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

Akihiko Nakatsuka,^{1,*} Akira Yoshiasa,^{2} Takamitsu Yamanaka,^{2} Osamu Ohtaka,^{2} Tomoo Katsura,^{3} and Eiji Ito^3

[1]Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan
[2]Department of Earth and Space Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
[3]Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori 682-0193, Japan

Abstract

Six single crystals of Mg$_3$(Mg$_x$Si$_x$Al$_{2-2x}$)Si$_3$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 $I4_1/acd$ (tetragonal), which is the maximal subgroup of the space group $Ia\bar{3}d$ (cubic). Given that the previous reports that crystals with $0.8 \leq x \leq 1.0$ have the tetragonal space group $I4_1/a$, the majorite solid-solution in this system undergoes the series of symmetry changes, $Ia\bar{3}d \rightarrow I4_1/acd \rightarrow I4_1/a$, with increasing MgSiO$_3$ component. The symmetry changes from $Ia\bar{3}d$ to $I4_1/acd$ 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 $I4_1/acd$ structure loses the center of symmetry with the symmetry reduction from $Ia\bar{3}d$ to $I4_1/acd,$ the symmetry reduction may be caused by the electronic polarization of the cations due to the neighboring cation-cation interaction.