Received 19 May 2006

Accepted 30 October 2006

Acta Crystallographica Section B Structural Science

Patrick H. J. Mercier,^a* Zhili Dong,^b Thomas Baikie,^b Yvon Le Page,^a T. J. White,^b Pamela S. Whitfield^a and Lyndon D. Mitchel^c

^aInstitute for Chemical Process and Environmental Technology (ICPET), National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, ^bSchool of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore, and ^cInstitute for Research in Construction (IRC), National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Correspondence e-mail: patrick.mercier@nrc-cnrc.gc.ca Ab initio constrained crystal-chemical Rietveld refinement of $Ca_{10}(V_xP_{1-x}O_4)_6F_2$ apatites

Extraction of reliable bond distances and angles for $Ca_{10}(V_xP_{1-x}O_4)_6F_2$ apatites using standard Rietveld refinement with Cu Ka X-ray powder data was significantly impaired by large imprecision for the O-atom coordinates. An initial attempt to apply crystal-chemical Rietveld refinements to the same compounds was partly successful, and exposed the problematic determination of two oxygen-metaloxygen angles. Ab initio modeling with VASP in space groups $P6_3/m$, $P2_1/m$ and Pm showed that both these angular parameters exhibited a linear dependence with the vanadium content. Stable crystal-chemical Rietveld refinements in agreement with quantum results were obtained by fixing these angles at the values from ab initio simulations. Residuals were comparable with the less precise standard refinements. The larger vanadium ion is accommodated primarily by uniform expansion and rotation of BO₄ tetrahedra combined with a rotation of the Ca-Ca-Ca triangular units. It is proposed that the reduction of symmetry for the vanadium end-member is necessary to avoid considerable departures from formal valences at the A^{II} and B sites in $P6_3/m$. The complementarity of quantum methods and structural analysis by powder diffraction in cases with problematic least-squares extraction of the crystal chemistry is discussed.

1. Introduction

Apatite-type structures combine crystallochemical flexibility with considerable durability, making them materials of interest for the long-term stabilization of toxic metals from municipal incinerators (Eighmy et al., 1998; Valsami-Jones et al., 1998; Crannell et al., 2000) and high-level nuclear waste (Ewing & Wang, 2002; Vance et al., 2003; Terra et al., 2006). The most common symmetry is $P6_3/m$, leading to the general formula $[A_4^{I}][A_6^{II}][(BO_4)_6]X_2$, although numerous low-symmetry derivatives have been reported. Topologically, apatites can be considered to be one-dimensionally microporous and zeolitelike, with a flexible framework created through the cornerconnection of $A^{I}O_{6}$ metaprism columns with isolated BO_{4} tetrahedra. The channels are occupied by A^{II} ions in the disposition of irregular $A^{II}O_6X$ polyhedra. A and B cation ordering is observed on occasion and usually leads to a reduction of symmetry.

In solid solution fluorapatite $[Ca_{10}(PO_4)_6F_2]$ can accommodate larger ions of valence 1+, 2+ and 3+ in place of Ca, and smaller 4+, 5+ and 6+ ions for P (White *et al.*, 2005). While apatites have the potential to immobilize a spectrum of elements, compositional tailoring is nevertheless required, as their adaptability is constrained to suitable combinations of ions that maintain charge balance and accept the steric and topological limitations of the structure. A model involving

O 2007 International Union of Crystallography Printed in Singapore – all rights reserved

electronic reprint