

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  $\sim 0.54$  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.