Low-temperature ordered phase of CaU(PO₄)₂: synthesis and crystal structure

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Abstract: The crystal structure of the new compound CaU(PO₄)₂ was determined from X-ray single-crystal data and refined to R(F) = 0.025 and Rw(F) = 0.023 for 993 independent observed reflections. The unit cell is orthorhombic, a = 13.926(4) Å, b = 6.958(3) Å and c = 6.136(2) Å, space group Pnma. The structure is Ca, U ordered and in some aspects similar to the xenotime and anhydrite structure. The coordination polyhedra for the large metal ions are described as semi regular trigonododecahedra.

Key-words: crystal structure, synthesis, CaU(PO₄)₂, xenotime, monazite-type.

Introduction

The structural study of the orthorhombic compound CaU(PO₄)₂ reported here is part of an ongoing study on the capacity of lanthanum orthophosphate for incorporating large amounts of radioelements. The stability of the (La₁₋₂₅[U, Th]ₓCaₓ)PO₄ compounds is demonstrated in companion papers (Podor et al., 1995; Podor & Cuney, submitted). The crystallographic data concerning the xenotime-type CaU(PO₄)₂ compound have been obtained, and the limits of its thermal stability under hydrothermal conditions are also reported here. The structural relationships between the low- and high-temperature forms of CaU(PO₄)₂ are discussed.

Synthesis and thermal stability

The CaU(PO₄)₂ single-crystals were obtained by a method originally described by Anthony (1957). The CaU(PO₄)₂ compound is precipitated by reaction between a stoichiometric mixture of UO₂·₁₂ and Ca(OH)₂ and a 30 m H₃PO₄ solution, at T = 500°C and P = 200 MPa. The oxygen fugacity was fixed at 10⁻²² atm by the Ni/NiO buffer (Podor et al., 1995).

The orthorhombic compound is stable in 30 m H₃PO₄ solution, at P = 200 MPa, in the temperature range 300-700°C. A high-temperature (Ca₀.₅U₀.₅)PO₄ compound crystallises under the same conditions of pressure and composition of the aqueous phase, at T > 700°C (Podor et al.,...