The high-temperature $P2_1/m \rightarrow C2/m$ phase transitions in synthetic amphiboles along the richterite–(^BMg)–richterite join

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ABSTRACT

The thermal behavior of three amphiboles along the join "Mg-richterite" [MRIC: $^{A}Na^{B}(NaMg)$ $^{C}Mg_{5}^{T}Si_{8}O_{22}^{W}(OH)_{2}$]-richterite [RIC: $^{A}Na^{B}(NaCa)^{C}Mg_{5}^{T}Si_{8}O_{22}^{W}(OH)_{2}$] was investigated by in situ synchrotron radiation powder diffraction between 90 and 873 K. The studied samples have B-site compositions $Na_{1}Mg_{1}$ (sample RN1), $Na_{0.97}Mg_{0.8}Ca_{0.24}$ (sample RN2), and $Na_{0.97}Mg_{0.58}Ca_{0.45}$ (sample RN6).

The evolution of cell parameters as a function of T shows a discontinuity in the two Mg-richer samples (RN1 and RN2), which is interpreted as evidence of a $P2_1/m \rightarrow C2/m$ phase transition, whereas the Ca-richer sample (RN6) shows no evidence of a phase transition. The transition in samples RN1 and RN2 follows a different thermodynamic behavior, being tricritical in end-member "Mg-richterite" (RN1) and second order in the ^BCa-bearing amphibole RN2. A thermodynamic analysis done according to the Landau formalism and allowing for order parameter saturation, gives $T_c = 462(3)$ and 378(1) K, and saturation temperature $\theta_s = 116(21)$ and 141(7) for RN1 and RN2, respectively.

Comparison with data from literature shows that the thermal strain of *C*-centered amphiboles with constant A-, C-, T-, and W-site occupancy equal to Na, Mg₅, Si₈, and (OH)₂, respectively, and a B-site occupied by variable amounts of Li, Na, Mg, and/or Ca, mainly expands about 70° from *c* toward the *a* cell-edge onto the 010 plane. Conversely, the spontaneous strain accompanying the thermal transition shows that the maximum expansion is oriented about 25° from *c* and is coupled with a contraction close to the *a* cell direction. On the other side, transition induced by solid solution at room-*T* follows an almost opposite deformation pattern.

The present data confirm the hypothesis of a first-order character of the transition induced by the increase of the B-site dimension for increasing ^BCa contents, similarly to the closely related $P2_1/c \rightarrow C2/c$ transition in pyroxenes.

Keywords: Synthetic amphibole, synchrotron XRPD, phase transition, lattice deformation