO₃ could be the dominant phase in the lower mantle.

Because of the special importance of perovskite-type MgSiO₃, Ito and Matsui (1978) and Yagi et al. (1978) studied its structure by X-ray powder-diffraction analysis. Their results revealed that its structure belongs to the orthorhombic system with probable space group *Pbnm* and deviates significantly from the ideal cubic-perovskite structure through the tilting of the relatively regular SiO₆ octahedra and the large distortion of the MgO₁₂ dodecahedron (Sasaki et al., 1983). However, structural refinement using a single crystal has urgently been needed because the results could provide a firmer basis for discussion of the physical and chemical properties of the phase.

Ito and Weidner (1986) recently succeeded in growing single crystals of perovskite-type MgSiO₃ that are large enough for X-ray diffraction and spectroscopic studies. It is the purpose of the present paper to report the detailed crystal structure of perovskite-type MgSiO₃ obtained by means of a single-crystal X-ray diffraction analysis.

Experimental details

The specimen used in this work was synthesized at approximately 27 GPa and 1830°C with a run time of 8 min, by means of an uniaxial split-sphere-type high-pressure apparatus. Synthetic orthoenstatite powder was used as the starting material. The single-crystal specimen used in the crystal-structure analysis was approximately $125 \times 85 \times 60$ μm³ in size. It was optically transparent and colorless.

X-ray photographs indicated systematic absences of reflections with $k = 2n + 1$ for $0kl$ and $h + l = 2n + 1$ for $h0l$, which are consistent with space group *Pbn2₁* or *Pbnm*. Cell dimensions of $a = 4.7754(3)$, $b = 4.9292(4)$, and $c = 6.8969(5)$ Å reported by Ito and Matsui (1978) were adopted throughout the analysis. The cell constants determined by means of a four-circle diffractometer, using 19 reflections of the 2θ range of 38 to 52° and employing the 0.71073-Å wavelength, were $a = 4.7787(4)$, $b = 4.9313(4)$ and $c = 6.9083(8)$ Å. The constants are slightly larger than the results from the powder-diffraction technique. The reason why we adopted the former results in this work is that the results of the four-circle diffractometer may have a systematic error introduced by the uncertainty of the wavelength because of using a pyrolytic graphite monochromator. From these crystallographic data, the calculated density and linear absorption coefficient are 4.108 g/cm³ and 14.07 cm⁻¹ for Mo*K*α radiation, respectively.

Mo*K*α radiation monochromatized by pyrolytic graphite was

TABLE 1. Refined atomic coordinates and temperature factors (×10⁵) for perovskite-type MgSiO₃

		Coordinates		
	x	y	z	B_{eq}* (Å²)
Mg	0.5141(1)	0.5560(1)	¼	0.46
Si	½	0	½	0.25
O(1)	0.1028(2)	0.4660(2)	¼	0.32
O(2)	0.1961(1)	0.2014(2)	0.5531(1)	0.34

	Anisotropic temperature factors†					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	480(19)	459(17)	257(9)	44(16)	0	0
Si	296(19)	298(10)	100(6)	−4(11)	2(8)	−9(7)
O(1)	376(30)	472(32)	90(15)	11(24)	0	0
O(2)	372(20)	365(20)	179(11)	70(17)	29(12)	48(13)

* B_{eq}: Equivalent isotropic temperature factors according to the relation $B_{eq} = \frac{4}{3} \Sigma\Sigma \beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$.
† Coefficients in the expression
$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

used for diffraction-intensity measurement. The intensities of 3580 reflections including crystallographically equivalent reflections in the hemisphere of reciprocal space within the range of $0° < 2\theta < 100°$ were obtained by the 2θ-ω scan technique on a four-circle diffractometer (RIGAKU AFC-5). All the observed reflections were processed to yield 895 unique reflections. Conventional polarization and Lorentz factor corrections were carried out in the process of the data collection. No absorption correction was applied because of the sufficiently small value of μr (<0.1).

REFINEMENT OF THE STRUCTURE

The structure refinement was initiated with the atomic coordinates reported by Ito and Matsui (1978). The space group *Pbnm* was assumed for the structure and was confirmed by structure refinement. The scattering factor curves of neutral atoms were applied for Mg, Si, and O (*International Tables for X-ray Crystallography*, 1974). All 895 unique reflections were used in the structure refinement, applying the weight $1/\sigma_{hkl}(F_{obs})^2$ for each reflection, where $\sigma_{hkl}(F_{obs})$ is a standard deviation of each reflection obtained from counting statistics.

The value of weighted R, roughly 0.15 for the initial atomic parameters, was reduced to 0.024 (R for unit weight; 0.035) for the final cycle of refinement with anisotropic temperature factors for all atoms. The final atomic parameters are given in Table 1 and interatomic distances and angles are shown in Table 2. Table 3, giving F_o and F_c values, has been deposited.[1] All computations for the least-squares refinement of structure parameters and for crystal-structure plotting were carried out using the programs RFINE (Finger, 1969) and ORTEP II (Johnson, 1971), respectively, at the Computer Center of the University of Tokyo.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is fundamentally obtained by substituting Mg for Ca and Si for Ti in the perovskite structure. Both MgO₁₂ and SiO₆ polyhedra occur in the structure,

[1] To obtain a copy of Table 3, order Document AM-87-329 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.
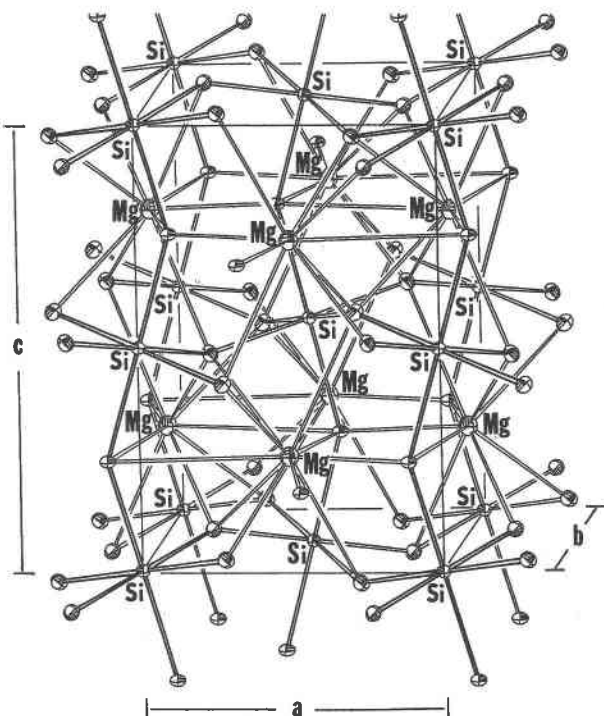

Fig. 1. A perspective view of the structure of perovskite-type MgSiO₃ drawn using the program ORTEP (Johnson, 1971). Si and Mg atoms are labeled, and nonlabeled atoms are oxygens.

TABLE 2. Interatomic distances (Å) and angles (degrees) of perovskite-type MgSiO₃

SiO₆ octahedron

Si–O distances		O–O distances		O–Si–O angles
Si–O(2)	1.7827(7) [2]	O(1)–O(2)	2.504(1) [2]	88.66(5)
–O(2)	1.7960(7) [2]	O(1)–O(2)	2.509(1) [2]	88.49(5)
–O(1)	1.8005(3) [2]	O(2)–O(2)	2.518(1) [2]	89.43(3)
	1.7931*	O(2)–O(2)	2.543(1) [2]	90.57(3)
		O(1)–O(2)	2.563(1) [2]	91.34(5)
		O(1)–O(2)	2.577(1) [2]	91.51(5)
			2.536*	90†

MgO₁₂ polyhedron

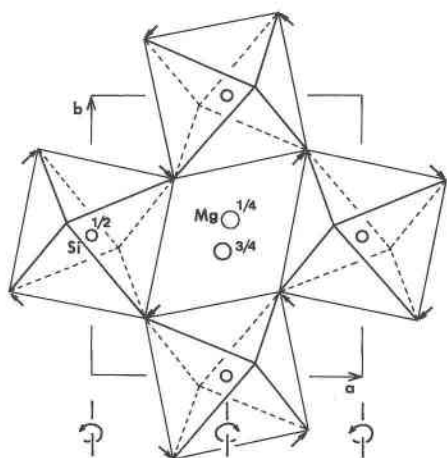| Mg–O distances		O–O distances		O–Mg–O angles
Mg–O(1)	2.014(1)	O(1)–O(2)	2.504(1) [2]	53.25(3)
–O(2)	2.052(1) [2]	O(1)–O(2)	2.504(1) [2]	66.76(3)
–O(1)	2.096(1)	O(1)–O(2)	2.509(1) [2]	59.01(3)
–O(2)	2.278(1) [2]	O(1)–O(2)	2.509(1) [2]	69.86(3)
–O(2)	2.427(1) [2]	O(2)–O(2)	2.518(1) [2]	52.19(3)
–O(1)	2.846(1)	O(2)–O(2)	2.518(1) [2]	70.89(4)
–O(1)	2.961(1)	O(2)–O(2)	2.543(1) [2]	54.28(3)
–O(2)	3.120(1) [2]	O(2)–O(2)	2.543(1) [2]	65.34(3)
	2.473*	O(1)–O(2)	2.563(1) [2]	58.16(3)
		O(1)–O(2)	2.563(1) [2]	58.78(3)
		O(1)–O(2)	2.577(1) [2]	50.05(2)
		O(1)–O(2)	2.577(1) [2]	70.23(3)
			2.536*	60†

* Mean.
† Ideal.

Fig. 2. Projection of the perovskite-type MgSiO₃ along the **c** axis. SiO₆ octahedra are shown diagrammatically by real lines. Rotation and tilting of SiO₆ octahedra are shown by arrows.

and each polyhedron shares all edges with the others. SiO₆ octahedra share all corners. Mg and Si atoms are assumed to be completely ordered. Figure 1 shows a perspective view of the structure. The results of refinement are essentially the same as those given by Ito and Matsui (1978) and by Yagi et al. (1978).

The Si atom is located at the center of the SiO₆ octahedron and is the center of symmetry. The Si–O distances in the SiO₆ octahedron range from 1.783 to 1.801 Å with a mean distance of 1.793 Å, which is slightly larger than that of stishovite, 1.774 Å (Sinclair and Ringwood, 1978) and is similar to that of ilmenite-type MgSiO₃ (Horiuchi et al., 1982). The small variations in Si–O distances and O–Si–O angles (88.5 to 91.5°) show that the SiO₆ octahedron is much more regular than those of stishovite and ilmenite-type MgSiO₃.

On the other hand, the position of the Mg atom deviates from the center of the MgO₁₂ polyhedron. Geometrically, the deviations result in a wide range of Mg–O distances and O–Mg–O angles: They range from 2.014 to 3.120 Å and from 52.19 to 70.89°, respectively. An ideal value of the O–Mg–O angle is 60° for a regular MgO₁₂ polyhedron. The variation of O–O distances in the MgO₁₂ polyhedra is the same as those in the SiO₆ octahedra because both polyhedra share all of their edges with each other.

The average value of the nearest-neighbor O–O distances in the structure, which shows face-centered cubic-closest-packing with Mg atoms, is 2.536 Å. Each deviation of the nearest-neighbor O–O distances is within about ±0.04 Å of the mean value. The second-nearest-neighbor O–O distance should ideally be 3.586 Å, from the calculation using the first-nearest-neighbor mean distance. However, some of the second-nearest-neighbor distances are very small (2.716 to 2.838 Å), whereas others are large (4.174 to 4.199 Å). Therefore, their deviations from the ideal value are as much as ±0.8 Å. These features contrast with the oxygen arrangements in ilmenite-type

MgSiO₃, in which the first-nearest-neighbor O–O distances show a wide range of 2.331 to 3.076 Å.

The small range of the nearest-neighbor O–O distances and the large range of the second-nearest neighbors is due to a rotation and tilting of rigid and nearly regular SiO₆ octahedra in the structure, as suggested in similar structures (Sasaki et al., 1983). These features are illustrated in Figure 2. The rotation around the O–Si–O bond along the **c** axis is about 11.2°, and the angle of tilt measured against **c**, which is equivalent to the rotation around the **b** axis, is about 16.7°. The rotation and tilting greatly distort the MgO₁₂ polyhedra and result in a structure that somewhat resembles the rigid and nearly regular SiO₄ tetrahedral frameworks of silicate minerals under ambient pressures. In such structures, the oxygen configuration around large cations depends on how the SiO₄ tetrahedra are linked to each other. From this point of view, perovskite-type MgSiO₃ can be explained as one of SiO₆ octahedral framework structures.

The degree of rotation and tilting in the perovskite-type structure of MgSiO₃ depends on applied pressure and temperature conditions (O'Keeffe et al., 1979). If the SiO₆ configuration is rigid, smaller amounts of rotation and tilting will make the unit-cell volume larger, because the straighter –O–O–O– arrangements along the **a** and **b** axes and the straighter –O–Si–O–Si–O– arrangement along the **c** axis make the values for a, b, and c larger. This situation will be less advantageous at higher pressure, but will be more advantageous at higher temperature. However, too much rotation and tilting will also cause a stronger repulsive force between the oxygen atoms with the shortest distances. The observed structure represents a balance of the two opposite effects.

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