

**o.m13.p17** Synthesis and crystal structures of fluorinated phases of potassium-indium hydroxiphosphate. M.G. Zhizhin, V.A. Morozov, L.N. Komissarova, A.A. Filaretov, F.M. Spiridonov, *Chemical Department, Lomonosov Moscow State University, 199899, Moscow, Russia, e-mail address: zhizhin@tech.chem.msu.ru*

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For several years our laboratories have been studying the synthesis and structures of phosphate compounds, searching for new materials that may have interesting and useful adsorption, ion exchange or catalytic properties.

Information about hydroxiphosphates of In-? ( $M=K, Rb^{1-2}$ ) is limited by hydrothermal synthesis ( $T=550-900^{\circ}C$ , 2.2-3 kbar pressure) of biphasic samples (+  $In_2O_3$  second phase) and single crystal determination of selected phases.

Pure  $KInPO_4OH$  (compound **I**),  $KInPO_4(OH,F)$  (**II** + 2%  $In_2O_3$ ) phosphates were synthesized by hydrothermal synthesis ( $T=200^{\circ}C$ , 20 bar pressure).  $KInPO_4F$  (**III**) was prepared by solid state reaction ( $T=500^{\circ}C$ ). They crystallize into a rhombic (**I**; sp.gr.  $P2_12_12_1$ ) and tetragonal (**II** and **III**; sp.gr.  $P4_32_12$ ) systems with unit cell parameters:  $a=9.2814(4) \text{ \AA}$ ,  $b=9.3369(4) \text{ \AA}$ ,  $c=11.2424(4) \text{ \AA}$ ,  $V=974.26(7) \text{ \AA}^3$  (**I**);  $a=9.2421(2) \text{ \AA}$ ,  $c=11.0914(5) \text{ \AA}$ ,  $V=967.99(5) \text{ \AA}^3$ ,  $Z=8$  (**III**). Their crystal structures were determined by the Rietveld analysis.

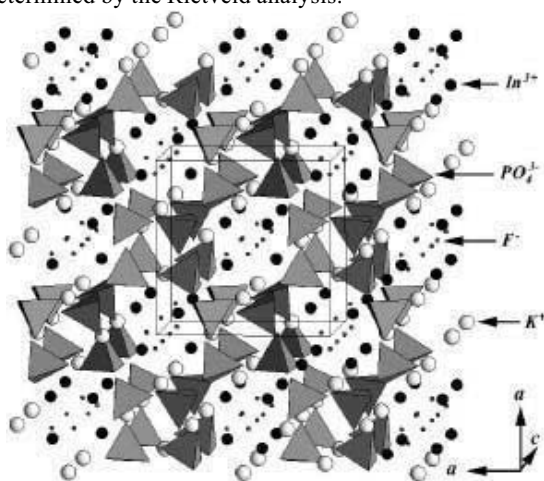


Fig. Stereoscopic view of  $KInPO_4F$  (**III**) structure along the  $[001]$  direction.

These compounds are built of  $InO_6$  (for **I**) or  $InO_5F$  (for **II**, **III**) octahedra that form spiral chains, parallel to the  $c$  axis, by corner-sharing of the  $F$  and  $OH$  groups. The chains are interconnected by tunnels along the  $z$  direction containing the  $K$  ions.

Both partial and full substitution of  $OH$ -groups on fluoride ion results in increase of unit cell symmetry. Structure, thermal stability and IR-spectroscopy of these compound details in the report will be discussed.

**o.m13.p18** Domains of actinide atoms in crystals.

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Keywords: atomic radii, atomic domains, actinides.

The program complex TOPOS is created allowing one to compute and analyse the characteristics of atomic domains (Voronoi-Dirichlet polyhedra or Wigner-Seitz cells) in crystal lattices of any complexity. By means of TOPOS 855 atomic actinide domains were investigated in 687 structures containing coordination polyhedra  $AX_n$ , where  $A=Th, U, Np, Pu$  or  $Am$  and  $X=O, F, Cl, Br$  or  $I$ .

It is discovered that actinide atoms keep the volume of their atomic domains ( $V_{VDP}$ ) irrespective of their coordination numbers at a given oxidation state and identical chemical sort of surrounding atoms. It is more convenient to use the radius of the spherical domain equal to  $V_{VDP}$  instead of volume of atomic domain to compare the size of an atomic domain with interatomic distances.

Thus, in crystal structures of  $BaPuO_3$ ,  $PuO_2$ ,  $Pu(SO_4)_2(H_2O)_4$ ,  $Na_{12}[Pu(CO_3)_5]_2 \cdot Na_2CO_3 \cdot 33H_2O$  and  $(NH_4)_2[Pu(NO_3)_6]$  the atoms  $Pu(IV)$  have coordination numbers 6, 8, 8, 10 and 12, respectively, and the interatomic distances  $r(Pu-O)$  change from 2.22 to 2.51  $\text{\AA}$  and differ from each other almost by 0.3  $\text{\AA}$ . However, varying of coordination numbers and  $r(Pu-O)$  in the compounds specified practically do not influence on the radii of the spherical domains of plutonium atoms (1.382, 1.382, 1.368, 1.369 and 1.369  $\text{\AA}$ , respectively). The constancy of volume of atomic domains is explained with the model of soft spheres and is used for calculation of actinide oxidation numbers in  $U_3O_8$ ,  $U_2F_9$ , etc.

The results of calculation of atomic domains in actinide sublattices have shown the predominance of tetradecahedra (54%), among which the Fedorov cuboctahedron is the most frequent (31%). The last one corresponds to body centred cubic lattice confirmed to the thinnest covering of space by equal spheres (or to their minimal deformation, if spheres are soft), that, in our opinion, explains the prevalence of tetradecahedra.

The correlation is found between the solid angles of atomic domain faces and the distances between atoms  $A$  and  $X$ , forming these faces. The value of solid angle is proposed as a characteristic of intensity of interatomic interaction in crystals.

A number of novel parameters characterizing atoms in crystals are introduced. These parameters can be determined using metrics of atomic domains and allow one to study more completely the interrelation composition – structure – property and to reveal the errors in structural data.

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