[b]University of Ulm, Institute of Inorganic Chemistry – Materials and Catalysis, Albert-Einstein-Allee 11, 89081 Ulm, (Germany). E-mail: frederik.bachhuber@chemie.uni-r.de

There is a big variety of structure types for MPn_2 (Pn = N, P, As, Sb, Bi) compounds with promising properties. Pyrite-type SiP_2 served as a model compound for DFT calculations on electronic structure in both direct and momentum space as well as IR- and Raman spectra [1] [2]. The calculations were extended to the system $SiP_{2-x}As_x$ where P was successively substituted by As [3]. An ordering scheme derived from the pyrite structure type according to [4] resulted in hetero- and homoatomic dumbbells with the first clearly preferred over the latter due to dipole momentums from the charges of P (-0.8 e) und As (-0.3 e).

Here we present an extension of the calculations to different structure types not only with dumbbell but also with strand-like structures. In addition to the system $SiP_{2-x}As_x$, related compounds with either different metal or different pnictogen atoms were taken into consideration. New ordering schemes could be derived leading to the occurrence of distinct preferences and tendencies within the 5th main group. With a special focus on the 1:1:1 stoichiometry, the examined compounds were evaluated in terms of thermodynamic stability and hence the possibility of being capable of synthesis.
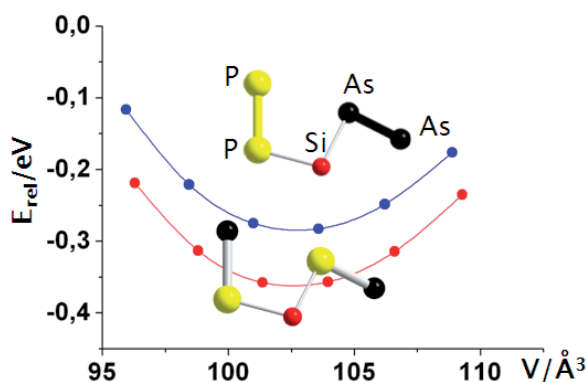

Fig. 1: Energy vs. volume plot of different structural variants of SiPAs derived from the marcasite structure type.

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Keywords: modelling, bonding, ordering

MS76.P07

Mercury-ordering in $Hg_3S_2Cl_2$ polymorphs

Florian Pielnhofer,[a] Frederik Bachhuber,[b] Jan Rothballer,[a] Richard Weihrich,[ab] [a]University of Ulm, Institute of Inorganic Chemistry – Materials and Catalysis, Albert-Einstein-Allee 11, 89081 Ulm, (Germany). [b]University of Regensburg, Institute of Inorganic Chemistry, Universitätsstr. 31, 93040 Regensburg, (Germany). Email: florian.pielnhofer@uni-ulm.de

The crystal structures of different modifications of mercury chalcohalides $Hg_3Ch_2X_2$ (Ch = S, Se, Te; X = F, Cl, Br, I) were first investigated in the 1960s. All of these structures can be described in terms of cationic $Hg_3Ch_2^{2+}$ partial structures. Different linking of ChHg₃

trigonal pyramids leads from zero-dimensional clusters over one-dimensional polymers and two dimensional layers to three-dimensional networks [1], [2], [3], [4], [5], [6]. Another possibility to understand the structures of those ternary compounds is the description as ordered half-antiperovskites, where only ½ of perovskite O-sites is occupied with Hg-atoms [7]. The mercury ordering with respect to primitive X-supercells points out the structural relation to cubic perovskite $SrTiO_3$ and allows for a systematical understanding of the whole family of the 3:2:2 mercury sulfo-, seleno- and tellurohalogenides which crystallize in a variety of different crystal systems.

There is a large amount of possibilities to synthesize $Hg_3S_2Cl_2$, but a specific reaction control is still missing.

The investigation of the relative and thermodynamic stabilities of those structures with DFT methods includes the newest polymorph (δ) [8] and leads to the prediction of more potential structures.

The chemical nature of the heavy element Hg requires calculations at a full relativistic level. To gain insight into the bonding situation, band structure calculations with the full potential local orbital method (FPLO) [9] have been performed and partial densities of states have been analysed.

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Keywords: superlattice, ordering, relativity

MS76.P08

Computational study with combined X-ray structure of dioxidom olybdenum(VI)Compound

Batoul Sheikhshoaie[a] Iran Sheikhshoaie,[b] [a]South of Kerman Electric Power Distribution Company, Jomhoury Blvd, Kerman (Iran). [b]Chemistry Department of Shahid Bahonar University of Kerman, (Iran). E-mail: ishoaie@gmail.com

The geometry of Methanol {6-[(2-oxidopropyl)iminometh-yl]phe nolato}dioxidomolybdenum(VI) complex optimized in the gas phase using density functional theory calculations. The agreement between theoretical and experimental data is for this metal complex. The electronic excitation energies and oscillator strengths f calculated by B3LYP/DZP method for this complex are summarized in this work. The longest wavelength transition is belonging to HOMO-LUMO with n→π*character [[(the percentage composition of the lowest unoccupied and highest occupied molecular orbital levels for this compound are: For HOMO level, %Mo=0, %O=2.24(p_x)+6.52(p_y)+ 13.04 (p_z), N=1.71(p_y)+3.24(p_z) and %C=18.6(p_y)+ 43.41(p_z). For LUMO level, %Mo=30.52(d_{xz})=, %O=17.05(p_x), %N=2.22(p_y)+8.46(p_z) and %C=8.73(p_y)+ 22.22(p_z)].

In the structure of the title compound, which was characterized by X-ray crystal analysis, and it has monoclinic space group $p2_1$/c, and a= 10.330(17) Å, b= 9.397(15) Å, c= 13.695(2) Å, V= 1252.1(3) Å³, and Z= 4. B3LYP theoretical method with DZP basis sets calculations nicely reproduces the X-ray experimental geometry, molecular orbital levels and the other structural properties for this complex.

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**Keywords: Mo(VI) complex, DFT, theoretical study, B3LYP**

MS77.P01

Photoinduced conductivity change and structure transformation.

Kiyotaka Asakura,[a] Takeshi Miyamoto,[a] Toshio Naito,[b] Yoshinori Kitajima[c] *[a]Catalysis Research Center, Hokkaido University, Sapporo, (Japan). [b]KEK-IMSS-PF, Tsukuba, (Japan). [c]Department of Chemistry, Hokkaido Universiy, Sapporo, (Japan).* E-mail:askr@cat.hokudai.ac.jp

$Ag(DM)_2$ is a metallic conductor with one-dimensional column. The conductivity and electronic structure are modified by the irradiation of UV Vis light. The electronic conductivity can be controlled from the metallic, semiconductor to insulator region only by the photo-irradiation and thus the $Ag(DM)_2$ is a promising material for the single material electronic device. We have investigated the origin of the photo-induced conductivity change by Ag K and $L_{2,3}$ edges EXAFS and XANES.

Figure 1 shows the Fourier transforms of Ag K-edge EXAFS. Fig.1 a shows the pristine $Ag(DM)_2$. Three peaks appeared corresponding to Ag-N, Ag-(N=), and Ag-(N=C)-N, respectively. Fig.1 c shows the insulator phase where only one Ag-N distance was found. XRD suggested the amorphous phase was formed. The disorder in the local structure around Ag broke the conduction path to convert the $Ag(DM)_2$ to insulator. In the other word, the insulator phase was produced by the vitrification of the crystalline structure.

Fig.1 b shows the semiconductor phase. There are three peaks similar to that in pristine. However, small modifications were found in the first and third peaks. Curve fitting analyses demonstrated that the formation of small number of shorter Ag-N bond. Thus the $Ag(DM)_2$ molecular structures were collectively modified and small part of the $Ag(DM)_2$ was involved in the modified structure domains. The boundary between original and modified domains form the conduction barrier for the electron and the semiconductor was formed.
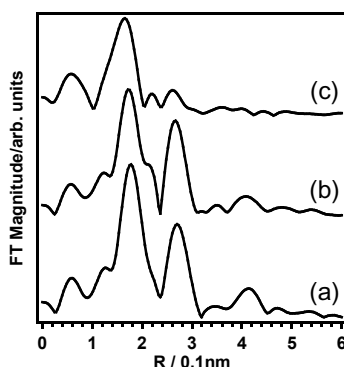
Figure.1 Fourier transforms of (a) pristine conductor, (b) semiconductor and (c) insulator Ag(DM)$_2$

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Keywords: XAFS, Ag(DM)2, photo-induced conduction change

MS77.P02

Industrial applications at the national synchrotron light source

Jun Wang, Vivian Stojanoff, *National Synchrotron Light Source, Photon Science Directorate, Brookhaven National Laboratory, Upton NY 11973.* E-mail: junwang@bnl.gov.

Synchrotron light provides an unique source of non-destructive methods for material characterization. At the National Synchrotron Light Source the industrial program benefits from a large collection of tools to analyze a wide range of materials. Embracing spectroscopic and diffraction methods it is possible to characterize a sample from molecular to atomic levels. Diffraction powder and macromolecular crystallography are typical examples providing useful tools for drug design. X-ray absorption spectroscopy are widely used by our industrial users in their quest to develop better batteries and catalysis studies. Specific examples will be presented and discussed in light of the needs of the industrial researcher.

Keywords: synchrotron, industrial applications, spectroscoy, diffraction

MS78.P01

The particular mechanisms of DNA recognition and dimerization of MITF

Vivian Pogenberg,[a] Morlin Milewski,[a] Viktor Deineko,[a] Alexander Schepsky,[b] Eirikur Steingrimsson,[b] Matthias Wilmanns,[a] *[a]EMBL-Hamburg, c/o DESY, Notkestrasse 85, 22603 Hamburg, (Germany) [b]Department of Biochemistry and Molecular Biology, Faculty of Medicine, University of Iceland, 101 Reykjavik, (Iceland).* E-mail: vivian@embl-hamburg.de

The Microphthalmia-associated Transcription Factor (MITF) is a key regulator of the expression of pigment-cell specific genes in melanocytes, the mature pigment producing cells of the skin and hair follicles. Moreover, in the past few years, MITF became one of the most studied macromolecule in the investigation of the mechanisms leading to melanoma, a particular skin cancer.

MITF is a member of the superfamily of basic Helix-Loop-Helix leucine zipper transcription factors (b-HLH-Zip). Like other b-HLH-Zip factors, MITF can bind a subset of the canonical palindromic E-box sequence (CANNTG) as well as related asymmetric motives like the M-box (TCATNTG); nevertheless the exact mechanism in which MITF recognizes the correct promoters of target genes is not yet fully elucidated. Within the b-HLH-Zip family, MITF can associate with the Tfe factors, but no heterodimeric complexes containing MITF and the related Myc, MAX or USF-1 have been observed, raising the question how this discrimination is achieved.

We solved three crystal structures: the one of MITF in absence of DNA and two structures of MITF in complex with DNA duplexes encompassing two different target motives (E-box and M-box). In addition, we analyzed interactions between these DNA motives and several MITF mutants with documented phenotypes in mice, using different techniques such as Isothermal Titration Calorimetry, Transactivation assays and EMSA. The comparison of our structural, biophysical and functional data together with available biological data reveals the particular mechanism of DNA recognition by MITF and how MITF discriminates between the E and M boxes. In addition, our data demonstrate an unusual mode of dimerization that might explain how MITF selects its heterodimerization partners.

Keywords: transcription, DNA, interactions.