[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.
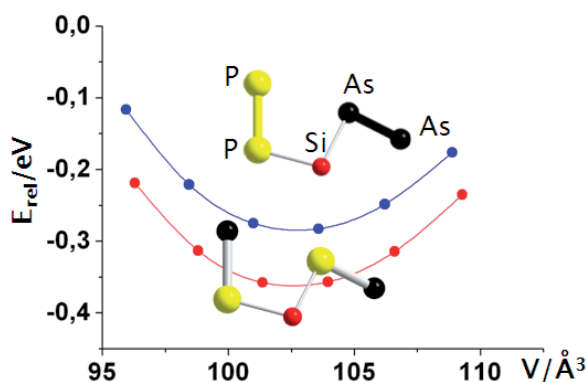

Fig. 1: Energy vs. volume plot of different structural variants of SiPAs derived from the marcasite structure type.

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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 ChHg$_3$

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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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_y)+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) Å^3, 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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