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

ERNESTO MESTO1, EKATERINA KANEVA1, EMANUELA SCHINGARO1, NIKOLAY VLADYKIN2, MARIA LACALAMITA1 AND FERNANDO SCORDARI1,*

1Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari “Aldo Moro,” via E. Orabona 4, I-70125 Bari, Italy
2Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk-33, 664053 Russia

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 [001]. 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) 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): (Ca₀.₃₉Ce₀.₆₁Y₀.₁₀)Zr₀.₅ₛSi₀.₄₅O₁₄.₉₇H₂O. 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[Si₅O₁₃] nH₂O (2 ≤ n ≤ 3), named after the American astronomer 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 (Salvi and Williams-Jones 1995; Roelofsen and Veblen 1999).

Armstrongite belongs to the group of Zr-silicates having general formula [ZrₜₙSi₅O₁₃₋ₙ]^{2n⁻}, and is characterized by a mixed framework of [Si₅O₁₃]ₙ⁻ silicate sheets interlinked via ZrO₆ octahedra through vertex connection of octahedra and tetrahedra. According to Liebau’s classification, armstrongite contains unbranched silicate single layers of {uB, 12'} [Si₅O₁₃] 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 (NaₙCaZr(Si₅O₁₃)H₂O) (Ilyushin et al. 1981a), gaidonnyite NaₕZr(Si₅O₁₃)H₂O (Chao 1973), bilaireite Na₂Zr(Si₅O₁₃)H₂O (Ilyushin et al. 1981b), elpidite NaₙZr(Si₅O₁₃)H₂O (Cannillo et al. 1973), lemoynite (Na₂Ca)Zr(Si₅O₁₃)H₂O (Le Page and Perrat 1976). All these phases constitute alkali 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). Kasharov 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 h0l → 4kl level precession pictures of two identical crystals of the Canadian armstrongite which gave a monoclinic cell with systematic absences consistent with space groups I2/m, I₂, 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)°]