American Mineralogist, Volume 93, pages 713–727, 2008

The crystal structure of vurroite, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$: OD-character, polytypism, twinning, and modular description

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Abstract

The crystal structure of the type specimen of vurroite from Vulcano (Aeolian Islands, Italy) has been solved and refined using single-crystal X-ray diffraction data collected at the Elettra synchrotron facility (Basovizza, Trieste). Vurroite has an OD (order-disorder) structure belonging to the category III of OD structures composed of equivalent layers. The OD-groupoid family (λ and σ partial operations) and MDO structures were derived by means of the application of the OD theory. The two theoretically possible polytypes with maximum degree of order (MDO polytypes) have pseudo-orthorhombic metric, with lattice parameters $a \approx 45.6$, $b \approx 8.4$, $c \approx 54$ Å, and $a \approx 22.8$, $b \approx 8.4$, $c \approx 54$ Å, and space group symmetries $F2/d11$ and $A2/d11$, respectively. Only the former polytype (MDO_1) could be identified in the analyzed crystals. The MDO_1 structure was solved and refined to $R = 6.26\%$ for 4968 reflections with $F_o > 4\sigma(F_o)$. In the standard $C2/c$ setting of the space group the unit-cell parameters of MDO_1 are $a = 8.371(2)$, $b = 45.502(9)$, $c = 27.273(6)$ Å, $\beta = 98.83(3)°$, $V = 10265(4)$ Å^3, $Z = 4$. Frequent twinning with (001) as the twin plane, together with the occurrence of disordered domains in the structure, was observed.

The crystal structure of vurroite contains lozenge-shaped composite rods made of coordination polyhedra of Pb and Sn, interconnected into layers parallel to (010) of the standard monoclinic setting. These layers are separated by ribbons of As and Bi, each in distorted octahedral coordination. The ribbons form wavy, discontinuous double layers of PbS archetype. Lone electron pairs of As and Bi are accommodated in the central portions of the PbS-like layers. The structure of vurroite contains building blocks topologically similar to those found in the zinckenite group and in the structure of kirkiite. It can be considered a box-work structure containing the smallest possible pseudo-hexagonal block in the form of a sole octahedron.

Keywords: Vurroite, Pb-Bi-As sulfosalts, crystal structure, OD-theory, polytypism, twinning