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Raman spectroscopic measurements on San Carlos olivine up to 14 GPa and 800 K: Implications for thermodynamic properties

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Abstract

Olivine, the most abundant mineral in the upper mantle, plays a key role in controlling the thermodynamic properties in the Earth's and planetary interiors, like the temperature distribution along the adiabatic geotherm. In this study, we conducted simultaneous high-pressure (P) and high-temperature (T) Raman measurements on a San Carlos olivine sample in an externally heated diamond-anvil cell (DAC). The intrinsic anharmonic parameters, a_i, are calculated as functions of both pressure and temperature, and the isochoric (C_V) and isobaric (C_P) heat capacities are computed at various P-T conditions with the anharmonic correction. The harmonic heat capacities are C_V = 807.7 J/kg/K and C_P = 815.4 J/kg/K at ambient conditions, with anharmonic contribution of ΔC = 7.9 J/kg/K. Relative to the previous vibrational measurements conducted at high-P or high-T conditions, this simultaneous high-P-T experiment indicates that the anharmonic contribution to heat capacities is overestimated if the anharmonic parameters (a_i) are treated as constants, as done previously. The pressure effect is marginal on the intrinsic anharmonic contribution to thermodynamic properties, whereas it has a much more significant effect on the external anharmonicity (thermal expansivity). The pressure dependence of C_P (dC_P/dP, in J/kg/K/GPa) increases from –3.14 at 300 K to –1.94 at 700 K, and then decreases smoothly to –5.03 at 1800 K. Combining the derived high-P-T capacity with a reliable P-V-T equation of state (EoS) for olivine, we further modeled the thermodynamic Grüneisen parameter, $\gamma(P\text{-}T)$. The Grüneisen parameter is important for the connection between isothermal and adiabatic compressions of minerals, which can be decreased by approximately 5% with the anharmonic correction at high temperatures. The modeled adiabatic bulk modulus and bulk sound velocity can be expressed as: $K_S(T,P)$ (GPa) = 127.5(1) + 4.32(5)$\cdot P$ – 0.018(1)$\cdot(T$ – 300) and $V_\Phi(T\text{-}P)$ (km/s) = 6.22(2) + 0.069(3)$\cdot P$ – [3.74(15)–0.075(13)$\cdot P$]$\cdot 10^{-4}\cdot(T$ – 300). The adiabatic temperature gradient, dT_S/dP, which is almost independent of pressure, equals 13.40(16) and 12.35(16) K/GPa in the harmonic and anharmonic models, respectively. This study provides a useful example for modeling the radial temperature distribution in adiabatic planetary mantles.

Keywords: Olivine, simultaneously high-P-T Raman spectra, intrinsic anharmonic parameter; heat capacity, thermodynamic Grüneisen parameter, adiabatic temperature profile