

MgSiO₃ perovskite: a HRTEM study

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Abstract

Selected-area electron diffraction patterns for the [110] zone of MgSiO₃ perovskite are consistent with the orthorhombic unit cell obtained by X-ray diffraction ($a = 4.775$, $b = 4.929$, $c = 6.897$ Å). Various areas of a crystal fragment show diffuse streaking along c^* , and well-developed satellite reflections that give a 3-fold repeat along $[1\bar{1}0]^*$. Another fragment shows doubled cell dimensions when viewed down $[\bar{1}30]$. The variable occurrence of the satellite reflections and diffuse streaking indicate subtle variations in ordering, chemistry, or both. Images obtained by high-resolution transmission electron microscopy contain perfectly ordered regions, out-of-phase boundaries, and intergrowths of the two orthorhombic forms of perovskite.

KEYWORDS: MgSiO₃ perovskite, HRTEM, satellite reflections, intergrowth, out-of-phase boundaries.

Introduction

MgSiO₃ perovskite is thought to be a major constituent of the lower mantle, and thus its crystal-chemical properties are of prime importance for understanding deep-mantle rheology (Reid and Ringwood, 1975). MgSiO₃ perovskite may be related to the seismic velocity discontinuities in the mantle at the 670 km depth (Liu, 1979; Jeanloz and Thompson, 1983). The perovskite structure in its several varieties is also of broader interest because, for example, the new superconductors have structures that are related to that of perovskite. Such significance in what is probably Earth's most abundant mineral has attracted the attention of scientists using many different techniques (see, e.g. Hazen, 1988; Kudoh *et al.*, 1987). Transmission electron microscopy (TEM) is well suited for investigating the small sizes and quantities of materials produced by high-pressure syntheses.

The orthorhombic modification of MgSiO₃ perovskite was found by Liu (1974). It was synthesized at about 300 kbar and 1000°C in a diamond-anvil cell coupled with laser heating (DAC-LH; Liu, 1975). Subsequently, Yagi *et al.* (1978) synthesized (Mg,Fe)SiO₃ perovskite using the DAC-LH method and determined the crystal structure, which was also determined by Ito and Matsui (1978); both studies used powder X-ray diffraction analyses. Madon *et al.* (1980) used TEM to examine (Mg,Fe)SiO₃ perovskite synthesized by the DAC-LH method. They reported a unit cell with $Z = 32$ and lattice parameters double those obtained from powder X-ray diffraction. Recently, Wang and Liebermann (1993) observed twinning and antiphase boundaries (APBs) in a CaTiO₃ perovskite with space group *Pbnm*, and they relate these structural features to the transition from space group *Pbnm* to *P4/mbm*. In the present study, we have used high-resolution transmission electron microscopy (HRTEM) to study MgSiO₃ perovskite. The goals were

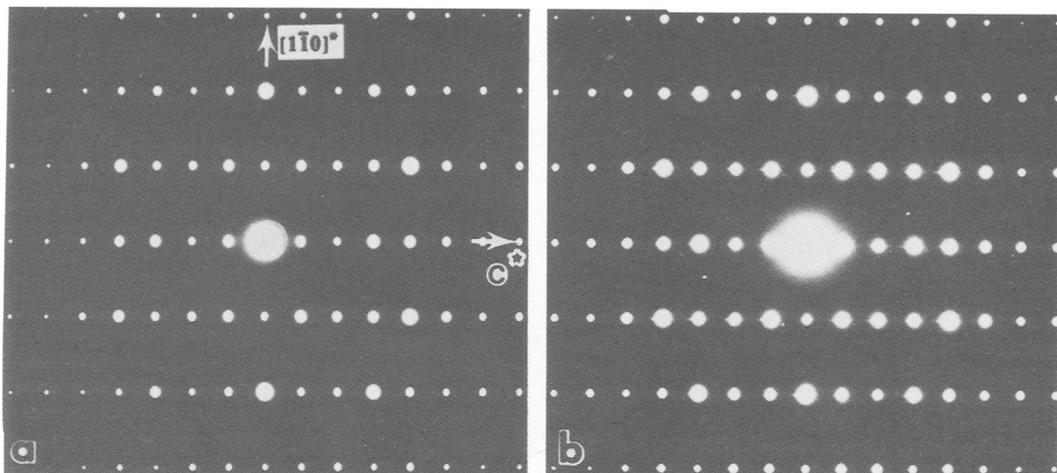


FIG. 1. $[110]$ -zone SAED patterns of MgSiO_3 perovskite. (a) Main reflections; (b) Main reflections and diffuse streaking along c^* .

(a) to see whether we confirm the TEM results of Madon *et al.* (1980) and (b) to search for unusual and distinctive microstructures that might reflect the high-pressure origin of MgSiO_3 perovskite. A preliminary report was given by Hassan *et al.* (1988).

Experimental

Good MgSiO_3 perovskite single crystals up to $200\ \mu\text{m}$ in diameter were synthesized using a uniaxial split-sphere apparatus. The structure of these crystals was determined at room pressure (Horiuchi *et al.*, 1987) and at high pressures (Kudoh *et al.*, 1987). Two pieces of this single-crystal MgSiO_3 perovskite, approximately $100\ \mu\text{m}$ in diameter, were used in the present study. These crystals appeared untwinned when viewed with a

petrographic microscope. The crystals were crushed using an agate mortar and pestle, and the fragments were placed onto holey carbon grids. The material was then examined with a JEOL 4000 EX transmission electron microscope operated at 400 keV. The small amount of material limited the data we could obtain. These problems were compounded by damage of MgSiO_3 perovskite in the electron beam. Radiation damage was also encountered in the study by Madon *et al.* (1980).

Selected-area electron diffraction (SAED) patterns

SAED patterns along the $[110]$ zone were obtained from different areas of two crystal fragments (Figs 1, 2). Streaking is absent in Fig. 1a, but Fig.

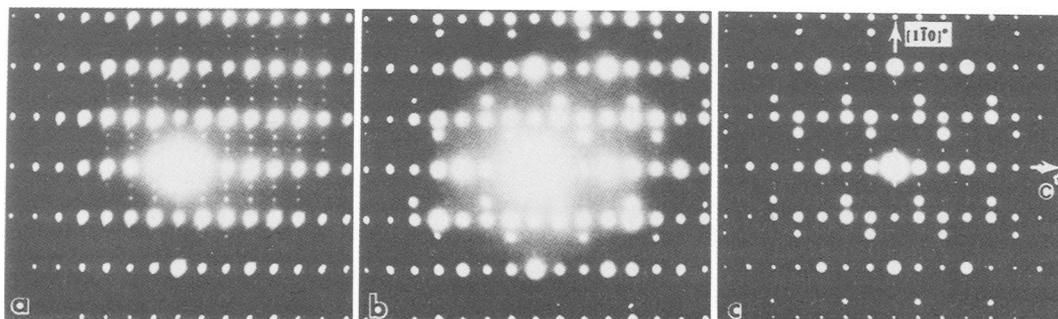


FIG. 2. $[110]$ -zone SAED patterns. (a) Satellite reflections give a 3-fold repeat along $[1\bar{1}0]^*$. (b) Two separate sets of main spots arising from an intergrowth. (c) Overlapping of patterns (a) and (b).

1b contains diffuse streaking along c^* . Figure 2a also shows well-developed satellite reflections that give a three-fold repeat along $[1\bar{1}0]^*$. In Fig. 2b, an extra set of spots occurs besides those in Fig. 1a. A combination of the spots from Figs 2a and b occurs in 2c. The main spots (substructure reflections) in Figs 1 and 2 are consistent with the known orthorhombic unit cell obtained by X-ray diffraction ($a = 4.775$, $b = 4.929$, $c = 6.897$ Å; space group $Pbnm$; e.g. Ito and Matsui, 1978; Horiuchi *et al.*, 1987). However, Fig. 3 cannot be indexed with this unit cell but requires an orthorhombic unit cell having dimensions double those given above; although the spacing of the spots along c^* is the same as that in Fig. 1, adjacent rows that are parallel to c^* are displaced by $\frac{1}{2}c_0^*$ requiring a doubling of the c -axis for the new cell. Figure 3, which is along the $[\bar{1}30]$ -zone axis, also contains continuous diffuse streaks along c^* (arrows). The streaks and satellite spots are readily lost by electron irradiation, indicating that they are associated with subtle features that require low energy for their destruction.

HRTEM images

The $[110]$ HRTEM images corresponding to the SAED patterns given above contain many distinctive features. Figure 4 shows a well-ordered region of crystal; the optical diffractogram (insert in Fig. 4) indicates that the image does not contain information about the satellite reflections in Fig. 2a, even though this pattern (Fig. 2a) was used to form the image. Attempts to image with the satellite reflections failed

because of their rapid disappearance in the electron beam.

Figure 5 shows fringe offsets parallel to the c direction (arrow). Such offsets are fairly abundant in some regions of crystal. They have not previously been observed in such high-pressure perovskites, and so they are of interest. We think they are out-of-phase boundaries, but the limited amount of material available for this study precluded definitive tests. These boundaries are not sufficiently periodic to give the satellite reflections.

Our identification of these features as out-of-phase boundaries is inferential and is based in large part on the elimination of alternative interpretations. In places of the image, the fringe displacements are parallel to the edges of the fragments, so that the offsets occur in small areas of constant thickness and therefore do not appear to arise from thickness variations. The optical diffractogram, obtained by passing a laser beam through the image negative, indicates that the crystal is well oriented, and so the illustrated offset does not arise from orientational effects. Since such offsets only occur in some fragments, they are not generated from thickness variations arising from radiation damage. The displacement of the fringes is about $\frac{1}{2}c_0$, so these boundaries could be antiphase domain boundaries

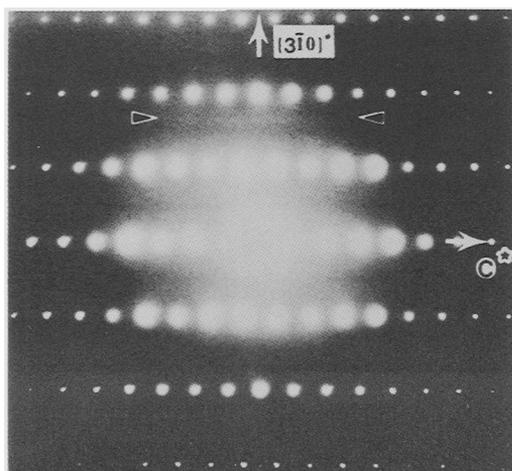


FIG. 3. $[\bar{1}30]$ -zone SAED pattern. This pattern is indexed with a doubled orthorhombic cell. Note the continuous, diffuse streaking parallel to c^* (arrows).

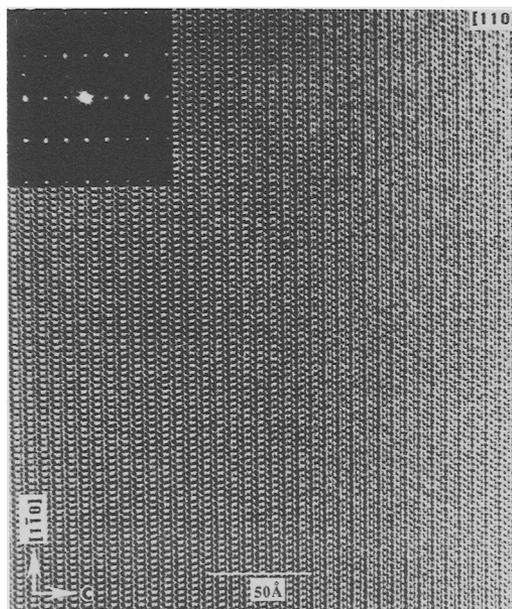


FIG. 4. $[110]$ image of MgSiO₃ perovskite. The crystal is well ordered and the optical diffractogram (insert) does not contain satellite reflections.

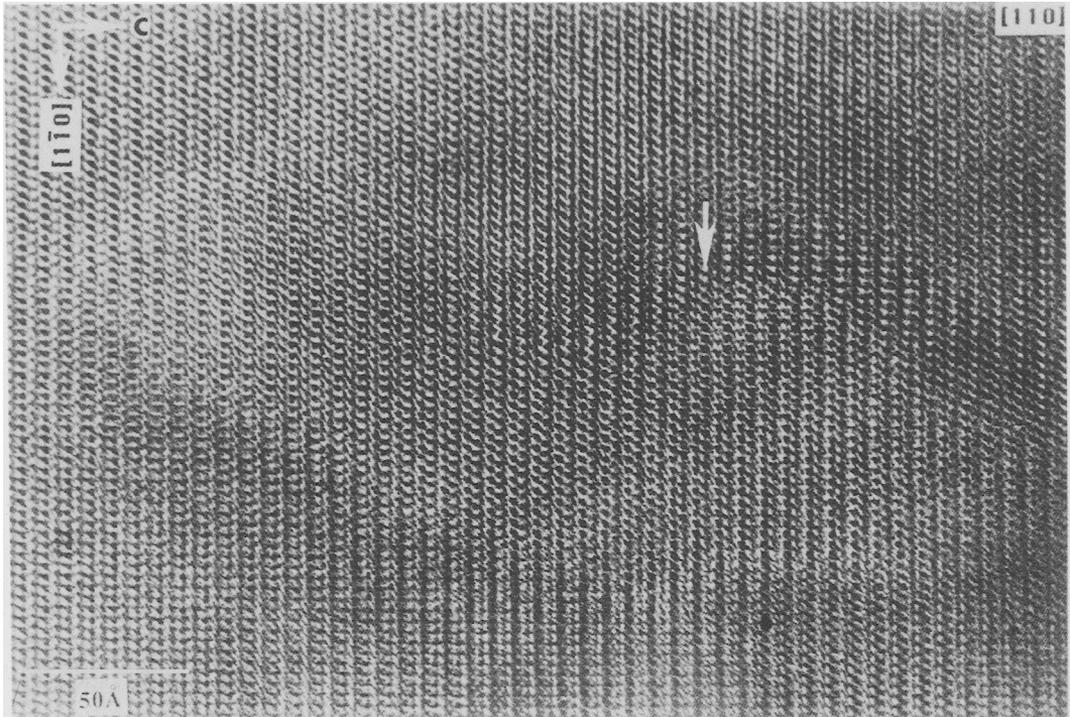


FIG. 5. [110] image. Presumed out-of-phase boundaries are observed as lateral shifts parallel to c of fringes that are perpendicular to c (arrow). The boundary has an ellipsoidal shape, with the long axis approximately parallel to c ; the enclosed ellipsoidal region has a lighter contrast relative to the surrounding areas. Such boundaries are common in some crystal fragments.

(APBs). Note that if the APBs are non-parallel with the incident electron beam, the offsets are not expected to be $\frac{1}{2}c_0$. These boundaries could arise from positional ordering of the Mg atoms if such atoms are displaced so that their environments are no longer symmetry equivalent. The boundaries would be analogous to the APBs in anorthite that arise from positional ordering of the Ca atoms (e.g. Van Tendeloo *et al.*, 1989). However, in the case of MgSiO_3 , the structure refinement (Horiuchi *et al.*, 1987) does not indicate positional ordering of the Mg atoms. It should be noted that $\frac{1}{2}c_0$ APBs were observed in CaTiO_3 perovskite (Wang and Liebermann, 1993).

The diffraction pattern in Fig. 2b was used to form the image in Fig. 6, which includes a central region (part b) that has a different orientation from the surrounding region (parts a). Drawings of the optical diffractograms from parts a and b are given in Fig. 6 (the experimental patterns contain too much diffuse scattering to make good illustrations). Overlapping of these two diffractograms yields the pattern of spots (a

+ b) shown at the bottom right of Fig. 6, which corresponds to the SAED pattern in Fig. 2b. The pattern corresponding to part a is along the $[\bar{1}\bar{1}0]$ zone of the regular perovskite cell, while that of part b is along the $[11, \bar{2}\bar{3}]$ zone of the doubled perovskite cell. For the intergrowth, c^* and $[\bar{1}\bar{1}0]^*$ of the regular perovskite cell (part a) are parallel, respectively, to $[\bar{1}\bar{2}\bar{5}]^*$ and $[254]^*$ of the doubled perovskite cell (part b). The boundaries between parts a and b are sharp (see bottom boundary), but they were somewhat enlarged by the electron radiation.

Discussion

This study indicates two types of orthorhombic unit cells; one is the same as that found by X-ray diffraction (e.g. Yagi *et al.*, 1978; Ito and Matsui, 1978), and the other has dimensions that are twice as large. The doubled cell is the same as that found by Madon *et al.* (1980). The two orthorhombic forms of perovskite are intergrown in one crystal fragment. Our results also show satellite reflections and diffuse

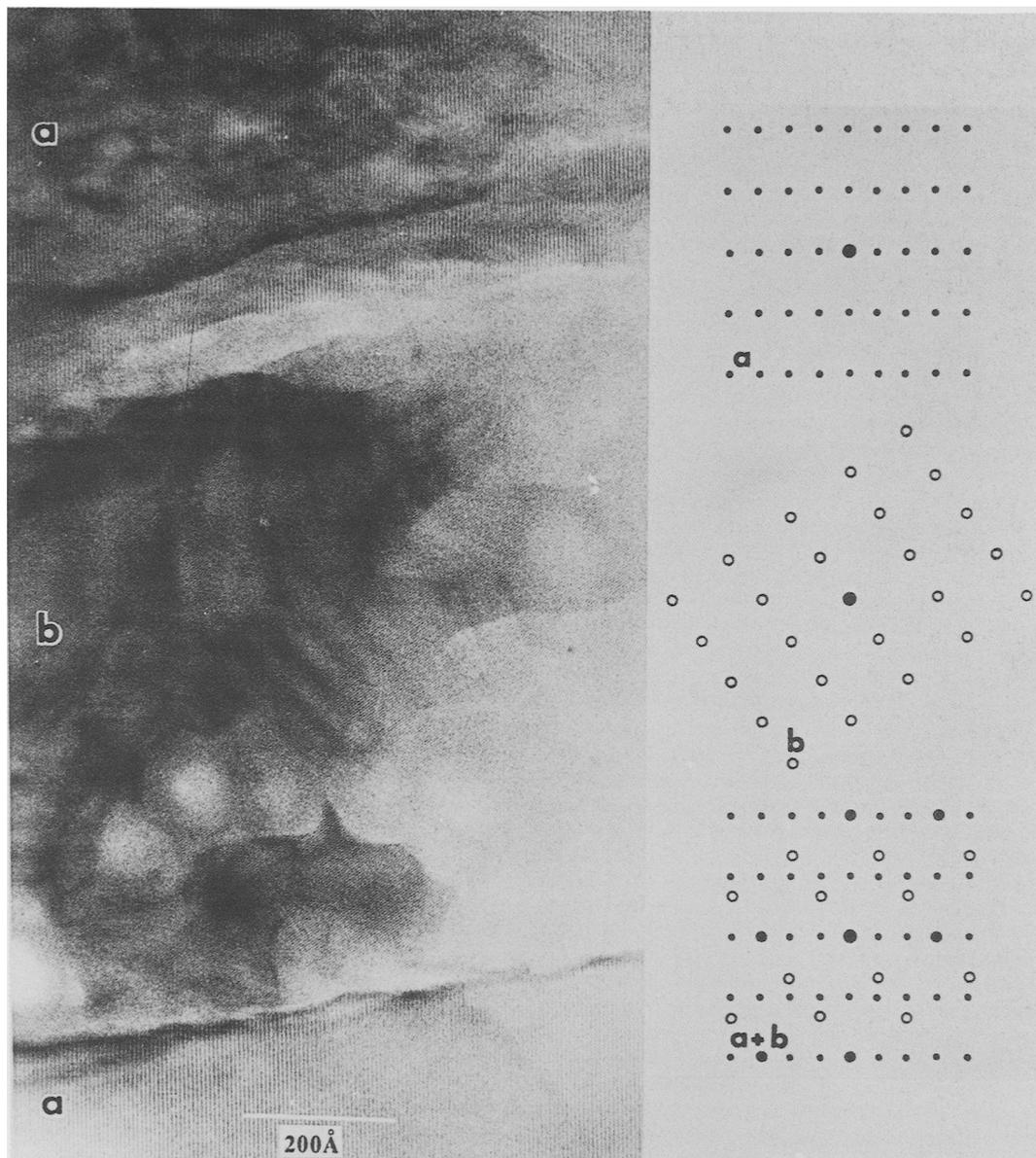


FIG. 6. TEM image showing an intergrowth of the two orthorhombic forms and schematic illustrations of their optical diffractograms. Area b of the image is surrounded by areas a to the top, bottom, and left (not shown). The schematic optical diffractograms (top two) were taken from areas a and b respectively; area a is along the $[110]$ zone of the normal orthorhombic cell, and area b is along the $[11,2\bar{3}]$ zone of the doubled cell. The bottom optical diffractogram shows the overlap from areas a and b (compare SAED pattern in Fig. 2b).

streaking in MgSiO₃ perovskite. The satellite reflections, which are easily destroyed by the electron beam, show a triple repeat along the

$[1\bar{1}0]^*$ direction, thus indicating the possibility of a commensurate superstructure for MgSiO₃ perovskite. However, other possibilities such as twinning or

lamellar intergrowths in two orientations, as in Fig. 6, cannot be ruled out although equal proportions of the two lamellae are required. Diffuse and continuous streaking also occur along c^* . The variability of the occurrence of the satellite reflections and the diffuse streaking indicate subtle variations in ordering, chemistry, or both.

Acknowledgements

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References

- Hassan, I., Kudoh, Y., Buseck, P.R. and Ito, E. (1988) MgSiO₃ Perovskite: a HRTEM Study. *EOS: Trans. Amer. Geophys. Union*, **69**, 1436.
- Hazen, R.M. (1988) AGU Chapman Conference on Perovskites. *EOS: Trans. Am. Geophys. Union*, **69**, 28.
- Horiuchi, H., Ito, E. and Weidner, D.J. (1987) MgSiO₃ (perovskite-type): single crystal X-ray diffraction study. *Amer. Mineral.*, **72**, 357–60.
- Ito, E. and Matsui, Y. (1978) Synthesis and crystal-chemical characterization of MgSiO₃ perovskite. *Earth Planet Sci. Lett.*, **38**, 443–50.
- Jeanloz, R. and Thompson, A.B. (1983) Phase transitions and mantle discontinuities. *Rev. Geophys. Space Sci.*, **21**, 51–74.
- Kudoh, Y., Ito, E. and Takeda, H. (1987) Effect of pressure on the crystal structure of perovskite-type MgSiO₃. *Phys. Chem. Minerals*, **14**, 350–4.
- Liu, L.G. (1974) Silicate perovskite from phase transformations of pyrope-garnet at high pressure and temperature. *Geophys. Res. Lett.*, **1**, 277–80.
- Liu, L.G. (1975) Post-oxide phases of fosterite and enstatite. *Geophys. Res. Lett.*, **2**, 417–9.
- Liu, L.G. (1979) Calculations of high-pressure phase transitions in the system MgO-SiO₂ and implications for mantle discontinuities. *Phys. Earth Planet Inter.*, **19**, 319–30.
- Madon, M., Bell, P.M., Mao, H.K. and Poirier, J.P. (1980) Transmission electron diffraction and microscopy of synthetic high pressure MgSiO₃ phase with perovskite structure. *Geophys. Res. Lett.*, **7**, 629–32.
- Reid, A.F. and Ringwood, A.E. (1975) High-pressure modification of ScAlO₃ and some geophysical implications. *J. Geophys. Res.*, **80**, 3363–70.
- Van Tendeloo, G., Ghose, S. and Amelinckx, S. (1989) A dynamical model for the $P\bar{1}-\bar{1}\bar{1}$ phase transition in anorthite, CaAl₂Si₂O₈. I. Evidence from electron microscopy. *Phys. Chem. Minerals*, **16**, 311–9.
- Wang, Y. and Liebermann, R.C. (1993) Electron microscopy study of domain structure due to phase transitions in natural perovskite. *Phys. Chem. Minerals*, **20**, 147–58.
- Yagi, T., Mao, H.K. and Bell, M. (1978) Structure and crystal chemistry of perovskite-type MgSiO₃. *Phys. Chem. Minerals*, **3**, 97–110.

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