



## Phase transitions at ambient and high- $T$ along the amphibole join richterite – “magnesorichterite”

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Ten amphibole compositions along the  $P2_1/m$   $\text{Na}(\text{NaMg})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  (“magnesorichterite”) -  $C2/m$   $\text{Na}(\text{NaCa})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  (richterite) join were synthesized at 800-850°C and 0.35-0.5 GPa. The run-products were characterized by a combination of SEM-EDS, EPMA-WDS, XRPD, SAED-TEM and FTIR OH-stretching spectroscopy. The microchemical data show that a complete solid-solution is obtained along the join, which is characterized by the  $^B(\text{Na}_1\text{Mg}_x\text{Ca}_{1-x})$  (with  $0 \leq x \leq 1$ ) substitutional vector. A slight departure from the nominal compositions following the  $^A\text{Na}_x^B\text{Na}_{1-x}$  vs  $^A\text{Mg}_{2-x}^B\text{M}^{2+}$  exchange (with  $\text{M}^{2+} = \text{Mg}$  or  $\text{Ca}$ ) is observed. Refinement of the X-ray powder diffraction-patterns shows a major variation for the  $a$  and  $\beta$  cell parameters, with only minor variations ( $< 1\%$  relative) for the  $b$  and  $c$  edges.

At room- $T$ , the FTIR OH-stretching spectra of the  $^B\text{Mg}$ -richer compositions show two intense absorptions, which are assigned to two independent O-H groups in the primitive structure. The frequency separations of these bands is progressively reduced as  $^B\text{Ca}$  increases. In agreement with this assignment, SAED patterns show  $h + k$  odd reflections for the same samples. Conversely, the amphiboles with B-site compositions between  $(\text{Na}_1\text{Mg}_{0.6}\text{Ca}_{0.4})$  and  $(\text{Na}_1\text{Ca}_1)$  show a unique and symmetric OH-stretching band, indicative of a  $C$ -lattice. Therefore, along the examined join the  $P2_1/m \leftrightarrow C2/m$  phase-transition at room- $T$  occurs at the  $\text{Na}(\text{Na}_1\text{Mg}_{0.7}\text{Ca}_{0.3})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  stoichiometry.

The Mg-richer  $P2_1/m$  amphiboles reverse their structure to  $C2/m$  at high- $T$  by a displacive transformation. The spontaneous strain parameters fitted by Landau expansions indicate that the end-member “magnesiorichterite” follows a tricritical behavior, whereas the presence of  ${}^B\text{Ca}$  induces a second order type transformation. The measured  $T_c$  is linearly related to the amount of  ${}^B\text{Mg}$  in the amphibole, i.e. is a linear function of the mean aggregate ionic radius at the  $M(4)$  site.