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LETTERS

Elasticity of $MgSiO_3$ orthoenstatite

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ABSTRACT

The single-crystal elastic moduli of the $MgSiO_3$ orthoenstatite end-member have been measured by Brillouin spectroscopy at ambient conditions. The aggregate elastic moduli at 1 atm are K_S = 107.6(15) GPa and μ = 76.8(7) GPa, for the adiabatic bulk modulus and shear modulus, respectively. These values are in excellent agreement with the results of previous acoustic studies of synthetic $MgSiO_3$. Comparison of our results with pressure-volume (*P-V*) measurements do not support the presence of a change in the *P-V* trajectory of orthoenstatite at ~4 GPa, as suggested previously on the basis of X-ray measurements to 8.5 GPa. The effects of chemical composition on the elasticity of orthopyroxenes are well represented by the variation of compressional and shear velocities with density, which exhibit well defined trends for both synthetic and natural samples.

INTRODUCTION

Orthopyroxene (Opx), with a simplified formula of $(Mg,Fe)SiO_3$, is an abundant mineral in mafic rocks of the crust and is a major constituent of all proposed models of upper mantle mineralogy to a depth of ~500 km. Knowledge of the elastic properties of orthopyroxenes, is therefore important for constraining mantle mineralogy through comparisons of seismic velocities with laboratory measurements of velocities and elastic properties. In addition, the elastic properties of end-member phases provide a baseline for assessing the effects of compositional variations on the elastic properties of solid solutions. This is especially true for the Mg end-member Opx, enstatite, because the compositions of most orthopyroxenes are dominated by the $MgSiO_3$ component.

Although the elastic moduli of Mg-rich Opx with up to 20% Fe have been measured previously, substantial uncertainties still exist. In particular, values reported for the bulk modulus of $MgSiO_3$ range from an isothermal K_T = 95.8(30) GPa (Hugh-Jones and Angel 1994a), to K_S = 107.8 GPa for the adiabatic bulk modulus (Weidner et al. 1978). It is unlikely that this 12% spread in values is due to the difference between isothermal and adiabatic measurements. Given the large uncertainty in *K* for end-member enstatite, it is presently not possible to identify the effects of chemical composition on the elasticity of Opx. In particular, the lowermost value of K_T = 95.8 GPa is significantly smaller than typical values of K_T for orthopyroxene solid solutions. This would imply that small (<1%) concentrations of elements such as Ca and Al may have major effects on the elasticity of Opx solid solutions close to the $MgSiO_3$-$FeSiO_3$ join (Hugh-Jones and Angel 1997). Chemical composition is not observed to have such a drastic effect on elastic properties in other mineral systems; if such effects can be verified they would be unique to Opx. To resolve discrepancies in the elasticity data base and further our understanding of elasticity-composition relationships for Opx, we performed Brillouin scattering measurements of sound velocities and elastic moduli on synthetic single crystals of $MgSiO_3$ orthoenstatite.

EXPERIMENTAL PROCEDURES

The orthoenstatite (OEN) samples used in this experiment are nearly pure $MgSiO_3$ with trace amounts of Li and V (<0.25 wt%) from the flux growth in lithiumvanadomolybdate (Ito 1975). The crystals were kindly provided by G. Rossman (Sample GRR 259). Lattice parameters were measured on a four-circle X-ray diffractometer, and from these the density was calculated (Table 1). Refractive indices were measured with a spindle stage at ~589 nm and ~514.5 nm wavelengths using index-matching fluids. The lattice parameters and refractive indices agree with literature values for pure orthoenstatite (Deer et al. 1997; Ito 1975; Cameron and Papike 1980).

The as-grown euhedral samples exhibited {010}, {100}, and {210} growth faces, and in addition to these {001} surfaces were ground and polished. Each sample was oriented with a four-circle X-ray diffractometer, and then transferred to a three-circle Eulerian cradle which is used to control the sample orientation on the Brillouin system. The orientation of each crystal was verified by optical goniometry and is believed to be accurate to within less than one degree. Any desired phonon direction can be chosen by appropriate choice of settings on the three-circle cradle.

In the Brillouin experiments a 90° scattering geometry was used, with an argon laser (λ = 514.5 nm) as the light source. The scattered light was analyzed by a tandem 6-pass Fabry-Perot interferometer and photon counting electronics (Bass 1989; Sinogeikin et al. 1998). Most spectra were collected in

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TABLE 1. Elasticity of orthoenstatite from acoustic experiments

	This Study	Weidner et al. (1978)	Flesch et al. (1998)
C_{11}, GPa	233(1)	224.7(23)	
C_{22}, GPa	171(1)	177.9(22)	
C_{33}, GPa	216(1)	213.6(36)	
C_{44}, GPa	83(1)	77.6(19)	
C_{55}, GPa	79(1)	75.9(11)	
C_{66}, GPa	77(1)	81.6(16)	
C_{12}, GPa	73(2)	72.4(42)	
C_{13}, GPa	56(2)	54.1(110)	
C_{23}, GPa	50(3)	52.7(46)	
ρ, g/cm^3	3.194(6)	3.204	3.18(3)
$K_{S,VRH}$, GPa	107.6(15)	107.8	104(2)
μ_{VRH}, GPa	76.8(7)	75.7	74.9(15)
V_P, km/s	8.11	8.07	8.00
V_S, km/s	4.90	4.86	4.85

Notes: Uncertainties reported here are 1 standard deviation based on an RMS deviation of 0.056 km/s.

air, but some were collected with the crystal immersed in an index-matching fluid (n = 1.524 at 514.5 nm) to minimize refraction and elastically scattered light. Refraction effects were accounted for in calculating phonon directions (Vaughan and Bass 1983).

RESULTS

Brillouin scattering spectra were collected in 53 distinct crystallographic directions (Fig. 1). At least two separate spectra were collected for each direction. In most directions both longitudinal and shear velocities were obtained, and in several directions two shear modes were well resolved (Fig. 1). The final data set consisted of 113 independent mode velocities. Most of the data were collected within or close to the (100), (010), and (001) crystallographic planes so that the on-diagonal elastic moduli are well constrained and highly independent of one another. A linear inversion technique was used to calculate a best-fit model of single-crystal elastic moduli, C_{ij}, from the velocity data (Weidner and Carlton 1977).

The only other single-crystal acoustic measurements on orthoenstatite are those reported by Weidner et al. (1978), which were performed on a nominally identical sample (also synthesized by J. Ito). A comparison with our results (Table 1) shows that nearly all of the C_{ij} values from the two studies agree within their mutual uncertainties at the two standard deviation (2σ) level. It is worth noting that although the results of Weidner et al. (1978) represent one of the first Brillouin studies from that laboratory, and the velocities were not corrected for refraction effects, their results are confirmed to be valid. However, the present results supersede those of Weidner et al. (1978), because our data set is over twice as large, and refraction corrections were applied. Isotropic aggregate properties [K_S, μ, longitudinal velocity (V_P), and shear velocity (V_S)] were calculated using the Hill averaging scheme, and show yet closer agreement between our results and those of Weidner et al. (1978): the values of K_S, μ, V_P, and V_S all agree within 1σ (Table 1). Both studies agree with ultrasonic velocities measured on the same samples (Weidner et al. 1978), indicating that velocity dispersion and relaxation are not significant at room temperature (~298 K). The accuracy of the single-crystal Brillouin measurements is further supported by a recent study of the sound velocities of hot-pressed polycrystalline $MgSiO_3$ orthoenstatite to 10 GPa by Flesch et al. (1998), whose reported elastic moduli agree with our results (Table 1).

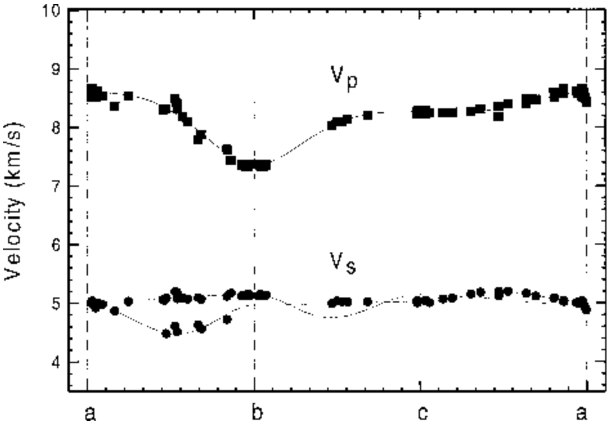

FIGURE 1. Acoustic velocities of orthoenstatite (solid symbols) as a function of crystallographic direction, projected on the *a-b, b-c, a-c* planes. The best-fit acoustic velocity model is shown by solid lines. Error bars are smaller than the symbols.

TABLE 2. Bulk modulus of $MgSiO_3$ orthoenstatite

Reference	$K_{S,V}$* (GPa)	$K_{S,R}$† (GPa)	K_T (GPa)
This Study	108.6(10)	106.6(10)	105.5(20)§
Weidner et al. 1978	108	107	105.9§
Hugh-Jones and Angel 1994‡ (to 4 GPa)			95.8(30)
Hugh-Jones and Angel 1994‡ (to 8.5 GPa)			103.1(19)
Zhao et al. 1995‡			102.8(2)

*Voigt bound.
†Reuss bound.
‡Static compression.
§Acoustically determined values, corrected to isothermal conditions using $K_S = K_T(1+\alpha\gamma T)$, α=32.2 × 10^{-6} K^{-1} (Hugh-Jones 1997), γ=1.05 (Zhao et al. 1995), and T = 300 K. For Brillouin experiments, K_T was calculated using the Reuss bound on the bulk modulus.

DISCUSSION

The P-V equation of state of orthoenstatite has been measured in several studies by static compression of samples in a diamond-anvil high-pressure cell (DAC), yielding values of K_T and its pressure derivative K'_T (Hugh-Jones and Angel 1994a; Zhao et al. 1995). To compare the bulk moduli from compression and acoustic experiments, one must use the Reuss value ($K_{S,R}$) of the bulk modulus calculated from the single-crystal moduli to match the stress conditions in the DAC experiment. Values of $K_{S,R}$ are then corrected to isothermal conditions through the equation $K_S = K_T(1+\alpha\gamma T)$, where α is the volume thermal expansivity, and γ is the thermal Gruneisen parameter. Values of K_T calculated from the Brillouin results are in Table 2. The adiabatic-isothermal corrections amount to ~1%, which is on the order of the experimental uncertainties.

Hugh-Jones and Angel (1994a, 1994b) reported K_T of 95.8(30) GPa for orthoenstatite which differs from our results by 10% (Table 1). These authors further suggested that pure

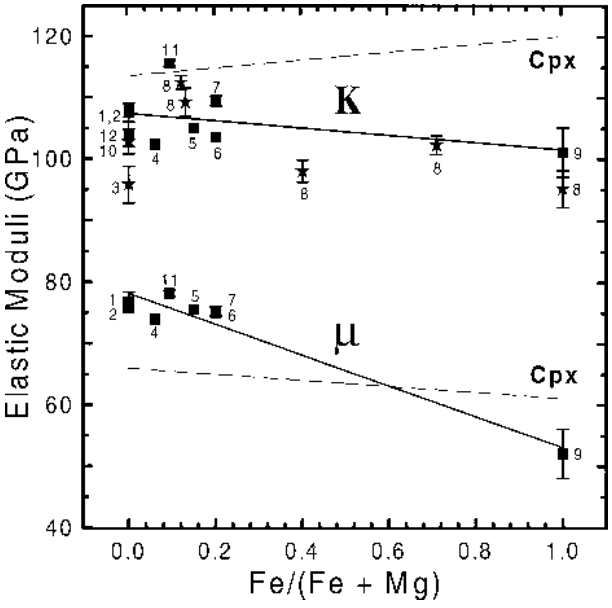

FIGURE 2. Aggregate elastic moduli of orthopyroxenes. Dashed lines indicate clinopyroxene trends defined by the diopside-hedenbergite solid solution series (Aleksandrov et al. 1964; Levien et al. 1979; Kandelin and Weidner 1988). The results of this experiment are plotted along with previous acoustic (squares) and compression (stars) results for the enstatite-ferrosilite solid solution series. Sources of data: 1 = This study; 2 = Weidner et al. 1978; 3 = Hugh-Jones and Angel 1994a; 4 = Duffy and Vaughan 1988; 5 = Kumazawa 1969; 6 = Frisillo and Barsch 1972; 7 = Webb and Jackson 1993; 8 = Hugh-Jones and Angel 1997; 9 = Bass and Weidner 1984; 10 = Zhao et al. 1995; 11 = Chai et al. 199; 12 = Flesch et al. 1998.

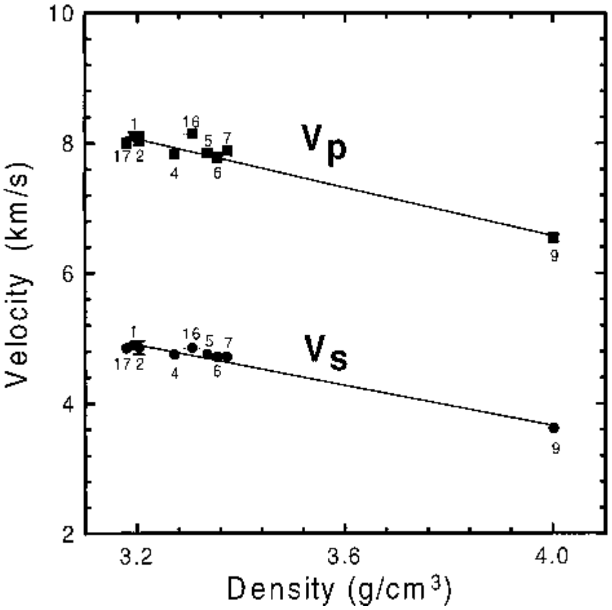

FIGURE 3. Compressional (V_P) and shear (V_S) velocities from this experiment and other acoustic measurements for the enstatite-ferrosilite solid solution series. Both V_P and V_S decrease linearly as density increases (Birch 1961). Sources of data are as in Figure 2.

Mg orthoenstatite is not a good representation of natural orthopyroxene solid solutions, which are generally characterized by larger values of K_T (Fig. 2). This discrepancy, which exceeds the mutual uncertainties in the experimental techniques, could significantly affect the results of geophysical modeling. Both studies utilized synthetic crystals of high purity, so differences between samples are not likely to explain this discrepancy.

In the study of Hugh-Jones and Angel (1994a), the *P-V* equation of state (EOS) of OEN was measured by X-ray diffraction from samples compressed in a diamond cell to P = 8.5 GPa. The value of K_T = 95.8(30) GPa they reported for OEN is based only on their data collected at P < 4 GPa. Hugh-Jones and Angel (1994a, 1994b) concluded that the higher pressure data collected at P > 4 GPa defines a distinct *P-V* trajectory, with a 1 atm cell volume of V_0 = 31.23(10) cm^3/mol, and K_T = 122.8(16.5) GPa. If the *P-V* measurements of Hugh-Jones and Angel (1994a) are not separated into two parts, and all of the measurements up to 8.5 GPa are fitted by a single equation of state, then a value of K_T = 103.1(19) GPa is obtained, which is in far better agreement with the results of this and earlier studies (Table 2). Our results argue strongly against their suggested change in the *P-V* EOS of orthoenstatite near P ~4 GPa. Furthermore, synthetic orthoenstatite does not exhibit any change in its velocity-pressure trajectory up to 10 GPa, and samples recovered from the high-*P* acoustic experiments show no textural evidence of having transformed to a phase with different properties (Flesch et al. 1998). Although it is possible that the crystal-structural mechanism by which strain is accommodated may change as pressure is increased above 4 GPa, as suggested by Hugh-Jones et al. (1994a), our results argue against an actual change in the equation of state of OEN near that pressure.

To assess the effect of chemical composition on the elastic properties of orthpyrozenes, we examined the variation of the aggregate bulk and shear moduli as a function of Fe/(Fe+Mg), because Fe-Mg substitution is the dominant chemical variable in most natural orthopyroxenes. The elastic moduli display is a great deal of scatter about the lines defined by the $MgSiO_3$ and $FeSiO_3$ end-member values for K and μ. The bulk modulus is relatively constant, with only a vague suggestion of a decrease in K with increasing Fe content, whereas μ shows a more significant decrease for the Fe end-member. Aside from the K_T value of Hugh-Jones and Angel (1994a), the most significant deviation from the Opx trend in Figure 2 is data point no. 16 for a natural alumina-rich sample with ~5 wt% Al (Chai et al. 1997). The large value of K for this sample indicates that Al has the strongest compositional effect on Opx elasticity of any common cations. In fact, K_S of the Al-rich sample lies closer to the trend for clinopyroxene than the trend for Al-free Opx. Thus, 5% Al has about the same effect on K_S as replacing half of the Mg with Ca. Note that the total ensemble of results for Opx and clinopyroxene do not support the notion that minute quantities (tenths of a weight percent) of Ca or Al drastically increase K_S or K_T by, for example, up to 14% (Hugh-Jones and Angel 1997).

The lack of a consistent trend in Figure 2 indicates that differences in elastic properties among orthopyroxenes depend on more than just the Fe content. Natural pyroxenes contain a wide range of minor chemical constituents (Deer et al. 1997), and sometimes have complex microstructures and fine scale heterogeneities (e.g., Webb and Jackson 1993). It is difficult to isolate the effects of these competing factors on elastic moduli. However, any heterogeneity or variability in chemistry will affect the density, suggesting the density as an appropriate measure of differences between samples. When the sound velocities are plotted as a function of density on a Birch diagram (Birch 1961), the data for Opx display clearer trends for both V_P and V_S (Fig. 3). Static compression results cannot be included in Figure 3 because those experiments do not yield information on shear properties or velocities. Nevertheless, the available velocity data clearly define decreases of V_P and V_S with increasing density. The velocity-density trends are linear within the resolution of the data and are described by the regression equations $V_P = -1.97\ \rho + 14.4$ and $V_S = -1.62\ \rho + 10.1$. Aluminous pyroxene (Chai et al. 1997) exhibits relatively high velocities and deviates from the average trends more than the other samples. However, the velocity-density variations of orthopyroxenes are typical of the trends displayed by most silicate minerals (Birch 1961). $MgSiO_3$ orthoenstatite is entirely consistent with the elasticity-composition behavior of other orthopyroxenes, and the trends in Figure 3 do not support any unusual compositional effects as proposed by Hugh-Jones and Angel (1997).

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