$(1,2\text{-DAPH}_2)_2Ge_9(OH)_4O_{18} \cdot 2\ H_2O$: A New Microporous Germanate Based on the Interconnection of Ge_9O_{18} Clusters Showing Reversible Water Emission and Uptake

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Treatment of germanium dioxide with a 33% aqueous solution of 1,2-diaminopropane (DAP) under solvothermal conditions leads to the formation of colourless octahedral crystals of the novel germanate $(1,2\text{-DAPH}_2)_2Ge_9(OH)_4O_{18} \cdot 2\ H_2O$. The compound crystallises in the orthorhombic space group *Pbca*, $a = 14.4155(10)$, $b = 12.9384(9)$, $c = 14.5417(8)$ Å, $V = 2712.2\ (3)$ Å^3; $Z = 4$. The structure consists of an anionic $[Ge_9(OH)_4O_{18}]^{4-}$ framework with isolated $[1,2\text{-DAPH}_2]^{2+}$ cations and water molecules in the channels of the structure. The primary building units of the anionic framework are GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra. The asymmetric unit consists of two GeO_5 units sharing a common edge to form a Ge_2O_8 unit. This Ge_2O_8 unit is corner-linked to two GeO_4 tetrahedra, and finally one GeO_4 tetrahedron is connected to a GeO_6 octahedron by corner-sharing. The connectivity yields a chain-like Ge_5O_{19} fragment as a secondary building unit (SBU). The chain fragments are interconnected with each other forming the three-dimensional framework. Three types of channels with diameters ranging from 5.98 to 8.025 Å intersect the three-dimensional germanate network. Upon heating the compound decomposes in three steps starting at about 125 °C losing the water and the 1,2-diaminopropane molecules.

In situ X-ray diffraction experiments show that the water molecules are removed retaining the integrity of the skeleton of the material. The removal of H_2O is accompanied with an anisotropic shrinkage of the structure. The original lattice parameters were obtained after the uptake of water.

Key words: Germanate, Hydrothermal Synthesis, Thermal Stability