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Phase transition induced by solid solution: The ^{B}Ca-^{B}Mg substitution in richteritic amphiboles

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Abstract

Eleven compositions along the join $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$-$Na(NaCa)Mg_5Si_8O_{22}(OH)_2$ ("magnesiorichterite"-richterite) have been synthesized at T = 800–850 °C and P_{H_2O} = 0.35–0.5 GPa. The run products have been characterized by electron probe microanalysis (EPMA), synchrotron and conventional X-ray powder diffraction (XRPD), Fourier transformed infrared (FTIR) spectroscopy, and selected area electron diffraction (SAED-TEM). Nominally, the chemical variation along the join can be expressed as $^{B}Mg_x{}^{B}Ca_{1-x}$ with $0 \leq x \leq 1$. A combination of EPMA and FTIR data in the OH-stretching region show that a complete solid solution is obtained under the conditions used. Nevertheless, a slight deviation from the nominal compositions involving a limited loss of Na at A and B sites, balanced by an increase of Ca at the B site, is present. Several indications of a displacive and coelastic $P2_1/m \rightarrow C2/m$ transformation induced by the Ca-Mg chemical substitution are observed. The phase transition occurs at B-site composition (X_c) close to $^{B}(Na_1Mg_{0.7}Ca_{0.3})$. $C2/m$ samples with a Ca content of 0.34, 0.45, and 0.54 apfu show a significant strain tail related to local compositional inhomogeneities. This residual strain disappears as the amount of ^{B}Ca significantly increases with respect to that of ^{B}Mg. The transformation behavior observed here mirrors that of pyroxenes along the join diopside ($CaMgSi_2O_6$)-enstatite ($Mg_2Si_2O_6$). The cell parameters of amphiboles with $^{C}Mg_5$, $^{T}Si_8$, and $^{W}(OH)_2$ and variable A- and B-site populations follow almost linear and continuous trends, indicative of small amounts of spontaneous strain accompanying these monoclinic phase transitions and the absence of significant miscibility gaps among different amphibole groups when quenched from higher temperatures of crystallization.

Keywords: Synthetic amphiboles, XRPD, EPMA, SAED-TEM, FTIR spectroscopy, cell parameters, phase transition