

SLS Symposium on Novel Materials

Tuesday, June 3, 2014

10:00 to 12:15, WBGB/019

10:00 In-situ crystallization of GeTe/GaSb phase change memory stacked films

Alin Velea, C.N. Borca, G. Socol, D. Grolimund, M. Popescu, J.A. van Bokhoven

10:30 Novel Metal-Organic Frameworks with Phosphine Functional Groups: Synthesis, Characterization and Applications in Metal-Supported Catalysis

Flavien L. Morel, X. Xu, M. Ranocchiari, J.A. van Bokhoven

11:00 Coffee

11:15 Investigation of high-pressure phases of $[\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})]$ with synchrotron powder X-ray diffraction

Arianna Lanza, M. Fisch, N. Casati, C. Fiolka, K. Krämer and P. Macchi

11:45 Nano-characterization of organic semiconductors

Peter Warnicke, N. Pilet, B. Watts, R. Fink, and J. Raabe

In-situ crystallization of GeTe/GaSb phase change memory stacked films

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Single and stacked phase change memory structures based on GeTe and GaSb thin films were deposited by pulsed laser deposition (PLD). Depending on the annealing temperature, different behavior was observed in the case of the single and the stacked structures. The as-deposited GeTe thin films were amorphous and crystallized after the annealing at transition threshold while the as-deposited GaSb films were partially crystalline and fully crystallized after reaching the transition temperature. Electrical resistance vs. temperature investigations using the four points probe method showed transition temperatures of 129 °C and 198 °C for the GeTe and GaSb thin films. X-ray diffraction measurements on the in-situ annealed GeTe/GaSb multilayer showed that the crystallization of GeTe initiates the crystallization of GaSb and decreases its crystallization temperature by 30 °C. In order to confirm the results, additional diffraction measurements were performed on ex-situ annealed stacked films at various temperatures below and above their transition temperature. Ge, Te and Sb phase segregations at high annealing temperatures were found whereas no mixing of the stacked films was observed even for long ex-situ annealing time. Extended X-ray absorption fine structure (EXAFS) measurements at the Ga and Ge K-edges revealed changes in their local atomic environments as a function of the annealing temperature. Simulations unveil a tetrahedral configuration in the amorphous state and octahedral configuration in the crystalline state for Ge atoms while Ga is four-fold coordinated in both states.

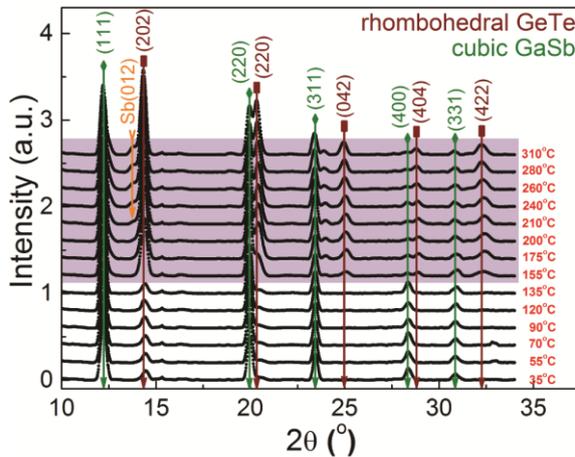


FIG. 1. The XRD spectra of the GeTe/GaSb stacked film, during the in-situ annealing between 35 °C and 310 °C. The crystallization of GeTe occurs at 149 °C (highlighted).

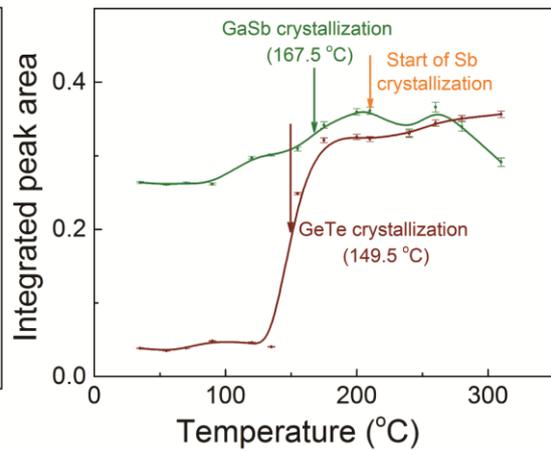


FIG. 2. The normalized integrated area of the GaSb (111) (green) and GeTe (202) (brown) peaks. The crystallization of GeTe activates the crystallization of GaSb. Sb starts to crystallize at 210 °C, diffuses into the GaSb matrix producing Ga – Sb bond breaking and the reduction of the GaSb crystalline phase.

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Novel Metal-Organic Frameworks with Phosphine Functional Groups: Synthesis, Characterization and Applications in Metal-Supported Catalysis

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Metal-organic frameworks (MOFs) are nanoporous coordination polymers, which attract great interest due to their potential applications in gas sorption, biomedical application and catalysis.[1] Their well-defined structures and flexibility toward the incorporation of chemical functional groups make MOFs ideal candidates for metal-supported catalysis.[2] Recently, phosphine functional groups have been incorporated into different MOFs topologies.[3] Organophosphines are well-known ligands in organometallic chemistry and are widely used to fine-tune the steric and electronic properties of a catalyst. Their incorporation into MOFs provides unique opportunities for the design of single-site catalysts.

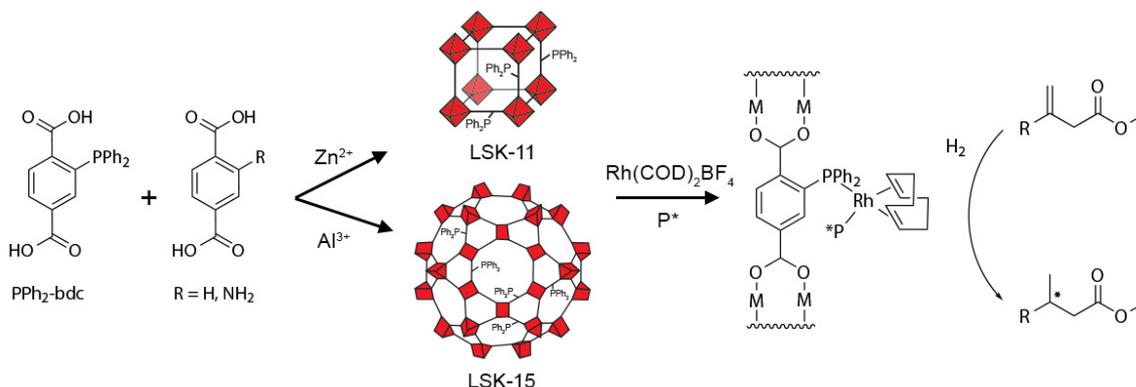


Figure 1. General strategy for the synthesis of phosphine-MOFs based on PPh₂-bdc.

Here, we present a series of novel phosphine-functionalized MOFs based on a substituted terephthalic acid (PPh₂-bdc).[4] We will demonstrate how NMR and X-ray absorption spectroscopy can be used to characterize subsumed phosphorus nuclei in the solid state. Finally, we will also illustrate that these structures act as support for organometallic complexes and can be applied for Rh-catalyzed asymmetric hydrogenation of olefins.

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Investigation of high-pressure phases of $[\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})]$ with synchrotron powder X-ray diffraction

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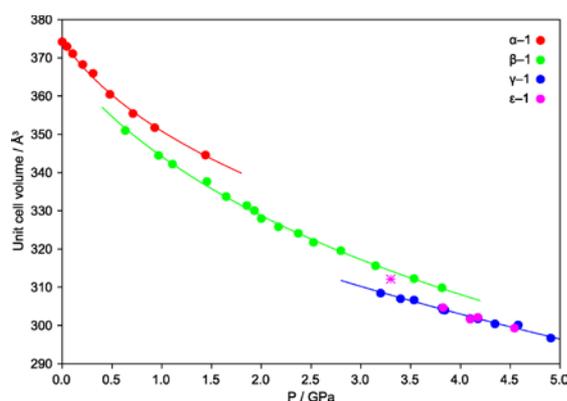
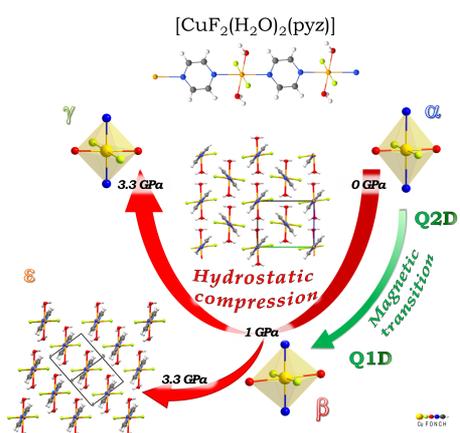
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In recent years, the interest for the behaviour of matter at non-ambient conditions and in particular at high pressure, has widely expanded from its original field of application (geosciences) towards the field of active materials in general. As a matter of fact, varying the pressure is a way to explore different thermodynamic conditions as much as varying the temperature, and therefore a way to induce changes in the structure and properties of the materials. The structure of crystalline materials (as powder or single crystals) under high pressure can be studied with X-ray diffraction using diamond-anvil cells, and in the case of powder diffraction synchrotron radiation is necessary.^[1]

The linear coordination polymer $[\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})]$ (pyz = pyrazine) is an ideal candidate to investigate the variation of the material properties as a function of pressure induced modifications of the coordination environment. In recent years, several crystallographic, magnetic and spectroscopic investigations have been carried out on it at “extreme conditions”, revealing the occurrence of many phase transitions, some of which induce important changes in the dimensionality of the magnetic exchange network.^[2-4] New single-crystal and powder X-ray diffraction experiments evidenced the occurrence of different phases at the same pressure value. Synchrotron powder X-ray diffraction was used to investigate the pressure space in small steps, in order to define the stability field of every phase. Coexistence of phases as well as shift of transition pressure values was observed depending on the experimental conditions and in particular on the pressure gradient applied.



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Nano-characterization of organic semiconductors

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Organic semiconductors show great promise as a replacement of conventional electronics due to their solution-based processability. However, with the convenience of solution-based processing comes the challenge of maintaining a well-defined structure. As the electronic properties of organic semiconductor devices are strongly dependent on both the chemical composition and local microstructure it is important to employ experimental techniques that provide information on both of these characteristics. Currently, such techniques are lacking and hence there is a great need for more complete characterization tools. Here, I will present a novel instrument "NanoXAS" which combines two powerful techniques, scanning probe microscopy (SPM) and x-ray absorption spectroscopy (XAS), in order to fully characterize organic semiconducting materials and devices. On one hand, SPM can measure physical properties such as sample topography, elasticity, adhesion, friction, electrostatic and magnetic properties with nanometer resolution [1]. Meanwhile, XAS provides access to the local chemical composition, electronic structure, molecular orientation, order, and absolute density. The instrument consists of a scanning probe microscope and a scanning transmission x-ray microscope (STXM). Owing to the coaxial design of the instrument several detection modes can be utilized simultaneously as a semi-transparent sample is scanned through the x-rays to provide real-space multidimensional datasets including element sensitivity. To demonstrate the function of the instrument, measurements on polymers, polymer blends, and lithographically defined nanostructures will be shown.

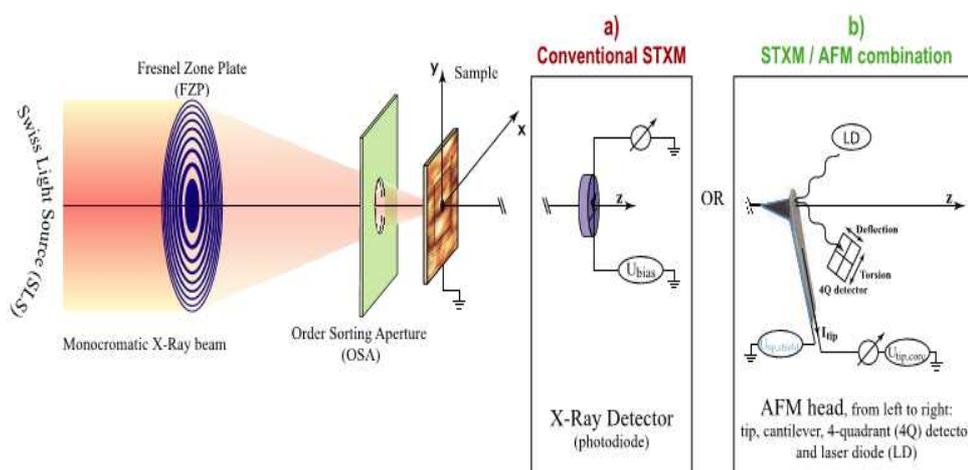


Figure 1. Operational modes of the instrument.

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