Journal of Solid State Chemistry 184 (2011) 937–944

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Structural study and physical properties of a new phosphate $KCuFe(PO_4)_2$

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ARTICLE INFO

Article history:
Received 11 January 2011
Received in revised form
16 February 2011
Accepted 16 February 2011
Available online 4 March 2011

Keywords:
Phosphate
X-ray diffraction
Mössbauer spectroscopy
Magnetic susceptibility
Electrical measurements

ABSTRACT

Single crystals of a new phosphate $KCuFe(PO_4)_2$ have been prepared by the flux method and its structural and physical properties have been investigated. This compound crystallizes in the monoclinic system with the space group $P2_1/n$ and its parameters are: $a=7.958(3)$ Å, $b=9.931(2)$ Å, $c=9.039(2)$ Å, $\beta=115.59(3)^\circ$ and $Z=4$. Its structure consists of FeO_6 octahedra sharing corners with Cu_2O_8 units of edge-sharing CuO_5 polyhedra to form undulating chains extending infinitely along the *b*-axis. These chains are connected by the phosphate tetrahedra giving rise to a 3D framework with six-sided tunnels parallel to the [101] direction, where the K^+ ions are located. The Mössbauer spectroscopy results confirm the exclusive presence of octahedral Fe^{3+} ions. The magnetic measurements show the compound to be antiferromagnetic with $C_m=5.71$ emu K/mol and $\theta=-156.5$ K. The derived experimental effective moment $\mu_{ex}=6.76\mu_B$ is somewhat higher than the theoretical one of $\mu_{th}=6.16\mu_B$, calculated taking only into account the spin contribution for Fe^{3+} and Cu^{2+} cations. Electrical measurements allow us to obtain the activation energy (1.22 eV) and the conductivity measurements suggest that the charge carriers through the structure are the potassium cations.

1. Introduction

In the last two decades, an extensive search has been carried out for new ferroelectric, piezoelectric, laser luminescent and other materials, which can be applied in quantum electronics and fiber optics and used as sorbents and catalysts. In this context, complex phosphates containing mono- and trivalent cations are of particular interest [1–3]. The structural properties of these compounds were discussed in detail and it was revealed that the sizes of the M^I and M^{III} cations and their ratio have a dominant role in their structure formation [4].

The targeted synthesis of new phosphates containing variable combinations of cations and predictions of their physico-chemical characteristics require revealing the composition–structure–property relations for different types of compounds. In this sense, the aim of this work is to study the relations between structure and properties of two phosphates, $KMgFe(PO_4)_2$ [5] and $KCuFe(PO_4)_2$. The stoichiometry of these compounds could be related with the $Ca_3(PO_4)_2$ one, where the Ca^{2+} can be substituted by various cations [6] and with the $Ca_3(VO_4)_2$ one which is a high temperature ferroelectric (FE) with a phase transition temperature of $T_c=1383$ K [7]. Other compounds of this type, e.g. $Ca_9R(PO_4)_7$ also possess ferroelectric (FE) phase transitions [8]. Sr-analogs of such phosphates, $Sr_9R(PO_4)_7$ have been shown to have a centrosymmetric monoclinically distorted β-$Ca_3(PO_4)_2$-type structure [9]. This compound exhibits an antiferroelectric (AFE) phase transition at 773 K [10].

In this paper, we report the synthesis, structural characterization and physical properties of a new phosphate $KCuFe(PO_4)_2$, and the electrical behavior is compared with $KMgFe(PO_4)_2$ which shows a bi-dimensional structure as we have recently reported [5].

2. Experimental section

2.1. Synthesis

Single crystals of $KCuFe(PO_4)_2$ were prepared by crystallization in a flux of potassium dimolybdate $K_2Mo_2O_7$, in an atomic ratio P:Mo=4:1. Appropriate amounts of KNO_3 (Fluka, 99%), $Cu(NO_3)_2\cdot 6H_2O$ (Acros, 99%), $Fe(NO_3)_3\cdot 9H_2O$ (Fisher, 98.6%), $(NH_4)_2HPO_4$ (Merck, 99%) and MoO_3 (Acros, 99%) were mixed by dissolving in aqueous nitric acid and the obtained solution was dried at 353 K. The resulting dry residue was ground in an agate mortar to ensure its best homogeneity, and then gradually heated

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doi:10.1016/j.jssc.2011.02.021

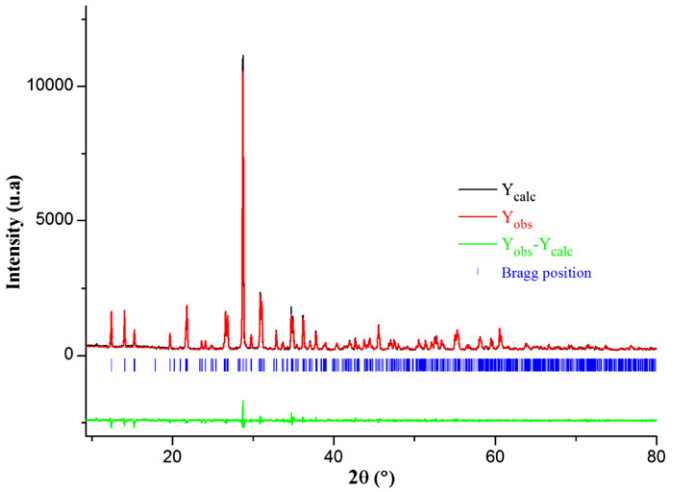

Fig. 1. The powder X-ray diagram of $KCuFe(PO_4)_2$.

Table 1
Details of the data collection and structural refinement for $KCuFe(PO_4)_2$.

Crystal data	
Chemical formula	$KCuFe(PO_4)_2$
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.958(3)
b (Å)	9.931(2)
c (Å)	9.039(2)
β (deg.)	115.59(3)
Z	4
ρ_{cal} (g cm^{-3})	3.59
Data collection	
Crystal dimensions	$0.4 \times 0.1 \times 0.1$ mm
Diffractometer	CAD4 (Enraf-Nonius)
Radiation	λ (Mo $K\alpha$)=0.7107 Å
Monochromator	Graphite
μ (mm^{-1})	6.7
Scan type	$\omega/2\theta$
Scan speed	Variable
$2\theta_{max}$ (deg.)	59.9
Number of unique reflections; R_{int}	1872; R_{int}=0.031
Number of observed reflections [$I > 2\sigma(I)$]	1771
F (000)	672
Structural refinement	
Intensity corrections	Lorentz–polarization
Absorption correction ($T_{min,\ max}$)	Analytical (0.20, 0.49)
Structure solution	Direct methods
Reliability factors	R_1=0.028; wR_2=0.089; S=0.98
Number of parameters	119
$(\Delta\rho)_{max,\ min}$ (e Å^{-3})	0.97; −0.84

up to 873 K in a platinum crucible. After being reground, the mixture was melted for 1 h at 1173 K and subsequently cooled at a rate of 10 K h^{-1} down to 673 K, after which the furnace was turned off. The crystals obtained by washing the final product with warm water, in order to dissolve the flux, are essentially composed by dark green and hexagonally shaped rod crystals of $KCuFe(PO_4)_2$.

After the structure determination, a polycrystalline sample was synthesized by a conventional solid state reaction starting from a stoichiometric mixture of KNO_3, $Cu(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_2HPO_4$. After an initial treatment, similar to that undertaken for the synthesis of the single crystals until 873 K, the sample was subjected to final calcinations at 1113 K for

Table 2
Atomic coordinates and displacement parameters U_{eq} (Å^2) for $KCuFe(PO_4)_2$.

Atom	*Wyckoff*	*x*(σ)	*y*(σ)	*z*(σ)	U_{eq} (σ)
K	8*d*	0.4179(2)	−0.1333(1)	0.0748(1)	0.0239(2)
Cu	8*d*	0.3695(1)	0.1201(2)	−0.5532(1)	0.0077(2)
Fe	8*d*	0.0143(1)	0.1253(1)	−0.2573(1)	0.0051(2)
P1	8*d*	0.1281(1)	0.1594(1)	−0.8587(1)	0.0050(2)
O11	8*d*	0.4496(2)	0.2635(2)	−0.3942(2)	0.0097(3)
O12	8*d*	0.3000(2)	0.2464(2)	−0.7429(2)	0.0075(3)
O13	8*d*	0.1483(2)	0.0375(2)	−0.7424(2)	0.0083(3)
O14	8*d*	0.1426(3)	0.1141(2)	−0.0127(2)	0.0096(3)
P2	8*d*	0.2677(2)	−0.0886(1)	−0.3511(1)	0.0047(2)
O21	8*d*	0.0970(3)	−0.1312(2)	−0.5042(2)	0.0100(3)
O22	8*d*	0.3580(3)	−0.2084(2)	−0.2403(2)	0.0090(3)
O23	8*d*	0.2221(2)	0.0137(2)	−0.2469(2)	0.0092(3)
O24	8*d*	0.4148(3)	−0.0236(2)	−0.3993(2)	0.0090(3)

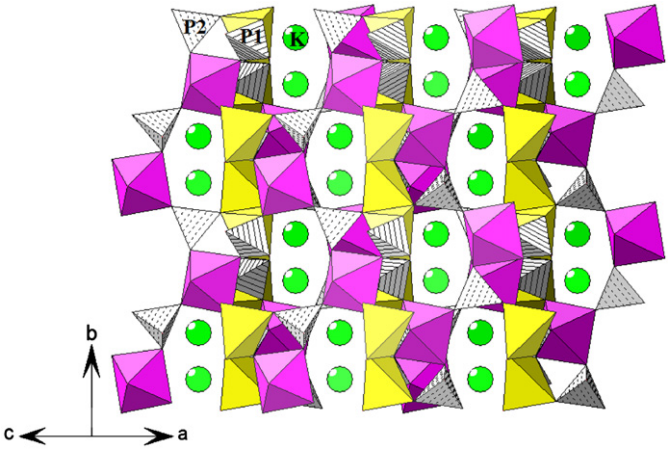

Fig. 2. A projection along the [101] direction of the structure showing the six-edged tunnels, occupied by the K^+ ions. *Legend*: CuO_5 polyhedra=yellow; PO_4 tetrahedra=hatched; FeO_6 polyhedra=purple; and K^+ cations=green circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

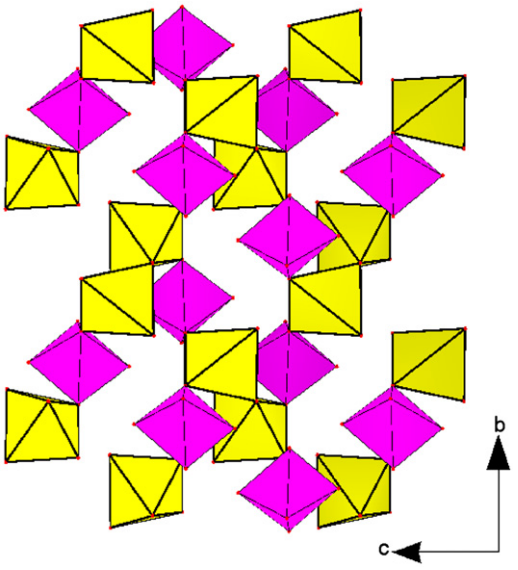

Fig. 3. The Cu/Fe/O sub-network forming sheet parallel to the *bc* plane. *Legend*: CuO_5 polyhedra=yellow and FeO_6 polyhedra=purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)