

New data on the crystal-chemistry of arrojadite: an HT study

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Arrojadite group minerals are very complex orthophosphates, with monoclinic symmetry. Ideally arrojadite has formula $A_2B_2Ca_1Na_{2-3}M_{13}Al(PO_4)_{11}(PO_3OH_{1-x})W_2$, where A sites are occupied by Ba, Sr, Pb, Na, K plus vacancy; the B site is occupied by divalent Fe, Mn, Mg, (Zn, Li) plus vacancy; the W site can be occupied by OH or F [1]. Their classification was approved by IMA-CNMMN and published by [1]. Their structure was described as C2/c by [2] and [3], and later revised by [4] who showed that the correct space group is actually Cc on the basis of new single-crystal X-ray diffraction data (SCXRD) and Raman spectroscopy. Recently the Cc model has been questioned [5] although very recent spectroscopic evidences confirm the lower symmetry [6].

The collaboration with AMI led us to examine new samples of arrojadite with compositions never described so far. In particular, we found the occurrence of a specimen with Mg dominant at the M group cation site coming from the locally known "Costa Balzi Rossi" locality, close to the village of Isallo (Liguria, Italy). This sample has a 16.3944(4), b 9.9477(2), c 24.4435(7) Å, β 105.661(3)°, and V 3838.41(16) Å³ and SCXRD data confirms that Mg is dominant in most of the M sites. Another specimen from Hagendorf (Germany) revealed to be F and (Na,Ba) dominant at W and A sites respectively. The relative proposals for new mineral names are being prepared to be submitted soon to IMA-CNMMN. Both samples show structural models in Cc s.g. which have the presence of residual density reproducing the C2/c model. This has been observed for other specimens, among them the arrojadite-(NaFe) from Nickel Plate (USA) studied also by [3] and [5].

Due to the controversy related to the choice of the C2/c versus Cc space groups, we performed annealing experiment of an arrojadite-(KFe) sample from Rapid Creek, Yukon (Canada). The natural crystal has Cc symmetry without any residue of density in the Fourier difference maps. A single crystal (0.080 0.30 0.35mm radius) was placed in a sealed and vacuumed quartz vial together with a Pt crucible containing iron-wüstite buffer and annealed at 650 °C for 24 hours. The vial was dropped into water and the crystal was studied by SCXRD at the same conditions used for the natural crystal. The results of structure refinement in the Cc space group showed the presence of disorder in a similar fashion to that found for natural samples coming from Nickel Plate. Therefore, the annealing clearly promotes the disorder of cations leading to an apparent centre of symmetry.

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Thermal expansion in bafertisite

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Bafertisite, ideally $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_4$, is a Ti-disilicate layered mineral with the TS (Titanium-Silicate) block, a central trioctahedral (O) sheet and two adjacent heteropolyhedral (H) sheets of [5-7]-coordinated polyhedra and Si₂O₇ groups [1, 2]. The topology of the H sheet dictates two translation vectors, t_1 and t_2 (~ 5.5 and ~ 7 Å, respectively; $t_1 \wedge t_2$ close to 90°). The structure of bafertisite was described by [3] as monoclinic cell, Cm , $a = 10.6$, $b = 13.64$, $c = 12.47$ Å, $\beta = 119.5^\circ$ $Z = 8$. Bafertisite belongs to Group -II minerals with $Ti = 2$ apfu in the H sheets and linkage 2 of H and O sheets in the TS-block: two Si₂O₇ groups link to two octahedra of the O sheet adjacent along t_2 .

We have studied a sample of manganoan bafertisite from Darai-Pioz (Tajikistan) with composition $(Ba_{1.9}Na_{0.1})(Fe^{2+}_{1.8}Mn^{2+}_{1.6}Fe^{3+}_{0.4}Zr^{4+}_{0.1})(Ti_{1.9}Nb_{0.1})(Si_2O_7)_2O_2(F_{2.2}OH_{1.8})$ on a very thin sample (0.15 X 0.07 x 0.01). Careful inspection of lattice parameters revealed a triclinic symmetry, with lattice constants: $a = 10.695(1)$, $b = 13.788(1)$, $c = 12.551(1)$ Å, $\alpha = 90.210(1)$, $\beta = 119.860(1)$, $\gamma = 89.994(1)$, $V = 605.2(3)$ Å³. Structure was therefore solved and refined in space group C-1, with the mirror plane imposed as a twin operation and agreement factor was as low as 2.8% for 4716 observations.

The thermal behaviour of bafertisite from Darai-Pioz (Tajikistan) was studied by an *in-situ* synchrotron radiation X-ray powder diffraction experiment. The data were collected in transmission geometry with a fixed wavelength of (0.8279 Å) at MCX beamline at Elettra synchrotron light source (Trieste-Italy). The sample was heated from RT to 700°C with a thermal gradient of 5°C/min. Diffraction patterns were collected every 25°C on a translating image plate. Full profile Rietveld refinements were performed to follow the evolution of cell parameters with temperature.

Lattice parameters expands showing $\alpha_{V300} = 3.02(18)$. The observed lattice expansion anisotropy is 1:1.09:1.22. At ca. 600°C β angle starts widening and crosses 120°. Contemporaneously c lattice parameters start decreasing while expansion increases within (001). The contraction of the [001] direction leads the cell volume variation that show negative thermal expansion (NTE) at $T > 600$ °C. Preliminary data point to a NTE driven by differential shift among the TS-block and a change in the coordination of Ba in the intermediate layer that brings closer the TS-blocks in order to achieve satisfactory coordination.

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