American Mineralogist, Volume 91, pages 1378–1384, 2006

Crystal chemistry and polytypism of tyrolite

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ABSTRACT

The crystal structures of the 1*M* and 2*M* polytypes of tyrolite have been solved from single-crystal X-ray diffraction data. The structure of tyrolite-1*M* [monoclinic, *P*2/*c*, $a = 27.562(3)$, $b = 5.5682(7)$, $c = 10.4662(15)$ Å, $\beta = 98.074(11)°$, $V = 1590.3(3)$ Å^3] has been refined to $R_1 = 0.086$ on the basis of 2522 unique observed reflections collected using synchrotron radiation at the Swiss-Norwegian beamline BM01 of the European Synchrotron Research Facility (SNBL at the ESRF). The structure of tyrolite-2*M* [monoclinic, *C*2/*c*, $a = 54.520(6)$, $b = 5.5638(6)$, $c = 10.4647(10)$ Å, $\beta = 96.432(9)°$, $V = 3154.4(6)$ Å^3] has been refined to $R_1 = 0.144$ on the basis of 2666 unique observed reflections obtained from a non-merohedrally twinned crystal using in-house X-ray radiation and a STOE IPDS II image-plate diffractometer. The structures are based upon complex nanolayers consisting of Cu, As, and Ca coordination polyhedra. The core of the nanolayer is a copper arsenate substructure consisting of **A** and **B** sublayers. The **B** sublayer consists of chains of edge-sharing Cu octahedra running along the *b* axis. The **A** sublayer contains trimeric units of Cu octahedra sharing corners with AsO_4 tetrahedra. Two adjacent **A** sublayers are linked by the octahedral chains of the **B** sublayer resulting in formation of the 18 Å thick **ABA** slab. The **ABA** slab is sandwiched between sublayers of Ca^{2+} cations and H_2O molecules. Adjacent nanolayers are connected by hydrogen bonds to the interlayer species (carbonate anions and H_2O molecules). The structures of tyrolite-1*M* and tyrolite-2*M* differ by the stacking sequence of the nanolayers only. The adjacent nanolayers in tyrolite-2*M* are shifted by $b/2 = 2.8$ Å in comparison to the relative position of the nanolayers in tyrolite-1*M*. The structural formula of tyrolite can be written as $[Ca_2Cu_9(AsO_4)_4(OH)_8(CO_3)(H_2O)_{11}](H_2O)_x$ where $x = 0–1$.

Keywords: Tyrolite, "clinotyrolite," crystal structure, copper arsenate, nanolayers, polytypes