Refinement of the crystal structure of pseudomalachite

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Abstract

The crystal structure of pseudomalachite, Cu₃(PO₄)₆(OH)₁₈ (from Rheinbreitenbach, Germany) has been refined by full-matrix least-squares techniques to a residual \( R = 0.040 \) \( (R_w = 0.047) \) using automatic diffractometer data. The lattice parameters (space group \( P2_1/c \)) are \( a = 4.4728(4) \), \( b = 5.7469(5) \), \( c = 17.032(3) \) \( \AA \), and \( \beta = 91.043(7) \). The copper ions lie in sheets of edge-sharing coordination polyhedra in the \( bc \) plane; the sheets are linked together in the \( a \) direction by highly distorted phosphate tetrahedra. This work confirms the essential features of an earlier structural study of pseudomalachite with increased precision. Through an analysis of bond distances, coordination, and bond valence sums, probable locations of hydrogen bonds were determined. Hydrogen bonds appear to be important in stabilizing the pseudomalachite structure.

Introduction

We recently reported (Anderson et al., 1977) the preparation and crystal-structure determination of synthetic Cu₃(PO₄)₆(OH)₁₈, a polymorph of pseudomalachite (PM). The structure of this synthetic phase (called PPM for convenience) differs from that of PM only in the difference in the polyhedral linkages in two-dimensional copper-containing sheets.

In our comparison of the two structures, the only difference in copper coordination seemed to occur about the Cu(2) ion, which we considered to be five-coordinated \((4 + 1)\) in PPM but which Ghose (1963) reports as six-coordinated \((4 + 1 + 1)\) in PM. As a result, we decided to complete a three-dimensional least-squares refinement of the structure of PM in order to compare the coordination polyhedra at the same level of accuracy. This paper reports the results of that refinement.

Experimental

Samples of pseudomalachite were obtained from the Harvard University Mineralogical Museum and from the Smithsonian Institution. The best crystals for X-ray diffraction were found in a sample from Rheinbreitenbach, Germany (Harvard #110744). According to published analyses, pseudomalachite from Rheinbreitenbach contains traces of iron, but an examination of fragments from our sample by electron microprobe showed none.

A sphere was ground to a radius of 0.0065(5) cm. Precession photographs revealed monoclinic symmetry with systematic absences corresponding to the space group \( P2_1/c \). The lattice parameters were determined in a PICK-II least-squares refinement program, using 50 reflections within the angular range \( 37^\circ < 2\theta < 50^\circ \): the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using \( \text{MoK} \alpha_1 \) radiation. At \( 22^\circ \text{C} \) the lattice parameters are \( a = 4.4728(4) \), \( b = 5.7469(5) \), \( c = 17.032(3) \) \( \AA \), and \( \beta = 91.043(7) \). Where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with \( Z = 2 \), is 4.367 \( \text{g cm}^{-3} \).

Diffraction intensities were measured using \( \text{Zr} \) filtered \( \text{MoK} \alpha_1 \) radiation at a take-off angle of 2.5° with the diffractometer operating in the \( \omega \) scan mode. 10-second background counts were taken at the ends of a 1.4° \( \theta - 2\theta \) scan corrected for dispersion. Of the 1694 independent data investigated in the angular range \( 2 \theta < 65^\circ \), 1411 were considered observable according to the criterion \( |F_o| > 3.00 \sigma_F \), where \( \sigma_F \) is defined as 0.02 \( |F_o| + [C + k^2B]^{1/2} |F_o| \). LP: the total scan count is \( C \), \( k \) is the ratio of scanning time to the total background time, and \( B \) is the total background count. Three reflections were systematically monitored and no variations in intensity greater than 5