

中塚晃彦 山口大学 (受入教官: 桂智男)

アルミナスペロフスカイトの単結晶育成 (H9 中塚)

MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> perovskite の結晶構造解析 (H10,11 中塚)

Symmetry change of majorite solid-solution in the system Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>-MgSiO<sub>3</sub>

Akihiko Nakatsuka,<sup>1,\*</sup> Akira Yoshiasa,<sup>2</sup> Takamitsu Yamanaka,<sup>2</sup> Osamu Ohtaka,<sup>2</sup>

Tomoo Katsura,<sup>3</sup> and Eiji Ito<sup>3</sup>

Am. Mineral. 84, 1135-1143 (1999).

Six single crystals of Mg<sub>3</sub>(Mg<sub>x</sub>Si<sub>x</sub>Al<sub>2-2x</sub>)Si<sub>3</sub>O<sub>12</sub> majorite solid-solution ( $x = 0.05, 0.13, 0.24, 0.38, 0.52,$  and  $0.64$ ) were first systematically synthesized at 20 GPa and 2000 °C with “6-8” type uniaxial split-sphere apparatus. The crystal structures were refined using single crystal X-ray diffraction method. The new discontinuities in compositional dependence of the molar volume, equivalent isotropic temperature factors ( $B_{eq}$ ), and mean bond lengths were found at a certain composition between  $x = 0.24$  and  $0.38$ . From the polarization-microscopic observation, the single crystals in the compositional range  $0 \leq x \leq 0.24$  show no birefringence, while those of  $x = 0.64$  slightly have an optical anisotropy. Moreover, the cell symmetry of  $x = 0.64$  obtained using synchrotron X-ray radiation resulted in tetragonal. From these results, the symmetry of majorite solid-solution in this system is considered to change from cubic to tetragonal at a certain composition within the range  $0.24 < x < 0.38$ . 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). In consideration of the previous reports that the crystals in the range  $0.8 \leq x \leq 1.0$  have the space group  $I4_1/a$  (tetragonal), 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<sub>3</sub> component. The symmetry changes from  $Ia\bar{3}d$  to  $I4_1/acd$  cannot be explained by the cation ordering on the octahedral site. The existence of the strong electrostatic interaction between the dodecahedral (Mg<sup>2+</sup>) and tetrahedral (Si<sup>4+</sup>) cations was observed from atomic thermal motion and electron density distribution. In consideration of the fact that 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.