American Mineralogist, Volume 92, pages 863–872, 2007

The geometric effects of $^{V}Fe^{2+}$ for ^{V}Mg substitution on the crystal structures of the grandidierite-ominelite series

Tashia J. Dzikowski,[1] Lee A. Groat,[1,*] and Edward S. Grew[2]

[1]Department of Earth and Ocean Sciences, University of British Columbia, 6339 Stores Road, Vancouver, British Columbia V6T 1Z4, Canada
[2]Department of Geological Sciences, University of Maine, 5790 Bryand Research Center, Orono, Maine 04469-5790, U.S.A.

Abstract

The electron microprobe compositions and crystal structure of seven members of the grandidierite-ominelite ($MgAl_3BSiO_9$–$Fe^{2+}Al_3BSiO_9$) series with $X = (Fe^{2+} + Mn + Zn)/(Fe^{2+} + Mn + Zn + Mg)$ ranging from 0.00 to 0.52 were studied to determine the geometric effects of Fe substitution for Mg on the crystal structures. Calculating Fe^{3+} from the electron microprobe analyses gave 0.04–0.06 Fe^{3+} apfu, but such small amounts at the Al sites could not be detected in the refinements. Regression equations derived from single-crystal X-ray diffraction data show that *b* increases by 0.18 Å from X = 0–1. The crystal structure refinements show that the most significant changes involve the $(Mg,Fe^{2+})O_5$ polyhedron, which increases in volume by 0.36 $Å^3$ (5.0%), largely as a result of expansion of the MgFe-O5, -O2, and -O6 (×2) bond distances, which increase by 0.09 (4.4%), 0.06, and 0.04 Å, respectively. Other significant changes include increasing O1-MgFe-O2 (3.44°) and -Al3-O5a angles (1.9°) and a decreasing O6-MgFe-O6b (–2.20°) angle. Significant increases are also seen in the lengths of the O1-O2 (0.13 Å) and O6-O5a (×2) (0.09 Å) edges. The SiO_4 tetrahedra appear to respond to changes in the surrounding polyhedra by changing O-Si-O angles such that the tetrahedral angle variance and mean tetrahedral quadratic elongation increase with X. The BO_3 triangles appear to behave as relatively invariant units in the crystal structure.

Regression equations obtained from the MgFe-O bond distances were used to determine a radius for $^{V}Fe^{2+}$ of 0.70 Å. Although our samples show little Mn, the presence of Mn^{2+} at the MgFe site would be expected to cause more distortion than an equivalent amount of Fe^{2+}. Substitution of Zn likely would have little effect. The presence of Cr^{3+} at any of the Al sites would be expected to increase the size of the coordination sphere, but the substitution of P^{5+} for Si at the Si sites would most likely decrease the Si-O bond distances.

Keywords: Grandidierite, ominelite, crystal structure, substitution, borosilicates