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LETTER

High-temperature behavior of metastable $MgSiO_3$ perovskite: A Raman spectroscopic study

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ABSTRACT

The thermal behavior of metastable magnesium silicate ($MgSiO_3$) perovskite has been investigated with Raman spectroscopy at ambient pressure. No evidence for previously predicted high-temperature crystal phase transformations or soft mode behavior is observed. Thermally induced vitrification of the perovskite to an amorphous phase with Si in tetrahedral coordination begins near 400 K and is complete by 750 K. Irreversible frequency shifts of the perovskite Raman bands accompany the vitrification. Residual Raman shifts of samples thermally cycled into the vitrification region indicate a contraction of the perovskite lattice of up to 0.5% in volume. This implies that structural and thermoelastic properties of silicate perovskite measured outside its thermodynamic stability field may not represent true metastable equilibrium values but may include irreversible contributions arising from the thermally induced transition from crystal to amorphous.

INTRODUCTION

Crucial to an understanding of the dynamic processes of the Earth's interior is an accurate characterization of the structural and dynamic stabilities of Mg-rich silicate perovskites, believed to dominate the mineral assemblage of the Earth's lower mantle (Knittle and Jeanloz, 1987). Magnesium silicate ($MgSiO_3$) crystallizes in a perovskite structure at pressures above about 23 GPa, corresponding to a depth greater than 650 km in the Earth's mantle. This high-pressure phase is metastable at ambient conditions and exists in an orthorhombic $GdFeO_3$-type structure (space group *Pbnm*) (Yagi et al., 1978; Horiuchi et al., 1987), a modification of ideal cubic perovskite through combined tilts and distortions of SiO_6 octahedra.

Theoretical lattice-dynamic studies have led to the controversial suggestion that orthorhombic $MgSiO_3$ perovskite undergoes antiferro-distortive transformations to higher symmetry tetragonal and ultimately cubic polymorphs at elevated temperatures because of a critical softening of vibrational modes associated with rotations of the SiO_6 octahedra (Wolf and Bukowinski, 1985, 1987). Of important geodynamical relevance is that, if transitions of this type do occur within the silicate perovskite phase of the Earth's mantle, they could have a significant influence on the seismic shear wave velocities and attenuation (which place strong constraints on mantle composition models), as well as on a number of thermal properties (i.e., thermal expansivity) that critically influence the convective processes within the mantle (Wolf and Bukowinski, 1985, 1987; Bukowinski and Wolf, 1988).

We have investigated the vibrational properties of $MgSiO_3$ perovskite as a function of temperature at ambient pressure using Raman spectroscopy. Raman scattering, a sensitive probe of symmetry changes, has been extensively employed in the study of distortive phase transformations in perovskite compounds. These transitions are principally driven by soft vibrational modes that are Raman active in the lower symmetry (low-temperature) phase and that approach zero frequency at the critical transition temperature.

RESULTS AND DISCUSSION

Raman spectra of $MgSiO_3$ perovskite synthesized in a multiple anvil press at 25 GPa and 1973 K were obtained with the micro-Raman system described by Durben et al. (1991). At least 11 Raman active modes can be resolved in the Raman spectrum of $MgSiO_3$ perovskite between 200 and 700 cm^{-1} (Fig. 1). The two low-frequency modes at 249 and 282 cm^{-1} have been assigned as the A_g modes related to octahedral tilting vibrations (Williams et al., 1987; Zimmerman and Wolf, unpublished data) typically associated with antiferro-distortive transitions in *Pbnm* perovskites. The weak modes resolved at 254, 338, 343, 392, and 666 cm^{-1} were not resolved in any previous Raman study of $MgSiO_3$ perovskite (Hemley et al., 1989; Williams et al., 1987). No additional modes were observed at lower frequencies (to 10 cm^{-1}), and only weak,

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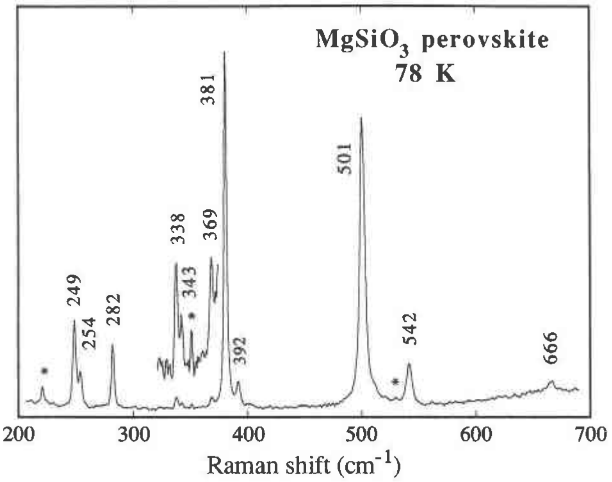

Fig. 1. The polarized (HH) Raman spectrum of polycrystalline $MgSiO_3$ perovskite at 78 K. Raman frequency shifts were calibrated against 488-nm Ar^+ laser plasma lines, indicated by asterisks, and are accurate to within less than 1 cm^{-1}.

broad glass bands were observed at higher frequencies (to 1500 cm^{-1}).

Upon heating at ambient pressure, the two low-frequency A_g modes (at 249 and 254 cm^{-1} in Fig. 1) show almost no temperature dependence, whereas all the other modes decrease slightly in frequency (Fig. 2). The unusually small temperature derivatives, on the order of -1 cm^{-1}/100 K, are consistent with highly harmonic vibrational modes and little change in the octahedral tilt angles with temperature. There is no indication in the Raman spectra of soft mode behavior nor evidence for any symmetry breaking transformations in $MgSiO_3$ perovskite to at least 700 K.

The Raman spectra, however, do reveal a gradual vitrification of $MgSiO_3$ perovskite with increasing temperature. An onset of this disordering is evident at temperatures as low as 400 K and is marked by a decrease in the intensity of the crystal bands and the emergence of two broad bands centered near 650 and 980 cm^{-1}. The emergence of these bands is consistent with formation of metasilicate $MgSiO_3$ glass, where Si is in tetrahedral coordination (Kubicki et al., 1992). Although the abundance of glass increases rapidly above 400 K, sufficient long-range order (~50 Å) must be maintained to at least 573 K to retain the sharp crystalline Raman bands displayed. At higher temperatures the perovskite bands rapidly lose intensity and cannot be detected above 750 K (nor can they be detected at ambient conditions in samples thermally cycled above 750 K).

When $MgSiO_3$ perovskite is thermally cycled to a peak temperature below 700 K, the Raman spectrum of the recovered sample at ambient temperature indicates a mixture of well-preserved perovskite and tetrahedral chain metasilicate glass (Fig. 3). It is interesting to note that the Raman bands are not broadened by thermal cycling. However, the crystal bands of samples thermally cycled into the vitrification transition region exhibit a strong residual shift to higher frequencies relative to their initial ambient frequencies. The direction of these residual Raman shifts suggests that the perovskite crystal lattice of thermally cycled samples is contracted relative to that of unheated samples.

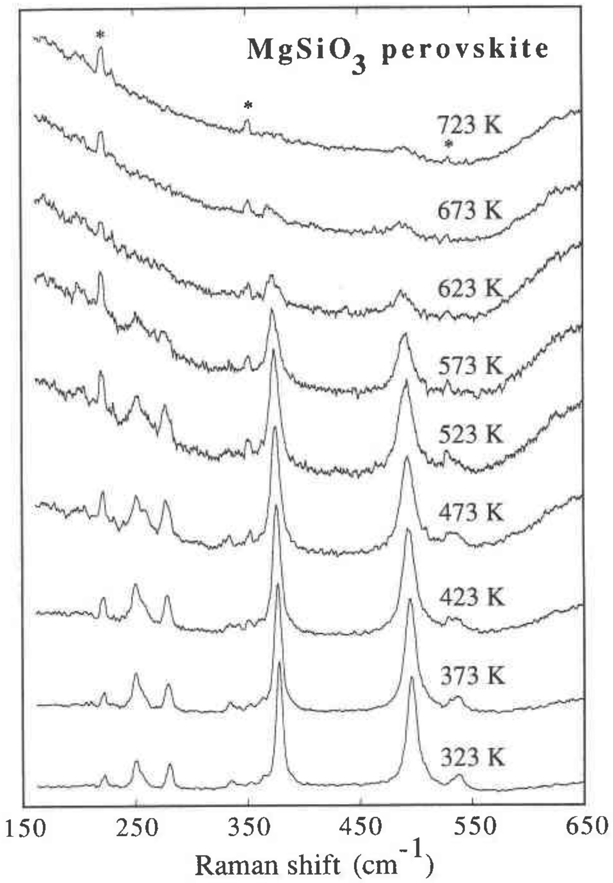

Fig. 2. The in situ Raman spectrum of $MgSiO_3$ perovskite as a function of temperature. There is no evidence of soft mode behavior to 700 K. The early onset of vitrification is indicated by the increase with temperature in the intensity of the broad metasilicate glass band centered near 650 cm^{-1}. Perovskite bands could not be resolved above 750 K. Ar^+ laser plasma lines are indicated by asterisks in the 723-K spectrum.

The residual frequency shifts observed in thermally cycled $MgSiO_3$ perovskite samples are similar to that produced by hydrostatic pressure and can be quantitatively correlated to lattice contraction through available data on the pressure dependence of the mode frequencies (Hemley et al., 1989) and the equation of state. For example, in the $MgSiO_3$ perovskite sample represented in Figure 3, which was thermally cycled to 573 K, the direction and magnitude of the residual frequency shifts indicate a 0.5% contraction of the lattice volume (Table 1). This residual volume contraction is equivalent to that which would be produced by a hydrostatic pressure of about 1.3 GPa.

The irreversible frequency shift in the Raman bands of

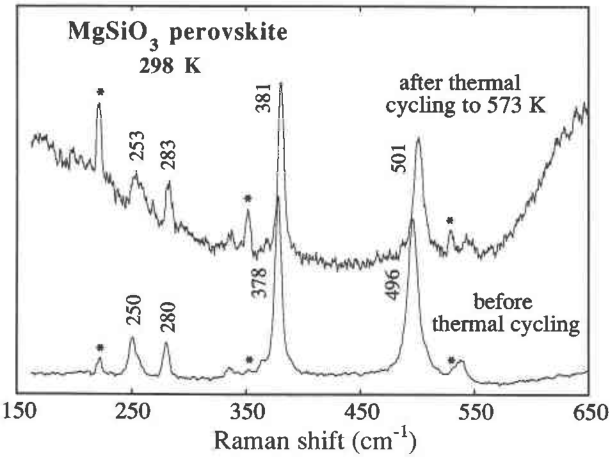

Fig. 3. The ambient Raman spectrum of a $MgSiO_3$ perovskite sample before and after thermal cycling to 573 K. The spectrum of the thermally cycled sample indicates an assemblage of perovskite and low-density chain metasilicate glass. All of the perovskite bands exhibit a residual positive frequency shift upon thermal cycling, indicating an irreversible contraction of the crystal lattice upon thermal cycling. Ar^+ laser plasma lines are indicated by asterisks.

Table 1. Residual Raman frequency shifts and irreversible lattice contraction in $MgSiO_3$ perovskite cycled to 573 K

Raman shift ν (cm^{-1}) at 298 K				
Before thermal cycling	Thermally cycled to 573 K	$\Delta\nu$ (cm^{-1})	$d\nu/dP$* (cm^{-1}/GPa)	$\Delta V/V_0$ (%)**
250.0	253.2	3.2	2.9	0.43
279.8	282.4	2.6	1.7	0.58
377.7	380.7	3.0	2.4	0.48
495.6	501.2	5.6	4.2	0.51
			mean $\Delta V/V_0$ = 0.50%	

Note: The residual frequency shifts ($\Delta\nu$) and mode pressure derivatives ($d\nu/dP$) indicate a contraction in the crystal lattice volume ($\Delta V/V_0$) of about 0.5%.

* From Hemley et al. (1989).

** Calculated using the bulk modulus K_0 = 261 GPa (Mao et al., 1991).

metastable $MgSiO_3$ perovskite clearly accompanies the thermally induced glass formation. One possible interpretation for the residual Raman shifts is that volume expansion associated with glass formation could produce an internal transformation stress in the crystalline perovskite phase, provided the vitreous phase is homogeneously nucleated throughout the sample. As suggested by the Raman data, the amorphous phase resulting from the thermal vitrification is structurally related to a tetrahedral chain metasilicate glass and thus has a density approximately 30% lower than that of the perovskite phase. Because of the low temperature of the crystal to amorphous transition compared with the normal liquid-glass transition temperature of $MgSiO_3$ perovskite (~1065 K) (Richet and Bottinga, 1986), the transformation stress would not fully relax over the time scales of the experiment (10^2–10^4 s). We note, however, that it is not presently possible to quantify the transformation stress without further information on the mechanism of the phase transformation and its nucleation process.

Other mechanisms for the irreversible Raman frequency shifts in metastable $MgSiO_3$ perovskite are possible. One is a gradual build-up of defects in the crystal with increasing temperature, although it is not clear how these low-density defects produce a contraction of the perovskite lattice. Alternatively, a chemical decomposition of the perovskite could result in an MgO- or SiO_2-deficient perovskite phase, which would be contracted relative to the stoichiometric phase. However, it is difficult to rationalize a spinodal chemical decomposition of this type because of the extremely low atomic mobilities that would be expected at such a low transformation temperature.

The irreversible behavior of the Raman modes suggests that the thermal path followed by $MgSiO_3$ perovskite is no longer a strict thermodynamic isobar once the crystal is heated into the crystal to amorphous transition region. One manifestation of this may be the small temperature derivatives measured for the Raman mode frequencies measured for $MgSiO_3$ perovskite. For comparison, the temperature derivatives of the Raman mode frequencies measured for $MgSiO_3$ perovskite are only about one-third of that observed for the isotypic $CaGeO_3$ perovskite (Durben et al., 1991). The smaller temperature derivatives of the mode frequencies in $MgSiO_3$ perovskite would be expected because of the lower thermal expansion of $MgSiO_3$ perovskite compared with that of $CaGeO_3$ perovskite (Knittle et al., 1986; Liu et al., 1991). This reduced thermal expansivity in $MgSiO_3$ perovskite may partly arise from the contribution of the residual contraction in the lattice, associated with the thermally induced vitrification, which is absent in $CaGeO_3$ perovskite. By compensating for this residual lattice contraction through reducing the $MgSiO_3$ perovskite Raman measurements to an ambient pressure isobar, comparable temperature derivatives of the mode frequencies for $MgSiO_3$ and $CaGeO_3$ perovskite are obtained.

CONCLUSIONS

The Raman spectrum of metastable $MgSiO_3$ perovskite has been measured as a function of temperature (278–750 K) at ambient pressure. The Raman data indicate that phase transformations of the anti-ferro-distortive type do not occur over this temperature range. Moreover, there is no evidence for soft mode behavior up to 700 K. At temperatures above 400 K, $MgSiO_3$ perovskite undergoes a direct crystal to amorphous transformation, to a lower density metasilicate glass where Si is in tetrahedral coordination. Vitrification is complete by 750 K. The relatively low temperatures at which $MgSiO_3$ perovskite vitrifies at ambient pressure suggest that the crystal to amorphous transformation may be driven by an underlying instability of the crystal lattice to some strain or chemical fluctuation that marks the extreme limit of metastability of the crystal lattice (Wolf et al., 1992).

The low-temperature vitrification of $MgSiO_3$ perovskite results in a departure from the isobaric thermodynamic path, causing irreversible behavior above 400 K. Thermally cycling $MgSiO_3$ perovskite into the region of the crystal to amorphous transition generates an irreversible contraction of the perovskite lattice, of up to 0.5%, clearly indicated by residual frequency shifts in the ambient Raman spectrum. This irreversible residual volume change is comparable in magnitude (although opposite in sign) to the thermal expansion of $MgSiO_3$ perovskite measured over the same temperature interval and is equivalent to that which would be generated by hydrostatic pressures as high as 1.3 GPa. Thus, the irreversible thermal behavior of $MgSiO_3$ perovskite can have a significant effect on thermoelastic properties, underscoring the importance of characterizing this behavior when determining the properties of $MgSiO_3$ perovskite from measurements that are made at conditions well outside its thermodynamic stability field.

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