

A multi-methodological characterization of new hydrated Bi sulphate minerals

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Two new hydrated bismuth sulfates have been discovered on a bismuth mineralization associated with quartziferous dikes intruding Pre-Triassic orthogneiss and garnet micaschist from Alfenza (Crodo), Antigorio Valley, Italian Alps (Capitani et al. 2011). The new minerals are found in "hortensia-like" aggregates of white, micrometre-sized crystallites or massive incrustations covering bismuthinite and quartz. At the SEM, they appear constituted of ~20 microns wide, few micron thick, randomly oriented, hexagonal platelets. EDS semi-quantitative analyses lead to the simplified chemical formula $[Bi_2SO_4(OH)_4]$. IR spectroscopy confirms the presence of hydroxyls and the absence of water molecules.

Due to the very small amount of material and the very small size of each crystallite, no X-ray diffraction analysis has been possible so far. On the contrary, transmission electron microscopy and diffraction, performed either by conventional zone orientation and automated diffraction tomography (Kolb et al. 2007), reveals two distinct phases, both without any natural or synthetic analogue; one phase is monoclinic, with $a = 17.2(4)$, $b = 15.9(3)$, $c = 20.3(4)$ Å, $\beta = 95(1)$, and $P2_1$ or $P2_1/m$ symmetry; the other phase is hexagonal, with $a = 9.6(2)$, $c = 15.3(3)$ Å, and $P-62c$ symmetry. The two phases can be recognized at the TEM not only by their unit cell geometry and symmetry, but also by their morphology and different beam sensitivity, whereas they are compositionally identical within the experimental error. The monoclinic phase has perfect basal cleavage that make its recognizable as (001) oriented platelets on TEM grids, show a strong diffuse scattering along the c^* direction, and is very beam sensitive. The hexagonal phase is more resistant under the electron beam and does not show any preferential cleaving orientation. By morphological similarity, we draw the conclusion that the first phase is representative of the hexagonal platelets, while it was not possible to unambiguously associate the second phase with a specific morphology in SEM images.

Structure solution for both the phases has been attempted on the basis of automated diffraction tomography data. The orthorhombic phase, since beam sensitive and affected by stacking disorder, gave only partial results. On the contrary, the hexagonal phase gave a sound and reproducible structure. This new phase is built up by laterally offset, stacked pairs of Bi_3O_3 (001) trigonal rings, capped by SO_4 tetrahedra, interleaved and further cemented by additional (001) BiO layers.