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Lecture

SOFT-MATTER-LIKE PROPERTIES AND REACTIVITY OF MOLECULAR CRYSTALS

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Elastic materials that are capable of stimuli-induced mechanical reconfiguration are indispensable for fabrication of mechanically tunable elements for actuation, including flexible electronics, artificial muscles, and microfluidics parts. The advanced materials that will qualify for these applications in the future must fulfill an extended list of requirements including reversible, rapid and controllable response that is proportional to the applied stimulus, and fatigueless operation over prolonged periods of time.

Despite that elasticity is counterintuitive for crystals, there is an increasing number of reports of serendipitous observations of molecular single crystals that can hop, leap, bend, curl, crawl, expand, contract, twist, spin, explode, split, roll, or respond otherwise to external stimuli akin to soft, mesophasic materials. These ***dynamic crystals*** provide extreme and visually impressive demonstrations of the mechanical strain that can accumulate in the interior of molecular crystals and be released as mechanical energy. Mechanically reconfigurable molecular crystals—ordered materials that can adapt to variable operating and environmental conditions by deformation, whereby they attain motility or perform work—are quickly shaping up a new research direction in materials science, ***crystal adaptronics***. Properties such as elasticity, superelasticity and ferroelasticity that are normally related to inorganic materials, and phenomena such as shape-memory and self-healing effects which are well established for soft materials, are now being reported for molecular crystals, yet their mechanism, quantification, and relation to the crystal structure are not immediately intelligible to the wider materials science research community. At the current stage of the understanding of their mechanical properties, the type of mechanical response from these materials remains hardly predictable, although it almost always is a result of the interplay between disintegrative and restorative factors.

This lecture will provides a condensed overview of the dynamic and self-healing single crystals, emerging new classes of materials that bridge the gap between the soft matter and inorganic materials. The occurrence and detection of their unconventional properties, and the underlying structural features of the related molecular materials will be discussed and highlighted together with prominent recent examples.

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THERMODYNAMICS AND KINETICS OF DEGRADATION REACTIONS IN SOLID-STATE BATTERIES

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While recent research has shown considerable progress in the increase of room temperature conductivity of lithium solid electrolytes, the interface kinetics of anodes and cathodes in SSLB still needs to be improved. In particular, the kinetics and the stability of the lithium metal anode still requires improvement. Also the stability of the best solid electrolytes – currently lithium thiophosphates – at the cathode side causes problems and requires interface modifications or protecting films. In this lecture the current knowledge on the interface stability and kinetics of thiophosphate based electrolytes will be reviewed. As all relevant electrode materials show volume changes during charge/discharge, the electrode interfaces not only suffer from (electro-)chemical degradation – but also from chemo-mechanical effects. In order to illustrate the role of mechanical effects during battery operation, I will present own data from thiophosphate based SSLB.

Financial support by BMBF (projects BENCHBATT and FELIZIA) and by BASF SE (International Network for Batteries) is gratefully acknowledged.

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RECENT PROGRESS IN GARNET-TYPE LITHIUM-ION CONDUCTING OXIDE MATERIALS

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Li-ion batteries (LIBs) are widely used for the rechargeable battery system from small-sized electric devices including smartphones to large-scaled power sources such EVs. However, they are required to be improved from a view point of higher safety and energy density for next generation LIBs. Especially, all-solid-state LIBs using oxide-type solid electrolyte have attracted attention as advanced LIBs without inflammable organic liquid electrolytes. There are many candidates of Li-ion conducting oxides as solid electrolyte materials for all solid-state LIBs, such LISICON-type phosphates and perovskite-type titanates. Recently, the garnet-type Li7La3Zr2O12 (LLZO) and the chemical variants are attracting the most attentions, after the first report of good lithium-ion conductivity by Prof. Weppner's group. LLZO has some advantages in lithium ion conductivity, chemical stability and wide electrochemical potential windows. In order to improve the Li-ion conducting properties of the garnet-type LLZO, a large number of studies on the chemical substitution using various cation species has been reported. Among them, Ta-doped LLZO exhibits a relatively higher Li-ion conductivity (c.a. 10^{-4} S cm^{-1} at room temperature). Recently, we extensively investigated the synthesis, crystal structure and electrochemical properties of Al-free $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ [1,2]. We successfully synthesized centimeter-sized single crystal specimens using zone-melting growth technologies [3]. The precise crystal structure including lithium-ion migration pathway was determined using single-crystal neutron diffraction data. On the other hand, low temperature synthesis of electrolyte materials is a key technology to fabricate electrolyte and/or composite electrode materials by co-firing method, because of the reactivity between electrolyte and electrode compounds at high temperatures. From this view point, we developed a novel low temperature synthetic process of $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ using a precursor material below 500 °C [4].

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Crystalline $Ba_{1-x}Ca_xF_2$ ($0 \leq x \leq 1$) prepared by ball milling: formation and quasi super-ionic conduction

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Fluorite-type $Ba_{1-x}Ca_xF_2$ shows a large miscibility gap between $x \approx 0.04$ and $x \approx 0.97$ at ambient temperature. Although solid solutions are formed up to $x \approx 0.60$ at a temperature of ca. 1270 K, they decompose on cooling. Also fast cooling leads to decomposition. For larger x even at high temperatures no phase pure $Ba_{1-x}Ca_xF_2$ could be observed.[1] However, the miscibility gap can be closed by low-temperature atom beam deposition, resulting in amorphous $Ba_{1-x}Ca_xF_2$ which can be turned into crystalline $Ba_{1-x}Ca_xF_2$ by annealing, pointing to non-diffusive crystallisation.[2] Another way to close the miscibility gap is ball milling of mixtures of BaF_2 and CaF_2.[3,4] At temperatures above ca. 700 K these labile solid solutions decompose[2,4]. Since also miscibility gaps of other fluoridic systems can be closed by ball milling mixtures of its constituent binary fluorides[5], it seems likely that ball milling in general enables non-diffusive crystallisation. As it turned out, the crystalline $Ba_{1-x}Ca_xF_2$ prepared by ball milling shows a by several orders of magnitude increased F ion conductivity, compared to its binary parents, with a broad conductivity maximum and an activation energy minimum at $x \approx 0.50$.[3,4] Using experimental techniques and molecular dynamics simulation we concluded that the origin of this conductivity increase is a decrease of migration activation energies due to geometric frustration.[4] Geometric frustration can be understood as the impossibility to build a perfect crystal structure from non-matching building units like the $Ba_{1-y}Ca_yF$ (y = 0, 1, 2, 3, or 4) tetrahedrons, leading to a locally highly disordered structure ('antiglass' structure[6]) in which interionic distances and coordination numbers deviate from their ideal values found in the non-frustrated crystals. Hence, a variety of local energetic minima for the ions are created, decreasing the migration activation energy for the F ions. As a consequence, $Ba_{1-x}Ca_xF_2$ exhibits the properties of a superionic fluorite already at low temperature which comprise: a disordered anion sublattice, excess volume, high ionic conductivity, low migration activation energy and collective ion transport.[4] The emergence of collective ion transport can be understood as homogeneous melting of the anion sublattice.[4,7]

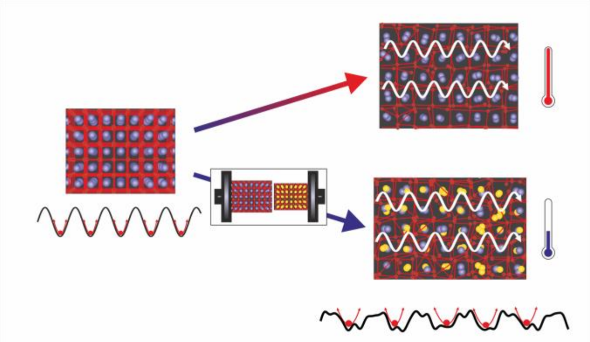

Fig. 1 BaF_2 can be turned into a geometrically frustrated system and, thus, superionic state by increasing its temperature or by introducing CaF_2 into its structure.

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NON-EQUILIBRIUM PHASE TRANSITIONS IN ELECTRODE MATERIALS OF METAL-ION BATTERIES STUDIED BY OPERANDO DIFFRACTION AND SPECTROSCOPIC TECHNIQUES

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Application of different diffraction and spectroscopic techniques to *operando* studies on the electrode materials became an integral part of the metal-ion battery research. Diverse material's properties can be monitored in *operando* regime: the electrochemical mechanism (single-phase intercalation vs two-phase intercalation, conversion reaction, pseudocapacity), phase transformations and stability, crystal structure transformations, volume change between the charged and discharged states, oxidation states of the involved atomic species (i.e. d-metals and oxygen), local crystal and electronic structure etc. A vital need in the *operando* methods stems from their inherent advantage in studying the electrochemical response of the materials at the non-equilibrium dynamic conditions mimicking a real battery. As an example, for olivine-type cathode materials application of X-ray diffraction in *operando* regime revealed a number of intriguing properties, e.g. dependence of the phase transformation behavior during Li^+ (de)intercalation on particle's size, charge/discharge rate and composition in d-cation sublattice [1-3].

To successfully meet the challenge of comprehensive *operando* studies of different types of materials at different regimes, we created a novel type of synchrotron electrochemical cell [4]. Single crystal sapphire X-ray windows provide good signal-to-noise ratio, excellent electrochemical contact because of constant pressure between the electrodes and perfect electrochemical stability at high potentials due to the inert and non-conductive nature of the sapphire windows. A number of diffraction and spectroscopic experiments was performed using the cell. We studied phase transitions, crystal structure evolution, changes of valence state and local coordination of Fe and other cations in phosphate, flouruphosphate and oxide materials for Li-ion and Na-ion batteries. The obtained results will be discussed in details in the present report.

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OPERANDO X-RAY DIFFRACTION INVESTIGATION OF ELECTROCHEMICAL REACTIONS WITH VANADIUM-CONTAINING PHOSPHATES AS ELECTRODES FOR Na-ION BATTERIES

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Polyanionic materials (phosphates in particular) are of special interest as positive electrodes for Li-in or Na-ion batteries since they offer competitive electrochemical performances compared to sodiated or lithiated transition metal oxides [1]. Polyanionic crystal structures of Na- or Li-containing materials are based upon stable *3D* frameworks, which provide long-term structural stability and demonstrate a unique variety of atomic arrangements in their crystal structures. Recent electrochemical and structural investigations of vanadium-based phosphate compounds ($LiVPO_4O$ - $LiVPO_4F$ [2], $Na_3V_2(PO_4)_2F_3$ [3], $Na_3V_2(PO_4)_3$ [4]…..) , revealed promising perspectives for these chemical systems.

In order to get in-depth understandings of theses materials, a series of new phases was synthesized and characterized by single crystal and *operando* powder X-ray diffraction analyses using laboratory and high-resolution synchrotron X-ray sources, as well as neutrons.

In this presentation, the electrochemical performance of $Na_3V_2(PO_4)_2F_{3-y}O_y$ compositions [5-7] in Na-ion batteries will be discussed in details. We also investigated the substitution of a part of vanadium by aluminum, iron or manganese in several alternative crystal structures. As a result of our work, we discovered and electrochemically characterized a novel mixed-valence $Na_{11}V^{3+}(V^{4+}O)(P_2O_7)_4$ compound, a new composition $Na_3V^{III}(PO_4)_2$ and two groups of new M^{3+}-substituted phases, namely, $Na_7V_{4-x}Al_x(P_2O_7)_4(PO_4)$ [8] (x = 2 and 1) and NASICON-type $Na_{3\pm y}V_{2-x}M_x(PO_4)_3$ (M = Al, Ti, Mn, Fe).

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Electrochemistry with Fluoride Ions: A Facile Route for the Topochemical Modification of Oxides and Oxyfluorides

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Topochemical fluorination of oxide materials, e. g., compounds with Ruddlesden-Popper type structure, became of increasing interest after the discovery of superconductivity in cuprate compounds [1]. Such fluorination reactions can be performed via a variety of reagents, e. g., gaseous F_2, XeF_2, NH_4F, PVDF, and metal fluorides. All reaction types have certain advantages and disadvantages, and the fluorination agent must be well adjusted to the respective oxide under investigation [2].

All-Solid-State Batteries are currently investigated for their potential of possessing increased intrinsic safety. Apart from the field of lithium ion systems, such batteries can also be based on a shuttling of fluoride ions [3] in a fluoride ion battery (FIB), see Fig. 1. In our group, we examine the potential to develop intercalation based electrode materials for such FIBs, and we found that the battery setup is well suitable to be used for electrochemical topochemical fluorination and defluorination reactions.

In this talk, we will show that the electrochemical reactions can contribute to a deeper understanding of the fluorination chemistry of such systems, which can be further complemented by DFT based calculations. We will show that the setup is suitable for the oxidative insertion of fluoride ions into anion-deficient perovskites [4], Ruddlesden-Popper type compounds [5, 6], or compound with schafarzikite type structure [7]. By appropriate choice of starting materials, fluorination potentials and charging time, the degree of fluorination can be well controlled, and high transition metal oxidation states can be obtained.

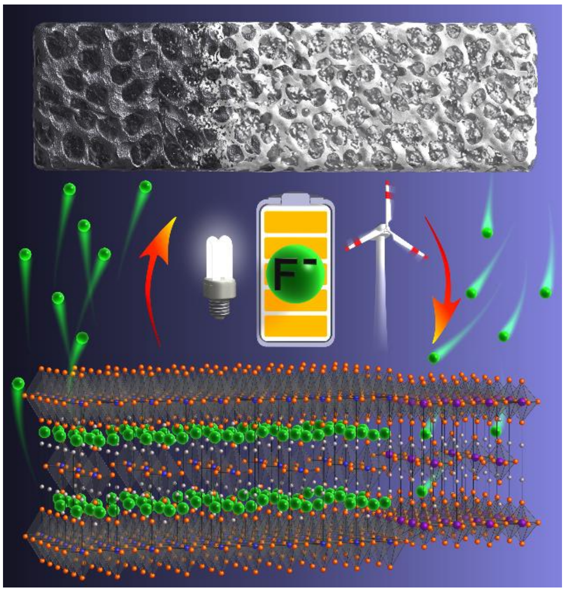

Fig. 1. Working scheme of a fluoride ion battery using a Pb/PbF_2 electrode as counter-electrode, https://pubs.acs.org/toc/cmatex/29/8

The electrochemical setup is not only suitable for oxidative fluorination reactions, but can also be used for the reductive defluorination of materials. By this, new compounds can be synthesized, which are hard to be approached via chemical routes. We will exemplify this on the electrochemical defluorination of $La_2NiO_3F_2$ to $La_2NiO_3F_{2-x}$ ($0 < x \leq 1$), which goes under the formation of low valent Ni^+ species.

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EPITAXIAL ELECTRODEPOSITION OF ELECTRONIC AND PHOTONIC MATERIALS UNTO WAFER-SIZE SINGLE CRYSTAL GOLD FOILS FOR FLEXIBLE ELECTRONICS

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Single-crystal silicon (Si) is the bedrock of semiconductor devices due to the high crystalline perfection that minimizes electron-hole recombination, and the dense SiO_x native oxide that minimizes surface states. There is interest in moving beyond the planar structure of conventional Si-based chips to produce flexible electronic devices such as wearable solar cells, sensors, and flexible displays. Most flexible electronic devices are based on polycrystalline materials that can have compromised performance due to electron-hole recombination at grain boundaries. In order to expand the palette of electronic materials beyond planar Si, there is a need for both an inexpensive substrate material for epitaxial growth, and an inexpensive and scalable processing method to produce epitaxial, grain-boundary-free films of metals, semiconductors, and optical materials. Recently, in our laboratory, we have developed a process for producing wafer-size, flexible, and transparent single-crystal Au foils by an electrochemical processing method.[1] The processing scheme is shown in Fig. 1. Au is epitaxially electrodeposited onto Si using a very negative applied potential. An interfacial layer of SiO_x is then produced photoelectrochemically by lateral undergrowth. The Au foil is then removed by epitaxial lift-off following an HF etch. We will report on the electrodeposition of epitaxial films of metal oxide semiconductors such as Cu_2O and ZnO onto the highly-ordered Au foils. We will also present new, unpublished results in which we spin-coat epitaxial films of perovskites, such as $CsPbBr_3$, directly onto these Au foils and onto other single crystals.

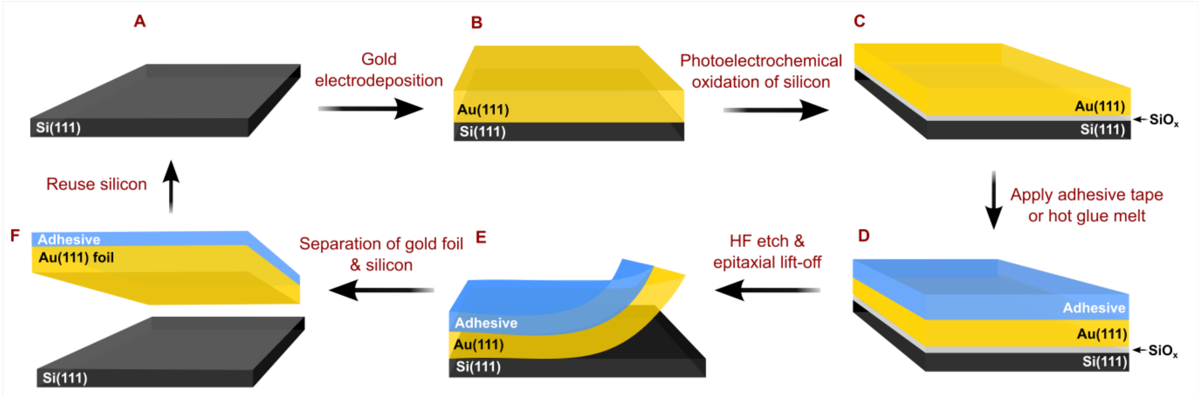

Fig. 1 Processing scheme to produce wafer-size, single-crystal Au foils by epitaxial lift off.

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ELECTROCHEMICAL SYNTHESIS OF THE FUNCTIONAL OXIDE MATERIALS

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Two essentially different types of oxide electrodeposition processes are compared: (1) the direct electrocrystallization and (2) electrochemically induced deposition.

The processes of type (1) are highly controllable because nucleation and growth of oxide is controlled by the electrode potential, can be effectively monitored by means of current-time responses, and the quantity of the product can be calculated from electric charge spent for deposition. The accuracy of coulometric techniques is high enough to control even submonolayer quantities. Well-known industrial processes of type (1) form a basis for technologies of lead and manganese oxides. Many other oxides can be fabricated by means of anodic or cathodic electrocrystallization (examples will be presented for deposition of Cu, Tl, V, W, Mo, Re, Co, Fe oxides from aqueous solutions, and also from certain melts). The most general requirement to deposition solution consists in the essential difference in solubility of reduced and oxidized species. The choice of deposition mode depends on minimization of by-side electrode processes (e.g. solvent decomposition).

The processes of type (2) are chemical reactions which occur in a thin solution layer near the electrode resulting from the local pH increase. The latter is induced by electrochemical reactions which themselves generate no solid products (e.g. hydrogen evolution, oxygen, or peroxide, or nitrate reduction). Controllability of type (2) processes is much lower as compared to type (1) processes, but certain regulation is possible because the rate of hydroxide-generating reaction can be precisely controlled by the electrode potential. The requirements to electrolysis bath are less sharp than for type (1) processes. Illustrations will be presented for a number of well-studied type (2) processes (Ni, Zn, Ce oxides).

Basic advantage of oxides electrosynthesis is a possibility to avoid high temperatures (the issue crucial for oxide films adhesion). Simultaneously, disadvantage of electrochemical synthesis is its ‘wet’ environment typically resulting in formation of interfacial or even bulk oxohydroxides. When ‘dry’ solid-state applications are considered, the electrosynthesis products usually require post-deposition treatment above room temperature. The most natural applications for electrosynthesized oxides assume that the material operates in the same ‘wet’ medium as was used for fabrication, and no special dehydration of the deposition product is required. A wide range of materials for energy storage (electrodes for batteries and fuel cells), electrochromic oxides, and various ‘wet’ sensors are the most usual examples. However successful oxides electrodeposition for ‘dry’ low-temperature devices is also possible.

Less pragmatically, electrochemical deposition of oxides forms a useful link between solution chemistry and solid state chemistry. This approach allows fabrication of some unusual solids, highly dispersed oxides (if necessary) or (alternatively) of large enough single crystals. The analysis of potential effect on the oxygen stoichiometry can be considered as an instrument to obtain new thermodynamic information. By these means electrochemistry meets solid state chemistry.

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Oxygen redox: what can HAXPES and RIXS tell us?

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The desire for high energy densities for next generation energy storage has led to widespread interest in Li-rich cathode materials.[1,2] By utilizing oxygen redox, Li-rich cathodes offer higher capacities beyond what is expected from the transition metal (TM) redox couples alone. This contrasts with conventional layered oxides where the extractable lithium is limited by the TM content, with oxygen participation considered solely through TM-O re-hybridization. Despite the growing range of Li-rich systems demonstrating oxygen redox, the mechanism remains poorly understood. The situation is further compounded by material specific issues among Li-rich systems, which complicate the interpretation of their electrochemistry. However, there is increasing recognition that local probes of the bulk oxygen chemical and electronic structure such as O K-edge Resonant Inelastic X-ray Scattering (RIXS) and Hard X-ray Photoemission Spectroscopy (HAXPES) are required for a complete description.

Here we report on O K-edge RIXS of conventional layered oxides, where a localized RIXS feature emerges for Ni-rich (and Co-rich) $LiMO_2$ systems at the very highest degrees of delithiation (Fig. 1). This feature has been identified as a unique signature of oxygen redox for Li-rich sytems,[3,4] but its origin remains unclear. The high electrochemical quality of the layered oxides presents fertile ground for evaluating various mechanisms proposed by the community. By combining RIXS and HAXPES with conventional structural probes (EXAFS, ND/XRD) we were able to rule out various structural candidates that have proposed.

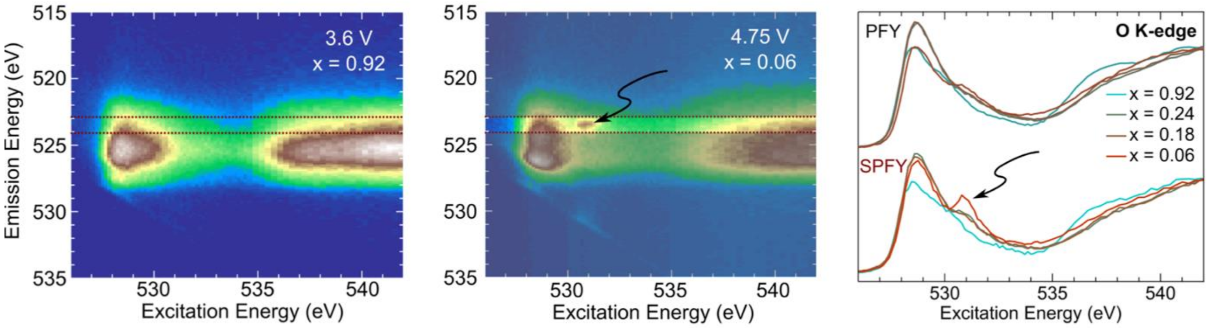

Fig. 1 Representative O K-edge RIXS maps of $Li_xNi_{0.80}Co_{0.015}Al_{0.05}O_2$ (NCA) at 3.6V (left) and 4.75V (right), revealing the formation of the localized loss feature associated with oxygen redox (arrow). The localized feature is also identified from the corresponding O K-edge x-ray absorption spectra (right, arrow) at the highest states of delithiation i.e x = 0.06.

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ON THE QUEST FOR CATHODE MATERIALS IN MULTIVALENT BATTERY TECHNOLOGIES

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The development of a rechargeable battery technology using light electropositive metal anodes would bring in a breakthrough in energy density. For multivalent charge carriers (M^{n+}), the number of ions that must react to achieve a certain electrochemical capacity is diminished by two (n=2) or three (n=3) when compared to Li^+. While proof-of-concept has been achieved for magnesium, the electrodeposition of calcium was thought to be impossible to date and research restricted to non rechargeable systems. Nonetheless, calcium is especially attractive amongst multivalent electropositive metals, as it is the fifth most abundant element on earth crust and its standard reduction potential is only 170 mV above that of lithium, enabling significantly larger cell potential than that achievable with magnesium. The feasibility of a calcium metal based technology had been poorly explored as it was generally admitted that calcium deposition was virtually impossible due to the lack of calcium ion transport through the surface layer formed at the electrode interface in conventional electrolyte solutions. Calcium is the fifth most abundant element on earth crust and its standard reduction potential is only 170 mV above that of lithium, thus enabling significantly larger cell potential than that achievable with magnesium. Moreover, the low polarizing effect (charge/radius) would *a priori* present some advantages towards the latter with respect to reaction kinetics and resulting power performances.

The talk will revisit these aspects discussing the feasibility of reversible calcium plating/stripping using conventional alkylcarbonate electrolytes which impacts the prospects of developing a new calcium based rechargeable battery technology.[1] The well known stability of these electrolytes at high potentials is maintained at 100ºC which paves the way to exploratory screening and testing of potential cathode materials which would reversibly insert and deinsert calcium to assemble a full calcium based cell and achieve proof-of-concept. Candidate compounds should have a redox center, typically a transition metal, and involve a couple operating within the stability range of the electrolyte. Moreover, the crystal structure must exhibit pathways to enable diffusion of calcium ions. Some compounds such as $CaMoO_3$ or $CaMn_2O_4$ which exhibit such features are found to exhibit too large barriers for calcium ion diffusion.[2,3] Results will also be presented on alternative compounds for which some electrochemical activity has been unravelled. The need to use diverse characterization techniques to assess calcium electrochemical insertion/extraction, will be emphasized. **[4]**

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Ionogels for safer energy storage: the determining effect of the interface

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Ionogels represent a route to biphasic materials, for the use of ionic liquids (ILs) for all-solid devices. Confining ILs within host networks enhances their averaged dynamics, resulting in improved charge transport. Fragility, short relaxation times, low viscosity, and good ionic conductivity, all them appear to be related to the IL / host network interface. The presence of ILs at interface neighborhood leads to the breakdown of aggregated, structured regions that are systematically found in bulk ILs. This "destructuration",[1] as well as segregative interactions at interface,[2] coupled with percolation of the bicontinuous solid/liquid interface,[3] make these materials very competitive among the existing solid electrolytes. Such approach could provide (i) a route to lower locally the viscosity of ILs, and (ii) an easier pathway for diffusion of charged species. Several types of ionogels demonstrate this effect, taking into account of fully inorganic, hybrid, polymeric or organic-inorganic host networks . This "all-solid" approach can be applied to several electrochemical energy storage sources, including lithium batteries (Fig 1)[2,4] and supercapacitors (Fig. 2).[5] Strikingly, high performance were shown on these devices, thanks to interfacial effects of confined ILs, with sometimes heightened properties of the chosen ILs as referred to their bulk properties.[2,3,6] Such solid electrolytes are particularly well suited for microdevices that we have been or are being developed (Fig. 3).[5,6] Herein we will emphasize the results of a systematic study of the effect of size of confinement.

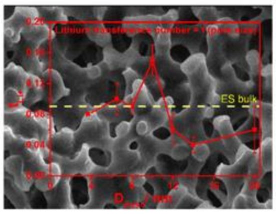

Figure 1: Lithium transport number shows an optimum for a given pore size.

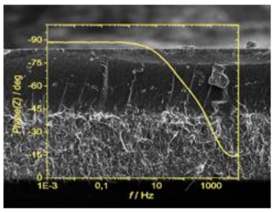

Figure 2**:** High time response for ionogel silicon wires SCap.

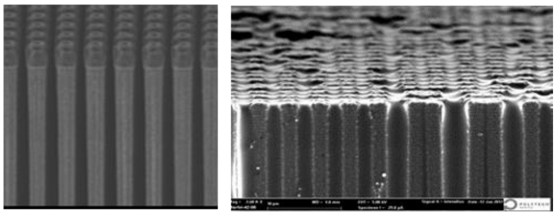

Figure 3: Silicon micropillars covered by MnO_2, without ionogel (left), with ionogel (right).

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NANOMATERIALS AT THE EDGE: PERVOVSKITE EXSOLUTIONS

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Understanding and controlling the processes occurring at electrode/electrolyte interface are key factors in optimising fuel cells and electrolysers. Metal particles supported on oxide surfaces promote many of the reactions and processes that underpin the global chemical industry and are key to many emergent clean energy technologies. At present, particles are generally prepared by deposition or assembly methods which, although versatile, usually offer limited control over several key particle characteristics, including size, coverage, and especially metal-surface linkage. In a new approach, metal particles are grown directly from the oxide support though in situ redox exsolution. We demonstrate that by understanding and manipulating the surface chemistry of an oxide support with adequately designed bulk (non)stoichiometry, one can control the size, distribution and surface coverage of produced particles. We also reveal that exsolved particles are generally epitaxially socketed in the parent perovskite which appears to be the underlying origin of their remarkable stability, including unique resistance of Ni particles to agglomeration and to hydrocarbon coking, whilst retaining catalytic activity

We also present the growth of a finely dispersed array of anchored metal nanoparticles via electrochemical poling on an oxide electrode, yielding a sevenfold increase in fuel cell maximum power density. Both the nanostructures and corresponding electrochemical activity show no degradation over 150 hours of testing. These results not only prove that in operando treatments can yield emergent nanomaterials, which in turn deliver exceptional performance, but also provide proof of concept that electrolysis and fuel cells can be unified in a single, high performance, versatile and easily manufacturable device. This opens exciting new possibilities for simple, quasi-instantaneous production of highly active nanostructures for reinvigorating Solid oxide cells during operation.

Solution-Based Lattice Engineering with 2D Oxide and Hydroxide Nanosheets

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We have successfully synthesized molecularly thin 2D oxides and hydroxides by delaminating precursor layered compounds [1,2]. Treatments with appropriate aqueous amine solutions or organic solvents could homogeneously prop open the interlayer gallery to over one hundred fold [3]. With appropriate mechanical agitation, such swollen crystals could be disintegrated into molecularly thin 2D nanocrystals, the lateral size, shape and yield of which are dependent on the process parameters. The resulting oxide and hydroxide nanosheets can be obtained in diverse compositions and structures, leading to a range of attractive properties. Furthermore, they are monodispersed in a colloidal suspension as polyanionic and cationic species, respectively, making them useful as a building block to construct highly organized nanostructures via solution-based processes [1,4,5]. Layer-by-layer assembly via electrostatic self-assembly, Langmuir-Blodgett deposition and special spin-coating process enable layer-by-layer assembly of nanosheets into multilayer and even superlattice films with precisely controlled nanostructures. Flocculation of two kinds of nanosheets having opposite charge enables bulk-scale production of a superlattice-like composite. Such artificially designed nanostructures can show advanced functionalities through synergistic interaction of constituent nanosheets. For example, interlayer coupling from heterostructures composed of ferromagnetic $Ti_{0.8}Co_{0.2}O_2$ and dielectric $Ca_2Nb_3O_{10}$ nanosheets led to multiferroic response. Flocculated products of graphene oxide and redox-active MnO_2 or $Co_{1/3}Al_{2/3}(OH)_2$ nanosheets showed superior electrochemical performance. Function design via this strategy like these examples will be presented.

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LAYERED DOUBLE HYDROXIDES AS CANDIDATE INCOMMENSURATE PHASES

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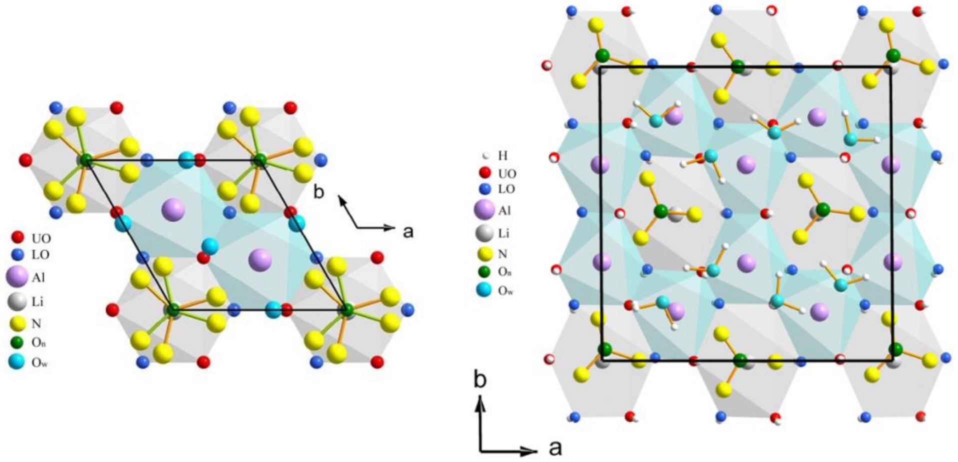
Aluminum hydroxide comprises charge neutral layers of the composition $[Al_2\square(OH)_6]$ ($\square$: octahedral vacancy). Layered double hydroxides (LDHs) of Li and Al are formed when Li^+ ions are imbibed into the octahedral vacancies, resulting in positively charged metal hydroxide layers of the composition $[LiAl_2(OH)_6]^+$, wherein the Li^+ ions are the seat of positive charge. Li^+ is in an ordered arrangement relative to the Al^{3+} ions. The unit mesh has a hexagonal symmetry (layer group p-31m, $a = b = 5.08$ Å). Anions, NO_3^- in this study, along with water molecules are included in the interlayer region to restore charge neutrality, giving these compounds an anionic clay character. Like their cationic clay counterparts, the LDHs undergo temperature and humidity-induced reversible dehydration. In the dehydrated crystal (T = 40 °C, in vacuo) (space group $P6_3/mcm$), the NO_3^- ions are located proximal to the Li^+ ions emphasizing the role of coulombic attraction between the positively charged layer and the negatively charged interlayer. There is a coincidence of the unit mesh of the interlayer with that of the metal hydroxide layer (Fig. 1, left panel).

On cooling (T = 25 °C) and rehydration (Relative Humidity 55%), there is ingress of water molecules into the interlayer region accompanied by an expansion in the basal spacing. Aggressive hydrogen bonding between the intercalated nitrates and the water molecules weakens the coulombic interaction between the layer and interlayer. Decoupling of the layer and the interlayer results in a displacive incommensurate structure wherein the unit mesh of the nitrate ions is no more coincident with the unit mesh of the metal hydroxide layer (Fig. 1, right panel).

One of the pre-requisites to generate an incommensurate structure is the presence of two subsystems: a rigid charge ordered metal hydroxide layer comprising cations with a difference of at least two units of positive charge, and a flexible network of intercalated anions, whose mesh size varies with hydration. The formation of the incommensurate phase is facilitated when the loss of coulombic energy is adequately compensated by the gain in energy due to hydrogen bonding between the nitrate ions and water molecules. Halide intercalated LDHs fail to generate incommensurate phases due to the inadequacy in their hydrogen bonding ability. LDHs with other oxo-anions can also potentially crystallize in incommensurate structures making this phenomenon more prevalent than is generally acknowledged.

Fig. 1 Commensurate structure (left panel, experimental), Schematic of an incommensurate structure (right panel, computed)



LINEAR INTERGROWTH AND LAYERED STRUCTURES BASED ON INTERMETALLIC FRAGMENTS: IODINE-ASSISTED SYNTHESIS AS A SILVER BULLET

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The focus of the work presented here is on linear intergrowth and layered structures combining the fragments of ordered intermetallics with structural units of other nature. Ordered polar intermetallic compounds in themselves are fascinating objects both due to their incredible structural diversity and the variety of unconventional and potentially useful physical properties. Quite often they feature complicated structure motifs and convoluted bonding patterns, as well as complicated structure-property relationships. Furthermore, if a 3D intermetallic system is infused with non-metallic fragments, new possibilities arise. This concept is exploited here using two types of compounds as examples: i) metal-rich mixed group 10 – group 13 chalcogenides and pnictides based on the Cu_3Au-type fragments; ii) intergrowth structures based on the LaOAgS structure type.

The first type of compounds can be regarded as linear intergrowth structures and is based on the group 10 – group 13 intermetallic fragments of the Cu_3Au structure type alternating with group 10 metal – chalcogen or pnictogen fragments of the Cu_2Sb, Li_2O, and $PtHg_2$ types. The second type of compounds is a layered one and features fairly simple atomic arrangement that consists of two alternating anti-isotypic (PbO- and FeS-type) layers. It is, in fact, its own anti-type and thus is a very convenient object for crystal chemical analysis. The compounds that we are interested in combine non-metallic (rare earth or alkali earth and fluorine or oxygen) and intermetallic (e.g. triel-tetrel: Al-Ge, Al-Si; *d*-metal-pnictogen: Zn-Sb, Mn-As, Mn-Sb, etc.) layers (Fig.1).

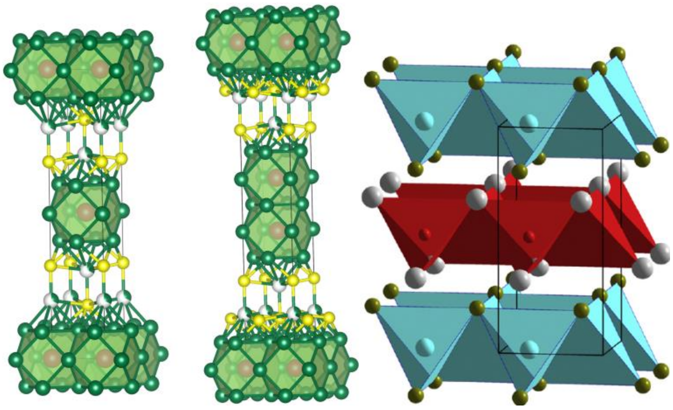

Fig. 1. Structure types investigated in this work (left to right): $Ni_{7-x}MQ_2$, $Ni_{10-x}M_2Q_2$, LaOAgS.

Crystal and electronic structures of both types of compounds, bonding schemes, as well as structure-property relationships are discussed in the presentation. Of particular note are synthetic difficulties: the synthesis of not only phase-pure, but even the samples featuring significant amount of these compounds is severely hindered. However, the use of the miniscule amounts of iodine during high temperature synthesis works wonders, although the exact nature of its effect is yet to be determined.

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Intercalation vs. Oxidation for Layered Iron Chalcogenides

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Tetragonal iron sulfide and selenide adopt the simplest crystal structures of the recently-discovered iron-based superconductors and are of considerable interest for the development of the structure-properties relationship. Iron-chalcogen layers are neutral allowing for the intercalation of various species in the interlayer space. Conventional high-temperature solid-state syntheses of alkali metal cations intercalates resulted in the red/ox processes in the iron-chalcogenide layers, i.e. the formation of vacancies in the Fe sublattice. Low-temperature solution-assisted intercalations provides an access to rich phase space of intercalates based on C,N,O,H-containing molecular species. The latter phases exhibit a large variety of thermodynamic transport properties. Structure-properties relationships are hindered by the unavailability of structural information because intercalated samples are often fine and not well-ordered powders. Analogously to alkali metal iron chalcogenides the red/ox component of the solution produced intercalates should not be ignored. To establish structure of the intercalated phases complimentary techniques to conventional powder X-ray powder diffraction, namely synchrotron pair distribution function (PDF), STEM, and 57Fe Mössbauer spectroscopy, were applied. On the example of the transition metal coordination complexes intercalates the intricate interplay between Fe vacancy formation, incorporation of the interstitial species and solvent molecules, structural distortion, and properties will be discussed.

SOFT CARBON SHEETS: SOME NEW INSIGHTS INTO AN OLD MATERIAL

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Graphene oxide (GO) sheets are made by exfoliation of graphite using century-old chemical reactions. Interest in this old material has resurged with the rapid development of graphene since 2004, as GO has been considered to be a promising precursor for bulk production of graphene. However, GO itself is a very interesting material in its own right. I will share a few curiosity-driven discoveries about GO, leading to new hypotheses and new applications of graphene-based materials. These include the discovery of GO's amphiphilicity, its use to construct 2D nanofluidic channels, the development of aggregation-resistant crumpled graphene balls, and the application of GO and graphene as a materials-based solution to a difficult chemical problem in hair dyes. The curiosity-driven enquiry may help to enhance student learning experience through their own innovations. One example of pencil drawn chemiresistors will be discussed.

VARIOUS TOPOTACTIC MECHANISMS FOR THE INTERCALATION INTO GRAPHITE OF METALS AND METALLIC ALLOYS

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Graphite is a noteworthy host material for intercalation reactions and especially in the case of metals and metallic alloys, because it appears easily as a good electron acceptor towards the electron donors such the strongly electropositive elements, which abandon easily their outlying electron(s).

Graphite is indeed a stacking of mono-atomic graphene layers. They are solidly built by means of strong covalent bonds, whereas the piling of these graphene planes is created by very weak van der Waals's bonds. During the intercalation reaction, two simultaneous phenomena occur: (1) an opening of the van der Waals's gaps manifests, allowing the putting up of the reagent between the graphene layers; (2) an electron transfer appears between graphene and reagent, generating an oxido-reduction reaction. The latter is obviously a topochemical reaction.

The intercalation reactions generally take place between solid graphite and a gaseous or liquid reagent: metal vapor, liquid metal, liquid alloy or dissolved metal into melting salts. It has been observed that the intercalation mechanisms are especially diversified. Various significant examples are described below.

a) Potassium vapor intercalates very easily into graphite. In a first time, one interval in *n* only is occupied by mono-atomic layer (stage *n* compound), then one interval in (*n*-1) etc… Finally, all the intervals are occupied (stage 1 compound) leading to a binary phase whose chemical formula is KC_8 [1].

b) Liquid KHg amalgam intercalates into graphite by means of two successive steps. First, potassium penetrates alone in the van der Waals's gaps giving the previously described first stage KC_8 compound. Afterwards, potassium and mercury intercalate simultaneously increasing again the spacing between the graphene planes and leading to thick three-layered KHgK intercalated sheets. The chemical formula of this ternary compound is $KHgC_4$ [2].

c) Liquid calcium-lithium alloys can react with graphite leading to a binary phase of formula CaC_6. Also in this case, two successive steps come into play. First of all, lithium intercalates alone between the graphene planes giving the saturated first stage LiC_6 binary compound (all the intervals are of course occupied by mono-atomic lithium layers). In a second time, calcium penetrates in the van der Waals's galleries getting rid of the lithium atoms in order to substitute this metal: that is how LiC_6 turns into CaC_6 [3].

a) Using the LiCl-KCl liquid eutectic in which europium metal was dissolved, it is possible to prepare a first stage EuC_6 compound, by plunging a graphite platelet in this molten salts medium. During this reaction, firstly the dissolved metal Eu reduces Li^+ ions into metal Li. The latter is then intercalated into graphite, giving rise to the first stage LiC_6 compound. Finally, Li atoms are substituted with europium ones until the formation of EuC_6 [4].

These four examples illustrate clearly the significant diversity of the behavior of the reactivity of solid graphite towards several media able to lead to the topotactic intercalation of metals and metallic alloys into this host structure. In some cases, occur even more complex mechanisms.

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CONTROLLING SOLID STATE REACTION PATHWAYS THROUGH NANOSCALE COMPOSITION FLUCTUATIONS

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The idea of an energy landscape containing free energy minima corresponding to both stable and metastable compounds is a powerful concept. Experimentally there are two challenges - 1) predicting the composition and structure of the local minima and 2) designing a synthesis of the desired structure that avoids competing free energy minima. The synthesis of a metastable solid under conditions where it is metastable has historically been a challenge because traditional solid-state synthesis conditions (high temperatures and long times, or high diffusion rates in fluid phases) enable the system to explore most of the energy landscape. A striking exception is topotactic reactions, where only some atoms are mobile. This limits the extent of the energy landscape explored to regions where the host lattice remains intact. Since diffusion rates of atoms depend on composition, similar differential diffusion rates might be possible by varying the composition of a precursor on a nanometer scale. We will present data that shows that it is possible to control local composition in a precursor on a nanometer scale by sequentially depositing elemental layers on a cold substrate the matrix. Annealing this precursor at low temperatures preserves the nanoscale composition variation as a layered solid forms via self-assembly. The composition of the precursor layers controls the structure of the layers formed. The structure, composition and properties of a number of new multinary solids containing Bi-Se layers will be presented.

Preparation and magnetic properties of spinel $Zn_{1-x}Ni_x Fe_2O_4$ ($0.0 \leq x \leq 1.0$) nanoparticles synthesized by microwave combustion method

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Abstract

Nano particles $Zn_{1-x}Ni_xFe_2O_4$ (x=0.0–1.0 in step of 0.2) ferrites are synthesized by microwave combustion method using glycine as a fuel. The structure, site occupancy and ferromagnetic property are characterized by X-ray diffraction (XRD), Mossbauer Spectroscopy (MS) and Vibrating Sample Magnetometer (VSM). Special emphasis is placed in the information provided by each of these techniques in the investigation the impact of the site occupancy on the magnetic properties. The results reveal that the formation of single phase cubic spinel with crystallite sizes in the range of 30-42 nm. The lattice constant and the lattice strain decrease gradually with increasing Ni-content. Two well defined Mossbauer sextets belong respectively to octahedral [B] and tetrahedral (A) sites in the spectra at 78K, are confirming the formation of $Zn_{1-x}Ni_xFe_2O_4$ spinel. The isomer shift (δ_{Fe}) values were assigned to Fe^{3+} ions distributed in both A and B sites. The quadrupole splitting (Δ) values showed also that the orientation of the magnetic hyperfine field (h_{int}) with respect to the principle axes of the electric field gradient (EFG) was random. The values of h_{int} inferred that the A-sites had stronger A-O-B super exchange interactions than the B-sites. The nano size features under applied magnetic field exhibit the hysterical loops of the ferromagnetic nature. The values of saturation magnetization increases with introducing Ni up to x=0.8 and then it decreases. The magnetic data parameters of this structure is discussed as a function of the content of Ni ions .

ELECTRON DIFFRACTION TOMOGRAPHY FOR ATOMIC STRUCTURE DETERMINATION, EX AND IN SITU

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Quantitative electron diffraction in the form of precession electron diffraction and electron diffraction tomography has been used for about a decade now to solve and refine structures of different types of compounds. For example, using electron diffraction tomography we solved and refined the changes in the structures of several lithium battery cathode materials upon cycling. We obtained the complete crystal structures including the sites and their occupations for the lithium atoms.

As some of the examples that will be shown, this allowed us to detect massive antisite disorder in Li_2FePO_4F showed after cycling, which is uncommon in polyanionic cathode materials, while the same investigation on $LiFePO_4$ did not show such antisite disorder. For $Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$, we could determine that the structure does not change much during charging and that the introduction of Mn^{3+} does not lead to a cooperative Jahn-Teller distortion. For $LiRhO_2$, a layered compound like $LiCoO_2$, a drastic structural change turns the structure from a layered into a tunnel structure, with ramsdellite and rutile channels. For each of these cases, electron diffraction tomography was the key technique to be able to answer the structural questions.

Initially, we performed this type of experiments using data from ex situ experiments, but recently we have been able to also refine the structure of a lithium based battery cathode material from in situ data obtained using an electrochemical cell. Up until now, X-ray (XRD) and neutron diffraction (ND) are typically applied for in situ tracking of structural changes during battery cycling. In situ electron diffraction in electrochemical cells has not yet been reported in literature. It will have a very important advantage: it can probe matter at a more local scale than the bulk diffraction techniques and therefore allows investigating nanoparticles and getting single crystal information from multi-phased bulk samples.

So far, in situ TEM experiments in closed electrochemical cells mostly showed direct low magnification images. It is not possible to image with atomic resolution in the filled electrochemical cells. Evaporating part of the liquid would allow to improve resolution, but contamination due to the strong electrolyte–beam interaction then creates further barriers for imaging. In this talk, I will demonstrate that in situ electron diffraction tomography in these electrochemical cells can give the much needed subangstrom information on the structural changes of cathode materials upon cycling but also highlight the problems that still need to be overcome before this can become an established technique.

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DECODING LOCAL STRUCTURES IN COMPLEX MOLYBDENUM AND VANADIUM MIXED OXIDES

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Concomitant optimization of catalytic and synthetic protocols in heterogeneous catalysis allows to address new challenges arising in the field of efficient energy conversion. Bulk and surface structure defects are intrinsic to solid catalysts and can significantly influence their catalytic performance.[1] Defects, nevertheless, tend to be neglected since they are, due to the lack of translational symmetry, hard to pinpoint. Qualitative and quantitative defect accounting could, however, reveal important defect - activity correlations, which will enhance the understanding in heterogeneous catalysis and will simplify prospective catalyst tailoring.

Recent developments in scanning transmission electron microscopy (STEM) allow for capturing details of structural and compositional features without 3-dimensional translational symmetry on the atomic scale.[2,3] We further developed a quasi in-situ TEM setup to track structural changes as a function of atmosphere and temperature.

This way local structural and compositional variations as well as distortions in orthorhombic Mo and V based mixed oxides were explored. For instance, for the complex structure of orthorhombic $(Mo,V)O_x$ 19 different local structures could be identified. They can be listed and classified into different structural motifs, intergrowth, channels, interstitial regions, and inclinations. The observed defects can be composed of Mo or V enriched metal sites and are expressed by the rearrangement of the $\{(Mo)Mo_5O_{27}\}$ building blocks. Furthermore, the evaluation of 31 orthorhombic $(Mo,V)O_x$ crystals yields an average defect concentration of 3.3% and indicates that all particles are different with respect to the details of the defect motifs. We have observed 54 of these rearranged structural motifs close to the surface of one (Mo,V)Ox particle ($100x50\ nm^2$). In addition, the local compositional differences between defect, bulk, and surface were investigated on the nanoscale by electron energy loss spectrometry (EELS) coupled with STEM imaging. Moreover, changes of the surface structure of identical $(Mo,V)O_x$ particles can be observed before and after thermal treatments using quasi in-situ TEM.

Understanding the diversity of defects generated by nanostructuring combined with a quantitative analysis will establish new defect - activity correlations that will allow explaining trends in heterogeneous catalysis in greater detail.

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Pushing PDF experiments – lab and synchrotron

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The pair distribution function (PDF) technique exploits the total, i.e. the Bragg and diffuse, X-ray scattering of crystallographically challenging materials to derive their structure - with nanoparticles being the biggest showcase in recent years. [1] The strong increase in flux at high X-ray energies combined with novel detector technologies (CdTe) at synchrotron radiation facilities allows in-operando studies of chemical reactions and nanoparticle formation on a time scale of seconds. [2] The improved signal-to-noise ratio provided the basis to probe weak scattering contrasts as in the case of solvation shells around colloidally dispersed nanoparticles or nanodiamonds. [3] Transferring the synchrotron know-how to lab PDF instruments necessitates rethinking about the relevance of monochromatization and suitable detector technology. The design of a novel PDF diffractometer will be presented herein which allows monochromatic (Ag Kα1) data collection of powder samples with unprecedented resolution and exposure time of only few hours.

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ADOR CHEMISTRY: CURRENT STATUS AND PERSPECTIVES

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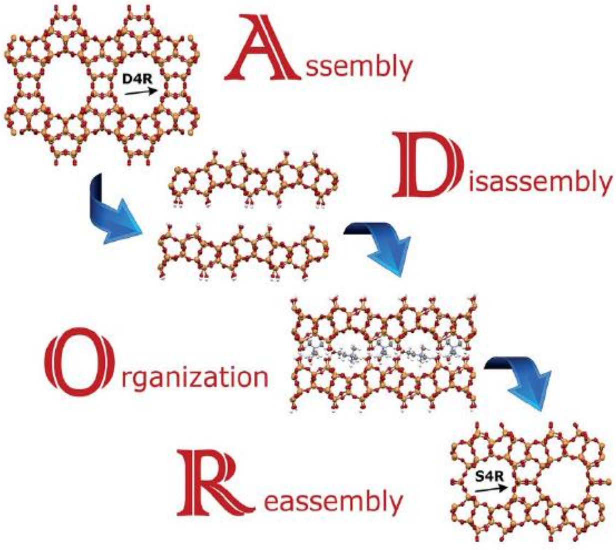
Zeolites are the most important heterogeneous catalysts for industrial applications being applied in oil upgrading, petrochemistry, environmental catalysis, and synthesis of chemical specialties. Despite their enormous success at commercial level, there are still many important challenges in their synthesis to be overcome.



The ADOR protocol

Recently, the **ADOR** strategy for synthesis of new zeolites was developed[1]. This process is based on 4 steps: i) **A**ssembly, the synthesis of initial 3D initial germanosilicate zeolites via hydrothermal method; ii) its **D**isassembly, the fabrication of lamellar material from the parent zeolite. The latter process can proceed due to the presence of chemically labile Ge-rich double four-rings (D4Rs) in the frameworks of germanosilicates; iii) post-synthetic **O**rganization of the layers, and final iv) **R**eassembly representing the condensation of 2D layers to form a new 3D zeolite.

Application of this strategy for zeolite UTL allowed us to synthesize a family of new zeolites such as IPC-2, IPC-4[1], IPC-9 and IPC-10[2], while novel IPC-12 material can be obtained starting from zeolite UOV[3].

This presentation will summarize the current state-of-the-art of the research of ADORable zeolites and will propose new directions for the future.

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Tungsten borides – on the reaction of tungsten with boron(III) bromide

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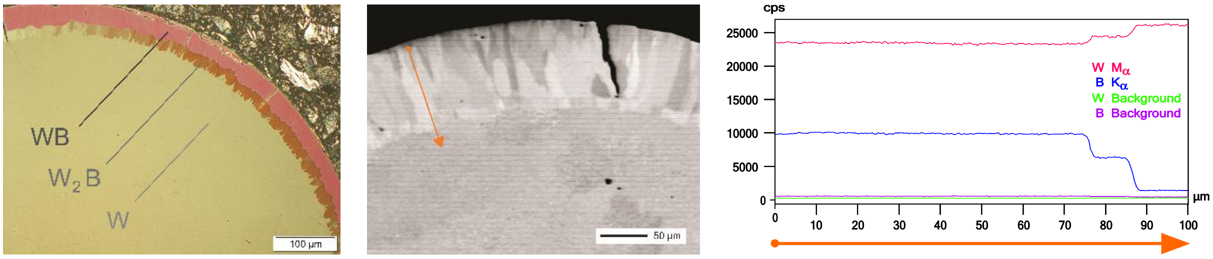
An innovative crucible-free technique was developed for the synthesis of transition metal borides yielding products exhibiting no significant chemical impurities (like oxides or carbides, frequently observed in borides prepared by other methods,). The procedure is based on the crucible-free reaction of a solid transition metal with a gaseous boron halogenide. A metal wire ($d = 1$ mm) is heated by an electrical current up to reaction temperatures of 1800 °C in an atmosphere of gaseous boron halide. Thereby a metal boride is formed in a gas/solid reaction. The applied experimental setup was described in [1] and reminds of van Arkel and de Boer's hot-wire method.

In our presentation, we will give an account on the reaction of tungsten wires with boron tribromide. Whereas in the hafnium-boride system the described hot-wire method led exclusively to phase-pure samples of HfB_2 [1], the reaction of W with BBr_3 is more complicated and does not lead directly to phase pure products. Multiple phases are obtained, for example, a WB layer separated from the tungsten core by a W_2B layer as presented in Figure 1.

Fig. 1 Reaction product obtained at 1600 °C after 10 minutes; from the left to the right: Polarized light microscopic image of the wires cross section (outer layer is false-coloured); Scanning electron microscope BSE image; Corresponding WDXS linescan (measurement along the orange arrow), step width 0.46 µm.



The experiments were carried out at various reaction temperatures and times, revealing the formation of W_2B, WB and WB_2 phases as evidenced by X-ray powder diffraction and wave-length dispersive X-ray spectroscopy.

The underlying reactions were analysed and described by using thermodynamic model calculations. The stability of the gaseous tungsten bromides was evaluated using quantum chemical methods. Within this reaction mainly free bromine and some tungsten bromides are formed in the gas phase.

While the developed synthesis of phase-pure borides is only possible to a limited extent, especially for this system, it offers a potential route for the formation of protective coatings with high chemical and thermal resistance.

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THE REACTIVITY OF As_4S_4 CAGE MOLECULES IN THE SOLID STATE AND IN SOLUTION

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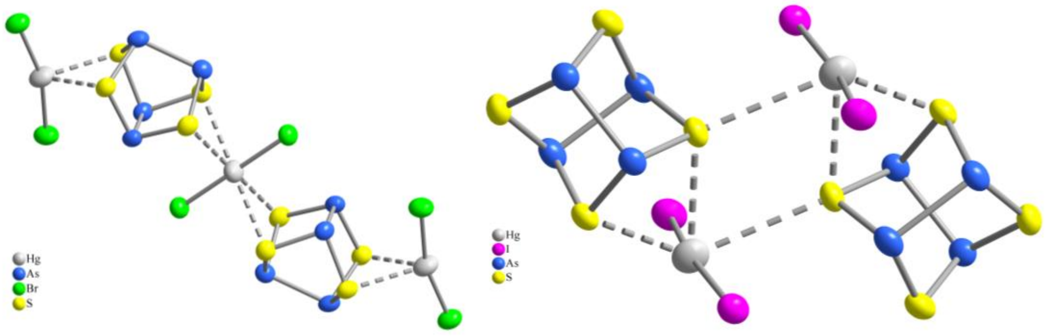
The mineral realgar consists of As_4S_4 cage molecules of the so-called α-type, see Figure 1. The reactivity of such As_4S_4 cage molecules with transition metals is quite limited and only very few examples for compounds with intact cages coordinated to transition metals are known in literature.[1] However, we found an access to new compounds with intact cage molecules exhibiting extremely weak interaction with linear HgX_2 (X = Br, I) moieties.[2,3] Due to the weak interaction between both molecular parts in the crystal structures, a visible light-induced transformation of the α-cage to the β-cage can be followed by Raman spectroscopy and also by X-ray diffraction experiments on single crystals.[4,5]

The talk will show our recent results of activation of As_4S_4 cage molecules and the competition of solvent – metal interaction and metal – cage molecule interaction in the case of the hard Lewis acids Ti^{4+} and Ta^{5+} in comparison with the soft Lewis acid Cu^{1+}.

Fig. 1 Sections from the crystal structures of $(HgBr_2)_3(As_4S_4)_2$ (left), and of $(HgI_2)_2(As_4S_4)$ (right). The dotted lines represent distances d(Hg-S) ≥ 3 Å, corresponding to very weak interactions between these atoms.



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TOPOTACTIC TRANSFORMATIONS AND CATALYSIS WITH LAYERED ZINTL PHASES

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The layered Zintl phases are a large family of solid-state materials whose atomic structure consists of two-dimensional honeycomb networks of main group elements separated by electropositive cations. Here, we describe our efforts utilizing these phases both as precursors for 2D van der Waals materials as well as heterogeneous catalysts with organic substrates. First, we will discuss the synthesis, characterization, properties and applications of hydrogen and organic-terminated group 14 graphane analogues, from the topochemical deintercalation of precursor Zintl phases, such as $CaGe_2$. These sp^3-hybridized 2D derivatives analogues are a unique family of 2D materials in which every atom requires a terminal ligand for stability. We will demonstrate that the interplay between the size and electron-withdrawing nature of the ligand can be exploited to tune the electronic structure, even changing the band gap by ~0.25 eV. Furthermore, we will highlight how the surface chemistry can lead to nonobvious interactions with other chemical species. Finally, we will show that these materials are excellent catalysts for a variety of organic transformations.

TOPOTACTIC OXYGEN REACTION PATHWAYS EXPLORED BY IN SITU SINGLE CRYSTAL AND POWDER DIFFRACTION METHODS IN NON-STOICHIOMETRIC PEROVSKITE DERIVATES

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Transition metal oxides are an important class of compounds showing interesting properties of academic and applied interest. Non-stoichiometric oxides present a special case, as they can undergo important variations of oxygen stoichiometry, enabling to tune physical and chemical properties. Combining neutron diffraction, inelastic neutron scattering and ab initio lattice dynamics calculations, we have recently evidenced the importance of lattice dynamics, i.e. soft phonon modes, triggering low temperature oxygen mobility in Brownmillerite type (Ca/Sr)FeO2.5, as well as Ruddlesden Popper type oxides, e.g. $La_2CuO_{4.07}$ and $(Nd/Pr)_2NiO_{4+\delta}$ [1-3]. This new concept, explaining why oxygen ions can diffuse in stoichiometric quantities already at ambient temperature, has technological relevance e.g. for optimization of oxygen membranes and electrolytes for sensors or membranes in SOFCs.

On the other hand, “hole-doping” via a topotactic oxygen intercalation, allows the controlled synthesis of strongly correlated oxides far away from thermodynamic equilibrium, as it proceeds at low temperatures, and thus results essentially in kinetically stabilized, metastable phases. Contrary to the cation substitution, requiring high reaction temperatures, oxygen intercalation reactions allow the controlled synthesis of kinetically stabilized and thus metastable phases.

Low temperature reactivity of solids may thus be used as a concept, to investigate the limits of structural and electronic complexity in transition metal oxides. The reaction pathway to insert oxygen at low temperatures in solid oxides becomes a decisive parameter to tune correlations, leading to extremely complex phase relations as physical and structural properties are not only depending on the overall stoichiometry, but on the sample history. Taking these oxides as oxygen ‘sponges’ operating at low reaction temperatures down to ambient, structural and electronic correlation lengths could then be influenced by the reaction conditions and kinetics.

We discuss here solid-state reaction mechanisms, associated with complex oxygen and domain ordering phenomena during oxygen uptake or release reactions in non-stoichiometric oxides with Brownmillerite and K_2NiF_4 type frameworks, essentially explored in situ by neutron scattering and synchrotron radiation using single crystals [4-5]. Following up chemical solid-state reactions on single crystals presents a powerful tool, allowing to scan the whole reciprocal lattice and to obtain valuable information about diffuse scattering, weak superstructure reflections, as well as information about possible twin domains associated to changes in the symmetry during of different domains during the reaction, to highlight a few examples which are difficult or impossible to access by powder diffraction. The understanding of phonon assisted diffusion mechanisms is not only important for the optimization strategies of oxide membranes and electrolytes, but much more general for all materials in solid state ionics.

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Regenerative Electroceramics for High Temperature Energy Converters

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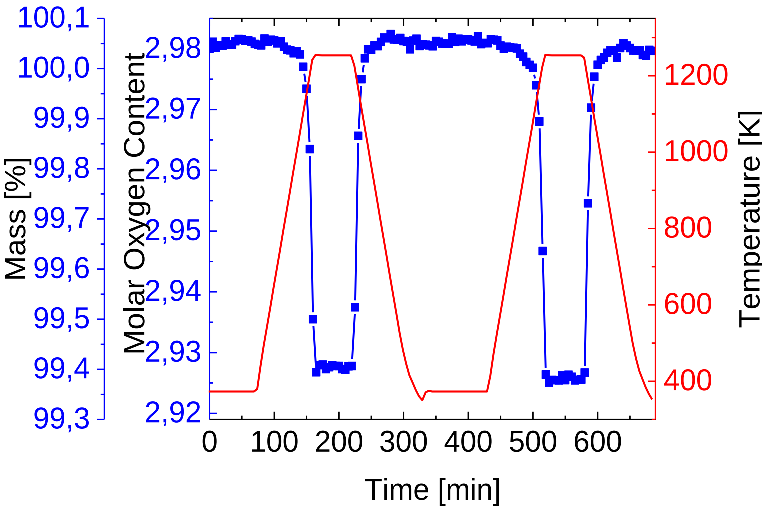
Electroceramics are needed for high temperature thermoelectric- and thermochemical energy converters[1,3]. The prerequisite for a durable active material in these applications is the constant regeneration of the structure under long term application cycles. Perovskite-type ceramics as well as their nanocomposites are prospective candidates for high temperature thermoelectric generators, membranes and catalysts. Their good performance relies on their flexible "breathing" crystal structure accommodating defects during thermal redox processes. The design of our materials is based on theoretical predictions and a deep knowledge on composition-structure-property relationships. The perovskite structure allows diverse substitution reactions to tune the band structure, charge carrier density and mobility as well as thermal and ionic transport. Mixed ionic/electronic mobility can become high while the thermal conductivity can be low. Strongly correlated electronic systems are employed as additional design elements for a targeted materials design.

The resulting CO_2 and air tolerant manganates[2], titanates[4], and ferrates[1] are characterized and tested in diverse high temperature applications to improve the efficiency and energy density of CO_2 converters, and thermoelectric conversion devices.

Fig. 1 Regeneration of a Calcium manganese oxide based thermoelectric material during heating cooling cycles. [2]



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SOFT-CHEMISTRY PRECURSORS FOR NEW OXYNITRIDE SOLID SOLUTIONS

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Perovskite oxynitrides with the general composition $AB(\mathrm{O,N})_3$ are of high interest for a number of possible applications such as pigments, semiconductors, dielectrics, LED-phosphors and in particular as photocatalysts for wastewater treatment, air purification or water splitting [1].

In all these applications the usually bright colors of oxynitrides play the key role. They result from higher energies of the nitrogen 2p-orbitals compared to the oxygen 2p-orbitals, leading to a reduction of the band gap and in turn a shift of the absorption edge from the UV to the visible region of the light spectrum. The size of the band gap is additionally affected by the crystal structure and electronegativity of the *B*-type element [2]. A lower symmetry, leading to *B*–O–*B* angles smaller than 180°, results in a decreased width of the conducting band (basically consisting of the d-Orbitals of *B*) and therefore in a larger band gap. Such changes in the crystallographic symmetry are commonly induced by the size of the *A*-type cation. On the other hand, a decreasing electronegativity of the *B*-element shifts the energy of the conducting band to higher energies, again resulting in a larger band gap and a blue shift of the absorption edge.

Thus by a proper choice of *A*- and *B*-type elements the band gap of oxynitrides can be altered and a fine-tuning can be achieved by (isovalent) substitutions on the two sites. While this concept seems rather straightforward, its experimental realization is quite demanding, since in many cases solid solutions do not form at all or at least not in the entire compositional range. One strategy to circumvent this problem is the use of suitable, highly reactive oxide precursors that contain the corresponding elements already mixed on the atomic scale and can be nitridated at comparatively low temperatures.

Against this background, we here report on the solid solutions $\mathrm{Ca_{1-x}Sr_xNbO_2N}$, $\mathrm{CaNb_{1-x}Ta_xO_2N}$, and $\mathrm{SrNb_{1-x}Ta_xO_2N}$. Partially amorphous precursors for these oxynitrides have been obtained by a hydrothermal synthesis in strongly alkaline solutions of calcium (strontium) nitrate and niobium (tantalum) chloride [3]. After drying the precursors were ammonolysed at temperatures between 750 °C and 930 °C, resulting in phase pure oxynitride powders.

The solid solution $\mathrm{Ca(Nb,Ta)O_2N}$ crystallizes in *Pbnm*, while for $\mathrm{Sr(Nb,Ta)O_2N}$ space group *I*4/*mcm* was found. In the case of the substitution series $\mathrm{Ca_{1-x}Sr_xNbO_2N}$ a transition from orthorhombic to tetragonal occurs around $x \approx 0.4$. For all three solid solutions a continuous change of the band gap width was observed.

For photocatalytic test measurements small oxynitride aliquots were loaded with $\mathrm{CoO_x}$ as co-catalyst. We investigated the photocatalyzed decomposition of a methyl orange solution upon illumination for 3 h with a Xe arc lamp. Optical filters with cut-off wavelengths of 300 nm and 420 nm were used to separate the photocatalytic activity in the visible light region. For the solid solution $\mathrm{Ca_{1-x}Sr_xNbO_2N}$ degradations up to 60 % could be achieved and the major effect results from irradiation with visible light.

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Systematic Valence Distribution Changes in Bi- and Pb-3d Transition Metal Perovskite Oxides

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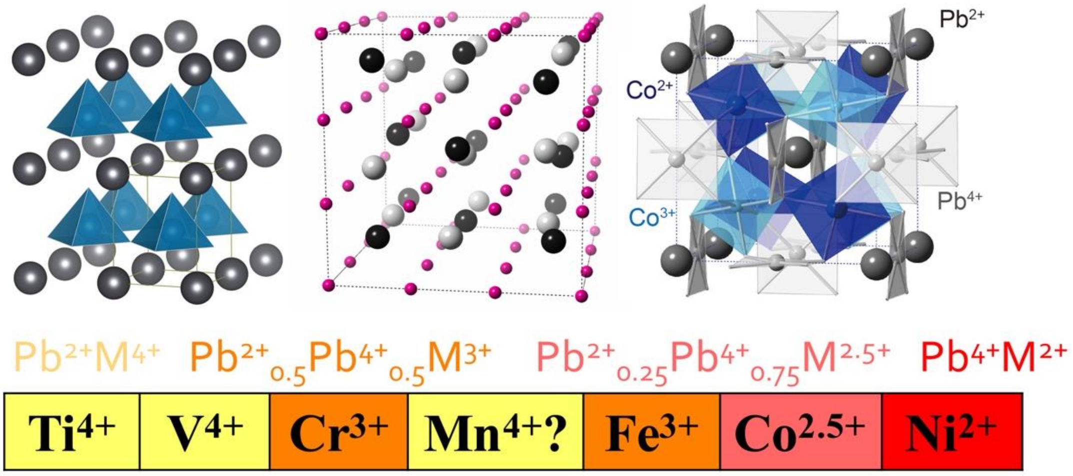
Bi and Pb are main group elements, but these have charge degree of freedom depending on the $6s^2$ and $6s^0$ electronic configurations. These are therefore called valence skippers. Since 6s states of these elements are close to the d level of transition metal and oxygen 2p level, $BiMO_3$ and $PbMO_3$ (M: 3d transition metals) exhibit systematic valence distribution changes [1].

From left to right in the periodic table, $BiCrO_3$ to $BiCoO_3$ are all $Bi^{3+}M^{3+}O_3$. However, $BiNiO_3$ has an unusual $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ valence state. An intermetallic charge transfer between Bi^{5+} and Ni^{2+} takes place under pressure leading to the $Bi^{3+}Ni^{3+}O_3$ high-pressure phase. $BiNiO_3$ decomposes on heating at 500 K, but La substitution for Bi or Fe substitution for Ni destabilizes the Bi charge disproportionation and $(Bi,La)^{3+}(Ni,Fe)^{3+}O_3$ appears on heating at an ambient pressure. Because of the contract of Ni-O bond owing to the oxidation of Ni^{2+} to Ni^{3+}, negative thermal expansion, shrinkage of volume on heating, is observed [2-4].

Similar charge distribution change is observed three times in $PbMO_3$. $PbVO_3$ is $Pb^{2+}V^{4+}O_3$ like $Pb^{2+}Ti^{4+}O_3$, but $PbCrO_3$ is found to be $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$ [5]. $PbCoO_3$ has turned out to be $Pb^{2+}Pb^{4+}_3Co^{2+}_2Co^{3+}_2O_{12}$ [6]. $PbNiO_3$ has a valence distribution of $Pb^{4+}Ni^{2+}O_3$ [7]. Namely, $PbMO_3$ changes from $Pb^{2+}M^{4+}O_3$ to $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$ (average valence state of $Pb^{3+}M^{3+}O_3$) to $Pb^{2+}_{0.25}Pb^{4+}_{0.75}Co^{2+}_{0.5}Co^{3+}_{0.5}O_3$ ($Pb^{3.5+}Co^{2.5+}O_3$) and to $Pb^{4+}M^{4+}O_3$ according to the order in the periodic table and the depth of d level.

Fig. 1 Crystal structures of $PbVO_3$, $PbCrO_3$ and $PbCoO_3$



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The Role of Transition Elements in the Design of New Inorganic Pigments

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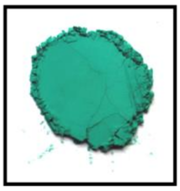
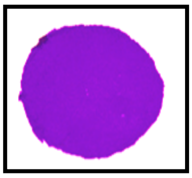
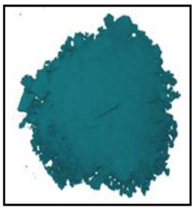
Crystalline inorganic oxides displaying bright colours attracted much attention from early days for application as gemstones and pigments. Ruby (Cr^{3+} doped Al_2O_3) and Emerald (Cr^{3+} doped $Be_3Al_2(SiO_3)_6$) and Azurite ($Cu_3(CO_3)_2(OH)_2$), Han blue ($BaCuSi_2O_6$) and Turquoise ($\underline{CuAl}_6(PO_4)_4(\underline{OH})_8 \cdot 4H_2O$) for example found application as gemstones and pigments since ancient times.[1] In addition to the naturally occurring gemstones and pigments, several man-made (synthetic) coloured solids were also developed to meet the demand.[1] Y_2BaCuO_5, copper substituted apatites, Mn(III) substituted $YInO_3$ and $CaTaO_2N$ – $LaTaON_2$ pervoskites are some of the more recent pigment materials for green, blue, red-yellow colours.[2,3] A scientific inquiry into the origin of colours of inorganic solids is essential for a rational design and synthesis of coloured materials. While there are several causes for the colour of solids, the main factor that causes colour in an inorganic oxide containing transition metal ion is the electronic transitions within the partially filled d-states arising from the ligand field effects around the transition metal ion. Octahedral and tetrahedral are the most common geometries where the colour and optical absorption spectra of all the transition metal ions have been well-documented. Transition metal ions in less symmetric geometries such as distorted octahedral and five-fold coordinated (square pyramidal and trigonal bipyramidal) geometries produce colours different from those in regular octahedral and tetrahedral geometries in materials. The present talk would address some of these issues and our efforts towards identifying new chromophores employing transition metal chemistry.[4-6]


$LiZn_{0.85}Co_{0.15}BO_3$


$Ba_3(V_{0.75}Mn_{0.25}O_4)_2$


Li_2MnO_3


$YGa_{1-x}Mn_xO_3$


$Ca_3Sb_2GaFeCoO_{12}$

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Mesostructured materials for solar energy conversion

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Photocatalytic and photoelectrochemical processes with stable oxide materials still lack the efficiency to justify industrial application, mainly due to insufficient light absorption, short charge carrier lifetimes, or dominant recombination. The presentation will present strategies including mesostructuring of complex semiconductor mixed oxide materials on the nanoscale to improve photocatalytic and photoelectrochemical activity for H_2 generation and water splitting. Mesoporous and fibroid photocatalysts exhibit shortened charge carrier diffusion lengths and enhanced surface area for improved photocatalytic performance, while the design of composite photocatalysts improves charge carrier separation for enhanced activity.

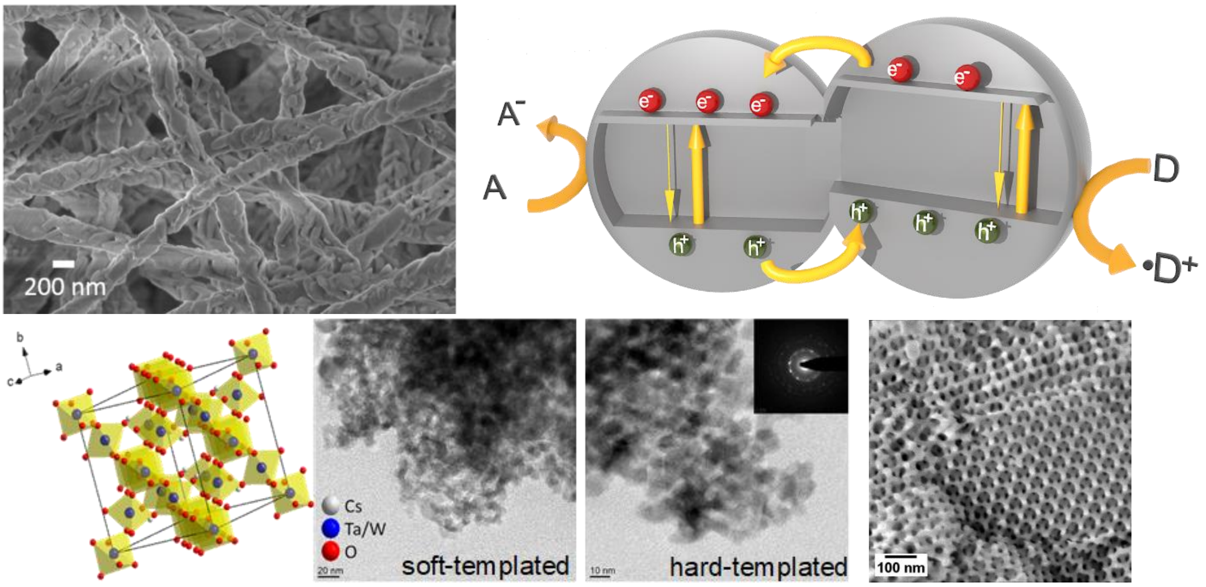

Fig. 1 Top row: electrospun oxide fibres of layered perovskite $Ba_5Ta_4O_{15}$ [1] & principle of charge carrier separation with semiconductor heterojunctions [2]; Bottom row from left to right: Defect-pyrochlore crystal structure of $CsTaWO_6$; TEM image of soft-templated mesoporous $CsTaWO_6$ [3]; TEM image of hard-templated mesoporous $CsTaWO_6$ [4]; SEM image of ordered mesoporous $CsTaWO_6$ [5].

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Photocatalytic CO_2 Reduction by 3*d* transition metal substituted $Ba_2In_2O_5\cdot(H_2O)_\delta$

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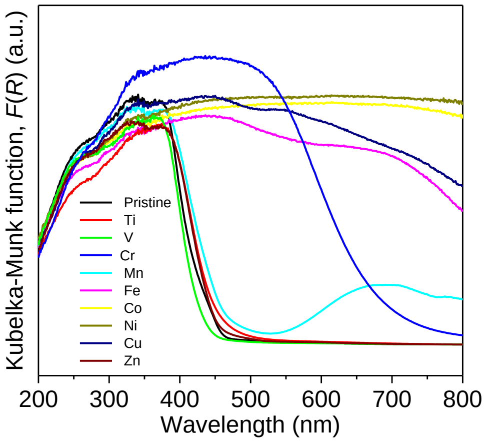
Photocatalytic reduction of CO_2 is a powerful approach to reduce global CO_2 emissions simultaneously achieving a sustainable generation of platform chemicals. Development of new photocatalysts is therefore very crucial and represents even a precondition for the successful future realization of photocatalytic CO_2 reduction. In this study brownmillerite-type (oxygen-deficient perovskite-related structure) $Ba_2In_2O_5$ phase has been investigated as one of the potential candidates for photocatalytic CO_2 reduction. $Ba_2In_2O_5$ has drawn much research interest regarding fast oxide ion and proton conduction due to its unique crystal structure [1,2]. Compositional variation in $Ba_2In_2O_5$ brings marked changes in crystal, defect, and electronic structure, resulting in a number of interesting magnetic, mechanical and transport properties for different technical applications. In this study, 3*d* transition metal substituted $Ba_2(In_{1.8}M_{0.2})O_5\cdot(H_2O)_\delta$ (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) powders were synthesized by solid state reaction to investigate the particularly crucial factors for the photocatalytic CO_2 reduction. Crystal structural analysis in combination with TGA and elemental analysis revealed that the Cr-substitution results in the highest unit cell expansion and the highest oxygen and hydrogen contents (hydroxide ion). In the UV–vis spectra of the Cr-substituted sample a distinctive shift of the absorption-edge energy from 430 to 690 nm was observed corresponding to a bandgap narrowing from 2.88 to 1.80 eV (Figure 1). The partial replacement of tetrahedral InO_4 units by octahedral CrO_6 units was found to be the main factor for the drastic change of the magnetic and optical properties. Consequently, an enhanced photocatalytic CO_2 reduction activity was observed with increasing Cr substitution, compatible with the state-of-the-art high surface area TiO_2 photocatalyst (P-25). Numerical calculations showed that the observed bandgap narrowing was due to 3*d* transition metal induced states in $Ba_2In_2O_5\cdot(H_2O)_\delta$. An enhanced photocatalytic CO_2 reduction activity up to 1.365 $\%\cdot g^{-1}$ was observed by 3*d* transition metal substitution, and the crucial factors and the possible reasons will be discussed in more detail.

Fig. 1 UV–visible diffuse reflectance spectra.



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From Ligand Exchange to Reaction Intermediates: What Does Really Happen During the Synthesis of Emissive Complexes?

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In-situ monitoring the formation of emissive complexes is essential to enable their rational synthesis, the control over their structure-related properties such as luminescence, besides the development and optimization of new compounds. Hence, the *in-situ* luminescence analysis of coordination sensors (ILACS) utilizes the sensitivity of lanthanide ions to the coordination environment to detect structural changes during crystallization processes. In this work, the formation of [Eu(bipy)$_2$(NO$_3$)$_3$] (bipy = 2,2'-bipyridine) was analyzed during co-precipitation synthesis by combining ILACS with different techniques e.g. synchrotron-based *in-situ* X-ray diffraction analysis (Fig. 1). The gradual desolvation of the Eu^{3+} ions and attachment of ligands were detected by the exponential increase of the intensity of the $^5D_0 \rightarrow ^7F_J$ (J = 0-4) transitions. Moreover, the *in-situ* emission spectra show the increase of crystallization rate and decrease in induction time in 21 min for reducing the concentration of the starting solutions e.g. in 12 mM, until ceasing crystallization for concentrations below 6 mM. Increasing the three times the concentration caused the formation of a reaction intermediate, which stability is also concentration-dependent. *In-situ* luminescence measurements show, in addition, the ligand exchange process occurring during the addition of phen (phen = 1,10'-phenanthroline) as a concurrent ligand to a [Eu(bipy)$_2$(NO$_3$)$_3$] solution for the formation of a new phen-containing emissive complex.

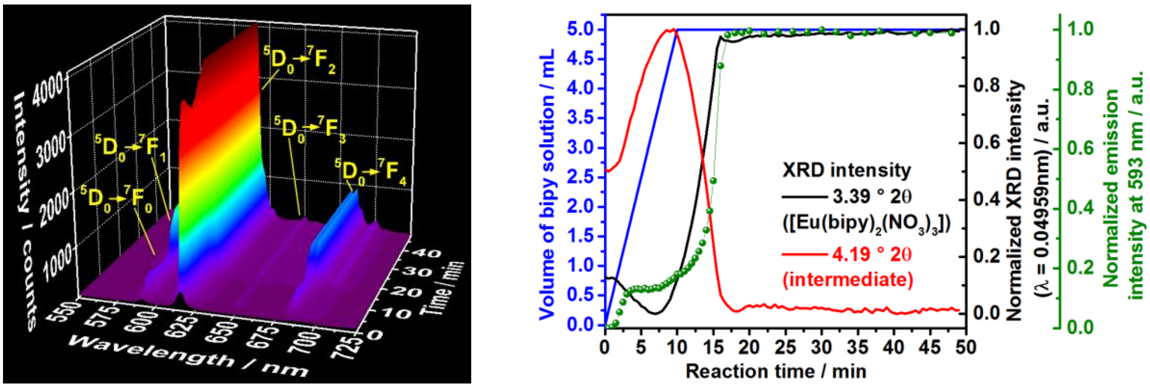

Fig. 1 *In-situ* luminescence spectra (λ_{ex} = 365 nm, left) and comparison between the added volume of the bipy solution (blue curve) with the emission intensity of the $^5D_0 \rightarrow ^7F_1$ Eu^{3+} transition at 593 nm (green curve), intensity of the Bragg reflections at 4.19 °2θ (intermediate, red curve) and at 3.39 °2θ ([Eu(bipy)$_2$(NO$_3$)$_3$], black curve), recorded simultaneously at the P08 DESY beamline during synthesis of [Eu(bipy)$_2$(NO$_3$)$_3$].

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CATALYIS WITH SOLID SOLUTIONS – INSIGHT FROM THE MATERIALS CHEMISTRY OF MIXED 3D TRANSITION METAL COMPOUNDS

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Solid high-performance catalysts often are nanostructured materials that have been synthesized by a two-phase approach *via* deposition of an active material onto a porous support. An alternative route to achieve an optimal inter-dispersion of two materials is to employ solid solutions as catalyst precursors (or directly as bulk catalysts). Such a one-phase approach yields the complex nano-scaled catalytic material with a uniform microstructure, which greatly facilitates the targeted establishment of structure-performance relationships in heterogeneous catalysis – a benefit that is also known as the single-source precursor concept. Synthetic inorganic chemistry of solid solutions thus takes a key role for a better understanding of high-performance catalysts that is often guided by such correlation.

One example from metal catalysis is the ammonia decomposition over Fe-based catalysts. Layered double hydroxides (LDHs) with a cationic sub-lattice containing iron, magnesium and an additional promoter cation can be synthesized by facile co-precipitation [1]. Thermal post-treatment of this solid solution precursor transforms it into MgO-supported Fe particles in presence of finely dispersed promoter species. It was found that if the promoter was Ga, a new solid solution was formed upon high-temperature reduction, Fe_3Ga. This intermetallic catalyst is further transformed into $GaFe_3N$ with a perovskite structure [2]. This phase exhibits a strong promoting effect on ammonia decomposition, while it is almost inactive in the synthesis of ammonia in accordance with the concept of microscopic reversibility [3].

Another example comes from the field of oxide catalysis. Solid solutions of the spinel-type are an attractive playground to study effects of morphology, composition, and cation distribution and ordering on oxidation reactions. We have used cobalt ferrite, $CoFe_2O_4$, as a starting point to compare different synthesis routes as well as cation substitutions with regard to their impact on the catalytic properties in the electrochemical water oxidation. Interesting effects were observed for Co,Ni- [4] and Fe,V-substitution [5], which both lead to a maximum in activity at partial substitution degrees. In addition to composition, also the morphology of cobalt ferrite played an important role in this reaction. A new LDH-based precursor method yields $CoFe_2O_4$ in form of monocrystalline holey platelets. This anisotropic form is a much better electrocatalyst than commercial cobalt ferrite [6]. Possible explanations for these findings are related to conductivity and structural inversion of the spinels and will be discussed.

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SEMI-HYDROGENATION OF ACETYLENE ON $Ga_{1-x}Sn_xPd_2$

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Selective hydrogenation is an important class of reactions in fundamental as well as industrial chemistry. Industrially, the semi-hydrogenation of acetylene is applied to reduce the acetylene content in the ethylene streams used for the production of polyethylene and ethylene oxide to a low ppm-level [1]. Thus, the ideal catalyst for this process has to be active and at the same time possess an excellent selectivity [2].

The electronic influences on the catalytic properties in the semi-hydrogenation of acetylene are addressed by applying unsupported intermetallic materials from the solid solution $Ga_{1-x}Sn_xPd_2$ ($0 \leq x \leq 1$) between the isostructural compounds $GaPd_2$ and $SnPd_2$ (Co_2Si-type of crystal structure [3]). The whole series shows an excellent selectivity to ethylene (~ 85%) and a maximum of the specific catalytic activity at the $x = 0.28$.

The series $Ga_{1-x}Sn_xPd_2$ (with two different crystallographic positions for the palladium atoms) falls within the active-site isolation concept, which is decisive for high selectivity in the semi-hydrogenation of acetylene [4], and follows Vegard's rule [5], thus corroborating the smallest possible extent of structural changes. On the other hand, the electronic properties are changing drastically – while the QTAIM charges in $GaPd_2$ are in agreement with the expectations ($Ga^{+0.60}Pd1^{-0.31}Pd2^{-0.29}$), the charge distribution in $SnPd_2$ is more differentiated ($Sn^{+0.8}Pd1^{-0.44}Pd2^{-0.36}$).

The coherent potential approximation (CPA) method was used to calculate the electronic structure for x values from the *operando* XPS around the maximum activity. Dependence of the specific activity of the materials on the centre of gravity of the *d*-band of the Pd1 atoms shows a very sharp maximum. The same behaviour is observed for Pd2. While the absolute value has to be different due to the different charge of the palladium atoms, the correlation in form of a volcano plot reveals an optimum of the electronic structure. A different picture is observed for the activity dependence on the electronic density of states (DOS) at the Fermi level – no optimum is found and it seems rather that the activity profits from a low DOS at E_F.

The results of our study, which comprises experimental characterization and catalytic testing of unsupported materials and is corroborated by quantum chemical calculations, reveal the strong influence of the electronic structure on the catalytic properties and demonstrate once more the high potential of intermetallic compounds in heterogeneous catalysis.

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NANOPOROUS (La, Sr)(Ti, Fe)$O_{3-\delta}$ SOLID SOLUTIONS AS HIGHLY EFFICIENT OXIDATION CATALYST MATERIALS

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The versatility of perovskite oxides is well known to be given by their ease in accommodating nonstoichiometry without compromising the structural stability. The rational introduction of doping species in A and/or B position of the perovskite lattice is a feature largely exploited for the design of catalysis devices, because it significantly influences both ionic and electronic mobility as well as surface oxygen exchange kinetics. Along with the optimization of the composition, the improvement of the oxide morphology properties is a further essential requirement for such applications. Hence, the design of perovskite oxides which combine large porosity with controlled doping represents an ultimate goal for the development of highly performing catalytic devices. [1] To the best of our knowledge, the simultaneous substitution of both cation lattice positions within a mesoporous structure has not been described yet.

Recently, our group achieved the synthesis of $SrTiO_3$ with very high surface areas based on a novel combination of chelate complex synthesis combined with silica endotemplating. The beneficial effect of enhanced porosity on the catalytic properties was demonstrated in a photocatalytic dye degradation reaction. [2] In this work we present the synthesis of mesoporous $La_{0.3}Sr_{0.7}Fe_xTi_{1-x}O_3$ as a robust and active catalyst for CO and CH_4 oxidation. The materials were prepared by employing a similar route to the synthesis procedure on ref. [2] and the concentration of the B-site dopant varied between 0.1 to 0.5. Diffraction and spectroscopic investigations revealed an increasing amount of iron (IV) species with the dopant content, thus enhancing the mixed ionic-electronic character of the materials. This feature, together with the high porosity, could explain the superior conversion of CO and CH_4. Kinetic studies showed reaction order to be <0.04 with respect to O_2, demonstrating excellent O_2 supply of the catalysts. Moreover, after the catalysis tests the materials maintained their microstructural and morphological characteristics evidencing high stability of the mesostructure of the multimetal oxides. Finally, employing silica endotemplating, homogeneous, phase pure $La_{0.3}$ $Sr_{0.7}Fe_{0.5}Ti_{0.5}O_3$ catalysts were obtained with much larger surface areas up to 220 m^2g^{-1}. Such porous oxides revealed to be excellent support for platinum nanoparticle catalysts. Their superior O_2 supply contributed to complete conversion of CO at temperatures as low as 170°C.

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TEMPERATURE-INDUCED TRANSFORMATIONS OF $Li_3[AlC_2O_4]·nH_2O$ COMPLEX

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The double oxalates $M^I[M^{III}(C_2O_4)_3]$ attract constant interest during last decades both due to their intrinsic physical and chemical properties and as precursors for the synthesis of the complex metal oxides. These salts are usually obtained in form of crystallohydrates with 0-6 water molecules per formula unit. The decomposition pathway of these hydrates is of special interest due to its multistage and often irreversible nature. Among possible compositions belonging to this group $Li_3[Al(C_2O_4)_3]$ was never described before.

The current work summarizes the results of the investigation of the crystal structure and stability of the different $Li_3[Al(C_2O_4)_3]$ hydrates. The structure transformations were investigated using *in situ* powder diffraction, *in situ* FTIR spectroscopy and thermal analysis. The powder diffraction and FTIR data were collected at the MSPD and MIRAS beamlines of the ALBA synchrotron light source respectively.

The freshly precipitated phase appeared to have a composition $Li_3[Al(C_2O_4)_3]·6H_2O$ while the most stable one at the ambient conditions is $Li_3[Al(C_2O_4)_3]·4H_2O$. Heating of this phase leads to the sequential formation of $Li_3[Al(C_2O_4)_3]·H_2O$ and anhydrous $Li_3[Al(C_2O_4)_3]$. All phases share the common building block consisting of the AlO_6 and LiO_6 octahedra bridged by the $C_2O_4^{2-}$ anion. However, the formation of $Li_3[Al(C_2O_4)_3]·H_2O$ includes the reorientation of these blocks. This reorientation results in the change of the space group from Pbcn to Pnna and is accompanied by the strong decrease of crystallinity.

The multistage decomposition of $Li_3[Al(C_2O_4)_3]$ begins above 350°C and includes sequential formation of $Li_2C_2O_4$, Li_2CO_3 and, finally, γ-$LiAlO_2$. This provides a way to prepare highly reactive precursors of the aluminates which usually require extremely high temperatures for the solid state synthesis.

DOS ENGINEERING FOR NEW NANO-MATERIALS

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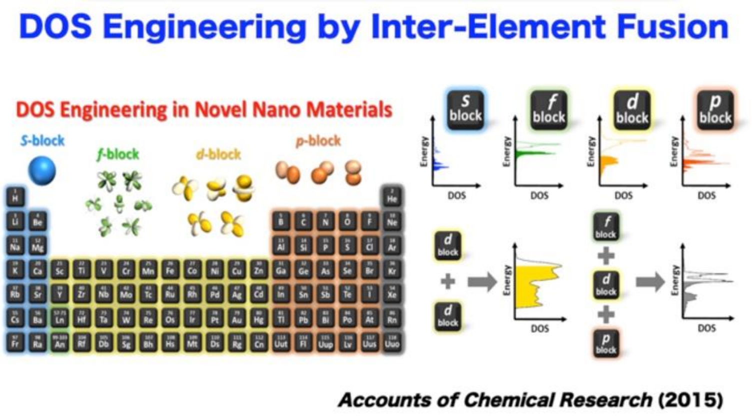
The property of element is correlated directly with its electron configuration. In a solid, the density of states (DOS) at the Fermi level affects the physical and chemical properties. The method of alloying elements has been used to improve the properties of materials for many years. In particular, the solid-solution-type alloy is advantageous because tuning the compositions and/or combinations of the constituent elements can continuously control the properties. However, the majority of bulk alloys are of the phase-separated type under ambient conditions, where constituent elements are immiscible with each other. To overcome the challenge of the bulk-phase metallurgical aspects, we have focused on the nanosize effect and developed methods involving "non-equilibrium synthesis" or "a process of hydrogen absorption/desorption". We propose a new concept of "density-of-states engineering" for the design of materials having the most desirable and suitable properties by means of "inter-element fusion". Novel solid-solution alloys of Pd-Pt, Ag-Rh, and Pd-Ru systems in which the constituent elements are immiscible in the bulk state are presented and discussed [1]. Our present work provides a guiding principle for the design of a suitable DOS shape according to the intended physical and/or chemical properties and a method for the development of novel solid-solution alloys [2-5].



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DIVERSE BEHAVIOUR OF CaAg UNDER OXIDATIVE CONDITIONS

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The direct epoxidation of ethylene using molecular oxygen and supported, promoted Ag catalyst is exploited worldwide for production of ethylene oxide [1]. The demand of a deep understanding of reaction mechanism, the nature of active sites and the role of support, promoters as well as Ag particle size forces the search of model system for such studies. In this case ordered intermetallic compounds have several advantages: unique crystal structure, preferential occupation of crystallographic sites, distinct electronic structure and well-defined chemical bonding pattern [2].

Binary compound CaAg with orthorhombic α-TlI type of crystal structure ($Cmcm$, a = 4.063(1) Å, b = 11.460(2) Å and c = 4.655(1) Å) was investigated as a catalyst for ethylene epoxidation [3]. A diverse chemical behaviour of CaAg under air and ethylene epoxidation conditions was revealed using a combination of experimental and quantum chemical techniques as well as real-space chemical bonding analysis. On one hand, under ethylene epoxidation conditions CaAg possesses an outstanding stability during long-term experiment (600 h). This stability is originated from the formation of a highly ordered, stable and dense CaO passivation layer with a small amount of embedded Ag atoms on the (010) surface which is also the preferred cleavage surface upon sample crushing (Fig. 1). As a result, (010) surface with CaO-overlayer builds a kinetic barrier for further reaction of CaAg with oxygen. On the other hand, it oxidizes quickly during exposure to air forming $CaAg_2$, Ca_2Ag_7, Ag, and Ca-containing products (e.g. CaO, $Ca(OH)_2$, $CaCO_3$). Contrary to ethylene epoxidation conditions, the amount of water vapour in air is significantly higher and causes the reconstruction of CaO-overlayer with the formation of hydroxyl groups. The latter leads to the oxidation of CaAg towards elemental silver (Fig. 1).

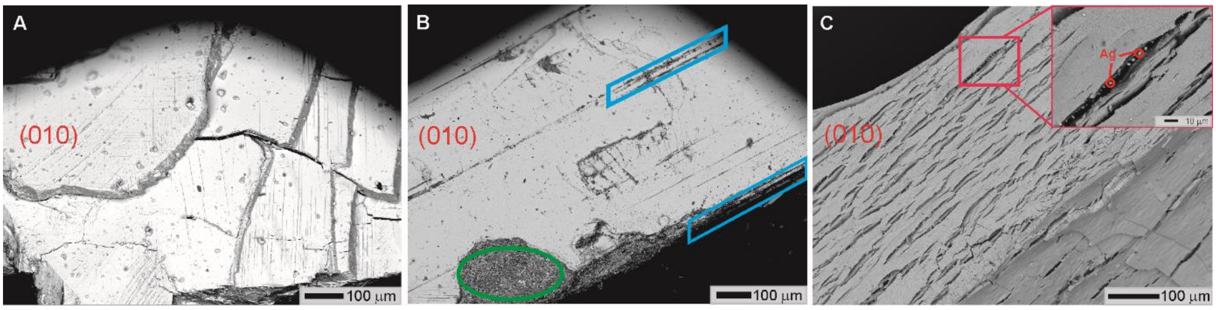

Fig. 1 CaAg particles (BSE images, 15 kV, material contrast):
(**A**) as-synthesized, (**B**) after ethylene epoxidation experiment, and (**C**) after exposure to air followed by catalytic test.
The preferential cleavage plane is (010). Steps (*blue*) and damaged regions (*green*) of CaAg undergo oxidation.

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Oxygen abstraction from V_2O_5 and SiO_2 by coexisting hydrocarbon under mechanical stressing

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Solid-state reduction processes from V_2O_5 and SiO_2 to VO_2 and SiO_{2-x}, respectively, by coexisting hydrocarbon compounds (HC) with and without halogen under mechanical stressing were examined and compared. Paraffin wax (PW), poly(propene) (PP), poly (ethylene) (PE) and poly(1,1-difluoroethylene) (PVDF) were chosen as HC sources. The starting oxides with the highest oxidation number were milled with 3 – 20 mass% of HC.

In the case of V_2O_5 + PW, phase pure VO_2 was attained after milling for 3h at ca 3 mass% PW, as shown in Fig. 1. The latent heat during tetragonal – monoclinic phases change was larger than commercial VO_2, as shown in Fig. 2. Mechanochemically reduced VO_2 exhibited larger thermal hysteresis, which usually leads smaller latent heat [1].

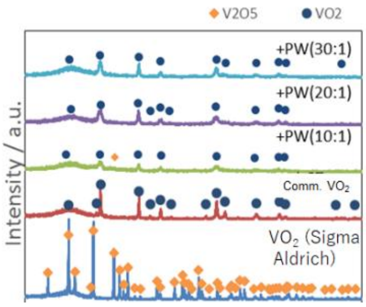

Fig. 1. X-ray diffractograms of V_2O_5 milled with PW for 3h with varying weight ratio of V_2O_5:PW.

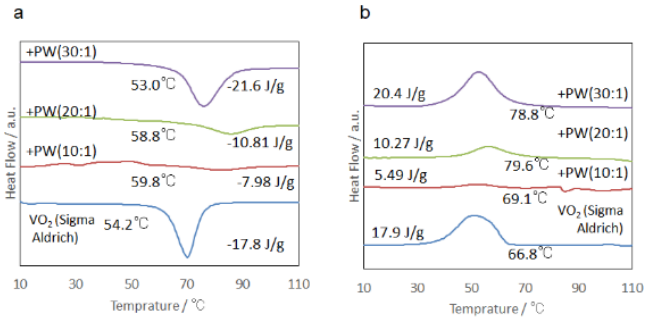

Fig. 2. DSC profiles of the samples for fixed milling time, 3h, with varying weight ratio of V_2O_5:PW. (a) Hearing, (b) cooling

With the combination, SiO_2 + 10 mass% PP, PE or PVDF, the chemical state of the product, examined by ^{29}Si MAS NMR, was homogeneous, in contrast to those prepared via a thermal route, passing through a gaseous state of SiO and subsequent disproportionation to SiO_2 and Si [2], exhibiting two distinct states, as shown in Fig. 3.

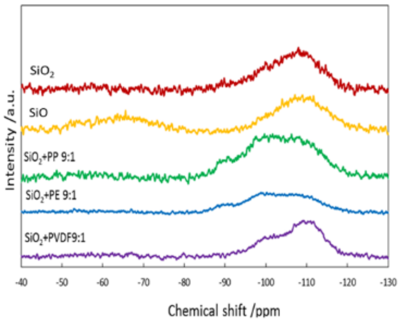

Fig. 3. ^{29}Si MAS NMR spectra of the mixtures with SiO_2:HC ratio 9:1.

All those reduction processes were different from conventional wet chemical or high temperature chemical processes. The unique feature of mechanochemical reduction is discussed in view of abstraction of lattice oxygen by HC serving as an electrophile [3]. Application of the reduced oxide nanoparticles for energy storage devices will be briefly mentioned.

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Postersession

SYNTHESIS AND APPLICATIONS OF SANDWICH-LIKE NANOPARTICLE@HECTORITE CATALYSTS

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Highly active catalysts require an ordered structure with a high specific surface area and an architecture that allows for an efficient mass transport. These criteria can be achieved by the ordered intercalation of nanoparticles in the interlayer space of clay materials where the nanoparticles act as pillars and reactive catalysts.

In this approach positively charged interlayer cations of synthetic hectorite are exchanged by nanoparticles. To grant bigger objects as nanoparticles (compared to discrete cations) access to the space between the layers, the layer distance has to be raised to several nanometers. An expeditious melt synthesis of a phase pure sodium hectorite $[Na_{0.5}]^{inter} [Mg_{2.5} Li_{0.5}]^{oct} [Si_4]^{tet} O_{10} F_2$ yields a superior charge homogeneous material that allows for swelling and quantitative delamination into individual platelets.[1-3]

When adding positively charged nanoparticles to the delaminated hectorite suspension, the oppositional charged objects heterocoagulate into a nanocomposite where the nanoparticles are sandwich-like stabilized by the clay platelets. This microporous structure grants good access to the reactive sites of the nanoparticles. For instance, a catalyst consisting of Palladium particles and hectorite exhibits high performance in high temperature gas phase oxidation reactions. Furthermore, the sandwich-like fixation leads to a better long term stability when compared to common supports as Al_2O_3. This catalyst might be a good alternative to established catalysts used for the cleaning of exhaust gases.

The sandwich-like catalysts can be used for photocatalytic applications as the clay sheets are transparent.[4] By use of semiconducting nanoparticles as iron oxide the composite catalyst shows interesting synergistic effects and high activity in the photocatalytic degradation of organic pollutants like dyes or drugs.

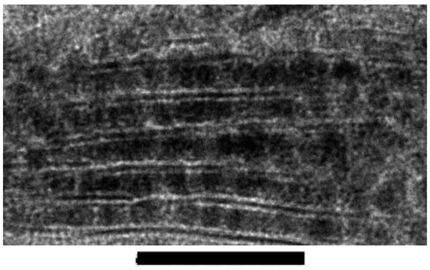

Figure 1: Cross section TEM of Palladium nanoparticles in the interlayer space of hectorite. The scale bar represents 20 nm.

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INTERMETALLIC COMPOUNDS AS CATALYSTS FOR OXYGEN EVOLUTION REACTION

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Coal, oil and natural gas are nearly reaching their end, and due to the current state of the global energy demand, it is necessary to find other sources. In addition, the use of fossil fuels leads the environment to rapid deterioration. For these reasons, it is necessary to provide enough clean and abundant sources of energy to supply the current and future population. One of the most efficient energy system is the water splitting to produce H_2 as a clean fuel.

The oxygen evolution reaction (OER) is the core reaction for the water splitting process; the formation of O_2 requires a transfer of four electrons, leading to the sluggish kinetics of this reaction. As result, large overpotentials to drive the reaction are required [1].

Electrocatalysts play an important role to overcome the slow kinetics of the OER. Intermetallic compounds (IMCs) are promising catalyst materials suitable for developing efficient catalytic systems. The superior activity of IMCs can result from the modification of the electronic states of the parent metals (electronic effect), which will influence the adsorption properties; and the modification of the geometrical environment at the catalyst surface (geometric effect), which will change the coordination number of the parent active metal forming preferential actives sites available to adsorbates [2, 3].

However, the assessment of the electrocatalyst activity and the establishment of reliable methods for reporting the performance of different materials under identical conditions are still very contradictory in the literature [4, 5]. Also, the stability of the materials is another point to take into account due to the harsh oxidative conditions, which require special stability protocols for catalyst evaluation as well as knowledge about the behavior of IMCs under oxidative conditions.

Therefore, in order to develop an efficient and suitable OER catalyst, it is necessary to approach the accurate evaluation of the activity and stability for intermetallic compounds as OER catalysts. Examples will be illustrated.

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SYNTHESIS OF TRANSITION METAL OXO-THIOSTANNATES AND INVESTIGATION OF THEIR PHOTOCATALYTIC PROPERTIES

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Many thiostannate compounds contain the $[Sn_2S_6]^{4-}$ unit as building unit. Compounds with sulfide and oxide anions are relatively rare. Prominent representatives are $[Sn_{10}S_{20}O_4]^{8-}$ [1, 2], $[Sn_{10}S_{16}O_4Cl_4]$ [3], $[Sn_8S_{12}O_4(SPh)_6]^{6-}$ [4], $[Sn_8S_{12}O_2(OH)_2Cl_6]$ [3] and $[Sn_4S_5(S_3)OCl_4]^{2-}$ [5]. Among these anions the $[Sn_{10}S_{20}O_4]^{8-}$ moiety is most common. We were able to synthesize two compounds with different tin-oxosulfide anions, namely $[Sn_6S_{12}O_2(OH)_6]^{10-}$ (**1**) and $[Sn_{10}S_{20}O_4]^{8-}$ (**2**) using $Na_4SnS_4 \cdot 14H_2O$ as precursor. Both compounds were obtained under hydrothermal conditions. Compound **1** could be obtained using the $[Ni(amine)](ClO_4)_2$ complex and compound **2** applying $[Ni(amine)(H_2O)_2](ClO_4)_2$. Compound **2** is a promising photocatalyst for hydrogen evolution (Fig. 1).

a) b)

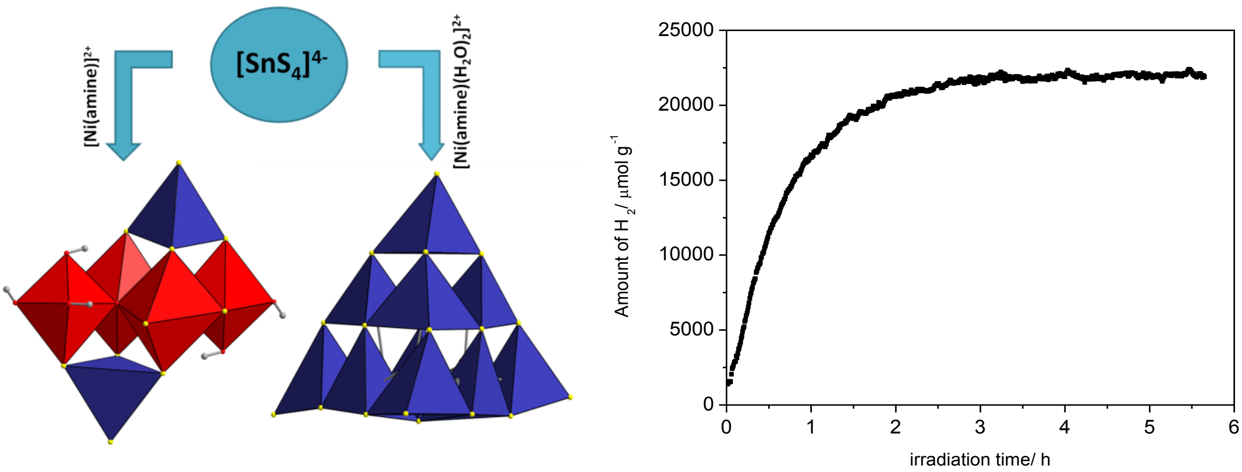

Fig. 1: a) Dependence of the formation of tin-oxosulfide anions on the complex, b) photocatalytic activity of compound **2**

Photocatalytic hydrogen evolution experiments were carried out with a system consisting of compound **2**, $[Ru(bpy)_3](PF_6)_2$ as photosensitizer, triethylamine as sacrificial additive and a acetonitrile-water mixture as solvent. The hydrogen evolution increases with irradiation time and reaches 21700 $\mu mol \cdot g^{-1}$ after 3h irradiation. Afterwards the hydrogen evolution remains constant. The stability of compound **2** during the photocataytic reaction was confirmed by XRD analysis. The X-ray powder patterns of the starting material and the catalyst after photocatalytic reaction are unchanged, indicating that H_2 is produced by a heterogeneous catalytic reaction.

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Revisiting the microwave-assisted water-free synthesis of $MgFe_2O_4$ nanoparticles towards applications in photocatalysis

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Spinel ferrites with the formula AFe_2O_4 have recently emerged as promising alternatives to well-investigated photocatalysts like TiO_2 and $BiVO_4$.[1] With a reported band gap of approx. 2 eV and band positions that would allow the splitting of water under illumination with visible light,[2] the partially inverse spinel $MgFe_2O_4$ stands out as a photocatalyst that offers a wide variety of possible applications addressing the increasing demand for green and sustainable chemical reactions. The material proves stable towards photocorrosion while the comprising elements are cheap and earth-abundant. Still to this day reports about the photocatalytic applications of this material are scarce, especially when the focus is laid on photocatalytic water splitting.

From diffraction patterns alone, nanocrystalline $MgFe_2O_4$ is hardly discernible from some of the common by-phases like magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3), which are readily formed when non-optimal synthesis conditions are chosen. Consequently such composites might be misinterpreted as a single phase material. In this work a procedure for a microwave assisted, water-free synthesis of single-phase $MgFe_2O_4$ nanoparticles will be presented.[3] Phase purity is ensured by X-ray diffraction, Raman spectroscopy and energy dispersive X-Ray spectroscopy as well as near-edge X-ray absorption spectroscopy. Furthermore (photo-)electrochemical measurements are shown and reasons will be discussed why the material might not live up to the expectations when it comes to photocatalytic water-splitting.

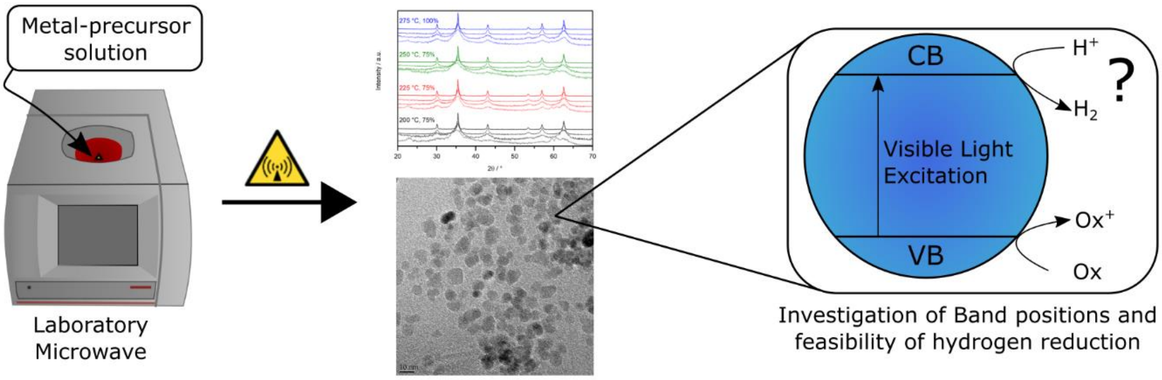

Fig. 1 Microwave assisted synthesis of $MgFe_2O_4$ nanoparticles and investigation of phase-purity and photocatalytic properties.

Acknowledgements: We thank Ralph Henning and the workgroup of Dr. Matthias Elm (Uni Giessen) for PLD preparation. We gratefully acknowledge financial support from the AiF within the program for promoting the Industrial Collective Research (IGF) of the German Federal Ministry of Economic Affairs and Energy (BMWi), based on a resolution of the German Parliament (project "QuinoLight", 18904N2). R.M. gratefully acknowledges funding in the Emmy-Noether program of the German Research Foundation DFG (MA 5392/3-1).

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POSTSYNTHETIC MODIFICATION OF MICROPOROUS ORGANIC POLYIMIDES

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The reduction of the anthropogenic greenhouse gas, as main factor of climatic change, has become a main topic for modern society. One medium term approach is to separate the main component carbon dioxide from flue gas and store it for long periods of time (carbon dioxide capture and storage CCS).[1] In this respect especially porous organic polymers (POPs) are a promising class of materials because of their distinctive properties such as variability in structure, pore size and high physisorptive gas uptake.[2] Since efficiency and investment costs for an implementation of CCS in power plants strongly depend on selectivity and uptake towards CO_2, the improvement of those properties is crucial.[1] Here, postsynthetic modification (PSM) is an convenient option to optimise various properties, like surface area or polarity of the inner surface.[4] Due to the harsh conditions needed for PSM, especially porous organic polyimides are particularly suitable because of their high thermal and chemical stabilities.[5] Here we present an optimised synthesis of the polyimide network MOPI-IV and its postsynthetic modification.[6] The networks were characterised by current methods like ^{13}C-, ^{19}F-NMR-, IR-spectroscopy and elemental analysis. The refinement of the synthesis conditions already led to an increase of the surface area from 896 m^2/g to 1090 m^2/g (NLDFT, CO_2) and an increase of the CO_2 uptake from 3.8 mmol/g up to 4.6 mmol/g. By introduction of covalently bound fluorine into the network both CO_2 uptake and surface area can be further increased significantly. This results in a ultramicroporous surface area of 1373 m^2/g and a superior CO_2 uptake up to 5.90 mmol/g. These values even exceed the state of the art microporous organic polyimide (MOPI) PI-NO_2-1 which at 4.03 mmol/g has the highest known CO_2 uptake for MOPIs to date.[7]

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The Onset of Osmotic Swelling in 2:1 Layered Silicates

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Delamination by osmotic swelling of layered materials is generally thought to become increasingly difficult, if not impossible, with increasing layer charge density because of strong Coulomb-interactions.[1-2] Nevertheless, for the class of 2:1 layered silicates, very few examples of delaminating organo-vermiculites were reported in literature.[3-4] We propose a mechanism for this repulsive osmotic swelling of highly charged vermiculites based on critically weakening the electrostatic attraction of adjacent layers above a certain threshold separation d*. Based on this mechanistic insight, we were able to identify several organic interlayer cations appropriate to delaminate highly charged, vermiculite-type layered silicates. Moreover, one of these organo-cations (N-Methyl-D-Glucosammonium) ensures a layer charge robust osmotic swelling irrespective of both, the layered silicate's charge density and its charge heterogeneity. These findings suggest that the osmotic swelling of highly charged organo-layered silicate is a generally applicable phenomenon rather than the odd exemption.

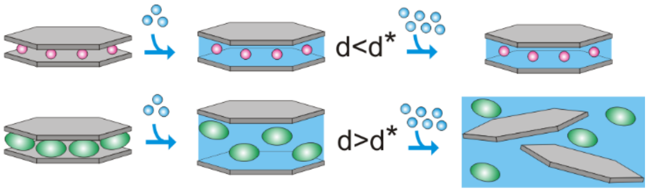

Fig. 1. A simple explanation for the onset of osmotic swelling of organo-layered silicates is offered. At a critical d-spacing electrostatic attraction is critically weakened. This d-spacing is achieved by the swelling of bulky organic but hydrophilic interlayer ions at a small enough charge equivalent area (high enough charge density) of the layered silicate.

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VAPOR-PHASE AMINE INTERCALATION FOR THE RATIONAL DESIGN OF PHOTONIC NANOSHEET SENSORS

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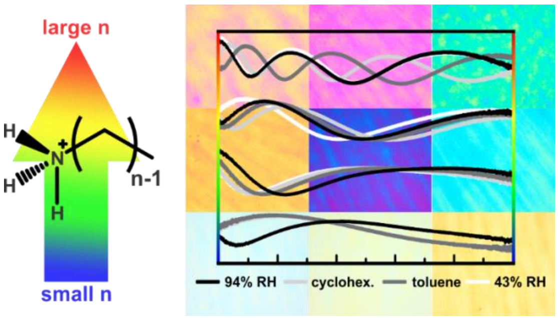
The development of vapor sensors with tunable sensitivity and selectivity based on rational molecular design is challenging, however at the same time of great interest due to the manifold applications in our everyday life, e.g. in air quality monitoring or food control. Here, we address this challenge by designing and tailoring vapor sensors based on stimuli-responsive 2D nanosheet materials.[1-4] $H_3Sb_3P_2O_{14}$ nanosheet-based Fabry-Pérot interference sensors are endowed with chemical selectivity by modifying the nanosheets with primary and tertiary alkylamines.[1] The photonic sensors allow to distinguish different amines based on the intercalation time and optical shift, arising from different amine sizes and thus varied chemical properties, such as polarity or vapor pressure. Apart from amine sensing, the amine intercalation can be applied to gradually and widely tune the sensor's sensitivity towards various analytes. The locally resolved amine intercalation allows the construction of single chip sensor arrays capable to distinguish between different volatile organic compounds. For both cases, amine sensing as well as analyte sensing, the color change of the sensor can be tracked with the naked eye. Moreover, we report a soft, fast and straightforward post-synthetic re-modification of the amine intercalated sensors, which allows an even broader application range.

Fig. 1: Schematic description of the color change induced by the modification of nanosheet-based Fabry-Pérot interference sensors.[1]



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CONTROLLING CRYSTALLIZATION OF POLYOXONIOBATES

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While metal oxide clusters based on V, Mo and W were in the focus of polyoxometalate chemistry for a long time, polyoxoniobates (PONbs) are less developed[1]. Most of the transition-metal containing PONbs are synthesized hydrothermally[2] but this method can be regarded as a trial-and-error method. Most recently, we were able to present a more systematic approach enabling the fast screening of the parameter space[3]. Applying the so-called dynamic conditions in glass tubes, where the slurry is stirred during solvothermal reactions, we discovered two new PONbs $K_5[Cu(H_2O)_2(cyclam)]_{1.5}\{[Cu(cyclam)][Cu(H_2O)(cyclam)]_2HSiNb_{18}O_{54}\}(NO_3)\cdot 30H_2O$ $\{SiNb_{18}O_{54}\}$ and $\{[Cu(cyclam)(H_2O)]_2[Cu(cyclam)][Nb_{10}O_{28}]\}_n\cdot 9nH_2O$ $\{Nb_{10}O_{28}\}$. We observed that the cluster geometry of the compounds is strongly dependent on the starting pH value of the reaction mixture (Fig.1a).

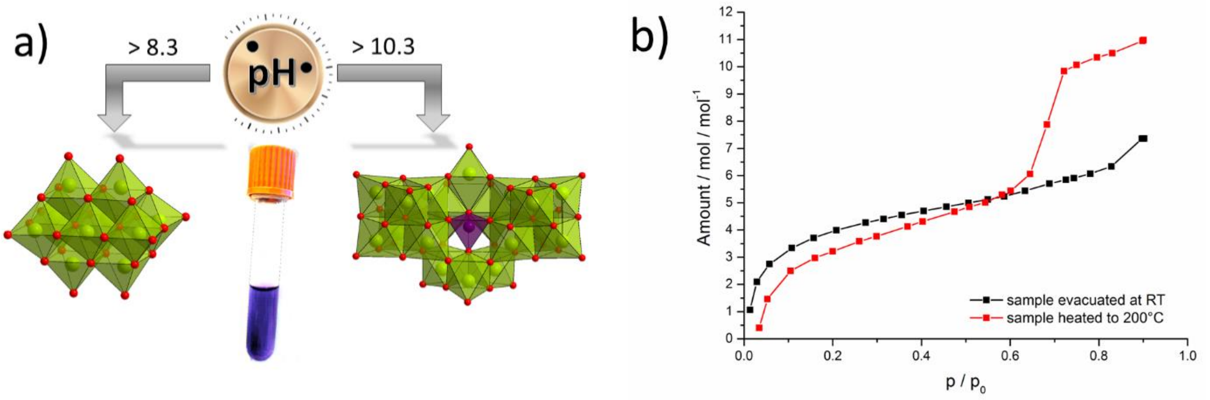

Fig. 1: a) pH value influences the crystallization of $\{Nb_{10}O_{28}\}$ and $\{SiNb_{18}O_{54}\}$. b) Water sorption isotherms of $\{Nb_{10}O_{28}\}$.

The compounds are characterized by a large number of co-crystallized water molecules that form complex patterns, the so-called water clusters[4]. Furthermore, the thermogravimetric (TG) curve reveals a pronounced plateau after removal of H_2O molecules from $\{Nb_{10}O_{28}\}$. Water sorption measurements proved that the sample can be totally or partially dehydrated, depending on the treatment prior to the measurement (Fig. 1b). In addition, we evaluated the role of the atmosphere during decomposition of $\{SiNb_{18}O_{54}\}$ and $\{Nb_{10}O_{28}\}$ and we have found significant differences concerning the evolution of the TG curves and the decomposition products, e.g. heating $\{Nb_{10}O_{28}\}$ under air atmosphere to 600 °C, a nanocrystalline material was obtained. Thus PONbs are promising precursors for the synthesis of novel nanosized materials.

Using stirring conditions, we were able to significantly reduce the reaction time from days/hours to the range of minutes for the synthesis of new PONbs, obtained high yields. Currently, we are successfully investigating reaction systems with different chemical compositions[5]. The synthetic approach presented here can also be utilized for the fast and efficient synthesis of Ti-PONbs.

Acknowledgements: The authors thank the Land of Schleswig-Holstein for the financial support.

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In-situ monitoring of the mechanism of formation of the Eu^{3+}-doped und undoped layered double hydroxides

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Layered double hydroxides (LDHs) are intercalation compounds represented by the general formula $[M^{2+}_{1-a}M^{3+}_{a}(OH)_2]^{a+}$ $(A^{n-})_{a/n}.yH_2O$ (abbreviated as $M^{2+}_{1-a}M^{3+}_{a}$-A), where $M^{2+/3+}$ is a divalent or trivalent metal cation. A^{n-} is the interlayer anion compensating the positive charge of the metal hydroxide layers[1]. Various forms of LDHs have attracted great attention because of the wide variety of elements and ions that can be incorporated in this layered structure, enabling them to be applied in areas like catalysis, adsorption, medical science[2] and fluorescence imaging[3]. Monitoring the LDHs formation process by means of *in-situ* characterization methods is important not only for understanding their crystallization mechanism but also for optimizing and predicting the synthesis of functional LDH materials. Here, using *in-situ* measurements of pH value, ion conductivity, light transmission and luminescence spectroscopy, the mechanism of formation of the $[Mg_{1-a}Al_a(OH)_2]^{a+}(CO_3^{2-})_{a/n}).yH_2O$ during different approaches of co-precipitation synthesis have been studied as well as the influence of key reaction parameters such as solution concentration and temperature. In addition, doping the LDH with Eu^{3+} allowed the application of the *in-situ* luminescence analysis of coordination sensors (ILACS) approach[4]. *In-situ* measurements of light transmission revealed that it was possible to control the targeted onset of the crystallization of the layered material, decreasing it from 20 min to 12.5 min and 6 min by increasing the initial concentration two and three times, respectively. Heating the reaction solution from 25 °C to 65 °C did not significantly influence the onset of the crystallization, but accelerated the reaction rate. Under visible light, undoped and doped LDH are colourless whereas they emit blue and red light under UV irradiation, respectively (Fig. 1a). Adding a solution of sodium carbonate and hydroxide to a solution containing magnesium, aluminium and europium nitrates, the intensity of the emission band at 615 nm (orange curve, Fig. 1b) corresponding to the $^5D_0 \rightarrow {}^7F_2$ electronic transition of Eu^{3+} ions started to increase after t = 9.15 min, indicating the formation of the layered material. The slower growth rate between 20 min and 90 min could be assigned to the crystal growth, in agreement with the decrease of light transmission, obtained during previous undoped LDH experiments. During the aging step increasing the temperature to 65 °C after 90 min, an additional growth rate indicated by the further increase of the Eu^{3+} intensity despite thermal quenching effects could be assigned to the additional crystallite growth, decreasing the number of lattice defects and therefore decreasing the luminescence quenching. In summary, the results obtained using *in-situ* characterization methods like the ILACS technique during the formation of LDH are especially important, since experiments at the DESY synchrotron facility indicate that the synthesized LDH crystal size is too small for monitoring the synthesis process by means of *in-situ* X-ray diffraction analysis.

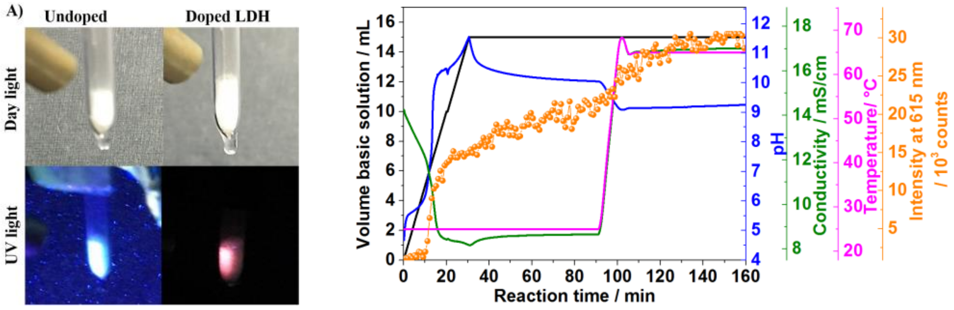

Figure 1: A) Undoped and doped LDH under visible and UV light. B) Time dependent *in-situ* emission spectrum of Eu^{3+} at 615 nm (orange curve), *in-situ* measurements of the ion conductivity (green curve), pH value (blue curve), temperature (magenta curve) and addition of Na_2CO_3 and NaOH solution to the solution of Al, Mg and Eu nitrates (black curve), recorded during the synthesis of Eu^{3+}-doped LDH.

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[Sm(1,10-phenanthroline)$_2$(NO$_3$)$_3$]·(2,2’-bipyridine): crystal structure, optical properties and mechanism of formation

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Luminescent lanthanide complexes have been intensively investigated over the past few decades, especially due to their diverse applications in e.g. optoelectronics and biomedicine, such as production of electroluminescent devices or emissive probes in biological systems. [1, 2] However, for the rational synthesis of these compounds and control over their structure-related properties like luminescence, it is important to monitor and control their crystallization process by means of *in-situ* characterization techniques. This work presents the crystal structure of the new [Sm(phen)$_2$(NO$_3$)$_3$]·bipy (phen = 1,10-phenanthroline, bipy = 2,2’-bipyridine) complex, the characterization of its luminescence properties and mechanism of formation monitored by e.g. the *in-situ* luminescence analysis of coordination sensors (ILACS) approach[3] and synchrotron-based *in-situ* X-ray diffraction (XRD) analysis. Hence, the crystallization process of this complex was applied for delivering the first *in-situ* XRD results measured at the new P23 beamline of the German Electron Synchrotron (DESY). In summary, [Sm(phen)$_2$(NO$_3$)$_3$]·bipy crystalizes isostructurally to [Eu(phen)$_2$(NO$_3$)$_3$]·bipy [4] in the space group C2/c and four formula units in the unit cell, with cell parameters a = 12.7776(10) Å, b = 15.9860(13) Å, c =17.2526(14) Å, α = 90 °, β = 102.3169(19) °, γ = 90 °. Under irradiation with UV light, this complex emits strong reddish light (Fig. 1), due to the $^4G_{5/2}\rightarrow{}^6H_{5/2\text{-}11/2}$ electronic transitions of Sm^{3+}. Upon the addition of the bipy and phen to the samarium nitrate solution during the *in-situ* experiments, an emission peak at ca. 500 nm is detected, assigned to the $\pi\rightarrow\pi^*$ electronic transitions of the organic ligands, which intensity increases until t = 18 min. Afterwards, the intensity of this band starts to decrease, simultaneously to the rise of sharp peaks assigned to the Sm^{3+} transitions, due to the antenna effect. These results show, for the first time by the ILACS approach, the transition of the organic molecules from the solution to the product incorporation. Increasing the reactant concentration to 150 % and 200 %, the product formation was shifted to t = 6 min and t = 4 min, respectively. Interestingly, the ILACS measurements additionally show that the increase of the temperature caused rather a delay instead of the acceleration of the product formation, most probably because of the increase of the complex solubility. These results were confirmed by simultaneous *in-situ* measurements of pH value and ion conductivity, while the *in-situ* XRD experiments characterized the crystallization profile from a saturated solution upon the decrease of the temperature.

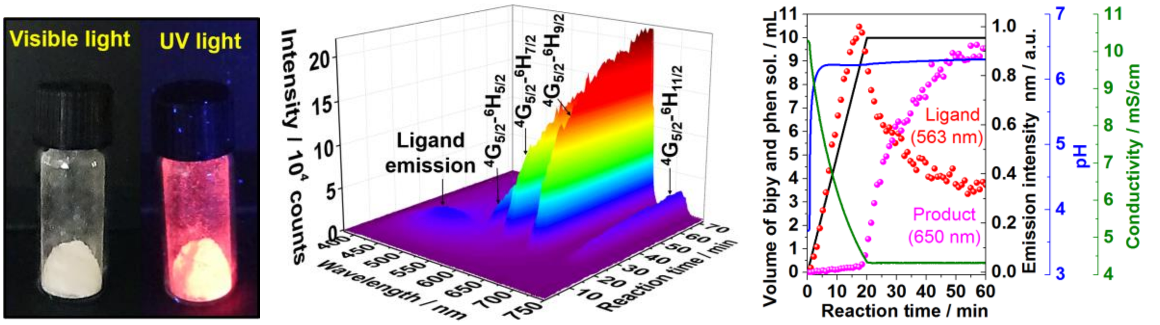

Fig. 1. Left: [Sm(phen)$_2$(NO$_3$)$_3$]·bipy complex under visible and UV light (left). Middle: Time-dependent *in-situ* luminescence spectra recorded during synthesis of [Sm(phen)$_2$(NO$_3$)$_3$]·bipy complex. Right: Time-dependence of the addition of the phen and bipy (black curve) to the Sm^{3+} nitrate solution, *in-situ* measurements of the pH value (blue curve), ion conductivity (green curve), normalized emission intensity (λ_{ex} = 365 nm) of the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ electronic transition of Sm^{3+} (magneta curve) at 650 nm and of the ligands at 500 nm (red curve).

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SYNTHESIS OF PEROVSKITE-TYPE NIOBIUM OXIDE NANOSHEETS INCORPORATED WITH MANGANESE IONS

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Layered materials, e.g., clays, layered metal oxides, chalcogenides, layered double hydroxides, can be delaminated into molecularly thin 2D materials, or nanosheets. They have attracted significant attention because they often exhibit new or enhanced physical properties based on their unique 2D structure. We have reported that a series of 2D oxide nanosheets with a progressively varied thickness were derived from a homologous family of layered perovskite niobates, $KNa_{n-3}Ca_2Nb_nO_{3n+1}$ (n = 3-6), through soft-chemical delamination processes [1]. In this work, we applied this synthetic strategy, or “solid-state templating method”, to produce new homologous compounds, ACa$_2$MnNb$_3$TiO$_{13}$ (A = K or Rb), containing manganese ions Then the obtained compounds were successfully exfoliated into new perovskite-type oxide nanosheets.

A stoichiometric mixture of the precursor layered perovskites, ACa$_2$Nb$_3$O$_{10}$ (A = K or Rb), and ilmenite-type manganese titanate, $MnTiO_3$ was heated at 1373 K for 48 h under an atmosphere. XRD data indicates the expansion of interlayer spacing by ca. 0.4 nm in comparison to the precursor, corresponding to the height of NbO_6 or TiO_6 octahedron. The Rietveld refinement of $RbCa_2MnNb_3TiO_{13}$ confirmed the layered perovskite structure having a host slab of n = 4 (Fig. 1). The obtained samples were converted into H^+-exchanged form, $HCa_2MnNb_3TiO_{13}\cdot nH_2O$ upon treatment with a 5 M HNO_3 solution. And then the H^+-exchanged sample was reacted with an aqueous solution containing tetrabutylammonium hydroxide. After reaction for 7days, a turbid colloidal suspension by a delaminated material was obtained. AFM observations after depositing onto a Si substrate detected micrometer-sized 2D objects with a uniform thickness of ca. 2.6 nm (Fig. 2). This result strongly suggests the delamination into unilamellar nanosheets. In-plane and out-of-plane XRD data further support the full exfoliation of the layered perovskite compound. The result of atomic ratio by XPS of the nanosheet film was confirmd to keep stoichiometric ratio in perovskite layer. These results indicate that new perovskite-type 2D nanosheets of $Ca_2MnNb_3TiO_{13}$ were obtained.

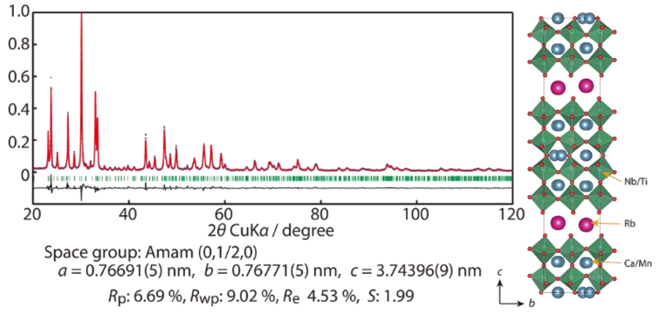

Fig. 1 Rietveld refinement of $RbCa_2MnNb_3TiO_{13}$.

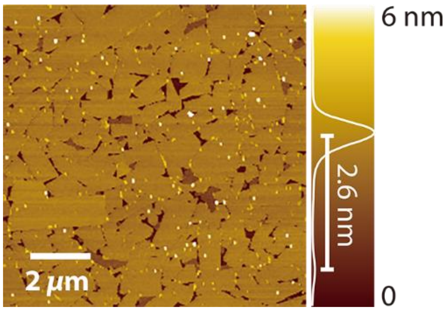

Fig. 2 AFM image of $Ca_2MnNb_3TiO_{13}$ nanosheets..

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OXYGEN EVOLUTION REACTION WITH MÖSSBAUERITE – INFLUENCE OF NICKEL DOPING ON THE STRUCTURE AND ACTIVITY OF A TRIVALENT IRON ONLY LAYERED DOUBLE HYDROXIDE

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The high overpotential of the oxygen evolution reaction (OER) represents the critical issue in electrocatalytic water splitting which ideally should be tackled by base metal catalysts. In particular, NiFe-based (oxy)hydroxides and layered double hydroxides (LDH) have been shown to be among the most active OER catalysts in alkaline electrolyte solutions, the best even surpassing state of the art noble oxides. Fe was shown to play a crucial role which, however, is not yet fully understood. Fougèrites are abundant natural minerals found under specific geological conditions (low T, moderate CO2 fugacity, alkaline pH). Minerals of the fougèrite group are the only members of the hydrotalcite supergroup where divalent and trivalent cations are of the same element (iron). Forced oxidation of the mixed-valence LDH green rust preserves the LDH structure and results in the oxidation-stable trivalent iron only mössbauerite. The fully oxidized carbonate interlayered iron LDH has recently been shown to be an efficient electrocatalyst with unexplored versatility towards morphology modification or doping [1].

While $Ni_{1-x}Fe_x$ OOH (oxy)hydroxide electrocatalysts have been under intense study for their superior performance and numerous work indicates that both, Ni and Fe are essential in decreasing the necessary overpotentials, the essential role of either one in the LDH structure has to be established, yet. A critical aspect is that the incorporation of Fe^{3+} in the brucite structure is restricted to 1/3 to result in a LDH with anions in the interlayer for charge balance. This issue can be addressed by the synthesis of LDHs with both divalent and trivalent iron and allows doping with foreign atoms in wide range without producing secondary phases.

In this work, we report the synthesis, characterization, and catalytic activity of phase pure NiFe LDHs containing with unusual high Fe content by simple coprecipitation. A continuous increase of the iron content results in several structural changes of the fully oxidized electrocatalyst. We observe a steady decrease in the d-spacing towards 7.0 Å which is in good agreement with the work of Vaysse on pillared layered hydroxides with grafted carbonate [2]. Indeed, IR spectroscopy indicates increased mono-grafting of carbonate to the hydroxyl slabs with increasing iron content. Furthermore, the amount of carbonate between the brucite layers is shown to be dependent on the metal ratio. The unusual wide variability of Ni/Fe ratio while preserving the LDH structure renders our approach with mixed valence iron as intermediate interesting for systematic screening and possible mechanistic studies regarding the electrocatalytic OER. Water oxidation experiments in basic media show that the catalytic activity increases with increasing Ni content. Those results confirm the existence of a synergistic mechanism between the two metal species but for the first time in phase pure LDH structures.

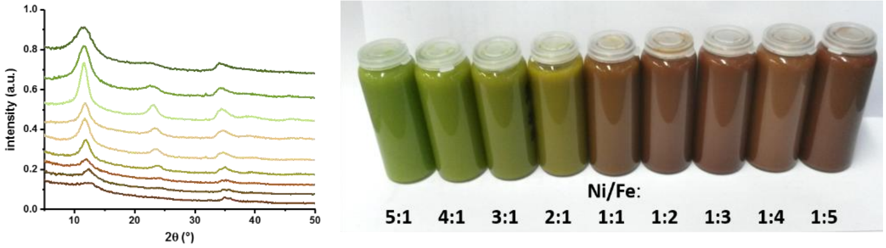

Fig. 1 PXRDs of NiFe LDHs with increasing Fe content show a lowering of the d-spacing from 7.7 Å to 7.0 Å.

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Reactivity of Intermetallic Phases in Ionic Liquids

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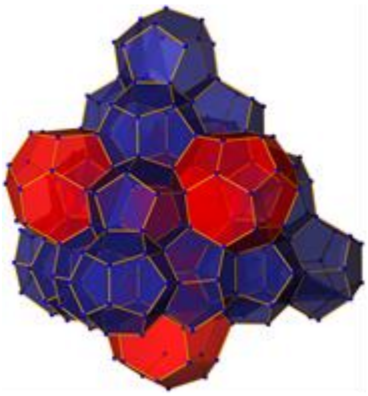
Redox reactions at low temperatures have been used for the preparation of metastable intermetallic phases and element modifications[1,2]. Also the applicability of protic ionic liquids such as quaternary ammonium tetrachloroaluminates in that kind of reactions has been demonstrated by the examples of the metastable allotrope Ge(*cF*136) [3], the related $K_{8.6}Ge_{136}$ [4] or a metastable intermetallic phase of Zn and Si [5]. Particularly a possible dissolvability of salt-like intermetallic starting materials in inert ionic liquids would provide prospects for homogeneous redox reactions to, e.g., solvent-free intermetallic phases with group-14 cluster polymers.[6] However, a more universal application of redox reactions in ionic liquids often suffers from the inherent and hardly controllable reactivity of protic ionic liquids [7]. This contribution summarizes recent results of studies on the reactivity of tailored non-protic imidazolium-based ionic liquids towards intermetallic and related salt-like phases, for which $Na_{12}Ge_{17}$ and Li_2C_2 have served as model materials providing a high sensitivity and promising oxidation products [3, 8] (Fig. 1).

Fig. 1 The metastable allotrope Ge(*cF*136) with empty type-II clathrate crystal structure, which may be accessed by the oxidation of $Na_{12}Ge_{17}$.



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Microphase separation of small amphiphilic molecules: DFT-based polymorph design

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Due to enhanced solubility and dissolution rates many new active pharmaceutical substances are marketed as salts of carboxylic acids. A major drawback of this method is the corresponding difficulty to crystallize these salts. Therefore they show a low degree of long range order in their structure. This is mainly caused by the widely differing sizes of small inorganic cations and large organic anions in conjunction with 1:1 stoichiometry. The aforementioned often leads to a frustration of coordination needs for the cations. Even rather small amphiphilic molecules like the widely used food preservative sodium benzoate (NaBz) are prone to this behavior. NaBz is marketed in semi-crystalline forms and no crystal structures were known until a first structure was published by Butterhof *et al.* in 2013[1] and a second one to be published soon.[2] In these crystal structures micro-phase separation takes place to form tube like structures. The core of these tubes consists of the polar groups and sodium cations which are surrounded by an unpolar corona.

Some samples of NaBz showed PXRD patterns that could not be indexed due to low crystallinity. Therefore we applied modelling techniques based on the basic tube motif modifying the size of the tubes. Simulations on density functional theory (DFT) level were used to elucidate the structures from our modelling approach. A potential third polymorph was found fitting to the PXRD pattern of a commercial sample of NaBz. Furthermore a potential fourth polymorph was found which has not been observed in experiments before. In contrast to the known polymorphs this phase exhibits a layered like structure as it is known for potassium benzoate (KBz).[1] Further guided experiments on crystallization show promising PXRD patterns for this structure. Additionally ^{23}Na solid state NMR (*ss*-NMR) STMAS experiments can be used for further structure elucidation as simulation of the quadrupole constants for the DFT based modelled structures is straight forward.

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^{1}H NMR CRYSTALLOGRAPHY ON NANOLITER RINGWOODITE CRYSTALS REVEALING ITS HYDROUS DEFECT CHEMISTRY

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High-pressure silicate minerals, like ringwoodite (γ Mg_2SiO_4), which make up the main proportion of the Earth's interior, can incorporate a significant amount of water in the form of OH defects.[1] The recent discovery of natural hydrous ringwoodite containing about 1 wt% H_2O is proving the presence of high water contents in the transition zone, which over the volume of the mantle equates to a potential mass of H_2O in the Earth's interior that exceeds that of the oceans.[2] Recently, we were able to qualitatively and quantitatively solve the defect chemistry of a ringwoodite sample containing about 0.1 wt% H_2O with the help of an NMR-crystallographic approach.[3,4] As such, we can show that four competing defect types are forming: additionally to low-valent Mg^{2+} defects (V_{Mg}``+ 2H**) high-valent Si^{4+} vacancies emerge, which are charge balanced either by four protons (V_{Si}````+ 4H****) or one Mg^{2+} and two protons (Mg_{Si}``+ 2H**). Furthermore, a significant proportion of coupled Mg and Si vacancies ($Mg_{Si}V_{Mg}$````+ 4H****) are present.[4]

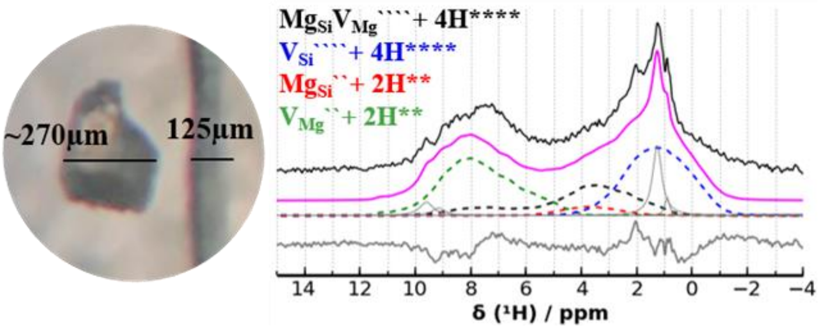

Fig. 1 Left: Hydrous ringwoodite crystal (~15nL) containing ~0.7 wt% H_2O. Right: corresponding ^{1}H MAS spectrum (black) recorded at 62.5 kHz MAS rate and at a Larmor frequency of 1 GHz corresponding to a magnetic field of 23.5 T. The spectrum was refined by fitting previously established ^{1}H chemical shift footprints of each defect type[4] allowing to determine the defect ratio.

Since the different defect types will significantly alter the chemical and physical properties of ringwoodite and thus transport properties, such as viscosity and thermal conductivity, of the Earth's mantle, it is essential to solve its defect chemistry as function of water concentration. Therefore, we prepared hydrous ringwoodite crystals of ~5-200nL volume with varying H_2O concentrations and used standard MAS, as well as μMAS piggyback techniques[5] to measure the ^{1}H MAS spectra of each nanoliter sample. By the use of a previously established description of the individual ^{1}H chemical shift footprints of each defect type,[4] we are able to fit the broad and overlapping ^{1}H MAS spectra (Fig. 1) and thus can extract the defect ratios for each crystal. Further detailed characterization via XRD and polarized FTIR of the same crystals may provide access to correlations between the crystal structure, water concentrations and defect ratios being the basis for thermodynamic descriptions of ringwoodites defect chemistry in the future.

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SPRAY COATING OF CLAY-BASED, (ULTRA) HIGH GAS BARRIER SYSTEMS

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Packaging materials for flexible optoelectronics devices like organic light emitting diodes require (ultra) high barrier properties with transmission rates for oxygen (OTR) and water vapor (WVTR) of less than 10^{-5} $cm^3/(m^2$ day bar) and 10^{-6} $g/(m^2$ day), respectively [1]. Next to the barrier properties of a system, even for food packaging applications, the biodegradability and the antimicrobial properties of a system are indispensable. Therefore, results concerning these functions will also be presented.

The Cussler model describes the dependence of the transmission rate on the filler content and the aspect ratio of the filler [2]. An expeditious melt synthesis of a phase pure sodium hectorite $[Na_{0.5}]^{inter}$ $[Mg_{2.5}\ Li_{0.5}]^{oct}$ $[Si_4]^{tet}$ O_{10} F_2 yields large tactoids of up to 20 µm in diameter [3,4]. The superior charge homogeneity of this material allows for swelling and quantitative delamination into individual platelets with aspect ratios of up to 20 000 [5].

According to Cussler, the tortuous path length is increased by a perfect alignment of the filler platelets into a textured nanocomposite film. Furthermore, due to the increased Coulomb interactions in one-dimensional (1D) crystalline smectic liquid crystalline films the free volume and, therefore, the permeability will be further decreased. We first observed such a 1D-crystallinity in a waterborne spider silk/clay nanocomposite made by sedimentation. These films show a reduced swelling behavior at elevated relative humidity (rh) and, furthermore, a surprisingly low water permeability [6].

Spray coating as method improves the crystallinity of such composite films. Within this processing large area liquid crystalline, smectite composite films are generated. The excellent positional order of the individual silicate layers in the polymer matrix are displayed by up to four higher-order reflections. OTR and WVTR values of down to 10^{-4} $cm^3/(m^2$ day bar) and 10^{-4} $g/(m^2$ day), respectively, are observed with water based liquid crystalline nanocomposite films (ethoxylated polyethyl-enimine/polyacrylic acid polymer) at 23 °C and 50 %rh [7]. Less ordered films made by doctor blading show lower transmission rates up to 2 orders of magnitude. This indicates, that the superb barrier performance is dependent on the quality of the liquid crystallinity.

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Synthesis routes and conversion reactions to functional ternary chalcogenides

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A range of fascinating compounds and properties was discovered within the ternary phase diagram MACh in recent years. Examples are the 2D half metal ferromagnetic system $Co_3Sn_2S_{2-x}Se_x$ [1] that is currently investigated with respect to skyrmions, superconducting $Ni_3Bi_2S_2$, topological $Pd_3Bi_2S_2$ and tunable semiconductors and thermoelectrics like Co_3InSnS_2, $Ni_3Sn_2S_2$, pyrite and skutterudite related compounds $Ir_2Sn_3Ch_3$ (Ch = S, Se, Te) [4]. The compounds are prepared by several solid state or liquid reaction routes. Within our recent research we developed routes for directed synthesis of targets within competing structures or compositions. Conversion reactions were applied for e.g. flux synthesis to $Ir_2Sn_3Se_3$ or Co_3Sn_2SeS. In a next step polyol routes syntheses were used to direct reactions and to study routes of formation. Thus, Ni^{2+} could be reacted with SnS to $Ni_3Sn_2S_2$, core-shell Ni@SnS or binary Ni3Sn2 or Ni_3S_2. On the other hand $Ni_3Bi_2Se_2$ and NiBiSe were shown to be formed from Bi_2Se_3 via decomposition to Bi and formation of NiBi. The soft chemistry methods are further applied to synthesize stable and metastable compounds as predicted by DFT modelling [5]. We present and discussed the mentioned investigations and recent results.

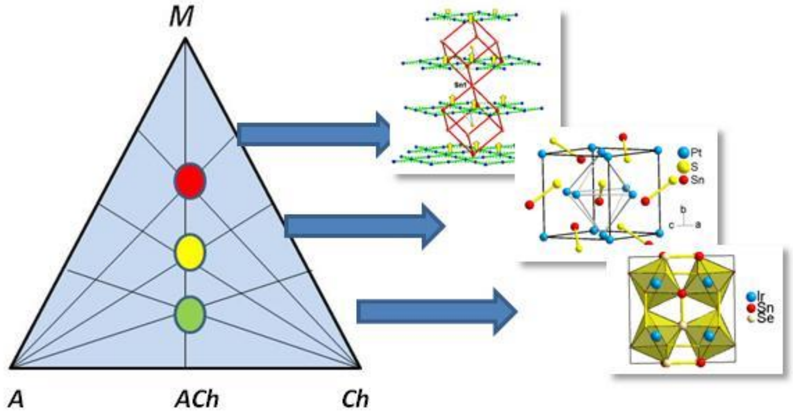

Fig. 1 Synthesis of MACh compounds with varying composition

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HIGHLY REACTIVE SOFT CHEMISTRY PRECURSORS FOR OXYNTRIDE SOLID SOLUTIONS

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$AB(O,N)_3$ perovskite oxynitrides are an extensively studied class of materials because of their versatile possible applications ranging from photocatalysts, pigments, dielectrics to semiconducting materials [1].

For the preparation of most oxynitrides it is possible to use conventional solid state synthesis starting either from stoichiometric oxide/carbonate mixtures or mixed oxides in the desired ratios like $Ca_2Ta_2O_7$. For $CaNbO_2N$ and other Ca/Nb containing oxynitrides it was found that this approach is not suitable and leads to the formation of niobium(oxy)nitrides as byproducts. A hydrothermal synthesis method was therefore developed as a suitable approach to obtain highly reactive precursors, which suppress the niobium(oxy)nitride formation by drastically lowering the necessary nitridation temperatures [2]. Such precursors can additionally be used to prepare oxynitrides with rather high surface areas, which is desired for an application as photocatalysts.

Based on these findings, we herein report on the thermal and structural properties of partially amorphous oxide precursors containing Ca and Nb. They were obtained by hydrothermal synthesis in alkaline solutions of calcium (strontium) nitrate and niobium chloride. Their thermal behavior was investigated using TG/MS-measurements combined with high temperature X-ray diffraction to obtain a complete understanding on the composition of these precursors and to investigate phase transitions leading to the enhanced reactivity during nitridation.

The Ca and Nb containing precursors exhibit a cubic pyrochlore structure. Upon heating, they release water and CO_2 and undergo a phase transition above 720 °C which leads to a distinct decrease of the cell volume. This apparently reactive phase is stable up to 930 °C where a second irreversible phase transition occurs and the layered perovskite high temperature phase is stabilized.

Phase pure oxynitrides of the $Ca_{1-x}Sr_xNbO_2N$ solid solution series were prepared for the first time without the occurrence of niobium(oxy)nitride impurities utilizing these reactive precursors and a comparatively low ammonolysis temperature of 750 °C. The photocatalytic properties of the obtained single-phase samples have been investigated. The oxynitrides were loaded with CoO_x as co-catalyst [3] and the decomposition of methyl orange solution under irradiation was used to test their photocatalytic suitability. As light source a Xe arc lamp equipped with different optical filters was used to investigate the effects of UV/Vis- and purely visible light. The members of the $Ca_{1-x}Sr_xNbO_2N$ solid solution exhibit rather high degradation values, reaching up to 60 % with a major visible light contribution.

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STABILIZATION OF THE THREE-LAYERED STACKING OF *P*3-$Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ BY Mg-DOPING FOR CATHODE MATERIALS FOR DUAL Na-Li-ION BATTERIES

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The growing demand for effective energy storage systems requires new generations of batteries that have not only high specific capacity and power density, but also high safety, long cycle life and low price. In the last few years, the sodium ion batteries have been advanced as an alternative to the lithium ion technology because of the low-cost and abundant sodium resources. Searching for efficient electrode materials, it has recently been proposed the using of environmentally friendly and low cost elements like magnesium ions as dopants in layered sodium transition metal oxides [1,2]. It has been demonstrated that the most attractive electrode materials are Mg-substituted oxides with two-layered stacking (i.e. *P*2-type structure) such as $Na_xMg_{0.11}Mn_{0.89}O_2$ [1] and $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ [2].

In order to combine the advantages of Li- and Na-ion batteries by avoiding their disadvantages, we propose a new approach, which consists in the development of the dual Na-Li-ion batteries, in which Li^+ and Na^+ ions are simultaneously engage to store energy in a way to achieve the synergetic effect [3,4]. This becomes feasible due to utilization of new structural modification of sodium nickel manganese oxides as a cathode material: i.e. *P*3-$Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ with a three-layered stacking.

Herein, we present new data on the stabilization of the *P*3-type structure of $Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ by Mg-doping: *P*3-$Na_{2/3}Ni_{1/2-x}Mg_xMn_{1/2}O_2$, $0 \leq x \leq 1/6$. For the preparation of oxides, we have adopted a simple precursor method that consists in thermal decomposition of mixed sodium-nickel-magnesium-manganese acetate salts obtained by freeze-drying. The solid state reaction proceeds at 700 °C, as a result of which well-crystallized $Na_{2/3}Ni_{1/2-x}Mg_xMn_{1/2}O_2$ with *P*3-type structure is formed. The structure of the sodium oxides were determined by powder X-ray diffraction in the framework of the Rietveld refinement method. The oxidation state of nickel ions was determined by electron paramagnetic resonance spectroscopy. The electrochemical performance of *P*3-$Na_{2/3}Ni_{1/2-x}Mg_xMn_{1/2}O_2$ was carried out in model two-electrode cells versus Li metal as an anode. The mechanism of the electrochemical reaction is monitored by cycling voltammetry using three electrode cells. It is found that the Mg-dopants improve dramatically the electrochemical performance of *P*3-$Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$: (i) the reversible capacity reaches a value of 130 mAh/g, which is two times higher than that of undoped oxide; (ii) the rate capability is also higher than that of the undoped oxide. These results demonstrate that *P*3-$Na_{2/3}Ni_{1/2-x}Mg_xMn_{1/2}O_2$ can serve as an effective electrode material for the dual Na-Li-ion batteries.

Acknowledgements: Authors are grateful for the financial support from the “Program for supporting young scientists in BAS” (No DFNP-17-24/25.07.2017).

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Exploring the pore space of CAU-1 using hyperpolarized ^{129}Xe-NMR

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The utilization of hyperpolarized (HP)-^{129}Xe-NMR for the analysis of porosity holds many advantages compared to conventional methods like gas physisorption because of the sensitivity enhancement by four to five orders of magnitude. The ^{129}Xe chemical shift is influenced strongly by the shape of pores as well as the interactions with the pore walls.[1,2] In this respect Fraissard et al. established a model to predict pore sizes for the material class of zeolites based on a direct connection between the pore sizes with the appearing chemical shift of isolated Xe atoms.[3]

Compared to purely inorganic zeolites, metal organic frameworks (MOFs) are demonstrating a different influence on the chemical shift caused by the influence of linkers or clustered metal ions. Here we show that the original Fraissard-model applied on microporous aluminum-based MOFs like CAU-1 or MIL-53 leads to large deviations. As model frameworks, CAU-1 as well as two postsynthetically modified derivatives with stepwise reduced pore sizes were utilized. Based on these frameworks, measurements of the chemical shift as a function of pore sizes together with DFT calculations were carried out to get a better understanding of the inherent adsorption processes. The experimental data is modeled by ab-initio calculations where all possible adsorption positions of Xe were scanned and the associated energy and chemical shifts were calculated. Therefore, we are able to determine the most favored adsorption sites for Xe within the network, lying in the smallest pores near the linker molecules. A Boltzmann weighted shift for the whole network was calculated and shows the arising influence of Xe-Xe-interactions at lower temperatures. Combining the obtained results with pore size distributions and Xe-concentrations from Ar-/Xe-physisorptions experiments allows the correlation between the measured chemical shift of ^{129}Xe and the structure of CAU-1 species.

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IMPACT OF ELECTRIC FIELD ASSISTED SINTERING ON THE CATALYTIC ACTIVITY OF $SrTiO_3$

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Perovskite oxides are versatile materials with applications in a variety of fields such as ferroelectrics and heterogeneous catalysis [1]. Performance in these applications is strongly influenced by the materials' defect chemistry and charge transport properties. Flash sintering is a sintering technique characterized by the application of an electric voltage to a green body during thermal treatment. At temperatures significantly below those usually required for sintering a flash event occurs densifying the material in a matter of seconds [2]. Joule heating alone and in combination with increased defect concentrations has been suggested as the cause of the rapid increase in power dissipation in conjunction with rapid densification [3-5].

In this work we investigate the impact of the electric field employed in the flash sintering process on the charge transport properties and on the catalytic activity of $SrTiO_3$, a well-known model perovskite oxide. Nanoparticles were prepared using a hydrothermal treatment, pressed into pellets and subsequently subjected to conventional and flash sintering. Structural and morphological characterization of the samples was carried out via x-ray diffraction and electron microscopy. Impedance spectroscopy was employed at different temperatures and oxygen partial pressures to investigate the charge transport properties, while electron spin resonance (ESR) measurements provided information on the defect species present in the sample. Moreover, the activity towards photocatalytic phenol degradation and methane oxidation as model reactions at low and high temperature, respectively, was investigated.

At high temperature (700 °C) samples subjected to flash sintering exhibited lower conductivity with respect to the conventionally sintered sample due to their lower grain size. Upon increasing the electric field, ESR measurements revealed an increased concentration of intrinsic defects, which have been shown to contribute to the interfacial reactivity of $SrTiO_3$ [6]. Room temperature catalysis may benefit from the increased amount of active centers, while high temperature catalysis might be hindered by the lower conductivity. Accordingly, the activity towards methane oxidation increased with the applied electric field, but decreased with respect to the conventionally sintered sample due to the low conductivity. Conversely, the activity of flash sintered samples towards photocatalytic phenol degradation was remarkably increased with respect to the conventionally sintered sample.

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INNOVATIONS IN POLYOXOVANADATE CHEMISTRY – NEW WATER SOLUBLE PRECURSORS

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Recently, we discovered the water soluble antimonato polyoxovanadates (Sb-POVs) $\{Zn(en)_3\}_3[V_{15}Sb_6O_{42}(H_2O)]\cdot 3en\cdot 10H_2O$[1] (**I**) $\{V_{15}Sb_6O_{42}\}$ and $\{Ni(en)_3\}_3[V_{15}Sb_6O_{42}(H_2O)_x]\cdot ca.15H_2O$[2] (**II**) (en = ethylenediamine) which are promising synthons for the preparation of new Sb-POVs. Electrospray ionization mass spectrometry (ESI MS) investigations evidenced that **I** is fully intact for 72 h in aqueous solution. After 14 d about 50 % of the $\{V_{15}Sb_6O_{42}\}$ cluster is transformed into the V-poorer cluster $\{V_{14}Sb_8O_{42}\}$. Applying **I** as starting material two new compounds, namely $\{Zn(phen)_3\}_2[Zn(en)_2V_{15}Sb_6O_{42}(H_2O)]\cdot 23H_2O$ and $\{(Zn(en)_2(H_2O)_2)(Zn(en)_2)\}[Zn(en)_2V_{15}Sb_6O_{42}(H_2O)]\cdot 8.5H_2O$ (Fig. 1a) could be synthesized within 24h at T = 150 °C.[1] The velocity of the $\{V_{15}Sb_6\} \rightarrow \{V_{14}Sb_8\}$ conversion can be enhanced by addition of an ammonia buffer affording the crystallization of new $\{V_{14}Sb_8O_{42}\}$ clusters within 24h at T = 150°C: $\{Zn(phen)_3\}_2[V_{14}Sb_8O_{42}(H_2O)]\cdot 0.5\ phen\cdot 17\ H_2O$, $[\{Zn(en)_2\}_2V_{14}Sb_8O_{42}]\cdot 7\ H_2O$ and $\{Fe(phen)_3\}_2[V_{14}Sb_8O_{42}(H_2O)]\cdot 11\ H_2O$ (Fig. 1a).[3]

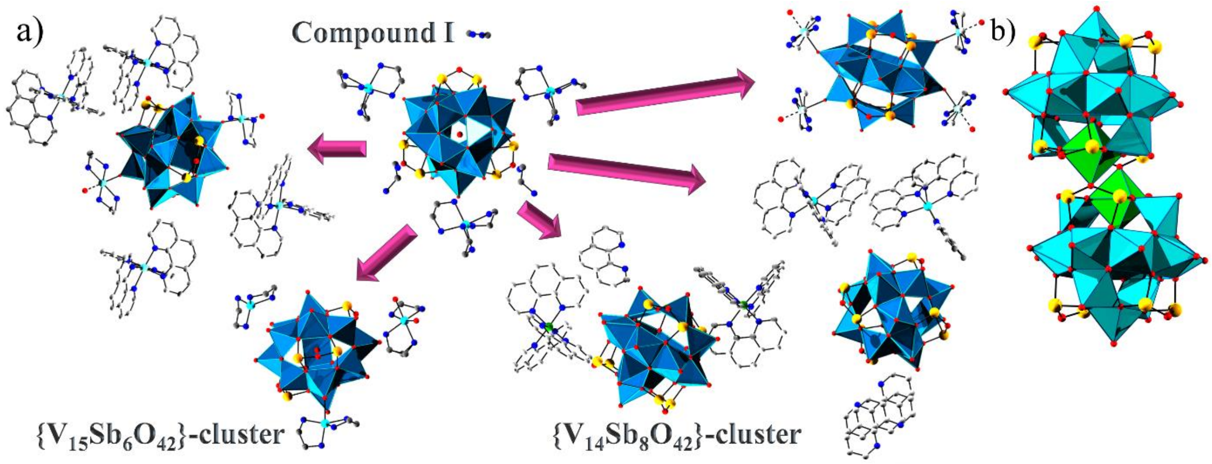

Fig. 1 a) Compound **I** and $\{V_{15}Sb_6O_{42}\}$ or $\{V_{14}Sb_8O_{42}\}$ cluster synthesized from this precursor; b) New isomer of the $\{V_{14}Sb_8O_{42}\}$ cluster outgoing from compound **II** as a synthon.

Using **II** as synthon leads to crystallization of a new isomer of the $\{V_{14}Sb_8O_{42}\}$ cluster observed in $\{Ni(cyclen)(en)\}_2[V_{14}Sb_8O_{42}(H_2O)]\cdot ca.10H_2O$[4] (Fig. 1b). One of the VO_5 pyramids is inverted into the interior of the cluster shell. Supramolecular Sb-O···V and Sb-O···Sb contacts lead to formation of $\{V_{14}Sb_8O_{42}\}_2$ dimers. ESI MS experiments confirmed the stability of these dimers in solution and in the gas phase. The usage of compounds **I** and **II** as synthons makes rational syntheses and design of new POVs possible.

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EXCITONIC COUPLING OF PSEUDOISOCYANINE IN LAYERED SILICATES

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Excitonic coupling is a phenomenon which can occur when the molecules are in close proximity. Due to relative orientation of molecules and Van der Waals interactions is the transition energy of dimers and higher aggregates shifted with respect to monomeric species to higher or lower energies [1]. In the case when the excitonic coupling results in a shift to lower energies, then the aggregate is called J-aggregate. Depending on used conditions J-aggregates can be organized in 2D brickwall fashion which is more advantageous than the 1D arrangements, because the 2D brickwall arrangement has better electron-hole and exciton transport properties. Materials with these kind of properties are essential in applications like thin-film organic semiconductors or light harvesting systems [2].

In this study we have prepared thin hybrid films consisting from synthetic saponite (SSA) and cationic organic dyes. The formation of monomeric and J-aggregate species in the interlayer space of SSA can be controlled by changing the height of the interlayer space of SSA [3]. Proposed method is based on the swelling properties of SSA and was developed to gain control over the formation of monomeric and J-aggregate species in the interlayer space of SSA. Swelling procedure has been done with dimethyl sulfoxide (DMSO), and the optical properties of prepared film under presence and absence of DMSO were investigated by conventional spectroscopy techniques.

Acknowledgements: This work was supported by JSPS KAKENHI Grants JP15F15742, JP15K13676.

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SYNTHON APPROACH TO STRUCTURE MODELS FOR THE BAYERITE-DERIVED LAYERED DOUBLE HYDROXIDES OF Li AND Al

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The Br^- ion intercalated layered double hydroxide (LDH) of Li and Al obtained from the bayerite-$Al(OH)_3$ precursor crystallizes in a structure different from that of the gibbsite-$Al(OH)_3$ derived counterpart. Additionally, it undergoes temperature and humidity induced reversible interpolytype transformations. The dehydrated LDH (T ~ 120 °C) adopts a structure of hexagonal symmetry (space group $P\bar{3}1m$) and comprises a stacking of the metal hydroxide layers arranged one above another. On cooling and rehydration, the LDH adopts a structure of monoclinic symmetry with a stepwise increase in the stacking angle, β. Using the structural synthon approach, based on the systematic elimination of the principal symmetry elements of the hexagonal crystal, structure models were generated for each of the two hydration steps (Relative Humidity ~ 50%, >70%) and the structures refined (space group $C2/m$). The refined structures show that the interpolytype transitions are a result of rigid translations of successive metal hydroxide layers relative to one another by translation vectors (1/6, 0, 1) and (1/3, 0, 1) respectively.

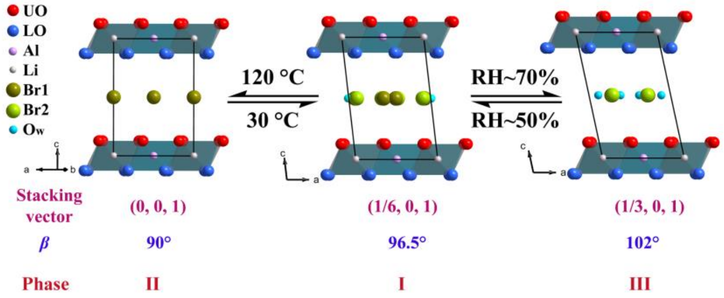

Fig. 1 A schematic of the rigid relative translations of the metal hydroxide layers leading to different polytypes.

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OPERANDO XRD DATA ANALYSIS OF LI-ION BATTERIES MEASURED ON LABORATORY DIFFRACTOMETERS

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X-ray diffraction is a powerful tool for the characterization of battery materials [1,2]. Operando X-ray diffraction experiments of Lithium-Ion batteries are typically carried out at high brilliance synchrotron beamlines due to the possibility to use high-energy radiation, which allows a very fast collection of diffraction data from rather thick batteries. However, a wealth of information can also be extracted by the analysis of diffraction data collected on a laboratory diffractometer, which is much more accessible compared to a synchrotron source. In this presentation we will show how high-quality diffraction data of Lithium-based batteries can be collected quickly and analysed during charge/discharge cycles on a laboratory XRD diffractometer, equipped with an X-ray tube with Silver or Molybdenum anode and an area detector optimized for high energy X-rays. Two main approaches will be demonstrated, in particular (a) transmission diffraction through single- and multi-layer pouch cells, and (b) reflection diffraction obtained with customized electro-chemical cells, which also allows the characterization of half cells.

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$CaAg_2$ UNDER ETHYLENE EPOXIDATION CONDITIONS: AN ELECTRONIC STRUCTURE AND CHEMICAL BONDING STUDY

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Ethylene oxide (EO) is an important industrial material used in the production of polyester fibers, surfactants, detergents and polyethylene terephthalate (PET). EO is industrially obtained by a selective oxidation process employing supported and promoted silver catalysts [1]. The highest selectivity values currently achieved are 85-90% implying there is still room for further improvement. A deeper understanding of the reaction mechanism and the changes taking place on the surface of the catalyst is necessary for developing new catalysts with superior performance. Intermetallic compounds (IMC) with their ordered crystal structure and well-defined chemical bonding features may serve as useful model systems to investigate and understand the behavior of the catalyst materials under reaction conditions.

The IMC $CaAg_2$ was tested as a catalyst for ethylene epoxidation [2]. Selectivity values of 60-65 % and conversion levels between 1.5 and 2.5 % were measured during the 600 hours of time on stream. Post-catalysis analysis of the samples showed the presence of $CaAg_2$, Ca_2Ag_7 and micron-sized elemental Ag particles as well as other oxidation products containing Ca. The strong dependence of selectivity on the presence of promoter (ethyl chloride) in the gas stream implies that catalysis is mainly due to the elemental Ag particles being formed as a result of the oxidation process. First-principles electronic structure calculations and position-space chemical bonding analysis were employed to understand these findings (Fig. 1).

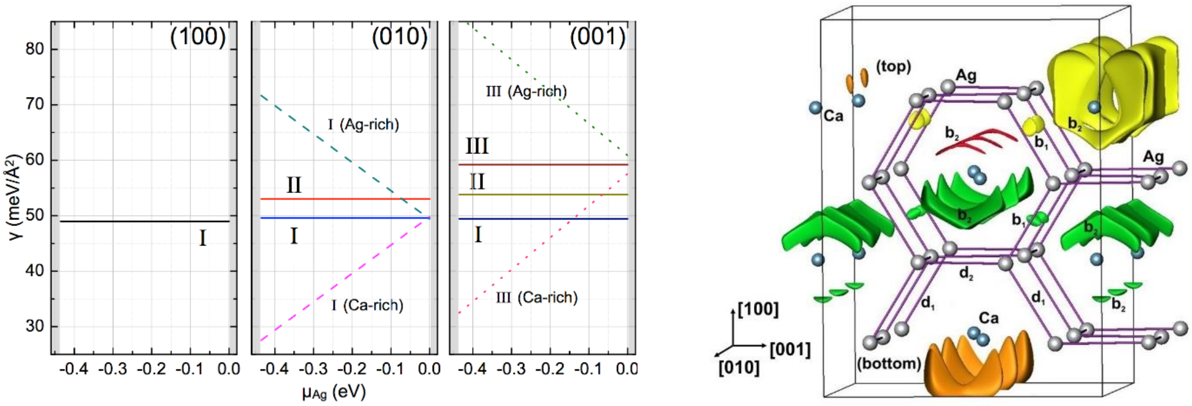

Fig. 1 Surface energies of the low-index surfaces (left) and the ELI-D distribution computed for the (100) surface (right).

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A REAPPRAISAL OF POLYTYPISM IN LAYERED DOUBLE HYDROXIDES: CONSEQUENCES OF CATION ORDERING IN THE METAL HYDROXIDE LAYER

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Recent diffraction studies on layered double hydroxides have shown that the three-layer polytypes that were thought to crystallize in rhombohedral symmetry are actually one-layer polytypes of monoclinic symmetry. However, the prevailing Bookin and Drits (1993) scheme of polytypism, which is based on the widely accepted cation-disordered structure model, fails to predict the occurrence of low symmetry (monoclinic and orthorhombic) polytypes among the layered double hydroxides. In this work, a cation-ordered metal hydroxide layer (layer group *p*-312/*m* or *c*12/*m*1) is chosen as the basic building block. Application of the structural synthon approach enables the description of the complete universe of polytypes comprising 1H, $1M_{1\text{-}7}$, 2H, 2O, 3R, 3H, 6H and 6R among others (M: Monoclinic; O: Orthorhombic). These polytypes are characterized by their unique stacking vectors. The polytypes of large unit cell volume are obtained by a combination of two or more stacking vectors. This work has relevance to the understanding of several mineral structures, specially those with large unit cells.

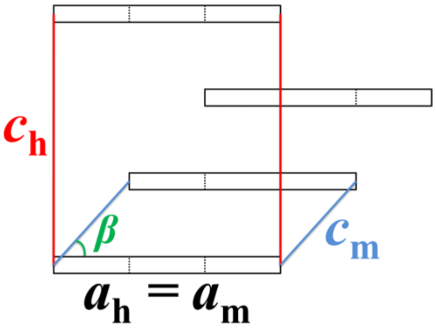

Fig. 1 Scheme illustrating the equivalence of a n-layer orthogonal cell to a one-layer monoclinic cell.

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WHERE FICK'S LAW FAILS: REAPPRAISAL OF GRAIN GROWTH IN NANOCRYSTALLINE METALS AND OXIDES

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Taking a fresh look at the fundamental process of grain growth (coarsening) in polycrystalline materials, we are struck by two realizations:

1. The immense change in the growth rate's dependence on size as one switches from the macroscale to the nanoscale is *quantitatively predictable* – it stems from a failure of Fick's law at the nanoscale, overlooked so far.

2. This change is also *empirically quantifiable* simply by applying elementary statistics to the vast amount of experimental data already accumulated in the literature – again, an avenue not taken before.

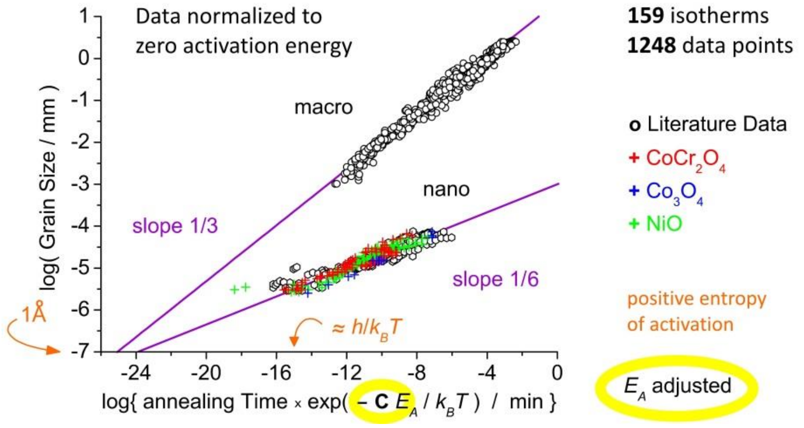
Spontaneous (stochastical) grain growth is the thermally induced coarsening observed in polycrystalline solids. The average grain size *s* increases with time *t* according to $s{\sim}t^n$ (growth isotherms). Here *n* is the characteristic exponent. At the macroscale, the *s*-*t* power-law relationship in general and the value of *n* in particular may be understood in terms of Herring's scaling laws of diffusion which ultimately derive from Fick's first law.

At the nanoscale, however, the experimental value of *n* turns out to be much too small, only about half that observed at the macroscale. This is of immense practical consequence – every doubling of the grain diameter, for instance, takes nearly ten times as long at the nanoscale than at the macroscale (after dividing by starting times).

Where does this massive shift in scale come from? We contend that the answer is unexpectedly simple, even elegant: Fick's first law, the foundation of Herring's laws, fails at the nanoscale! Simply because the average distance between sources and sinks becomes smaller than the average separation between the diffusing species. Hence, diffusion is reduced to random walks of individual atoms. Herring's laws, therefore, have to be supplemented by this elementary mode of diffusion. We are thus able to predict, for the first time we believe, that $n={}^1/_6$ at the nanoscale, in contrast to $n={}^1/_3$ at the macroscale.

Next, we collate plentiful experimental data from the literature as well as from our laboratory – spanning both length scales and comprising *metals*, *intermetallics*, *oxides* and *mixed oxides* – to obtain what is in our opinion an impressive "big picture" of unprecedented revelatory quality (159 isotherms evaluated, Fig. 1). It corroborates the postulated failure of Fick's law at the nanoscale. But it also points to the merits of examining the literature.

Fig. 1 Failure of Fick's law at the nanoscale – corroborated by empirical data (*n* corresponds to the slope of the *log*/*log* plots)



Finally, the new findings illustrate the fruitfulness of looking at solid state transformations in the light of their classical atomistic nature, applied here to the mechanism of diffusion (for another example see reference [1]).

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REACTION OF K_2Se WITH NbO_2: SYNTHESIS, CRYSTAL GROWTH AND STRUCTURAL CHARACTERIZATION OF A NEW OXY-SELENIDE $K_3NbSe_2O_2$

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Water splitting via photocatalysis and photoelectrolysis is a potential means to produce clean and renewable hydrogen as a storable high-density energy carrier. At present, the main concern is how to develop semiconductor materials for efficiently converting sunlight energy.

Inorganic semiconductors are predominantly utilized for water splitting over organic/organometallic dye molecules because of their superior photochemical stability. Specifically, mixed anion semiconductors, oxynitrides and oxysulfides have been demonstrated to be promising materials for water splitting under visible light. In this report, the synthesis of a new quaternary mixed anion semiconductor, $K_3NbSe_2O_2$ by solid state technic is described. We started from NbO_2 oxide and an excess K_2Se as a reactive flux to promote large single growth. We observed large single crystals of the title phase in the form of transparent orange plates. The crystal structure was determined X-ray diffraction methods. A projection of the structure of $K_3NbSe_2O_2$ is given in Figure 1. The potential of the title phase as promising photocatalyst is investigated with the support of theoretical electronic band structure calculations.

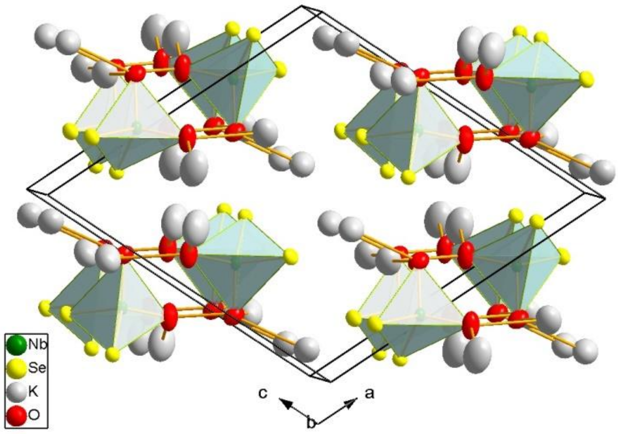

Fig. 1 View of the crystal structure of $K_3NbSe_2O_2$ along the b-axis

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A NON-CLASSICAL CARBONATE CRYSTAL GROWTH BY LOWER ENERGETIC PATHWAY VIA AMORPHOUS AND NANOPHASE PRECURSORS

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Carbonate crystal growth has been studied extensively as it forms by several different pathways in both synthetic and natural environments. Some of these pathways involve formation of prenucleation clusters, metastable liquid like binodal phase, polymer induced liquid precursors, mesocrystals, amorphous and nanophase in the early stages of crystal growth [1]. The energetic barrier associated with formation of such complex metastable phases could have kinetic or/and thermodynamic underpinnings. In order to understand the energetics of carbonate crystal growth, experimental thermodynamic study was performed on synthetic and biologically produced amorphous calcium carbonate (ACC). Energetically different hydrated and dehydrated ACC phases as well as nanophase metastable precursors were identified during the early stages of carbonate formation. These precursors were found to provide the energetically downhill calcium carbonate crystallization through stepwise evolution of series of metastable phases in chemical and biologically mediated processes [2]. This study was extended to Ca-Mg-Fe-Mn-CO_3 systems and amorphous/nano metastable precursors were identified for minerals such as (a) magnesite, $MgCO_3$ and dolomite, $CaMg(CO_3)_2$ [3], (b) siderite, $FeCO_3$ [4], and (c) rhodochrosite, $MnCO_3$ [5]. These results suggested a possible existence of a non-classical method of carbonate crystal growth by a lower energetic pathway via amorphous and nanophase metastable precursors in synthetic, biomineralization, geological and CO_2 sequestration environments [6].

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SnIP A FLEXIBLE 1-DIMENSIONAL SEMICONDUCTOR

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Electronic devices were downscaled remarkably during the last decade. To further decrease their size semiconductor nanowires or low-dimensional semiconductors are required. One interesting one-dimensional semiconductor is the ternary compound SnIP [1], which we have investigated regarding its flexibility for implementing in bendable electronic devices.

SnIP is composed by two helices, a ${}_{\infty}^{1}[P^{-}]$ chain as inner helix which is surrounded by an outer ${}_{\infty}^{1}[SnI^{+}]$ helix with a diameter of 0.98 nm. Each unit cell contains one left-handed (M-Helix) and one right-handed (P-Helix) helix, which are aligned along the a-axis. SnIP shows a direct band gap of 1.86 eV and an indirect band gap of 1.80 eV.

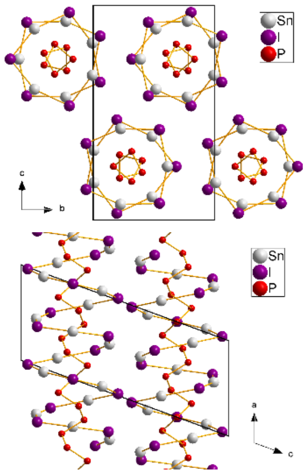

Fig. 1 Crystal Structure of SnIP.

The P and Sn-I helices themselves are bonded covalently, in between those helices dative-ionic interactions can be found. Finally, double helical SnIP rods are only bonded via weak van der Waals interactions. Therefore, the intrahelical interactions are much stronger compared to the relatively weak interhelical interaction. To investigate this bonding situation, we measured high pressure XRD using a diamond anvil cell under isostatic conditions. In a pressure range from 0.1 GPa up to 11.5 GPa the pressure dependent lattice parameters were refined. The cell parameter *a* along the double helix axis decreases linearly, while non-linear behaviour is found for cell parameters *b* and *c*.

The pressure dependent cell volumes can be used to calculate the bulk modulus using the Birch-Murnaghan equation of 3rd order, which resulted in a bulk modulus of 15.7 GPa. This extremely low value compared to other group II-VI, III-V or group IV semiconductors (see figure 2) illustrates the exceptional mechanical properties of SnIP. Other semiconductors show values of 50-90 GPa. With 15.7 GPa SnIP has a “softness” that can be compared to the soft metals lithium and potassium and even liquids like Glycerin.

This unusual property makes SnIP an interesting candidate for the application in electronic devices. Especially flexible electronics like bendable displays require soft and reversible flexible semiconductors.

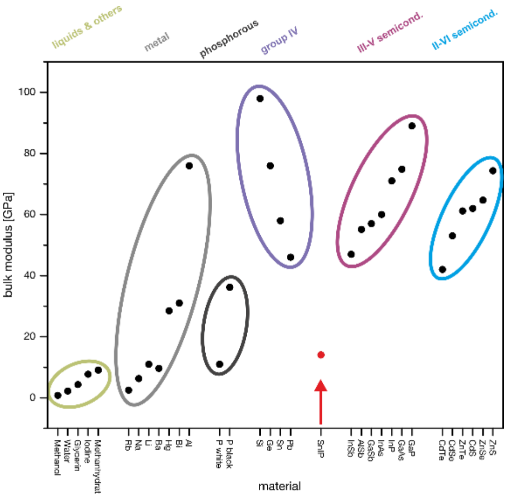

Fig. 2 Bulk modulus of different semiconductors.

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STRUCTURAL DYNAMISM IN MICROPOROUS ORGANICALLY PILLARED LAYERED SILICATES

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The development of efficient, energy saving and sustainable separation processes for chemical mixtures is intensely attractive to meet the needs of our modern society for sustainable technologies. The recognition and selective adsorption of gases is hereby of particular significance as they are key resources in the manufacturing of bulk chemicals.[1,2] Since in conventional porous materials the pore sizes and shapes essentially dictate the performance of adsorptive separations it is especially challenging to achieve high selectivity between molecules of similar physical properties and shapes like CO and N_2 or CO_2 and C_2H_2. In this context, porous solids with structural flexibility (Soft Porous Crystals, SPC), which are able to specifically respond to guest molecules under appropriate conditions, have attracted much interest.[3]

However, structural dynamism for controlling the adsorption properties is no longer a unique characteristic of SPCs. Pillaring charge homogenous synthetic clays with cationic molecules, such as organocations or metal complexes, provides access to a largely unnoticed class of microporous hybrid materials. These so called Microporous Organically Pillared Layered Silicates (MOPS) are conceptually similar to SPCs and combine the concepts of functional porosity and component modularity with a continuously porosity tuning in the sub-Ångström range.[4-6] It was found that MOPS are capable of discriminating very similar gases (CO_2/C_2H_2 or CO/N_2) by a new fully reversible and selective gate-opening mechanism.[7,8] Contrary to conventional gate-opening as observed for SPCs the additional adsorption capacity in MOPS is mostly realized without macroscopic volume changes as it is triggered solely by freezing pillar dynamics. The gate-opening is restricted to CO_2 and CO. Moreover, we found that the selectivity of this unprecedented type of gate-opening is primarily attributed on polarization effects among the adsorbates and adsorbent. The present type of gate-opening can therefore be altered by tuning the electrostatic interaction among pillar and silicate by varying the charge density of the latter. A decrease of the pillar density entails, that simultaneously the Coulomb attraction of cationic interlayer space and anionic host layers is reduced, which modifies the gate-opening mechanism to a conventional structural gate-opening involving an increase in volume.

The structural flexibility of MOPS in respect to systematic variation of charge density of the host, equivalent area of the molecular pillar and their chemical functionality are the building blocks for a straightforward rational design of microporous materials tailored for separation of various industrially relevant gas mixtures.

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SPRAY COATING OF LARGE AREA SMECTIC LIQUID CRYSTALS AND THEIR MECHANICAL PROPERTIES

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Nacre, the material of seashells, is a lightweight biological nanocomposite, which combines stiffness, strength and toughness in a unique way. The brick-and-mortar structure of the material is mainly build up by aragonite platelets (95 vol%), which are surrounded by a soft and ductile matrix of biopolymers. The key for the extraordinary mechanical properties lies in the hierarchical arrangement of the hard and soft constituents.[1]

Hitherto, we proved that the aspect ratio of clay in combination with the dispersion quality and the compatibility between the filler and the polymer is important for an improvement of the mechanical properties of nanocomposites with low filler content (< 2 vol%).[2][3][4] Inspired by nacre, it is our goal to fabricate lightweight hierarchically ordered nanocomposites with up to 50 vol% of clay.

Phase pure sodium hectorite $[Na_{0.5}]^{inter}[Mg_{2.5}Li_{0.5}]^{oct}[Si_4]^{tet}O_{10}F_2$, obtained by melt synthesis[5][6] is a promising inorganic component. The superior charge homogeneity of this material allows for swelling and quantitative delamination into individual platelets with aspect ratios of up to 20 000.[7] Applying a wrinkling technique, the in-plane-modulus of a single clay lamella was determined to be 150 GPa.[8]

The hectorite-PVP system allows us for the first time to build up highly ordered structures of hectorite platelets and polymer without any phase segregation. Furthermore, the system allows for tuning the interlayer space from 20 Å to 40 Å by adjusting the amount of polymer. Spray coating, for processing the aqueous suspensions, yields large area crystalline smectic self-supporting films. PXRD patterns and the TEM picture (Fig. 1) reveal the quality of the 1D crystalline order. The hectorite platelets are perfectly parallel aligned with PVP in the interlayer space. The resulting film has a high tensile strength of 150 MPa and a stiffness of 10 GPa. Compared to nacre, the stiffness is about a factor 6 lower whereas the strength of the film is in the same range.

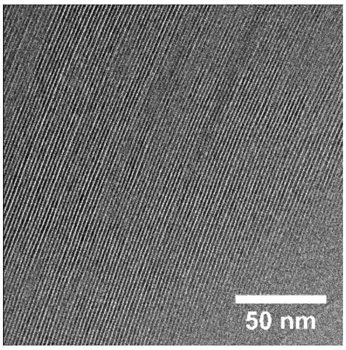

Fig. 1 TEM picture of the hierarchical long-range structure in the hectorite-PVP system.

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REORIENTATIONAL DYNAMICS LINKED TO THERMO-RESPONSIVE BREATHING IN FUNCTIONALIZED METAL-ORGANIC FRAMEWORKS

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Metal-organic frameworks (MOFs) are a class of porous networks with inorganic and organic units, which show potential in a range of applications like gas separation, gas storage or catalysis.[1] Besides the control over pore volumes and shapes by using different linkers, MOFs specifically allow to introduce a large variety of functional groups to the network. Based on the building units and linkers chosen, many systems have shown to exhibit a breathing behavior with strong and reversible changes in cell parameters between narrow pore and large pore configurations.

Breathing transitions are typically accessible through selective host-guest-interactions when passing a certain pressure of the guest species. However, for some alkyl-ether-functionalized pillared-layer frameworks $[Zn_2\text{fu-}L_2\text{dabco}]_n$ (fu-L = functionalized 1,4-benzenedicarboxylic acid, dabco = 1,4-diazabicyclo-[2.2.2]octane), this reversible pore opening has been observed as a mere thermo-responsive effect, without any contribution of additional guest molecules.[2] We expect that this phase transition is triggered by reorientational dynamics of the alkyl side chains coupling with phonons in the host framework.

Here we present a combination of ^2H solid-state line shape and relaxation studies with energy rankings and molecular dynamics (MD) simulations to deduce the dynamic behavior of the system. To access the reorientations of the entire side chain, the methyl end groups of the alkoxy-functionalization had been deuterated. For the large-pore configuration at high temperatures, we were able to explain the ^2H line shapes merely by the energy hypersurface of the alkyl torsions without any influence of the MOF framework (see figure 1). For the narrow pore variant, MD simulations indicate the framework influence increases and leads to at least two subspecies of the chemically equivalent side chains with strongly different degrees of mobility.

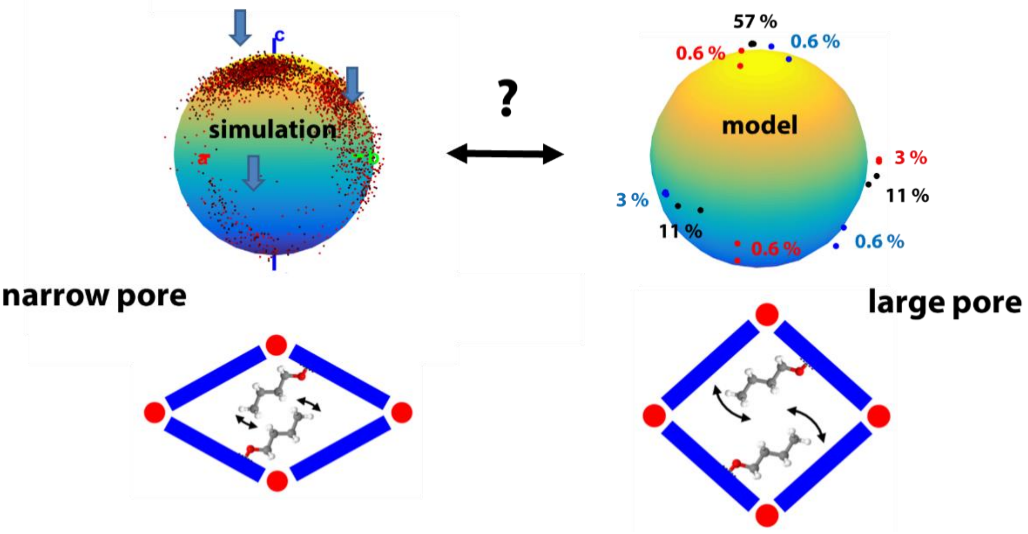

Fig. 1 Based on our solution for the reorientational dynamics of the large pore configuration (right), molecular dynamics simulations help formulate refined jump models including the framework influence in the more restricted narrow pore configuration (left). The color code of the sphere is only for perspective.

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Development of a humidity tolerant lithium superionic conductor

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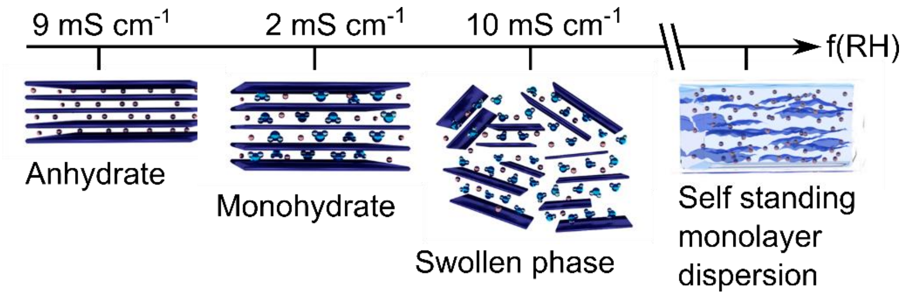
Today's requirements for cheap and safe high-performance electrical energy storage devices are currently outpacing new improvements to state-of-the-art battery technology. One promising attempt to enhance lithium ion battery (LIB) performance and safety is the design of all solid-state battery (ASSB) with high rate capabilities and energy density. This concept requires the use of a solid electrolyte instead of a liquid electrolyte solution of organic carbonates and lithium salts in combination with a porous polymer membrane, which is currently seen as a major safety (flammable, toxic) and performance (low capacity anode materials) bottleneck in improving LIBs. However, the ionic conductivities of liquid electrolytes are typically two to three orders of magnitude higher than those of commercially available polymeric solid electrolytes. Therefore, identification of fast lithium solid electrolytes reaching conductivities of at least 1 mS cm^{-1} is crucial to boost the commercial success of ASSB. Among different inorganic Li electrolytes, the polarizable lattice of sulfide-based systems provides the highest Li ion conductivities. A recently discovered layered sulfide-based lithium electrolyte $Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]$ shows a room temperature Li diffusivity of σ_{NMR} = 9.3 mS cm^{-1} as measured by pulsed field gradient (PFG) NMR spectroscopy and confirmed by electrochemical impedance spectroscopy.[1] Besides the high ionic conductivity at inert conditions we herein demonstrate the improved environmental stability of $Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]$, compared to other prominent thio(-phosphate)-based lithium electrolytes, such as $Li_{10}GeP_2S_{12}$ (LGPS). Exposing $Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]$ to ambient humidity results in a fast two-step hydration process yielding first a stoichiometrically sharp monohydrate, which is further hydrated to continuously form a swollen phase with a broad range of hydration. Lithium ion conductivity of $Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]\cdot H_2O$ is slightly reduced (σ_{NMR} = 2 mS cm^{-1}) compared to the anhydrate, whereas the swollen phase $Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]\cdot x\ H_2O$ ($x > 1$) has a slightly higher conductivity (σ_{NMR} 10 mS cm^{-1}).[2] These findings bode well for the design of environmentally robust sulfide solid electrolytes showing both high conductivity and chemical stability.

Fig. 1 Schematic hydration behavior of the lithium superionic conductor $Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]$ with the corresponding Lithium diffusivities σ_{NMR} as measured by PFG NMR.



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MECHANOSYNTHESIS OF PYROXENE–BASED NANOCOMPOSITES

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Pyroxenes are a group of remarkable natural minerals and synthetic compounds with the general crystal-chemical formula $M2M1T_2O_6$. The positions *M2* (distorted five- to eightfold coordinated polyhedron) and *M1* (regular octahedron) can host a wide range of mono-, di- or trivalent metal cations, whereas the positions *T* (tetrahedron) can be occupied only by tetravalent Si or Ge, the latter occurs in the synthetic systems only. Li- and Fe- containing pyroxenes with the formula $LiFeX_2O_6$ (*X* is tetravalent cation) attract attention due to great variety of their structural and functional properties. Various conventional preparation methods requiring a number of stages have been described for the synthesis of these materials.

In the present work, the non-conventional one-step mechanosynthesis [1] of analogous pyroxenes, $LiFeGe_2O_6$, $LiFeSi_2O_6$, and $LiFeTi_2O_6$, is attempted via high-energy milling of the stoichiometric mixtures of powdered precursors. In the case of the α-Fe_2O_3 + Li_2O + GeO_2 mixture, the mechanosynthesis of *nanocrystalline* $LiFeGe_2O_6$ is preferred in the initial stage of the processing, whereas the simultaneous mechanochemical reduction reaction leading to the formation of *nanoglassy* Li_2FeGeO_4 occurs at the prolonged mechanical treatment. The final mechanosynthesized product is the $LiFeGe_2O_6/Li_2FeGeO_4$ nanocomposite [2]. Similarly, the mechanical treatment of the α-Fe_2O_3 + Li_2SiO_3 + 3 SiO_2 mixture results in the formation of the *nanoglassy* $LiFeSi_2O_6/Li_2FeSi_2O_6$ composite [3]. On the other hand, milling of the α-Fe_2O_3 + Li_2O + TiO_2 mixture leads solely to the mechanosynthesis of *nanoglassy* $LiFeTi_2O_6$ [2]. On the short-rage scale, the structural state of the mechanosynthesized pyroxenes is characterized by broadly distorted geometry of their constituent structural units (FeO_6 octahedra and XO_4 tetrahedra).

The present work is supported by the Deutsche Forschungsgemeinschaft (project SE 1407/4-1): Partial support by the Slovak Grant Agency VEGA (2/0175/17) and by the Visegrad Group (V4) – Japan Joint Research Program on Advanced Materials "Structure-Function Relationship of Advanced Nanooxides for Energy Storage Devices (AdOX)" is gratefully acknowledged.

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INVESTIGATION OF CARBON NITRIDES USING SOLID-STATE NMR

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Carbon nitrides, an earth-abundant family of polymeric materials, have developed into an interesting field of research due to their properties and their wide range of applications. In particular, the cyanamide functionalized polyheptazine has shown very high photocatalytic activities for hydrogen evolution. This high activity has been attributed to the insertion of the NCN- moiety which could be a preferential docking site for the platinum co-catalyst and facilitate the transfer of photogenerated charges into the hydrogen.[1,2] More recently, this material was also reported to enable both light harvesting and electrical energy storage, two key functions of energy conversion.[3] However, despite the large potential of this material, its polymeric network remains unsolved.

Using a series of NMR experiments and with the help of some previous NMR study on similar materials,[4] we attempt to get a better understanding of the structure of the NCN-polyheptazine. We show that the polymer is a combination of the fully condensed 2D polymer of melon (g-C_3N_4) and the 2D polyheptazine imide (PHI) network with a ratio of about 1/1. The NCN- groups, although having an important role on the polymer properties, functionalize only about 25% of the heptazine rings.

Finally, a comparison of the ^{13}C and ^{15}N NMR spectra from the platinized and non-platinized samples, reveals a weakening of the resonances from the fully condensed C_3N_4 region for the platinized samples, hinting that this region is the closest one to the Pt nanoparticles.

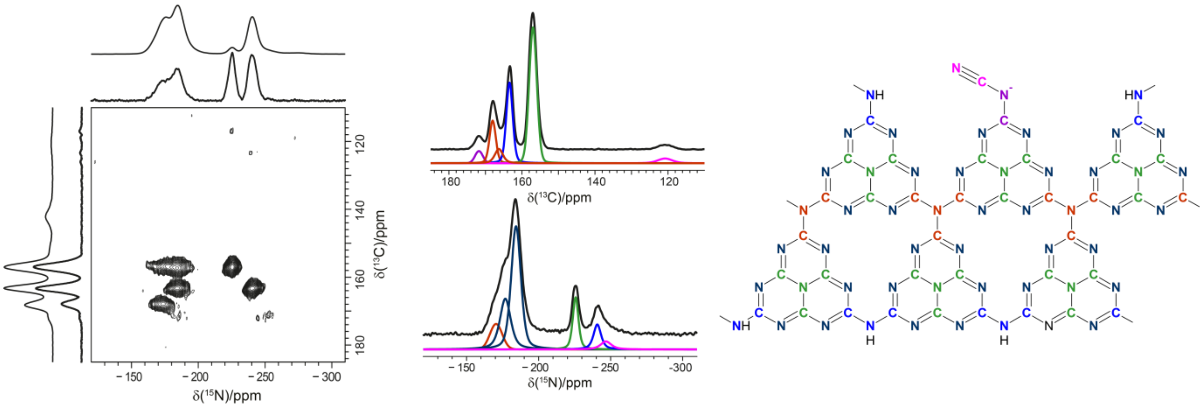

Fig. 1 2D ^{13}C-^{15}N HECTOR DNP NMR spectrum (left), ^{13}C (middle, top) and ^{15}N (middle, bottom) single-pulse spectra with their respective deconvolution and schema of the polymer network of the NCN-polyheptazine (right).

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MEASUREMENT OF BULK AND THIN FILM POROSITIES OF PCN-221 BY HYPERPOLARIZED ^{129}XE-NMR

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The study of porosities via hyperpolarized (hp) ^{129}Xe-NMR has proven its versatility over the last years. [1] Due to the highly-polarizable electron cloud of the xenon atom, any distortion of its chemical environment, like the size and shape of pores as well as interactions with pore walls, influences the ^{129}Xe chemical shift. An additional advantage in the analysis of porosities with hp ^{129}Xe-NMR is the sensitivity enhancement by up to five orders of magnitude compared to conventional NMR spectroscopy.

In the aim of utilizing porous materials deposited on electrodes for photoelectrocatalysis, the characterization of porosities is indispensable. Due to its high sensitivity, hp ^{129}Xe-NMR poses as a promising technique. For a first application, we examine the porosities of the metal-organic framework (MOF) PCN-221. This framework is characterized by a Zr_8O_6 Cluster bridged by porphyrin-type linkers. The structure features two types of pores. A small octahedral pore with a cavity diameter of ~1.1 nm and a large hexahedral pore with an edge length of approximately 2 nm. [2]

Our goal is to probe the capabilities of hp ^{129}Xe-NMR for the study of porosities to thin films. In a first step, porosity measurements were performed on a PCN-221 bulk sample (cf. Fig 1). The variable temperature (vt) hp ^{129}Xe-NMR spectra show one distinct adsorption site for Xenon in the framework at moderately low temperatures. With decreasing temperature, the chemical shift increases. At 220 K several overlapping resonances become distinguishable revealing several independent adsorption sites. At lower temperature, 160 K, these adsorption sites are even more distinguishable as their resonances span over a range of 70 ppm. For investigation of porous thin films of deposited PCN-221 with different thicknesses, a new sample holder design with inboard NMR-coil was crafted (Fig. 2). This allowed the first comparison of porosities of PCN-221 as bulk sample and deposited on a thin film.

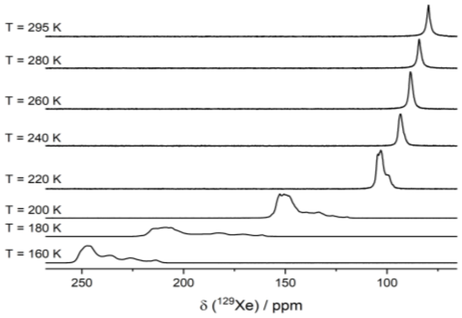

Figure 1. vt hp ^{129}Xe-NMR spectra illustrating different adsorption sites in PCN-221 (bulk sample)

Figure 2. Sample holder for HP-129Xe-NMR measurements on porous thin films.

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REVERSIBLE FLUORESCENT COLOR SWITCHING OF SMECTITE-ORGANIC HYBRID FILMS INDUCED BY SWELLING AND DRYING OF A SMECTITE

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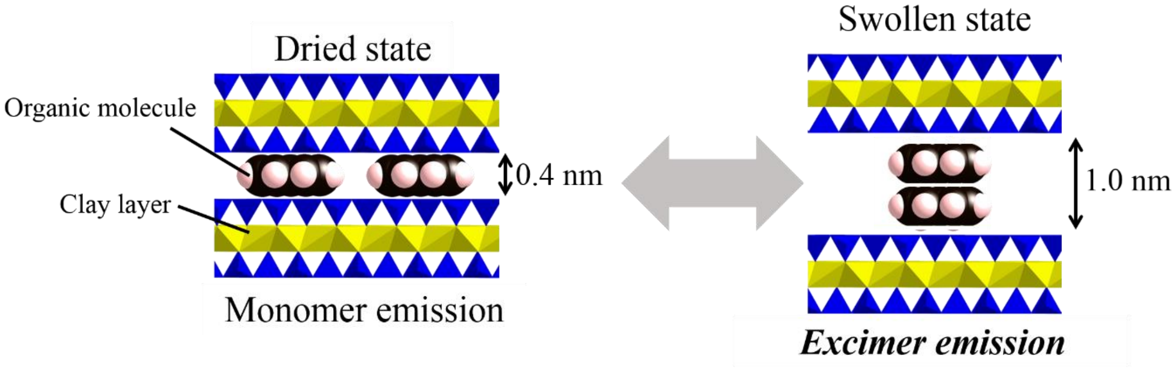
A smectite clay is a layered inorganic material. The interlayer space incorporates hydrated cations because each layer of the smectite is negatively charged. The hydrated cations can be exchanged by cationic organic molecules. As a result, a hybrid material in which organic molecules are intercalated in the interlayer space of smectite is obtained. At a lower loading level of organic molecules, the organic molecules are often confined in monomer form. When a π-conjugated organic molecule with high planarity is confined, under such a situation, typical gallery height of the hybrids is ca. 0.4 nm, which is similar to the thickness of π-electron system of the intercalated cationic molecule.

Smectites have a swelling property. They can be swollen by incorporating water or polar organic solvents into their interlayer space. Smectite-organic hybrid materials can also be swollen and the resulting gallery height is up to 1.0 nm. This interlayer space is large enough for confined organic molecules to form π–π stacked assembly because it is about twice the thickness of a planar π-conjugated system. In this study, utilizing switchable interlayer distance, accompanied by swelling and drying of a smectite-organic hybrid film, we have demonstrated switching between monomer and excimer forms of the confined organic molecules [1].

We fabricated hybrid films that consisted of synthetic saponite and fluorescent planar organic molecules with π-conjugated system. As guest organic molecules, 1-methyl-4-[(1*E*)-2-phenylethenyl]pyridinium iodide, 4,4′-[4,1-phenylenedi-2,1-ethynediyl]bis[1-methylpyridinium] diiodide, 4,4′-[4,1-phenylenedi(1*E*)-2,1-ethenediyl]bis[1-methylpyridinium] diiodide, 4,4′-[2,6-naphthylenedi(1*E*)-2,1-ethenediyl]bis[1-methylpyridinium] diiodide, and 4,4′-[2,6-anthrylenedi(1*E*)-2,1-ethenediyl]bis[1-methylpyridinium] diiodide were used.

The smectite-organic hybrid films with an appropriate loading level of the guest organic molecules exhibited fluorescent color attributed to the monomer in the as-prepared state. By adding dimethylsulfoxide (DMSO) as a polar solvent to the films, fluorescent color was remarkably red-shifted due to the formation of excimer. When DMSO was removed, fluorescence returned to the original fluorescent color. This reversible fluorescent color change occurred at least 50 cycles with no change of the fluorescence maxima. Thus, the swelling property of smectite-organic hybrids can be utilized to develop novel materials that exhibit switching properties.

Fig. 1 Mechanism of monmer and excimer emission in a smectite-organic hybrid fim.



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IMPACT OF STRUCTURAL DISORDER ON BREATHING AND ADSORPTION IN METAL-ORGANIC FRAMEWORKS

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Sorption of flexible metal-organic frameworks (MOFs) is defined and manipulated by framework functional groups, and the ability to adjust pore geometries upon external stimuli, which makes them promising for applications like gas storage and separation, drug delivery and catalysis.

Here we show, that formamide groups[1, 2] in MIL-53-X alter the water adsorption isotherm from a one-step breathing in MIL-53-H to a S-shaped two-step process. By validating sorption, diffraction and solid-state NMR spectroscopic data against structure models and their properties derived by Monte Carlo and Molecular Dynamics simulations, we were able to link the formamide group disorder to the water adsorption.

We deduce that such transitions might readily be induced within flexible MOFs, if the space requirement of the side groups and their functionalities offer confined environments with close contacts between the side chains and attractive binding spots for guest molecules. We found these to be located predominately at boundaries of mesoscopic domains, in each of which the side chains are aligned parallel. These regions take up most of the guest molecules leading to an inhomogeneous spatial distribution.

As such we present a concept, where side group disorder on the mesoscale governs the macroscopic sorption properties. With this, we envision a new pathway to porous materials with tailored switchable chemical and physical properties in the future.

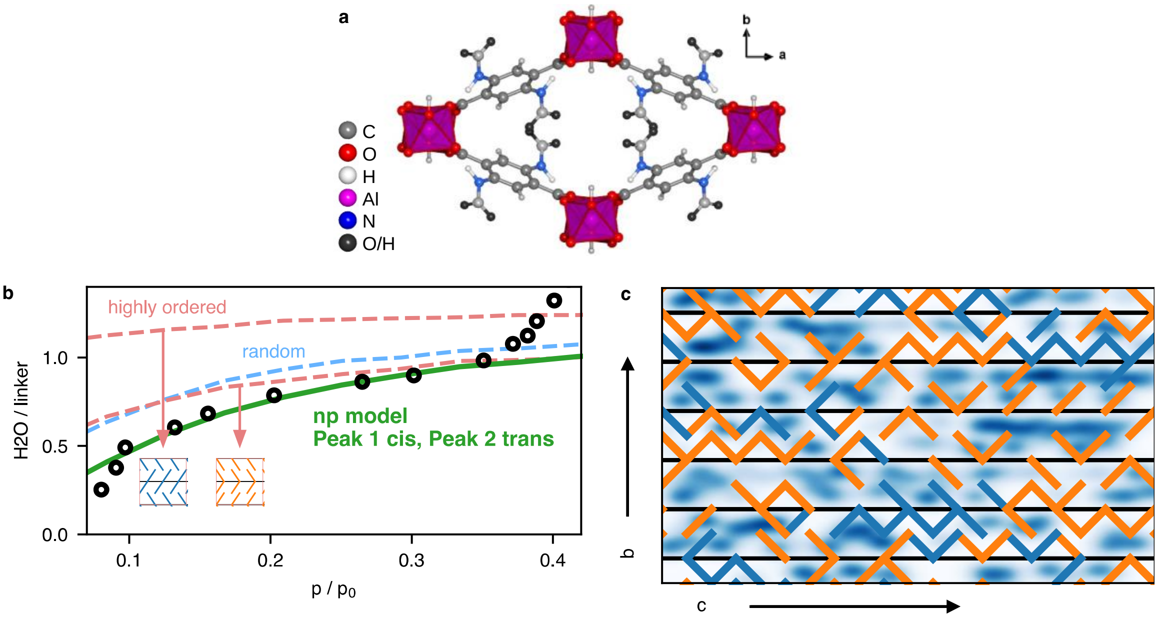

Fig. 1 **a** Structure of MIL-53-NHCHO. **b** Experimental (symbols) and calculated (lines) water adsorption isotherms of MIL-53-NHCHO. The green line is the calculation of our structure model derived from solid-state NMR spectroscopy analysis depicted in c. **c** Depiction of formamide groups as lines along the *bc* plane. Groups in cis configuration are blue, trans orange.

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CRYSTAL STRUCTURE SOLUTION OF TWO SERIES OF SUPRAMOLECULAR POLYMER ADDITIVES WITH PLATLET-LIKE STRUCTURE

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Supramolecular polymer additves have gained significant attention in recent years. This is because they dissolve in a polymer melt and can so be homogeneously distributed in the polymer. Upon cooling, they self-assemble to supramolecular nanoobjects and by this influence the polymer properties like their nucleation behavior.[1] Knowing the crystal structure of these additives is essential to understand the way these additives effect the polymer.[2] So far, research focused mostly on 1D supramolecular nanoobjects.[1] Now we explore the properties of 2D nanoobjects.

In this work we present the crystal structures of two series of benzene bisamides. The first set consists of three molecules with two symmetric perfluorinated chains of the same length bound to the amide. The second set consist of three asymmetric substituted bisamides. In this series one side group is always t-butyl. The other side group is a perfluorinated chain.

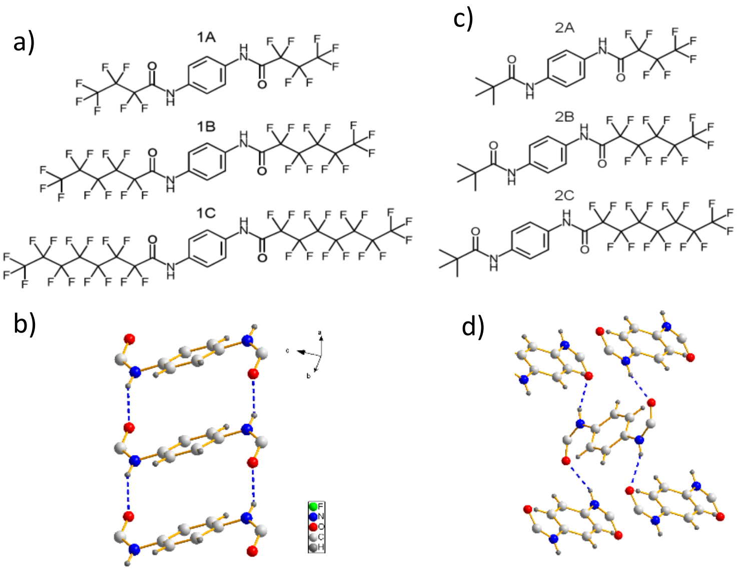

Figure 1. Molecular structure a),c) and packing pattern b)d) structure of series 1 and 2, respectively. For the sake of clarity, the side chains are omitted.

For both series it was possible to get a single crystal which was big enough to solve the crystal structure by single crystal x-ray-diffraction measurements for at least one compound. The other structures of the series were solved by NMR crystallography.

The results show that the two series crystallise in a completely different packing pattern. The symmetric series shows a hydrogen bond pattern where one molecule only binds to two other molecules. The asymmetric series shows an H-bond pattern where one molecule is bound to four other molecules. This second packing pattern was previously observed for a bisamide with two t-butyl end groups.[3] To investigate the origin of the different packing patterns geometry optimisations of the molecules in the packing pattern of the other series were performed with the DFT programm CASTEP. Thereby, we saw that the shortest possible H-bond is the driving force for a specific packing pattern.

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$Cu_9Te_4Cl_3$ and $Ag_{10}Te_4Br_3$ – INVESTIGATIONS ON THE MECHANISM OF P-N-P-SWITCHING IN THERMOELECTRIC COMPOUNDS

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Polymorphism is a common observed phenomenon in solid materials, often accompanied by a change of properties undergoing the phase transitions. The class of materials designated the ‘pnp compounds’ is a class of ion conductors capable of reversible switching between p- and n-type of semi conduction. These compounds undergo ion mobility-driven order-disorder phase transitions, showing typical phonon softening effects and modulations in the thermoelectric properties. This has been confirmed to be usually attended by closing of the band gap and increasing in the density at the fermi level leading to an intermediate quasi-metallic state in which valence electron conduction increases. [1, 2]

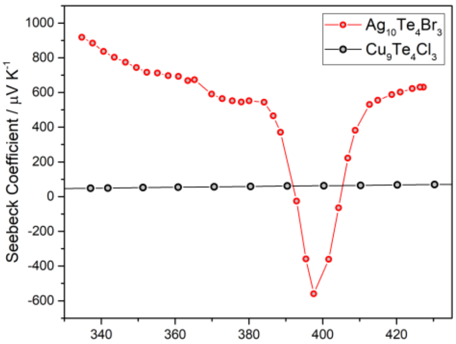
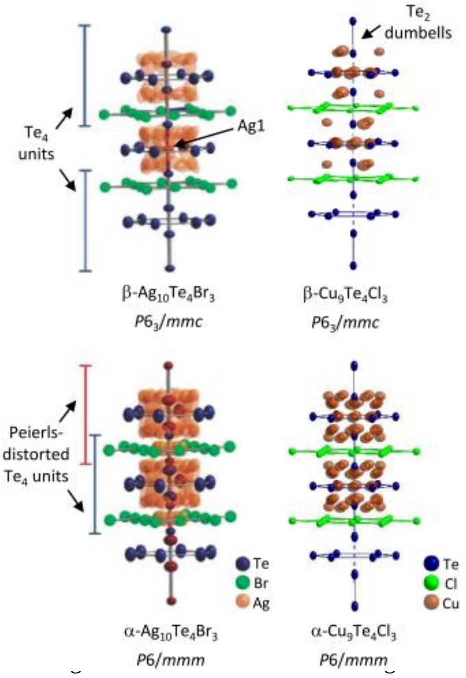


Figure 1. Seebeck Coefficient of $Ag_{10}Te_4Br_3$ and $Cu_9Te_4Cl_3$ in dependence of the temperature.

The first representative in this class is the tetramorphic coinage metal polychalcogenide halide $Ag_{10}Te_4Br_3$ recently presented by our group. [3, 4] It undergoes p-n-p switching accompanied by a huge jump of the Seebeck coefficient released by the variation of temperature. [5]

The new compound $Cu_9Te_4Cl_3$ is built on virtually the same structure motifs as present in $Ag_{10}Te_4Br_3$, and also shows polymorphism, but does not exhibit any pnp-switching or discontinuities of the Seebeck coefficient. By the examination of the new compound and comparison with the structural related pnp compound the features leading to p-n-p switching are carved out. Thus the results serve as a proof of concept concerning the mechanism of p-n-p switching and may offer possibilities for the discovery and optimization of pnp compounds concerning potential applications in energy conversion, like thermoelectrics.



temperature polymorphs of $Ag_{10}Te_4Br_3$ and $Cu_9Te_4Cl_3$.

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ELECTROSPUN ALKALI METAL SALT@PEO-MEMBRANES FOR LITHIUM ION BATTERIES

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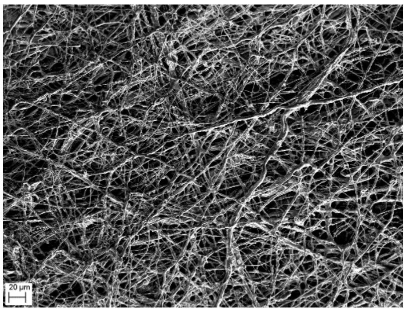

Fig. 1 SEM image of a PEO:SN:$LiBF_4$ membrane.

Solid Polymer Electrolytes (SPEs) for Lithium Ion Batteries (LIBs) could offer a safer and more stable alternative to conventional liquid electrolyte systems.[1] More than 40 years ago it has been shown that poly (ethylene oxide) (PEO) can be mixed with alkali metal salts and that these systems show reasonable ionic conductivity.[2] Since then, polymer-alkali metal ion hybrids where prepared via different techniques, *e.q.* hot pressing and solution casting. Our group recently showed that electrospinning of thin fiber conductive salt@polymer membranes is beneficial to aim for higher ionic conductivity. If $LiBF_4$ is added to PEO in molar ratio of 18:1, an ionic conductivity up to 1.5×10^{-6} Scm^{-1} at 293 K can be reached. When a solid plasticizer like succinonitrile (SN) is applied to system, the ionic conductivity can be raised to 2.0×10^{-4} Scm^{-1} at 293 K for a PEO:SN:$LiBF_4$ (36:8:1) membrane. Only half the amount of expensive conductive salt is used in that case. Further increase of SN does not lead to higher conductivity. If a molar ratio of 36:14:1 is applied, the conductivity is not further increased.[3] Sodium Ion Batteries (SIBs) are recently investigated as alternative for LIBs because Na is more abundant. Therefore we tried to transfer the knowledge gained from Li to Na membranes.[4] PEO mixed with $NaBF_4$ in a molar ratio of 18:1 shows ionic conductivity of 3×10^{-5} Scm^{-1} at 293 K, which is one magnitude higher than the respective Li sample. For sodium again the highest ionic conductivity is also reached if SN is added. A membrane with a molar composition PEO:SN:$NaBF_4$ of 36:8:1 shows an ionic conductivity of 10^{-4} Scm^{-1} which seems to be the upper limit for electrospun conductive salt@PEO membranes. All obtained membranes where investigated by means of impedance spectroscopy, differential scanning calorimetry, x-ray powder diffraction, scanning electron microscopy, cyclic voltammetry and solid state NMR.

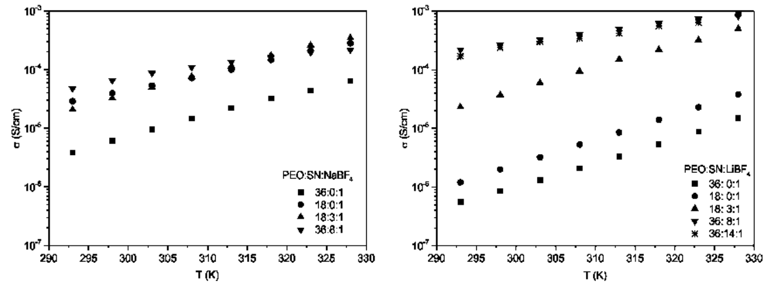

Fig. 2 Ionic conductivity over temperature for A) PEO:SN:$LiBF_4$ and B) PEO:SN:$NaBF_4$ membranes with different molar composition in a temperature range from 293 K to 328 K.

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Sn(II) EXCHANGE FOR VISIBLE LIGHT ABSORPTION OF $KTaWO_6$ WITH DEFECT-PYROCHLORE STRUCTURE

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The quest for developing a sustainable energy source to satisfy the ever-growing energy demand of an increasing world population is arguably one of the most important goals of scientific research nowadays. Heterogeneous photocatalysis using semiconductors is a promising way to use solar energy and store it in the form of chemical fuels, e.g. hydrogen or methane. Unfortunately, the large band gap of most metal oxides only enables the absorption of UV light, which is only a minor part of the solar spectrum. Here we present a method using ion exchange at ambient conditions to decrease the band gap of $KTaWO_6$ nanoparticles by approximately 1.3 eV down to 2.3 eV, thus enabling absorption of larger part of solar light.

The defect-pyrochlore structure of $KTaWO_6$ consists of corner-sharing TaO_6- and WO_6-octahedra, which form hexagonal tunnels (Figure 1 left). Inside these channels, the K^+ ions are located and only weakly bound, therefore they can easily be exchanged. For $KTaWO_6$ we found that water molecules can enter the channels, resulting in a widening of the crystal structure, greatly enhancing the ion exchange process.

The incorporation of Sn^{2+} ions is of special interest, since the lone electron pair of Sn^{2+} is located in the Sn 5s states. These states are located above the oxygen 2p states, which form the valence band of most metal oxide semiconductors. The incorporation of Sn^{2+} therefore results in the formation of a new valence band, greatly diminishing the band gap (Figure 1 right).

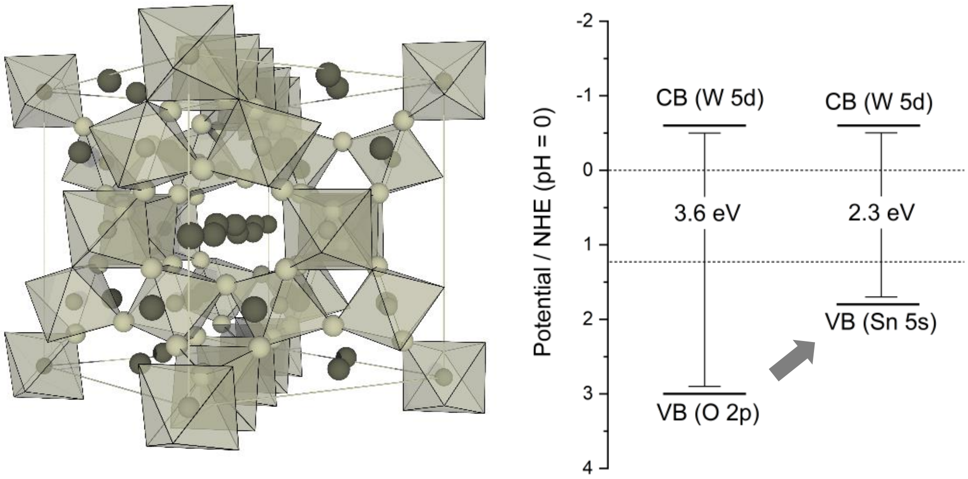

Figure 3: Crystal structure (left) and band scheme (right) of $KTaWO_6$.

To conclude, we show a method to decrease the band gap of quaternary metal oxide semiconductor using a simple ion-exchange reaction. The ion exchange is greatly facilitated by water molecules within the crystal structure. [1]

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UNUSUAL SOLID-SOLUTION BEHAVIOR OF NASICON-STRUCTURED CATHODE MATERIALS FOR SODIUM-ION BATTERIES

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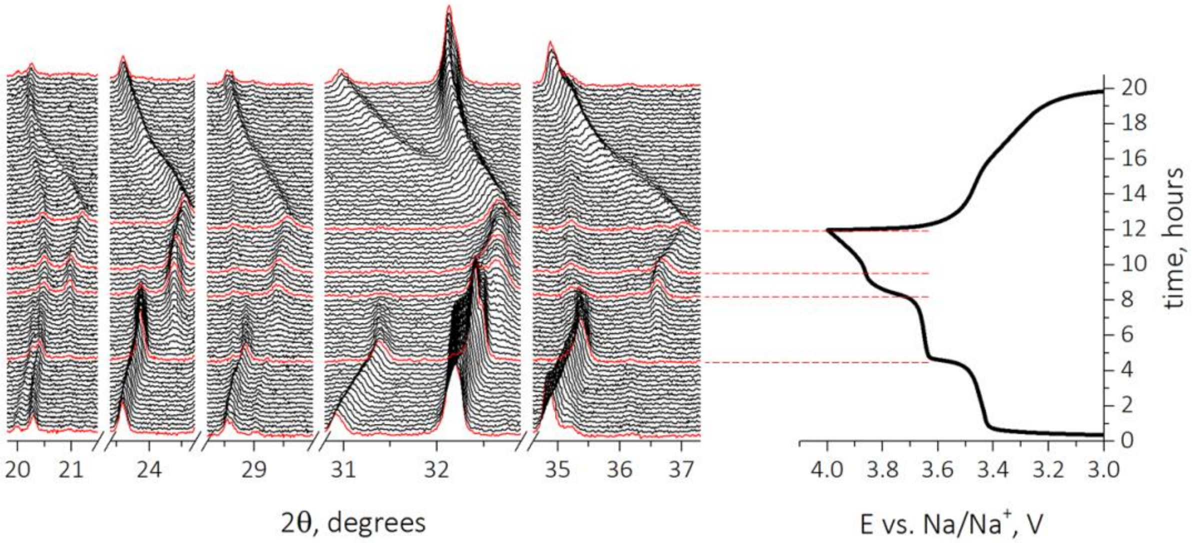
$Na_3V_2(PO_4)_3$ is known to crystallize in NASICON-type structure, which consist of corner-shared transitional metal octahedra and phosphate tetrahedra. It delivers a highly reversible capacity of more than 110 mAh/g, showing a biphasic voltage plateau at 3.4 V corresponding to the V^{4+}/V^{3+} redox couple [1].

In $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$, introduction of Mn(II) leads to the voltage increase and materials cost decrease compared with the $Na_3V_2(PO_4)_3$ [2]. The aim of our work was to study the phase transformation behavior of $Na_4MnV(PO_4)_3$ during cycling within different potential limits.

In $Na_4MnV(PO_4)_3$ two well-defined steps are observed when charged to 3.8 V [2]. After the increase of the cut-off voltage on charge up to 4.0V the electrochemical behavior on discharge changes, namely a gradual slope is observed instead of two steps as in the case of cut-off at 3.8V.

By *operando* X-Ray Diffraction we've found that on charge $Na_4MnV(PO_4)_3$ demonstrate consequently solid-solution and then biphasic deintercalation mechanisms, which is symmetric on discharge when cut-off is 3.8 V, however only solid-solution intercalation mechanism was found on discharge in the case of charge up to 4.0 V.

Fig. 1 *Operando* X-ray diffraction pattern for $Na_4MnV(PO_4)_3$, galvanostatically charged and discharged at a current rate corresponding to 2 Na^+ per 10 hours



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CUBOCTAHEDRAL INTERMETALLIC MOTIFS IN PALLADIUM AND PLATINUM TERNARY COMPOUNDS: QUASI-LAYERED STRUCTURES WITH HETEROMETALLIC BONDS

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We have recently reported several new palladium- and platinum-rich compounds, such as Pd_5InSe, Pd_8In_2Se, $Pd_{17}In_4Se_4$, Pd_5InAs, Pt_5InAs, and Pt_8In_2As, all of which feature cuboctahedral [$T_{12}In$] (T = Pd/Pt) fragments that are encountered in binary intermetallics of the Cu_3Au structure type. The compounds with 5:1:1 atomic ratios belong to the Pd_5TlAs structure type, a relatively uncommon type that was established in early 1970s [1] and until recently included only a few structurally characterized compounds, e.g. Pd_5CdSe, Pd_5CdAs [2], and Pd_5HgSe [3]. The compounds with 8:2:1 atomic ratio belong to the Pd_8In_2Se-type, that we have discovered, which features double-stacked along the c axis [$T_{12}In$] (T = Pd/Pt) fragments, and thus are essentially second homologues to the Pd_5TlAs type of structures. Although several other palladium and platinum ternary pnictides, tetrelides and selenides, belonging to the Pd_5TlAs structure type, were suggested in the same paper [1], no structural data was provided and the compositions were not established properly. And, surprisingly, neither structures nor any properties of most of the suggested compounds were never studied since then.

Here we report the results of our purposeful synthesis of the compounds of the Pd_5TlAs- and Pd_8In_2Se-type in Pd-In-P, Pt-In-P, Pd-Zn-Se, Pd-Zn-P, Pt-Zn-P systems, their crystal and electronic structures, bonding analysis, as well as magnetic properties and the response to hydrogenation. High-temperature ampoule technique was used for the synthesis. Crystal structures of compounds were determined using powder or single-crystal diffraction data. Electronic structures were established based on the DFT calculations. New compounds are built in a similar way to previously characterized ones belonging to the Pd_5TlAs structure type. Their structures can be described either in terms of linear intergrowth structures of Cu_3Au- and $PtHg_2$-type blocks, or as layers of Pd- or Pt-based cuboctahedra separated by sheets of pnictogen or chalcogen. We have found no new second homologues neither for palladium, nor for platinum under equilibrium conditions.

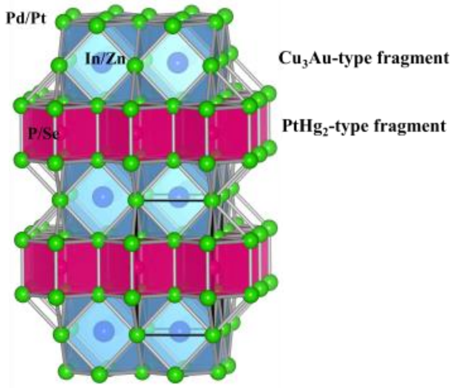

Fig. 1 Polyhedral representation of the crystal structures of Pd_5InP / Pt_5InP / Pd_5ZnSe / Pd_5ZnP /Pt_5ZnP

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PROTON CONDUCTION MECHANISMS IN METAL ORGANIC FRAMEWORKS

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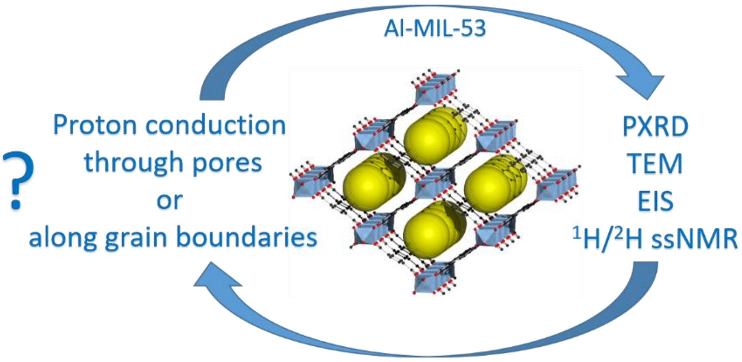
Power storage and renewable energy sources have become a major topic for the human society for the last decades.[1] A promising approach for renewable energy sources are fuel cells, which convert chemically bound energy into electrical energy with high efficiency [2]

The efficiency and operating conditions of fuel cells depend on the membrane material used.[4] To date for low temperature polymer electrolyte fuel cells Nafion is the state of the art membrane material.[5] For an optimisation of membranes it is crucial to entirely understand the current mechanisms of water mediated proton movement in those materials. In comparison to polymer electrolytes the conduction mechanism in metal organic frameworks (MOFs) should be straight forward because of their detailed crystal structure.[6, 7]

Cheetham *et al.*[8] suggested that proton conduction in MOFs mostly originates from interparticle phases. They proved their concept by experimental evidence and their additional survey of the literature seemed to confirm the high contribution of interparticle phases on proton conduction.[8] We claim that the conduction mechanism, either along grain boundaries or through the pores depends on the specific structure of the framework. Our aim is to take the whole investigation even further and examine the specific mechanism, Grothuss[9] or vehicle mechanism[10], which prevails in MOFs showing conductivity through the pores.

Herein we present a systematic study using size selectively synthesised Al-MIL-53, and its derivatives Al-MIL-53-NH_2 and Al-MIL-53-OH. The phase purity is analysed using powder X-ray diffraction (PXRD). The size distribution and structure of the nanoparticles is determined by dynamic light scattering (DLS) and transmission elecron microscopy (TEM). The conductivity of MOF nanoparticles is determined employing impedance spectroscopy (EIS). We expect that in MOFs with a conduction along grain boundaries the conductivity is higher in small crystals while conduction through the pores leads to a higher conductivity in large crystals. Finally proton mobility in MOFs, in which proton conduction is observed, is further analysed employing ^{1}H and ^{2}H solid state NMR spectroscopy to get information on the molecular level.



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LUMINESCENT AND CATALYTIC PROPERTY MODULATION OF GERMANOSILICATE ZEOLITE AFI BY POST-SYNTHESIS ALUMINATION

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Germanosilicates with AFI [1] topology were synthesized for the first time and further utilized for the chemically selective removal of Ge from the framework positions followed by alumination with the methods of one-step alumination and two-step degermanation/alumination procedure [2]. It was found that extraction of Ge did not lead to the change of zeolite structure but to the formation of silanol nests. Taking full advantage of this unique change, one dimensional large pore Al-AFI zeolites were obtained. On one hand, the original AFI samples exhibited ultralong fluorescence lifetimes up to about 300 ms at ambient temperature and atmosphere, one-step alumination created new phosphorescence center, while prior acid treatment in the two-step procedure quenched luminescent phenomena, this is due to the modulation of in-situ confined carbon dots in the zeolite matrices [3]. On the other hand, both alumination methods could incorporate Al into AFI zeolite framework by substitution of Ge for Al, however the leached Ge cannot move out efficiently, causing to block the pores and channels in one-step alumination, only two-step procedure retained the porosity and introduce acidity simultaneously. The catalytic performance of Al-AFI zeolites was investigated in the alkylation of toluene with isopropyl alcohol and compared to that of MTW zeolite possessing similar type of pore system (one-dimensional system of channels with 12-member ring openings).

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