The crystal structure of namibite, Cu(BiO)\textsubscript{2}VO\textsubscript{4}(OH), and revision of its symmetry

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ABSTRACT

The crystal structure of namibite, Cu(BiO)\textsubscript{2}VO\textsubscript{4}(OH) [triclinic, space group \(\overline{P\overline{T}}\), \(a = 6.210(1), b = 7.398(1), c = 7.471(1)\,\text{Å}, \alpha = 90.10(1), \beta = 108.73(1), \gamma = 107.47(1)^\circ\), \(V = 308.22(8)\,\text{Å}^3\)], was determined using single-crystal X-ray diffraction data. The refinement, based on 2140 unique reflections with \(F_o > 4\sigma(F_o)\), gave \(R1 = 3.61\%\). The structure determination showed namibite to be triclinic-pseudomonoclinic; previously reported C-centered monoclinic cell is a pseudocell. The structure contains two unique Bi atoms, with nine Bi-O bonds between 2.17 and 3.39 Å. The Bi coordinations show some stereochemical influence of the lone pair of electrons on Bi\textsuperscript{V}. A three-dimensional network is formed by linkages of Bi-O polyhedra to one slightly distorted V\textsuperscript{V}O\textsubscript{4} tetrahedron that decorates chains of corner-sharing CuO\textsubscript{4} polyhedra extending parallel to the \(b\) axis. The CuO\textsubscript{4} polyhedra show the Jahn-Teller-distorted \([\text{tetrahedron} \times 2]\)-coordination of Cu\textsuperscript{II}. Layers of Bi atoms parallel to (100) alternate with layers of parallel heteropolyhedral \([\text{Cu(VO}_4\text{)O}_2(OH)]\) chains. According to bond-valence calculations and geometrical considerations, the H atom of the OH group is probably involved in disordered or trifurcated H bonding. The structure of namibite represents a slightly distorted ordered variant of the monoclinic structure of brendelite, (Bi,Pb)\textsubscript{3}(Fe\textsuperscript{III},Fe\textsuperscript{II})\textsubscript{2}O\textsubscript{4}(OH)(PO\textsubscript{4}). Further relations to synthetic Cu\textsubscript{3}Bi\textsubscript{4}V\textsubscript{2}O\textsubscript{14}, to the 7 Å chain-structure phosphates and sulfates, and to linarite are outlined.

INTRODUCTION

Namibite is a rare dark-green Cu-Bi-V-mineral originally described from Namibia (von Knorring and Sahama 1981). Recently, it has been found at an increasing number of localities (see overview by Dunning and Cooper 1998). Originally assumed to be an oxide with the formula CuBi\textsubscript{2}VO\textsubscript{4}, namibite was redefined by Mrázek et al. (1994) as a vanadate with the formula Cu\textsuperscript{II}(BiO)\textsubscript{2}V\textsuperscript{V}O\textsubscript{4}(OH), based on a new wet chemical analysis, IR spectroscopical and thermoanalytical data, and a hydrothermal preparation of synthetic namibite. The suggested presence of vanadate is also corroborated by the fact that crystals of namibite are monoclinic (\(C\)-centered monoclinic, probably \(C2/m\)), on the basis of precession photographs obtained by the first authors. A platy \{100\} habit and cleavage parallel to (100) were reported by von Knorring and Sahama (1981), but Mrázek et al. (1994) inferred that the cleavage is parallel to (001), based on an X-ray powder pattern strongly affected by preferred orientation of the cleavage fragments. According to von Knorring and Sahama (1981), type namibite shows common interpenetration twinning on (011), often in a polysynthetic manner. An IR absorption spectrum of namibite did not indicate “any notable H\textsubscript{2}O or OH” (von Knorring and Sahama 1981), whereas Mrázek et al. (1994) report clear evidence for a hydroxyl group, based on their IR investigations and chemical analyses of both natural and synthetic material. To clarify these inconsistencies, we determined the atomic arrangement of namibite and report the results here.

CRYSTAL STRUCTURE DETERMINATION AND REFINEMENT

Namibite crystals were taken from a small specimen from the Iron Monarch deposit, South Australia (Pring et al. 1992, 2000). The platy crystals are black-green, translucent, and occur in intimate association with finely crystalline bayerite. Energy-dispersive spectroscopic chemical analyses of the namibite showed that the crystals are of ideal composition within detection limits. Preliminary investigations of selected crystal fragments were done with a Nonius KappaCCD diffractometer equipped with a 300 mm diameter capillary-optics collimator to provide increased resolution. They showed that subparallel intergrowth is common. Optically, no twinning features were recognizable. Tiny grains of high crystal quality clearly showed a triclinic cell, \(a = 6.210(1), b = 7.398(1), c = 7.471(1)\,\text{Å}, \alpha = 90.10(1), \beta = 108.73(1), \gamma = 107.47(1)^\circ, V = 308.22(8)\,\text{Å}^3\), that has pseudo-monoclinic symmetry, with a \(C\)-centered pseudocell \(a \approx 10.51, b \approx 10.52, c \approx 6.21\,\text{Å}, \alpha \approx 91.0, \beta \approx 116.1, \gamma \approx 89.4^\circ, V \approx 616.5\,\text{Å}^3\), the transformation matrix being (011,0\(\overline{1}\),1,100). Frames obtained from poor-quality fragments resulted in large errors and did not allow distinction between the triclinic and the pseudomonoclinic cells. The previously reported, smaller monoclinic \(C\)-centered cell, \(a = 11.87, b = 3.70, c = 7.49\,\text{Å}, \beta = 109.7^\circ, V = 310\,\text{Å}^3\) (von Knorring and Sahama 1981; Mrázek et al. 1994) is a monoclinic pseudocell that shows interesting relations to the true triclinic cell (see discussion below).

A tiny, irregular, somewhat platy fragment with approximate dimensions 0.05 \(\times\) 0.03 \(\times\) 0.02 mm\(^3\) was selected for the