Crystal structural changes in titanite along the join TiO-AlF

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Abstract: We investigated the crystal structural changes in titanite solid-solution Ca(Ti,Al)(O,F)SiO₄ along the binary join TiO-AlF, on the basis of X-ray powder data and Rietveld refinement of seven synthetic titanites of intermediate compositions. Investigations with the transmission electron microscope allow us to narrow down the space group transition from P2₁/a to A2Ia to compositions between Xₐ₁ = 0.09 and Xₐ₁ = 0.18 [Xₐ₁ = Al/(Al+Ti)]. The changes in most of the unit-cell dimensions along the binary join are non-linear, resulting in a small excess volume of mixing with a maximum at Xₐ₁ = 0.54. The commonly observed trend of positive deviation of the excess volume of mixing near the large end-member, and negative deviation towards the small end-member seems to be reversed in this case. At AlF-contents larger than Xₐ₁ = 0.6 the Ca-site and the O₁-site in the titanite structure become increasingly over-bonded with Al-F substitution. At about Xₐ₁ = 0.4 the octahedral cation-oxygen distances change significantly, indicating that the titanite structure undergoes a major atomic rearrangement at high AlF-contents in order to accommodate the increasingly different ionic size and charge. Generally, with increasing AlF content the polyhedra are being deformed rather than rotated. The changes in unit-cell dimensions, bond lengths and bond valence sums along the binary join suggest the presence of structural strain in AlF-rich titanite, especially at Al-F contents exceeding Xₐ₁ = 0.4. The structural problems are obviously not significant enough to prevent the formation of Al-rich titanite in simple chemical systems as in our experiments. However, the structural strain may be significant enough to decrease the thermodynamic stability of Al-rich titanite in natural rocks compared to other Al- and F-bearing phases. This could partly explain the rare natural occurrence of titanite with Xₐ₁ > 0.54.

Key-words: titanite, solid solution, crystal structure, crystal chemistry, Rietveld refinement.

Introduction

The mineral titanite CaTiOSiO₄ is a common accessory phase in a broad range of igneous, metamorphic, and even some sedimentary rocks. The composition of titanite is variable, depending on bulk-rock and fluid composition, pressure and temperature. The Al-content in titanite was the focus of numerous previous studies (e.g., Smith, 1981; Enami et al., 1993) because the two coupled exchange reactions

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\begin{align*}
\text{Ti}^{4+} + \text{O}^{2-} &= \text{Al}^{3+} + \text{F}^- \\
\text{Ti}^{4+} + \text{O}^{2-} &= \text{Al}^{3+} + \text{OH}^{-}
\end{align*}
\]

are very sensitive to pressure and temperature, and thus could be of interest for geothermobarometry. Many Al-rich titanites were reported from high-