Armstrongite from Khan Bogdo (Mongolia): Crystal structure determination and implications for zeolite-like cation exchange properties

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ABSTRACT

The results of a combined electron probe microanalysis, single-crystal X-ray diffraction, and Fourier transform infrared study of a crystal of armstrongite from Khan Bogdo deposit (Gobi, Mongolia) are reported. Major element analysis provided (wt%): CaO 9.2(1), ZrO₂ 20.9(2), and SiO₂ 62.5(2). Significant concentrations of REE (0.45 wt%) were also detected. From single-crystal structural refinement, armstrongite resulted monoclinic [space group C2/m, a = 14.0178(7), b = 14.1289(6), c = 7.8366(3) Å, β = 109.436(3)°, V = 1463.6(1) Å³, Z = 4] and twinned with two individuals rotated around a twin twofold axis parallel to [100]. The analyzed crystal was refined up to R = 3.3% (Rw = 2.9%). The structural refinement showed that the investigated armstrongite has only two water groups per formula unit consistent with the infrared analysis. Indeed, the occurrence in the infrared spectrum of the armstrongite (here reported for the first time) of two bending vibration bands at about 1640 and 1610 cm⁻¹ testifies to the presence of two water groups environments. The results of this integrated approach converged to the following empirical formula (based on Si = 6 atoms per formula unit): (Ca₀.₉ЄCa_i₀.₁₀Y₀₂i₀.Y₂i₀)Zr₉₀Si₁₅O₄₅₋₂₋₂H₂O. Finally, the studied mineral shows a framework density (FD = 21.86) lying in the range of zeolites and microporous heterosilicates with tetrahedral-octahedral frameworks. The determined crystal chemical features are relevant for the possible employment of this mineral or of its synthetic analogs for technological applications.

Keywords: Armstrongite, microporous Zr-silicates, single-crystal structure refinement, EPMA, infrared analysis, water groups

INTRODUCTION

Armstrongite, CaZr[Si₆O₁₅]nH₂O (2 ≤ n ≤ 3), named after the American astronaut Neil A. Armstrong, is a rare mineral identified for the first time by Vladykin et al. (1973) in granite pegmatite and alkaline granites of the Khan Bogdo massif (Mongolia). From the same locality Vladykin (1983) and Vladykin and Kovalenko (2006) reported data from crystals of two generations of armstrongite. This mineral was also described in the Canadian peralkaline granite Strange Lake alkalic complex of the Québec-Labrador boundary (Jambor et al. 1987) in association with elpidite and gittinsite (Sali and Williams-Jones 1995, Roelofsen and Veblen 1999).

Armstrongite belongs to the group of Zr-silicates having general formula [ZrₙSi₆O₁₅]²⁻, and is characterized by a mixed framework of [Si₆O₁₅]²⁻ silicate sheets interlinked via Zr₆O₈ octahedra through vertex connection of octahedra and tetrahedra. According to Liebau’s classification, armstrongite contains unbranched silicate single layers of [Si₆O₁₅]²⁻ [Si₆O₁₅] composition with only tertiary [SiO₄] tetrahedra (Liebau 1985).

The stability of such polyhedral topology depends on the formation of almost equivalent Si-O-Si or Si-O-Zr bonds (Zubkova and Pushcharovsky 2008 and references therein).

Ghose et al. (1980) classified the armstrongite as a Zr-silicate belonging to the Zr-zeolite family together with catapleiite (Na₉₋₁₀Ca₇₋₁₀Zr(Si₁₅O₄₅₋₂₋₂)·2H₂O (Ilyushin et al. 1981a), gaidonnayite Na₉₋₁₀Zr(Si₁₅O₄₅₋₂₋₂)·2H₂O (Chao 1973), bilaireite Na₉₋₁₀Zr(Si₁₅O₄₅₋₂₋₂)·3H₂O (Ilyushin et al. 1981b), elpidite Na₉₋₁₀Zr(Si₁₅O₄₅₋₂₋₂)·8H₂O (Le Page and Perrault 1976). All these phases constitute alkal rocks and relative veins (Khomyakov 1995).

Structural details of armstrongite such as space group, content and location of water groups were still a matter of debate until this study. Possible space groups (C2, Cm, and C2/m) were initially reported for Mongolian armstrongite polysynthetic twin with lattice parameters a = 14.04, b = 14.16, c = 7.81 Å, and β = 109.55° (Vladykin et al. 1973). Kashaev and Sapozhnikov (1978) proposed the C2 space group for a twinned crystal from the same locality, basing on 319 reflections measured with photographic methods (De Jong-Bouman camera). However, their structure refinement converged to relatively high-R value (13%) and gave negative temperature factors.

Jambor et al. (1987) studied hk0 → hk3, 0kl → 4kl, and hkl → hkl level precession pictures of two blade crystals of the Canadian armstrongite which gave a monoclinic cell with systematic absences consistent with space groups C2/m, C2, or Im. The authors also obtained refined unit-cell parameters [a = 13.599(9), b = 14.114(9), c = 7.833(4) Å, and β = 103.41(5)°]...