Phase behavior of protoenstatite at high pressure studied by atomistic simulations

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ABSTRACT

Structural phase transformations of MgSiO3 protoenstatite at high pressures are studied by atomic scale simulation techniques. Molecular-dynamics simulations and electronic-structure calculations reveal two metastable polymorphs with space groups P21/cn and Pbn, respectively. They are related to protoenstatite by displacive transition mechanisms via subsequent change of the silicate chain rotations from O- to S-type. Metadynamics simulations in combination with molecular dynamics reveal possible mechanisms for the martensitic transition from protoenstatite to high-pressure clinoenstatite. Two different shear mechanisms in the (100) plane are activated during the transition. The first consists of four partial displacements in (100)[001] and (100)[010], whereas in a second step only a single shear in (100)[010] is observed.

Keywords: Molecular dynamics, metadynamics, phase transition, enstatite, MgSiO3, protopyroxene, clinopyroxene

INTRODUCTION

Pyroxenes are important crustal and upper mantle minerals (Ringwood 1975; Anderson 1989). Their common structural features are tetrahedral chains usually of SiO4 units that are separated by parallel chains of octahedral edge-sharing M1O6 units containing cations on the M1 site. Differences between pyroxene structures such as the stacking sequence of the chains, the rotation angles within the chains or the oxygen coordination of cations on the second site, M2, (Downs 2003) control the physical properties of the respective crystals, e.g., their density or elastic properties, and thus influence geophysical and rheological properties of crustal and upper mantle rocks.

The thermodynamic stability of different pyroxene structures depends on P, T, and chemical composition. Enstatites with MgSiO3 composition are known to exist in at least five different structures (Fig. 1). At low T and low P, monoclinic low-clinoenstatite with space group P21/c is the stable phase. A displacive phase transition at high P results in high-P clinoenstatite with space group C2/c (Angel et al. 1992). Orthoenoanstatite (Pbca) occurs at high T and pressures up to about 7 GPa, whereas protoenstatite (Pbcn) and high-T clinoenstatite (C2/c) have small stability fields at high T and low P (Presnall 1995).

Crystallographic considerations suggest several additional pyroxene phases (Thompson and Downs 2003), some of which may exist as metastable enstatite phases. For instance, experimental (Lin 2003; Kung et al. 2004) and atomistic simulation studies (Jahn 2008) suggest at least one high-pressure orthopyroxene phase. Other phases have stability fields at compositions slightly different from enstatite such as high-T orthopyroxene (Pbca) of (Ca0.06Mg1.94)Si2O6 (Ohi et al. 2008) or high-P proto-

pyroxene (P21/cn) of (Mg1.54Li0.23Sc0.23)Si2O6 (Yang et al. 1999).

For a systematic understanding of the complex phase behavior in pyroxenes, not only the thermodynamics have to be known, but also the kinetics of the transitions may be of importance. Transmission electron microscopy has been used extensively to study the transitions in pyroxenes, especially from orthopyroxene to clinopyroxene (Coe and Müller 1973; Coe and Kirby 1975; McLaren and Etheridge 1976; Hugh-Jones et al. 1996). It was concluded that the dominant transition mechanism is...