The synthesis and crystal structure of CaAlFSiO₄, the Al-F analog of titanite

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ABSTRACT

Aluminum-rich titanites [Ca(Ti,Al)(O,F)SiO₄] with Xₐl > 0.53 [Xₐl = Al/(Al+Ti)], including the pure end-member CaAlFSiO₄, were synthesized for the first time in a high-pressure experimental study. The crystal structure of CaAlFSiO₄ was determined by Rietveld analysis of an X-ray powder diffraction pattern. CaAlFSiO₄ is monoclinic, belongs to the space group A2/a, and has the unit-cell dimensions a = 6.9149(2) Å, b = 8.5064(1) Å, c = 6.4384(2) Å, and β = 114.684(2)°. The unit-cell volume is less than 93% of CaTiOSiO₄, which is consistent with the natural occurrence of Al-rich titanite in high-P rocks. Although previous studies suggested that titanite with Xₐl > 0.5 is possibly not stable, this study demonstrates that complete solid solution occurs between CaTiOSiO₄ and CaAlFSiO₄. The similarity of the crystal structures of titanite and CaAlFSiO₄ explains why in natural Al-rich titanite the end-member CaAlFSiO₄ generally dominates over the hypothetical end-member CaAlOHSiO₄, which under geological conditions is stable in a different crystal structure.

INTRODUCTION

Al-rich titanites [Ca(Ti,Al)(O,F)SiO₄] has been the focus of many previous mineralogical studies (Higgins and Ribbe 1976; Smith 1981; Oberti et al. 1991) because Al is one of the most common and abundant substituents for Ti in natural titanite (Franz and Spear 1985; Sobolev and Shatsky 1990; Krogh et al. 1990; Carswell et al. 1996). Moreover, the substitution appeared to be pressure and temperature dependent and thus could be of interest for geothermobarometry (Smith 1981; Enami et al. 1993). The two coupled substitution reactions that account for the formation of Al-bearing titanite are Ti⁴⁺ + O²⁻ = Al³⁺ + F⁻ and Ti⁴⁺ + F⁻ = Al³⁺ + OH⁻. Hence Al-rich titanite is made up of the three end-members CaTiOSiO₄ [titanite], CaAlFSiO₄, and CaAlOHSiO₄. Although the end-member titanite occurs in nature and its crystal structure is known (Speer and Gibbs 1976), to our knowledge CaAlFSiO₄ has never been found or synthesized before, and neither has the pure CaAlOHSiO₄ end-member been reported. The mineral vuagnatite [CaAlOHSiO₄] is chemically equivalent to the AIOH end-member of Al-rich titanite, but its crystal structure (McNear et al. 1976) is different to that of titanite and thus it does not represent the AIOH-component of titanite solid solution.

The extent of solid solution between these end-members was previously discussed. Because the maximum amount of Al-substitution (Xₐl = 0.5) reported from natural titanite (Franz and Spear 1985) is comparable to that of the first and only high-PT experimental investigation of Al- and F-bearing titanite with Xₐl = 0.53 (Smith 1981), previous studies (Franz and Spear 1985; Oberti et al. 1991) pointed out that the Al-content in titanite appears to be restricted to Xₐl < 0.5 (note that earlier studies usually did not distinguish between the two aluminum-end-members due to lack of OH- and F-analyses). Oberti et al. (1991) investigated several natural Al-rich titanites (Xₐl < 0.37), documenting changes in the crystal structure with increasing Xₐl. They discussed various crystal structural features that might be responsible for the apparent mixing gap at Xₐl > 0.5, but clear evidence for a crystal structural constraint was still missing.

The present study extends the information on Al-rich titanite summarized by Oberti et al. (1991) by providing crystal structural data for the end-member CaAlFSiO₄. Results from high-PT experiments in the binary system CaTiOSiO₄-CaAlFSiO₄ are reported that show complete solid solution.

EXPERIMENTAL METHODS

Synthesis of CaAlFSiO₄

The synthesis of CaAlFSiO₄ was carried out at 35 to 38 kbar and 1100 °C using the piston cylinder apparatus at the Geology Department, Australian National University. Run times varied from 21 to 24 h (see Table 1 for individual run conditions; samples G-295, G-296, G-297). The starting material was a powder of synthetic fluorite (Specpure) and anorthite in equal molar proportions, seeded with about 10 wt% CaAlFSiO₄. CaAlFSiO₄ does not nucleate without the presence of seeds. Thus CaAlFSiO₄ seeds had to be prepared in several cycles from titanite, anorthite and fluorite. In the first cycle, a mix of fluorite and anorthite (1:1) and about 1 wt% titanite seeds was run at 35 kbar and 1100 °C for 24 h, resulting in titanite solid solution with about 99 mol% of the CaAlFSiO₄ end-member, besides smaller amounts of zoisite, fluorite, and kyanite (G-274, Table 1). This product was then used as seed material for subsequent cycles. After three cycles, titanium could no longer be detected using scanning electron microscopy, and the material was used as seeds for CaAlFSiO₄ synthesis. The anorthite of the starting mix was crystallized from glass at 1000 °C, 1 atm for 24 h with several cycles of crushing and heating. The glass was prepared by melting Al₂O₃, SiO₂, and CaCO₃ at 1600 °C and 1 atm, with subsequent quenching in water.