

Estimates of mantle relevant Clapeyron slopes in the MgSiO_3 system from high-pressure spectroscopic data

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ABSTRACT

The phase diagram for MgSiO_3 was estimated using the entropy, enthalpy, thermal expansivity, and volumes of all the phases. Entropy at the various P - T conditions in the phase diagram was estimated using statistical thermodynamics and spectroscopic data at ambient and high pressures for each of the phases. Nearly complete 1 atm polarized Raman spectra of end-member MgSiO_3 orthoenstatite and new high-pressure Raman data on orthoenstatite ($Pbca$) to 24.5 GPa and majorite to 33.6 GPa are presented. Both of these minerals exhibit profound changes in their spectra as pressure is increased and the pressure dependence of the Raman modes changes substantially at 5 GPa for orthoenstatite and 26 GPa for majorite. These, like MgSiO_3 perovskite, appear to change symmetry even at room temperature. The slopes for the following transitions are reported: clinoenstatite ($C2/c$) to majorite, -12 bar/K; majorite to ilmenite, 46 bar/K; ilmenite to perovskite, -46 bar/K, majorite to perovskite, 26 bar/K. A volume change of 0.6 cm^3/mol for the orthopyroxene to high-pressure clinopyroxene transition was estimated using the previously measured phase boundary and the present entropy data. Clapeyron slopes are overestimated by 20 to 100% if the pressure dependence of ΔS across the transitions at various P - T conditions is not included in the thermodynamic calculations.