

The crystal structure of synthetic autunite, $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$

ANDREW J. LOCOCK* AND PETER C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, Indiana 46556-0767, U.S.A.

ABSTRACT

Autunite, $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$, is amongst the most abundant and widely distributed of the uranyl phosphate minerals, yet because of its pseudo-tetragonal symmetry and rapid dehydration in air, the details of its symmetry, stoichiometry, and structure were previously uncertain. The crystal structure of synthetic autunite was solved by direct methods and refined by full-matrix least-squares techniques to agreement indices $R_1 = 0.041$, calculated for the 1497 unique observed reflections ($|F_o| \geq 4\sigma_F$), and $wR_2 = 0.119$ for all data. Autunite is orthorhombic, space group $Pnma$, $Z = 4$, $a = 14.0135(6)$, $b = 20.7121(8)$, $c = 6.9959(3)$ Å, $V = 2030.55(15)$ Å³. The structure contains the well-known autunite type sheet with composition $[(\text{UO}_2)(\text{PO}_4)]^-$, resulting from the sharing of equatorial vertices of the uranyl square bipyramids with the phosphate tetrahedra. The calcium atom in the interlayer is coordinated by seven H_2O groups and two longer distances to uranyl apical O atoms. Two symmetrically independent H_2O groups are held in the structure only by hydrogen bonding. Bond-length-constrained refinement provided a crystal-chemically reasonable description of the hydrogen bonding.