Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a new vanadium sublimate from Izalco volcano, El Salvador: crystal structure

LARRY W. FINGER

Geophysical Laboratory, Carnegie Institution of Washington
Washington, D. C. 20008

Abstract

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, is triclinic with $a = 8.1576(6)$, $b = 8.2691(5)$, $c = 8.0437(7)$ Å, $\alpha = 107.144(5)^\circ$, $\beta = 91.389(7)^\circ$, $\gamma = 105.441(5)^\circ$, $Z = 1$, and space group $P\overline{1}$. The crystal structure has been solved and refined to a weighted $R$ of 0.044 from 2875 intensities measured on a four-circle diffractometer. The structure consists of vanadium in tetrahedral coordination and copper in octahedral and trigonal bipyramidal coordination with Jahn-Teller distortions typical for $\text{Cu}^{2+}$. The octahedron form a sheet with holes and are cross-linked by vanadium tetrahedra and copper trigonal bipyramids.

Introduction

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a fumarolic mineral from Izalco volcano, El Salvador, is described in the preceding paper (Hughes and Hadjadiacos, 1985). It is a double honor to have the mineral named after me and to have the opportunity to solve and present its crystal structure.

Experimental

A crystal of fingerite, $0.09 \times 0.09 \times 0.15 \text{ mm}$, was mounted on a four-circle diffractometer, and the orientation matrix and reduced unit cell were determined by an automatic indexing algorithm similar to that suggested by Jacobson (1976). The cell proposed by Hughes and Hadjadiacos (1985) was confirmed. In the final orientation the axis of crystal rotation was approximately parallel to [328]. Unit-cell and orientation parameters were refined from the positions of 20 independent observations with $39^\circ \leq 2\theta \leq 54^\circ$ measured by the eight-reflection centering method of King and Finger (1979). The unit cell and other crystal data are listed in Table 1. The intensity data for one hemisphere ($l \equiv 0$) of the triclinic mineral were measured to $60^\circ$ with omega step scans and Nb-filtered Mo radiation. The resulting data were integrated by application of the Lehmann and Larsen (1974) technique for optimum background selection. In accordance with the suggestions of Gabr (1980), the inner edge of the background region was selected two steps outside the point corresponding to the minimum in $\sigma I$. Integrated intensities were corrected for Lorentz-polarization and absorption effects ($\mu_1 = 143.2 $ cm$^{-1}$) with the program of Burnham (1966). A total of 2875 intensities were measured. Of these, 2257 had values greater than twice the standard deviation.

Solution of the crystal structure was accomplished through use of the tangent formula as implemented in MULTAN-80 and associated programs (Main et al., 1980). Pseudosymmetry of the copper and vanadium atoms resulted in some difficulty in the solution (cf. Hai-Fu et al., 1983). In addition, the formula as derived from electron microprobe analyses was thought to be $\text{Cu}_9\text{V}_2\text{O}_{25}$. Despite these difficulties, successive cycles of Fourier syntheses revealed the positions of all atoms, the correct stoichiometry and confirmation of the space group $(P\overline{1})$.

Program REFIN4 (Finger and Prince, 1975) was used to refine the structure. Effective standard deviations, $\sigma'$, used to calculate least-squares weights, were calculated from the formula $\sigma'^2 = \sigma^2 + (0.012F)^2$, where $\sigma$ is the standard deviation derived from counting statistics and $F$ is the structure factor. All structure-factor calculations were performed with neutral atom scattering curves selected from the data of Cromer and Mann (1968). Anomalous dispersion coefficients were taken from International Tables for X-Ray Crystallography, Vol. IV (1974). The refined structure converged to an $R$ factor of 7.6% with isotropic temperature factors and an isotropic secondary extinction coefficient. After conversion to anisotropic temperature factors, the structure converged to a weighted $R$ of 4.4% and an unweighted $R$ of 4.6%. The anisotropic refinement is significantly better than the isotropic calculation (Hamilton, 1965). Robust/resistant techniques (Prince, 1982) were employed in the final stages of the refinement. Final observed and calculated structure factors are listed in Table 2. Refined atomic coordinates and equivalent isotropic temperature factors are listed in Table 3.

Description of the structure

The anion arrangement of $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ may be described as essentially a close-packed array of oxygen. Octahedrally coordinated copper ions form a sheet with holes (Fig. 1). These edge-shared polyhedra have Jahn-Teller distortion typical for $\text{Cu}^{2+}$ (Shannon and Calvo, 1973). Each octahedron has four equatorial oxygen ions at distances approximately equal to 2 Å (Table 4) and two apical oxygens at greater distances. For Cu3 and Cu4, the