

Keywords: metal-organic framework, fluorescence, hydrothermal synthesis

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**Hydrothermal synthesis and characterization of transition metal gallophosphates**

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Open-framework metal phosphates have been widely studied for their applications in ion exchange, separation, and heterogeneous catalysis. It is well known that the inclusion of heteroatoms in open-framework phosphates can lead to the modification of the physical and chemical properties of the parent compounds. Many transition metals have recently been incorporated into gallium phosphate frameworks to give MGaPOs (M = Mn, Fe, Co, Zn, Ni, Ti, U,...) with both zeolitic and new structure types. In this research we explored transition metal gallophosphates which have been synthesized under hydrothermal conditions and structurally characterized by single crystal X-ray diffraction. The characterization of MnGaPO phase is described: the 3D open-framework consists of discrete bioctahedra of Ga<sub>2</sub>O<sub>10</sub>(H<sub>2</sub>O) and GaO<sub>5</sub> trigonal bipyramids connected via MnO<sub>4</sub> and PO<sub>4</sub> tetrahedra to generate intersecting tunnels within which piperazinium cations reside.

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Keywords: hydrothermal, gallophosphates, transition metal

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**Elastic layered zincophosphate intercalated with ice-like water cluster or superamolecular chains**

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Remarkable discrete water hexamers (H<sub>2</sub>O)<sub>6</sub> have been observed in pseudo neutral layers of amine-anchored zincophosphate host. Molecular structures of (H<sub>2</sub>O)<sub>6</sub> have been studied in several reports in which the cyclic topology as well as hydrogen bonding were clearly illustrated. However, no previous work showed that water hexamers could exist in solid-state under ambient conditions. We report here a kind of discrete water hexamers confine in-between zincophosphate strata with a chair conformation. The confined hexamers could sustain heating up to 150°C and then get off the host at higher temperatures. We observed that the host would become

amorphous upon prolonged heating. Interestingly, after exposing to moisture, the dehydrated host could restore to its originally crystalline state with absorbed water molecules being self-assembled into cyclic water hexamers again. The amorphous -to-crystalline transition was able to proceed reversibly via a repeated dehydration / rehydration process. Without heating, we found that water hexamers could still be driven out of host by reacting with terephthalic acid (TA), which could self assemble into infinite supramolecular chains within the host layers. The interchange between (H<sub>2</sub>O)<sub>6</sub> clusters and organic supramolecular entities involved very interesting and complicated guest-to-host and guest-to-guest hydrogen bonding interactions.

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**Gas adsorption process on silica mesoporous crystals obtained by *in-situ* SR powder diffraction**

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Structure of silica mesoporous crystal MCM-48 and argon gas adsorption process were studied by synchrotron powder diffraction. The diffraction intensity data were analyzed by the combination of maximum entropy method (MEM) and electron crystallographic approach[1] to solve three-dimensional structure of mesoporous crystals. In the analysis, the total electron number in the unit cell of mesoporous crystal, which is used for one of the constraint conditions in MEM calculation, was obtained from the pore volume estimated from gas adsorption isotherm. The silica wall structure of MCM-48 was confirmed to follow a Gyroid surface, which is one of the periodic minimum surfaces. The resultant MEM charge density was less affected by termination effect and has clearer distribution than that obtained by the conventional Fourier synthesis. The *in-situ* synchrotron powder diffraction experiment of gas adsorption was carried out at BL02B2 in SPring-8[2]. The changes of diffraction pattern by the gas adsorption, corresponding to the gas adsorption isotherm, were clearly observed. The argon gas adsorption process was directly observed as the change of charge density distribution inside the mesopore of MCM-48. It was clearly observed that argon gradually adsorbs on the surface of pore walls at low gas pressures, and suddenly filled mesopore by a capillary condensation as argon gas pressure increased. Comparing gas adsorption behavior obtained from the observed data and the isotherm calculated by the quenched solid density functional theory (QSDFT) model is now in progress.

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#### Nanoporous metal phosphates with photoluminescence property

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For the past two decades, research about metal silicate and phosphate with microporous structure has always played an important role in the field of materials chemistry due to their wide application potential from traditional catalyst, molecular sieve and ion exchange to recently developed low-k materials and zeolitic dye laser. In recent years, we have discovered several gallium phosphates containing transition metal with pore size around 1 nm and intriguing photoluminescence property. For example, 24-member ring NTHU-11 and the first organo-metallo phosphates NTHU-2,2 can emit blue light when excited with UV light. The photoluminescence phenomenon is a new property of nanoporous metal phosphate with emission mechanism apparently different from that of existing inorganic phosphor since the later is doped with metal activator or added with sensitizer in host lattice in order to illuminate. At present, the photoluminescence property of nanoporous metal phosphate is substantiated. Besides blue light, zinc gallophosphate that can emit yellow light or even white light have been synthesized. In this presentation, we are going to present a series of nanoporous gallophosphates and zinc gallophosphates via the synthetic strategy of employing the large 4,4'-trimethylenedipyridine (tmdp) amine as a template. Their structures will be described and photoluminescence property will be examined.

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Keywords: metal phosphate, photoluminescence, nanoporous

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#### Crystal growth, structure and physical properties of $Ln(\text{CuGa})_{13}$ compounds ( $Ln = \text{La-Nd, Eu}$ )

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Single crystals of  $Ln(\text{CuGa})_{13}$  ( $Ln = \text{La-Nd, Eu}$ ) compounds have been synthesized by flux-growth methods and characterized by single

crystal X-ray diffraction.  $Ln(\text{CuGa})_{13}$  ( $Ln = \text{La-Nd, Eu}$ ), which are isostructural to  $\text{NaZn}_{13}$ , crystallize in the cubic  $Fm-3c$  (No. 226) space group, with  $Z = 8$  and lattice parameters  $a \sim 11.8 \text{ \AA}$ . Magnetic susceptibility data show paramagnetic behavior down to 2 K for Ce, Pr, Nd, and Eu compound, respectively. Metallic behavior is observed below 300 K for each compound. A large positive magnetoresistance up to 154 % at 9 T is also observed for  $\text{Pr}(\text{CuGa})_{13}$ . The structure, magnetic, heat capacity and transport properties of these compounds will be presented and compared to  $Ln(\text{CuGa})_{12}$  ( $Ln = \text{Y, Gd-Er, Yb}$ ) family of compounds.

Keywords: magnetism, magnetoresistance, flux growth

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#### Structure and magnetic properties of a iron(III) spin crossover complex

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New complex,  $[\text{Fe}(\text{3-OMe-salMen})_2]_2[\text{Ni}(\text{mnt})_2]\text{CH}_3\text{CN}$ , (3-OMe-salMen=2-([2-(methyl-amino)ethyl]imino)methyl)-3-methoxyphenol; mnt=maleonitriledithiolate) is synthesized and characterized. (at 298 K, triclinic  $P-1$ , cell parameters  $a = 9.402(2)$ ,  $b = 10.476(2)$ ,  $c = 16.636(3) \text{ \AA}$ ,  $\alpha = 87.17(3)$ ,  $\beta = 77.38(3)$  and  $\gamma = 75.21(3)^\circ$ ). The Fe (III) is an octahedrally coordinated ( $\text{N}_4\text{O}_2$ ) by two tridentate ligand. The bond lengths of Fe-N and Fe-O suggests the Fe(III) is in a low spin (LS) state configuration. From the thermally dependent magnetic measurements, the title complex is in the LS state ( $S=1/2$ ) at temperature range of 5~350K. As the temperature higher than 350 K, the compound becomes at HS state (high spin,  $S=5/2$ ) based on the magnetic data. According to the TGA, the spin transition may be due to the removal of the solvent molecule of  $\text{CH}_3\text{CN}$ . The non-solvated species then displays a gradual spin transition between HS and LS with  $T_{1/2}$  of 290K. When the non-solvated compound was treated with water vapor, the magnetic property of this hydrated sample appears to have different spin transition temperature at 122K. It is known that solvent molecules sometimes do play important roles in the spin transition; the title complex did show different spin transition behaviors in the presence of  $\text{CH}_3\text{CN}$  or of water as a solvent; the one with acetonitrile prefers in LS at room temperature, however the non-solvated one is in HS at room temperature. With the presence of water, a spin transition occurs at lower temperature. The process of removing and retaking solvent molecule is reversible by referring to powder pattern and magnetic measurements. The structure and magnetic relationship, especially in the presence or absence of solvent molecules, is currently under investigation.

Keywords: spin crossover, iron (III), reversible

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#### The local structure & dielectric properties of the cubic pyrochlore $\text{Bi}_{1.67}\text{M}_{0.75}\text{Nb}_{1.5}\text{O}_7$ ( $\text{M} = \text{Mg}$ and $\text{Ni}$ )

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