# Synthesis, Structure and Magnetic Characterization of a New Phosphate $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ with the Langbeinite-type Structure

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A new complex phosphate $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ has been synthesized by the self-flux technique. The X-ray single crystal structure and magnetic properties were studied. The compound crystallizes in the cubic system with space group $P2_13$ ($a$ = 9.9404(10) Å) and belongs to the langbeinite structure type. The structure contains $[M_2P_3O_{18}]$ building units. "Closed" fragments $[M_8P_9O_{60}]$ provide space for location of two potassium atoms. Antiferromagnetic interactions were detected at low temperatures which originate from superexchange through a $M(1)$–O–P–O–$M(2)$ pathway with corresponding $J = -5.5(1)$ cm$^{-1}$. The relationship between the UV/vis absorption and the structure is discussed.

*Key words:* Phosphates, Crystal Structure, Langbeinite, Magnetic Measurements

## Introduction

In recent years complex phosphates with langbeinite-type structure have been intensively investigated due to their intriguing structures and interesting applications resulting therefrom. Anionic frameworks of common formula $\{[M_2(PO_4)_3]^{n-}\}_\infty$ ($M$ = polyvalent metal) form a large family of compounds which exhibit a rich structural variety. The structures of langbeinite, garnet, $ScWO_4$, NASICON (Na Supersonic Conductor) [1] and alluaudite-type synthetic compounds [2 – 6] could be described with a common formalism based on the different mutual orientation of $[M(1)O_6(PO_4)_3M(2)O_6]$ building units. The octahedral site $M$ may accommodate *s*-, *p*-, *d*- and *f*-elements [7 – 12], and rigid langbeinite frameworks could be obtained thereby. Previous results exhibit that the aliovalent pair of Nb(V) and Fe(III) is suitable to build up KTP ($KTiOPO_4$) isomorphs [13]. This principle was extended to langbeinite structures because of the predominant six-fold environment of those cations in oxide compounds. The high thermal stability and chemical resistance of compounds with an anionic framework $\{[M_2(PO_4)]_3\}^{n-}$ give prospects for design and development of materials with pre-programmed properties, particularly magnetic and luminescent effects.

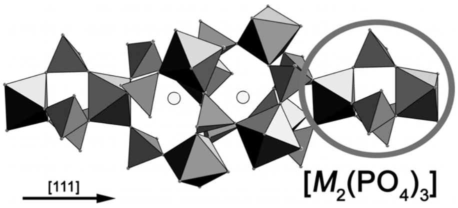

Fig. 1. The building units $[M_2P_3O_{18}]$ linked in the $[M_8P_9O_{60}]$ assembly. The $[M_2P_3O_{18}]$ fragment is highlighted by a light grey line.

Herein we present a novel complex phosphate $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ with langbeinite-type structure. In this work a model for magnetic susceptibility data fitting is proposed as based on the structural results.

## Results and Discussion

Pale brown crystals of $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ were synthesized from mixtures of $KPO_3$, $K_4P_2O_7$, $Fe_2O_3$, and $Nb_2O_5$ in platinum crucibles at 1293 K using the self-flux technique.

The complex phosphate $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ is isostructural to the mineral langbeinite [14]. Three orthophosphate groups are linked to two neighboring $[M(1)O_6]$ and $[M(2)O_6]$ octahedra through common oxygen vertices producing the building unit $[M(1)O_6(PO_4)_3M(2)O_6]$ (**1**) ($M$ = Fe, Nb) (Fig. 1). The main structure motif (Fig. 1) results from these elementary building blocks which are assembled in three mutually orthogonal directions. Conditional intersections of the described units (**1**) form closed $[M_8P_9O_{60}]$ fragments containing cavities where two K atoms are located (Fig. 1). The $[MO_6]$ octahedra are slightly distorted, corresponding Fe(Nb)–O bond lengths being in the range 1.962(6) – 2.004(6) Å and bond angles O–Fe(Nb)–O varying between 83.2(3) – 92.7(3) and 172.5(3) – 178.1(3)° (Table 1). Phosphorus atoms are

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Table 1. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ with estimated standard deviations in units of the last significant digit in parentheses[a].

| | | | |
|---|---|---|---|
| Fe1/Nb1–O1$^{i,ii}$ | 1.976(6) × 3 | K1–O1$^{ix,x,xi}$ | 2.885(7) × 3 |
| Fe1/Nb1–O2$^{iii,iv,v}$ | 1.984(7) × 3 | K1–O2$^{ix,x,xi}$ | 3.073(8) × 3 |
| Fe2/Nb2–O3$^{iii,iv\,v}$ | 2.006(6) × 3 | K1–O2$^{xii,xiii,xiv}$ | 3.238(7) × 3 |
| Fe2/Nb2–O4$^{vi,vii,viii}$ | 1.961(6) × 3 | K1–O4$^{xii,xiii,xiv}$ | 2.956(7) × 3 |
| P1–O1 | 1.534(6) | K2–O2$^{ix,x,xi}$ | 3.162(7) × 3 |
| P1–O2 | 1.543(7) | K2–O3$^{i,ii,xi}$ | 2.855(7) × 3 |
| P1–O3 | 1.547(6) | K2–O4$^{ix,x,xi}$ | 3.053(7) × 3 |
| P1–O4 | 1.546(6) | | |
| O1–Fe1/Nb1–O1 | 92.7(3) × 3 | O1–P1–O2 | 108.2(4) |
| O1–Fe1/Nb1–O2 | 172.5(3) × 3 | O1–P1–O3 | 110.8(4) |
| O1–Fe1/Nb1–O2 | 83.2(3) × 3 | O2–P1–O3 | 111.5(4) |
| O1–Fe1/Nb1–O2 | 93.8(3) × 3 | | |
| O1–Fe1/Nb1–O2 | 90.7(3) × 3 | | |
| O4–Fe2/Nb2–O4 | 89.5(3) × 3 | O4–P1–O3 | 109.2(4) |
| O4–Fe2/Nb2–O3 | 89.7(2) × 3 | O1–P1–O4 | 111.5(4) |
| O4–Fe2/Nb2–O3 | 88.7(3) × 3 | O2–P1–O4 | 105.6(4) |
| O4–Fe2/Nb2–O3 | 178.1(3) × 3 | | |
| O3–Fe2/Nb2–O3 | 92.0(3) × 3 | | |

[a] Symmetry codes: (i) $z, x, y$; (ii) $y, z, x$; (iii) $-y+1, z+1/2, -x+3/2$; (iv) $z+1/2, -x+3/2, -y+1$; (v) $-x+3/2, -y+1, z+1/2$; (vi) $x+1/2, -y+3/2, -z+1$; (vii) $-y+3/2, -z+1, x+1/2$; (viii) $-z+1, x+1/2, -y+3/2$; (ix) $-x+1, y-1/2, -z+1/2$; (x) $y-1/2, -z+1/2, -x+1$; (xi) $-z+1/2, -x+1, y-1/2$; (xii) $x-1/2, -y+1/2, -z$; (xiii) $-y+1/2, -z, x-1/2$; (xiv) $-z, x-1/2, -y+1/2$.

tetrahedrally coordinated with quite regular P–O bond lengths of 1.530(6) – 1.547(6) Å and O–P–O bond angles of 105.8(4) – 111.4(4)°. Both metal atoms $M1$ and $M2$ occupy special positions on a three-fold axis. Unequivalent distribution of Fe and Nb atoms over the sites $M1$ and $M2$ is observed. The $M1$ position is preferably occupied by Fe atoms having an effect on the Fe(Nb)–O distances of 1.976(6) – 1.984(7) Å, typical for iron phosphates [15, 16]. Selective occupation of the $M2$ sites by Nb atoms agrees well with an enlargement of the corresponding distances in the coordination polyhedron which lie in the range of 1.961(6) – 2.006(6) Å [17]. K1 is surrounded by twelve oxygen atoms, assuming a cut-off value for the contact lengths of 3.238(7) Å (the next nearest contact is at 3.53 Å). K2 forms nine K–O contacts in the range 2.855(7) – 3.162(7) Å. These bonding parameters and occupations are dictated by the rigidity of the $\{[M_2P_3O_{12}]\}^{n-}$ framework.

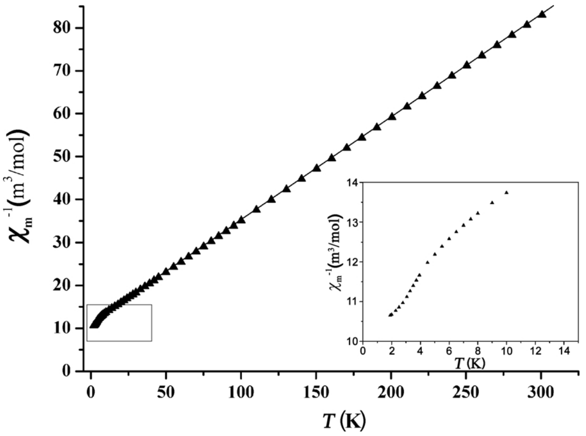

Fig. 2. The $1/\chi_m$ *vs.* $T$ plot. The non-linear part is given as an enlarged inset.

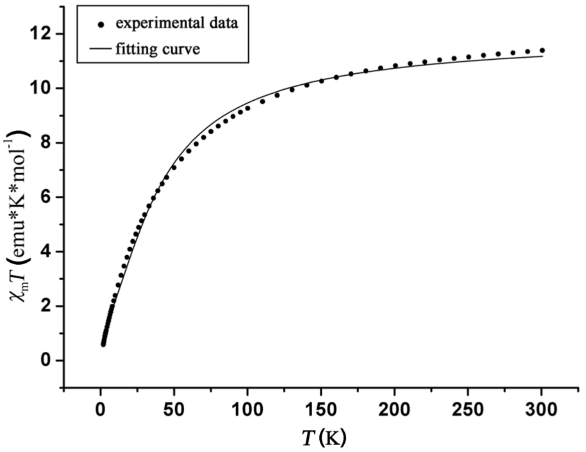

Fig. 3. Plot of experimental and calculated values of $\chi_m T$ *vs.* $T$.

*Magnetic properties of $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$*

The magnetic behavior is shown in Fig. 2 in the form of $1/\chi_m$ *vs.* $T$ and $\chi_m T$ vs. $T$ plots, where $\chi_m$ is the molar magnetic susceptibility. In the region of 50 – 300 K the measured values depend linearly on the temperature (Curie-Weiss law). Values calculated from the linear fit for the Curie constant ($C$) and the Weiss constant ($\theta_p$) are 4.17 emu · K · mole$^{-1}$ and −46.25 K (Fig. 2). The effective magnetic moment ($\mu_{eff}$) was estimated from the equation $\mu_{eff} = 2.828\ (\chi_m T)^{1/2}$ at $T$ = 300 K to be 5.38 $\mu_B$ while the expected value is 5.92 $\mu_B$, thus indicating the presence of spin-orbital interactions. The paramagnetic centers are the Fe(III) atoms ($S$ = 5/2) which partially occupy both $M1$ and $M2$ positions. In the range 2 – 50 K the fit deviates from linearity. This phenomenon was previously observed for langbeinite-type phosphates containing paramagnetic cations like Cr(III), Fe(III) or V(III) [18 – 21]. However the existing explanations of this fact are ambiguous. Taking into account that paramagnetic centers are rather far apart from each other (> 4.6 Å), the most reasonable explanation is spin superexchange through a $M(1)$–O–P–O–$M(2)$ pathway. All measured data were fitted (Fig. 3) using the equation [22]:

$$\chi T = \frac{2Ng^2\beta^2}{k}\,\frac{e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x}}{1 + e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x}} + \mathrm{TIP},$$

where $x = J\,(kT)^{-1}$ ($J$ = superexchange constant; $N$ = Avogadro number; $g$ = $g$-factor; $\beta$ = Bohr magneton; $k$ = Boltzmann constant; TIP = temperature independent paramagnetism). All performed calculations assumed the $g$-factor to be isotropic. The fitting process converges with the final parameters of $g = 1.963(5)$, $J = -5.5(1)$ cm$^{-1}$ ($|r^2| = 0.998$) justifying the assumption of an antiferromagnetic type of interaction.

### *Electron spectroscopy*

Diffuse scattering electronic spectra of $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ contain three absorption bands, two of which are related to the *d*-*d* transitions at 19450 ($^4T_{1g} \rightarrow {}^6A_{1g}$) and 23870 cm$^{-1}$ ($^4T_{2g} \rightarrow {}^6A_{1g}$), common for the high-spin state of Fe(III) in octahedral oxygen environment [23]. All transitions are theoretically prohibited by spin and Laporte for a $d^5$ ($^6S$) state. It should be assumed that trigonal distortions ($C_{3v}$ symmetry, see Table 1) of octahedra make spin transitions allowed. The most intensive band at 29550 cm$^{-1}$ is caused by the charge transfer $O^{2-} \rightarrow Fe^{3+}$.

## Conclusion

Our study has shown that langbeinite-type complex phosphates $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ can be prepared at high temperatures from oxidic precursors. The magnetic behavior of $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$ indicates the presence of antiferromagnetic interactions below 50 K. The superexchange pathway $M(1)$–O–P–O–$M(2)$ is suggested as a model for the fitting of the experimental magnetic susceptibilities.

## Experimental Section

All reagents were of analytical grade. Elemental analyses were performed by energy dispersive spectroscopy using a Link Isis analyzer mounted on a Phillips XL 30 FEG scanning electron microscope. FTIR spectra were collected with a Nicolet Nexus 470 FTIR spectrometer (KBr pellets; spectral range = 400 – 4000 cm$^{-1}$; spectral resolution = 0.5 cm$^{-1}$). UV/vis spectra were registered with a Specord-40 automatic PC controlled spectrometer operating in a diffuse scattering mode (frequency limits = 12000 – 38500 cm$^{-1}$).

Table 2. Crystal structure data for $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$.

| | |
|---|---|
| Formula | $K_{1.84}Fe_{1.42}Nb_{0.58}P_3O_{12}$ |
| $M_r$ | 490.25 |
| Crystal size, mm$^3$ | $0.1 \times 0.1 \times 0.1$ |
| Crystal system | cubic |
| Space group | $P2_13$ |
| $a$, Å | 9.9404(10) |
| $V$, Å$^3$ | 982.23(17) |
| $Z$ | 4 |
| $D_{\mathrm{calcd}}$, g · cm$^{-3}$ | 3.32 |
| $\mu(\mathrm{Mo}K_\alpha)$, mm$^{-1}$ | 4.11 |
| $F(000)$, e | 947.1 |
| *hkl* range | $0 \le h \le 13$, $-7 \le k \le 13$, $-3 \le l \le 13$ |
| $((\sin\theta)/\lambda)_{\max}$, Å$^{-1}$ | 0.66 |
| Refl. measured | 1383 |
| Refl. unique | 463 |
| $R_{\mathrm{int}}$ | 0.069 |
| Param. refined | 65 |
| $x$(Flack) | 0.10(8) |
| GoF ($F^2$) | 1.06 |
| $R(F)/wR(F^2)^a$ (all refl.) | 0.037/0.079 |
| $\Delta\rho_{\mathrm{fin}}$ (max/min), e Å$^{-3}$ | 0.64/−0.56 |

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2] / \Sigma[w(F_o{}^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (0.0297P)^2]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Magnetic measurements were performed at 5kOe using a Quantum Design MPMS XL SQUID magnetometer. Gelatin capsules were used as sample containers for measurements taken in the temperature range 1.9 – 300 K. Crystalline samples were ground in an agate mortar into a fine powder, and 79.31 mg of the sample was taken for data recording. Experimental susceptibilities were corrected for the diamagnetic component using Pascal's constants.

### *Synthesis of $K_{1.84}Fe_{1.42}Nb_{0.58}(PO_4)_3$*

A finely ground mixture of 8.66 g $KPO_3$, 1.34 g $K_4P_2O_7$, 0.902 g $Fe_2O_3$, and 1.5 g $Nb_2O_5$ was placed into a platinum crucible and heated up to 1293 K to obtain a homogeneous solution. The resulting melt was cooled to 1033 K at a rate of 25 K · h$^{-1}$ and kept for 2 h at the final temperature. A crystalline product was separateded from the rest of the melt with plenty of hot deionized water. Fine tetrahedrally shaped crystals were obtained. The calculated ratio of K, Fe, Nb, and P was 3.7: 2.8 : 1.2 : 6. – FTIR data (cm$^{-1}$): $\nu_{as}$, $\nu_s$ (P–O) 1225 (sh), 1163 (sh), 1110 (s), 1042 (sh), 1008 (m), 950 (sh), 900 (sh), 860 (s); $\delta$ (O–P–O) 632 (s), 582 (m), 524 (s).

### *Crystal structure determination*

Single crystal X-ray diffraction measurements were performed on a $\kappa$-geometry Nonius CAD-4 Express diffractometer [24] at 273(2) K. Cell parameters were determined from 25 reflections collected in the range $15 < \theta < 25°$.

Intensities were corrected for Lorentz and polarization effects [25]. Two standard reflections were used to confirm the absence of decay and stability of the sample during the experiment.

The structure was solved with Direct Methods using the program SHELXS-97 [26]. The structure refinement calculations were done with SHELXL-97 [27]. Coordinates of iron and niobium atoms and their anisotropic displacement parameters were appropriately constrained during the crystal structure refinement to allow for the mutual occupation of the 3*d*-metal position by Fe and Nb atoms, respectively. Crystal data and further experimental details are summarized in Table 2 together with the parameters of the structure refinement. Selected bond lengths and bond angles summarized in Table 1.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-418532.

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