LETTERS

A pressure-induced phase transition in MgSiO$_3$-rich garnet revealed by Raman spectroscopy

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Abstract

Raman spectra of two synthetic, noncubic garnet samples rich in MgSiO$_3$ component were measured in a diamond-anvil cell to 200 kbar at room temperature. Sample 1 was pure MgSiO$_3$ majorite; sample 2 was a solid solution with 93.4 mol% MgSiO$_3$ and 6.6 mol% Mg$_3$Al$_2$(SiO$_4$)$_3$. Although the X-ray patterns of both samples can be indexed assuming tetragonal symmetry, it cannot be completely ruled out that sample 2 is orthorhombic. High-pressure Raman spectra of sample 1 show a continuous shift of all bands to higher frequency with increasing pressure; there are no indications of phase transitions. Sample 2, however, undergoes a phase transition between 51 and 85 kbar on compression; this phase transition is completely reversible between 54 and 38 kbar on decompression. In the frequency range between 300 and 800 cm^{-1}, several bands that are present in the low-pressure phase disappear or merge in the high-pressure spectra, whereas some of the remaining bands intensify. The high-pressure spectrum of sample 2 is very similar to the room-pressure spectrum of sample 1. The phase transition could possibly be the result of a symmetry change from an orthorhombic to a tetragonal space group.

Introduction

Garnet containing large amounts of MgSiO$_3$ in solid solution was first obtained in high-pressure experiments by Ringwood and Major (1966). Pure MgSiO$_3$ garnet (majorite) was synthesied by Kato and Kumazawa (1985) and Sawamoto (1987), whereas a similar phase had been previously reported to occur in shock-metamorphosed meteorites (Mason et al. 1968). Garnet rich in majorite component was soon recognized to be an important constituent of the transition zone of the Earth's mantle (Ringwood 1967; Ito and Takahashi 1987; Sawamoto 1987). In the structure of majorite-rich garnet (Angel et al. 1989), two Al^{3+} ions that would normally fill the octahedral sites are replaced by Mg^{2+} and Si^{4+}. Accordingly, majorite contains both fourfold and sixfold-coordinated Si. Majorite samples synthesized in the laboratory are tetragonal at room temperature (*T*) and pressure (*P*), with space group *I*4$_1$/*a*. These crystals always contain polysynthetic twin lamellae, which suggests that the garnet was cubic at high *T* and *P* and acquired tetragonal symmetry because of Mg-Si ordering in the octahedral sites during cooling (Hatch and Ghose 1989; Wang et al. 1993). However, whether complete ordering occurred upon cooling is questionable (Angel et al. 1989).

Because of its importance as a major constituent of the Earth's mantle, the physical and thermodynamic properties of majorite have been intensively studied (Keppler and McCammon 1996; McMillan et al. 1989; Yagi et al. 1987). Obviously, a phase transition between a tetragonal and a cubic polymorph of majorite would strongly affect these properties. In the present study, we conducted a high-*P* Raman spectroscopic study of two noncubic, MgSiO$_3$-rich garnet samples to detect possible *P*-induced phase transformations.

Experimental methods

Garnet samples were synthesized in a multi-anvil apparatus using Re capsules, MgO as a pressure medium, and LaCrO$_3$ heaters. Fast isobaric quenching of samples was achieved by switching off the electrical power of the heater. Starting materials were glasses of the desired compositions. Experimental products were single-phase materials according to X-ray diffraction and optical examination. Pure MgSiO$_3$ majorite was synthesized at 196 kbar and 2000 °C with an experiment duration of 15 min. The product looked like a perfectly clear, millimeter-size single crystal filling the entire capsule. Upon opening the capsule, the sample even showed distinct rectangular
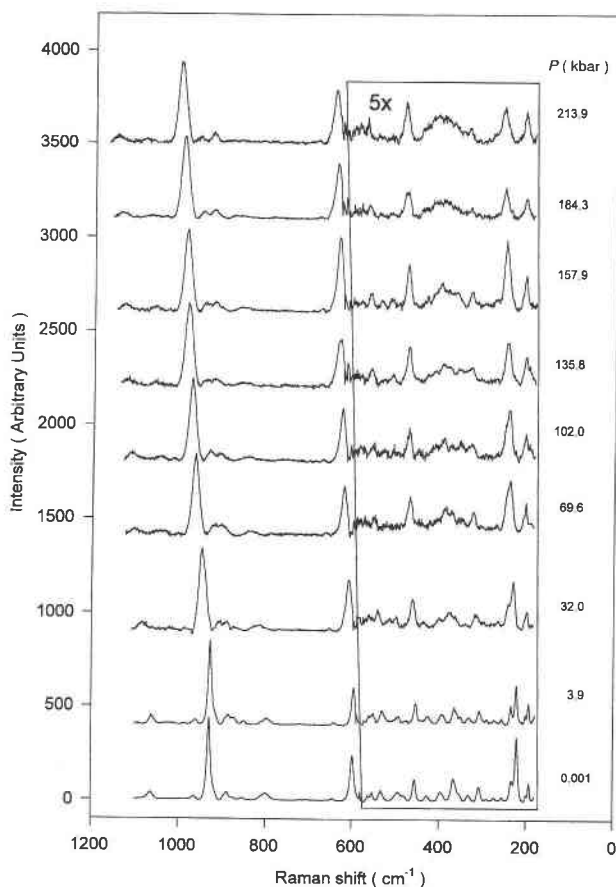
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FIGURE 1. High-*P* Raman spectra of MgSiO₃ majorite (sample 1). The spectrum at 1 atm was measured on a sample outside the diamond cell. The other spectra were obtained in the diamond cell with increasing pressure.

TABLE 1. Raman frequency shifts of MgSiO₃ majorite

Raman frequency ν_0 (cm^{-1})	$d\nu/dP$ (cm^{-1}/kbar)	$(1/\nu_0)(d\nu/dP)$ (10^{-3}/kbar)
196.1	0.092(4)	0.47(2)
200.0	0.072(6)	0.36(3)
222.0	0.198(6)	0.89(3)
233.9	0.125(8)	0.53(3)
255.2	0.19(2)	0.74(8)
273.2	0.169(6)	0.62(2)
307.9	0.173(9)	0.56(3)
332.4	0.217(8)	0.65(2)
354.9	0.205(8)	0.58(2)
365.9	0.26(1)	0.71(3)
396.6	0.27(1)	0.68(2)
427.8	0.21(2)	0.49(5)
456.4	0.162(6)	0.35(1)
493.6	0.144(5)	0.29(1)
515.8*	0.161(5)	0.31(1)
533.1	0.211(7)	0.40(1)
554.0	0.25(1)	0.45(2)
599.0	0.249(8)	0.42(1)
646.7	0.231(6)	0.357(9)
800.0	0.38(1)	0.47(1)
852.8	0.39(3)	0.46(3)
884.7	0.38(1)	0.43(1)
929.6	0.37(1)	0.40(1)
964.0	0.39(3)	0.40(3)
1064.7	0.41(1)	0.385(9)

Note: Estimated standard deviations are given in parentheses.
* Extrapolated to normal pressure, measured from 8.9 to 189.7 kbar.

parting. X-ray diffraction, however, proved that the sample was polycrystalline, with weak birefringence under the polarizing microscope. Lattice constants based on a tetragonal unit cell are $a = 11.5171(2)$ and $c = 11.4234(3)$ Å. A garnet sample with a composition of 93.4(1) mol% MgSiO₃ and 6.6(1) mol% Mg₃Al₂(SiO₄)₃ was synthesized at 190 kbar and 2000 °C in 3 min. This sample is polycrystalline with a grain size less than 50 μm. The composition was determined by electron microprobe analysis. Lattice constants, assuming tetragonal symmetry, are $a = 11.509(2)$ and $c = 11.442(3)$ Å. However, the possibility of this sample having symmetry lower than tetragonal cannot be ruled out, as discussed below.

High-*P* Raman spectra were collected using a Holzapfel-type diamond-anvil cell (Keller and Holzapfel 1977) equipped with low-fluorescence, type-IIa diamonds. The pressure medium was a 4:1 mixture of methanol and ethanol, containing small amounts of water. Main components of the home-built Raman spectrometer were a Coherent Innova 70 argon ion laser, a 0.6 m Spex 1877 triple monochromator, and a liquid-nitrogen–cooled Photometrix CCD camera. The monochromator contained a grating with a groove density of 1800 mm^{-1}. Raman spectra were excited using either the 514 or 488 nm lines of the argon laser. The angle between the incident laser beam entering the diamond cell and the scattered radiation reaching the triple monochromator was about 45°. The laser beam was focused on a spot with a diameter of 10 μm; laser power at the sample was 100 mW. The wavenumber resolution of the Raman spectrometer was 2 cm^{-1}. *P* was measured by ruby fluorescence with the use of the same spectrometer. The wavenumber scale of this system was calibrated before every measurement by recording the emission spectrum of a neon discharge lamp.

RESULTS AND DISCUSSION

High-*P* Raman spectra of pure MgSiO₃ majorite (sample 1) are shown in Figure 1. There is no evidence of any phase transformations up to 214 kbar. All bands shift to higher frequencies with increasing *P*. Within the limits of experimental uncertainty, the *P* dependence of band frequency is linear over the *P* range studied; frequency shifts for prominent bands are listed in Table 1. Aside from improvements in signal/noise ratio, the data in Figure 1 are similar to a room-*T* spectrum of majorite at 1 bar reported by McMillan et al. (1989) and a single high-*P* spectrum at 185 kbar reported by Böhler and Chopelas (1992). The small line width of the Raman bands (about 5 cm^{-1}) suggests essentially complete ordering of Mg and Si in the structure (McMillan et al. 1989).
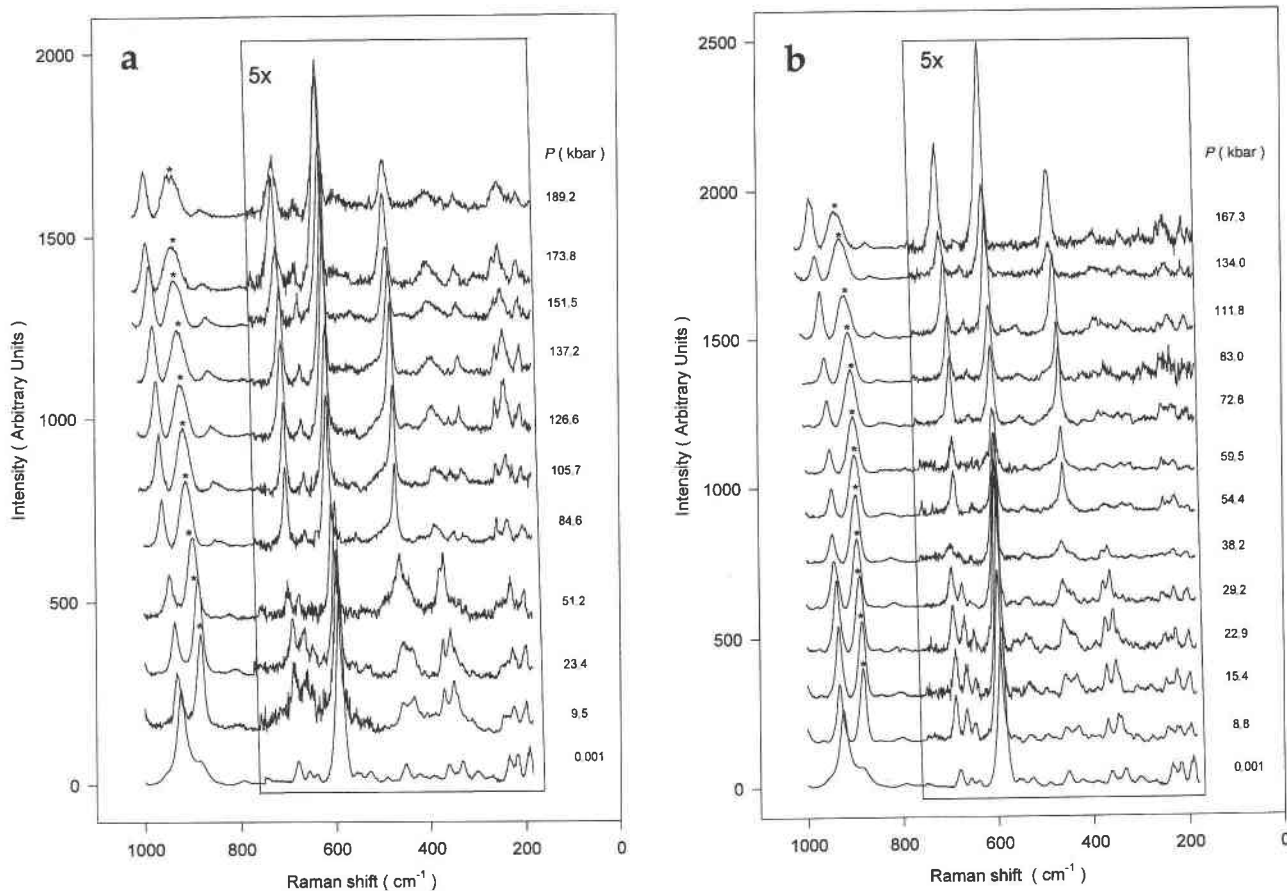
FIGURE 2. High-P Raman spectra of a garnet solid solution with 93.4 mol% $MgSiO_3$ and 6.6 mol% $Mg_3Al_2(SiO_4)_3$ (sample 2). (a) Spectra measured in diamond cell with increasing pressure; (b) spectra measured with decreasing pressure. Spectra at 1 atm were measured on a sample outside the diamond cell. Asterisk denotes a peak resulting from the methanol-ethanol pressure medium.

The fact that no phase transformation was observed upon compression of majorite to 214 kbar at room T does not necessarily imply that the tetragonal $I4_1/a$ structure is stable at the conditions of synthesis. Rather, a possible phase transformation may be too sluggish to be observed at 20 °C. Indeed, if this phase transformation involved disordering of Mg^{2+} and Si^{4+} in the octahedral sites (Hatch and Ghose 1989; Wang et al. 1993), the high activation energies required for Mg-Si exchange would make it extremely unlikely to occur at room T.

Garnet sample 2, which consists of a solid solution of 93.4 mol% majorite and 6.6 mol% pyrope, behaves very differently from pure $MgSiO_3$. The typical band widths of 11 cm⁻¹ are appreciably broader than those of pure majorite because of partial cation disorder induced by the presence of Al in the octahedral site. Upon compression, the Raman spectra showed clear evidence of a phase transition between 51.2 and 84.6 kbar (Fig. 2a); this phase transition is completely reversible between 54.4 and 38.2 kbar upon decompression (Fig. 2b). The transition is most clearly seen in the spectra in the ranges between about

600 and 700 cm⁻¹ and between 300 and 500 cm⁻¹. The room-P spectrum contains three well-resolved peaks between 600 and 700 cm⁻¹, at 644, 660, and 683 cm⁻¹ (Table 2). Above the phase-transition P, the 660 cm⁻¹ band disappears, whereas the 683 cm⁻¹ band intensifies. According to McMillan et al. (1989), the bands around 600 cm⁻¹ could be due to Si-O-Si bending vibrations; however, an unambiguous assignment is not possible. The most interesting changes in the spectra occur among the lattice vibrations between 300 and 500 cm⁻¹. There are two doublets of bands in the room-P spectrum that appear to merge just at the phase-transformation P: 335, 363 cm⁻¹, and 395, 454 cm⁻¹. Inspection of Table 2 shows that these pairs of bands merge because one band in each pair has an exceptionally large P shift, more than twice the value of all other bands: The 335 cm⁻¹ band has $d\nu/dP = 0.68$ cm⁻¹/kbar, and the 395 cm⁻¹ band has $d\nu/dP = 0.64$ cm⁻¹/kbar; the latter value may have larger systematic errors because of the broadness of the band. If one assumes that the phase transition occurs exactly at the pressure where the 335 and 363 cm⁻¹ bands merge,

TABLE 2. Raman frequency shifts of garnet solid solution with 93.4 mol% $MgSiO_3$ and 6.6 mol% $Mg_3Al_2(SiO_4)_3$

Raman frequency ν_0 (cm⁻¹)	$d\nu/dP$ (cm⁻¹/kbar)	$(1/\nu_0)(d\nu/dP)$ (10^{-3}/kbar)
196.8	0.101(7)	0.51(4)
219.8	0.192(5)	0.87(2)
236.8	0.16(2)	0.68(8)
272.9	0.14(2)	0.51(7)
303.0	0.22(1)	0.73(3)
331.0*	0.26(3)	0.78(9)
335.1	0.68(7)	2.0(2)
363.0	0.21(1)	0.58(3)
388.2**	0.32(5)	0.8(1)
394.7	0.64(9)	1.6(2)
453.9	0.235(5)	0.52(1)
528.1	0.36(2)	0.68(4)
593.1	0.239(6)	0.40(1)
644.8	0.223(8)	0.35(1)
660.1	0.27(5)	0.41(8)
683.5	0.261(8)	0.38(1)
792.8	0.46(2)	0.58(2)
888.8	0.33(1)	0.37(1)
926.6	0.373(7)	0.402(7)

Note: Estimated standard deviations are given in parentheses.
* Extrapolated to normal pressure, measured from 22.9 to 189.2 kbar.
** Extrapolated to normal pressure, measured from 8.8 to 189.2 kbar.

one can calculate from the measured values of dν/dP that the transition P is 59 kbar, in good agreement with the observation. Above the phase-transition P, there are again strong changes in band intensities in the range between 300 and 500 cm⁻¹.

The observed behavior of bands merging at the phase-transition P suggests a second-order, displacive phase transformation. It is interesting that aside from one additional band near 700 cm⁻¹, the high-P spectrum of the garnet solid solution (sample 2, Fig. 2) is actually almost identical to the spectrum of pure majorite (sample 1, Fig. 1). This suggests that the high-P phase of sample 2 probably has the tetragonal $I4_1/a$ structure. Because there are additional bands in the Raman spectrum of the low-P phase, it should have lower symmetry. In the present sample, no splittings of X-ray reflections indicating symmetry lower than tetragonal were observed; however, these splittings may simply be too small to be detected. Accordingly, it is possible that what is observed in the spectra in Figure 2 is actually a P-induced displacive phase transformation between an orthorhombic and a tetragonal garnet structure. The precise nature of this phase transition, however, remains unknown.

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