Isosymmetric structural phase transition of orthoenstatite: Molecular dynamics simulation

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ABSTRACT

An isosymmetric phase transition from orthoenstatite to a new high-temperature orthorhombic phase of enstatite was observed at about 1230 K in molecular dynamics (MD) simulations for the Mg end-member composition, Mg$_2$Si$_2$O$_6$. This new phase has the same space group as orthoenstatite, P_bca. The discontinuous changes of the cell volume and cell parameters during the transition indicate a first-order transition. The transition is characterized by the switching of bonds between Mg atoms at the M2 sites and the coordinated O3 atoms. This new phase corresponds to the high-temperature state of enstatite observed in the in situ high-temperature X-ray studies and probably to orthopyroxene appearing in the phase diagram of the quadrilateral pyroxenes, indicating the possibility of its existence as a stable phase at high temperature.

INTRODUCTION

Enstatite (Mg$_2$Si$_2$O$_6$) is an end-member of orthopyroxene, (Mg,Fe)$_2$Si$_2$O$_6$, one of the major constituent minerals in the Earth’s crust and upper mantle. Enstatite is known to have five polymorphs; orthoenstatite (space group: P_bca), protoenstatite (space group: Pbcm), low-temperature clinoenstatite (space group: P2$_1$/c), high-temperature clinoenstatite (space group: C$2$/c) and high-pressure clinoenstatite (space group: C2/c). Orthoenstatite and low-temperature clinoenstatite have two crystallographically distinct SiO$_3$ chains (A and B chains). On the other hand, protoenstatite, and high-temperature and high-pressure clinoenstatite have only one type of chain.

Ito (1935) proposed that the orthorhombic unit cell with space group P_bca is composed of two monoclinic cells with space group C2/c (diopside and high-temperature clinoenstatite) twinned by a b-glide plane parallel to (100), which is one of the cell-twin operations. Ito (1950) re-examined the hypothesis and suggested that the monoclinic subunit has P2$_1$/c symmetry rather than the C2/c of diopside owing to a slight change in the Mg (Fe) positions. After the discovery of natural Ca-poor clinopyroxene, pigeonite, with space group P2$_1$/c (Morimoto 1956), the orthorhombic cell was shown to be composed of two monoclinic cells of clinopyroxene with P2$_1$/c symmetry (Morimoto and Koto 1969). The C2/c-P2$_1$/c transition in clinopyroxene with increasing temperature was suggested by Morimoto and Tokonami (1969) and was confirmed by Smith (1969). In this transition, two crystallographically distinct SiO$_3$ chains in P2$_1$/c change to one type in C2/c. Based on the analogy of the C2/c-P2$_1$/c transition, Ohashi and Finger (1973) suggested the existence of a high-temperature orthorhombic phase (P_bca), composed of two monoclinic cells of clinopyroxene with space group C2/c. Pannhorst (1979) also proposed a high-temperature orthopyroxene with one crystallographically equivalent silicate chain, which may correspond to the same structure as that proposed by Ohashi and Finger (1973).

In addition to the two proposals for high-temperature orthopyroxene, high-temperature X-ray studies by Murakami et al. (1982) and Yang and Ghose (1995) suggested the existence of an orthorhombic phase as a transitional state during the phase transition in orthopyroxene.

Furthermore, the orthorhombic phase has been shown to have two stable regions at high and low temperatures in the phase diagram of the system Mg$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ (e.g., Longhi and Boudreau 1980; Jenner and Green 1983; Biggar 1985; Carlson 1985, 1986). However, until now, the differences in the crystal structures of the two orthorhombic phases at high and low temperatures have not been clarified.

Computer simulation has been recognized as a potential method for studying the structure and phase transitions in enstatite (e.g., Matsui and Price 1992; Choudhury and Chaplot 2000; Shimobayashi et al. 1998, 2001; Miyake et al. 2002). Using MD simulations, the phase relation and phase transitions among the three clinoenstatite phases of Mg$_2$Si$_2$O$_6$ were successfully observed (Shimobayashi et al. 1998, 2001; Miyake et al. 2002). In the present paper, we report the behavior of orthoenstatite at high temperature by using the same MD simulation technique. Using MD simulation, the isosymmetric structural phase transition was observed for the first time. Orthoenstatites below and above the transition temperature are hereafter referred as the low-temperature and high-temperature phases of orthoenstatite, respectively. Here, we report details of the transition and the crystal-chemical differences between the low- and high-temperature phases of orthoenstatite.

MOLECULAR DYNAMICS SIMULATIONS

In the study described here, we used the same MD simulation technique as in our previous molecular dynamics (MD) studies of clinoenstatite (Shimobayashi et al. 1998, 2001; Miyake et al. 2002). In the MD simulations, an interatomic potential function between two atoms $(i,j)$ consists of Coulombic, short range repulsion, van der Waals attraction, and Morse potential terms, as given by the relation;

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