

MS21 P01

Structural investigations of novel β -aminophosphonic acids Jakub Wojciechowski^{a*}, Henryk Krawczyk^b, Łukasz Albrecht^b, Wojciech M. Wolf^{ab} ^a*Institute of General and Ecological Chemistry, ^bInstitute of Organic Chemistry, Technical University of Łódź, Łódź, Poland.*
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Investigated compounds represent a novel group of α -substituted- β -aminophosphonic acids which show similarity to phosphorus herbicides commonly used in agriculture. On the contrary to α -aminophosphonic acids, structural information on their β -analogs is limited to eight compounds only [1]. An X-ray analysis based on a low temperature data accompanied by the *ab initio* MP2 and B3LYP [2] calculations revealed that strong electron density delocalizations exist in all structures. In particular, the phosphorus – oxygen double bond has a strongly pronounced dipolar character. This situation prompts electron density back-donation from the oxygen lone-pairs towards the phosphorus atom bearing the large positive charge. Investigated compounds adopt *anti* conformation with the central P-C-C-N torsion angles close to 180°. This arrangement prompts mutual $\sigma(\text{C-N})$ - $\sigma^*(\text{C-P})$ interactions. All oxygen and nitrogen atoms are involved in hydrogen bonding. In particular, the strongest symmetrical hydrogen bonds link oxygen atoms of the neighbouring phosphoryl groups. Additionally, several intra- and intermolecular interactions exist in the crystals. All those interactions are analysed using the Natural Bond Orbital [3] and Atoms in Molecules [4] approach at the *ab initio* level of theory. Wavefunctions are calculated either for the isolated molecules or within the periodic boundary conditions framework.

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Surface Modification of Calcium-Nickel Hydroxyapatite by Grafting Organic Moieties Abdallah Aissa^a, Aggougui Hassen^a, Mongi Debbabi^a, Michel Gruselle^b, René Thouvenot^b ^a*Laboratoire de Physico-Chimie des Matériaux, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia* ^b*Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR-CNRS 7071, FR-CNRS 2769, Université Pierre et Marie Curie, 4 place Jussieu, case courrier 42, 75252 Paris cedex 05, France.* E-mail: hamad_2001ab@yahoo.fr

Solid solutions of mixed calcium-nickel hydroxyapatite $\text{Ca}_{(10-x)}\text{Ni}_x(\text{PO}_4)_6(\text{OH})_2$ were obtained by precipitation in aqueous medium. Apatitic surface has been modified by grafting phenyl phosphine or phenyl phosphonate in dichloromethane. All samples were analyzed and identified using: IR spectroscopy, DRX powder diffraction pattern, MAS-NMR ³¹P and thermographic analysis. X-ray powder analysis has shown that solid solutions are limited to $x=3$, and the crystallinity has been affected by the presence of organic moieties.

IR spectroscopy shows a new vibration modes appearing essentially at 2950 cm^{-1} , 1648 cm^{-1} , 1440 cm^{-1} , 720 cm^{-1} , 770 cm^{-1} and 696 cm^{-1} , related to phosphonate and phosphine groups.

An isotropic ³¹P NMR signal is observed for mixed calcium-nickel hydroxyapatite corresponding to the $(\text{PO}_4)^{3-}$ anion [1]. After reaction, the ³¹P spectrum for reacted apatite consists on two signals, one around + 2.8 ppm $(\text{PO}_4)^{3-}$ and – 6.3 ppm (phosphonate) respectively. The phenyl (C_6H_5) groups are removed by thermal treatment around 450°C. According to the results founded a mechanism was proposed for the formation of covalent P-O-P bonds as the result of a reaction between the organic reagent and $(\text{HPO}_4)^-$ ions of the apatite.

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MS21 P03

Phosphate Mineral Equilibria At The Galiléia Pegmatite Fields, Minas Gerais, Brazil. Fernando Roberto Mendes Pires^a, Marco Antonio Fonseca^b, Maira da Costa de Oliveira Lima^a ^a*Departament of Geology, University Federal of Rio de Janeiro, Brazil,* ^b*Department of Geology, University Federal of Ouro Preto, Brazil.*
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The numerous important phosphate-rich pegmatites from the Galiléia fields, studied under the chemographic viewpoint allowed us to show the relative similarity between the diagrams and the behavior of some phosphate minerals. Vivianite and laueite presence constitute a clear boundary in the increasing hydration conditions of the system, interrupting the developing of the less hydrated parageneses. Their absence will constrain the system to a restrict control in μH^+ , which determines changes in phase stability. Whiteite, on the other hand, constitute a limit in the μH^+ of the paragenesis, by blocking their development. Scorzalite may restrict the whiteite development, by forming barbosalite, hureaulite and it is allowed to predict that the association of scorzalite and frondelite constrains the appearance of the other phases, maintaining the system strongly μH^+ dependent. At least six distinct fields can be depicted in the $\mu\text{H}_2\text{O}$ - μH^+ diagrams:

- 1) A less acid and moderately oxidized field dominated by cyrilovite, dufrénite, roscherite, faheyite, rockbridgeite, referred as basic iron phosphates and frondelite.
- 2) A less acid and less hydrated zone is dominated by the Be-Na rich assemblages, herderite, beryllonite and brazilianite, apatite and the more hydrated moraesite. These minerals were derived by partial acid leaching of beryl, and reaction with apatite.
- 3) Moderately acid and hydrated ($\mu\text{H}_2\text{O}$ - μH^+) field corresponds to the lipscombite, beraunite, barbosalite, whitmoreite, rockbridgeite and bermanite. Leucophosphite, phosphosiderite, phosphoferrite and hureaulite and wicksite could be included in this intermediate or transitional group.
- 4) The field dominated by the supposedly primary phases consisting of apatite, triphylite, triplite, beusite, wyllicite, alluaudite, arrojadite, johnsomervilleite and amblygonite-montebrazite is stable under low $\mu\text{H}_2\text{O}$ conditions. Ferrisicklerite may also participate of this group.

5) A field dominated by the Al-rich phosphates, scorzalite-lazulite, wardite, gordonite, jahnsite-whiteite, childrenite-eosphorite, souzalite-gormanite, variscite, angelite and berlinite Al corresponding to high μH^+ and low to moderate $\mu\text{H}_2\text{O}$ conditions.

6) The more hydrated and oxidized portion of the diagrams is composed by strengite, strunzite, ferristrunzite, laueite and vivianite under higher μH^+ conditions. These group of more oxidized phases, also corresponds to the highest hydration stage. Heterosite and tavorite are situated in the lower hydrated portion of all diagrams and represent local dehydration process. The sequence of gradual increasing hydration strengite→strunzite→laueite or strengite→vivianite is relatively clear, and to certain broad extent heterosite→tavorite→strengite→ferristrunzite→laueite is also obvious, according to the chemography. Vivianite corresponds to the more hydrated and acid phosphate. Carbonates, siderite, rhodochrosite and sideroplesite, and some arseniates, scorodite and pharmacosiderite, formed at the beginning of the oxidation process are relatively widespread, even in small amounts. The last diagram reflects a general tendency of the metasomatic alteration of the phosphate minerals, marked by the strong positive slopes of the reactions, with successive destabilization from the less to more hydrated phosphates, in terms of the chemical potentials considered. The large field dominated by the oxidic, basic and considerably hydrated phosphate, cyrilovite defines and limits the paragenetic evolution together with vivianite and moraesite. It could also be perceived that moraesite is the more hydrated phosphate of the system.

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Crystal Structures and Properties of Organically Templated Metal Phosphates and Metal Phosphites
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Keywords: Open-framework structure, zinc phosphate, zinc phosphite

Organic-inorganic hybrid metal phosphates have exhibited a variety of interesting open-framework structures as well as a wide range of applications such the traditional use in catalysis, gas sorption and ion exchange and modern modern low-*k* materials, zeolite-dye micro-laser, or even inorganic phosphor. Recently, we have investigated the tetrahedral zinc phosphate materials and discovered several phases with distinctive microporous structures and interesting photo luminescence property. Herein, we report the NTHU-n series ($n = 1-5$) which include a neutral 24-ring channel structure, a novel three-dimensional highly porous organic-inorganic hybrid framework with bimodal porosity, an elastic layered lattice with capability of molecular recognition by encapsulating supramolecular molecules, a unique mixed-metal zincophosphate with intrinsic yellow/white emission, and the first 26-ring channel structure of mixed metal phosphites.

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MS21 P05

Crystal structure and magnetic properties of $\text{LiCr}_y\text{Fe}_{1-y}\text{P}_2\text{O}_7$ diphosphates
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During the past decade, research on positive electrode materials for lithium batteries mainly focused on the layered oxides LiCoO_2 and LiNiO_2 , the spinel LiMn_2O_4 , and all their substituting derivative compounds. Nevertheless, polyanionic compounds built on PO_4 tetrahedra and MO_6 octahedra (M: 3d element) deserve special attention [1]. Efforts towards this relatively novel class of intercalation hosts focused on iron-containing systems. In order to compensate for the low intrinsic electronic conductivity of this kind of sample, we develop a 'wet' method based on mixing stoichiometric aqueous solutions of precursors followed by thermal treatment at low temperature compared to those used for classical solid state reactions. The solid solution series $\text{LiFe}_{1-y}\text{Cr}_y\text{P}_2\text{O}_7$ was synthesized and their crystal structures were refined using Fulprof program. In the whole composition range $0 \leq y \leq 1.0$, a single phase, with a colour depending on the chromium amount, was obtained. The XRD patterns exhibited very sharp peaks and can be indexed in the monoclinic system (S.G. P2_1). In the structure of these condensed phosphates, each MO_6 (M: $\text{Fe}_{1-y}\text{Cr}_y$) octahedron is linked to five different P_2O_7 groups, one of them acting as a "chelating" sequence around the transition metal. These MP_2O_7 units are interconnected in a 3D network so as to create cavities in which lithium ions are located in a distorted tetrahedral environment. Unit cell parameters of the end members of this solid solution are: $a = 4.8331(4) \text{ \AA}$, $b = 8.1006(6) \text{ \AA}$, $c = 6.9474(6) \text{ \AA}$, $\beta = 109.36(1)^\circ$ for LiFeP_2O_7 and $a = 4.8125(7) \text{ \AA}$, $b = 8.0670(7) \text{ \AA}$, $c = 6.9158(8) \text{ \AA}$, $\beta = 109.26(1)^\circ$ for LiCrP_2O_7 . Substitution of chromium for iron leads to a continuous small decrease of the unit cell parameters as a result of the difference in size between these two transition elements. Their valence state and the magnetic interactions were determined by measuring the thermal evolution of the magnetization. Fe^{3+} and Cr^{3+} adopt their high spin configuration (Fe^{3+} : $t_2^3e^2$; Cr^{3+} : $t_2^3e^0$). LiFeP_2O_7 presents an antiferromagnetic behaviour below 20 K with negative paramagnetic Curie temperature ($\chi_p = -68 \text{ K}$). Similar results were obtained by G. Rouse et al. by studying this diphosphate by neutron diffraction [2]. The increase of the chromium amount leads to decrease of the Fe-Fe strong antiferromagnetic interaction.

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