Symmetry change of majorite solid-solution in the system \( \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} - \text{MgSiO}_3 \)

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INTRODUCTION

Considerable efforts have been devoted to the investigations on crystal chemistry of garnets because of their importance in Earth’s crust and in the upper mantle. A garnet phase called majorite is stable under pressure-temperature condition corresponding to the transition zone in Earth’s mantle between the 400 and 670 km seismic discontinuities (e.g., Ringwood 1967; Liu 1977; Akaogi and Akimoto 1977; Ito and Takahashi 1987). Majorite in Earth’s mantle is considered to be solid-solution having complex chemical composition of Mg-Ca-Fe-Cr-Al-Si-O system. As the simplest model, the chemical composition of majorite in Earth’s mantle can be approximated by the solid-solution \( \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} - \text{MgSiO}_3 \). The structure formula of this majorite solid-solution can be expressed as \( \text{Mg}_3\text{Al}_{2-x}\text{Si}_{3-x}\text{O}_{12-x} \). It has been reported that the cubic symmetry (\( \text{Ia}3d \)) in this system is stable for \( 0 \leq x < 0.8 \), whereas the symmetry in the range \( 0.8 \leq x \leq 1.0 \) is tetragonal (\( \text{I}_4/\text{acd} \)) and the ordering of Mg\(^{2+}\) and Si\(^{4+}\) cations occurs on the two nonequivalent octahedral sites (e.g., Kato and Kumazawa 1985; Sawamoto 1987; Angel et al. 1989; Parise et al. 1996; Heinemann et al. 1997).

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ABSTRACT

Six single crystals of \( \text{Mg}_3\text{Si}_x\text{Al}_{2-x}\text{Si}_3\text{O}_{12} \) with \( x = 0.05, 0.13, 0.24, 0.38, 0.52, \) and 0.64 (the majorite solid-solution) were synthesized at 20 GPa and 2000 °C with a “6-8” type uniaxial split-sphere apparatus. Single-crystal X-ray diffraction studies revealed discontinuities in compositional dependence of the molar volume, equivalent isotropic temperature factors (\( B_{eq} \)), and mean bond lengths between \( x = 0.24 \) and 0.38. Single crystals in the compositional range \( 0 \leq x \leq 0.24 \) show no birefringence, whereas those of \( x = 0.64 \) have a slight optical anisotropy. Moreover, the cell symmetry for \( x = 0.64 \) obtained using synchrotron X-ray radiation is tetragonal with a slight deviation from cubic. On the basis of site splitting expected from compositional dependence of \( B_{eq} \) obtained by cubic refinement, the most probable space group in the range \( 0.38 \leq x \leq 0.64 \) is \( \text{I}_4/\text{acd} \) (tetragonal), which is the maximal subgroup of the space group \( \text{Ia}3d \) (cubic). Given that the previous reports that crystals with \( 0.8 \leq x \leq 1.0 \) have the tetragonal space group \( \text{I}_4/\text{a} \), the majorite solid-solution in this system undergoes the series of symmetry changes, \( \text{Ia}3d \rightarrow \text{I}_4/\text{acd} \rightarrow \text{I}_4/\text{a} \), with increasing \( \text{MgSiO}_3 \) component. The symmetry changes from \( \text{Ia}3d \) to \( \text{I}_4/\text{acd} \) cannot be explained by the cation ordering on the octahedral site. Strong electrostatic interaction between the dodecahedral (Mg\(^{2+}\)) and tetrahedral (Si\(^{4+}\)) cations was observed from atomic thermal motion and electron density distribution. Because one of the site symmetries of the two nonequivalent tetrahedral sites in \( \text{I}_4/\text{acd} \) structure loses the center of symmetry with the symmetry reduction from \( \text{Ia}3d \) to \( \text{I}_4/\text{acd} \), the symmetry reduction may be caused by the electronic polarization of the cations due to the neighboring cation-cation interaction.

Angel et al. (1989) reported from transmission electron microscopic (TEM) observation that the two different types of merohedral and pseudomerohedral twins were invariably observed in \( \text{MgSiO}_3 \) majorite synthesized at 17 GPa and 1800 °C. They argued that Mg-Si ordering process is unlikely to be completed within only a few seconds during the quenching and these twins will arise during crystal growth; and thus, that \( \text{MgSiO}_3 \) majorite is tetragonal (\( \text{I}_4/\text{a} \)) under high pressure-temperature condition corresponding to the transition zone in Earth’s mantle. However, from the symmetry analysis based on group theory, Hatch and Ghose (1989) interpreted the observed twinning in \( \text{MgSiO}_3 \) majorite as evidence of a phase transition from \( \text{Ia}3d \) to \( \text{I}_4/\text{a} \) caused during the quenching, and argued that \( \text{MgSiO}_3 \) majorite in the transition zone is cubic with complete Mg-Si disordering on octahedral site. Wang et al. (1993) concluded from the synthetic temperature dependence of microstructures that the phase transition from \( \text{Ia}3d \) to \( \text{I}_4/\text{a} \) in \( \text{MgSiO}_3 \) majorite arises around 22 GPa and 2300–2350 °C and that the ubiquitous twins in \( \text{I}_4/\text{a} \) phase synthesized below this temperature are produced during the growth process. Consequently, they considered that \( \text{MgSiO}_3 \) majorite in the transition zone is probably tetragonal (\( \text{I}_4/\text{a} \)). Recently, in \( \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} - \text{MgSiO}_3 \) majorite solid solution, Heinemann et al. (1997) proposed that the phase transition of the end-mem-