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Structure refinement of Ag-free heyrovskýite from Vulcano (Aeolian Islands, Italy)

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Abstract

The first single-crystal structure refinement of Ag- and Cu-free heyrovskýite was performed in this study. Crystals investigated were sampled from the high-temperature fumaroles of La Fossa crater of Vulcano, Aeolian Islands, Italy. Electron microprobe analyses gave the average chemical formula $(Pb_{5.86}Cd_{0.03})_{\Sigma 5.89}Bi_{2.04}(S_{8.52}Se_{0.53}Cl_{0.03})_{\Sigma 9.08}$, which is very close to the ideal composition of heyrovskýite, $Pb_6Bi_2S_9$. Lattice parameters are $a = 13.7498(4)$, $b = 31.5053(8)$, $c = 4.1475(1)$ Å, $V = 1796.7(1)$ Å^3, space group *Bbmm*. The structure refinement converges to $R = 4.17\%$ for 1312 reflections with $F_o > 4\sigma(F_o)$.

In Ag-free heyrovskýite from Vulcano, as well as in the synthetic $Pb_6Bi_2S_9$, the trigonal prismatic coordinated position Me1, as well as the octahedrally coordinated position Me3 are occupied only by Pb. Me2, also octahedrally coordinated, is dominated by Pb, whereas the octahedra situated at the edges of the octahedral layers (Me4 and Me5) are centered around mixed (Pb,Bi) positions, with almost equal occupancy. The octahedrally coordinated site Me3 was found to incorporate vacancies (□), created by the substitution $3Pb^{2+} \rightarrow 2Bi^{3+}+\square$, which allows for the observed deviations from the ideal composition, $Pb_6Bi_2S_9$. Selenium is preferentially ordered at the fivefold-coordinated anionic sites. Taking into account vacancies, as well as Se for S substitutions the structural formula of Ag-free heyrovskýite from Vulcano is $Pb_{5.82}Bi_{2.12}\square_{0.06}S_{8.70}Se_{0.30}$.

Comparison with the Ag-bearing heyrovskýite structures shows that during the $2\,Pb \rightarrow Ag(Cu)+Bi$ substitution the increased content of Bi is incorporated preferentially in the Me5 site until 2/3 Bi occupancy and thereafter in the two central octahedrally coordinated sites (Me2 and Me3). Silver occupies exclusively marginal octahedrally coordinated Me4 site like in the other members of the lillianite homologous series. The observed crystal chemical characteristics of the Ag-free heyrovskýite are in accordance with a model suggested by Callegari and Boiocchi, which describes the monoclinic form, aschamalmite, as an ordered polymorph of $Pb_6Bi_2S_9$, and heyrovskýite as a fully disordered polymorph of the same compound. Ag incorporation is expected to increase the Pb/Bi disorder and to stabilize the orthorhombic heyrovskýite form.

Keywords: Ag-free heyrovskýite, crystal structure, Pb-Bi sulfosalts, lillianite series, Vulcano, Italy