

## 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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### ABSTRACT

Six single crystals of  $\text{Mg}_3(\text{Mg}_x\text{Si}_x\text{Al}_{2-2x})\text{Si}_3\text{O}_{12}$  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 ( $B_{\text{eq}}$ ), 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  $B_{\text{eq}}$  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  $\text{MgSiO}_3$  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 ( $\text{Mg}^{2+}$ ) and tetrahedral ( $\text{Si}^{4+}$ ) 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.