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Gungerite, $TlAs_5Sb_4S_{13}$, a new thallium sulfosalt with a complex structure containing covalent As-As bonds

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Abstract

Gungerite, $TlAs_5Sb_4S_{13}$, is a new mineral from the Vorontsovskoye gold deposit in Northern Urals. It occurs in limestone breccias composed of calcite and dolomite and cemented by orpiment, pyrite, realgar, stibnite, and minor baryte and quartz. It belongs to the latest phases among sulfosalts (chiefly Tl-As-Sb ones) present in the ore. The empirical formula (based on the sum of all atoms = 23 pfu) is $Tl_{0.99}As_{5.29}Sb_{3.77}S_{12.95}$. The Raman spectrum exhibits bands corresponding to As-S and Sb-S stretching vibrations, and a band at 263 cm^{-1} that is assigned to As–As stretching vibrations. Gungerite is bright orange with an orange streak, greasy luster, and perfect cleavage on {010}. It is translucent in thin fragments. The calculated density is 4.173 g/cm^3. In reflected light, the mineral is yellowish-white with very weak bireflectance. In crossed polars, it is distinctly anisotropic but anisotropy effects are masked by strong internal reflections of bright orange color. Gungerite is orthorhombic, with the space group *Pbcn*. Unit-cell parameters determined from the single-crystal X-ray diffraction data are as follows: a = 20.1958(3) Å, b = 11.5258(2) Å, c = 20.1430(2) Å, and V = 4688.74(12) $Å^3$ (Z = 8). The crystal structure consists of doughnut-shaped (As,Sb)-S clusters, which have van der Waals contacts to most of the surroundings, and are connected to them only by sparse cation-sulfur bonds. These clusters are formed by a chelating mirror-symmetrical group, which is "stacked" on, around, and along rods of the TlS_9 coordination polyhedra; these rods are oriented parallel to [010]. An individual doughnut-shaped cluster with a central TlS_9 polyhedron half-inserted into it contains one As–As bond 2.449 Å long. The polar Tl rods form a chessboard arrangement with occasional stacking errors leading to twinning on (101). The large and complex structure of gungerite shows remote similarities to that of gillulyite and the rod-like structure of lorándite.

Keywords: Gungerite, new mineral species, Tl-As-Sb sulfosalt, Raman spectroscopy, crystal structure, covalent bonds; Vorontsovskoe gold deposit