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Argesite, $(NH_4)_7Bi_3Cl_{16}$, a new mineral from La Fossa Crater, Vulcano, Aeolian Islands, Italy: A first example of the $[Bi_2Cl_{10}]^{4-}$ anion

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Abstract

The new mineral argesite, ammonium bismuth chloride $(NH_4)_7Bi_3Cl_{16}$, was found in a medium-temperature (~250 °C) active fumarole at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. The mineral occurs on a pyroclastic breccia as pale-yellow crystals up to 0.15 mm in length, in association with bismuthinite, adranosite, brontesite, demicheleite-(Br), demicheleite-(Cl), and panichiite. Argesite is trigonal, space group: $R\bar{3}c$ (no. 167) with $Z = 18$; the unit-cell parameters are (single-crystal data): $a = 13.093(1)$, $c = 102.682(1)$ Å, and $V = 15245(2)$ Å^3. The six strongest reflections in the X-ray powder diffraction pattern are: [d_{obs}(Å) (I) (hkl)] 3.164 (100) (0 3 18), 3.808 (44) ($\bar{2}$ 2 20), 2.742 (78) ($\bar{2}$ 4 21), 6.14 (16) ($\bar{1}$ 2 6), 1.906 (16) (0 0 $\bar{54}$), 1.686 (13) ($\bar{5}$ 6 34). The mineral is uniaxial (–), with $\omega = 1.731(2)$, $\varepsilon = 1.725(2)$ (589 nm). The IR spectrum shows absorptions at 3188(vs), 3060(s), and 1397(vs) cm^{-1}, in agreement with the presence of the ammonium ion. Chemical analyses obtained by EDS electron microprobe gave (average wt%) Bi 42.26, Cl 32.57, Br 13.06, I 0.95, K 2.46, Tl 0.88, NH_4 7.82 (by difference) total 100.00, corresponding to the empirical formula: $[(NH_4)_{6.29}K_{0.91}Tl_{0.06}]_{\Sigma 7.26}Bi_{2.93}(Cl_{13.33}Br_{2.37}I_{0.11})_{\Sigma 15.81}$. The measured density is 2.88(1) g/cm^3. The structure was refined, using single-crystal diffraction data, to a final $R = 0.0345$ for 1289 independent observed reflections [$I > 2\sigma(I)$]. It contains $Bi_2Cl_{10}^{4-}$ and $BiCl_6^{3-}$ anions where the Bi atoms are octahedrally coordinated, and NH_4^+ cations are partially replaced by K^+ and Tl^+ ions.

Keywords: Argesite, new mineral species, crystal structure, ammonium bismuth chloride, bismuth(III) complexes, sublimates, Vulcano, Italy