Structural insights and elasticity of single-crystal antigorite from high-pressure Raman and Brillouin spectroscopy measured in the (010) plane

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ABSTRACT

We report high-pressure Raman and Brillouin spectroscopy results measured in the (010) plane of a natural antigorite single crystal. We find that structural changes at >6 GPa lead to (1) an intensity crossover between Raman modes of the Si-O-Si bending vibrations, (2) changes of the compression behavior of Raman modes related to the SiO₄ tetrahedra, (3) changes of the pressure derivative of the Raman shifts associated with OH stretching vibrations, (4) the emergence of a new Raman band in the OH spectral region, (5) a softening of the elastic constants c₃₃ and c₁₁, and (6) a directional change of the slowest compressional wave velocity in the a-c plane. In addition to the structural insights at high-pressure, the unique characteristics of our single-crystal sample allows for first direct measurements of the acoustic velocity anisotropy in a plane perpendicular to the basal a-b plane. Comparison to previously published data indicates that the elastic anisotropy of antigorite strongly depends on the FeO and/or Al₂O₃ content. In contrast, it seems not to be affected by increasing temperature as inferred from an additional high-temperature experiment performed in our study. These constraints are important for the interpretation of seismic anisotropy observations in subduction zone environments.

Keywords: Antigorite, serpentine, elasticity, Brillouin, Raman, seismic anisotropy

INTRODUCTION

Serpentine group minerals are characterized by a layered structure, where sheets of SiO₄ tetrahedra alternate along the c direction with sheets of MgO₆(OH)₈ octahedra. In antigorite, the high-pressure high-temperature (HP/HT) monoclinic form of serpentine, the layers show a pronounced curvature along the basal plane, which is accompanied by changes in the polarity of the tetrahedral layer (Capitani and Mellini 2004, 2006). Antigorite is a major mineral phase in subduction environments and serves as an important carrier of water from Earth’s surface to the upper mantle (e.g., Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997). Its breakdown reaction has been associated with local melting of the mantle wedge and deep Earth seismicity (Ulmer and Trommsdorff 1995; Dobson et al. 2002; Hilairet et al. 2007). Recently, the markedly anisotropic frictional strength of the antigorite (001) basal surface has been related to the dynamics of slab motion and seismic activity at convergent margins (Campione and Capitani 2013). A detailed characterization of the HP/HT physical properties and chemical behavior of antigorite is important to understand its potential role for geophysical and geochemical processes in subduction zone settings. As a consequence of its layered structure, antigorite is expected to show a strong direction dependence for many physical and chemical properties, including elasticity (e.g., Bezacier et al. 2010). Knowledge of the anisotropic elastic properties of antigorite as a function of chemical composition at pressure and temperature conditions relevant to subduction environments is essential to understand its contribution to observed seismic anisotropy and map its abundance, distribution, and breakdown reaction (e.g., Katayama et al. 2009; Long 2013; Reynard 2013).

In a high-pressure Raman study in a diamond-anvil cell (DAC) on synthetic antigorite, Reynard and Wunder (2006) observed changes in the pressure-derivative of OH-related Raman modes at a pressure of about 7 GPa. In a later single-crystal X-ray diffraction study, this observation was assigned to a pressure-induced structural modification that occurs in antigorite at a pressure of about 6 GPa, evidenced by discontinuous changes of volume and β-angle (Nestola et al. 2010). The experimental findings were confirmed by computations that provided additional details on the associated structural re-arrangements in antigorite (Capitani and Stixrude 2012). Computational studies also predicted that the pressure-induced structural re-arrangement affects the elastic properties of serpentine at HP (Mookherjee and Stixrude 2009; Mookherjee and Capitani 2011; Tsuchiya 2013). The maximum effect was predicted for some of the elastic constants describing properties in the crystallographic c direction (c₃₃ and c₁₁) (Tsuchiya 2013). An effect of the structural change on elasticity was later confirmed by high-pressure Brillouin spectroscopy (Bezacier et al. 2013). However, because minerals of the serpentine group show a strongly layered crystal structure and therefore exhibit pronounced cleavage, sample platelets were restricted to the basal a-b plane (the natural cleavage plane). Because of this experimental limitation, the previous Brillouin