The crystal structure of hopeite

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Abstract

The crystal structure of hopeite, Zn$_3$(PO$_4$)$_2$·4H$_2$O, has been solved by the Heavy Atom method from 1421 graphite-monochromatized MoKα data and refined by full matrix least-squares to $R = 0.026$ ($R_w = 0.036$). The structure is orthorhombic, $P_{nma}$, $a = 10.597(3)$, $b = 18.318(8)$, $c = 5.031(1)$ Å, and $Z = 4$. The Zn atoms occur in two crystallographically distinct sites, one six-coordinated and deficient in Zn, the other four-coordinated. The α and β modifications of this mineral are discussed in relation to its thermal dehydration and infrared absorption properties.

Introduction

Following the discovery of abundant material on a bone breccia in a cave at the Broken Hill mine, Zambia (Spencer, 1908), the mineral hopeite, Zn$_3$(PO$_4$)$_2$·4H$_2$O, has been the subject of considerable study. Much of this research has centered on the characterization of the α and β modifications first proposed by Spencer (1908) on the basis of differences in optics, density, and thermal behavior. Although most studies of the P$_2$O$_5$-ZnO·H$_2$O system support the existence of two varieties of hopeite displaying different optical and/or thermal properties, the characterization of these phases remains in a state of disarray: Takahashi et al. (1972) suggested that the α form of hopeite occurs in nature, while the β form corresponds to specimens prepared in the laboratory; Goloshchapov and Filatova (1969) seem to have been able to prepare both forms; the material synthesized by Nriagu (1973) has been identified as α-hopeite.

Two-dimensional crystal structure analyses of various natural and synthetic hopeite specimens were completed by Mamedov et al. (1961), Gamsidov et al. (1963), and Liebau (1962, 1965), but the topology of the structure was not confirmed until three-dimensional studies of synthetic hopeite (Kawahara et al., 1972, 1973) and of natural material (Whitaker, 1975) were published; this latter work came to our attention only after the refinement detailed in the present study was completed.

Experimental

Unit-cell dimensions for natural hopeite from Broken Hill, Zambia, (obtained through the courtesy of the South Australian Museum) were determined by a least-squares fitting (Appelman and Evans, 1973) of calculated to observed d-spacings; the data were collected at 21°C by powder diffractometry using LiF monochromatized CuKα radiation ($λ = 1.5418$ Å), and Si powder ($a = 5.4305$ Å) as an internal standard. These and other physical constants for hopeite are: $a = 10.597(3)$, $b = 18.318(8)$, $c = 5.031(1)$ Å, $V = 976.60$ Å$^3$, formula weight = 458.1, $F(000) = 896e$, $D_m$ (toluene immersion) = 3.065(9) g·cm$^{-3}$, $D_4$ (for $Z = 4$) = 3.116 g·cm$^{-3}$, $\mu_{MoKα} = 79.49$ cm$^{-1}$.

Two approximately cubic cleavage fragments, of dimensions 0.20 mm and 0.25 mm, were mounted about $a^*$ and $c^*$ respectively on a Stoe equi-inclination automated diffractometer. A total of 2797 reflections consistent with space group $Pn\overline{a}$ (suggested from systematic absences) were measured (a axis, 0kl-12kl; c axis, k=0-6) of which 97 percent were within the positive octant of the reflecting sphere. The data set was collected at 21°C with graphite-monochromatized MoKα radiation ($λ = 0.7107$ Å), utilizing the ω-scan technique; details of the procedure are described by Snow (1974).

Absorption corrections were applied to the data collected from each crystal using a local modification of the program-AUSCOR (Busing and Levy, 1957). Lorentz and polarization corrections were then applied, incorporating functions appropriate for use...