Gungerite, TlAs₂Sb₄S₁₃, a new thallium sulfosalt with a complex structure containing covalent As-As bonds

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ABSTRACT

Gungerite, TlAs₂Sb₄S₁₃, is a new mineral from the V orontsovskoye 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 Tl₀.₉₉As₂.₂₉Sb₁.₇₇S₁₂.₉₅. 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/cm³. 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) Å³ (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 TlS₈ coordination polyhedra; these rods are oriented parallel to [010]. An individual doughnut-shaped cluster with a central TlS₉ 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

INTRODUCTION

Thallium and its compounds play a very important role in a wide variety of industrial applications (Gresham and Lawrey 2018; https://www.usgs.gov/centers/nmic/thallium-statistics-and-information): they are applied in the manufacture of electronic devices, optical lenses with a high-refractive index, semiconductor materials, alloys, γ radiation detection equipment, infrared radiation detection and transmission equipment, crystal-line filters for light diffraction for acoustic-optical measuring devices, low-temperature thermometers, in the synthesis of organic compounds, and in a high-density liquid for sink-float separation of minerals. Also, research activity with thallium is ongoing to develop high-temperature superconducting materials for such applications as magnetic resonance imaging, storage of magnetic energy, magnetic propulsion, and electric power generation and transmission. Trace amounts of thallium are used as a contrast agent in the visualization of cardiac function and tumors. On the other hand, thallium compounds show a very strong level of toxicity and should be strictly controlled to prevent harm to humans and the environment. Although thallium is moderately abundant in the Earth’s crust [for instance, the average content of Tl in granites is 1.5 ppm (Turekian and Wedepohl 1961)], it is mostly dispersed in association with potassium minerals in clays, granites, and soils, and is not generally considered to be commercially recoverable from those materials. The major sources of recoverable thallium are gold and complex sulfide ores (Ikrumuddin 1985; Karbowska 2016). Because of the above, much attention of geologists and mineralogists is given to the research of gold deposits that bear Tl-mineralization and to the study of new Tl-bearing mineral species and their structures.

Herein, we describe the new sulfosalt mineral gungerite