A first-principles calculation of the elastic and vibrational anomalies of lizardite under pressure

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ABSTRACT

Lizardite, being one of three serpentine minerals is of considerable interest in connection with understanding the geological processes occurring at subduction zones where serpentinitized ocean floor is recycled into the Earth’s mantle. The crystal structure, elasticity, and vibrational properties of lizardite under pressure were determined using first-principles techniques. Above 10 GPa, a stable and a metastable structures were obtained. The hydrogen bond geometry of the stable structure indicates the disappearance of hydrogen bonds above 10 GPa, whereas the metastable structure does not show any noticeable change of the hydrogen bond strength throughout the pressure range up to 20 GPa. At 10 GPa, a very sudden softening of the elastic constants was observed for the stable structure, which is associated with a slight change in the compressibility of the c axis. This elastic softening causes a sudden reduction in the seismic velocities $v_p$ and $v_s$ by about 16 and 24%, respectively. These velocities then steeply increase with further compression. Shear velocity $v_s$, on the other hand, gradually decreases with pressure and then abruptly increases about 14% at 10 GPa. The calculated OH stretching frequencies also increase suddenly at ~10 GPa. Previous Raman measurement reported that the highest OH stretching frequencies also increase steeply above 6 GPa. Therefore, there is a possibility that this elastic anomaly can be observed experimentally at about 6 GPa.

Keywords: Lizardite, first principles, elasticity, vibration, high pressure

INTRODUCTION

Serpentine is a common rock-forming hydrous magnesium phyllosilicate, and it is known to form in the mantle wedge due to a reaction between peridotite and upwelling water, which is released by the decomposition of hydrous minerals in the subducting slab under pressure (e.g., Schmidt and Poli 1998; Iwamori 1998). Partially serpentinitized peridotite may be a significant reservoir for hydrogen in the mantle wedge and be the convectional lubricant of subducting plates (Hilairet et al. 2007). The dehydration of serpentine is thought to contribute to the generation of arc magmatism and was also extensively investigated in connection with intermediate and deep earthquakes (e.g., Irifune et al. 1996; Dobson et al. 2002). There are three polymorphs in the serpentine group: antigorite, chrysotile, and lizardite. Although antigorite is the most relevant mineral in these serpentine polymorphs at the subduction zone, lizardite is expected to exist in very cold regions below ~400 °C (Evans 2004). Despite the geophysical and mineralogical importance of serpentine, its structural and physical properties have not been sufficiently determined. An in situ synchrotron X-ray diffraction study previously reported the compressibility of lizardite, antigorite, and chrysotile up to 10 GPa (Hilairet et al. 2006). Later, Nestola et al. (2010) reported the anomalous softening of antigorite at 6 GPa by single-crystal X-ray diffraction. Although, Mookherjee and Stixrude (2009) reported the structure and elasticity of lizardite beyond 100 GPa, finding an elastic anomaly at 7–22 GPa, and discovering an elastic instability at 50 GPa, their data points are sparse in the vicinity of the anomaly and more detailed calculations and analyses are needed. In this study, first-principles calculations on the structural and elastic properties of lizardite up to 20 GPa, with a small pressure interval of less than 2 GPa were performed. To achieve a more detailed analysis, the vibrational properties such as the OH stretching frequencies and the Raman spectra of lizardite under pressure were also determined by using the density functional perturbation theory (DFPT).

METHOD

First-principles computations were based on the generalized gradient approximation (GGA-PBE) within the density functional theory (Hohenberg and Kohn 1964; Perdew et al. 1996). It is known that the local density approximation (LDA) overestimates the strength of the hydrogen bond and underestimates the volume, while GGA slightly overestimates the experimental volume (e.g., Lee et al. 1992; Hamann 1997). Since first-principles structural optimization is usually conducted at static 0 K conditions, whereas the structural refinement experiments are usually conducted at ambient conditions, the difference between experiments and LDA calculations might be less if the temperature effects are included in the calculations (e.g., Stixrude 2002). Actually, the differences in the physical properties calculated by GGA and LDA should be smaller when they are compared at the same volume, and the qualitative behaviors under pressure are usually similar between GGA and LDA (e.g., Demuth et al. 1999). In this study, GGA-PBE is employed for the elasticity calculation. The Troullier-Martins type norm-conserving pseudopotentials (Troullier and Martins 1991), which were extensively tested in previous calculations (e.g., Tsuchiya and Tsuchiya 2008, 2009) were used for this study.

The lizardite-1T polytype Mg$_5$Si$_2$O$_7$(OH)$_4$ has trigonal symmetry with the space group $P3_1m$, and the lizardite primitive cell contains 18 atoms (Mellini 1982). The electronic wave function was expanded in plane waves using a kinetic energy cutoff of 80 Ry. The irreducible Brillouin zone of the lizardite primitive cell was sampled on a $5 \times 5 \times 4$ Monkhorst-Pack mesh (Monkhorst and Pack 1976)....