

5) A field dominated by the Al-rich phosphates, scorzalite-lazulite, wardite, gordonite, jahnsite-whiteite, childrenite-eosphorite, souzalite-gormanite, variscite, augelite and berillite Al corresponding to high  $\mu\text{H}^+$  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  $\mu\text{H}^+$  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.

#### MS21 P04

**Crystal Structures and Properties of Organically Templated Metal Phosphates and Metal Phosphites**  
Sue-Lein Wang, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, ROC  
E-mail: [slwang@mx.nthu.edu.tw](mailto:slwang@mx.nthu.edu.tw)

**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.

[1] Liao, Y. C.; Lin, C. H.; Wang, S. L. *J. Amer. Chem. Soc.* 2005, 127, 9986.

[2] Liao, Y. C.; Jiang, C. J.; Wang, S. L. *J. Amer. Chem. Soc.* 2005, 127, 12794.

[3] Liao, Y. C., Liao, F.L., Chang, W.K., Wang, S.L. *J. Amer. Chem. Soc.* 2004, 126, 1320.

[4] Lin, C.H.; Yang, Y.C.; Chen, C.Y., Wang, S. L. *Chem. Mater.* 2006, 18, 2095-2101

[5] Lin, C. H.; Wang, S. L.; Lii, K. H. *J. Amer. Chem. Soc.* 2001, 123, 4649.

#### MS21 P05

**Crystal structure and magnetic properties of  $\text{LiCr}_y\text{Fe}_{1-y}\text{P}_2\text{O}_7$  diphosphates** Hssain Bih, Ismael Saadoun, Mohammed Mansori, Helmut Ehrenberg<sup>b</sup> and Hartmut Fuess<sup>b</sup>. <sup>a</sup>*Equipe Chimie des Matériaux et de l'Environnement, LP2E2M, FST Marrakech, UCAM, Morocco*, <sup>b</sup>*Material Science Department, TUD, Germany*.  
E-mail : [hssain\\_bih@yahoo.fr](mailto:hssain_bih@yahoo.fr)

**Keywords :** Rietveld Refinement, Phosphates, Magnetism

During the past decade, research on positive electrode materials for lithium batteries mainly focused on the layered oxides  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ , the spinel  $\text{LiMn}_2\text{O}_4$ , and all their substituting derivative compounds. Nevertheless, polyanionic compounds built on  $\text{PO}_4$  tetrahedra and  $\text{MO}_6$  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.  $\text{P2}_1$ ). In the structure of these condensed phosphates, each  $\text{MO}_6$  (M:  $\text{Fe}_{1-y}\text{Cr}_y$ ) octahedron is linked to five different  $\text{P}_2\text{O}_7$  groups, one of them acting as a "chelating" sequence around the transition metal. These  $\text{MP}_2\text{O}_7$  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  $\text{LiFeP}_2\text{O}_7$  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  $\text{LiCrP}_2\text{O}_7$ . 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.  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  adopt their high spin configuration ( $\text{Fe}^{3+}$ :  $t_2^3e^2$ ;  $\text{Cr}^{3+}$ :  $t_2^3e^0$ ).  $\text{LiFeP}_2\text{O}_7$  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.

[1] Wurm C., et al., *Chem. Mater.*, 2002, 14, 2701-10.

[2] Rouse G., et al., *Solid State Ionics*, 2002, 4, 973-78.

*This work has been supported by the CNRST-DFG collaboration*