The high-temperature $P_{2/1m} \rightarrow C2/m$ phase transitions in synthetic amphiboles along the richterite–(6Mg)–richterite join

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ABSTRACT

The thermal behavior of three amphiboles along the join “Mg-richterite” [MRIC: $^6$Na$^8$(NaMg)$^6$Mg; $^8$Si$_8$O$_{22}$(OH)$_{22}$]–richterite [RIC: $^8$Na$^8$(NaCa)$^8$Mg; $^6$Si$_8$O$_{22}$(OH)$_{22}$] was investigated by in situ synchrotron radiation powder diffraction between 90 and 873 K. The studied samples have B-site compositions Na$_x$Mg$_{1-x}$ (sample RN1), Na$_{0.97}$Mg$_{0.03}$Ca$_{0.24}$ (sample RN2), and Na$_{0.97}$Mg$_{0.24}$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 $P_{2/1m} \rightarrow C2/m$ 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 $^6$Ca-bearing amphibole RN2. A thermodynamic analysis done according to the Landau formalism and allowing for order parameter saturation, gives $T_x = 462(3)$ and $378(1)$ K, and saturation temperature $0_x = 116(21)$ 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, Mg$_6$, Si$_8$, 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 $^6$Ca contents, similarly to the closely related $P_{2/c} \rightarrow C2/c$ transition in pyroxenes.

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

INTRODUCTION

The $C2/m \rightarrow P_{2/1m}$ phase transition in amphiboles has been the subject of repeated investigations since the first refinement of a $P_{2/1m}$ cummingtonite by Prewitt et al. (1970). At room temperature, the $P_{2/1m}$ phase occurs in the Mg-richer portion of the cummingtonite-grunerite join (Hirschmann et al. 1994; Yang and Prewitt 2000; Boffa-Ballaran et al. 2004). Recent works have also shown that synthetic “magnesiorichterite” [MRIC: Na(NaMg)Mg$_6$Si$_8$O$_{22}$(OH)$_{22}$] and amphiboles along the join Na(NaMg)Mg$_6$Si$_8$O$_{22}$(OH)$_{22}$–Na(LiMg)Mg$_6$Si$_8$O$_{22}$(OH)$_{22}$ have $P_{2/1m}$ symmetry (Iezzi et al. 2004, 2006a; Cámara et al. 2008). In situ high-$T$ or $-P$ investigations have shown that the $P$-lattice polymorph is stable at higher $T$ and lower $P$ when the B-site is progressively reduced in dimension by the Li-Na substitution (Iezzi et al. 2005a, 2009; Della Ventura et al. 2008; Welch et al. 2007). At room conditions, $C2/m$ symmetry is stabilized when the B-site is Li-free and 6Mg is progressively substituted by 6Ca; the transition occurs at the Na$_x$Mg$_{6-x}$Ca$_{6}$ B-site stoichiometry (Iezzi et al. 2010).

The aim of this study is to characterize the thermodynamic behavior of the $P_{2/1m} \rightarrow C2/m$ transition as a function of $T$ (90–873 K) in synthetic Mg-richer amphiboles along the join “magnesiorichterite”–richterite [RIC: Na(NaCa)Mg$_6$Si$_8$O$_{22}$(OH)$_{22}$]. The study was done using high-resolution synchrotron X-ray powder diffraction (XRPD), so as to detect subtle changes in cell parameters through the phase transition. This study is part of a larger project on the crystal-chemical behavior of synthetic amphiboles in the LNMClSH (Li$_2$O-Na$_2$O-MgO-CaO-SiO$_2$-H$_2$O) system aimed at characterizing their transitional features as a function of $T$, $P$, and $X$ (Cámara et al. 2003, 2008; Iezzi et al. 2004, 2005a, 2005b, 2006a, 2006b, 2009; Della Ventura et al. 2008; Welch et al. 2007). Synthetic LNMClSH amphiboles, although not found in nature, indeed provide a sim-