STRUCTURAL STUDY OF Pb-Bi SULFOSALTS FROM VULCANO (AEOLIAN ISLAND, ITALY) BY TRANSMISSION ELECTRON MICROSCOPY

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INTRODUCTION

The first Transmission Electron Microscopy (TEM) investigations are performed on some Pb-Bi sulfosalts from the high-temperature fumaroles (T ~ 400°C) of Vulcano, Aeolian Islands, Italy.

Among the sulfosalts belonging to the $PbS-Bi_2S_3$ system, the TEM investigation has been performed on two natural sulfosalts of the Lillianite Homologues Series (LHS) (Makovicky, 1981), lillianite and heyrovskýite, which are very abundant at Vulcano and unique examples Ag- and Cu-free sulfosalts known in nature, and on one analogues synthetic Phase II (85.7 mol.% PbS). In addition, TEM investigation was also extended to natural crystal of galenobismutite, which was never structurally investigated by transmission electron microscopy.

The structure of lillianite, ideally $Pb_3Bi_2S_6$, and heyrovskýite, ideally $Pb_6Bi_2S_9$, is based on ordered intergrowths of "galena-like" slabs cut parallel to $(131)_{PbS}$ and stacked along $[010]_{lill}$ (*Bbmm* setting). Any two slabs are twin related and diverse members of this series differ by the thickness of the "galena-like" slabs and, consequently, by the frequency of the *chemical twinning* (Makovicky, 1977).

The most of studies on natural heyrovskýite and lillianite concern minerals containing monovalent cations, such as Ag, Cu. It is also known that these monovalent cations play a role in stabilizing structure (Price & Yeomans, 1984; Skowron & Tilley, 1990).

Due to the particular sensitivity of sulfosalts, to the heating effect of the ion beam during preparation and electron beam during observation (Loginov & Brown, 1992; Skowron & Tilley, 1986; Tilley & Wright, 1982), a particular attention has been given to the preparation techniques of the samples and some precautions were also taken during TEM observations (*i.e.*, low intensity of the electron beam and low exposition of the crystal to the electron beam).

Three different methods, ion-milling, crushing and ultramicrotomy, have been used to prepare several sufficiently thinned samples for TEM investigation. Among these, the ion-milling technique is resulted to be one of the most powerful techniques to prepare sulfosalts, allowing to obtain uniformly and widely thin transparent regions of sulfosalts samples, following the procedure suggested by Barna (1992).

Two different electron microscope have been used to specimens investigation: JEOL JEM 2010 and JEOL JEM 4000, operating at 200 kV and 400 kV, respectively.

The investigated lillianite and heyrovskýite from Vulcano appear as discrete phases, showing a perfectly ordered sequence of slabs 4,4 and 7,7, respectively, with very few stacking faults and/or dislocations. In addition, all the lillianite crystals and few heyrovskýite crystals result non modulated structure. Also the natural galenobismutite crystals appear as a well-ordered structure. On the contrary the most of heyrovskýite crystals showed interesting modulations. This is the first report of the presence of modulations in the natural heyrovskýite structure, never observed in natural Ag-bearing sample (Makovicky *et al.*, 1991) and in synthetic analogue (Pring *et al.*, 1999; Pring & Etschmann, 2002; Prodan *et al.*, 1982).

ORDERED NON MODULATED STRUCTURES

The lillianite crystals from Vulcano show a well-ordered structure with a constant average periodicity of approximately 20.6 Å along *b* direction (Fig. 1a). All the analyzed crystal fragments do not show streaks and/or additional reflections, but only sharp reflections corresponding to the lillianite-like structure (Fig. 1b). Really, subordinate and little areas with low crystallinity could be seen only in the ion-milled lillianite, explained as either a reaction effect under the electron beam or a sublimation phenomenon under the vacuum conditions during the preparation of the sample (Skowron & Tilley, 1986). But, during TEM observations, no dynamic processes, like formation of other phases or chemical reaction, were observed in the lillianite crystals from Vulcano. As a consequence, we exclude that the observed low crystallinity is related to the electron beam and we consider highly probable that it can be ascribed to sublimation phenomena of the sample under the vacuum conditions of the Precision Ion-Polishing System (PIPS) instrument.
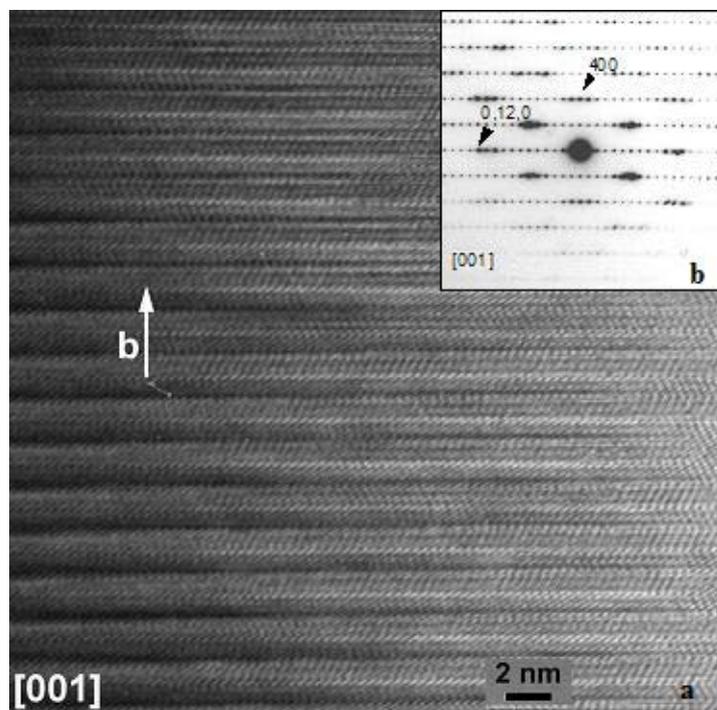
Fig. 1 – HRTEM image (a) and SAED pattern down the [001] zone (b) of well-ordered lillianite (crushed sample).

Analogous ordered structures without any modulation have been observed in some ultramicrotomed heyrovskýite crystals (Fig. 2a), both natural and synthetic (85.7 mol.% PbS), as testified by the absence of streaks and satellite reflections in electron diffraction patterns (Fig. 2b). No substantial differences between natural and synthetic crystals could be observed, except rare stacking faults in the synthetic Phase II observed at low magnification. A perfect constant periodicity of the slabs of approximately 31.2 Å was determined for both the natural phase and its synthetic analogue. This lead us to confirm the structural similarity between the Ag-free heyrovskýite from Vulcano and the synthetic analogue here analyzed. The results obtained in this work on synthetic heyrovskýite are highly comparable with those obtained by Prodan *et al.* (1982) for the same material but prepared and analyzed under different conditions (crushed sample, investigated at 125 kV). This analogy of the results indicates that ultramicrotomy and crushing are preparation tecniques substantially equivalent each other, which can

be usefully used in TEM investigations on sensitive materials. In addition, the absence of structural defects in the samples from Vulcano, support the evidence that disorder stacking sequences are connected with the induced heating during TEM investigations (Skowron & Tilley, 1986, 1990; Colaïtis *et al.*, 1981), rather than with the sample preparation procedure.
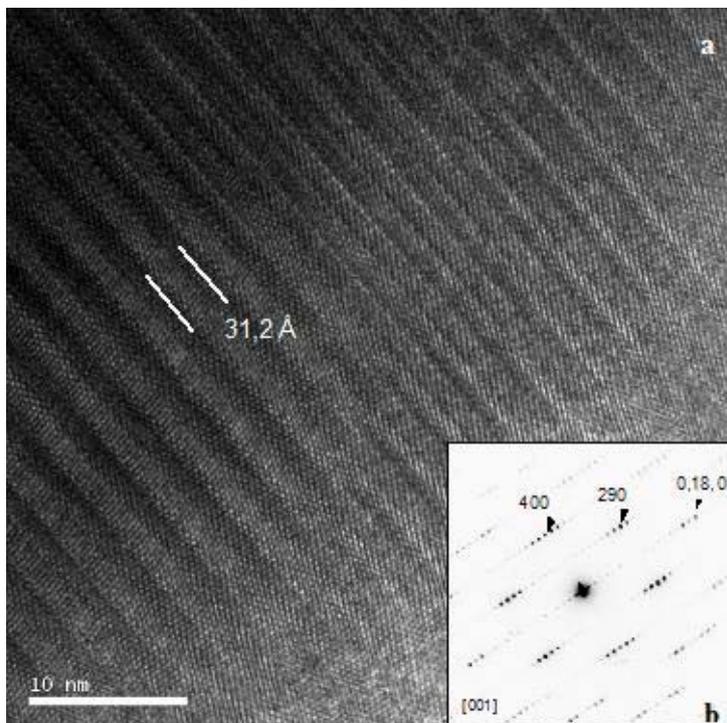
Fig. 2 – HRTEM image (a) and electron diffraction pattern down the [001] zone (b) of heyrovskýite (ultramicrotomed sample).

Also ordered structures without any modulation have been observed in the ultramicrotomed galenobismutite crystal from Vulcano. A perfect constant periodicity of the slabs of approximately 11.8 Å was determined. No HRTEM images, which refers to for comparison, are available in literature neither on natural or synthetic galenobismutite. Only some SAED patterns on synthetic Phase IV are reported (Colaïtis *et al.*, 1981; Tilley & Wright, 1986). Our preliminary results are highly comparable with those reported by Colaïtis *et al.* (1981) for the synthetic Phase IV, suggesting that natural galenobismutite is characterized by an ordered structure without modulations. More experimental work on this matter is obviously desirable for the future.

INTERGROWTHS

A lamella of heyrovskýite (about 145 nm wide) intergrown in a lillianite crystal has been observed in one sample prepared by ion milling. This is a structural features quite uncommon in lillianite and heyrovskýite from Vulcano, but frequently occurring in analogues natural Ag-bearing samples from other localities (Pring & Etschmann, 2002; Pring *et al.*, 1999; Makovicky *et al.*, 1991). In this case too, lillianite presents a well-ordered structure but heyrovskýite appears again as an ordered incommensurate modulated structure. In addition, some planar defects, like edge dislocations, are clearly visible near the observed boundary between lillianite and heyrovskýite. These defects, whose occurrence is well documented in literature, play an important role in the detwinning process. As a matter of fact,

detwinning would be facilitated by the movement of the dislocation from sheet to sheet of the twinned structure, because the dislocation movement decreases substantially the number of chemical bonds that have to be broken to allow the structural change and makes it an energetically feasible process (Skowron & Tilley, 1986). Similar processes were observed as artefacts in transformations of lillianite and heyrovskýite into a galena matrix (Skowron & Tilley, 1986), and they were interpreted as due to the combined effect of the heating induced by the electron beam and of the surrounding vacuum with loss of Bi atom or Bi_2S_3, rather than as due to chemical reaction (Tilley & Wright, 1982; Skowron & Tilley, 1986). In the investigated sample the interruption of the slabs of heyrovskýite are clearly evident, and the presence of the edge dislocations near the boundary of heyrovskýite and lillianite phases suggests that elastic strain energy may also be significant.

Stacking disorder is also observed in the crushed, natural heyrovskýite crystal investigated at 400 kV. This evidence is suggested by the presence of pronounced streaks along the **b*** direction in the electron diffraction pattern. Taking into account that the damage rate induced by electron beam decreases with the increase of operating voltage (Klimentidis & Mackinnon, 1986) and the secondary microstructural defects increase linearly with increasing electron beam flux (Loginov & Brown, 1992), we exclude that the observed disorder could be associated to the different working conditions used for TEM observations (400 kV accelerating voltage instead than 200 kV).

ORDERED INCOMMENSURATE MODULATED STRUCTURES

Ordered incommensurate modulated structures have been observed in a number of natural heyrovskýite crystals investigated in this work. Such modulated structures are characterized by long-range fluctuations visible as dark bands which break the original arrangement of the atomic structure. These fluctuations appear continuous and well developed in two directions, with an average wavelength of about 80 Å (Fig. 3a). The incommensurability has been deduced from the electron diffraction pattern showing satellite spots surrounding the Bragg reflections, making an angle of 15° with **b*** (Fig. 3b). The attempt to investigate structure modulations observed from HRTEM images by means of a single-crystal synchrotron X-ray diffraction experiment did not give the expected results. Although data collection at the synchrotron facility was performed by increasing the crystal-to-detector distance (90 mm), no satellite reflections with period of 80 Å could be observed. The absence of satellite reflections in the synchrotron X-ray single-crystal pattern can be explained by the presence of a modulation diffused in very narrow domains of the crystal structure.

The observed structure modulations in the heyrovskýite from Vulcano can be related either to a cation ordering in the metal sites or to the presence of vacancies. According to Balić-Žunić *et al.* (2007) in the Ag-free heyrovskýite from Vulcano, the M1 site, situated on the mirror plane that connects the adjacent, mirror-related galena-type layers, is a pure Pb site (Fig. 4). The octahedral sites Me2 and Me3, located in the central zone of PbS-like slabs, are pure Pb sites, whereas those closer to the boundary $(311)_{PbS}$ planes (M4 and M5 sites) are mixed (Pb, Bi) sites, with almost equal occupancy. The compositional nature of the modulation in Ag-free heyrovskýite from Vulcano can be related to a sort of ordering between Pb and Bi through the mixed sites Me4 and Me5. It can be expected that if Me4 has Bi then the nearby Me5 will have Pb, and so on. However, the occurrence of vacancies could also lead to the modulations. The presence of vacancies connected to the substitution $3Pb^{2+} \rightarrow 2Bi^{3+} + \square$ were first proposed by Takeuchi & Takagi (1974) in the pure synthetic heyrovskýite $Pb_{6-x}Bi_{2+2x/3}S_9$ and, recently, the structure refinement of an Ag-free heyrovskýite crystal from Vulcano suggested ~ 0.04 *pfu* of vacancy

in the sole Me3 site (Balić-Žunić *et al.*, 2007). It is noteworthy that the M3 lies at about 15° with respect to the b axis, thus forming an angle comparable with the angle that the satellite reflections form with respect to **b*** axis (Fig. 3).
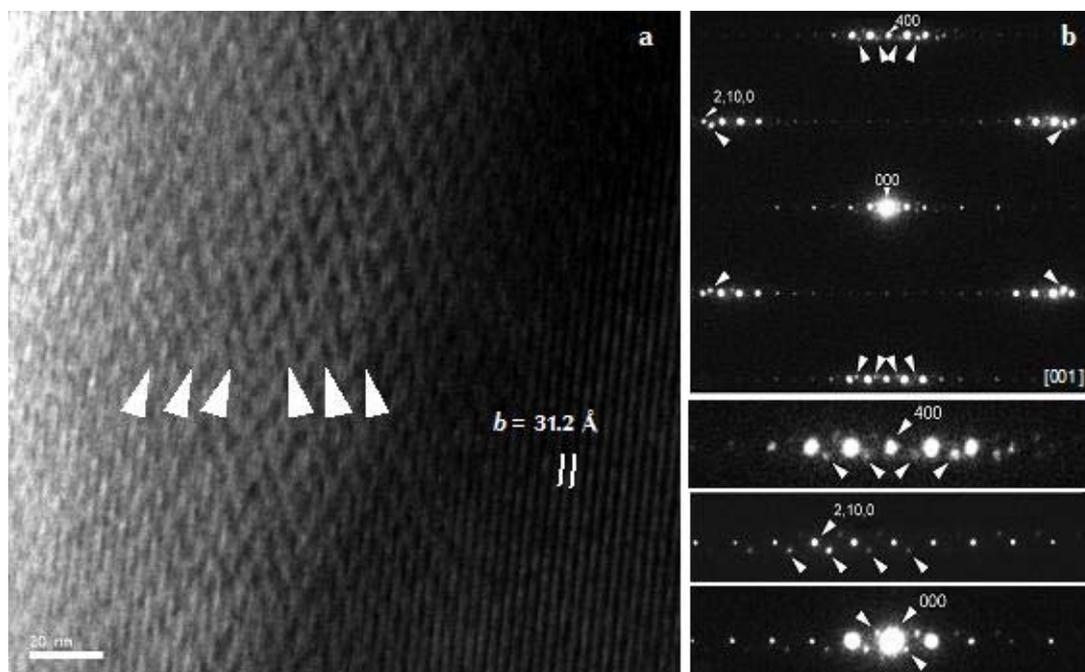
Fig. 3 – Modulated structure (arrows) of heyrovskýite from Vulcano (ion-milled sample): (a) low magnification image; (b) SAED patterns down the [001] zone.

Whereas, the presence of modulations only in Ag-free heyrovskýite and not in Ag-free lillianite can be found by looking at the structure peculiarities of the two mineral phases. As a matter of fact, lillianite and heyrovskýite are two homologues of the lillianite series (Makovicky, 1977; Makovicky & Karup-Møller, 1977a, 1977b) which differ only in the width of the PbS-like slabs mirror related on $(311)_{PbS}$ planes, represented by the number N of octahedra running diagonally across an individual slab, N = 4, for lillianite, and N = 7, for heyrovskýite. Recent studies have shown that, in the structure of Ag-free lillianite from Vulcano, Pb and Bi are statistically distributed among the only two cation sites of the PbS-like slabs (*i.e.* M1 and M2), with almost the same occupancy in both sites (Pinto *et al.*, 2006). Thus, the greater stability of Ag-free lillianite with respect to Ag-free heyrovskýite from Vulcano can be due to either the different thickness of the galena-like slabs or the different distribution of Pb and Bi among the cation sites inside the slabs of these two structures. According to Aizawa and co-workers (Aizawa *et al.*, 1983), the stability of members of the lillianite homologous series is related to their elastic strain energy (*E*), described as a force performed in twin planes from their unstrained state (E_s) less any energy dissipated by inelastic deformation (E_r). They demonstrated that the total strain energy depends on the distribution of cations, *i.e.* Pb and Bi, over the cation sites of the structure and that, although lillianite and heyrovskýite are the most stable sulfosalts of PbS-Bi_2S_3 system, a rather small change in cation distribution, affects greatly the elastic strain energy of these two phases, thus influencing their stability. Moreover, they noted that, depending on the cation distribution, the elastic strain energy could decrease

or increase when the width of the slabs increases. Thus, this local/widespread "instability" of Ag-free heyrovskýite, can be associated to the higher elastic energy and that the variation in the Pb/Bi ordering would allow to achieve a minimum strain energy that stabilize the structure.
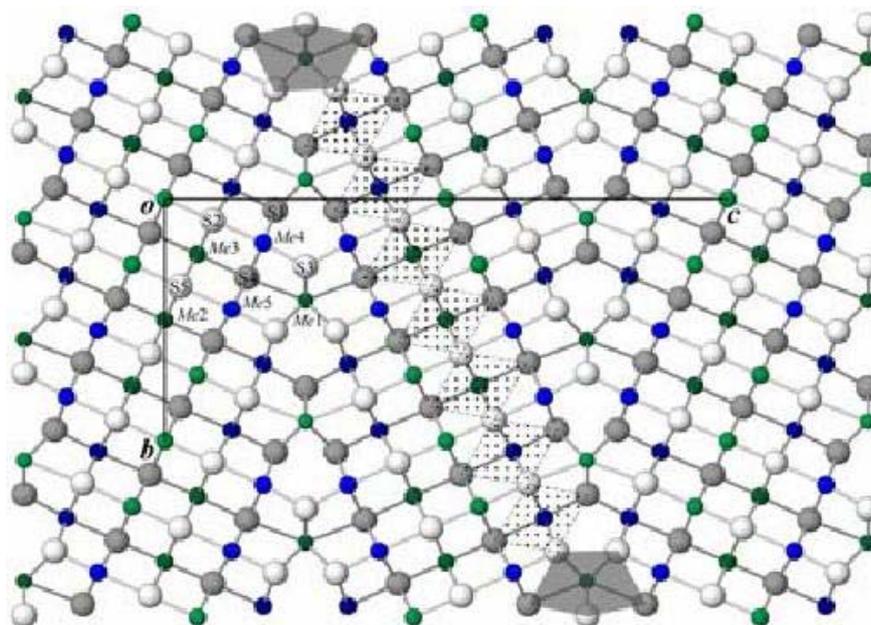
Fig. 4 - The crystal structure of Ag-free heyrovskýite from Vulcano. Projection on (001). Green: Pb; blue: mixed Pb-Bi sites; grey: S. Lightly and darkly shaded circles indicate atoms at $z = ½$ and $z = 0$, respectively, along the ~ 4 Å axis. Stippled: chain of octahedra running diagonally across the PbS-like layer, grey shaded: bicapped trigonal prisms of Me1 (by Balić-Žunić *et al.*, 2007).

Taking into account that the presence of small amounts of monovalent cations as Ag (or Cu) allow to stabilize these crystal structures (Makovicky, 1977; Makovicky & Karup-Møller, 1977a, 1977b), it is possible to explain why no structure modulations were observed to date from previous HTREM studies of heyrovskýite, which were only performed on Ag-bearing samples (Makovicky *et al.*, 1991; Takéuchi & Takagi, 1974).

This evidence allows to conclude that the modulations in the heyrovskýite from Vulcano are originally present in the crystals and they are not artefact induced by ion beam and/or surrounding vacuum. It is highly probable that their nature is connected to the very particular depositional environment of these phases, which at Vulcano is characterized by:

1. rapid cooling of the fumarolic fluid from which they form;

2. extreme variability of the Pb/Bi ratio in the fluid phase;

3. continuous variation in the abundance of compounds acting as carriers for the metals (HCl, H_2S etc.);

4. dynamism of the environment of formation which gave reason of the mineral deposition under non-equilibrium conditions.

Finally, the TEM analyses lead us to affirm with a good approximation that no sub-phases in the natural Ag-free phases of lillianite homologous series are present, although in the recent investigations on

heyrovskýite from Vulcano Borodaev and coworkers (Borodaev *et al.*, 2003) suggested the existence of a number of "heyrovskýites", with N_{chem} values substantially different from the ideal value N = 7 (N ~ 5 or N ~ 6).

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