$K_2Fe^{III}_{0.5}Ti^{III}_{0.5}Ti^{IV}_{1.0}(PO_4)_3$: Preparation and Characterization of a Langbeinite-related Phosphate Containing Iron(III) and Mixed-valent Titanium

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A potassium mixed iron(III)-titanium(III)-titanium(IV) phosphate $K_2Fe^{III}_{0.5}Ti^{III}_{0.5}Ti^{IV}_{1.0}(PO_4)_3$ has been obtained using a two-step flux interaction in evacuated sealed silica tubes. It forms tetrahedrally-shaped dark violet crystals which belong to the cubic system (space group $P2_13$) with the cell parameter $a = 9.8592(5)$ Å. The structure was refined from single-crystal X-ray diffraction data. $[MO_6]$ octahedra and $[PO_4]$ tetrahedra share their vertices forming a rigid 3D framework. The potassium cations are located in large closed cavities of the framework. A distribution of the $3d$ metals' valence states in $K_2Fe^{III}_{0.5}Ti^{III}_{0.5}Ti^{IV}_{1.0}(PO_4)_3$ has been proposed on the basis of magnetic measurements, structure investigations and bond-valence calculations as well as UV/vis and EPR spectroscopy.

Key words: Phosphate, Langbeinite, Flux Method, Mixed-valent, Magnetic Measurements

Introduction

A great number of langbeinite-related phosphates containing trivalent titanium are known. Different preparation methods were applied for their synthesis combining various redox processes during solid state, hydrothermal or flux interactions. $K_2Ti_2(PO_4)_3$ and $K_{1.75}Ti_2(PO_4)_3$ were obtained by Leclaire using a two-step solid state technique from a mixture of Ti and TiO_2 [1]. $K_2Ti_2(PO_4)_3$ was also prepared from TiN by the interaction in a potassium phosphate flux in air [2] or from Ti_2O_3 and TiO_2 by a hydrothermal method [3]. Another interesting mode of preparation of langbeinite-like phosphates is the crystallization of phosphate fluxes which contain titanium(IV) and tri- or divalent ions. Formation of phosphates containing mixed-valent titanium with a general composition $K_{1+y}Ti^{III,IV}_{2-x}M^{III}_x(PO_4)_3$ (M^{III} = Al, Sc, Cr, Fe, In, Y; $0 < x \leq 1$; $0 \leq y \leq 1$; $x \leq y$) [4, 5] were observed in fluxes of the systems K_2O-P_2O_5-TiO_2-$M^{III}_2O_3$. Similar behavior of titanium was observed in the melts containing Yb where $Rb_2YbTi(PO_4)_3$ and $Rb_2Yb_{0.32}Ti_{1.68}(PO_4)_3$ were obtained [6]. Later it has been observed that an injection of ZnO [7] into fluxes of the system K_2O-P_2O_5-TiO_2 is accompanied by self-reduction of titanium(IV). The fact of self-reduction of Ti(IV) to Ti(III) was explained by insertion of polyvalent metal ions (for example Al^{3+}) into positions of alkali metal cations. Partial substitution of a monovalent ion by a polyvalent metal leads to a change in the charge of the framework, which favors reduction of Ti^{4+} [8].

The behavior of titanium in the fluxes containing FeO has been investigated in the present work. A langbeinite-related potassium mixed iron(III)-titanium(III)-titanium(IV) phosphate $K_2Fe^{III}_{0.5}Ti^{III}_{0.5}Ti^{IV}_{1.0}(PO_4)_3$ was obtained and characterized using single-crystal X-ray diffraction, FTIR, UV/vis and EPR spectroscopy. Magnetic susceptibility measurements were carried out to characterize the valence state of the transition metal cations.

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Experimental Section

$K_2Fe_{0.5}Ti_{1.5}(PO_4)_3$

The synthesis of the title compound was performed using a two-step high-temperature flux technique. In the first step, a homogeneous phosphate glass containing a calculated amount of TiO_2 was prepared in a platinum crucible in air. Secondly, definite amounts of the solid glass and FeO were melted and crystallized in evacuated silica tubes. The crystallization was investigated in fluxes of the compositions $K_2O \times P_2O_5 \times 0.3TiO_2 \times n$FeO, where n = 0.6, 0.45, 0.3, and 0.15.

Reagents used for the synthesis were of extra pure grade (TiO_2) or pure grade (KPO_3, FeO). Initial FeO used was analyzed for the total iron and iron(III) content by ICP-AES. Total iron content was found to be 78.0 %, while the calculated value is equal to 77.78 %. The content of iron(III) was found to be less than 1 % of the total quantity of iron. For the preparation of the initial glass, a mixture of 50 g KPO_3 (0.424 mol) and 5.09 g TiO_2 (0.064 mol) was placed into a platinum crucible, heated to 1373 K and kept for 6 h to reach homogeneity. Then the flux was poured out from the crucible onto a sheet of copper to avoid crystallization. The solidified melt was dispersed in an agate mortar. At the next synthetic stage four portions of the powdered glasses obtained (8 g, containing 61.54 mmol of KPO_3 and 9.23 mmol TiO_2) were mixed with 1.329 (18.46), 0.997 (13.85), 0.665 (9.23), and 0.332 g (4.61 mmol) of FeO keeping the Fe/Ti ratios equal to 2.0, 1.5, 1.0, and 0.5, respectively. These mixtures were placed in silica ampoules, which were evacuated and sealed. The ampoules were heated to 1273 K and kept for 2 h to dissolve FeO. Then the fluxes were cooled to 873 K at a rate of 20 $K\,h^{-1}$, and at this temperature the furnace was turned off. At r. t. the ampoules were opened, and dark brown glassy solids with dark violet (practically black) tetrahedrally shaped crystals were found. The crystals were recovered by washing with hot water. The dimensions of the crystals varied from 0.15 to 3 mm.

The chemical compositions of the compounds were determined by X-ray fluorescent analysis using an "Elvax Light" spectrometer and by energy dispersive spectroscopy using a Link Isis analyzer mounted on a Philips XL 30 FEG scanning electron microscope. The analyses were performed for crystals with different dimensions obtained in all syntheses. For several samples similar element ratios close to K : Fe : Ti : P = 2.0 : 0.5 : 1.5 : 3 were found, which differs insignificantly from the values calculated from the structure investigations. Impurities such as Si, Cu *etc.* were not detected in the samples.

X-Ray structure determination

A tetrahedrally shaped crystal with verified composition, obtained in the experiment with an initial Fe/Ti ratio equal to 1.0 was selected for structure investigation. A single crystal X-ray diffraction experiment was carried out on an Oxford-Diffraction XCalibur 3 diffractometer equipped with a 4 MPixel CCD detector using monochromated MoK_α radiation (λ = 0.71073 Å). Space group and cell parameters were determined on the basis of all reflections ($2.92 < \theta < 34.98°$). A multi-scan absorption correction was applied to the collected data.

Table 1. Crystal structure data for $K_{1.928}Fe_{0.485}Ti_{1.515}(PO_4)_3$.

Formula	$K_{1.928}Fe_{0.485}O_{12}P_3Ti_{1.515}$
M_r	459.91
Cryst. size, mm^3	$0.12 \times 0.08 \times 0.05$
Crystal system	cubic
Space group	$P2_13$
a, Å	9.8592(5)
V, Å^3	958.35(8)
Z	4
D_{calcd}, g cm^{-3}	3.19
μ(MoK_α), cm^{-1}	34.04
F(000), e	894.3
hkl range	±15, −15 + 10, ±15
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.807
Refl. measured	24722
Refl. unique	1418
R_{int}	0.0649
Param. refined	62
$R(F)/wR(F^2)$[a] (all refls.)	0.027/0.054
x (Flack)	−0.02(2)
GoF (F^2)	1.272
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.42/−0.39

[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 $P = (F_o{}^2 + 2F_c{}^2)/3$.

The structure was solved by Direct Methods using SHELXS-97 [9] and refined anisotropically with SHELXL-97 [9]. Two iron and two potassium atoms were located on three-fold axes and one phosphorus atom in a general position. The remaining oxygen atoms were found in general positions as four peaks with high electron density. Titanium atoms were placed in the positions of iron. Their coordinates and anisotropic displacement parameters were constrained during the occupancy refinement. An extinction correction was applied in the final stage of the refinement, but as its value was found negligible comparing with its esd, it was omitted. The experimental parameters are listed 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-418185.

Physical characterization

The purity of the crystals was checked using powder X-ray diffraction (Siemens D500 diffractometer; CuK_α radi-

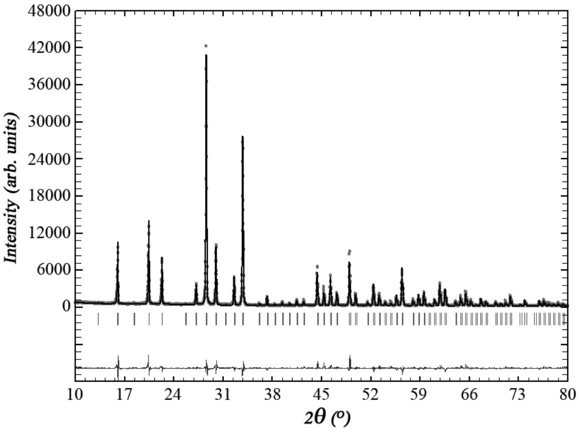

Fig. 1. Observed, calculated and difference X-ray patterns for $K_{1.928}Fe_{0.485}Ti_{1.515}(PO_4)_3$.

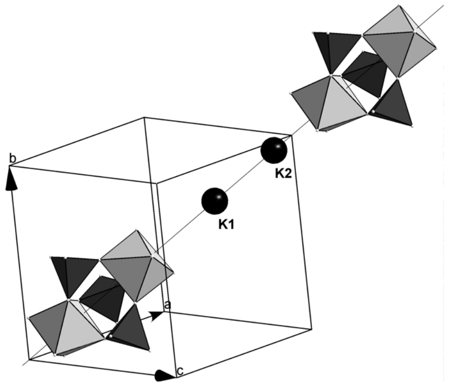

Fig. 2. Arrangement of $[M_2P_3O_{18}]$ units along the three-fold axis. Light grey octahedra are Ti(Fe)O_6, dark grey tetrahedra are orthophosphate groups, and black circles are potassium cations.

ation, λ = 1.54184 Å; curved graphite monochromator on the counter arm). All samples were well crystallized and single-phased. The X-ray powder patterns coincided well with those generated from the single-crystal data (Fig. 1).

Magnetic measurements were performed for the sample with the initial Fe/Ti ratio equal to 1.0. The temperature dependence of magnetic susceptibility was measured with a Quantum Design Squid MPMS-XL magnetometer over the range 1.9 – 300 K under a constant magnetic field of 0.5 T. Several crystals with average dimensions close to 1 × 1 × 1 mm^3 were dispersed in a sapphire mortar, and then the measurements were performed on the powdered sample. The temperature and field dependence of the susceptibility of the container was previously determined, and their effect on the total susceptibility was found negligible.

The FTIR spectra were recorded at r. t. on KBr discs using a Nicolet Nexus FTIR spectrometer at 400 – 4000 cm^{-1}. UV/vis spectra were collected in the diffuse reflectance mode using a SPECORD-40M spectrometer at 12000 – 40000 cm^{-1}. Electron paramagnetic resonance spectra (EPR) on powdered polycrystalline samples were measured at X-frequencies (9.438 GHz at 298 K and 9.249 GHz at 77K) with a Radiopan spectrometer.

Results and Discussion

Synthetic procedure

Preparation and investigation of langbeinite-related compounds $K_2M^{II}{}_{0.5}Ti_{1.5}(PO_4)_3$, where M^{II} = Mn, Co, Ni, were previously reported [10, 11]. It appeared to be reasonable to expect a complex phosphate $K_2Fe_{0.5}Ti_{1.5}(PO_4)_3$, where iron(II) and titanium(IV) are octahedrally coordinated network cations. Under the experimental conditions two possible oxidation states of iron (+2 and +3) and titanium (+3 and +4) were possible. As it was noted above, the presence of iron(III) in the molten phosphates can promote self-reduction of titanium(IV) to titanium(III). On the other hand, both iron(II) and titanium(III) are highly reducing agents which can be oxidized by the air oxygen. Thus, we performed syntheses in evacuated sealed silica tubes to prevent the oxidation processes. Taking into account that the synthesized compounds could contain mixed-valent iron and titanium we proposed the following flux interaction schemes:

$$\begin{aligned} &8KPO_3 + FeO + 3TiO_2 \\ &\rightarrow 2K_2Fe^{II}{}_{0.5}Ti^{IV}{}_{1.5}(PO_4)_3 + K_4P_2O_7 \end{aligned} \quad (1)$$

$$Fe^{II} + Ti^{IV} \rightarrow Fe^{III} + Ti^{III} \quad (2)$$

The first equation describes simple interactions without redox processes and admits the presence of Fe^{2+} and Ti^{4+} in the resulting phosphate. The second shows a possible redox interaction, which suggests heterovalent substitution of iron(II) and titanium(IV) by iron(III) and titanium(III) in the framework of the synthesized langbeinite.

Crystal structure

The investigated compound crystallizes in the cubic system and is isostructural to the naturally occurring mineral langbeinite $K_2Mg_2(SO_4)_3$ [12]. The framework contains isolated tetrahedra and octahedra which are interconnected *via* oxygen vertices. Two nearest octahedra are joined into pairs by three bridging orthophosphate groups forming $[M_2P_3O_{18}]$ units. Each phosphate tetrahedron shares its four corners with four

Table 2. Selected bond lengths (Å) and angles (deg) for $K_{1.928}Fe_{0.485}Ti_{1.515}(PO_4)_3$ with estimated standard deviations in parentheses.

Fe1/Ti1–O1^{i,ii}	1.992(2) ×3	Fe1/Ti1–O2^{iii,iv,v}	1.970(2) ×3
Fe2/Ti2–O3^{vi,vii,viii}	1.940(2) ×3	Fe2/Ti2–O4^{i,ii}	1.966(2) ×3
K1–O1^{vi,vii,viii}	2.838(2) ×3	K1–O2^{ix,x,xi}	3.006(2) ×3
K1–O4^{ix,x,xi}	3.147(2) ×3		
K2–O3^{ix,x,xi}	2.879(2) ×3	K2–O2^{xii,xiii,xiv}	2.928(2) ×3
K2–O4^{ix,x,xi}	2.988(2) ×3	K2–O4^{xii,xiii,xiv}	3.278(2) ×3
P1–O1	1.528(2)	P1–O2	1.528(2)
P1–O3	1.531(2)	P1–O4	1.533(2)
O1–P1–O2	109.25(10)	O1–P1–O3	110.52(9)
O1–P1–O4	111.65(9)	O2–P1–O3	111.65(9)
O2–P1–O4	106.28(10)	O3–P1–O4	107.43(10)

Symmetry codes: ^{i} z, x, y; ^{ii} y, z, x; ^{iii} $-z, x-1/2, 1/2-y$; ^{iv} $1/2-y, -z, x-1/2$; ^{v} $x-1/2, 1/2-y, -z$; ^{vi} $1/2+y, 1/2-z, 1-x$; ^{vii} $1/2-z, 1-x, 1/2+y$; ^{viii} $1-x, 1/2+y, 1/2-z$; ^{ix} $1-y, 1/2+z, 3/2-x$; ^{x} $3/2-x, 1-y, 1/2+z$; ^{xi} $1/2+z, 3/2-x, 1-y$; ^{xii} $3/2-y, 1-z, 1/2+x$; ^{xiii} $1-z, 1/2+x, 3/2-y$; ^{xiv} $1/2+x, 3/2-y, 1-z$.

[MO_6] octahedra. Two coaxial [$M_2P_3O_{18}$] units are located at a distance equal to 10.23 Å (Fig. 2). The K1 atom is nine-coordinated with K–O lengths limits at 2.838(2) and 3.147(2) Å, while K2 is twelve-coordinated by oxygen atoms with K–O interatomic distances ranging from 2.879(2) to 3.278(2) Å. The orthophosphate tetrahedron is slightly distorted. The O–P–O angles are close to the tetrahedral angle and the P–O bond lengths are normal for orthophosphate groups [13]. Selected geometric parameters are listed in Table 2.

Both octahedral sites are occupied by iron and titanium. The distribution of iron over these sites has similar values, but the $M1$ [Ti1/Fe1 = 0.739(14)/0.261(14)] site has a slightly higher occupancy factor for iron than the $M2$ [Ti2/Fe2 = 0.775(15)/0.225(15)] site. Taking into account the M–O bond lengths, a distribution of Ti(III) and Ti(IV) was assumed. On the basis of a bond-valence calculation [14] we found that Ti(III) is preferably located in the $M1$ site (BVS for Ti1 is equal to 3.822) while Ti(IV) occupies preferably the $M2$ site (BVS for Ti2: 4.128). Corresponding M–O distances for the [$M1O_6$] have insignificantly larger values than for the [$M2O_6$] octahedra.

FTIR and UV/vis spectroscopy

The FTIR spectrum of $K_{1.928}Fe_{0.485}Ti_{1.515}(PO_4)_3$ is typical for langbeinite-related phosphates (Fig. 3). The great number of observed bands correlates with a low (C_1) local symmetry of the [PO_4] tetrahedron. The bands which belong to the P–O stretching frequencies in the [PO_4] tetrahedron are limited to the range of 1200 – 850 cm^{-1} and coupled into two subgroups. Three bands were found in the first subgroup: 1099s, 1141sh and 1052sh cm^{-1}. Only two bands are well observed in the second subgroup: 993s and 938s cm^{-1}. P–O bond bending vibrations are located in the 670 – 540 cm^{-1} region and appear as symmetric singlets at 646m, 587m and 545m cm^{-1}. The low energy region indicates the presence of M–O vibrations at 456 and 431 cm^{-1}.

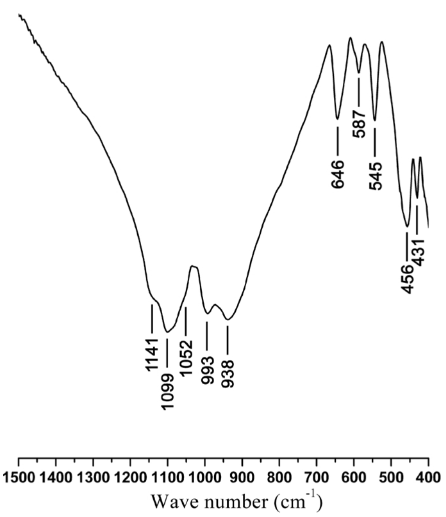

Fig. 3. FTIR spectrum of $K_2Fe_{0.5}Ti_{1.5}(PO_4)_3$.

The diffuse reflectance electronic spectrum of the title compound could be presented as a superposition of the electronic spectra of Ti(III) and Fe(III) in octahedral oxygen environments (Fig. 4). Multi-peak fitting of the obtained data gave five single Gauss peaks. The distortion of the [MO_6] octahedra can be described by C_{3v} symmetry. For the d^5 shell of the high-spin Fe^{3+} ion electron transitions are prohibited by spin (term ^6S). According to the local symmetry, the energy levels of Ti^{3+} (d^1, term ^2D) should be split (Fig. 5). The ground state level $^2T_{2g}$ is split into two states: $^2A_1$ (ground state under trigonal distortion) and ^2E ($^2T_{2g}$); ^2E_g transforms into ^2E (^2E_g). Two possible electron transition bands could be observed in the low-energy region: $^2A_1 \rightarrow {}^2E(^2T_{2g})$ (13900 cm^{-1}, ν_1) and $^2A_1 \rightarrow {}^2E(^2E_g)$ (20500 cm^{-1}, ν_2). The next three bands at 27200 (ν_3), 31500 (ν_4) and 38600 cm^{-1} (ν_5) were found in the high-energy region. They could be assigned as charge transition bands from oxygen to iron $O^{2-} \rightarrow Fe^{3+}$ [15].

Magnetic properties and EPR spectroscopy

The temperature dependence of the reciprocal molar magnetic susceptibility is shown in Fig. 6. All

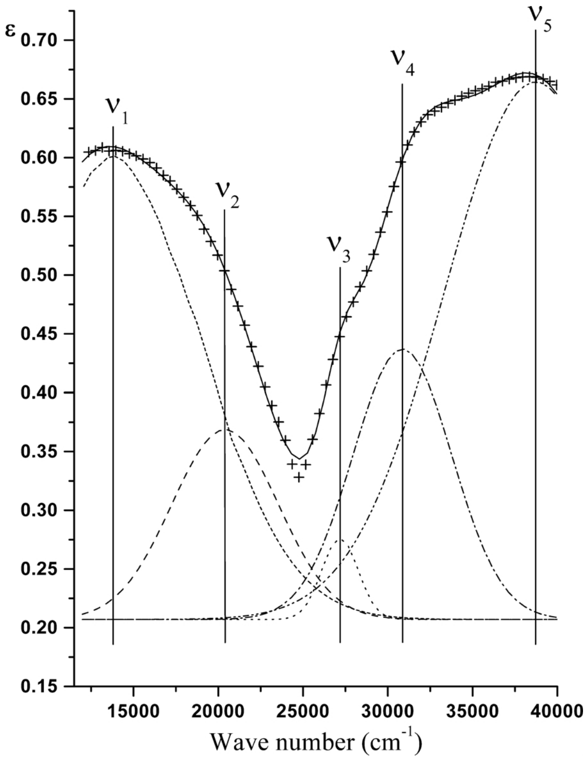

Fig. 4. Diffuse reflectance electronic spectrum of $K_2Fe_{0.5}Ti_{1.5}(PO_4)_3$. The collected spectrum is marked by (+), the solid line corresponds to the fitted spectrum, while dash and dash dotted lines are fitted components.

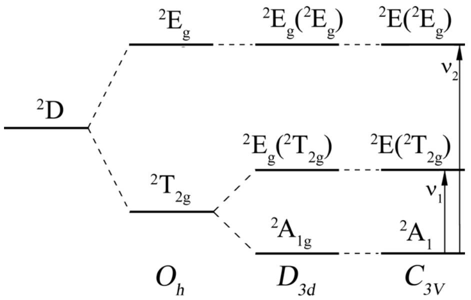

Fig. 5. Energy level splitting of the ^2D term under trigonal distortion.

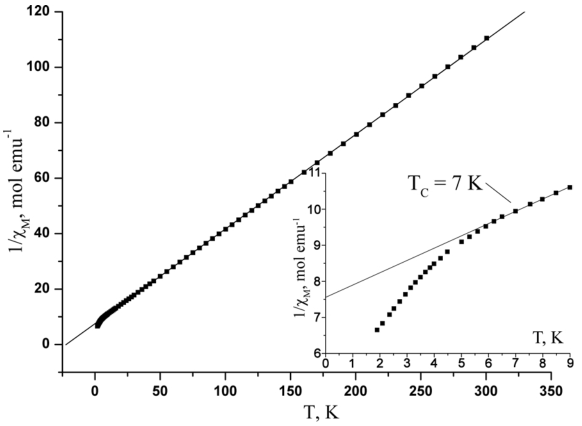

Fig. 6. Thermal variation of the reciprocal molar magnetic susceptibility of $K_2Fe_{0.5}Ti_{1.5}(PO_4)_3$. The insert enlarges the low temperature behavior.

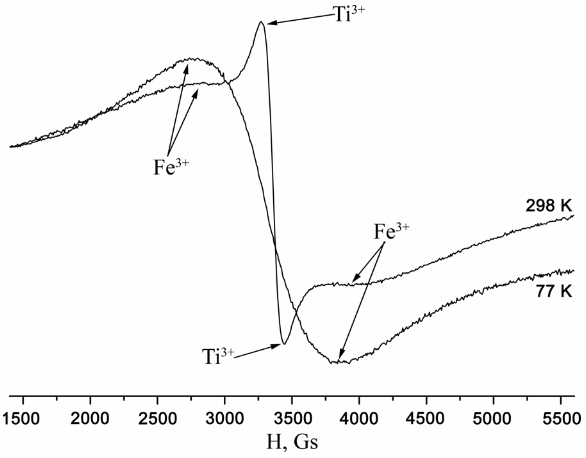

Fig. 7. EPR spectra of $K_2Fe_{0.5}Ti_{1.5}(PO_4)_3$ at 298 and 77 K.

calculations were performed for 1 formula unit with the general composition $K_2Fe_{0.5}Ti_{1.5}(PO_4)_3$. The investigated compound displays a Curie-Weiss behavior at temperatures above 7 K, $\chi = C/(T - \Theta)$. Below this temperature the deviation of the reciprocal magnetic susceptibility from Curie-Weiss law (Fig. 6, insert) can be explained by the existence of ferromagnetic interactions between Fe(III)-Fe(III), Ti(III)-Ti(III) and Fe(III)-Ti(III) ion pairs. These interactions are possible because of their joining into pairs of transition metal atoms *via* the three bridging orthophosphate groups; the interatomic distances between the metal atoms are near 4.5 Å. The calculated Weiss temperature and Curie constant are $\Theta = -22.14$ K and $C = 2.93$ emu·K·mol^{-1}, respectively. The effective magnetic moment was found equal to 4.66 μ_B. On the basis of the chemical analysis, the structure investigations and the electron spectroscopy study the formula $K_2Fe^{III}{}_{0.5}Ti^{III}{}_{0.5}Ti^{IV}{}_{1.0}(PO_4)_3$ of the compound was proposed. The spin-only value of the magnetic moment was calculated taking into account the quantities of paramagnetic ions per formula unit and was found equal to 3.825 μ_B ($0.5 \times \mu Fe^{III}(HS) + 0.5 \times \mu Ti^{III}$). For $Fe^{2+} + Ti^{4+}$ instead of $Fe^{3+} + Ti^{3+}$ the calculated value of μ_{eff} should be significantly lower (down to the value of 2.45 μ_B, or 2.74 μ_B including spin-orbit coupling, for 0.5 Fe^{2+} per formula unit). This fact suggests that all iron atoms are trivalent. The deviation of μ_{eff} from the theoretical value can be explained by a high contribution of the orbital magnetic moment of the titanium ions under trigonal distortion [16].

The EPR spectra of the compound differ significantly at the two temperatures investigated (Fig. 7). At r.t. bands with $g_1 = 2.009$, $\Delta H_1 = 110$ Gs and $g_2 = 2.004$, $\Delta H_2 = 700$ Gs were found. The first belongs to Ti(III) and the second can be assigned to Fe(III). The line width and the g_1 value are characteristic for Ti(III) in a langbeinite phosphate matrix [8, 17]. At 77 K only one broad line with the parameters $g = 1.997$, $\Delta H = 700$ Gs belonging to Fe(III) could be observed. Taking into account the chemical composition of the compound and the g factors for Ti(III) and Fe(III), we calculated the value of 4.48 μ_B which is in agreement with the value of $\mu_{eff} = 4.66$ μ_B.

Conclusion

The interaction between iron(II) oxide and titanium(IV) oxide in a potassium phosphate flux is accompanied by oxidation of the iron and the reduction of titanium centers. The resulting product of the interaction under the conditions described above in the absence of oxygen is a potassium mixed iron(III)-titanium(III)-titanium(IV) phosphate. This compound is isostructural to the mineral langbeinite. The magnetic behavior of $K_2Fe^{III}{}_{0.5}Ti^{III}{}_{0.5}Ti^{IV}{}_{1.0}(PO_4)_3$ indicates the presence of ferromagnetic interactions below 7 K. The high value of the effective magnetic moment can be explained by contributions of magnetic moments of iron(III) and titanium(III). The presence of any iron(II) should significantly reduce the magnetic moment of the compound. Thus, the presence of iron in the trivalent state only and titanium in both tri- and tetravalent states is proposed. The value of the effective magnetic moment correlates with the results of EPR investigations.

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[1] A. Leclaire, A. Benmoussa, M. M. Borel, A. Grandin, B. Raveau, *J. Solid State Chem.* **1989**, *78*, 227 – 231.

[2] I. V. Zatovsky, N. S. Slobodyanik, D. A. Stratiychuk, K. V. Domasevitch, J. Sieler, E. B. Rusanov, *Z. Naturforsch.* **2000**, *55b*, 291 – 298.

[3] E. S. Lunezheva, B. Maximov, O. K. Mel'nikov, L. A. Muradyan, *Kristallografiya* **1989**, *34*, 611 – 614.

[4] N. S. Slobodyanik, N. V. Stus, P. G. Nagornyi, A. A. Kapshuk, *Russ. J. Inorg. Chem.* **1991**, *36*, 1554 – 1556.

[5] I. V. Zatovskii, N. S. Slobodyanik, T. I. Ushchapivskaya, I. V. Ogorodnik, A. A. Babarik, *Russ. J. Appl. Chem.* **2006**, *79*, 10 – 15.

[6] J. C. M. Gustafsson, S. T. Norberg, G. Svensson, J. Albertsson, *Acta Crystallogr.* **2005**, *C61*, i9–i13.

[7] I. V. Ogorodnyk, I. V. Zatovsky, N. S. Slobodyanik, *Dopov. Akad. Nauk Ukr.* **2007**, 148 – 151 (in Ukrainian).

[8] A. P. Shpak, A. M. Korduban, V. V. Trachevskii, N. S. Slobodyanik, *Theor. Exp. Chem.* **2000**, *36*, 241 – 253.

[9] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**.

[10] I. V. Ogorodnyk, I. V. Zatovsky, N. S. Slobodyanik, V. N. Baumer, O. V. Shishkin, *J. Solid State Chem.* **2006**, *179*, 3461 – 3466.

[11] I. V. Ogorodnyk, I. V. Zatovsky, N. S. Slobodyanik, *Russ. J. Inorg. Chem.* **2007**, *52*, 121 – 125.

[12] A. Zemann, J. Zemann, *Acta Crystallogr.* **1957**, *10*, 409 – 413.

[13] D. E. C. Corbridge, *Phosphorus. An Outline of its Chemistry, Biochemistry and Technology*, Vol. 2, 2nd ed., Elsevier, Amsterdam, **1980**, pp. 89 – 141.

[14] I. D. Brown, Accumulated list of bond-valence parameters, **2002**: http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/

[15] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd Russian ed., Elsevier, Amsterdam, **1984**, pp. 76 – 79.

[16] R. L. Carlin, *Magnetochemistry*. Springer-Verlag, Berlin, Heidelberg, **1989**.

[17] I. V. Zatovsky, N. S. Slobodynik, G. T. Ostapenko, T. I. Ushchapivska, B. M. Mitsyuk, *Vestn. Otd. nauk Zemle RAN* **2003**, *21*, 1 – 2; http://www.scgis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/hydroterm-2e.pdf