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Elastic properties of hydrous forsterites under high pressure: First-principle calculations

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ABSTRACT

Elastic and electronic properties of anhydrous (Mg_2SiO_4) and hydrous forsterite crystals with 3.2 wt% ($Mg_{1.75}H_{0.5}SiO_4$) and 1.6 wt% water ($Mg_{1.875}H_{0.25}SiO_4$) under high pressure were investigated using first-principle calculations within local density approximation. Different hydrogen locations around the Mg cation vacancy (as structurally bound OH) have been compared in terms of total energy and elastic properties. Comparison of the anhydrous and hydrous forsterite crystals shows that hydration reduces the mass density, elastic moduli, and sound velocities. Adding 3.2 wt% and 1.6 wt% water leads to reductions of compressional and shear wave velocities (V_P and V_S) of forsterite by 3.1–7.1% and 3.6–9.7%, and by 2.4–4.1% and 3.3–6.6% at pressures from 0 to 14 GPa, respectively. The reduction of sound velocity of hydrous forsterite decreases with water content. This may be the main reason for formation of the low velocity zones in the Earth mantle. However, substitution of hydrogen with Mg cation in forsterite has little effect on its electronic state. The band gap of hydrous forsterite crystals is comparable to the gap of anhydrous one and slightly increases with increasing pressure.

1. Introduction

The behavior of the minerals at high pressure is critical to understanding the structure, dynamics, and compositions of the deep Earth. Olivine (α-phase) of orthosilicate ($(Mg,Fe)_2SiO_4$) is considered to be one of the main constituents of the upper mantle. Determining the elastic parameters of olivine under high pressure, such as seismic velocities, Young's and shear moduli, crystal anisotropy and Poisson's ratio, is of importance for Earth science because these properties are related to geophysical properties including seismic velocities and Poisson's ration in understanding the structure and composition of the Earth's interior. The pressure dependence of the geophysical properties plays an important role in interpreting seismic data and understanding the Earth's interior.

Nominally anhydrous minerals (NAMs) are able to incorporate small amounts of hydrogen as point defects within the crystal structures (Martin and Donnay, 1972). The colloquial use of water or hydration of mantle minerals refers to the incorporation of hydrogen as structurally bound hydroxyl $(OH)^-$, typically associated with point defects such as cation vacancy. Small amount of hydrogen may lead to defect structures and modifications of physical and chemical properties (conductivity, viscosity, and diffusion) of the host phases and mantle dynamics (Kubo et al., 1998; Kleppe et al., 2002; Smyth et al., 2003; Smyth, 2006; Jacobsen et al., 2004; Jacobsen, 2006; Kohlstedt et al., 1996; Mosenfelder et al., 2006).

For interpreting seismological observations of the crust and mantle, hydration effect on the elastic moduli and sound velocities of nominally anhydrous minerals has been investigated via measuring the V_P and V_S from the seismic discontinuities near 410 and 660 km (Van der Meijde et al., 2003; Blum and Shen, 2004; Jacobsen and Smyth, 2006), the sound velocities of hydrous forsterite (hy-Fo100) and hydrous olivine (hy-Fo97) containing 0.8–0.9 wt% H_2O at 12 GPa and 1250 °C (Jacobsen et al., 2008), the second-order elastic constants of hydrous wadsleyite containing 0.37, 0.84, and 1.66 wt% H_2O (Mao et al., 2008), and the sound velocities and single-crystalline elastic moduli of hydrous γ-Mg_2SiO_4 (ringwoodite) containing 2.3 wt% of H_2O at high pressures up to 23.4 GPa (Wang et al., 2006a,b). In addition to the elastic properties, a study of vertical electrical conductivity profile at 200–1000 km of the French Alps revealed that olivine contains 1–1.5 wt% water in cold mantle (Tarits et al., 2004). Xu et al. (1998, 2004) measured the conductivity of $Mg_{1.8}Fe_{0.2}SiO_4$ olivine and its high-pressure polymorphs wadsleyite under mantle conditions and inferred that the conductivity increases approximately 30% along with the transition from olivine to wadsleyite, corresponding to the 410 km discontinuity. Huang et al. (2005) found that the electrical conductivity of wadsleyite and ringwoodite depends strongly on water content but only weakly on temperature, and they draw the conclusion that the water con-

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Table 1
Lattice parameters (*a*, *b*, and *c*) and cell volume (*V*) for anhydrous and hydrous forsterite crystal at ambient conditions from different experimental and theoretical studies.

		a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	Method	Reference
Anhydrous							
	Experiment	4.752	10.192	5.978	289.53	Synchrotron single crystal X-ray diffraction	Kirfel et al. (2005)
		4.757	10.198	5.983	290.22	X-ray diffraction	Downs et al. (1996)
	Theory	4.710	10.150	5.960	284.92	CETEP:GGA	Brodholt (1997)
		4.682	9.953	5.837	272	VCSMD:LDA	Wentzcovitch and Stixrude (1997)
		4.793	10.281	6.041	297.68	VASP:GGA	Durinck et al. (2005)
		4.643	9.988	6.074	281.67	CETEP:LDA	Brodholt et al. (1996)
		4.723	10.127	5.946	284.39	CASTEP:LDA	This work
Hydrous							
	Experiment	4.756	10.208	5.988	290.7	$Mg_{1.985}Si_{0.993}H_{0.006}O_4$	Kudoh et al. (2006)
	Theory	4.752	10.231	5.833	283.4	$Mg_{1.75}SiH_{0.5}O_4$	This work
		4.748	10.136	5.915	284.6	$Mg_{1.875}SiH_{0.25}O_4$	

tent in the mantle transition zone of the Pacific is 0.1–0.2 wt%. Karato (1990) proposed that the electrical conductivity of olivine is sensitive to water content, and hydrogen enhances electrical conductivity in olivine either directly through charge transport by protons or indirectly through enhancement of ionic conductivity by Mg–Fe diffusion. The electrical conductivity of San Carlos olivine with 0.01–0.08 wt% water was determined by AC impedance measurements at pressure of 4 GPa in temperature range of 873–1273 K (Wang et al., 2006a,b). Their results indicated that the electrical conductivity is sensitively to water content, but depends weakly on temperature.

The hydration effects on the elastic and electronic properties of olivine, however, are poorly understood due to difficulty in directly experiment. Recently, atomistic modeling of mineral materials based on first-principle quantum mechanics has become an important technique in the geoscience for investigating the Earth's interior under extreme conditions (Gillan et al., 2006; Piekarz et al., 2002; Stixrude and Peacor, 2002; Churakov et al., 2003; Walker et al., 2006; Tsuchiya et al., 2005, 2006; Wright, 2006). For α-phase olivine, previous first-principle efforts have been focused on the compressional behavior (Brodholt et al., 1996), elastic tensor (Jochym et al., 2004), electronic structure and magnetism (Jiang and Guo, 2004), phase transition (Matsui, 1999; Liu et al., 2008), and hydrous structure (Churakov et al., 2003). However, the elastic and electronic properties of the hydrous crystals are rarely reported.

Inspired by the achievements of first-principle simulations of mineral materials, in this paper we employed first-principle methods to investigate the effects of water content on the elastic moduli, sound velocities, and electronic structures of forsterite at pressures up to 22 GPa. We find that the incorporation of small amount of water (3.2 wt%) can efficiently reduce the density, elastic moduli, and sound velocity of forsterite with regard to the anhydrous values. But such effects become much less pronounced as pressure increases. The electronic structures of forsterite crystal are moderately modified via hydration. These computational results, together with the seismic and experimental data, might provide some useful insights on the properties of hydrous forsterite at upper mantle conditions.

2. Theoretical method

First-principle calculations were performed using density functional theory (DFT) and the planewave pseudopotential technique, as implementing in the CASTEP codes (Clark et al., 2005). Local density approximation (LDA) with CA–PZ parameterization (Ceperley and Alder, 1980; Perdew and Zunger, 1981) was used to describe the exchange–correlation interaction. Ultrasoft Pseudopotentials (Vanderbilt, 1999) was used to model the electron-ion interaction. A 3 × 1 × 2 Monkhorst Pack grid of **k** points was adopted for sampling the Brillouin zone. The energy cutoff for the planewave basis was chosen as 700 eV. Test calculations show that the denser **k** point grid and higher energy cutoff affect slightly the computational results.

Within the planewave pseudopotential framework, the stress tensor on the unit cell of a crystal can be directly calculated using the stress theorem (Nielsen and Martin, 1983). At a given hydrostatic pressure, both the lattice constants and atomic positions of the crystal were simultaneously optimized by minimizing the Hellmann–Feynman forces on the atoms and the stress components on the unit cell. The space group of the anhydrous forsterite crystal was preserved during the optimization of crystal lattice. Though incorporation of hydrogen in the crystal breaks the original symmetry, space groups in the hydrous systems were still treated as orthorhombic. Based on the equilibrium structure of forsterite crystal under different pressures, band structure calculations were performed to determine the electronic density of states (DOS) and the band gaps of the anhydrous and hydrous forsterites.

Forsterite (Mg_2SiO_4) crystallizes in orthorhombic lattice with *Pbnm* space group and 28 atoms per unit cell ($Z=4$), resulting in nine independent elastic constants: c_{11}, c_{22}, c_{33}, c_{12}, c_{13}, c_{23}, c_{44}, c_{55}, c_{66} (Hill, 1952). The overall elastic properties of a crystal can be described by its bulk modulus (K) and shear modulus (G). For orthorhombic crystals, therefore, the isotropic K and G can be derived from the set of nine elastic constants c_{ij} using the VRH (Voigt–Reuss–Hill) average scheme (Hill, 1952):

$$K = \frac{(c_{11}+c_{22}+c_{33})+2(c_{12}+c_{23}+c_{13})}{9} \quad (1)$$

and

$$G = \frac{(c_{11}+c_{22}+c_{33})}{15} - \frac{(c_{12}+c_{23}+c_{13})-3(c_{44}+c_{55}+c_{66})}{15} \quad (2)$$

For crystalline materials, V_P and V_S can be calculated from the elastic moduli via:

$$V_P = \sqrt{\frac{(3K+4G)}{3\rho}},$$

$$V_S = \sqrt{\frac{G}{\rho}},$$

respectively, where ρ is mass density that is determined by the equilibrium volume of the crystal lattice from first-principle optimization and molecular mass of the forsterite.