



Crystal structure of leucophosphite, $\text{KFe}^{3+}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, from the João pegmatite, Minas Gerais, Brazil

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ARTICLE INFO

Submitted: March 2019

Accepted: April 2019

Available on line: May 2019

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DOI: 10.2451/2019PM865

How to cite this article:

Rotiroti N. and Vignola P. (2019)

Period. Mineral. 88, 325-332

ABSTRACT

The crystal structure of leucophosphite, $\text{KFe}^{3+}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, was fully characterized using single-crystal X-ray data, collected on a crystal from the João pegmatite, Minas Gerais, Brazil. This crystal belongs to the same fragment accurately analysed by electron microprobe. The refinement was carried out in the $P2_1/n$ space group and with unit-cell $a=9.7734(3)$ Å, $b=9.6606(2)$ Å, $c=9.7429(5)$ Å, $\beta=102.447(5)^\circ$ and $V=898.27(6)$ Å³ for $Z=4$. The known crystal-structure, based on tetramers of octahedrally coordinated sites connected by the (PO_4) -tetrahedra in a complex tridimensional framework with K atoms located in channels aligned along b axis, is confirmed. Difference Fourier map allowed to unambiguously locate the hydrogen positions that were refined at the final steps of the crystal structure anisotropic refinement leading to an $R1$ index of 2.12%. 162 parameters were refined on the basis of 2406 observed [$I>3\sigma(I)$] reflections. The H-bonding scheme in the structure of leucophosphite is now fully defined. One hydroxyl group and two H_2O groups are exhaustively described. OH group has donor-acceptor distance of 2.96 Å and D-H...A 172°. H_2O groups show donor-acceptor distances less than 2.9 Å whereas angles D-H...A are 161-176° and 162-176° for OW10 and OW11, respectively. The OW11 atom behaves twice as donor (with H111 and H112) and twice as acceptor (with H91 and H101), results in a distorted tetrahedron with OH9, OW10, O6, and O4. A very good agreement against microprobe chemical analysis was found, also confirmed by bond valence calculation showing expected values for all the atomic sites.

Keywords: leucophosphite; crystal structure; single-crystal X-ray diffraction; hydrogen bonding; João pegmatite; Minas Gerais; Brazil.

INTRODUCTION

Leucophosphite, $\text{KFe}^{3+}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, was found and described for the first time in phosphate-bearing veins (phosphate content from bird guano) in the serpentinitic rocks at Ninghanboun Hills, Weelhamby Lake, Perenjori Shire, Western Australia (Simpson, 1931-32). Leucophosphite of non-sedimentary or biogenic origin was firstly described in Brazil at the Sapucaia pegmatite by Lindberg (1957). It is a typical low temperature

product of hydrothermal alteration of Fe-bearing primary phosphates in granitic pegmatites where it occurs in evolved phosphate-bearing pegmatites from the beryl-columbite-phosphates to the spodumene subtype, according to the classification of Černý and Ercit (2005). Leucophosphite single crystals are tabular on $\{101\}$ with a typical “diamond shape”. The single crystals often cluster in groups to form spherical polycrystalline aggregates. The color spans from colorless, yellowish-brown up to



purplish with a vitreous to adamantine luster (Lindberg, 1957).

The crystal structure of leucophosphate, was solved and refined for the first time by Moore (1972). He described the structure in the space group $P2_1/n$ with $a=9.782(9)$ Å, $b=9.658(9)$ Å; $c=9.751(9)$ Å, and $\beta=102.24(12)^\circ$, $V=900.3(15)$ Å³ and providing with a theoretical position for the H ions.

A compound with formula $K_3[Fe_{3.26}V_{0.74}(OH)O(PO_4)_4(H_2O)_2] \cdot 2H_2O$ and space group $P2_1/n$, with $a=9.6391(7)$ Å, $b=9.8063(7)$ Å, $c=9.7268(7)$ Å, $\beta=100.71(1)^\circ$, and $V=903.38(11)$ Å³ was synthesized by Silva-Galaz et al. (2013). A transformation according to (001/010/100) results in the cell $a=9.7268(7)$ Å, $b=9.8063(7)$ Å, $c=9.6391(7)$ Å, $\beta=100.71(1)^\circ$ which well compares with that reported by Moore (1972) for leucophosphate. Crystal structure without determination of H atoms position was deposited by authors.

Dick and Zeiske (1997) studied the synthetic analogue of leucophosphate with formula $K[Fe_2(PO_4)_2(OH)(H_2O)] \cdot H_2O$ and unit-cell $a=9.756(3)$ Å, $b=9.664(3)$ Å, $c=9.769(4)$ Å, $\beta=102.43(2)^\circ$. Also in this case a transformation according to (001/010/100) should be applied resulting in the cell $a=9.769(3)$ Å, $b=9.664(3)$ Å, $c=9.756(4)$ Å, $\beta=102.43(2)^\circ$ to be compared with that by Moore (1972). By neutron powder diffraction they were able to locate H atoms and correct a misprint of a K parameter in the paper of Moore (1972) which was the reason for the unacceptable short K-O bond distances. In their paper they report in Table 1 mixed data part of which from the redetermination of the structure with a single crystal from Těškov (Bohemia, Czech Republic) and only parameters of H-atoms determined by neutron scattering of synthetic material.

Shi et al. (2008) could also localize and refine the H-atom positions for a synthetic crystal with 50% V^{3+} in the metallic sites occupied by Fe^{3+} (with formula $K[(Fe,V)(PO_4)_2(OH)(H_2O)] \cdot H_2O$; the H-atom positions are not printed but deposited) with $P2_1/c$, $a=9.7210(19)$ Å, $b=9.6500(19)$ Å, $c=12.198(4)$ Å, $\beta=128.569(18)^\circ$, $V=894.7(4)$ Å³. In this case applying a transformation matrix (101/010/100) a reduced cell with space group $P2_1/n$, and $a=9.791(4)$ Å, $b=9.650(2)$ Å, $c=9.721(2)$ Å, $\beta=102.51(2)^\circ$, $V=894.7(4)$ Å³ is obtained to be compared with that in Moore (1972).

The aim of this paper is to describe the crystal structure of the secondary phosphate leucophosphate from João pegmatite using single-crystal X-ray diffraction data obtained from the same crystal fragment well characterized from the chemical point of view by accurate EMPA analysis. Structure refinement from single crystal X-ray diffraction data allows to unambiguously position H ions and fully describe the hydrogen bonding environment.

The novelty in this report is the fact that the sample is not sedimentary but pegmatitic, as all the samples previously studied. Furthermore, Dick and Zeiske (1997) report mixed data (see Table 1 in their work) derived by single crystal X-ray diffraction experiments on a natural sample (from Těškov, Bohemia, Czech Republic) and neutron powder diffraction data on a synthetic material. Here, the first complete structural study is given.

Table 1. Averaged (10 points) electron microprobe analysis of leucophosphate from João.

| | wt% | esd | | apfu* |
|--------------------------------|--------|------|------------------|--------------|
| P ₂ O ₅ | 35.81 | 0.40 | P | 2.000 |
| Fe ₂ O ₃ | 41.06 | 1.04 | Fe ³⁺ | 2.038 |
| MnO | 0.03 | 0.02 | Mn | 0.002 |
| CaO | 0.01 | 0.01 | Ca | 0.001 |
| MgO | 0.03 | 0.02 | Mg | 0.003 |
| Na ₂ O | 0.01 | 0.01 | Na | 0.001 |
| K ₂ O | 11.53 | 0.15 | K | 0.970 |
| H ₂ O** | 11.59 | | sum | 0.977 |
| Total | 100.07 | | H | 5.098 |

* calculated considering 2 P atoms per formula unit (apfu); ** calculated to have 2 H₂O molecules and 1.098 OH⁻ groups (to balance charges) in stoichiometry.

SAMPLE DESCRIPTION AND MINERALOGY

The single-crystal data collection was carried out on a fragment of a tabular, pale brown 0,7 mm long single crystal of leucophosphate perched on mitridatite in green hemispheric aggregates which cover an hydrothermal cavity hosted by albite (var. cleavelandite). The specimen was found in the mine dumps (Cigana) of João pegmatite, Conselheiro Pena, Minas Gerais, Brazil.

The João pegmatite, as well as the Sapucaia, and Eduardo pegmatites, belongs to the Eastern Brazilian Pegmatite province, cropping out in the Conselheiro Pena pegmatite district in the middle part of the Doce river basin (Pedrosa-Soares et al., 2011; Bajjot et al., 2014; Bajjot, 2015). The granitic pegmatite dike is hosted in high grade sillimanite-, staurolite- and garnet-bearing mica schists of the São Tomé Formation belonging to the Araçuaí mobile belt during the Brasiliano orogeny (Almeida, 1977; Pedrosa-Soares et al., 2011; Bajjot et al., 2014; Bajjot, 2015). The pegmatitic dike belongs to the spodumene subtype in the classification of Černý and Ercit (2005) and shows a very complex secondary phosphates association

(Baijot et al., 2014; Baijot, 2015).

The João pegmatite, first mined for feldspar and gem material, is type locality for correianevesite, and worldwide famous for the spectacular specimens showing secondary phosphates (Chukanov et al., 2014; Baijot, 2015). The secondary phosphates association hosting the leucophosphite crystals investigated in this work belongs to the association III described by Baijot et al. (2014) and Baijot (2015), which is interestingly rich of Ca-bearing secondary phosphates such as mitridatite, robertsite, and fairfieldite (detected as divergent groups of tabular white crystals up to 2 cm in length and directly perched on mitridatite with hureaulite; this last phosphate was determined by XRPD and qualitative EDS microprobe analyses).

ANALYTICAL METHODS

Quantitative electron-microprobe analyses were performed on a polished mount of the same crystal used for the single-crystal data collection, using a JEOL JXA-8200 microprobe in wavelength-dispersive mode at the Earth Sciences Department (ESD) of the University of Milano. Electron-microprobe analytical conditions are the same as for phosphate triplite (Vignola et al. 2014). The raw data were corrected for matrix effects using the protocol implemented in the JEOL suite of programs. The averaged and normalized analysis is shown in Table 1.

Single-crystal X-ray diffraction data were collected with an Xcalibur - Oxford Diffraction diffractometer equipped with a CCD, using graphite-monochromatized MoK α radiation, and operated at 50 kV and 40 mA at the ESD (University of Milano) with a step size of 1° and an exposure time per frame of 20 s. Complete details on data collection and unit-cell parameters are contained in Table 2. Intensity data were corrected for Lorentz-polarization and absorption (empirical; ABSPACK) effects with the CrysAlis software (Oxford Diffraction, 2006).

After checking for systematic extinctions, the structure refinement was performed in the confirmed space group $P2_1/n$ using the JANA2006 software (Petříček et al. 2006), starting from the site coordinates of leucophosphite and isotropic displacement parameters as reported by Moore (1972), in which the H sites were not experimentally located. The neutral X-ray scattering curve of K, Fe, P, O and H were used according to the *International Tables for Crystallography C* (Wilson and Prince, 1999). Secondary extinction effects were corrected using the isotropic model of Type I (Becker and Coppens, 1974) with a Gaussian mosaic spread distribution as implemented in the JANA2006 package (Petříček et al. 2006).

Five maxima were found in the difference-Fourier map of the electron density and attributed to five independent H sites that were added to the structure. The relative O-H

distances were restrained to a target value of 0.85 ± 0.05 Å. After including isotropic model for H atoms, the convergence was rapidly achieved and the variance-covariance matrix showed no high correlation (larger than 0.65) among the refined parameters; atomic displacement parameters for the five H sites were restrained to be equal. No peaks larger than $\pm 0.45 e^{-\text{Å}^3}$ were present in the final difference-Fourier maps of the electron density. The final agreement index ($R1$) for the anisotropic refinement was 0.0212 for 2406 unique reflections with $I > 3\sigma(I)$ and 162 refined parameters (Table 2). Atomic coordinates and displacement parameters are reported in Table 3; relevant bond lengths are listed in Table 4. Table 5 reports the bond-valence calculation for leucophosphite (including hydrogen atoms). Table 6 shows the hydrogen-bonding scheme in leucophosphite. Additional data are reported in the deposited .cif.

Table 2. Details pertaining the data collection and the structure refinement of leucophosphite.

| | |
|--|---|
| a (Å) | 9.7734(3) |
| b (Å) | 9.6606(2) |
| c (Å) | 9.7429(5) |
| β | 102.447(5)° |
| V (Å ³) | 898.27(6) |
| Chemical formula | KFe ³⁺ ₂ (PO ₄) ₂ (OH)·2H ₂ O |
| Z | 4 |
| Space Group | $P2_1/n$ |
| Crystal Size (mm) | 0.17x0.14x0.10 |
| Total collected reflections | 24862 |
| Range hkl | -16< h <16, -15< k <15, -12< l <13 |
| Redundancy | 8.007 |
| Total unique reflections | 3105 |
| Observed reflections ($I > 3\sigma I$) | 2406 |
| Parameters (refinement) | 162 |
| $R_{\text{int}}(\text{obs/all})$ | 3.58/3.94 |
| Final $R1$ (obs/all) (%) | 2.12/3.59 |
| Final $wR2$ | 2.45/2.57 |

$$R_{\text{int}} = \frac{\sum |F_{\text{obs}}^2 - F_{\text{obs}}^2(\text{mean})|}{\sum F_{\text{obs}}^2}; R_1 = \frac{\sum (|F_{\text{obs}} - F_{\text{calc}}|)}{\sum |F_{\text{obs}}|}; wR2 = \frac{[\sum (w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2)]^{0.5}}{[\sum (wF_{\text{obs}}^2)]^{0.5}}, w = 1/[\sigma^2(F_{\text{obs}}^2)].$$

Table 3. Refined positional and anisotropic displacement parameters (\AA^2) for leucophosphite.

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₁₂ | <i>U</i> ₁₃ | <i>U</i> ₂₃ | <i>U</i> _{iso/eq} |
|------|-------------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|----------------------------|
| K | -0.10101(6) | 0.19593(5) | 0.51724(7) | 0.0203(3) | 0.0342(2) | 0.0271(3) | 0.0064(2) | 0.0031(3) | 0.0037(2) | 0.0275(2) |
| Fe1 | 0.36950(3) | 0.55121(2) | 0.39185(3) | 0.0055(1) | 0.0073(1) | 0.0060(2) | 0.0003(1) | 0.0006(1) | 0.0003(1) | 0.0063(1) |
| Fe2 | 0.30973(3) | 0.22781(2) | 0.59694(3) | 0.0059(1) | 0.0069(1) | 0.0058(2) | -0.0003(1) | 0.0004(1) | 0.0006(1) | 0.0064(1) |
| P1 | 0.35479(5) | 0.52857(4) | 0.70932(6) | 0.0066(2) | 0.0064(1) | 0.0060(3) | 0.0002(1) | 0.0017(2) | -0.0010(2) | 0.0063(1) |
| P2 | 0.12869(5) | 0.32210(4) | 0.28933(6) | 0.0061(2) | 0.0063(1) | 0.0059(3) | -0.0007(1) | -0.0006(2) | 0.0003(2) | 0.0064(1) |
| O1 | 0.3013(1) | 0.5934(1) | 0.5636(1) | 0.0090(6) | 0.0117(5) | 0.0060(8) | 0.0024(4) | 0.0006(6) | 0.0018(5) | 0.0090(4) |
| O2 | 0.1751(1) | 0.1210(1) | 0.6745(1) | 0.0105(7) | 0.0122(5) | 0.0080(8) | -0.0021(4) | 0.0018(6) | 0.0045(5) | 0.0102(4) |
| O3 | 0.4847(1) | 0.4920(1) | 0.2610(1) | 0.0068(6) | 0.0131(5) | 0.0070(8) | 0.0019(4) | 0.0011(6) | -0.0009(5) | 0.0090(4) |
| O4 | 0.2837(1) | 0.3865(1) | 0.7159(2) | 0.0123(7) | 0.0082(5) | 0.0128(8) | -0.0017(4) | 0.0057(7) | -0.0008(5) | 0.0107(4) |
| O5 | 0.1550(1) | 0.2689(1) | 0.4399(2) | 0.0092(7) | 0.0172(5) | 0.0076(8) | -0.0023(5) | -0.0018(7) | 0.0041(5) | 0.0119(4) |
| O6 | 0.1951(1) | 0.4677(1) | 0.2853(1) | 0.0099(6) | 0.0076(5) | 0.0093(8) | -0.0019(4) | -0.0012(6) | 0.0007(5) | 0.0094(4) |
| O7 | 0.3055(1) | 0.7278(1) | 0.3056(2) | 0.0096(7) | 0.0097(5) | 0.0140(8) | 0.0014(4) | 0.0031(7) | 0.0045(5) | 0.0110(4) |
| O8 | 0.4714(1) | 0.1622(1) | 0.7349(2) | 0.0068(6) | 0.0120(5) | 0.0122(8) | -0.0003(4) | -0.0025(6) | 0.0020(5) | 0.0110(4) |
| OH9 | 0.4387(1) | 0.3571(1) | 0.4970(2) | 0.0079(6) | 0.0088(5) | 0.0084(8) | -0.0001(4) | 0.0023(6) | -0.0008(5) | 0.0083(4) |
| OW10 | 0.3427(2) | 0.0467(2) | 0.4885(2) | 0.0329(11) | 0.0206(7) | 0.0088(9) | 0.0123(6) | 0.0001(9) | -0.0035(6) | 0.0214(6) |
| OW11 | 0.5331(2) | 0.1535(1) | 0.3099(2) | 0.0232(9) | 0.0192(7) | 0.0454(13) | -0.0089(6) | 0.0176(10) | -0.0102(7) | 0.0277(6) |
| H91 | 0.459(3) | 0.313(3) | 0.446(3) | | | | | | | 0.032(4) |
| H101 | 0.387(3) | -0.005(3) | 0.530(3) | | | | | | | 0.032 |
| H102 | 0.328(3) | 0.026(3) | 0.407(3) | | | | | | | 0.032 |
| H111 | 0.474(3) | 0.103(3) | 0.268(3) | | | | | | | 0.032 |
| H112 | 0.600(3) | 0.144(3) | 0.280(3) | | | | | | | 0.032 |

CRYSTAL-CHEMISTRY OF LEUCOPHOSPHITE

The empirical formula found using the averaged chemical analysis normalized on the basis of 2 P atoms per formula unit (Table 2) is: $\text{K}_{0.97}\text{Fe}^{3+}_{2.04}(\text{PO}_4)_2(\text{OH})_{1.098} \cdot 2\text{H}_2\text{O}$. The minor amounts of Mn, Ca, Mg and Na are not significant in the empirical formula. This formula is very close to the theoretical one, $\text{KFe}^{3+}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, for this species (Lindberg, 1957).

The crystal structure of leucophosphite, as described by Moore (1972), is based on a Fe-centered octahedra tetramer (Figure 1). Each tetramer is formed by two edge-shared octahedra (centered by Fe1) laterally linked the other two octahedra (centered by Fe2) by the common corner. These distorted tetramers are joined in a three dimensional framework by the PO_4 tetrahedra. The K atoms are located inside channels aligned along the *b* axis of the framework (Figure 2). Each K atom is coordinated to six oxygen atoms giving an irregular polyhedron with average K-O bond length of 2.924 Å (Table 4) which is in good agreement with 2.927 Å found by Moore (1972).

The polyhedron shares an edge with Fe2- O_6 octahedron and an edge with the P1- O_4 tetrahedron (Figures 1 and 2). According to the hydrogen bonding scheme proposed by Moore (1972) we identify OH9=(OH)⁻ and OW10, OW11=(H₂O) evidencing his hypothetic scheme. In particular, the OW11 oxygen atom is the only one not directly connected to the framework and receives 2 bonds and donates 2 bonds resulting in a distorted tetrahedron with O6, O4, OH9, and OW10. The geometry and geometrical parameters of the hydrogen bonding are summarized, respectively, in Figure 3 and Table 6.

DISCUSSION

The chemical analysis of leucophosphite from the João pegmatite shows a composition close to the end-member $\text{KFe}^{3+}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$ which is in very good agreement with inferences from structural data. The crystal structure refinement shows very complicated atomic arrangement, based on distorted tetramers of Fe centered octahedra linked by the (PO_4) tetrahedra.

Table 4. Bond distances (Å) in the crystal structure of leucophosphate.

| | | | |
|-----------|----------|----------|----------|
| K- O1a | 2.816(1) | Fe1-O1 | 1.972(2) |
| K- O2 | 2.894(1) | Fe1-O3 | 1.959(1) |
| K- O3b | 2.964(1) | Fe1-O6 | 1.967(1) |
| K- O4c | 3.016(2) | Fe1-O7 | 1.944(1) |
| K- O5 | 2.852(2) | Fe1-OH9e | 2.144(1) |
| K- O7d | 3.001(2) | Fe1-OH9 | 2.173(1) |
| <K-O> | 2.924 | <Fe1-O> | 2.026 |
| Fe2- O2 | 1.948(1) | P1-O1 | 1.537(1) |
| Fe2- O4 | 1.971(1) | P1-O2f | 1.518(1) |
| Fe2- O5 | 1.947(1) | P1-O3g | 1.545(1) |
| Fe2- O8 | 1.947(1) | P1-O4 | 1.546(1) |
| Fe2- OH9 | 2.151(1) | <P1-O> | 1.536 |
| Fe2- OW10 | 2.104(2) | | |
| <Fe2-O> | 2.011 | P2-O5 | 1.523(2) |
| | | P2-O6 | 1.553(1) |
| | | P2-O7h | 1.535(2) |
| | | P2-O8c | 1.522(1) |
| | | <P2-O> | 1.533 |

a: -x,-y+1,-z+1; b: x-1/2,-y+1/2,z+1/2; c: x-1/2,-y+1/2,z-1/2;
d: -x, -y+1,-z+1;
e: -x+1,-y+1,-z+1; f: -x+1/2,y+1/2,-z+3/2; g: -x+1,-y+1,-z+1;
h: -x+1/2,y-1/2,-z+1/2;

The structure of leucophosphate can be described in terms of octahedral cluster Fe_4O_2 building units (the four iron atoms lying in a plane almost perpendicular to the $[\bar{1}11]$ axis). The cluster consists of an edge-sharing doublet whose two common corners each fuse by corner-sharing to two other octahedra forming the tetramer Fe_4O_2 (Moore, 1972). The tetramer are formed by a central pair of edge sharing FeO_6 octahedra [$2x\text{Fe}(1)$ connected via O(9)], to which two additional FeO_6 octahedra are attached by corner sharing [$2x\text{Fe}(2)$ via O(9)]. Each of the two phosphate tetrahedra is connected with two Fe(1) and two Fe(2) octahedra, thus creating a three-dimensional framework of PO_4 tetrahedra and tetramers Fe_4O_2 . This framework contains intersecting channels which run parallel to the b -axis and which are centered at $(x, z)=(1/2, 0)$ and $(0, 1/2)$. These channels are occupied by ordered K^+ cations located across the inversion centers whose inner sphere of coordination includes six oxygen atoms with average K-O distances of 2.924. As reported in Table 5 the bond-valence calculation (Brown 1996) for K atom is still underestimated even considering enlarged shell of coordination including distances with O8, OW10 and OW11 (3.284, 3.319 and 3.217 respectively). The examination of atomic displacement parameters indicates values that are relatively higher for K atom with respect to those of the other atom positions and similar to those of H_2O groups. This may be due to local disorder of K atoms within the structural channels.

Difference-Fourier maps allowed the identification of five independent H positions; their positions agree with the bond-valence sums, indicating an undersaturation

Table 5. Bond-valence calculation for leucophosphate from Jocêo.

| | K | Fe1 | Fe2 | P1 | P2 | H91 | H101 | H102 | H111 | H112 | Σ |
|----------|------|------|------|------|------|------|------|------|------|------|----------|
| O1 | 0.16 | 0.56 | | 1.24 | | | | | | | 1.96 |
| O2 | 0.13 | | 0.60 | 1.31 | | | | | | | 2.04 |
| O3 | 0.11 | 0.58 | | 1.22 | | | | | | | 1.91 |
| O4 | 0.09 | | 0.56 | 1.21 | | | | | | 0.21 | 2.07 |
| O5 | 0.14 | | 0.60 | | 1.29 | | | | | | 2.03 |
| O6 | | 0.57 | | | 1.19 | | | 0.24 | 0.21 | | 2.21 |
| O7 | 0.10 | 0.61 | | | 1.25 | | | | | | 1.96 |
| O8 | 0.05 | | 0.60 | | 1.29 | | | | | | 1.94 |
| OH9 | | 0.35 | 0.35 | | | 0.83 | | | | | 1.86 |
| | | 0.33 | | | | | | | | | |
| OW10 | 0.04 | | 0.39 | | | | 0.83 | 0.77 | | | 2.03 |
| OW11 | 0.05 | | | | | 0.17 | 0.19 | | 0.76 | 0.78 | 1.95 |
| Σ | 0.87 | 3.00 | 3.10 | 4.98 | 5.02 | 1.00 | 1.02 | 1.01 | 0.97 | 0.99 | |

Table 6. Bond distances and angles in the hydrogen bonding of leucophosphite from João.

| donor | | acceptor | D-H | H...A | D-A | D-H...A |
|-------|------|-------------------|---------|---------|----------|---------|
| OH9 | H91 | OW11 | 0.74(3) | 2.23(3) | 2.961(2) | 172(3) |
| OW10 | H101 | OW11 ⁱ | 0.74(3) | 2.12(3) | 2.836(2) | 161(3) |
| OW10 | H102 | O6 ⁱⁱ | 0.82(3) | 1.90(3) | 2.723(2) | 176(3) |
| OW11 | H111 | O6 ⁱⁱ | 0.83(3) | 2.06(3) | 2.857(2) | 162(3) |
| OW11 | H112 | O4 ⁱⁱⁱ | 0.80(3) | 2.02(3) | 2.820(3) | 176(3) |

i: $-x+1,-y,-z+1$; ii: $-x+1/2,y-1/2,-z+1/2$; iii: $x+1/2,-y+1/2,z-1/2$

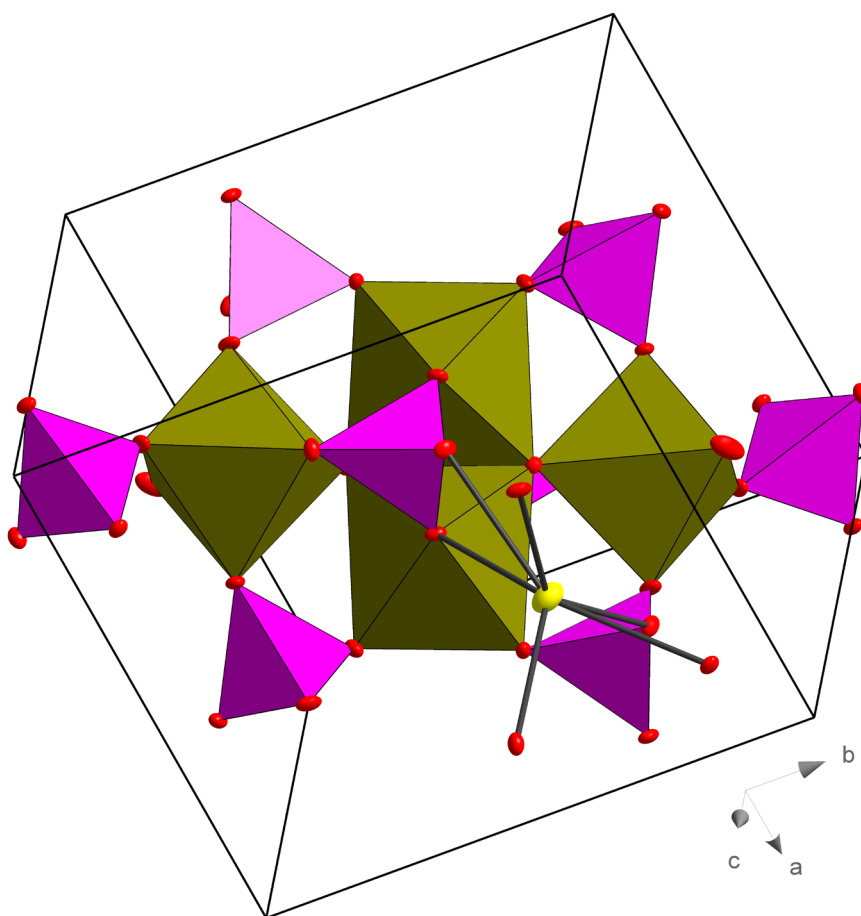


Figure 1. The octahedral tetramer (green) with the connecting P-centered tetrahedra (pink). The position of K-ions (yellow) hosted in the channels aligned along *b* is also indicated.

at the OH9, OW10, and OW11 sites (Table 5). The relative O-H distances were restrained to a target value of 0.85 ± 0.05 Å. The hydrogen bonding scheme proposed in the present paper works satisfactorily for all crystallographic sites and it is in good agreement with the scheme proposed by Moore (1972) in which the H atoms were not located (Figure 3 compare to Figure 6 in

Moore 1972). We confirm that $\text{OH9}=(\text{OH})^-$ and $\text{OW10}, \text{OW11}=(\text{H}_2\text{O})$ with the geometry proposed in Table 6.

All H-bonds are favorable being distances and angles between donors and acceptors almost ideal both for hydroxyl and H_2O groups. In particular in water molecules donor-acceptor distances are less than 2.9 Å and D-H...A angles are 161-176° and 162-176° for OW10 and OW11

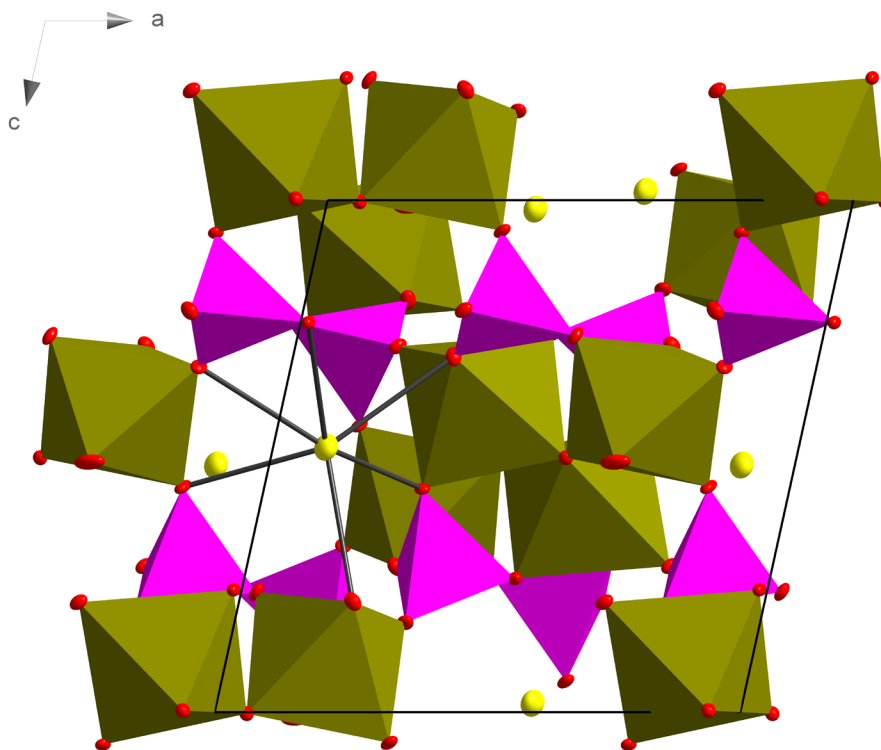


Figure 2. The crystal-structure of leucophospite down to b (green=Fe-centered octahedra, pink=P-centered tetrahedra, yellow=K ions).

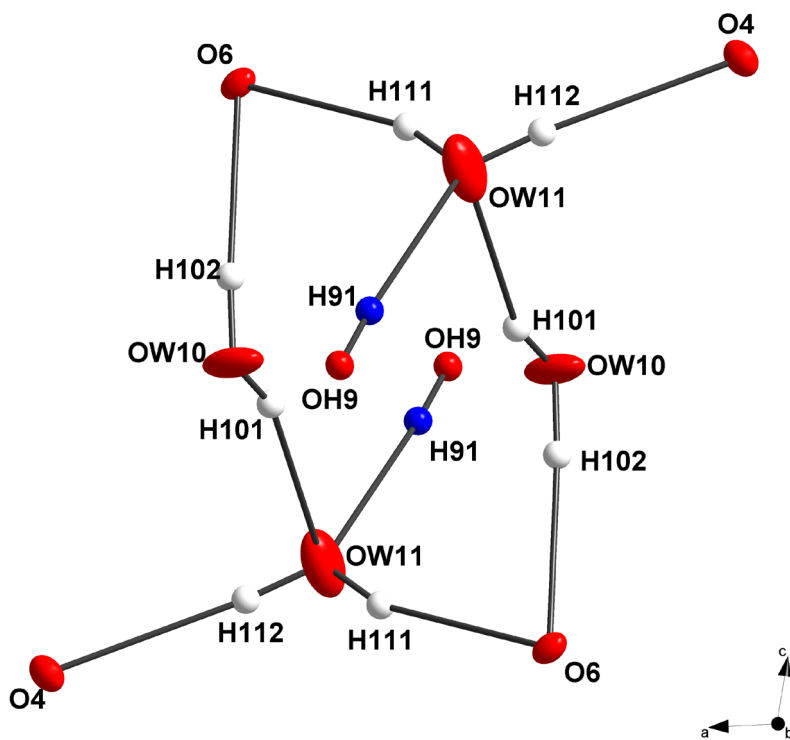


Figure 3. Hydrogen-bond structure as derived from the crystal-structure refinement. Hydrogen of the OH^- group in blue.

respectively. Moreover, being OW11 twice donor (with H111 and H112) and twice acceptor (with H91 and H2), results in a distorted tetrahedron with OH9, OW10, O6, and O4. Nevertheless, D-H distances are rather short due to inaccurate location of hydrogen atoms as obtained by structure refinement from x-ray data. Like in some zeolitic H₂O this oxygen is firmly accommodated in the cavity. The most common situation is that described in hureaulite and bjarebyite which crystal-structure was recently described (Gatta et al., 2015; Rotiroti et al., 2016).

ACKNOWLEDGEMENTS

The authors are indebted to Luca Bindi and two anonymous reviewers for critical comments and helpful suggestions. Sergio Varvello is thanked for providing the specimen used in the present work. Andrea Risplendente is thanked for the help during the electron microprobe session. NR acknowledges the support of the Italian Ministry of Education (MIUR) through the project “Dipartimenti di Eccellenza 2017”.

REFERENCES

- Almeida F.F.M., 1977. O Craton do São Francisco. *Revista Brasileira de Geociencias* 7, 349-364 (in Portuguese).
- Baijot M., Hatert F., Dal Bo F., Philippo S., 2014. Mineralogy and petrography of phosphate mineral associations from the Jocoá pegmatite, Minas Gerais, Brazil. *The Canadian Mineralogist* 52, 373-397.
- Baijot M., 2015. Les phosphates des pegmatites du district de Conselheiro Pena, Brésil: Minéralogie, pétrographie et relations avec les silicates. Ph.D. thesis, University of Liège, Belgium, 467 p.
- Becker P.J. and Coppens P., 1974. Extinction within the limit of validity of the Darwin transfer equations. I. General formalism for primary and secondary extinction and their applications to spherical crystals. *Acta Crystallographica A* 30, 129-147.
- Brown I.D., 1996. Valence: a program for calculating bond valences. *Journal of Applied Crystallography* 29, 479-480.
- Černý P. and Ercit T.S., 2005. The classification of granitic pegmatites revisited. *Canadian Mineralogist* 43, 2005-2026.
- Chukanov N.V., Scholz R., Zubkova N.V., Pekov I.V., Belakovskiy D.I., Van K.V., Lagoeiro L., Graça L.M., Krambrock K., de Oliveira L.C.A., Menezes Filho L.A.D., Sa Carneiro Chaves M.L., Pushcharovsky D.Y., 2014. Correianevesite, Fe²⁺Mn²⁺₂(PO₄)₂·3H₂O, a new reddingite-group mineral from the Cigana mine, Conselheiro Pena, Minas Gerais, Brazil. *American Mineralogist* 99, 811-816.
- Dick S. and Zeiske T., 1997. Leucophosphite K[Fe₂(PO₄)₂(OH)(H₂O)]·H₂O: Hydrogen bonding and structural relationships. *Journal of Solid State Chemistry* 133, 508-515.
- Gatta G.D., Redhammer G.J., Vignola P., Meven M., McIntyre G.J., 2015. Single-crystal neutron diffraction and Mössbauer spectroscopic study of hureaulite, (Mn,Fe)₅(PO₄)₂(HPO₄)₂(H₂O)₄. *European Journal of Mineralogy* 28, 93-103.
- Lindberg M.L., 1957. Leucophosphite from the Sapucaia Pegmatite mine, Minas Gerais, Brazil. *American Mineralogist* 42, 214-221.
- Moore P.B., 1972. Octahedral tetramer in the crystal structure of leucophosphite, K₂[Fe³⁺₄(OH)₂(H₂O)₂(PO₄)₄]·2H₂O. *American Mineralogist* 57, 397-410.
- Oxford Diffraction, 2006. *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Pedrosa-Soares A.C., Campos C.M., Noce C.M., Silva L.C., Novo T.A., Roncato J., Medeiros S.M., Castañeda C., Queiroga G.N., Dantas E., Dussin I.A., Alkmim F., 2011. Late Neoproterozoic-Cambrian granitic magmatism in Araçuaí orogen (Brazil), the Eastern Brazilian Pegmatite Province and related mineral resources. Geological Society, London, Special Publications 350, 25-51.
- Petříček V., Dušek M., Palatinus L., 2006. Crystallographic Computing System JANA2006: General Features. *Zeitschrift für Kristallographie* 229, 345-352.
- Rotiroti N., Vignola P., Bersani D., Simmons W.B., Falster A.U., Whitmore R.W., Nizamoff J.V., Lotti P., Risplendente A., Pavese A., 2016. On the crystal-chemistry of bjarebyite, BaMn²⁺₂Al₂(PO₄)₃(OH)₃, from the Palermo #1 pegmatite, Grafton County, New Hampshire. *The Canadian Mineralogist* 54, 1033-1041.
- Silva-Galaz C., Saldias M., Garland M.T., Vega A., Paredes-García V., Spodine E., Venegas-Yazigi D., 2013. K₃[Fe_{3.26}V_{0.74}(OH)O(PO₄)₄(H₂O)₂]·2H₂O: a synthetic leucophosphite. *Journal of Coordination Chemistry* 66, 1830-1836.
- Shi F.N., Moreira dos Santos A., Cunha-Silva L., Costa B.F.O., Klinowski J., Almeida Paz F.A., Amaral V.S., Rocha J., Trindade T., 2008. Synthesis, structure and magnetic behaviour of mixed metal leucophosphite. *Journal of Solid State Chemistry* 181, 1330-1336.
- Simpson E.S., 1931-32. Contributions to the mineralogy of Western Australia. *Journal of Royal Society of Western Australia* 18, 61-74.
- Vignola P., Gatta G.D., Hatert F., Guastoni A., Bersani, D., 2014. On the crystal-chemistry of a near end-member triplite, Mn²⁺₂(PO₄)F, from the Codera Valley (Sondrio province, central Alps, Italy). *The Canadian Mineralogist* 52, 235-245.
- Wilson A.J.C. and Prince E., 1999. *International Tables for X-ray Crystallography, Volume C: Mathematical, physical and chemical tables (2nd Edition)*. Kluwer Academic, Dordrecht.



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