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Synthesis, characterization, and structural study of $K_2FeZrP_3O_{12}$ with the langbeinite structure

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Abstract

A potassium iron zirconium phosphate, $K_2FeZrP_3O_{12}$, was synthesized by thermal treatment of a material obtained by the sol–gel method, mixing two aqueous solutions, the first containing KCl, $FeCl_3$ and $ZrOCl_2$, and the second, H_3PO_4. The crystal structure was refined using powder X-ray diffraction data. The unit cell is cubic, $a = 10.0554(3)$ Å, space group $P2_13$. This compound is the first iron zirconium phosphate described with a langbeinite-type structure.

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1. Introduction

Compounds with the NASICON structure ($Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, space group R-$3c$) exhibit fast ion conduction [1], low thermal expansion [2], and are envisaged as materials for nuclear-waste storage and in thermal-shock-resistance applications [3]. The flexibility in these structures, which allows chemical substitution, gives rise to a large number of isostructural phases. In general, these can be used as model systems to study the effects of cation size, occupancy and valence [4] in corner-shared polyhedral network compounds.

Besides $NaZr_2P_3O_{12}$ [5], one end member of the NASICON series, popularly known as NZP, and many other phosphates with architecture motive $[M_2P_3O_{12}]^{n-}$ have a rhombohedral structure of the NASICON type [6]. Although the NASICON-type structure is the most frequent in phosphates with a similar composition to NZP, some other structures have been reported. The cubic structural type of langbeinite ($K_2Mg_2S_3O_{12}$, space group $P2_13$) [7] is one possible structural modification in compounds with a $[M_2P_3O_{12}]^{n-}$ network.

The langbeinite-type mineral family are sulfates with the general formula $M^I_2M^{II}_2S_3O_{12}$ (M^I = K, Rb, Cs, Tl, NH_4; M^{II} = Mg, Ca, Mn, Co, Ni, Zn, Cd, Fe) [8]. A characteristic feature of such compounds is the presence of large one-valent cations in interstitial holes and relatively small two-valent cations in the network.

At the present time, the phosphates with a langbeinite structure constitute a small group of compounds. In the majority, the network cations are Ti^{III}, Ti^{IV}, Cr^{III}, and Fe^{III}, while the interstitial cations are Na^I, K^I, and Ba^{II}: $KTi_2P_3O_{12}$ [9], $K_{1.75}Ti_2P_3O_{12}$ [10], $K_2Ti_2P_3O_{12}$ [10,11], $KBaFe_2P_3O_{12}$ [12], $KBaCr_2P_3O_{12}$ [13], $Na_2CrTiP_3O_{12}$ and $Na_2FeTiP_3O_{12}$ [14]. The number of compounds including zirconium, $K_2YZrP_3O_{12}$ and $K_2GdZrP_3O_{12}$ [15] or hafnium, $K_2BiHfP_3O_{12}$ [16] is even smaller.

Notable differences exist between NASICON- and langbeinite-type structures [17]. In NASICON, four interstitial sites (holes in the network) are present, while langbeinite has only two. These sites are large enough to accommodate the cations that compensate the charge of the network. In the NASICON structure, the holes can be completely empty. This is not possible in the langbeinite structure. Moreover, in the latter, the channels between the network holes have narrow

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windows. This fact prevents cation transport. As a consequence, the cations of a sufficiently large size remain captive in the holes and lose their ability to migrate. This fact can be useful in developing materials for the immobilization of toxic cations from wastes, including radioactive waste.

We report here the synthesis and structural characterization of a new phosphate with a langbeinite structure $K_2FeZrP_3O_{12}$.

2. Experimental

2.1. Reagents

All reagents were of analytical grade (Aldrich) and were used without further purification.

2.2. Synthesis

The potassium iron zirconium phosphate (dark-gray), $K_2FeZrP_3O_{12}$, was prepared as follows: 6.4 mL of 1 M H_3PO_4 was slowly added, with constant stirring, to an aqueous solution containing stoichiometric quantities of KCl (2 M), $FeCl_3$ (1 M) and $ZrOCl_2$ (1 M). The resultant gel was dried at 85°C for 25 h, thoroughly dispersed in an agate mortar and then heated in stages to 600°C, 800°C, 1000°C and 1100°C for 24 h at each stage, cycling heating stage and dispersion. After each heating step, the sample was examined by powder diffraction, which allowed the formation of the final product and the presence of admixture phases in the sample to be controlled. Crystallization of $K_2FeZrP_3O_{12}$ takes place at 800°C. The thermal treatment to higher temperatures provokes an increase in the crystallinity of the synthesized phosphate.

2.3. Analytical procedures

The potassium, iron, zirconium and phosphorus contents were determined using a SpectraSpectrometer DCP-AEC after dissolving a weighed amount of sample in HF(aq). Elemental analysis (in wt.): 15.1% K, 10.9% Fe, 17.9% Zr, 18.4% P (calculated for $K_2FeZrP_3O_{12}$: 15.33% K, 10.95% Fe, 17.88% Zr, 18.21% P). The infrared spectra were recorded with a Carl Zeiss Jena SPECORD-75 FT-IR spectrophotometer. Micrographs were obtained with a JEOL JSM-6100 electron microscope operating at 20 kV.

2.4. X-data collection and structure refinement

The X-ray powder diffraction pattern was collected using a conventional powder diffractometer Philips 1050, using graphite monochromatized Cu*Kα* radiation operating in Bragg–Brentano ($\theta/2\theta$) geometry. The sample of $K_2FeZrP_3O_{12}$ was gently ground in an agate mortar and the data were collected at room temperature over the angular range 11–110° 2θ with a step of 0.02° and a count time of 10 s/step. The pattern was indexed using the program TREOR [18] from the angular positions of 26 low-angle accurately measured, unambiguously indexed reflections. A cubic cell was obtained: $a = 10.0511(3)$ Å (figures of merit: $M_{26} = 86$ [19] and $F_{26} = 83$ (0.007, 46) [20]). As a starting set for Rietveld analysis, the coordinates were taken from those of $KTi_2P_3O_{12}$ [9] with the Fe and Zr atoms initially sharing, with half occupancy, both Mg langbeinite sites and two independent K atoms, with full occupancy, in the two K langbeinite sites. Refinement was carried out in the $P2_13$ space group using the FULLPROF program [21]. The peak shape was described using a split pseudo-Voigt function. The background was modeled using a linear interpolation between 23 points. Free atomic coordinates refinement led to excessively deviated P–O distances from ideal ones. In order to obtain accurate values for the more structurally relevant metal–oxygen distances, soft constraints were introduced for the PO_4 tetrahedron. This does not significantly affect the fit ($R_{wp} = 11.6$ versus 11.5). In the last stages of refinement, the occupancies of metal sites were refined using linear constraints to fix total sites occupancies and formula content.

Fig. 1 shows the powder X-ray diffraction pattern and the difference between the calculated and the observed pattern. The crystallographic parameters are presented in Table 1. Final atomic coordinates, isotropic displacement parameters, bond distances and angles are reported in Table 2. A polyhedral representation of the crystal structure is shown in Fig. 2.

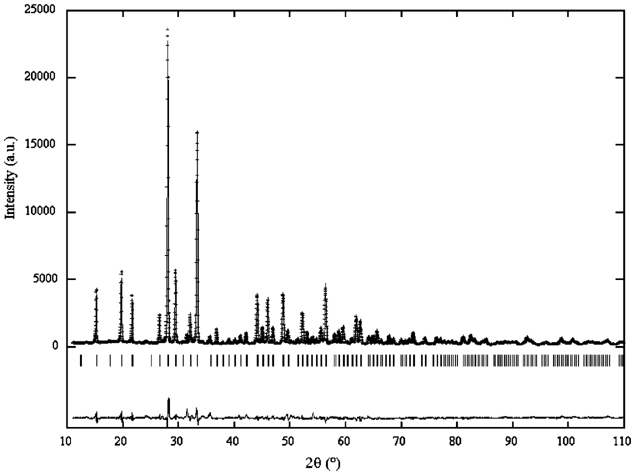

Fig. 1. Powder X-ray diffraction pattern and Rietveld analysis for $K_2FeZrP_3O_{12}$. Plus signs correspond to observed data; the solid line is the calculated profile. Tick marks represent the positions of allowed reflections, and a difference curve on the same scale is plotted at the bottom of the pattern.

3. Results and discussion

Fig. 3 shows the electron micrographs of the iron potassium zirconium phosphate. The particles appear mainly as irregular plates with micrometric dimensions. The IR spectra of $K_2FeZrP_3O_{12}$ (Fig. 4) exhibit all the bands predicted by group theory. The space group is T^4-$P2_13$. The PO_4 tetrahedron is somewhat distorted. The local symmetry of PO_4 is C_1. By assuming separation of the vibration into internal and external modes, factor group analyses lead to the following internal modes of the PO_4 anion. Thus, we expect $\nu_1 - F$ and $\nu_3 - 3F$ for

Table 1
Crystallographic parameters for the powder X-Ray diffraction study of $K_2FeZrP_3O_{12}$

Crystal system	Cubic
Wavelength (Å)	1.5418
2θ range (°)	11–110
a (Å)	10.0554(3)
V (Å^3)	1016.71(5)
Z	4
Space group	$P2_13$ (No. 198)
Structural parameters	29
Profile parameters	10
Reflections	260
R_{wp}	0.116
R_{exp}	0.043
R_F	0.058

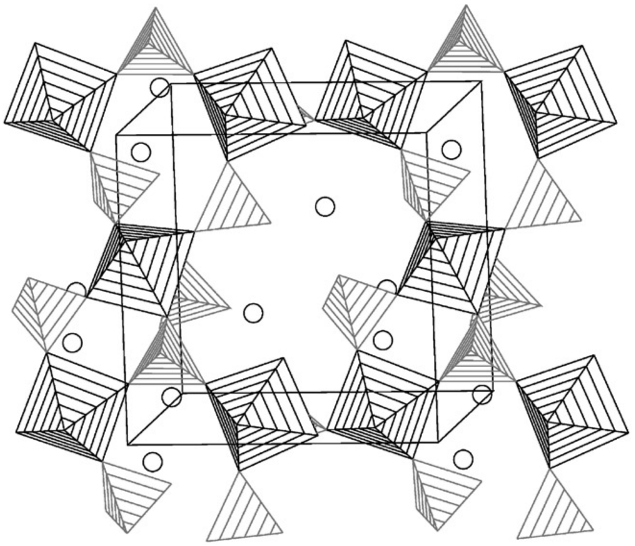

Fig. 2. Partial projection of the crystal structure of $K_2FeZrP_3O_{12}$ along the b-axis showing the cages where the K atoms lie. Black polyhedra: ZrO_6 and FeO_6 octahedra; grey polyhedra: PO_4 tetrahedra; and small circles: K atoms.

Table 2
Fractional atomic coordinates, isotropic displacement parameters (Å^2) and main geometrical data (Å, °) for $K_2FeZrP_3O_{12}$

Atom	Wyckoff	x	y	z	B
K(1)	4c	0.2977(4)	0.2977(4)	0.2977(4)	5.0(2)
K(2)	4c	0.0666(5)	0.0666(5)	0.0666(5)	4.1(2)
Fe/Zr[a]	4c	0.8561(2)	0.8561(2)	0.8561(2)	1.9(1)
Zr/Fe[b]	4c	0.5861(2)	0.5861(2)	0.5861(2)	1.77(9)
P	12b	0.6267(5)	0.4576(4)	0.2699(5)	2.4(1)
O(1)	12b	0.6442(9)	0.5020(7)	0.4125(5)	2.2(3)
O(2)	12b	0.7536(7)	0.4776(9)	0.1912(9)	5.5(5)
O(3)	12b	0.5821(8)	0.3146(5)	0.2661(8)	2.6(3)
O(4)	12b	0.5192(7)	0.5460(8)	0.2049(8)	4.1(3)
Fe/Zr–O(3)	2.037(7) × 3		P–O(1)	1.512(7)	
Fe/Zr–O(4)	2.009(8) × 3		P–O(2)	1.516(9)	
Zr/Fe–O(1)	2.026(7) × 3		P–O(3)	1.507(7)	
Zr/Fe–O(2)	2.031(9) × 3		P–O(4)	1.544(9)	
O(1)–Zr/Fe–O(1)	90.5(5) × 3		O(1)–Zr/Fe–O(2)	95.0(5) × 3	
O(1)–Zr/Fe–O(2)	172.8(7) × 3		O(1)–Zr/Fe–O(2)	84.8(5) × 3	
O(2)–Zr/Fe–O(2)	90.0(6) × 3		O(3)–Fe/Zr–O(3)	91.1(5) × 3	
O(3)–Fe/Zr–O(4)	91.6(5) × 3		O(3)–Fe/Zr–O(4)	87.5(5) × 3	
O(3)–Fe/Zr–O(4)	177.0(6) × 3		O(4)–Fe/Zr–O(4)	89.9(6) × 3	
O(1)–P–O(2)	111.0(8)		O(1)–P–O(3)	109.9(7)	
O(1)–P–O(4)	108.3(8)		O(2)–P–O(3)	111.3(8)	
O(2)–P–O(4)	107.0(8)		O(3)–P–O(4)	109.3(7)	
K(1)–O(2)	3.26(1) × 3		K(2)–O(1)	2.99(1) × 3	
K(1)–O(3)	2.883(9) × 3		K(2)–O(2)	3.16(1) × 3	
K(1)–O(4)	3.129(9) × 3		K(2)–O(4)	2.99(1) × 3	

[a] Refined occupancies: Fe (0.70), Zr (0.30).

[b] Refined occupancies: Zr (0.70), Fe (0.30).

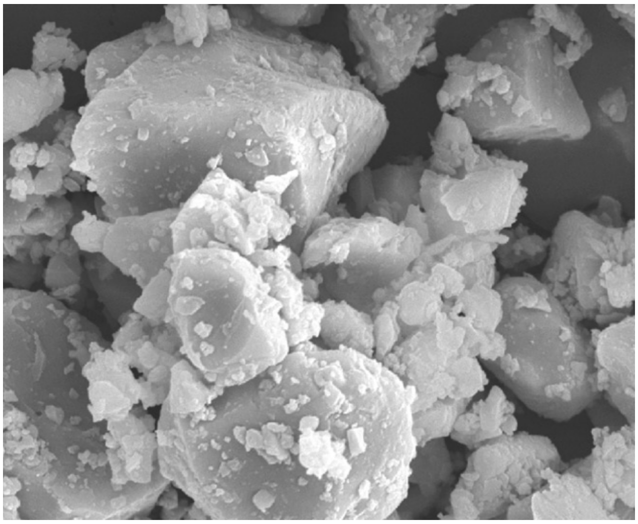

Fig. 3. Electron micrograph of $K_2FeZrP_3O_{12}$ at a magnification of 4000 × .

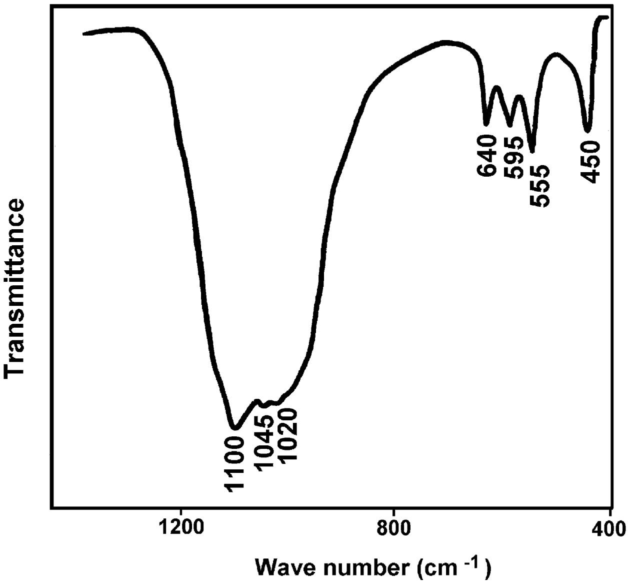

Fig. 4. IR spectrum of $K_2FeZrP_3O_{12}$.

the IR active stretching vibrations, and $\nu_2 - 2F$ and $\nu_4 - 3F$ for the bending vibrations [22]. The bands in the range 1100–990 cm^{-1} are due to the P–O stretching frequencies in the PO_4 tetrahedron: ν_3—1100, 1045, 1020 cm^{-1}, ν_1—shoulder 990 cm^{-1}. The 640–550 region shows three bonds expected for ν_4 bending vibrations: 640, 595, and 555 cm^{-1}. The 450 cm^{-1} peak could be attributed to ν_2.

Metal phosphates with the structure of langbeinite are known in three forms depending of cation charge: (i) $A^{I}M_2^{IV}P_3O_{12}$, (ii) $A^{I}A^{II}M_2^{III}P_3O_{12}$ and (iii) $A_2^{I}M^{III}M^{IV}P_3O_{12}$ where the A^{I} and A^{II} occupy one or the two fourfold K-sites of the langbeinite, whereas M^{III} and M^{IV} occupy the two fourfold Mg-sites of the langbeinite. The actual compound belongs to group (iii), where $A^{I}=K$, $M^{III}=Fe$ and $M^{IV}=Zr$. An open question regarding case (iii), two different metals or the same metal in different oxidation states, is whether there is a random or ordered distribution over the two Mg(II) sites. Isasi and Daidouh [14] propose an ordered structure for $Na_2FeTi(PO_4)_3$, but is not apparent from the paper whether the authors have explored the disordered possibility. Wulff et al. [15], who made intensity calculations based on different models, indicate a random distribution of Zr^{IV} and Y^{III}/Gd^{III} for $K_2MZr(PO_4)_3$ ($M=Y$, Gd), but they did not carry out a Rietveld refinement. For the non-stoichiometric titanophosphate, $K_{2-x}Ti_2(PO_4)_3$, the evolution of the Ti–O distances and calculations of the mean oxidation state for titanium allow the authors [10] to propose a distribution of the Ti^{III} and Ti^{IV} ions on both types of site. Our structure refinement clearly indicates the existence of occupational Fe/Zr disorder with a relative occupancy of ca. 70/30.

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