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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

P.08.04.5

Acta Cryst. (2005). A61, C318

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]

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

P.08.04.6

Acta Cryst. (2005). A61, C318

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.

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Keywords: excited structure, photoreaction, equilibrium state

P.08.04.7

Acta Cryst. (2005). A61, C318

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

P.08.06.1

Acta Cryst. (2005). A61, C318-C319

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

for intermolecular interactions in the monoclinic paraffins. This value sharply decreases in the region of “rotator” phases existence and equals to zero in H_{rot} . A statistic and dynamic model was proposed, which provides an adequate description of the observed effect [2].

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Keywords: *n*-paraffins, polymorphism, X-ray - FTIR

P.08.06.2

Acta Cryst. (2005). A61, C319

Structure and Properties of [4-NH₂C₅H₄NH][BiCl₄]

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The halogenoantimonates(III) and halogenobismuthates(III) of the general formula $R_aM_bX_{3b+a}$ (where R denotes organic cations, X = Cl, Br, I and M = Sb, Bi) form a large group of ferroelectric crystals [1]. The title crystal [4-NH₂C₅H₄NH][BiCl₄] (abbreviation – 4APCB) is closely related to the recently found antimonate(III) analog [4-NH₂C₅H₄NH][SbCl₄] [2], which reveals interesting ferroelectric properties with intermediate incommensurate phases. 4APCB undergoes at 252 K structural phase transition (PT) of first order. The room temperature structure (phase I) is monoclinic, space group Cc with $a = 13.229$, $b = 13.505$, $c = 7.350$ Å and $\beta = 120.31^\circ$. The structure is composed of BiCl₄⁻ ions which form infinite chains through the crystals via chloride linkages. Each bismuth lies in a distorted octahedral environment. The 4-aminopyridinium cation reveals substantial disorder. The low temperature phase (II) is monoclinic, space group P2₁/c with $a = 11.1660(7)$, $b = 13.5857(8)$, $c = 7.2750(4)$ Å and $\beta = 93.777(5)^\circ$. Over the phase II the organic cations are fully ordered. The structural analysis, calorimetric (DSC) and spectroscopic studies (IR) show that the PT is governed by the dynamics of the 4-aminopyridinium cations.

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Keywords: halogenobismuthate(III), disorder, phase transition

P.08.06.3

Acta Cryst. (2005). A61, C319

Structure Transformations in the Saturated Hydrides ZrV₂H₄₋₆

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We have studied, by means of neutron powder diffraction, the structure transformations caused by hydrogen redistributions in the Laves saturated hydrides ZrV₂H_x, 4 < x < 6. In the range of 4 < x < 5, the uncommon order-disorder phase transition has been found [1]. Unlike the known transitions in the unsaturated hydrides, x < 4, it results in change of hydrogen surroundings when hydrogen ordering. As a result, the novel hydrogen superstructure ZrV₂H₅, with the atypical hydrogen surroundings, forms [2]. At maximum hydrogen saturation, near x=6, whatever phase transitions are eliminated. The maximum hydride ZrV₂H₆ exists only as ordered, and any attempt to disarrange the hydrogen results in hydrogen discharge down to x=5. The crystal structure of ZrV₂H₆ has been determined [3]. It is advance of the Spinel-type structure found earlier in the saturated hydrides ZrTi₂H₄ and HfTi₂H₄. The work was partly supported by the Russian Foundation for Basic Research and Russian State Program HIII-2037.2003.2.

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50, 356-357.

Keywords: hydrides, neutron powder diffraction, phase transitions and structure

P.08.06.4

Acta Cryst. (2005). A61, C319

Structure and Phase Transitions of Some Crystals Containing [(CH₃)₃NH₂]⁺ and MeCl₄

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Results of our investigation of crystal structure and phase transitions of some crystals containing a bivalent metal, chlorine anion, and dimethylammonium (DMA) cations are reported. Studies of the crystals are of great interest, since data of the crystal structure of this compound are very scarce and mechanisms of phase transitions in them are not available. It was established that the crystal were grown from solution with copper chlorides have the composition [(CH₃)₂NH₂]₂CuCl₄[(CH₃)₂NH₂]Cl and, in room temperature are describes by orthorhombic space group *Pna*2₁. The structure of the crystals is built of CuCl₄ tetrahedral, three structure nonequivalent DMA groups, and individual chloride ions, which are links via an extended hydrogen bond system into three-dimensional framework. The unit cell parameters are measure as function of temperature. The crystals undergo jump-wise phase transition into incommensurate modulated phase at 279 K and commensurate modulated phase at 253 K, respectively. The result of our studies demonstrated that the crystals obtained from solution containing cadmium were grown in orthorhombic system [(CH₃)₂NH₂]₅Cd₃Cl₁₁ as well as monoclinic system [(CH₃)₂NH₂]₂CdCl₄. The temperature curves of unit cell parameter and the vicinity of phase transition are reported. At room temperature [(CH₃)₂NH₂]₂CoCl₄ belong to the *P2*₁/*c* space group and have ferroelectric properties in the temperature range 227-260 K. The crystals of this family has complicated system of hydrogen bonds and are a great interest because of ordering of hydrogen bonds and changes in cation dynamics pay an important role in the processes of phase transitions.

Russian Foundation supported this study for Basic Research, project no.03-02-16190

Keywords: crystal structure, phase transition, ferroic

P.08.06.5

Acta Cryst. (2005). A61, C319-C320

Striking Effect of Pressure and Temperature on PdSe₂ Allotropes

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Under ambient conditions, PdSe₂ adopts the PdS₂-type structure (o-PdSe₂). Its crystal structure at high pressure (up to 30 GPa) was investigated at 20°C and at 300°C by X-ray energy-dispersive diffraction. Le Bail refinements and ab initio calculations evidenced a solid-solid phase transition to the pyrite-type structure (c-PdSe₂), strongly related to the o-PdS₂. Using the experimental data obtained at 20°C and 300°C, we examined the order of the PdSe₂ phase transition and its dependence on temperature. For this purpose, we calculated and analyzed the thermodynamical potential and the entropy generation by numerically calculating the equation of state.

We also found that the cell volume of c-PdSe₂ was smaller at 300°C than at 20°C by nearly 40%. Such a dramatic decrease in the unit cell volume meant a strong reorganization of the bonding and was suggestive of an incoming phase transition. This possibility has been experimentally confirmed by fledgling high pressure experiments at ESRF. We surprisingly found that the new allotropic phase was a 2D CdI₂-type structure. It probed that all MSE₂ (M=transition metal) structures are linked. We evidenced the interconversion path between