The crystal structure of pararobertsite and its relationship to mitridatite

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ABSTRACT

The crystal structure of pararobertsite, Ca₆(PO₄)₉[Mn³⁺O₆(PO₄)₃]·3H₂O, P2₁/c, a = 8.814(4), b = 13.233(5), c = 11.056(4) Å, α = 101.184(7)°, V = 1265.0(9) Å³, Z = 4 has been solved by direct methods and refined to R = 0.042 for 1319 Fᵢ > 4σ(Fᵢ) using MoKα X-ray data. In the structure of pararobertsite, Z-shaped edge-sharing chains of Mn³⁺O₆ octahedra link to one another via shared O vertices and PO₄ tetrahedra to form a compact sheet of composition 2⁻[Mn³⁺O₆(PO₄)₃]₄⁻ oriented parallel to {100}. The space between the compact sheets is filled with a thick open assemblage of CaO₅(H₂O)₂ polyhedra and isolated water molecules. The structure bears strong similarities to the mitridatite (Fe³⁺) structure and, therefore, to its robertsite (Mn³⁺) isotype.

INTRODUCTION

The mineral pararobertsite from from the Tip Top pegmatite, Custer County, South Dakota was described by Roberts et al. (1989), who named the mineral for its close chemical and crystallographic relationship to robertsite, Ca₆(H₂O)₆[Mn³⁺O₆(PO₄)₃]·3H₂O in the asymmetric unit, Z = 4. Robertsite is isostructural with mitridatite, Ca₆(H₂O)₆[Fe³⁺O₆(PO₄)₃]·3H₂O, whose structure was determined by Moore and Araki (1977). This study was undertaken to elucidate the structural relationship between pararobertsite and robertsite.

STRUCTURE DETERMINATION

Single-crystal X-ray precession and diffractometer studies showed pararobertsite to be monoclinic, space group P2₁/c, a = 8.814(4), b = 13.233(5), c = 11.056(4) Å, α = 101.184(7)°, V = 1265.0(9) Å³, Z = 4. The cell parameters were refined from the peak positions obtained from the structure data collection. These cell parameters compare closely to those reported by Roberts et al. (1989), a = 8.825, b = 13.258, c = 11.087 Å, α = 101.19°.

X-ray intensity data were collected from a thin tabular crystal of pararobertsite of dimensions 0.14 × 0.11 × 0.01 mm³ using a Bruker PLATFORM 3-circle goniometer equipped with a 1 K SMART CCD detector. The operating conditions were: room temperature, 50 kV, 45 mA, graphite-monochromatized MoKα radiation (λ = 0.71069 Å). Frame widths of 0.3° in ø were used to acquire each frame for 120 s. A total of 1271 frames of data was collected, providing a half sphere of three-dimensional data. Data were collected for 4.7° ≤ 2θ ≤ 56.6°. Fifty duplicate frames acquired at the end of the data collection indicated that no significant decay had taken place. The 7946 measured intensities (1 ≤ h ≤ 11, 3 ≤ k ≤ 17, 4 ≤ l ≤ 14) were corrected for Lorentz and polarization effects using the program SAINT and an empirical absorption correction was applied using the program SADABS. The final data set reduced to 3014 unique reflections. The absorption correction lowered RINT from 3.8 to 3.1%.

The SHELXL97 software (Sheldrick 1997) was used for the determination and refinement of the structure. The metal atoms (Ca, Mn, and P) and several of the O atoms were readily located by direct methods. The positions of the remaining O atoms were obtained from subsequent difference-Fourier syntheses. In subsequent refinement cycles, anisotropic displacement parameters for all non-hydrogen atoms were refined to a conventional R index of 0.043 and wR₂ = 0.105 [weighted R factor on F², as defined by Sheldrick (1997)] for 1319 measured reflections with Fᵢ > 4σ(Fᵢ), R = 0.137 and wR₂ = 0.153 for all 3014 data, and goodness of fit = 0.619. At this point examination of the highest peaks in the difference-Fourier synthesis coupled with valence-bond and geometrical considerations allowed the location of all H atoms. With H atom positions and isotropic displacement parameters (0.05) held invariant, the final refinement cycles yielded R = 0.042 and wR₂ = 0.099 for 1319 measured reflections with Fᵢ > 4σ(Fᵢ), R = 0.136 and wR₂ = 0.149 for all 3014 reflections, and goodness of fit = 0.601. Maximum and minimum heights in the final difference Fourier synthesis were +1.15 and −0.76 e/Å³.

Table 1 includes the final fractional coordinates and displacement parameters, Table 2 the observed and calculated structure factors, Table 3 interatomic distances and angles, and Table 4 the bond valences.

DESCRIPTION OF THE STRUCTURE AND COMPARISON TO MITRIDATITE

In the structure of pararobertsite, Z-shaped edge-sharing chains of Mn³⁺O₆ octahedra link to one another via shared O vertices and PO₄ tetrahedra to form a compact sheet of composition 2⁻[Mn³⁺O₆(PO₄)₃]₄⁻ oriented parallel to {100} (Fig. 1a). (The notation 2⁻ indicates a structural unit that extends infinitely in two dimensions, i.e., a sheet.) The space between the compact sheets is filled with a thick open assemblage of CaO₅(H₂O)₂ polyhedra and isolated water molecules. The structure bears strong similarities to the mitridatite (Fe³⁺) structure and, therefore, to its robertsite (Mn³⁺) isotype.