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Crystal structure and chemistry of skarn-associated bismuthian vesuvianite

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Abstract

Due to its strong chalcophile character and the influence of its s^2 lone-pair electrons on the crystal structure trivalent bismuth is extremely rare in silicate minerals, with Bi-contents in common silicates typically below 1 ppm. In the present paper, we report on an exceptionally Bi-rich variety of the rock-forming mineral vesuvianite with up to ca. 20 wt% Bi_2O_3, occasionally in combination with enhanced Pb contents up to ca. 5 wt% PbO. The mineral occurs as small (≤300 μm) idiomorphic, black crystals in a sulfide-free silicate skarn in the Långban Mn-Fe deposit, central Sweden. The major skarn minerals comprise Ba-rich potassium feldspar, albitic plagioclase, Pb-rich scapolite, and phlogopite, while Pb-rich epidote, vesuvianite, and calcic garnets are minor phases. The vesuvianite grains are intensely zoned displaying Bi-rich cores surrounded by thinner Bi-poor rims. Although generally high in bismuth, the crystal cores invariably show oscillatory zoning. In addition to high Bi- and Pb-contents, the crystals are occasionally enriched in copper, cerium, antimony, and arsenic, thus reflecting the complex chemistry and evolution of the Långban mineralization.

Chemical analyses demonstrate a strong negative correlation between Ca and Bi, hence confirming that Bi replaces Ca at X sites of the vesuvianite structure. Concentrations of Si and Al are lower, while Fe and Ti contents are somewhat enhanced in the Bi-rich cores. Maximum Bi and Pb contents analyzed in the present vesuvianite crystals correspond to 3.19 and 0.87 atoms per formula unit, respectively. This exceeds by far previous reports in the literature. X-ray single-crystal diffraction studies of a crystal splinter with intermediate Bi-content (1.08 apfu) show that the space group *P4/nnc* is the most appropriate to describe the crystal structure; the refinement converged to an *R*1 index of 0.0493. The recorded unit-cell parameters, a = 15.7018(6), c = 11.8648(6) Å, and V = 2925.2(2) Å^3, are to our knowledge the largest ones observed so far for *P4/nnc* vesuvianite. Bismuth was demonstrated to order at the X3′(Bi) site that is only 0.46 Å distant from the nearest X3(Ca) site. Consequently, the X3 and X3′ sites cannot be simultaneously fully occupied.

Keywords: Vesuvianite, bismuth, crystal structure, Långban, Sweden, skarn, crystal chemistry