Phase Formation in the Flux Systems K_2O-P_2O_5-Fe_2O_3-$M^{II}O$-MoO_3

M.M. Yatskin[1,*], I.V.Zatovsky[1], N.Yu. Strutynska[1], V.N. Baumer[2] and N.S. Slobodyanik[1]

Abstract. *$KMg_{0.09}Fe_{1.91}(PO_4)_2$ is isotypic with $KM^{II}Fe(PO_4)_2$ (M^{II} – Fe, Cu) (monoclinic system, space group $P\ 2_1/n$). The framework is built up from $[FeO_5]$ and $[Fe(Mg)O_6]$ polyhedra sharing vertices, edges and connected by two types of bridging PO_4 tetrahedra. The K atoms are nine-coordinated and are located in hexagonal channels running along the direction of c-axis.*

Key words: complex phosphates, molten system, substitution, BVS (Bond Valence Sums).

I. INTRODUCTION

Complex oxide compounds possess a huge diversity of functional properties. Among them, phosphates occupy a leading position due to wide applications in luminescence and non-linear materials, ionic conductors, cathodic materials for portative energy sources, medical implants etc. The main reason for its common use is the presence of a variety of structural types and the fact that main properties of the phosphates are considerably dictated by the crystallographic features.

Iso- and aliovalent substitution within phosphate network is a key lever to change functional properties by structural changes.

In this case the nature and a number of substitutes have a significant influence on the type of crystalline matrix originated giving rise to find conditions of mild and direct influence on the properties. Having established the correlations between composition, structure and properties in light of nature of substitutes more evidence should be found for direct materials design.

II. EXPERIMENTAL SECTION

The crystallization trends were investigated in K_2O-P_2O_5-Fe_2O_3-$M^{II}O$-MoO_3 (M^{II} – Mg, Ni, Co, Cu, Zn) molten system in temperature region of 1273–873 K having fixed ratios Fe/P = 0.3, Fe/M^{II} = 1.0 and Mo/P = 0.2. To achieve necessary ratio of K/P starting from initial KPO_3 two approaches have been used: adding either H_3PO_4 for acidic region of high-temperature solutions or $K_4P_2O_7$ for basic one. Polyvalent metals have been immersed in a form of oxides, carbonates or hydroxocarbonates. As a source of molybdenum (VI) double molybdate $K_2Mo_2O_7$ has been used proving inert behavior toward phosphate compounds. After annealing at high temperature the homogenization has been reached and slow cooling has been performed with a rate of 1 K/min. Under these conditions the appearance of crystalline phase and viscosity has been controlled. In case of viscosity increase the molten system has been kept in isothermal conditions and afterwards crystalline products have been separated from remaining melt.

III. RESULTS

The types of compounds obtained depending M^{II} metal and ratio K/P are given in Table 1.

Table 1 Compounds obtained from K_2O-P_2O_5-Fe_2O_3-$M^{II}O$-MoO_3 molten system

M^{II} | K/P	0.75	0.9	1.3
Mg	$KMg_{1-x}Fe^{II}_xFe^{III}(PO_4)_2$ + $KFeP_2O_7$	$KMg_{0.09}Fe_{1.91}(PO_4)_2$	glass
Mn	glass		$KMnPO_4$
Co	$KCoFe(PO_4)_2$	$KCoFe(PO_4)_2$	$KCoPO_4$
Ni	$KNiFe(PO_4)_2$	$KNiFe(PO_4)_2$	$KNiPO_4$
Cu	$KCuFe(PO_4)_2$ + $KFeP_2O_7$	$KCuFe(PO_4)_2$	glass
Zn	$KZnFe(PO_4)_2$ + $KFeP_2O_7$	$KZnFe(PO_4)_2$	$KZnPO_4$

The main crystalline product obtained from molten salts enriched in P_2O_5 is double phosphate $KM^{II}Fe(PO_4)_2$. In case of cooper and iron-containing systems not only $KM^{II}Fe(PO_4)_2$ has been observed for K/P = 0.9, but also double pyrophosphates with lower K/P ratio. Manganese-containing systems significantly differ from other ones presenting only vitreous products even under comparatively low temperatures. On the contrary, K_2O-P_2O_5-Fe_2O_3-MgO-MoO_3 molten salts originates solid solutions with general formula $KMg_{1-x}Fe^{II}_xFe^{III}(PO_4)_2$ ($x \leq 0.12$). Having the ratio K/P shifted to basic molten solutions only orthophosphates $KM^{II}PO_4$ have been prepared. Exceptional behavior has been determined for manganese and copper-containing systems showing only glassy products after cooling. The composition and structure of compounds obtained has been determined by IR and atomic emission spectroscopy, X-ray powder and single crystal diffraction analysis.

Detailed analysis of experimental data indicates that simultaneous presence of two polyvalent metals in the melts provokes formation of polymetal compounds with a unique framework. The main feature of network formed is redistribution bi- and trivalent metals under different crystallographic positions. Chemical interaction between them may cause redox reactions that influence the cationic framework obtained. Thus, in case of K_2O-P_2O_5-Fe_2O_3-MgO-MoO_3 system a set of solid solutions have been prepared containg iron (II) and (III). X-Ray single crystal analysis indicates that these compounds belong to $KFe_2(PO_4)_2$ [1] and $KCuFe(PO_4)_2$ [2] structural families. The main difference from the parent compounds is the presence of iron (II)/(III) in different crystallographic positions.

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[1] Kiev National Taras Shevchenko University, Chemical department, Kyiv, Ukraine

[2] STC "Institute for Single Crystals", National Academy of Science of Ukraine, Kharkiv, Ukraine

[*] yats_13@ukr.net

The asymmetric unit of $KMg_{0.09}Fe_{1.91}(PO_4)_2$ (sp.gr. $P2_1/c$, a = 7.8444(3) Å; b = 10.0033(3) Å; c = 9.0371(4) Å; β = 114.838(5)°;) consist of one K, two Fe (one is partially occupied by Mg), two P and eight oxygen positions. The main building block involves two $[Fe(Mg)O_6]$ octahedra and two $[FeO_5]$ trigonal bipyramid connected by four orthophosphate tetrahedra. The blocks are aggregated into 2D-network which can be described by general formula $[Mg_{0.09}Fe_{1.91}(PO_4)_2]_\infty$ (Fig. 1).

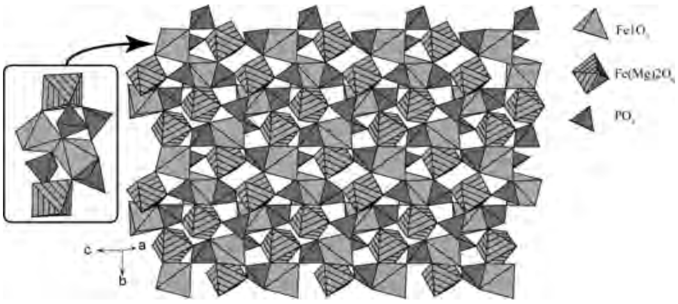

Fig. 1. Elementary fragments and 2D layers in the title compound.

It should be noted, that Mg was determined only in six-coordinated position during structure refinement while five coordinated position is occupied only by Fe. Fe(Mg)2 atoms lie in a quite distorted octahedron having vertices shared by two types of orthophosphate tetrahedral (Fe2–O distances varies between 1.947(3) and 2.133(3) Å). Completeness of the Fe1 environment is achieved by three orthophosphate tetrahedra connected to the metal atom only by one vertex and one orthophosphate tetrahedron connected via two vertices in a bidentate manner (distances Fe1–O lie in the range 1.955(3)–2.060(3) Å). As it can be compared to $KCuFe(PO_4)_2$ [2] the bond lengths of Fe2-O are very close in both structures. In $KCuFe(PO_4)_2$ this position is occupied by Fe^{III}, but in the structure of $KMg_{0.09}Fe_{1.91}(PO_4)_2$ it is occupied by both Mg and Fe. The analyses of Fe-O lengths in both positions showed that they are very close for both positions ($d(Fe1–O)_{average}$ = 2,00 Å; $d(Fe2–O)_{average}$ = 2,01 Å). It can be assumed that Fe^{II} and Fe^{III} are distributed over both positions. This fact can be confirmed by Bond Valence Sums calculations [3]. Thus, for both positions the values of BVS were found to be much higher than 2 (Fe1 position: 2.6 with Fe^{III} parameters and 2.4 with Fe^{II} parameters; Fe2 position: 3.0 with Fe^{III} parameters and 2.5 with Fe^{II} parameters). The geometry of orthophosphate tetrahedra is close to regular with P–O bond length ranging from 1.513(3) to 1.567(3) Å. The BVS values for both P atoms are close to 5 (4.91 for P1; 4.95 for P2). Potassium atoms are located in hexagonal channels running along the c-axis direction (Fig. 2).

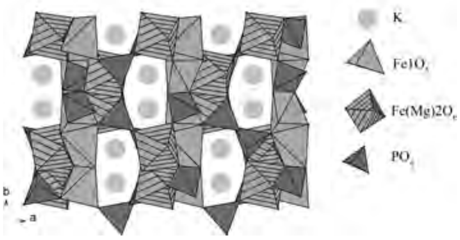

Fig. 2. A projection for $KMg_{0.09}Fe_{1.91}(PO_4)_2$ in *ab* plane.

The coordination polyhedron of the K is formed by nine O atoms assuming a cut-off distance of 3.2 Å.

IV. CONCLUSIONS

A new phosphate $KMg_{0.09}Fe_{1.91}(PO_4)_2$ was synthesized and found to exhibit an original three-dimensional structure consisted by $Fe(Mg)O_6$ octahedra sharing corners with Fe_2O_8 units of edge-sharing FeO_5 polyhedra to form ondulating chains extending infinitely along the c-axis.

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