Water effects on the anharmonic properties of forsterite

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ABSTRACT

To quantify the effects of hydration on anharmonicity of olivine thermodynamics, we have measured in situ Raman spectra of an extremely hydrous forsterite with 4500 ppm (wt) H2O at temperatures up to 1273 K. All the Raman modes in hydrous forsterite shift linearly to lower wavenumbers with increasing temperature. The calculated isobaric mode Grüneisen parameters related to SiO4 internal stretching and bending vibrations are much lower than lattice vibrations. Additionally, compared with anhydrous forsterite, except for the modes at 919, 858, and 227 cm⁻¹, water greatly reduces the isobaric mode Grüneisen parameters of the Raman modes in forsterite. Water also has a large effect on the anharmonic parameters related to lattice vibrations, whereas it has little effect on the anharmonic parameters related to SiO4 internal stretching and bending vibrations. Those results have the implications to the variations of local structure with temperature and estimation of water effects on the thermodynamics of forsterite.

Keywords: Water, anharmonic properties, Raman mode, forsterite

INTRODUCTION

Olivine is a major constituent of the upper mantle (Akimoto et al. 1976). It is known to contain significant amounts of water as OH defects in the structure and can be considered as a large reservoir of water in the upper mantle (Bell and Rossmann 1992; Bolfan-Casanova 2005; Beran and Libowitzky 2006; Koch-Müller et al. 2006). The presence of water in olivine has a profound influence on the physical properties of olivine, thereby on the dynamics of the upper mantle (Hirth and Kohlstedt 1996; Jung and Karato 2001; Mei and Kohlstedt 2000; Karato 2006; Wang 2010). Moreover, water has great effects on structure and thermal expansion of olivine (Smyth et al. 2006; Ye et al. 2009). However, it is not clear whether water affects such thermodynamic functions as heat capacity and entropy. Direct measurements of those thermodynamic properties of the minerals under deep earth conditions are difficult (Gillet et al. 1991, 1997; Fujimori et al. 2002), so it is desirable to have another method for estimating those properties. One of the important contributions of vibrational spectroscopy is the calculation of those thermodynamic functions (Kieffer 1979).

The lattice anharmonicity refers to the vibrational effects that do not follow simple harmonic motion. It is indispensable to understand such ubiquitous phenomena as thermal expansion and thermal conductivity, which cannot be explained in a harmonic system. Moreover, anharmonicity is especially remarkable and can dramatically modify the thermodynamic properties of material at high temperature (e.g., Karki et al. 2000; Wu 2015). So understanding anharmonic effects is one of the current problems in physics and draws more and more interests from physicists and geophysicists (e.g., Gillet et al. 1991, 1997; Fujimori et al. 2002; Zucker and Shim 2009; Deshpande et al. 2014; Silva et al. 2014; Sumita and Yoneda 2014; Wu 2015). Because the mantle temperatures are expected to be higher than 1000 K, the contribution of anharmonicity to thermodynamics of minerals of deep earth cannot be neglected. As a Mg-end-member of the olivine group and the main mineral in the upper mantle, the anharmonic properties of dry forsterite was widely studied (Gillet et al. 1991, 1997; Reynard et al. 1992). However, the anharmonicity of hydrous forsterite has not yet been reported. In this study, we carry out in situ high-temperature Raman spectroscopic investigations on a hydrous forsterite to obtain the isobaric mode Grüneisen parameters (γi,p). Combined with the isothermal mode Grüneisen parameters (γi,T) and thermal expansion coefficient (α) of the hydrous forsterite of the same batch reported by Ye et al. (2009) and Hushur et al. (2009), respectively, the anharmonicities of hydrous forsterite can be calculated. Then, water effect on the anharmonicities can be estimated compared with the data of dry forsterite (Gillet et al. 1991, which is consistent with their later paper Gillet et al. 1997).

EXPERIMENTAL METHODS

Sample description

The hydrous forsterite single crystal (SZ0410B) was synthesized at Bayerisches Geoinstitut by Smyth et al. (2006). The synthesis was carried out in double-capsule experiments in the 5000 ton multi-anvil press at 12 GPa and 1673 K. The water content was measured by polarized FTIR spectroscopy on previously oriented grains based on the calibration of Bell et al. (2003) and the sample SZ0410B contained 4505 ppm (wt) water (Smyth et al. 2006). The size of the crystal used in this study is about 150 μm.

FTIR spectroscopy

The Mid-IR spectra (2500 to 4000 cm⁻¹) of O-H stretching vibrations before and after in situ high-temperature Raman spectroscopic study were recorded (Fig. 1) to check the retention of water during the heating process. The spectra were obtained from a Nicolet 5700 FTIR spectrometer coupled with a Continuum microscope,