

Spain, Facultad de Ciencias Físicas y Matemáticas. <sup>b</sup>Universidad de Chile, Santiago, Chile. E-mail: dianez@icmse.csic.es

A set of Cu-30%Zn, Cu-49%Zn, Cu-65%Zn and Cu-86%Zn (that are in composition range of the phases  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\epsilon$ , 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  $\epsilon$  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  $\alpha$  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

#### P.08.04.5

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#### Studies on the Solid State Structures and Properties of Metal Arenedisulfonates

Jiwen Cai, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China. E-mail: pusejw@zsu.edu.cn

Recent progress in the solid state coordination and structural chemistry of aromatic disulfonates, as well as the amine interaction properties of crystalline  $\text{Cd}^{2+}$  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  $\text{Cd}^{2+}$  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

Yuji Ohashi, Manabu Hoshino, Akiko Sekine, Hidehiro Uekusa, Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan. E-mail: yohashi@cms.titech.ac.jp

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.

**Keywords:** excited structure, photoreaction, equilibrium state

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#### X-ray Induced Changes in Organic and Biological Crystalline Materials

Fabrice Camus<sup>a</sup>, C. Besnard<sup>a</sup>, M. Fleurant<sup>a</sup>, I. Margiolaki<sup>b</sup>, P. Pattison<sup>a,c</sup>, M. Schiltz<sup>a</sup>, <sup>a</sup>Laboratory of Crystallography, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland. <sup>b</sup>ESRF, Grenoble, France. <sup>c</sup>Swiss-Norwegian Beamlines, ESRF, Grenoble, France. E-mail: fabrice.camus@epfl.ch

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

Galyna Puchkovska<sup>a</sup>, I. Gnatyuk<sup>a</sup>, E. Kotelnikova<sup>b</sup>, N. Platonova<sup>b</sup>, S. Filatov<sup>b</sup>, <sup>a</sup>Institute of Physics of National Academy of Sciences of Ukraine, 46 pr. Nauki, Kyiv 03022, UKRAINE. <sup>b</sup>St. Petersburg State University, 7/9 Universitetskaya Naberezhnaya, St. Petersburg, RUSSIA. E-mail: puchkov@iop.kiev

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:  $\text{O}_{\text{rot1}}$ ,  $\text{O}_{\text{rot2}}$ ,  $\text{M}_{\text{rot1}}$ ,  $\text{H}_{\text{rot}}$ . IR spectra temperature dependencies showed, that up to  $T_{\text{melt}}$  paraffin molecules are in the completely extended *trans*-configuration. Davydov splitting value of deformation vibrations of methylene chains is characteristic