

structure $[\text{Ga}_3\text{F}(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_2](\text{C}_5\text{H}_5\text{N})$ (**I**) is not currently known, and the nitrogen atom from the pyridine molecular has coordinated with metal gallium to form strong N-Ga bonds in an octahedral GaO_4FN unit, and pyridine molecules sit in the channels which are formed by building unit, connected by diphosphonate. The structure $[\text{Ga}_4\text{F}_2(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_3]^{2-} 2[\text{C}_5\text{H}_5\text{N}]^+$ (**II**) contains pyridine cations within the channels formed by building unit, connected by diphosphonate and has a stronger hydrogen contact between oxygen from diphosphonate and nitrogen from pyridine. The new structures (**I**) and (**II**) are good examples to present three dimensional structures with channels constructed by two novel building units connecting diphosphonate groups, and two kinds of pyridine moieties. One pyridine has linked through Ga-N bond and another is free as cation, which has been found in channels as a template. The two materials exhibit microporous frame-work materials with pyridine template within the pores.

Keywords: gallium 1,2-ethylenediphosphonate, framework, pyridine

P.11.15.5

Acta Cryst. (2005). A61, C403

Mechanism of Phase Transition Caused by Water Absorption in FAPO-34

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It was made clear that the phase transition mechanism caused by the water absorption in FAPO-34 using the single-crystal X-ray (SCX) analysis and EXAFS Fourier transform spectra analysis.

FAPO-34 is known as the one of the Chabazite type zeolite. [1] The crystals of FAPO-34 including organic template in the framework (**as-made**) were obtained by hydrothermal synthesis method. To utilize as the water absorption material, the **as-made** crystals were baked in some temperature conditions to remove the organic template. The **as-made** crystals baked at high temperature (**HT**) caused phase transition, but the one baked at low temperature (**LT**) kept the structure after the water absorption.

As the results of SCX and EXAFS analysis, it was made clear that the specific water coordination to Fe on the framework causes the phase transition of **HT**. SCX analysis showed the direct coordination of the water to Al and Fe on the framework and the structural skew of the framework caused by the specific water coordination to Fe of **HT**. EXAFS analysis showed that Fe of **LT** is covered by something else other than water.

[1] Ristic A., Tusar N.N., Arcon I., Thibault-Starzyk F., Hanzel D., Czyniewska J., Kaucic V., *Micropor. Mesopor. Mater.*, 2002, **56**, 303-315.

Keywords: absorption material, phase transitions, structure analysis

P.11.15.6

Acta Cryst. (2005). A61, C403

Direct Observation of Hydrogen Molecules adsorbed in a Coordination Polymer

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Hydrogen is a very important material for the development of a clean energy system. The use of physisorption in microporous coordination polymers is one of the most promising candidates for the hydrogen gas storage. The fundamental structural information of adsorbed H_2 molecules is indispensable for the rational synthetic strategy of these materials. Although the weakest X-ray scattering amplitude of hydrogen has made it difficult to determine the structure of H_2 molecules, we have succeeded in direct observation of H_2 molecules adsorbed in the nanochannels of the coordination polymer

by the *in-situ* synchrotron powder diffraction experiment of gas adsorption and the MEM/Rietveld charge density analysis [1].

The H_2 molecules were found to be adsorbed without any chemical bonding to the host framework, in the condition that they can be easily adsorbed and released. The position of H_2 molecule was displaced from the center of the nanochannel. It was located near the metal-oxygen unit near one corner of the rectangular nanochannel. The size of the H_2 molecule is suited to the size of the pocket of the cavity. The structural information of H_2 molecule at the beginning stage of gas adsorption was obtained. That gives us the guideline for the design of high performance hydrogen gas storage materials.

[1] Y. Kubota, et al., *Angew. Chem. Int. Ed.*, 2005, **44**, 290-293.

Keywords: gas storage materials, microporous coordination polymer, synchrotron powder diffraction

P.11.15.7

Acta Cryst. (2005). A61, C403

Magnetic and Structural Properties of Rare Earth Hybrid Frameworks

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Aliphatic dicarboxylates (**AD**), $-\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2-$, have shown to be excellent ligands for crystal engineering transition metal molecular magnets [1]. With the aim of extending these studies to rare earth systems we have synthesized a series of organic inorganic hybrids of Ln(III) and **AD** anions, with $1 \leq n \leq 4$, from solutions under ambient conditions. Their single crystal x ray structural analysis show the formation of inorganic polymeric arrangements of different dimensionalities. AC susceptibility, χ' , measurements performed within the temperature range $13 < T < 330\text{K}$ show noticeable changes in the $\chi'T$ curve slope at different T values. To investigate the potential structural contribution to those magnetic ordering variations, we performed single crystal x-ray analysis in the temperature ranges of interest in steps of 2K. We discuss possible links between modifications in superexchange paths connecting cations —and eventually in hydrogen bonds networks— and magnetic response.

[1] Rodríguez-Martín Y., et al., *Cryst Eng Comm*, 2002, **87**, 522.

Keywords: organic inorganic hybrid materials, framework structures, molecular magnets

P.11.15.8

Acta Cryst. (2005). A61, C403-C404

Novel Modular Coordination Frameworks

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Crystal Engineering of Coordination Frameworks has been experiencing a great growth in recent years. Despite the majority of the compounds reported in the literature could only be usually isolated in small amounts due to inherent limitations of the synthetic techniques employed, we have optimised the hydrothermal synthetic approach for the synthesis of large and phase-pure quantities of such materials [1]. N-(phosphonomethyl)iminodiacetic and etidronic acids are precursors of multidentate organic ligands which not only exhibit unusual and flexible coordination properties, but also contain a number of potentially interesting nuclei to study using, e.g., solid-state NMR techniques. We have focused our research in the *in situ* synthesis of rigid building blocks (*i.e.*, Secondary Building Units, SBUs) formed by these ligands and V^{4+} which, along with various metal centres (e.g., Co^{2+} , Mn^{2+} and Ce^{3+}) and rod-like bridging organic molecules (such as 4,4'-bipyridine and pyrazine), self-assemble into peculiar frameworks of various topologies and dimensionalities [2], [3].

[1] Paz F.A.A., Klinowski J., *J. Solid. State Chem.*, 2004, **177**, 3423. [2] Paz F. A.A., Shi F.-N., Klinowski J., Rocha J., Trindade T., *Eur. J. Inorg. Chem.*, 2004, **13**, 2759. [3] Paz F.A.A., Shi F.-N., Klinowski J., Rocha J., Trindade T., *submitted*.

Keywords: coordination polymers, frameworks, materials

P.11.15.9

Acta Cryst. (2005). A61, C404

Structure Fingerprints of Ordered Mesoporous Silica

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Mesoporous materials present structural complexity, that together with the small volume of ordered domains, make it difficult the precise assignment of their structure. The combination of many different characterization techniques, like X-ray diffraction (XRD) or scattering (SAXS), transmission electron microscopy (TEM) and electron diffraction (ED) are necessary to properly determine the mesoporous structure. The use of different templates, like block copolymers (PEO-PPO-PEO; PEO-PBO-PEO) and methylammonium compounds (CTAB), gives hexagonal and cubic silica structures having different pore's diameter and wall thickness. In this work, the optimized synthesis of hexagonal $P6_3/mmc$ SBA-15 and MCM-41 and, cage-like cubic $Fm\bar{3}m$ FDU-1 and $Im\bar{3}m$ SBA-16 are described. The samples were prepared with commercial TEOS and Cab-O-Sil silicon sources. The as-synthesized and calcined (at 540°C) powders were analyzed by SAXS, TEM and N₂ gas adsorption, allowing a precise determination of the different material's structure, by the recognition of typical results.

The cubic structures present larger lattice parameter; the FDU-1 has a ~20 nm and, SBA-16 has a ~14 nm. The hexagonal SBA-15 and MCM-41 have a ~ 5 nm. Besides the analysis of the diffraction peaks, information on the non-ordered pores and micropores in the silica walls were also obtained from the SAXS data. The extent of pore's shrinkage effect, due to the calcination process, was also analyzed.

Keywords: porous solids, silicon oxides, small-angle diffraction

P.11.15.10

Acta Cryst. (2005). A61, C404

Design of Porous Bilayer Compounds Containing 1D Channels

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In the concept of reticular synthesis of porous metal-organic framework (MOF) structures [1], the inorganic secondary building units (SBU) described most often consist of a limited number of metal centres. However, larger structural motifs may also lead to porous MOF structures. In particular, Kitagawa et al. [2] have shown how 2D layered structural motifs can be pillared into 3D porous structures.

Recently, Wu et al. [3] reported a novel MOF structure based around infinite 2D layers of tetrahedral Zn and 5-aminoisophthalic acid (aip) ligands showing a dense triangular topology. By introduction of 4,4-bipyridine, 1,2-di(4-pyridyl)ethylene, 1,2-di(4-pyridyl)ethane and 1,3-di(4-pyridyl)propane, respectively, into mixtures of dimethylformamide and water with Zn(NO₃)₂ and aip, we are able to synthesize a series of isostructural pillared bilayer compounds built around these triangular Zn(aip) layers. In all four compounds, the pillars are creating spaces inside the bilayers resulting in 1D channels with dimensions of 3.5x6.7 Å². Inside these channels there are water molecules that can be removed upon heating to 150°C. The structural integrity of the compounds is maintained after removal of the water molecules, resulting in porous structures with estimated free volumes in the range of 20.7 to 25.5% of the unit cell volumes.

[1] Yaghi O.M., O'Keeffe M., Ockwig N.W., Chae H.K., Eddaoudi M., Kim J., *Nature*, 2003, **423**, 705. [2] Kitagawa S., Kitaura R., Noro S., *Angew. Chem. Int. Ed.*, 2004, **43**, 2334. [3] Wu C.D., Lu C.Z., Yang W.B., Zhuang H.H., Huang J.S., *Inorg. Chem.*, 2002, **41**, 3302.

Keywords: single-crystal structure determination, coordination

polymers, porous materials

P.11.16.1

Acta Cryst. (2005). A61, C404

Si Crystal Mirrors prepared by Plastic Deformation for Solar Cell Systems

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No one has ever intentionally undertaken to obtain shaped Si crystal wafers by plastic deformation. If plastically deformed Si crystals could be freely obtained, new applications based on various creative concepts could be actively developed in a wide range of fields. In this paper, we report on the successful plastic deformation of Si crystal wafers for the preparation of wafers with various shapes. A Si wafer was set Fig. 1 A Si crystal mirror between dies and pressed at high temperatures.



One application of shaped wafers is as well-shaped concave Si crystal lenses or mirrors [1,2] as shown in Fig. 1. The lattice plane of such a crystal lens has a curvature exactly along the surface.

A new solar cell system is proposed and demonstrated with the concave Si crystal mirror used as both a solar cell and a focused mirror. The effective number of total photons is the sum of photons from both the mirror solar cell and the small cell set at the focused spot, and it determines the efficiency of the entire system. The total conversion efficiency of the present system using the focused solar beam increases to 12.2 % comparing with the conversion efficiency of 9.2 % only for the concave Si mirror solar cell. This system can make effectively use of the reflected photons from solar cells.

[1] Nakajima K., Fujiwara K., Pan W., Okuda H., *Nature Materials*, 2005, **4**, 47. [2] Nakajima K., Fujiwara K., Pan W., *Appl. Phys. Lett.*, 2004, **85**, 5896.

Keywords: deformation, silicon crystals, solar cells

P.11.16.2

Acta Cryst. (2005). A61, C404

Low Temperature Anomaly of Plasticity and a Local Arrangement in Pb-In Alloys

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The temperature dependencies of the yield stress and the strain rate sensitivity of flow stress for Pb-1; 5; 10 and 20 at. % In single crystals were studied by tension in the temperature range 0,5 - 295 K. For Pb-1;5 and 10 at. % In the dislocation-impurity interaction parameters estimated from the experimental data were found typical for thermally activated depinning of dislocations from solute atoms at deformation temperatures 30 - 140 K. The anomaly of plasticity in these alloys below 30 K is consistent with the inertial unzipping of dislocations from impurity atoms. However, a further increase in indium concentration up to 20 at. % it was found affect the experimental dependencies, contradicting the above conclusions. The estimated plasticity parameters of concentrated alloy are seems to be atypical for the case of impurity atom as an effective barrier for mobile dislocations. For understanding this contradictions the Cowley's local order parameters α was estimated from the diffuse X-ray scattering measurements. The expected positive values of α indicate that clustering takes place in this system. For Pb-1 at. % In alloy $\alpha = 0$, but as the indium concentration increase the clustering becomes more dominant. The interaction of clusters with mobile dislocations leads to modify the mechanisms of low temperature plasticity and can explain the experimental data for concentrated alloy.

Keywords: low temperature, plasticity, local order