American Mineralogist, Volume 99, pages 35–43, 2014

Phase transitions and equation of state of forsterite to 90 GPa from single-crystal X-ray diffraction and molecular modeling

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Abstract

Forsterite, Mg_2SiO_4, the magnesian end-member of the olivine system, is the archetypal example of an orthosilicate structure. We have conducted synchrotron-based single-crystal X-ray diffraction experiments to 90 GPa on synthetic end-member forsterite to study its equation of state and phase transitions. Upon room-temperature compression, the forsterite structure is observed to 48 GPa. By fitting a third-order Birch-Murnaghan equation of state to our compression data, we obtain the zero-pressure isothermal bulk modulus, K_{0T} = 130.0(9) GPa and its pressure derivative, K'_{0T} = 4.12(7) for a fixed room-pressure volume, V_0 = 290.1(1) Å^3, in good agreement with earlier work. At 50 GPa, a phase transition to a new structure (forsterite II) occurs, followed by a second transition to forsterite III at 58 GPa. Forsterite III undergoes no additional phase transitions until at least 90 GPa. There is an ~4.8% volume reduction between forsterite and forsterite II, and a further ~4.2% volume reduction between forsterite II and III. On decompression forsterite III remains until as low as 12 GPa, but becomes amorphous at ambient conditions. Using our X-ray diffraction data together with an evolutionary crystal structure prediction algorithm and metadynamics simulations, we find that forsterite II has triclinic space group $P\bar{1}$ and forsterite III has orthorhombic space group $Cmc2_1$. Both high-pressure phases are metastable. Metadynamics simulations show a stepwise phase transition sequence from 4-coordinated Si in forsterite to mixed tetrahedral and octahedral Si (as in forsterite II), and then fully sixfold-coordinated Si (as in forsterite III), occurring by displacement in [001](100). The forsterite III structure is a member of the family of post-spinel structures adopted by compositions such as $CaFe_2O_4$ and $CaTi_2O_4$.

Keywords: Compressibility measurements, olivine, forsterite composition, single-crystal XRD data, synchrotron source, high-pressure olivine phase transition, diamond-anvil cell