The Bi sulfates from the Alfenza Mine, Crodo, Italy: An automatic electron diffraction tomography (ADT) study

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ABSTRACT

We report about three bismuth sulfates from mineralized quartz dikes from Alfenza (Crodo, Italy), two new phases and a rare mineral, cannonite, all growing on bismuthinite. The first new phase occurs as white, “hortensia-like” aggregates of pseudo-hexagonal platelets, with perfect basal cleavage, ~20 µm wide and few micrometers thick. The approximate composition is Bi2O4(SO4), and cell parameters and symmetry, as determined by automatic diffraction tomography, are a = 22.0(4), b = 16.7(3), c = 15.9(3) Å, β = 102.9(5)°, space group Pc or P2/c. A major stacking disorder is detected by HR-SEM images and electron diffraction data.

The second new phase was detected only by TEM. It can be distinguished by its random orientation on the TEM grid (i.e., absence of preferential parting), the higher resistance under the electron beam, and different cell parameters and structure, whereas the composition is similar (Bi/S ~ 2.2/1), apart for the presence of tellurium up to ~6 cations percents. The unit cell is hexagonal, space group P62c, a = 9.5(2) and c = 15.4(3) Å. In this case, a structure model was obtained ab initio from electron diffraction data. Interestingly, the mineral has a porous structure with one dimensional porosity (diameter of the channel ~7 Å).

Finally, within the same centimeter sized hand-specimens, we detected also cannonite. Its identification was done by automatic diffraction tomography. The measured cell parameters are a = 7.7(2), b = 13.9(3), c = 5.7(1) Å, β = 109.8(5)°, the space group P21/c. Cannonite at Alfenza forms radiating, acicular aggregates of colorless, transparent crystals with “scalpel-like” habit, elongated along e, up to 200 µm in length.

Keywords: Electron crystallography, automatic diffraction tomography, bismuth sulfate, cannonite, porous phase

INTRODUCTION

Many natural and synthetic materials crystallize in grains not large enough or sufficiently ordered for conventional single-crystal X-ray structural analysis, or not in sufficiently large amounts for powder X-ray diffraction. The latter, moreover, suffers of peaks superposition problems that limit any ab initio structure solution. Synchrotron radiation X-ray micro-diffraction can be applied to this kind of materials, but its application is very problematic since the very limited beamtime available at synchrotron facilities. Electron crystallography may be the solution to such cases, since crystallographic information can be extracted from nanosized volumes of material thanks to the strong electron-matter interaction, 103–106 times stronger than for X-ray. However, the strong electron-matter interaction is at the same time the main drawback of electron diffraction, since it causes multiple scattering, which makes the mathematical treatment of the diffraction process difficult. Because of this limitation, electron crystallography has never turned into a routine technique for crystal structure solution.

Things seem to take a different trend since the recent advent of the automatic electron diffraction tomography (ADT). This is a transmission electron microscopy (TEM) technique working similarly to an area detector single-crystal X-ray diffractometer: the reciprocal space is explored and sampled rotating the crystal around an arbitrary axis and image frames are acquired every degree and integrated alike X-ray intensities. Working out of zone axis orientation, the dynamical nature of the electron diffraction is significantly reduced. Moreover, ADT can be combined with the precession electron diffraction (PED), in which the electron beam is precessed around the optical axis of the microscope—a descans operation below the sample allows a stationary view of the electron diffraction pattern—with the net result that only a limited number of reciprocal nodes are excited.

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