

Chem. B., 2005, **109**, 1304. [3] Urabe H., Sugawara Y., Kasuya T., *Phys. Rev. B*, 1995, **51**, 5666.

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A Novel Spin Transition Curve in [tris(2-picolylamine)Fe(II)]Cl₂ Allyl Solvate

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The title compound exhibits a temperature dependent spin crossover with an intermediate plateau in the spin transition curve (STC) around 111K at an unusual high-spin concentration of about 30%. This is well below the plateau with a 50% concentration observed for the isomorphous ethanol solvate [1].

We report here single crystal diffraction data collected at 200, 132, 111 and 94K. The systematic absences are consistent with *B*₂₁/*c* space group symmetry at 200 and 132K. At 111K, *i.e.* in the range of the plateau, a superstructure is observed. The consequential reflections violate the original *B*-centering and lead to *P*₂₁/*c* space group symmetry with a doubled unit cell volume. At 94K the original *B*₂₁/*c* symmetry is recovered, thus indicating a reentrant sequence of phase transformations [2].

This observation shows that, as in the cases of the ethanol and 2-propanol solvates [1,3], a plateau in the STC reflects the appearance of a new ordered structure. The plateau region is likely a result of the coupling of the spin conversion with the concurrent conformational ordering of the crystal architecture.

[1] Chernyshov D., Hostettler M., Törnroos K. W., Bürgi H.-B., *Angew. Chem. Int. Ed.* 2003, **42**, 3825. [2] Chernyshov D., Bürgi H.-B., Hostettler M., Törnroos K. W., *Phys. Rev. B*, 2004, **70**, 094116. [3] *in preparation.*

Keywords: spin crossover, phase transition, order-disorder

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Solid State Synthesis and Characterization of Some Novel Sodium Rare Earth Phosphates

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Recently, much attention has been paid to the rare earth phosphates because of their potential applications for optical materials, including laser, phosphors, and more recently, anti-UV materials [1]. MOPO₄ type materials possess properties that make them potentially useful for catalytic, electronic and ion exchange applications[2].

In this work, Ln₂O₃ (where Ln= La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb) were used as a rare earth source, NH₄H₂PO₄ was used as a phosphate source and Na₂CO₃ was used as a sodium source to obtain sodium rare earth oxyphosphates. Reactants were heated at 1100 °C for 20 hours. X-ray diffraction patterns, IR and Raman analysis, SEM pictures and EDX analysis were taken for characterization. According to these results, structures of these products were compared with previous ones[2-3].

[1] Hirai H., Masui T., Imanaka N., Adachi G., *J. Alloys and Compounds*, 2004, **374**, 84-88. [2] Gönen Z.S., Kizilyalli M., Pamuk H.Ö., *J. Alloys and Compounds*, 2000, **303-304**, 416-420. [3] Uztielik- Amour A., Kizilyalli M., *J. Solid State Chem.*, 1995, **120**, 275-278.

Keywords: rare-earths, oxyphosphates, solid-state

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The Systems Li-Ho-P-O and K-Ho-P-O: A Study in Inert Atmosphere

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The phosphates with open frameworks are materials that are composed by (PO₄) tetrahedral and by others polyhedral as octahedral (XO₆) and dodecahedral (XO₈) units. So, this structural conformation prove several applications of such materials as ionic conductors, ion exchangers, scintillating materials for gamma ray detection [1], catalysts [2], anticorrosive [3], etc. As part of our phosphates with open frameworks research, we study the phases present in the systems Li-Ho-P-O and K-Ho-P-O using different temperatures reaction and atmospheres. In this work, different phosphates compound like rare earth phosphate (Xenotime-type HoPO₄), alkali metaphosphate (APO₃, A= Li, K) and an alkali-rare earth pyrophosphate (LiHoP₂O₇) [4] were synthesized. These phases were characterized by X ray powder diffraction, differential thermal analysis and microscopy methods. A crystallochemistry study relating the crystal structures was performed.

[1] Natarajan S., Eswaramoorthy M., Cheetham A.K., Rao C.N.R., *Chem. Commun.*, 1998, 1561, and references there in. [2] Clearfield A., Thakurb D.S., *Applied Catalysis.*, 1986, 1. [3] Deyá M.C., Blustein G., Romagnoli R., Del Amo B., *Surf.Coat.Tech.*, 2002, 133. [4] Hamady A., Fauzi Zid M., Jouini T., *J.Solid State Chem.*, 1994, 120.

Keywords: phosphates, phase identification, X-ray diffraction

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Studies of Spin Crossover Complexes via Solvo-thermal Syntheses and their Thermal Relaxation of Light Excited Kinetic Phenomena

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The unique spin crossover 1D ladder complex [Fe₂(bpt)₂(NCS)₂(bpy)₂] · MeOH (**1**) have been synthesized successfully by one-step solvo-thermal syntheses or directly transformed from *trans*-[Fe(abpt)₂(NCS)₂] complex by hydrothermal process.

The magnetic measurement reveals that the 1D spin-crossover complex **1** has an abrupt spin transition at 130 K and possesses an unusual magnetic behavior. The π-π interactions of **1** do vary slightly with spin transition. The distances along the (110) and (101) planes are 3.65(1) Å and 3.52(5) Å at 295 K but 3.53(3) Å and 3.45(2) Å at 100 K.

The novel dinuclear Double bridging complex [Fe₂(μ-bpt)₂(NCS)₂(CH₃OH)₂](**2**) and [Fe₂(μ-bpt)₂(NCS)₂(py)₂](**3**) have also been synthesized and characterized by x-ray diffraction. The bond lengths of Fe-N are 2.292(3) Å, 2.094(3) Å for complex **2** and 2.110(2) Å, 2.321(2) Å for complex **3** at HS state.

The variable-temperature magnetic susceptibility measurement reveals that **2** and **3** are in high-spin state during 60-400 K. Interestingly, the complex **3** has a spin transition from HS to LS at low temperature under 808 nm radiation and the thermal relaxation behavior of such induced LS state will be discussed.

Keywords: LIESST, spin crossover, thermal relaxation

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Study of the Mechanism of Cu-Zn Mechanical Alloying by X-ray Powder Diffraction

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A set of Cu-30%Zn, Cu-49%Zn, Cu-65%Zn and Cu-86%Zn (that are in composition range of the phases α , β , γ and ϵ , respectively) have been synthesized by mechanical alloying of the stoichiometric mixtures of pure copper and zinc powders in a planetary mill of high grinding energy by using a ratio weight of the balls/weight of sample (RBS here after) equal to 3.3.

The results obtained have shown that the full alloying of the starting mixtures of copper and zinc powders is attained after 3 hours of grinding. The study of the intermediate phases as a function of the grinding time pointed out that the reaction is started with the formation of phases very rich in zinc, like the ϵ phase, and continue reacting with copper until the full alloying is achieved. This behavior suggests that the mechanical alloying takes place through a mechanism that implies the diffusion of copper into the zinc matrix.

On the other hand, the grinding under more severe conditions (RBS equal to 13.3) extends considerably the composition range at which α phase becomes stabilized. A mechanochemical Cu-Zn binary phase diagram at room temperature is proposed.

Keywords: Cu-Zn alloys, mechanical alloying, Cu-Zn phase diagram

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Studies on the Solid State Structures and Properties of Metal Arenedisulfonates

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Recent progress in the solid state coordination and structural chemistry of aromatic disulfonates, as well as the amine interaction properties of crystalline Cd^{2+} sulfonate complexes with amines will be presented. [1]

Due to the weak coordination strength, most of the metal monosulfonates obtained from aqueous solution are water-coordinated metal sulfonate salts. [2] However, by employing arenedisulfonates, which can provide multiple coordination sites, stable frameworks sustained by sulfonate-metal interactions can be obtained with various dimensionalities. [1] Moreover, due to the flexible coordination modes, the 1,5-naphthalenedisulfonate ligand shows variant coordination modes in complexes obtained from different reaction conditions, resulting in polymorphism. [3] Finally, layered sulfonate- and water-coordinated Cd^{2+} complexes can selectively uptake amine vapor via solid-state substitution reaction, which is a reversible process at room conditions. [4,5]

[1] Cai J., *Coord. Chem. Rev.*, 2004, **248**, 1061. [2] Côté A. P., Shimizu G. K. H., *Coord. Chem. Rev.*, 2003, **245**, 49. [3] Cai J., Wang L., unpublished results. [4] Cai J., Zhou J.-S., Lin M.-L., *J. Mater. Chem.*, 2003, **13**, 1806. [5] Zhou J.-S., Cai J., Wang L., Ng S. W., *J. Chem. Soc., Dalton Trans.*, 2004, 1493.

Keywords: sulfonate, coordination chemistry, solid state structure and property

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Structure Analysis of the Excited Molecules in the Equilibrium State

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When the crystal is irradiated with UV or visible light at low temperatures, the averaged molecule in the crystalline lattice reaches the equilibrium state composed of ground and excited states. The structure of the excited molecule in the equilibrium state can be analyzed by X-rays if the occupancy factor of the produced excited molecules exceeds the limiting value (>5%). This method is called equilibrium analysis of excited molecule. Recently we obtained the excited structure of the diplatinum complex with the equilibrium

method[1]. The Pt-Pt and Pt-P distances of the diplatinum complex are shortened at the excited state.

The same method was applied to the other complex crystals and was successful to observe the structures of the excited molecules. The first example is the $(\text{VO})(\text{acac})_2$ complex. The unit-cell was expanded at the equilibrium state and the molecular structure indicated that one $\text{V}=\text{O}$ and four $\text{V}-\text{O}$ bonds around the central vanadium atom were expanded by 0.0043(8) and 0.0045(7)Å. The second example is the $[\text{Au}(\text{PPh}_3)_2]\text{Cl}$ complex. The unit-cell of the crystal shrank and the Au-P and Au-P distances decreased 0.0055(4) and 0.0057(4)Å in the equilibrium state. The structural changes at the equilibrium state suggest that the excited molecules are produced more than 5% in the crystal and the changes of the bond distances well explain the structures of the excited molecules.

[1] Yasuda N., Uekusa H., Ohashi Y., *Bull. Chem. Soc. Jpn.*, 2004, **77**, 933.

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X-ray Induced Changes in Organic and Biological Crystalline Materials

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The investigation of radiation-induced processes in organic and biological molecules is of importance for gaining a better understanding of the fundamental mechanisms by which certain compounds (e.g. halogenated nucleotides) induce a radio-sensitizing action and can thus be used to improve anticancer radiotherapies. The study of radiation-induced processes in macromolecules is also of considerable interest in the fields of structural biology and genomics, since current progress in synchrotron protein crystallography is hampered by radiation damage in the samples.

We have carried out powder diffraction measurements to investigate structural changes as a function of X-ray irradiation in organic and biological crystals. In these experiments, synchrotron radiation is used to both irradiate the samples and collect diffraction data. Powder diffraction is employed to monitor changes in the unit cell and microstructural parameters (crystallite size and lattice strain) in crystals of native and halogenated nucleobases as well as on other small-molecule model compounds under X-ray irradiation. Similar experiments were also carried out on macromolecular crystals. Our aim in these studies is to investigate radiation-induced changes as a function of temperature, wavelength and X-ray dose rate. Attempts to interpret the observed unit-cell expansions in terms of radiation-induced structural modifications in the crystal will be discussed.

Keywords: synchrotron powder diffraction, radiation chemistry, radiation damage studies

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Polymorphic Transitions in Even Paraffins $n\text{-C}_{24}\text{H}_{50} \div n\text{-C}_{34}\text{H}_{70}$. X-ray and Spectral Studies

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Polymorphic transitions in even n -paraffins ($n\text{C}_{24}\text{H}_{50} \div n\text{C}_{34}\text{H}_{70}$) were investigated by X-ray diffraction and IR spectroscopy at 20-70°C. Such phase transitions were studied for paraffins with $n \leq 24$ before [1]. Effects of our samples thermal prehistory on the sequence of phase transitions were considered. Different "rotator" phases were found for all studied paraffins: O_{rot1} , O_{rot2} , M_{rot1} , H_{rot} . IR spectra temperature dependencies showed, that up to T_{melt} paraffin molecules are in the completely extended *trans*-configuration. Davydov splitting value of deformation vibrations of methylene chains is characteristic