

**DESIGNING ANTHRACENE BASED BINARY SYSTEMS
DEDICATED TO THE SOLID-STATE SYNTHESIS**

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Recently, vigorous search for new synthetic methodologies has been observed in the area of chemistry. It has been found that solid state with conformational restriction of molecules can be effectively used in various non-solvent processes, including solid-state synthesis. Majority of chemical reactions performed in the solvent-free conditions consider chemical transformation (photochemical, thermal etc.) of the single substrate. From the practical reason however, binary systems containing two different partners are of higher significance. Designing crystals of organic and organometallic compounds with appropriate orientation and distances between reacting groups is a new, challenging field in crystallochemistry. We propose the use of supramolecular synthons library (i.e. hydrogen bonding, ionic forces, π - π -stacking etc.) for construction of such materials, dedicated for the non-solvent processes. The presented model system is based on anthracene derivatives that are functionalized in order to form binary crystals, further used for condensation reactions. The result of chemical transformation can be always rationalized on the basis of knowledge of crystal construction.

Keywords: NON-SOLVENT, REACTION, CRYSTAL ENGINEERING

**CHANGES IN SOLID STATE : WHAT CAN BE EXPECTED FROM
CHARGE DENSITY ANALYSIS?**

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Besides accurate structural information, high resolution X-ray diffraction allows the determination of the experimental electron density distribution in crystals. It has been used to derive many information on chemical bonding since the last few decades, especially in the case of metal-ligand and intermolecular interactions. Numerous molecular modifications taking place in solid state, like phase transition, solid state isomerization or neutral-ionic transition, involve structural and/or electronic alterations. Charge density analysis seems a particularly attractive and suited tool to investigate these latter ones. In transition metal complexes, it allows for example to monitor charge transfer effects (ligand-to-metal or metal-to-ligand) or electron redistributions over the atomic d orbitals, correlated to the change of system states. An overview of this approach will be presented, based on preliminary results on spin-crossover iron(II) complexes, in which thermal and light driven solid state changes are followed by charge density analysis. In these systems, the conversion in the solid state from high spin species to low spin below a critical temperature involves large structural modifications associated to important changes in coordination bonding. The analysis of the electron density distribution and its topological properties in both states (high and low spin) should provide new insights on the mechanism of their molecular bistability and spin transition properties. Example systems will be discussed (J. Jętic, ENSCR, Rennes, France), (N. Lugan, LCC, Toulouse, France) and (J.F. Letard et al., ICMCB, Bordeaux, France).

**Keywords: ELECTRON DENSITY MOLECULAR CRYSTAL
TOPOLOGICAL ANALYSIS**

**LIGHT-INDUCED METASTABLE STATES IN NITROSYL-
COMPOUNDS AND THEIR PECULIAR PHYSICAL PROPERTIES**

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Long-living metastable states are very attractive for basic research in the field of electron density and structure as well as for technical applications like holographic data storage. Such metastable states can be excited in nitrosyl-compounds by irradiation with light in the blue-green spectral range cooling below about 260 K. In this presentation it will be shown with different spectroscopic methods the change of the electron density (Moessbauer spectroscopy), the energetic shift of the absorption bands (absorption spectroscopy), the energetic positions of the metastable states (Differential Scanning Calorimetry), the structural problems (neutron diffraction) and data storage using holography.

Keywords: LIGHT INDUCED METASTABLE STATES

PHASE RELATIONS IN THE Sr-Re-O SYSTEM

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A new complex oxide, Sr_3ReO_6 , has been synthesized using ceramic techniques in an evacuated silica tube under controlled partial oxygen pressure $p(\text{O}_2) = 4.6 \times 10^{-17}$ bar at 700°C for 48h. The Sr_3ReO_6 compound has a C-centered monoclinic cell with $a = 10.013(1)$ Å, $b = 17.717(2)$ Å, $c = 10.0928(9)$ Å; $V = 946$; $\beta = 107.644(9)^\circ$ and adopts a new type of perovskite structure distortion with Sr and Re ordered on the B-sites in 'rock-salt' manner. This compound is stable in the narrow range of partial oxygen pressure from 4.6×10^{-17} to 2.3×10^{-15} bar only. at a higher partial oxygen pressure the Sr_3ReO_6 oxide decomposes to a mixture of SrO and $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$. The formal Re valence in Sr_3ReO_6 increases from +6 to +6.5 due to a formation of cation vacancies in the A-sublattice, that leads to a change in the coordination number of the Sr atoms in the B-sublattice from 6 to 8. A further increase of the partial oxygen pressure to 1.1×10^{-3} bar leads to decomposition of $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$ to $\text{Sr}_5\text{Re}_2\text{O}_{12}$ and SrO. In this case all Re atoms with the oxidation state +6 in $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$ are oxidized to Re^{7+} , and vacancies in the B-sublattice are formed. This oxidation sequence can be considered as a stepwise increase of the amount of cation vacancies in the A- and B-sublattices from $\text{Sr}_6\text{Re}_2\text{O}_{12}$ through $\text{Sr}_{5.5}\text{Re}_2\text{O}_{12}$ to $\text{Sr}_5\text{Re}_2\text{O}_{12}$. Sr_3ReO_6 orders with a weak ferromagnetic component below the Curie temperature of $T_C = 10$ K. Hysteresis loops were observed at different temperatures: 5.0, 7.0 and 9.0 K.

**Keywords: PEROVSKITE DISTORTION, FERROMAGNETIC
ORDERING, TERNARY RHENIUM OXIDE**