

materials, magnetic behaviour

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Insight into the mechanisms of metal ion binding in hexagonal tungsten bronze

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Tungsten trioxides and their alkali-metal-intercalated products $MzWO_3^+$ show potential for application in electrodes, as ion exchangers, catalysts and the treatment of radioactive waste. Hexagonal tungsten bronze (HTB) features hexagonal channels, of diameter ~ 0.54 nm, that may be useful for selective and reversible binding of metal ions. In particular doping of HTB with molybdenum (Mo-HTB) has been reported to enhance the uptake of Cs^+ and Sr^{2+} . We have conducted a powder diffraction study, using both x-rays and neutrons on a series of $MzHTB$ ($M = Na^+, Mn^{2+}, Ba^{2+}, Ce^{3+}, Pb^{2+}$), including some doped with molybdenum (Mo-HTB) synthesized using hydrothermal methods. Rietveld refinement of the diffraction patterns show that doping with Mo rapidly degrades the crystallinity of HTB by creating a high degree of disorder in the a-b planes, suggesting that the presence of Mo retards the hydrothermal crystallization process. The refinements confirm previous reports of an exchangeable metal ion binding site that displays varying degrees of affinity for the various metal ions studied. The solution binding affinity behaviour of the Mo-HTB's was also investigated for selected ions ($M = Co^{2+}, Gd^{3+}, Ce^{3+}, Ce^{4+}, Tl^+, Pb^{2+}$ doped with respective radiotracer) in a range of concentrations of acid and electrolytes solutions. These results show that the optimum condition for metal ion binding depends not only on the Mo doping level, but also the charge and redox chemistry of the exchange cation. In combination, the structure information and the solution chemistry indicate that the loading capacity of the each metal ion is also dependent on the microstructure of the HTB.

Keywords: inorganic ion exchanger, powder diffraction analysis, tungsten bronze

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Dynamics phase transition of water nanotube cluster stabilized in molecular nanoporous crystal

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Moving water molecules in a limited space within a nanometer-scale region, different from the molecular motion of bulk water, have imposed a remarkable nature affected by strong interfacial interactions with a surrounded outer wall. For examples, it has

been theoretically predicted that water molecules impacted on a hydrophobic interface inside carbon nanotube lead to osmotic water transport with a one-dimensional chain hydrate in its internal space instantly, have a critical point of the water-ice phase transition depending on the tube widths, and freeze at a novel ice polymorph with a multi-layered helix structure. Experimentally, it is demonstrated that melting point of each confined tube-like water clusters constructed from 5- to 8-membered rings, which is not supported to decrease melting points in inverse proportion to the pore sizes by theoretical expectation, increases as the widths of single-walled carbon nanotubes. A tube-like three-layered water cluster, called a water nanotube (WNT), forms into each internal channel space and regulates by hydrogen bonds (H-bonds) with the outer wall. In this study, the structure of WNT confined to the channel pores has been investigated by a neutron structure analysis, and revealed to stabilize by an anchor effect of the structural water. Furthermore, by the neutron scattering, a few water molecules around a center of WNT can definitely move about four times faster than those of bulk water, despite of restricting by H-bonds with the surrounded structural water. Investigation of the behavior of the mobile water molecules within WNT would link the elucidation of a mechanism for structural water bearing on vital functions on the cell surface.

Keywords: water cluster, crystal engineering, hydrogen bond

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A fluorescent two-dimensional Zn(II) framework containing 2,2'-bipyridine-5,5'-dicarboxylic acid

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Metal-organic frameworks (MOFs) are interesting nanoporous materials in the material research area because of their large void spaces and unique geometrical structures. These zeotype materials often maintain thermally robust crystalline frameworks with a permanent porosity. The porosity makes MOF potentially useful for catalysis as well as gas storage. Most MOFs are constructed by a unit of a symmetric molecule, which can bridge neighboring metal ions. Choosing a suitable ligand is an important step to prepare functional MOFs because the structural characteristics and physicochemical properties of MOFs primarily depend on the ligand. Multidentate ligands are usually chosen for preparing MOFs. The ligand, 2,2'-bipyridine-5,5'-dicarboxylic acid (bpdca), can work not only as a bridging molecule but also as a chelating ligand. The two nitrogen atoms of the ligand generally chelate to a metal ion, and two carboxylates can connect other metal ions additionally in one of the three possible modes: 1) solely to nitrogen atoms, 2) only to oxygen atoms from carboxylate groups, and 3) to both atoms. These multiple coordination ways of the bpdca ligand would provide interesting structures with a metal ion and apply for preparing the MOFs containing mixed metal ions with selective preference for an oxygen atom or a nitrogen atom. In addition, the ligand is weakly fluorescent. Thus, the corresponding MOF may possess sufficient fluorescence and the resulting materials are valuable for other applications. Herein, we present we present an infinite two dimensional MOF using 2,2'-bipyridine-5,5'-dicarboxylic acid and zinc nitrate. The compound was hydrothermally prepared and characterized by X-ray crystallography. The compound showed fluorescence in solid state at room temperature.

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 Ga₂O₁₀(H₂O) and GaO₅ trigonal bipyramids connected via MnO₄ and PO₄ tetrahedra to generate intersecting tunnels within which piperazinium cations reside.

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

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Remarkable discrete water hexamers (H₂O)₆ have been observed in pseudo neutral layers of amine-anchored zincophosphate host. Molecular structures of (H₂O)₆ 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 (H₂O)₆ 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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