Estimating compositions of natural ringwoodite in the heavily shocked Grove Mountains 052049 meteorite from Raman spectra

L. Feng,1,2 Y. Lin,1,* S. Hu,1,2 L. Xu,3 and B. Miao4

1Key Laboratory of the Earth’s Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
2Graduate School of Chinese Academy of Sciences, Beijing 100118, China
3National Astronomical Observatory, Chinese Academy of Sciences, Beijing 100029, China
4Department of Resources and Environmental Engineering, Guilin University of Technology, Guilin 541004, China

Abstract

A combined Raman spectroscopy and electron probe microanalysis study of the heavily shocked Grove Mountains (GRV) 052049 meteorite revealed the largest chemical fractionation of natural ringwoodite, and composition-dependent variation of the intensities and/or wavenumbers of Raman bands. With Fa content [atomic ratio of Fe/(Fe+Mg)] of ringwoodite varying from 27.8 to 81.6 mol%, the peak position of the single band around 290 cm⁻¹ (SB1), which relates to the SiO₂ symmetric stretching mode, shifts from 296.0 to 284.6 cm⁻¹, and one of the doublets around 790 cm⁻¹ (DB1), which relates to the SiO₂ symmetric stretching of SiO₂, shifts from 796.3 to 782.7 cm⁻¹. In addition, the relative intensities of SB1 and the other band of the doublet around 840 cm⁻¹ (DB2), which relates to asymmetric stretching of SiO₂, increases with Fa content. Based on the paired Raman-EPMA data, single-peak and two-peak calibrations were established, which can be used to derive Fa contents of ringwoodite from the Raman spectra. The accuracy of Raman-derived Fa content of ringwoodite is better than ±5 mol%. The correlation of SB1 intensity with the Fa content of ringwoodite suggests that the vibration of SB1 is enhanced with the substitution of Mg²⁺ by Fe²⁺. The correlation between Raman spectra and the chemical composition of ringwoodite have potential applications in on-line measurement of high-pressure experiments and in situ mineralogical determination in future planetary explorations.

Keywords: Raman spectroscopy, ringwoodite, chemical compositions, shocked meteorite

Introduction

As pressure increases, olivine, α-(Mg,Fe)₂SiO₄ is transformed to wadsleyite (β phase) at 13–16 GPa (at 1200 °C) and then ringwoodite, γ-(Mg,Fe)₂SiO₄, at 18–22 GPa (at 1200 °C) (Katsura and Ito 1989; Agee 1998). Both of the high-pressure polymorphs are predicted to be the predominant minerals in the Earth’s transition zone (400–660 km), and ringwoodite is predicted to occur in the lower part (Ringwood 1991). Thermodynamical, physical, and crystallographic properties of ringwoodite have been extensively studied to understand the dynamical processes of the Earth’s mantle and to determine properties of the lower part of transition zone. Raman spectra are related to the lattice vibration and are critical for identifying ringwoodite (Guyot et al. 1986; Yamanaka and Ishii 1986; McMillan and Akaogi 1987; Chopelas et al. 1994). However, little attention has been devoted to the effect of substitution of cations on the lattice vibration. McMillan and Akaogi (1987) noticed a significant shift of the lowest-frequency F₃g mode of Ni₂SiO₄ spinel (190 cm⁻¹) in comparison to γ-Mg₂SiO₄ (302 cm⁻¹) and interpreted this shift as a result of substitution of Ni²⁺ by Mg²⁺. Later study showed that the different translations of SiO₄ and M³⁺ are strongly coupled (Chopelas et al. 1994).

Previous studies of Raman spectra of olivine revealed a correlation between the Raman band shift and chemical composition, which was used to extract chemical compositions of the olivine-group minerals (fayalite content) (Kuebler et al. 2006; Mouri and Enami 2008). Analog studies were extended to pyroxenes (Wang et al. 2001), chromite (Al, Fe, Cr cation substitution), ilmenite (Fe, Ti), hematite (Fe, Ti) (Wang et al. 2004), and feldspars (Na, K, Ca) (Freeman et al. 2003, 2008). These studies provided unique and promising methods for space exploration to estimate both mineralogical and compositional information with the Raman spectrometer. In principle, the chemical composition of ringwoodite can also be determined from its Raman spectra if a calibration between them can be established. However, the effects of cation substitution between Mg²⁺ and Fe²⁺ on the vibrational mode frequencies of ringwoodite are unknown.

Natural ringwoodite has been found only in severely shocked meteorites, formed by solid-solid transformation of olivine (e.g., Putnis and Price 1979; Chen et al. 1996; Ohtani et al. 2004; Xie and Sharp 2007) or crystallization from olivine melts (Miyahara et al. 2008a, 2009) under high-pressure conditions created by impact events on planets or asteroids. Many ringwoodite grains in L-group chondrites have homogeneous compositions with a narrow range of fayalite contents (Fa₃₈–₃₉), overlapping with the composition of olivine in the same host meteorites (Putnis...