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Materials and Sustainable Development: Issues and Challenges of the 21st Century

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KEYNOTE SPEAKERS

EMERGENCE OF POLYNITROGEN NETWORKS IN LEAD-NITROGEN PbNx PHASES UNDER PRESSURE

G. Frapper

University of Poitiers/IC2MP UMR 7285 UP-CNRS

gilles.frapper@univ-poitiers.fr

This talk will tentatively illustrate the use of evolutionary (genetic) algorithms and first-principles calculations for predicting materials. Determining the crystal structure of a compound based solely on its chemical composition is a major challenge in materials science. This task involves identifying the lowest-energy structural arrangement from among millions of possible structures using numerical simulation. To demonstrate this challenge, arranging twenty atoms in a box - a repeating lattice of varying shape and volume - can potentially generate over 10^{21} structures on the potential energy surface (PES). If each optimized structure's energy were numerically determined, taking one hour of computing time, the required computing time would exceed the age of the universe... The problem at hand is how to access the lowest energy well, which is the global minimum on the PES, while using minimal computational resources.

This lecture will discuss a self-learning method for exploring the PES of a crystalline compound. The method combines an evolutionary algorithm (EA) with DFT calculations (here PBE and r2SCAN levels of theory). The CSP EA algorithm, which is based on the concepts of the Darwinian evolutionary theory, will be briefly outlined. Then, the *in silico* exploration of lead-nitrogen binary phase diagram under pressure from EA-DFT will be presented. The variety of (meta)stable PbN_x crystal structures in the pressure range of 0-100 GPa can be classified into three categories; (1) molecular anionic units, such as N_2^{q-} dumbbells in PbN_2, PbN_3 and PbN_4, exp. N_3^- azide in PbN_6 and 5-rings pentazolate N_5^- in PbN_{10}, (2) 1D infinite polynitrogen chains in PbN_8 and PbN_{10}, and (3) 2D covalent polynitrogen layers, such as fused 18-rings in *Cc* PbN_8 (see below).
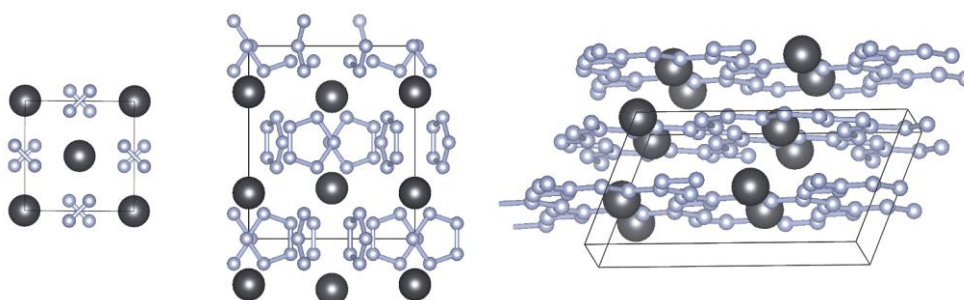
N$_2^{2-}$ dimers in *I4/mcm* PbN$_2$ pentazolate N$_5^-$ in *I4/m* PbN$_{10}$ 2D fused 18-rings in PbN8

Their crystal structures, bonding, and electronic properties will be presented. Finally, I will discuss the recoverability of each thermodynamically stable high-pressure phase to ambient pressure, as well as their thermal, kinetic, and dynamical stabilities, through *ab initio* molecular dynamic simulations. This "*Computational Materials Discovery*" study also emphasises the significance of pressure in obtaining polymerized nets from molecular unsaturated species. For instance, anionic polynitrogen species from N_2 precursor in high-energy density materials like PbN_x and others proposed in my *Applied Quantum Chemistry* group[1-6].

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PDC CHEMISTRY AS A POWERFUL TOOL FOR THE DESIGN OF FUNCTIONAL INORGANIC MATERIALS

M. Ben Miled[1], M. Cheype[1], A. Habrioux[2], S. Bernard[1]

[1]Univ. Limoges, CNRS, IRCER, UMR 7315, F-87000, Limoges, France.

[2]Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), Université de Poitiers, CNRS, F-86073 Poitiers, France

Samuel.bernard@unilim.fr

The PDC (Polymer-Derived Ceramics) method is an attractive synthetic approach in the design of advanced catalytic formulations that are based on non-noble transition metals with high degree of structural and compositional homogeneity. Nowadays, PDC chemistry gathers plenty of fascinating strategies to prepare materials from solution state precursors. Low temperature chemistry, reproducibility, and high surface to volume ratios of obtained products are features that add merit to this route. The development of different and fascinating procedures was fostered by the availability of preceramic polymers and transition metal complexes with the great advantage of tailoring the physico-chemical properties of the materials through the manipulation of the synthesis conditions. Thus, the synthesis of preceramic polymers offers a number of features particularly advantageous to trigger the formation of metal NPs and trap them in a high SSA matrix upon heat-treatment at significantly lower temperatures than conventional processes. In addition, the shaping richness of preceramic polymers allows for 3D printing offering some unique properties for heterogeneous catalysis.

The aim of this talk is to introduce an overview of the PDC synthesis of tailored and multifunctional inorganic materials and their application in the main domain of electrocatalysis. One of the main achievements is to stress the versatility of PDC preparation by highlighting its advantage over other preparation methods through some specific examples of the synthesis of catalysts and 3D architectures.

INVITED SPEAKERS

ACTIVE LEARNING APPLIED TO MATERIALS SCIENCE

G. Lambard
National Institute for Materials Science
LAMBARD.guillaume@nims.go.jp

In this talk, we will introduce the active learning principle assisted by Bayesian optimisation and its application to design new materials. We will demonstrate the capabilities of an active learning pipeline through the process of an epoxy resin with improved adhesive strength [1], the synthesis of a mesoporous PtPdAu alloy for electrochemical oxidation of methanol [2], the optimal combination of additives for rechargeable Li–O2 batteries [3], the optimisation of the direct extrusion process for Nd-Fe-B magnets with improved magnetic properties [4], and the synthesis of thermoelectric materials like the binary alloy of GeTe as well as a quaternary alloy of $Cu_{2.125}Zn_{0.875}SnS_4$ (kesterite) with improved thermoelectric properties [5]. We will demonstrate that an active pipeline coupled with experimental data can deliver novel perspectives on material behaviours regarding their synthesis process. Additionally, we will introduce our dedicated and open graphical user interface (GUI) system that should allow any experimentalist to leverage our active learning pipeline with no previous coding experience [6].

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THERMOELECTRIC MATERIALS: A LONG-TERM AND FRUITFUL COLLABORATION BETWEEN EXPERIMENTALISTS AND THEORETICIANS IN THE FRAMEWORK OF LINK

R. Gautier[1], D. Berthebaud[2,3], T. Mori[4] and J.-F. HALET[1,3]
[1]ISCR, Université de Rennes – CNRS – ENSC Rennes, Rennes, France
[2]IMN, Nantes Université, CNRS, Nantes, France
[3]LINK, CNRS – Saint Gobain – NIMS, Tsukuba, Japan
[4]MANA, NIMS, Tsukuba, Japan
regis.gautier@ensc-rennes.fr

Since the pioneering work of Goldsmid and Slack in the sixties,[1] thermoelectric energy conversion has been the chimera of power generation, energy recovering systems, and refrigeration in nano- and macro-systems alike.[2] One bottleneck to achieve competitive conversion performance is the efficiency of the active materials used to engineer the devices. These materials must satisfy several contradictory requirements both in the electrical and thermal transport channels in order to maximize the thermoelectric efficiency. Material performance is determined by the figure of merit, ZT, which involves the Seebeck coefficient, the electrical conductivity, and both the electronic and lattice contribution to the thermal conductivity. Optimizing simultaneously these four transport quantities at the desired operating temperature is very difficult.

First-principles modelling approaches based on density functional theory (DFT) are essential in materials science. In the context of thermoelectricity, computing their electronic and vibrational structures is often helpful to better understand their structural and transport properties. DFT calculations can also be useful to identify and predict the transport properties of promising thermoelectric materials. This presentation will show few examples of combined theoretical & experimental approaches to study thermoelectric materials in the exciting context of the Laboratory of Innovative Key Materials and Structures hosted in Tsukuba, Japan.

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MATERIALS INFORMATICS: UTILIZING AI TO ASSIST PRODUCT FORMULATION DESIGN

J. Zhu, Y. Zhao, W. Sun
Saint-Gobain Research Shanghai
jia.zhu@saint-gobain.com

Materials Informatics involves using data-centric approaches, including Artificial Intelligence (AI) and Machine Learning, to assist scientists and engineers in materials R&D. This process has the potential to transform materials development, leading to huge cost savings and quicker routes to market for its users.

At SGR Shanghai, by close collaborating with Composite R&D team, we piloted this Material Informatics approach with AI-assisted formulation design of PU (Polyurethane) foams for Tape Solutions. For PU compression pad product, the Compression Force Deflection (CFD) is one of the key mechanical properties since compression pad with adequate compression force can provide support to EV battery during expansion in charging and extend battery life.

The conventional product development follows a few steps: selection of available materials, sample preparation, sample test, followed by back-and-forth formulation modifications to achieve desired CFD curves before trials in plant. This process can take months or even longer. This is the part where we expect to accelerate through data analytics and obtain a better understanding of structure-process-property correlation.

An experiment-database was built, including raw materials, formulations, test methods and test result data, and a web application tool was developed. Users can retrieve formulations by code or range of CFD values. Details of the formulation can be reviewed, including the ratios of various ingredients, the properties of the ingredients, and the profiles of the tested CFD. Users can also perform a benchmark by simple clicks on multiple formulations to compare differences in ingredient ratios and differences in properties.

Furthermore, users can virtually design a new formulation by configuring and tuning the rates of various selected ingredients and viewing the predicted property curves in parallel. Existing formulations can also be selected as a reference and basis of the new design. With the AI algorithm behind, the tool can recommend multiple formulations based on desired properties and what is in development is to add constraints with the expertise from material scientists to optimize recommendations.

Materials informatics, as a long-term R&D topic at Saint-Gobain, provides a promising vision and a joint point among data science, modeling, and materials science.

DESIGNING HYDRIDES FOR HYDROGEN STORAGE USING MACHINE LEARNING

J.-C Crivello[1,2], A Sultanov[2], Z. Nefzi[2], Baturin[2], L. Levrel[2], C. Barreteau[2]

[1]CNRS-Saint-Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK), 1-1 Namiki, 305-0044 Tsukuba, Japan

[2]Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France

jean-claude.crivello@cnrs.fr

Hydrogen has proven to be a highly effective and environmentally friendly energy carrier that can be converted into electricity through fuel cells. However, its potential is hindered by the challenge of storage. Metal or complex hydrides offer a promising solution, as they are capable of storing significant amounts of hydrogen efficiently.

These materials, for which incremental research has limited efficacy, require real breakthroughs that can only be achieved through predictive methods. Presently, high-throughput first principles calculations and machine learning offer promising avenues to propel material design research forward, as illustrated by examples in this paper.

Using a combination of computational methods such as high-throughput SQS and DFT methods, supported by machine learning to expedite research, three topics of interest are presented: (1) disordered multi-component solid solutions with interstitial H atoms to design metal hydrides, (2) prediction of new mixed complex hydride phases using evolutionary algorithms, and (3) diffusion methods that provide training stability and efficient results in the generation of new crystallographic structures [1].

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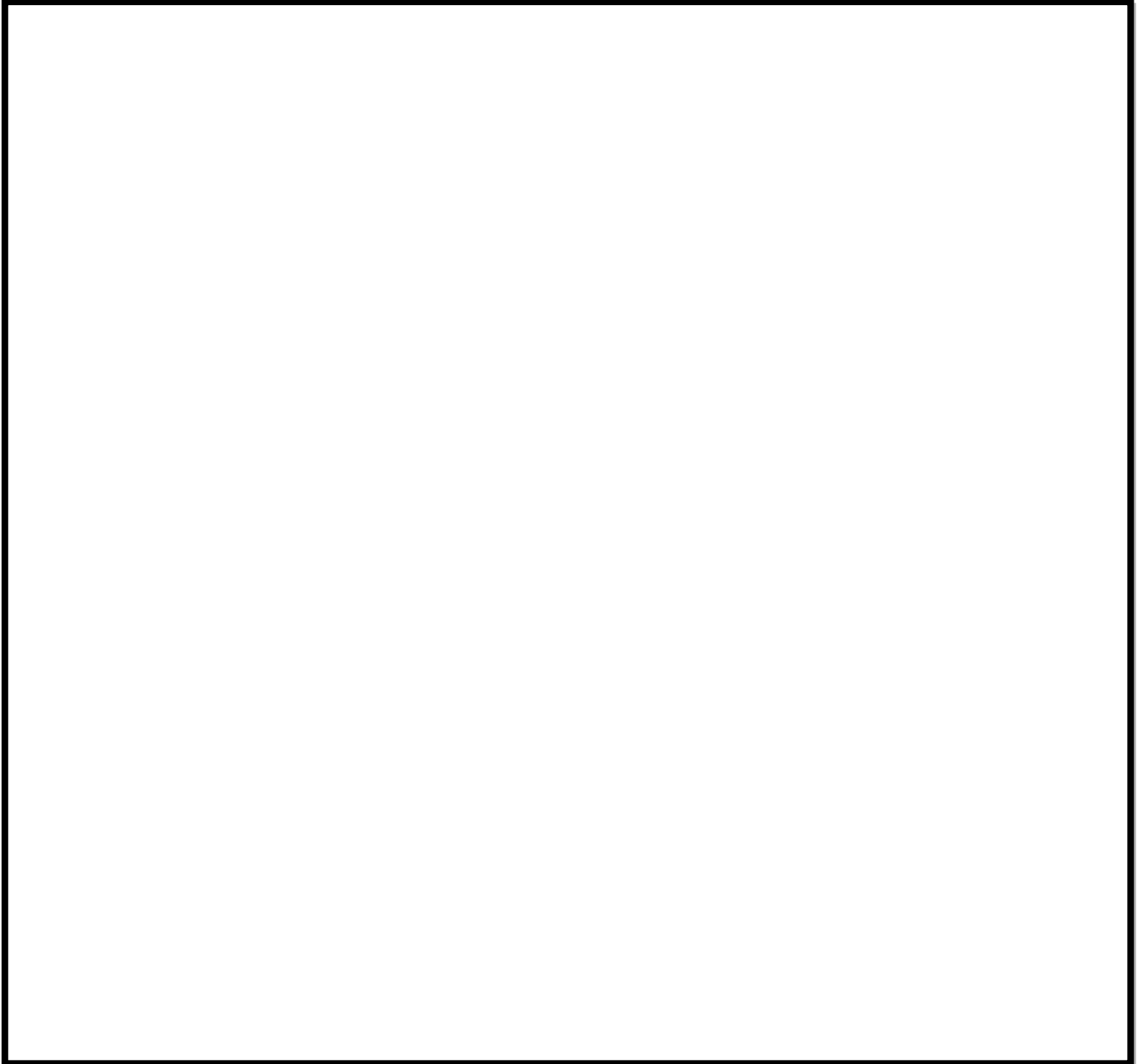
MATERIAL INFORMATICS FOR SG MATERIALS

L. Le Tiran
Saint-Gobain Research Paris
Loic.LeTiran@saint-gobain.com

FAST OPTIMIZATION OF MATERIAL SYNTHESIS VIA BAYESIAN OPTIMIZATION: A CASE STUDY ON MAGNETOCALORIC $Mn_{5-x}Fe_xSi_3$

S. Le Tonquesse

Laboratoire CRISMAT UMR 6508 CNRS ENSICAEN, 14050 Caen Cedex 04, Caen, France

sylvain.letonquesse@cnrs.fr

Optimizing synthesis parameters and chemical compositions are crucial in material science for developing high-performance materials with desired properties. Traditional trial-and-error approaches are time-consuming and often inefficient due to the complex interplay of synthesis parameters. To address this challenge, we explored Bayesian Optimization (BO) as a more effective method for fine-tuning the magnesioreduction synthesis of magnetocaloric $Mn_{5-x}Fe_xSi_3$, a non-toxic and rare-earth-free material [1], from metal oxides precursors. Magnesioreduction synthesis is an ideal study case for this optimization approach, given the critical need to optimize multiple experimental parameters which significantly influence the outcome [2]. Unlike conventional machine learning methods that require extensive data prone to noise, BO leverages a smaller dataset and incorporates prior knowledge to accelerate the optimization process [3]. Our approach utilized open-source GpyTorch and BoTorch libraries, focusing on reducing total reaction time while maintaining high purity and achieve large magnetocaloric effect near room temperature by tuning the chemical composition. The optimized process significantly improved the efficiency of synthesizing $Mn_{5-x}Fe_xSi_3$, demonstrating BO's potential to optimize complex material processes. This presentation discusses the methodology, results, and the broader implications of applying BO in the synthesis of advanced materials, underscoring its value in reducing experimental overheads and accelerating materials development.

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THE CALPHAD METHOD FOR MATERIALS DESIGN

J.-M. Joubert
ICMPE-CNRS, Thiais
jean-marc.joubert@cnrs.fr

The Calphad method relies on the thermodynamic description of different systems, from the known experimental data, which, when combined with each other in databases, can yield to the prediction of phase equilibrium in multi-component systems. This has been used for materials design. Sometimes, the accuracy obtained with commercial databases is not sufficient due to the poor description of some of the constitutive systems. One then need to go back to the original description of ternary or even binary systems. One may discover that the deficiencies are often caused by a poor experimental knowledge of some systems. Experimental effort is then needed in order to build new databases.

Various examples of materials design will be presented some with commercial databases, some for which a database has been constructed using new experimental data.
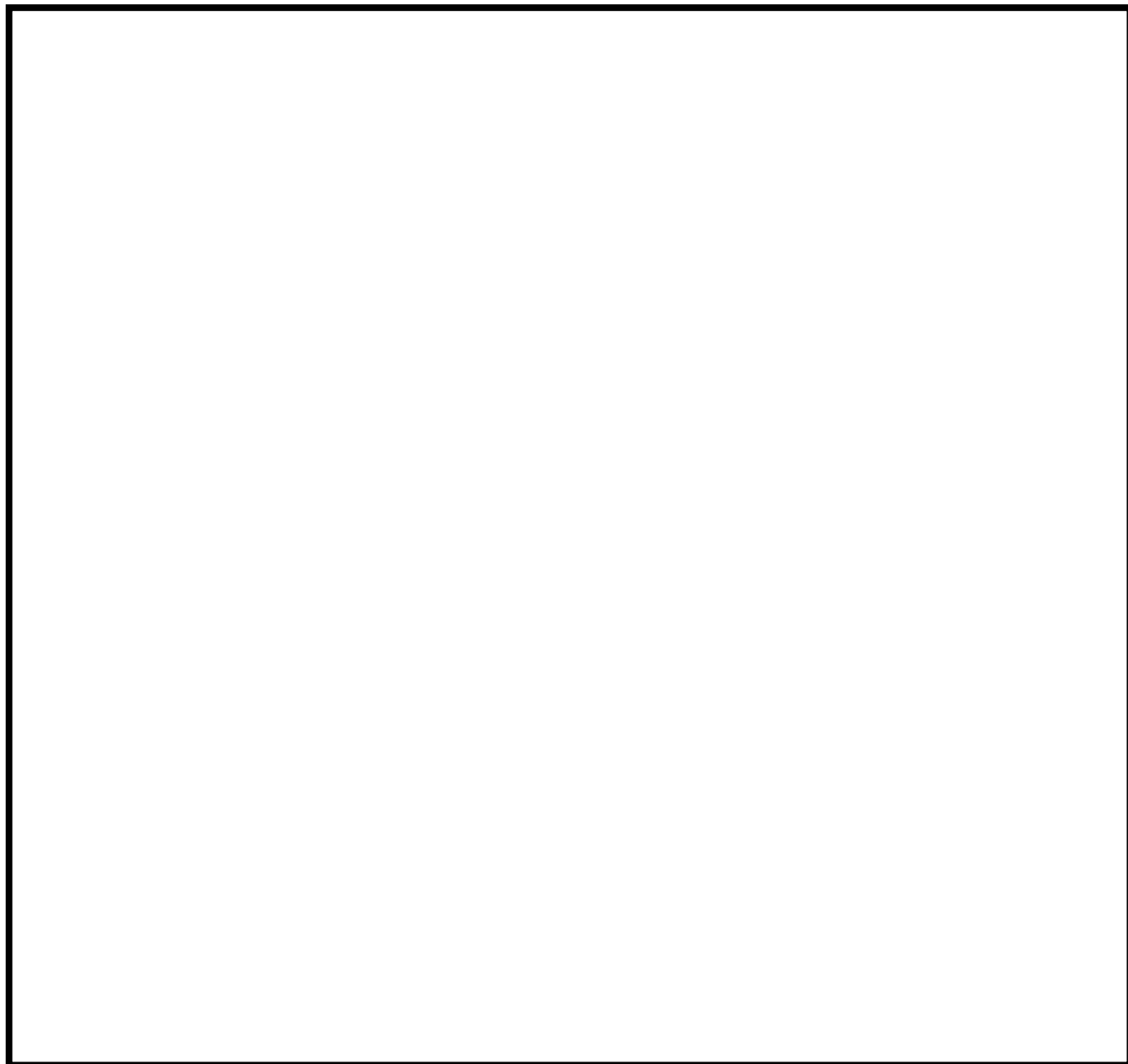
SOME INSIGHTS ON Mo6 CLUSTER COMPLEX AND ITS RELATED COMPOUNDS FROM RECENT INVESTIGATION

N. Ohashi

National Institute for Materials Science

ohashi.naoki@nims.go.jp

OCTAEDRAL METAL CLUSTER-BASED BUILDING BLOCKS: TOWARDS THE ENGINEERING OF NEW AMBIPOLAR PHOTOELECTRODES FOR SOLAR ENERGY CONVERSION

A. Renaud,[1] T. Lappi,[1,2] Y. Gayfulin,[2] N. Naumov,[2]
T. Uchikoshi,[3,4] F. Grasset,[1,3] S. Cordier[1]

[1]Univ Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France
[2]Nikolaev Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russian Federation
[3]CNRS–Saint-Gobain–NIMS, IRL 3629, LINK, NIMS, 1-1 Namiki, 305-0044 Tsukuba, Japan
[4]Research Center for Functional Materials, NIMS, 1-1 Namiki, Tsukuba, Japan
adele.renaud@univ-rennes.fr

Ambipolar materials are a class of compounds that can intrinsically transport and transfer simultaneously both charge carriers, holes and electrons in a comparable way.[1] Unlike conventional unipolar semiconductors in which a type of charge carrier is predominant, ambipolar materials can display p-type and n-type characteristics, which makes them attractive materials for many different application fields such as sunlight conversion.[2,3] Only few materials such as semiconducting polymers, carbon nanotubes, 2D materials or organic-inorganic hybrid perovskites exhibit ambipolar behaviors.[1,3] Their intriguing intrinsic physical properties result from their specific electronic structures that are not only related to the chemical compositions but also to morphology and size effects.[1,3]

Recently, the authors have completed this family of materials by a new series of compounds, namely the transition metal cluster (MC) compounds based on Mo_6, Re_6, and mixed $(Mo,Re)_6$ clusters.[4,5,6] $[\{M_6(Q,X)^i_8\}L^a_6]$ (M = Mo or Re, Q = S ou Se, X = I and L = Cl, I or H_2O) cluster-based building blocks have a nanosize scale restriction giving them fascinating optical and electronic properties such as molecule-like energy gaps, strong absorption in the visible and/or NIR spectral regions, deep red luminescence or high (photo)catalytic effectiveness.[4-8] They are particularly well suited for nanoarchitectonics[4,5,6,9] whose the concept is based on the assembly of nanoscale units to reach new original physical properties.

The design of photoelectrodes built on cluster core building blocks will thus be presented in this communication. The control of their composition and design led to the development of new ambipolar photoelectrodes with tailored optoelectronic properties. Beyond the deposition route, the origin and the engineering of the photoconductivity properties of MC-based layers will be discussed before to consider their interest as new light-harvesting layer for the solar energy conversion.

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LIGHT AND HUMIDITY SENSING BY MO$_6$ CLUSTER FILM FABRICATED BY ELECTROPHORETIC DEPOSITION

T. Uchikoshi[1,2] T. K. N. Nguyen[1,2], K. Harada[2,3], F. Grasset[2,4], S. Cordier[4],
N. Dumait[4] and M. Matsuda[3]
[1]National Institute for Materials Science (NIMS)
[2]CNRS–Saint-Gobain–NIMS, IRL3629, LINK, NIMS
[3]Kumamoto University
[4]Univ. Rennes-CNRS-Institut des Sciences Chimiques de Rennes

A new environment-sensing device based on opto ionic-electronic phenomena using octahedral molybdenum metal (Mo6) clusters have been developed. When the Mo6 clusters are deposited on a transparent electrode in an organic solvent containing a trace amount of water, by the electrophoretic deposition (EPD) process, an electrochemical method, water in the solvent is incorporated into the deposited film. In the process, some of the ligand species which stabilize the frame structure of the Mo6 cluster are partially substituted with hydroxyl groups, and the negatively-charged frame structure of the Mo6 cluster units are stabilized with hydronium ions as counter ions. As a result, the transparent film of the Mo6 cluster fabricated by this method exhibited mixed conduction of hydronium ions and electrons. The ionic conduction greatly changes depending on the temperature and humidity, and the electronic conduction greatly changes depending on the wavelength and intensity of the irradiated light[1]. These unique multi-sensing properties would present new possibilities for environmental sensor applications.
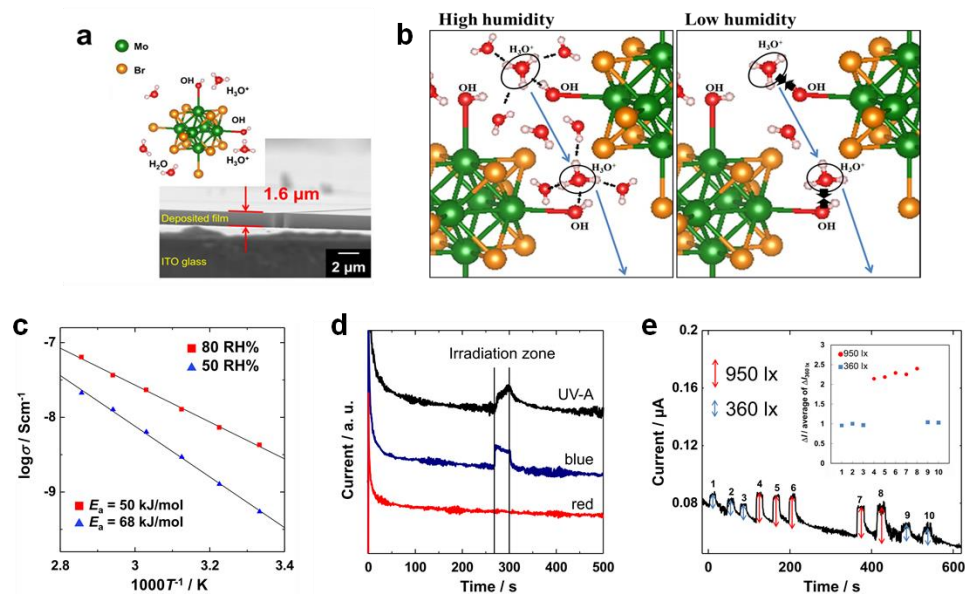

Fig. 1 Mo$_6$ cluster film formed on an ITO glass substrate by anodic EPD from a suspension of Cs$_2$[{Mo$_6$Br$^i_8$}Br$^a_6$] clusters in acetone: (A) schematic diagram of the octahedral framework structure of the Mo$_6$ cluster unit and cross-sectional SEM photograph of the Mo$_6$ cluster film; (b) schematic diagram of the internal structure of the Mo$_6$ cluster film; (c) temperature and humidity dependence on proton conductivity; (d) irradiation light wavelength dependence on electron conductivity; (e) irradiation light intensity dependence on electron conductivity.

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ELABORATION OF HYBRID THIN FILM BY ELECTROPHORETIC DEPOSITION: FROM NANOPARTICLES TO DEVICES

C. Lebastard

CNRS-Saint-Gobain-NIMS, IRL 3629, LINK, NIMS, 1-1 Namiki, Tsukuba, Japan

lebastard.clementhugo@nims.go.jp

Electrophoretic deposition (EPD) is a simple and flexible processing technique that can produce thin films (from a nano to a micro scale) of a variety of materials. The technique requires conductive substrates and a suspension of charged nanoparticles (NPs). The application of a voltage migrates the NPs on oppositely charged electrodes (*i.e.* the substrates). Among numerous advantages (low-cost, simple to set up, orientation of anisotropic NPs), EPD can be applied to flat surfaces but also to objects with numerous geometries (curved, with holes…).

The first part of the talk will concern antimony trisulfide, known as an optical phase change material. It displays a strong optoelectronic difference between the amorphous and crystalline form and is promising for various applications: battery, photonic and optoelectronic display and also as an emerging and attractive solar absorber. Sb_2S_3 has a bandgap of 2.2-2.7 eV (amorphous) and 1.5-1.7 eV (after crystallization in the orthorhombic P*nma* space group). It can be combined with c-Si technology as an extra subcell in based tandem dual-junction solar cells to increase the power conversion efficiency (PCE). Starting from suspension containing charged NPs, thin films of amorphous Sb_2S_3 were obtained, optimized and characterized before and after annealing.[1] Doping and integration of Sb_2S_3 in a device were also studied.

The second part will involve metal clusters (MCs), used as light harvesters for solid photoelectrode applications (ANR NanoLEtsGOs project). They are molecular nano-objects (< 2 nm) built of $[Mo_6X^i_8L^a_6]$ units (with X = chalcogen or halogen, L = two-electron ligands) with a molecular aspect when solubilize in a suitable solvent. Easily deposed by EPD, MCs can generate an efficient photo-induced current when enlightened. Based on an inverse opal structure, nanostructure and interfaces of the photoelectrode are the key parameters to enhance the photoconductivity.[2]

This work presents how EPD, a low-cost, efficient and simple technique, can be applied to a wide range of research areas, to develop environmentally friendly devices. Advantages and challenges that need to be overcome are also discussed.

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HYBRID LEAD HALIDE PEROVSKITE SINGLE CRYSTAL: STRUCTURAL, OPTICAL, AND THERMAL PROPERTIES

F. Pawula,[1,2*] A. Fakih,[3] S. Péchev,[4] R. Daou,[3] D. Mantione,[1] O. Lebedev,[3] A. Maignan,[3] G. Hadziioannou,[1] S. Hébert,[3] and G. Fleury[1]

[1]*Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600 Pessac, France*
[2] *Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes F–44000, France*
[3]*Normandie Univ., ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen, France*
[4]*Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France*

florent.pawula@cnrs-imn.fr

For many years the hybrid halide perovskites have received great attention by the scientific community due to their very promising potential for technological applications. The hybrid perovskites ABX_3 family gathers the compounds where A is an organic cation, B is an inorganic cation and X is a halide. The most studied members are those constituted of A = MA$^+$, FA$^+$; B = Pb^{2+}, Sn^{2+}; and X = I$^-$, Br$^-$, Cl$^-$, where MA$^+$ and FA$^+$ stand for methylammonium $CH_3NH_3^+$ and formamidinium $NH_2CHNH_2^+$, respectively. This family includes materials with a range of interesting properties such as optoelectronic, semiconductivity, low thermal conductivity, or large Seebeck coefficients, which hold great promise for many applications, including photovoltaics, thermoelectricity and thermal insulation [1–3].

Lead halide hybrid perovskite single crystals have been grown using antisolvent vapor-assisted crystallization. The chemical composition and structural model of the crystals have been established using nuclear magnetic resonance and single crystal x-ray diffraction, leading to the formula $FA_{0.9}MA_{0.1}PbI_{2.23}Br_{0.77}$. The hexagonal crystallographic structure with $P6_3/mmc$ space group has been confirmed by transmission electron microscope study. Through a detailed analysis of the single crystal XRD data, the locations of FA$^+$ and MA$^+$ in the unit cell have been identified, and the off-centering of Pb^{2+} on the octahedral sites has been unveiled, probably due to the Pauli repulsion of the lone pair. This material is a wide-gap semiconductor with Eg = 2.27 eV and demonstrates photoluminescence activity. The thermal conductivity is disorder-dominated with an extremely low value of 0.17 Wm^{-1}K^{-1} from about 75 K up to 325 K. The present investigation on $FA_{0.9}MA_{0.1}PbI_{2.23}Br_{0.77}$ single crystal demonstrates that low values of thermal conductivities are obtained in this hexagonal family of hybrid halide perovskites, with mixed cationic and anionic disorder.

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STRATEGIES FOR ACHIEVING A LARGE OPTICAL TRANSPARENCY WINDOW IN CORRELATED TRANSPARENT CONDUCTORS

A. Cheikh[1], E. Oualyd[1], M. Rath[1], U. Lüders[1], W. Prellier[1], A. Fouchet[1], C. Labbé[2] and A. David[1]

1 NORMANDIE UNIV, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 CAEN, France.
2 CIMAP, Normandie Université, ENSICAEN, UNICAEN, CNRS, 14050 Caen Cedex 4, France.

adrian.david@ensicaen.fr

Correlated transparent conducting oxides TCOs have gained great attention because of their unique combination of transparency conducting character. The oxide $SrVO_3$ (SVO) was identified as a high performance transparent conducting oxide TCO in the visible range. However, the functional properties of SVO have never been subject to extensive optimization in order to explore the limits of this technology. Here, we used two different strategies by exploiting the band lling and width of the bands derived from Vanadium in $SrVO_3$ to tune the screened plasma frequency $\omega * p$ and the inter-band transition E_{p-d} energy, which are the transparency window edges. For the control of band lling strategy, it is found that as $SrVO_3$ becomes Titanium-rich, the transparency window widens but such composition does not maintain the high electrical conductivity required for TCO applications. Concerning the bandwidth strategy, the gradual doping of $SrVO_3$ by Calcium shows that $\omega * p$ remains localized in the IR range, while E_{p-d} is blue-shifted into the UV region due to reinforced electronic correlations. By an appropriate choice of bandwidth strategy, we have demonstrated that the transparency window of Calcium-doped SVO widens to cover the UV-VIS-NIR range when it satises to strong electronic correlation.
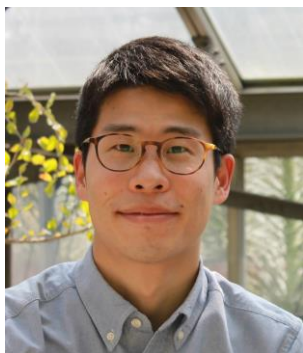
MOLECULAR CONTROL OF THE STEREOCHEMICAL ACTIVITY OF PB(II) LONE PAIR FOR DESIGNING ORGANIC-INORGANIC VALENCE BAND DISPERSIONS

D. Umeyama and S. Iimura

National Institute for Materials Science

umeyama.daiki@nims.go.jp

Controlling the lone-pair formation of post-transition metal ions with ns^2np^0 electronic configuration is an important issue as it influences various physical properties.[1] In this talk, we present a molecular method to control the stereochemical activity of Pb^{2+} lone pair in extended hybrid solids. While the science of the lone pair of these metal ions has been developed in the field of inorganic chemistry, we relied on a molecular approach to predetermine the coordination number of Pb^{2+} by properly designing the structure of organic anions, where nitrogen-based coordination sites are embedded in the five-membered ring of azolate anions. Using these molecular anions, we succeeded in limiting the coordination numbers of Pb^{2+} to be 4, 6, and 8. At the highest coordination number, the formation of lone pairs was almost completely suppressed, which is attributed to the preference of maximizing the interaction points by adopting the isotropic coordination environment. Different from inorganic lead chalcogenide (PbX; X = O, S),[2] most important bonding in lead azolates stems from the interaction between Pb orbitals and molecular orbitals of the anions, which are far from the frontier level. Briefly, this phenomenon stems from to the inherent complexity of the molecular anions. We will discuss how the energy level, symmetry, and topology of the molecular orbital anions dictate the interaction with Pb orbitals and govern overall band structures of the hybrid solids.
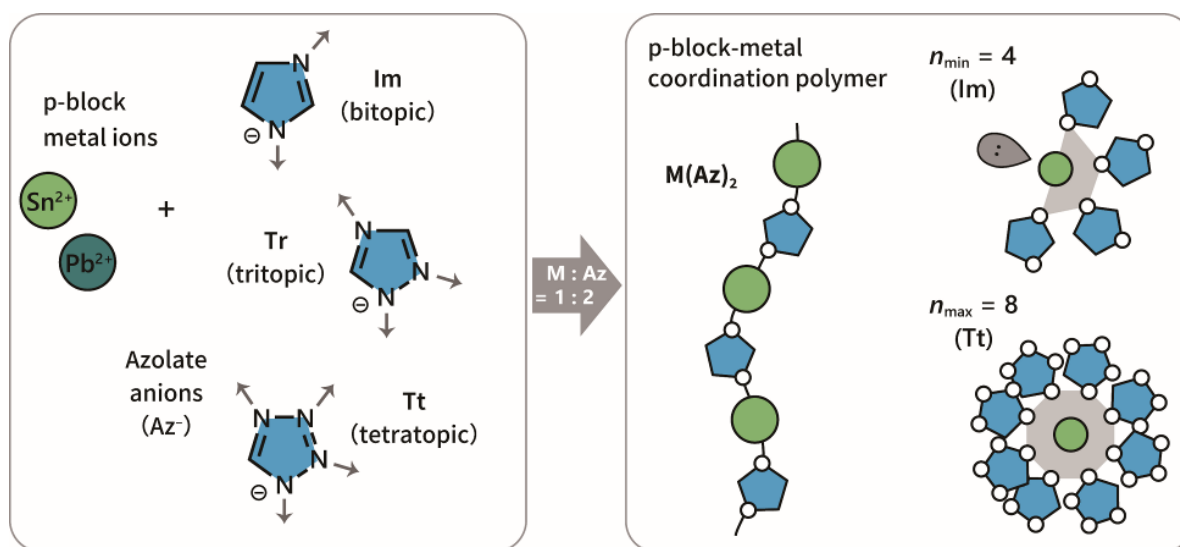
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# FABRICATION AND CHARACTERIZATION OF PORES: FROM NANO TO MACRO

Sadaki Samitsu[1,2]

[1] Data-driven Polymer Design Group, Research Center for Macromolecules and Biomaterials (RCMB), National Institute for Materials Science (NIMS)

[2] Faculty of Science and Engineering, Waseda University

SAMITSU.Sadaki@nims.go.jp

The introduction of pores imparts unique functions to materials. Porous structures impart physicochemical properties such as permeability, separation, and adsorption, in addition to mechanical properties such as light weight, improved deformation and toughness, and shock absorption. The size and shape of the porous structure, and whether the pores are interconnected or not, contribute significantly to its functionality. It is necessary to design porous structures that are optimal for the desired functionality and to realize the porous structure through advanced material processes. In order to optimize the fabrication process, it is necessary to visualize and evaluate the obtained porous structure not only in two dimensions but also in three dimensions, and to feed back the material characterization cycle to the process conditions of porous material fabrication. In this presentation, examples of nanoporous structure of cross-linked polymer-based reverse osmosis membrane for seawater desalination, nanoporous polymers fabricated by crystallization in polymer solutions, 3D microporous structure of polymer separation membrane, and polymer foam will be presented.
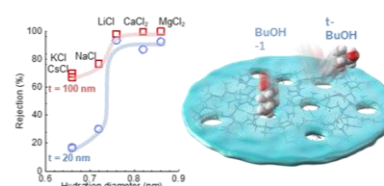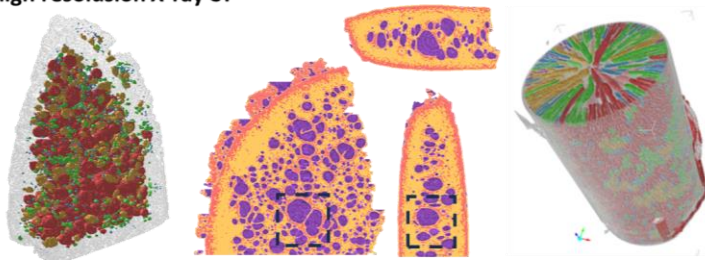
Fabrication of mesoporous polymers by flash freezing method
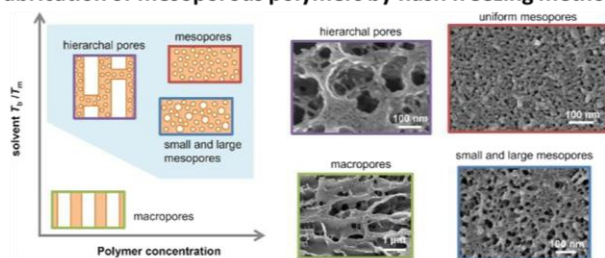
Crosslinked polymer-based reverse osmosis membranes and structural characterization
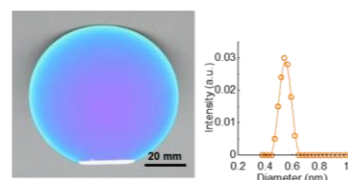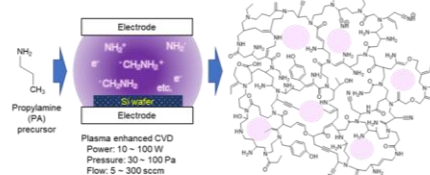
Macropore analysis of polymer foam and membranes by high resolution X-ray CT

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HYBRID CALIX[4]ARENE-PLATINUM NANOPARTICLES FOR RECONCILING ORR AND MOR ELECTROCATALYSES

C. Lagrost[1], Q. Lenne[1], Y. R. Leroux[1], I. Jabin[2], A. Mattiuzzi[3]

[1] *Univ Rennes, CNRS-ISCR UMR 6626, Campus de Beaulieu, F-35000 Rennes (France)*
[2] *Laboratoire de Chimie Organique, Université Libre de Bruxelles (ULB), CP 160/06, avenue F.D. Roosevelt 50, B-1050 Brussels (Belgium)*
[3] *X4C, 48 Auguste Piccard, B-6041 Gosselies (Belgium)*
corinne.lagrost@univ-rennes.fr

Catalytic materials are pivotal components for energy conversion devices that target small (and often highly stable) fuel molecules such as O_2, H_2O, CO_2, H_2 and MeOH. For ORR and MOR, Pt is still the best material but rare, expensive and easily poisoned in MOR process. A traditional strategy to boost the Pt electrocatalysts performance is the manipulation of size/shape of metallic nanomaterials or engineering of their topmost layers with foreign metals such as Ru. While being very efficient for MOR, this strategy is found poor for ORR, and besides Ru is also an expensive component.

Herein, we will describe a new design of electrocatalysts using a molecules@materials concept. The strategy is to keep the heterogeneous catalytic efficacy of Pt nanomaterials and to boost their performance, notably toward durability for both ORR and MOR processes through a deliberate surface functionalization of the nanoparticles[1]. The NPs are chemically modified with a well-organized covalently bound monolayer of calix[4]arene molecules[2]. The macrocycle provide a highly robust interface, able to control the interfacial reactivity at the molecular level and prone to enhance catalytic performance[3]. We will show that the carbon-supported hybrid calix[4]arene-Pt nanoparticles $Pt_{CF3}NPs/C$ exhibit better electrocatalytic performance as dual catalysts for both ORR and MOR compared with those of a commercial supported platinum ink (PtNPs/C)[4]. This new design leads to a highly versatile catalytic materials, bringing an original contribution toward the tuning of interfacial properties.
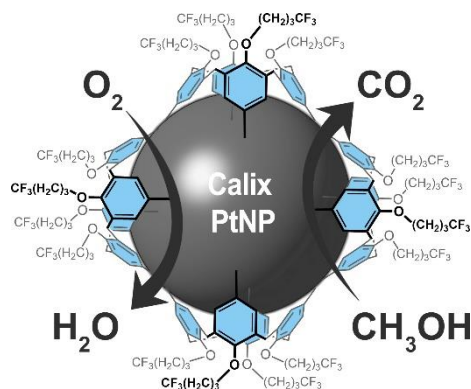
Schematic representation of $Pt_{CF3}NPs/C$ as a dual catalyst for ORR and MOR.

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USE OF AN IRON-DOPED COBALT-MOLYBDENUM-DITHIOOXAMIDE COMPLEX FOR ELECTROCATALYTIC WATER OXIDATION

Y. Sugahara and Y. Guo

Department of Applied Chemistry, Waseda University

ys6546@waseda .jp

Electrochemical water splitting is an important technology for producing clean energy from water, and it consists of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).[1] One of the important issues, however, is to reduce the electrical energy required for water splitting. In particular, for OER, which involves a kinetically sluggish four-electron transfer process, development of highly efficient electrocatalysts is required. Typical OER catalysts are RuO_2 and IrO_2, both of which are not sufficiently stable.[2] Thus, various studies have been reported for developing non-noble metal oxides and metal (oxy)hydroxides for OER, and also non-oxides such as metal chalcogenides, metal nitrides and metal phosphides for OER have been explored. In our work, we have prepared porous metal sulfide-based electrocatalysts by thermally decomposing a precursor containing cobalt, iron, dithiooxamide and phosphomolybdic acid, $H_3PMo_{12}O_{40}$, and by adding block polymers, pyrolyzed products exhibited high surface areas. By adding polystyrene-poly(acrylic acid) diblock copolymer, the resulting product exhibited mesoporosity, and demonstrated bifunctional catalytic activities for both HER and OER.[3] By adding polystyrene-poly(acrylic acid)-poly(ethylene oxide) triblock copolymer, a hollow bifunctional catalyst for both HER and OER was obtained.[4] On the other hand, the iron-doped precursor without pyrolysis could also work as an OER catalyst.[5] Co^{2+} ions formed complex with dithiooxamide, while Fe^{3+} ion did not interact with dithiooxamide. $H_3PMo_{12}O_{40}$ was likely to interact with dithiooxamide *via* an acid-base reaction. These interactions caused self-assembly of the starting compounds to form the precursor. The precursor was analyzed by X-ray photoelectron spectroscopy. Co was mainly present as Co^{3+} and a small amount of cobalt was in a divalent state. On the other hand, molybdenum was mainly in a hexavalent state with the presence of Mo^{5+} ions. In addition, the presence of iron and sulfur was also confirmed. The catalytic activity of the precursor was tested in a 1.0 M KOH aqueous solution. The overpotential (*vs*. RHE) required for a current density of 10 mA cm^{-2} was 294 mV for the precursor, which is very close to that of commercial RuO_2 (291 mV). Morphological change of the precursor under OER conditions was monitored by scanning electron microscopy. The morphology changed from original spherical shape. After 20 CV cycles, the nanorods formed, and growth of nanorods caused the collapse of the original spherical shape after 100 cycles. After 500 cycles, hexagonal nanoparticles were observed. The X-ray diffraction pattern of the sample after 500 cycles showed the formation of MoO_3, $CoMoO_x$, $Co(OH)_2$, and CoOOH. Thus, the precursor was converted into their corresponding oxide/hydroxide/(oxy)hydroxide mixture under the OER conditions.

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OUTSTANDING STRAIN-HARDENING OF A NEW METASTABLE BETA-TITANIUM ALLOY ELABORATED BY IN SITU ADDITIVE MANUFACTURING L-PBF PROCESS

H. Schaal[1], P. Castany[1] and T. Gloriant[1]

[1]*University of Rennes/INSA Rennes/Institut des Sciences Chimiques de Rennes, ISCR 6226*

Thierry.Gloriant@insa-rennes.fr

Metastable beta-titanium alloys are promising for biomedical applications, thanks to their low Young's modulus, preventing stress-shielding effect, and their excellent biocompatibility due to the use of non-toxic alloying elements for the stabilization of the beta phase, such as Ta, Nb, Zr.

Additive manufacturing, and especially the laser powder bed fusion (L-PBF) technique, is of great interest for the medical fields, because of the capability of the process to manufacture very complex parts, and therefore patient specific biomedical devices. However, elaboration of metastable beta-titanium alloys by L-PBF process is challenging due to the poor diversity of pre-alloyed powders available for sale, which are mainly commercial alloys (Ti-6Al-4V, CoCr alloys, stainless steels, superalloys…).

Consequently, we have investigated the manufacturing capability of the in situ technique, which promotes the manufacturing of parts with a blend of elemental powders instead of pre-alloyed powders, achieving alloying operation during the scanning of the laser beam [1].

We present in this communication recents results on a new Ti-22Zr-9Nb-2Sn (%at) alloy composition, which was successfully manufactured from a blend of elemental powders thanks to the in situ L-PBF technique. After a stress-relieved treatment at 700°C followed by a water quench, microstructure is composed of fully-beta restored columnar grains, with a strong <100> texture along the building direction. The mechanical characterization of the alloy was achieved through cyclic tensile tests. The stress-strain curve displays a very high strain-hardening, with an outstanding maximal strain-hardening rate of about 15 GPa, which is greatly higher than those commonly observed in literature for such alloys. Post mortem characterization by XRD, EBSD and TEM shows that the alloy undergoes a non-reversible stress-induced martensitic transformation during tensile test. As the stress-induced martensitic transformation triggers, the formation of new martensitic alpha'' laths is shown to be important, as their growth is limited. This important formation of new interphase boundaries hinders the dislocation slip and increase the strain-hardening rate [2].

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GAS SENSOR APPLICATIONS OF
SEMICONDUCTOR NANOPARTICLES

N. Saito
National Institute for Materials Science
saito.noriko@nims.go.jp

Highly sensitive and reliable gas sensors are useful for monitoring of air quality, detection of toxic gases and medical diagnosis. The advantages of semiconductor gas sensors are simple structure, low cost, rapid response and high sensitivity. Their ability to detect gases is based on the reversible change in the electrical conductivity induced by gas-surface interactions. When the sensor device is exposed to reduced gases, the gas molecules are oxidized by the oxygen ions adsorbed on the semiconductor surface and the electrons are released back into the conduction band, which increases the conductivity.

As an *n*-type semiconductor metal oxide, ZnO nanoparticle gas sensors were studied [1,2]. Isoprene gas, which is present in human breath at 0.02 to 1 ppm, is expected as a biomarker of physical condition due to sleepiness. When we controlled the ZnO crystal surfaces, we succeeded in detecting 0.01 ppm even under high humidity. We also showed that the loading of gold nanoparticles is effective for selective isoprene gas detection.

As a *p*-type semiconductor metal chalcogenide, WS_2 nanosheets gas sensors were studied [3,4]. Since doping into WS_2 is difficult by conventional ways, ion implantation was tried. We implanted trivalent Ru and pentavalent Sb in WS_2, where W is tetravalent. As a result, the Fermi level was controlled and Sb-implanted WS_2 shows *n*-type behavior. The ion implantation resulted in improving sensor response. Inplantation makes sulfur vacancies (Fig. 1), which act as oxygen adsorption sites in air, and the adsorbed oxygens react with the target gas. We succeeded in good repeatability through the repeated tests (Fig. 2).
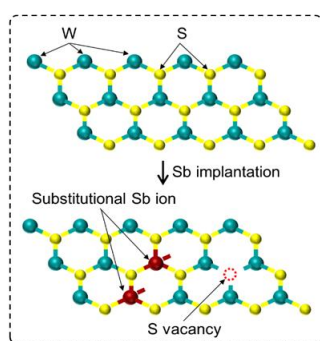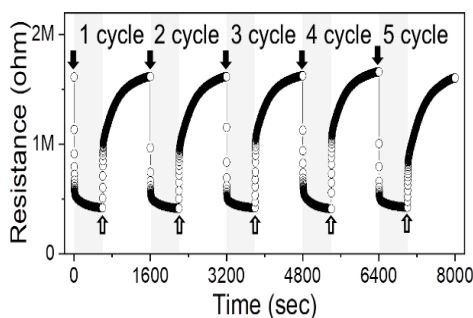

Fig. 1 Sulfur vacancies generated by ion-implantation.

Fig. 2 Repeatability of Au-decorated Sb-implanted WS_2 sensor to 50 ppm CO gas.

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CERAMIC POWDERS FOR HYDROGEN PRODUCTION THROUGH ALKALINE ELECTROLYSIS

M. Thibault and S. Marlin

Saint-Gobain Research Provence

Marielle.thibault@saint-gobain.com

Saint-Gobain is fully committed to the energy transition and aims to develop solutions to decarbonize industries. Among the various materials that play a crucial role in this transition, ceramics exhibit numerous advantages, such as chemical and mechanical stability in harsh environments and unique surface chemistry. ZirPro, a ceramic business of Saint-Gobain, is actively involved in energy transition through various products and applications, including the development of ceramic powders for hydrogen production via alkaline electrolysis (AEL). AEL involves the splitting of water molecules into H_2 and O_2 through thanks to electricity. The role of membranes that contain ceramic fillers is central in this process. The aim of this study is to improve our understanding of the role of fillers in membranes and develop the next generation of fillers.

HYDROGEN GAS SEPARATION OF ORGANIC–INORGANIC HYBRID SI-C MEMBRANES DERIVED FROM POLYCARBOSILANE

R. Mochida[1,2] and H. Segawa[1,2]

[1]NIMS, [2]Tokyo Institute of Technology
SEGAWA.Hiroyo@nims.go.jp

Hydrogen has garnered significant attention as a CO_2-free renewable energy source. In hydrogen production processes such as water electrolysis, it is essential to selectively separate hydrogen from other gases. As a method for hydrogen separation, membrane development has been actively pursued, with various materials under consideration. Particularly, organic-inorganic hybrid membranes containing hydrophobic organic functional groups have attracted attention [1]. This study focuses on the fabrication of hydrogen separation membranes using polycarbosilane (PCS), which exhibits hydrophobic properties. The membranes prepared under different heat treatment conditions were investigated in the gas separation performance. Additionally, the hydrophobicity was evaluated by permeating humidified gas. Since PCS membranes require formation on a porous support due to the difficulty in self-supporting, we also examined the formation process of the separation membrane, including the formation of a porous support.

Two types of silica particle solutions with different particle sizes were mixed at various volume ratios and subjected to vacuum filtration. After filtration, they were sintered and a silica particle solution containing PVA was dip-coated, resulting in porous supports after calcination. PCS was spin-coated onto the porous support and dried to fabricate the separation membrane. The resulting membranes were subjected to heat treatment at temperatures ranging from 200 to 400°C in air, nitrogen, and ammonia atmospheres. Permeation tests of H_2, He, and N_2 gases were conducted at room temperature for each sample. Permeation tests of humidified H_2 and N_2 gases were performed at 50°C.

The selectivity of the PCS membrane for H_2 improved in membranes subjected to heat treatment at 300°C in both air and ammonia atmospheres. Raman and XPS measurements suggested that in air atmosphere, cross-linking progressed due to the oxidation of Si-H, while in ammonia atmosphere, cross-linking progressed due to the dehydration of Si-OH by water and the cross-linking by N, thereby restricting the permeation of N_2 and improving selectivity of H_2. Results of permeation tests with humidified gas indicated the importance of avoiding oxygen incorporation during membrane fabrication to maintain hydrophobicity and improve permeability.

In summary, this study contributes to the ongoing advancements in hydrogen separation membrane technology, offering valuable insights into the optimization of PCS-based membranes for enhanced performance in diverse environmental conditions.

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GOING ON STRONG: MORE THAN A DECADE OF THERMOELECTRIC COLLABORATION BETWEEN NIMS AND CNRS/LINK

T. Mori[1,2], Je-F Halet[3], R. Gautier[3], M. Pasturel[3], D. Berthebaud[4]
1NIMS/MANA, 2U Tsukuba, 3U Rennes, 4Nantes U
MORI.Takao@nims.go.jp

Development of thermoelectric (TE) materials is important, for energy saving via waste heat power generation, and IoT power sources. For high TE performance, namely high figure of merit $ZT = S^2\sigma T/\kappa$ we must find ways to overcome the traditional tradeoffs between the properties, namely, between Seebeck coefficient S and electrical conductivity σ, and between the electrical and thermal conductivity κ [1].

For overcoming the first tradeoff, at NIMS we have found that magnetism can be utilized to enhance the Seebeck coefficient, and as a result, the overall power factor $PF = S^2\sigma$. Recent advancements in magnon drag, discovery of paramagnon drag, spin fluctuation, spin entropy, etc. For the latter aspect, in addition to various nanostructurings such as utilizing nanomicroporosity, intrinsic low κ mechanisms have also been demonstrated. Crystal structure derived mecahnisms, materials informatics approach, heterogeneous bonding from mixed anions, etc. Novel NIMS material rivalling the long-time champion bismuth telluride has also been recently developed.

Within the framework of our NIMS CNRS collaboration, we have developed successful strategies over the years to improve and optimize various thermoelectric materials.

This has led to >40 common papers in reputable international journals [2].

In the available time, I would like to describe several of these strategies. For example, particular doping into SnTe was discovered to lead to significant lattice softening. The thermal conductivity reduction effect was actually much larger than phonon scattering, and as a result, notable high ZT was achieved. Ways were found to manipulate the crystal field effect in GeTe leading to valence band convergence and a Seebeck coefficient enhancement. Various advancements have been made in abundant and relatively inexpensive materials like silicides; $FeSi_2$, $CrSi_2$, $MnSi_\gamma$, sulfides, and skutterudites, etc. From theoretical aspects, in general, the role that orbital interactions play on the power factor was investigated by applying sensitivity analysis to material science for the first time. In a further work, the high mobility in Bi alloyed Mg_3Sb_2 was indicated to be related to long-range p-orbital interactions.

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CARBODIIMIDES: ANOTHER CLASS OF N-CONTAINING INORGANIC MATERIALS

F. Cheviré, E. Leysour de Rohello, O. Merdrignac-Conanec, Y. Suffren
Univ Rennes, INSA Rennes, CNRS, ISCR – UMR 6226, F-35000, Rennes, France
francois.chevire@univ-rennes.fr

Over the last decade, inorganic carbodiimide materials with general formula $M_x(NCN)_y$ (M=alkali, alkaline-earth, rare-earth, transition metals or metalloids) have gained increasing attention due to their high thermal and chemical properties, and have been investigated for application as host materials for luminescence or negative electrodes for alkali-ion batteries. The $[N=C=N]^{2-}$ linear molecular ion can be seen as a nitrogen-containing pseudo-chalcogenide anion where bonding with the metal cations occurs through the nitrogen atoms. Indeed, $M_x(NCN)_y$ carbodiimides crystal structures are usually strongly related to well-known structures encountered in oxides or sulphides for example. The $[N=C=N]^{2-}$ group has an electronegativity value of 3.36 within those of N^{3-} and O^{2-}, 3.04 and 3.44, respectively, thus a lower nephelauxetic effect on activators *nd* states is expected compared to nitrides in regard to oxides hosts when Ce^{3+}, Eu^{2+} or Mn^{2+} doping. We have recently reported a simple and efficient synthetic route for the preparation of highly crystallized carbodiimides compounds in only one hour at moderate temperatures under NH_3 atmosphere using carbon nitride (C_3N_4) and oxygen-containing precursors (i.e. oxides, carbonates, oxalates) as starting materials. This talk will cover some of the recent results obtained in the lab when investigating the synthesis and optical properties of Ce^{3+} and/or Mn^{2+} doped alkaline-earth or rare-earth carbodiimides.

ADVANCED PHOSPHORS FOR LIGHTING AND DISPLAYS

T. Takeda
National Institute for Materials Science
TAKEDA.Takashi@nims.go.jp

Phosphor-converted light-emitting diodes (pc-LEDs) have replaced conventional cold cathode fluorescent lamps in lighting and display backlights. To improve the pc-LEDs performance and expand into new applications, new phosphors surpassing the current luminesence properties are required.

One is the narrowing the peak of the emission spectrum to improve the luminescent efficiency for solid-state lighting and expand the color gamut of displays. In the synthesis of phosphors, the luminescent center is added in the host crystal. The selection of the host crystal is most important. The luminesnce properties of phosphor are largely influenced by the local structure of the luminescent center consisting of center cation and surrounding anions. However, it is still difficult to accurately calculate the luminescence spectra of Eu^{2+} and Ce^{3+} phosphors. One of the efficient approaches is to use the crystal structures that have a similar local structure to that in a known narrow-band emitting phosphor.

We have developed the method to evaluate the (dis)similarity between local structures consisting of center cation and coordination anions using the Wasserstein distance.[1] Candidates for narrow band emitting phosphor extracted from the crystal structure database by the local structure similarity are experimentally examined. In the synthesis of complex compositions or structures, it is sometimes difficult to synthesize the candidate material as a single phase and the product is contaminated with impurity phases. In such a case, one particle of the candidate material is pick-uped from the mixture product and its crystal structure and luminescence properties are analyzed by single crystal XRD and microspectroscopy (single particle diagnosis approach).

An example of the phosphor is shown. As a reference of narrow-band emitting phosphor, the Ba-site in $BaSi_2O_2N_2$ was used. The K1 site of $K_2ZnP_2O_7$ was located near the Ba-site in $BaSi_2O_2N_2$ in the scatter plot using the t-SNE method. We synthesized $K_2ZnP_2O_7:Eu^{2+}$. As the product was contaminated by impurity phases, the $K_2ZnP_2O_7:Eu^{2+}$ particle was selected and characterized. $K_2ZnP_2O_7:Eu^{2+}$ particle showed a narrow-band emission at 440 nm with a full width at half maximum (FWHM) of 30 nm.[2]

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MICROSTRUCTURE AND ANISOTROPY ISSUES IN THE DEVELOPMENT OF NANOCRYSTALS WITH ORIGINAL OR OPTIMIZED OPTICAL PROPERTIES

T. Gacoin,[1] J.-M. Kim,[1] L. Daugas,[1] Y. Cheref,[1] J. Kim[1]

1CNRS – Ecole Polytechnique – Institut Polytechnique de Paris
91128 Palaiseau cedex, France

Thierry.gacoin@polytechnique.edu

Elaboration of colloidal nanocrystals has been a subject of intense research motivated by original properties emerging in the nanometer size range. In term of chemistry, main issues are related to the control of various parameters including particles crystallinity, size distribution, doping, surface functionalization, spatial organization… Improvement of elaboration processes as well as large extension of the available nanoparticles composition were obtained through a better understanding of elaboration mechanism, many of which deviating from classical nucleation/growth theory. In the last decade, our group has focused its research on the case of oxide nanocrystals with optical properties such as luminescence, plasmonics and photocatalysis. A special attention has been payed on properties associated to the particles microstructure and to the interplay between shape and crystalline anisotropy. This research will be illustrated in two specific cases. The first one concerns luminescent rare earth doped vanadates and phosphates. While microstructure issues are the basis of light emission efficiency and sensitivity to chemical environment, crystalline anisotropy leads to polarized light emission. These particles find interesting application in biolabelling, biosensors and biofluidics. The second case concerns plasmonic oxides derived from tungsten bronzes. These particles exhibit plasmonic properties that can be largely modulated by carrier doping, shape and crystalline anisotropy. The engineering of these particles will be presented toward their application as functional nanocomposite coatings suitable for solar NIR shielding in building windows.
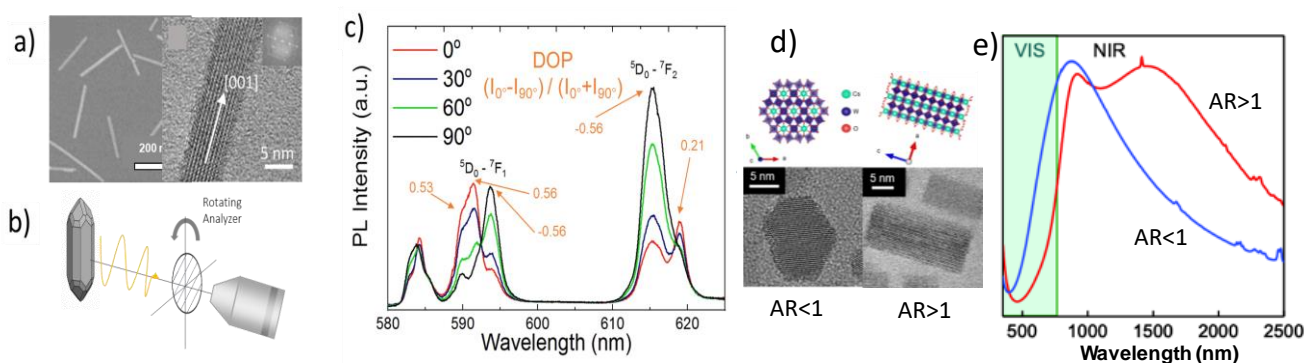
TEM image of LaPO$_4$:Eu nanorods (a), scheme of the polarized luminescence measurment (b) and polarized spectra under various analyzer angles with respect to the rod axis (c).
TEM image and associated cristalline orientation of Cs$_x$WO$_3$ nanoplatelets (left, AR<1) and nanorods (right, AR>1) (d); corresponding absorption spectra in the NIR showing the impact of the anisotropy.

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IONIC AND ELECTRONIC CONDUCTION IN
RARE-EARTH METAL OXYHYDRIDES

S. Iimura

National Institute for Materials Science
IIMURA.Soshi@nims.go.jp

Hydride ion (H^-) is a unique anionic species that exhibit high reactivity and chemical energy. H^- conductors are key materials to utilize advantages of H^- for applications, such as chemical reactors and energy storage systems. However, low H^- conductivity at room temperature (RT) in current H^- conductors limits the applications. Recently, we have reported a H^- conductivity of ~1 mS cm^{-1} at RT, which is higher by 3 orders of magnitude than that of the best conductor, in lightly oxygen-doped lanthanum hydride, $LaH_{3-2x}O_x$ with $x < 0.25$ [1] (Fig.1a). The oxygen concentration (x) is crucial in achieving fast H^- conduction near RT; the low activation barrier of 0.3–0.4 eV is attained for $x < 0.25$, above which it increases to 1.2–1.3 eV. Molecular dynamics simulations using neural-network potential successfully reproduced the observed activation energy, revealing the presence of mobile and immobile H^-. In this talk, in addition to the ionic conduction properties, the thin film device using the H^- conducting rare-earth oxyhydrides [2] (Fig.1b) as well as the unique electronic structure revealed by photoelectron spectroscopy [3] (Fig.1c) are also presented.
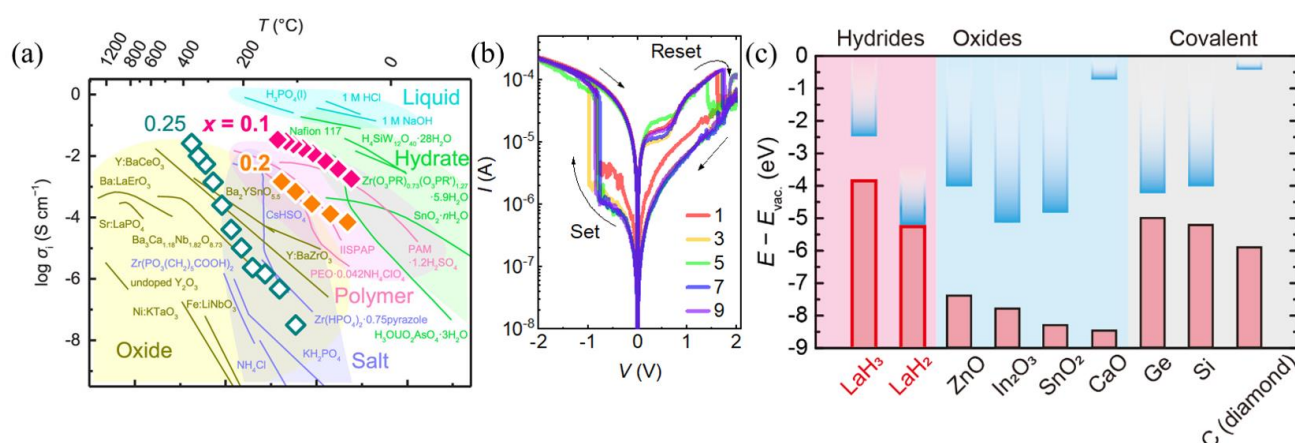

Figure 1:(a) Arrhenius plots of ionic conductivity (σ_i) in $LaH_{3-2x}O^x$ (diamond symbols) and representative H^+ electrolytes (solid lines): PAM = polyacrylamide, IISPAP = imidazole-intercalated sulfonated polyaromatic polymer, PEO = poly(ethylene oxide), $R = C_6H_4SO_3H$, R' = CH_2OH in $Zr(O_3PR)0.73(O_3PR')_{1.27} \cdot 5.9H_2O$. (b) *I–V* sweep curve of the $Ti/YH_{1.3}O_{0.85}/MoO_x$ device. (c) Band alignment of metal hydrides, oxides, and some covalent semiconductors.

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MICROSTRUCTURE CONTROL IN BULK CERAMICS BY EXTERNAL FIELDS

T.S. Suzuki and T. Uchikoshi
National Institute for Materials Science
suzuki.tohru@nims.go.jp

Microstructure control in ceramics is important and effective for improving their properties. We focus on crystallographic orientation as a parameter of microstructure control as well as grain size, grain boundary, second phase, etc. Since the agglomeration of particles forms large residual pores in green bodies using the conventional processing, elevated temperatures are necessary for densification. Colloidal processing is an effective technique for controlling the pore size distribution in green compacts before sintering, and a strong magnetic field can be used for controlling the orientation even in diamagnetic ceramics.

When a strong magnetic field is applied to the particles in a stable suspension, the particles were rotated to an angle minimizing the system energy by a magnetic torque generated from the interaction between the magnetic anisotropy and the applied magnetic field. In this processing, dispersion of powders in a suspension is necessary to effective work of a magnetic field, because large interaction between the agglomerated particles restrains the powder in a suspension from rotating by a magnetic field. Colloidal processing was used for particle dispersion because of developing for consolidating fine particles to avoid heterogeneous agglomerates by electrostatic repulsion due to surface charge.

In the case of Al_2O_3, SiC and $CrSi_2$, the c-axis of hexagonal crystal structure was aligned parallel to the magnetic field. The thermal conductivity perpendicular to the c-axis was superior to that parallel to the c-axis in textured SiC. A maximum ZT∥c-axis was consistent with values reported for a single crystal and represents a 50% improvement compared to untextured polycrystalline $CrSi_2$.

Electrophoretic deposition (EPD) is also effective technique for cotrolloing the miscortrucute in layered and functionally graded materials, thin films, high performance ceramic. The layered Al_2O_3 with alternative different orientation can be fabricated by EPD in a magnetic field and the residual stress is introduced due to the different coefficient of thermal expansion depnding on the crystal axes. The bending strengths were 1GPa more of the specimen with the compression residual stress in the bottom layer.
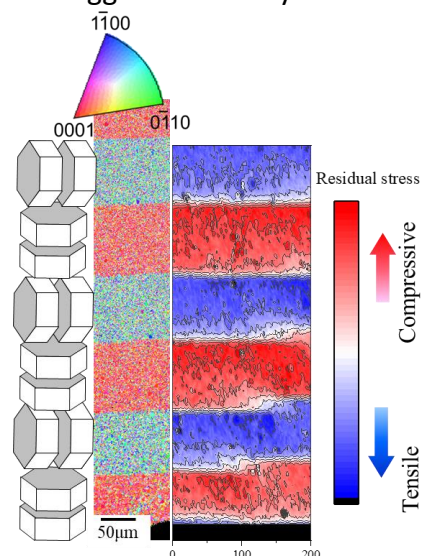

Figure 1 Crystal orientation analysis by EBSD and residual stress by Raman mapping.

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DESIGN OF NEW REFRACTORY ALLOYS FOR
MOLTEN GLASS PROCESSING

C. Condolf
*Saint-Gobain Research Paris*
Cyril.Condolf@saint-gobain.com

Computational thermochemistry is a powerful tool as it allows the theoretical exploration of the energetic behavior of multicomponent and multiphasic systems for a wide range of conditions at a small computational cost. It can be used for the simulation of processes and/or for material selections in extreme operation conditions.

In Saint-Gobain Research Paris this tool is used notably to optimize glass composition or to evaluate the corrosion of refractories in glass furnaces. New studies also concern the design of new refractory alloys for glass processing with an innovative approach.

This approach, recently developed in collaboration with NIMS, combines computational thermochemistry and active learning methods to propose potential promising compositions [1]. Preliminary results were obtained for some ternary Refractory High Entropy Alloys (RHEAs) and the methodology will be extended to higher order multicomponent systems.

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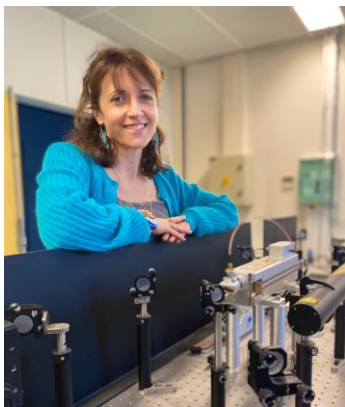
INFRARED PHOTONIC SENSORS BASED ONCHALCOGENIDE THIN FILMS FOR MONITORING OF WATER POLLUTANTS

V. Nazabal[1], R. Chahal[1], S. Meziani[2], A.Hammouti[2], M. Vrazel[1,4], R. Kadar Ismail[1,5], A. Benardais[1], C. Boussard-Pledel[1], L. Bodiou[2], J. Lemaitre[2], R. Courson[3], K. Boukerma[3], O. Fauvarque[3], P. Němec[4], W. Giraud[6], S. Le Floch[6], P. Michel[7], K. Michel[5], G. Maison[8], M. Carras[8], K. Milczarek[9], W. Kołkowski[9] and J. Charrier[2]

[1]*Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France,* [2]*Univ Rennes, CNRS, Institut FOTON - UMR 6082, F-22305 Lannion, France,* [3]*Ifremer, RDT, F-29280 Plouzané, France,* [4]*Department of Graphic Arts and Photophysics, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic,* [5] *BRGM, 45060 Orléans, France,* [6]*Cedre, CS 41836,29218 Brest, France,* [7]*SCIRPE, 69110 Sainte Foy les Lyon, France,* [8]*Mirsense, 1 Rue Jean Rostand, Campus Eiffel, 91400 Orsay, France,* [9]*Vigo, Poznańska Street 129/133, 05-850 Ożarów Mazowiecki, Poland*

virginie.nazabal@univ-rennes.fr

Chemical molecules in water place high demands on monitoring: high stability, sensitivity, multiplexing capabilities, wide detection range, compactness and short response time. The need for reliable, fast, multivariate, and cost-effective portable sensors continues to grow intensely. The sensor development for in situ detection of organic molecules in water using an optical method is a broad environmental challenge.

The implementation potential of MIR photonics is considerable, including for (bio)chemical sensors, environmental monitoring, security and medical diagnostics. Among the different classes of optical sensors, including conventional attenuated total reflectance, detection using the evanescent field is one of the possible ways to enable miniaturization of the sensor device with integration of mid-infrared photonic components and low-cost production.

Chalcogenide glasses have attracted attention for sensing applications due to their high transparency in the infrared range, their ability to be fabricated into thin films by PVD and to be processed into integrated photonic components by photolithography and etching.

We will present the development of a chalcogenide-based mid-infrared platform dedicated to mid-infrared spectroscopy using evanescent waves. The choice of the chalcogenide glass composition, the synthesis of chalcogenide films by RF magnetron sputtering, the structural, morphological, topographic and optical characterization of the thin films, the theoretical approach to define the analytical design of the evanescent optical field sensor for the detection of pollutants in water, the patterning of the films using photolithography and reactive ion etching, the optical losses and the surface functionalization by a hydrophobic polymer of the chalcogenide thin films will be described and discussed. This study represents an important step towards the development of an optical sensor in the MIR spectral range using chalcogenide materials for the detection of organic molecules in water.

PHASE SEPARATION IN GLASS THIN FILMS FOR SURFACE NANOSTRUCTURATION

B. Bouteille[1,2] D. Vandembroucq[2], J.-T. Fonné[1] and E. Gouillart[1]

[1]Surface du Verre et Interfaces, UMR 125, CNRS/Saint-Gobain
[2]PMMH, CNRS, ESPCI Paris, Université PSL, Sorbonne Université,
Université de Paris
barbara.bouteille@saint-gobain.com

This work aims at creating nanostructures which size can be controlled from a planar glass thin film of 100 nm deposited by reactive magnetron sputtering, thanks to phase separation phenomenon.

The model ternary system used is a barium borosilicate because its immiscibility domain is large. After demixing the barium rich phase has strong electronic contrast favorable for SEM imaging. Moreover, this less polymerized phase can be selectively dissolved to reveal nanostructures. Three different morphologies are finally obtained varying thin films composition: holes, pillars or interconnected roughness.

Image processing from SEM and AFM measurements allows quantitative measurements of characteristic lengths such as vertical and horizontal size and lateral correlations. Coarsening kinetics in ultra-confined media are studied for both mechanisms, nucleation and growth and spinodal decomposition [1].

Particularly, for droplets assembly with only one object into the thickness, confinement slows down diffusion. This impact is shown experimentally and numerically, it gives a power law slower than classical models [2].

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POSTERS

PEROVSKITE SOLAR CELLS WITH ADDITIVES
AND INTERFACIAL ENGINEERING

D. Heo
National Institute for Materials Science
HEO.doyeon@nims.go.jp

Technologies to increase the amount of power generation of new and renewable energy are being developed around the world, and among them, solar cells are attracting attention as a clean energy source. Monocrystalline or polycrystalline silicon solar cells made by melting silicon at a high temperature are commercially available and used. However, single-crystal silicon solar cells have high conversion efficiency and good durability but have the disadvantage of being expensive, and polycrystalline silicon solar cells are inexpensive but have somewhat lower efficiency. On the other hand, perovskite solar cells (PSCs), considered next-generation solar cells, can be made inexpensively through a solution process, unlike commercially available silicon solar cells, and can be made thin, light, and flexible. In addition, the perovskite solar cell is also used as an upper cell of a tandem cell bonded to a silicon solar cell (lower cell). The tandem cell exhibits a high-power generation efficiency that surpasses the theoretical limiting efficiency of the crystalline silicon cell even in a short research period. Since the single-cell efficiency of the upper cell, a perovskite solar cell, also affects the efficiency of a tandem cell, research to improve the efficiency of a single cell is important. Therefore, in this study, we present two approaches to improve the efficiency of perovskite solar cells; additives [1] and interfacial engineering [2].

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POLYMER-DERIVED CERAMICS (PDC) ROUTE TOWARDS ENCAPSULATED NON-NOBLE METAL NANOCATALYSTS FOR ALKALINE WATER ELECTROLYSIS

M. Ben Miled[1,2], A. Habrioux[2], O. Masson[1], S. Bernard[1]

[1]CNRS, IRCER, UMR 7315, Univ. Limoges, F87068 Limoges
[2]CNRS, IC2MP, UMR 7285, Univ. Poitiers, F86073 Poitiers
marwan.ben_miled@unilim.fr

Hydrogen is considered as a promising energy carrier to assure the needs of humanity. Its combustion in a fuel cell (FC) emits only water and does not involve any noise pollution. However, in order to be used inside a FC, H_2 needs to be at a very high level of purity, which can be achieved by using the water electrolysis process. This clean reaction only represents 4% of the actual method of H_2 production around the world. This process i) uses noble metal catalysts that are difficult to substitute in the Proton Exchange Membranes (PEM) technologies, ii) has limited electrical performance due to anode overpotential, inducing a sluggish kinetic because of a multiple electron transfer and several intermediates of reaction. The recent development of anion exchange membrane materials has led to the emergence of a new technology: the anion exchange membrane electrolyser. This device allows the use of non-noble transition metals in the composition of catalysts for hydrogen (HER) and oxygen (OER) evolution reactions in alkaline media. However, their nanoscale synthesis is highly challenging to limit the overpotential, particularly at the anode (OER).

The PDC (Polymer Derived Ceramics) route is a non-conventional way of designing ceramics by using pre-ceramic polymers as precursors. The coordination (or direct reaction) of these precursors with metal complexes via the functional groups and/or ligands of the polymer makes it possible to trap transition metal nanoparticles in a PDC matrix which plays the role of a support. It is important to keep in mind that pre-ceramic polymers display an intrinsic ability to form and maintain a micro- and mesopores range at low temperature pyrolysis, the resulting nanocomposites produced at low temperature are expected to : (i) display long-term stability due to stronger nanoparticle-matrix interaction and high corrosion resistance of the support in alkaline media; (ii) expose more active sites because of high porosity; (iii) avoid active sites aggregation during electrochemical process leading thereby to a constant catalytic activity; and (iv) have practical applicability. This poster discusses our recent works on the *in situ* growth of non-noble transition metal nanoparticles in an amorphous Si-C-N-O(H) ceramic network at very low temperatures (500°C). The large specific surface area of the materials associated with the nanometric size (20-50 nm) of the particles made it possible to boost OER performances, which suggests very promising prospects for the development of anion exchange membrane electrolysers [1]
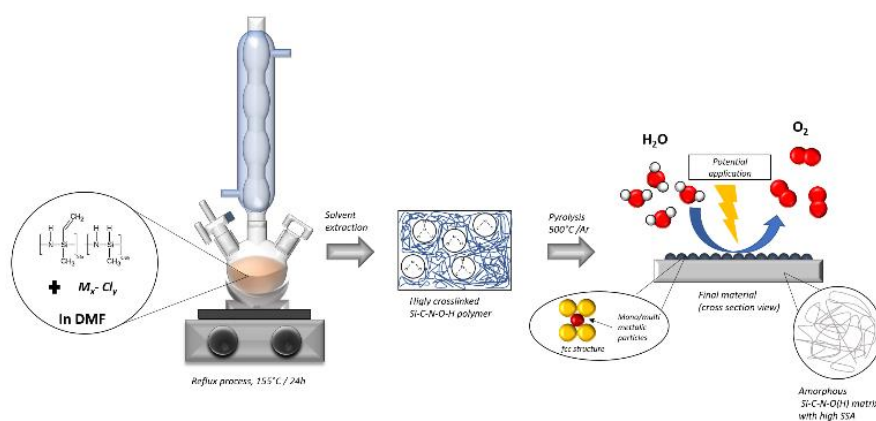
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INORGANIC ALL-SOLID SOLAR CELLS BASED ON OCTAHEDRAL MOLYBDENUM CLUSTERS

A. Le Gendre and A. Renaud
Université de Rennes/ISCR
antoine.le-gendre@univ-rennes.fr

Transition metal cluster-based halides are nano-objects that exhibit fascinating optical and electronic properties such as molecule-like energy gaps, strong absorption in the visible or deep red luminescence that make them promising light-harvester for solar energy conversion.[1,2] The integration of the molybdenum cluster iodides based on the $\{Mo_6I_8\}^{4+}$ cluster cores as light-harvester in photoelectrochemical solar cells and more recently in all solid solar cells demonstrated unambiguously the ambipolar character of such cluster-based layers. These ambipolar properties appears promising because the charge transfer is not limited by a charge carrier type. The challenge is now to design optimized solar cells by improving the charge transport and extraction. Two strategies are thus developed: a) the incorporation of clusters in a conductive polymeric matrix and b) the controlled condensation of clusters.

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PREDICTION AND DESCRIPTION OF MULTI-COMPONENT CENTERED CUBIC ALLOYS FOR HYDROGEN STORAGE

Z. Nefzi,[1,2] C. Barreteau,[1] L. Levrel,[1] and J.-C. Crivello[1,2]

1 Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France

2 CNRS-Saint-Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK), 1-1 Namiki, 305-0044 Tsukuba, Japan

Zeineb.nefzi@cnrs.fr

Hydrogen is a game-changer for clean energy, but we need better ways to store it safely.

High entropy alloys (HEAs) are of growing interest as materials for hydrogen storage due to their diverse and tunable properties [1].

In order to identify new relevant and appropriate hydride compositions among a large number of possible multi-component HEA solid solutions, our project is based on numerical calculation methods coupled with machine learning to screen these possibilities. For this purpose, a dataset of 18 elements has been carefully selected according to primary results and research findings, resulting in 185 possible systems. To ensure the smooth running of this project, several steps are required: first, the electronic structure calculations, in the frame of DFT, of all possible unary (M_1H) and binary (M_1M_2H) systems have been performed to start building a learning database. Then, for metallic bcc quinary alloys and their corresponding mono- and dihydrides (PtS and CaF2 structures), supercells are generated using the Special Quasi-random Structures (SQS) method.

To complete our database, some quinary SQS systems have been calculated by DFT to obtain the enthalpy of mixing and gather information about their stability. Given the large number of possible quinary systems and the size of each supercell (80 metal atoms), machine learning methods are then used to predict all the systems based on supervised statistical learning applied on our database.

The methodology is well defined. The supercells for metallic quinary systems as well as their corresponding hydrides have been designed, and DFT calculations on these supercells have been done for 440 selected systems. This subset of the 8568 possible quinary compositions provides sufficient data for our machine learning model to predict the outcomes for the remaining 8128.

We have built our supervised learning model by adding appropriate descriptors. It allows to predict the enthalpy of formation of equimolar HEAs with an accuracy of a few kJ/mol without resorting to DFT. Based on the prediction results, we have identified some promising high-entropy alloy systems for effective hydrogen storage. This innovative approach holds great promise for shaping the future of energy using hydrogen as a clean carrier.
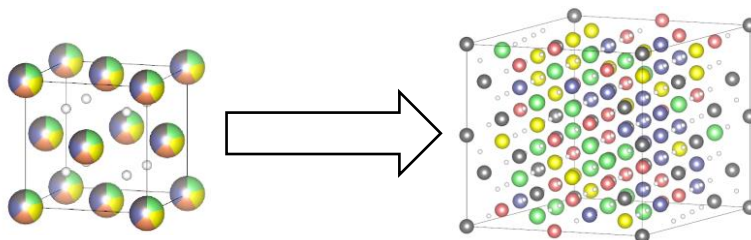

Figure 1. generation of the SQS cell of a quinary hydride (5 disordered metals + 2 hydrogen distributed)

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TRANSITION METAL NITRIDES SYNTHESES FROM METALLIC CLUSTERS: APPLICATIONS TO THE WATER-GAS SHIFT (WGS) REACTION

S. Mathivet[1], N. Dumait[1], H. Kaper[2], T. Uchikoshi[3], N. Ohashi[3], F. Grasset[3], S. Cordier[1], F. Tessier[1].

[1] Univ. Rennes, CNRS, Institut des Sciences Chimiques de Rennes – UMR 6226, F-35000 Rennes, France

[2] CNRS - Saint-Gobain Research Provence, LSFC– UMR 3080, F-84300 Cavaillon, France

[3] CNRS - Saint-Gobain – NIMS, Laboratory for Innovative Key Materials and Structures – IRL 3629, NIMS, 1-1 Namiki, Tsukuba 305-0044, Japan

sebastien.mathivet@univ-rennes.fr

The water gas-shift (WGS) reaction ($H_2O + CO \rightarrow CO_2 + H_2$) is used in non-stationary fuel cells to transform toxic carbon monoxide (CO) for the cell membrane into CO_2. In addition, it produces hydrogen (H_2) from water vapor, useful for the operation of the fuel cell. Currently, this reaction is catalyzed by noble metals, such as platinum. In recent years, there is a renewed interest in finding alternatives to the very expensive and rare noble metals listed as critical raw materials [1]. Several groups have studied the synthesis of new cost-efficient catalysts, among them transition metal nitrides [2].

We report the synthesis of Mo_2N and Mo_5N_6 from an original route using transition metal cluster-based precursors. [3] The resulting nitrides are characterized by several complementary techniques (XRD, BET, SEM, etc.) and TEM under NH_3 as an original structural contribution to the study of Mo_5N_6. This innovative synthesis produces nanostructured compounds that are evaluated as catalysts for the WGS reaction.

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SOFT PATHWAY FOR MOLYBDENUM CARBIDE AND NITRIDE SYNTHESES: APPLICATION TO THE HYDROGEN EVOLUTION REACTION (HER).

G. Dubois[1], C. Lagrost[1], N. Dumait[1], T. Uchikoshi[2], S. Cordier[1], F. Grasset[1,2], F. Tessier[1].

[1] *Univ. Rennes, CNRS, Institut des Sciences Chimiques de Rennes – UMR 6226, F-35000 Rennes, France*

[2] *LINK, IRL 3629 CNRS - Saint-Gobain - NIMS, NIMS, 1-1 Namiki, Tsukuba 305-0044, Japan*

guillaume.dubois@univ-rennes.fr

Transition metal carbides and nitrides show interesting properties in heterogeneous catalysis.[1,2] Several authors report the use of Mo_2C and Mo_2N to catalyse the Hydrogen Evolution Reaction (HER).[3,4] When synthesized by the urea route,[5] Mo_2C shows an electrocatalytic activity superior to that of other catalysts (Mo_2N, and MoB) in acidic and basic aqueous media, although still inferior to that of platinum.[6] Nevertheless, the use of Mo_2C carbide would be an alternative to platinum that would make the technology more economically viable.

Herein we report the synthesis of Mo_2C and Mo_5N_6 from an original route which consists to use transition metal cluster-based precursors.[7] The resulting carbides and nitrides are characterized by using several complementary techniques (XRD, S_{BET} measurement, SEM, etc...). This innovative mode of synthesis affords nanostructured compounds that were evaluated as catalysts for the HER reaction both in acidic and basic conditions (respectively H_2SO_4 0.5M and KOH 0.1M).

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IMPROVING VERY HIGH TEMPERATURE THERMOELECTRIC PERFORMANCE OF Yb$_4$Sb$_3$ THROUGH DUAL SUBSTITUTIONS: A THEORETICAL STUDY

V. Pelletier, [1] H. Bouteiller,[2] S. Le Tonquesse,[3] B. Fontaine,[1,4] D. Berthebaud,[5,8] F. Gascoin,[3] T. Mori,[6,7] J.-F. Halet,[1,8] R. Gautier[1]

[1] *Univ. Rennes, ENSCR, CNRS, ISCR UMR 6226, F-35000 Rennes, France*
[2] *Pprime Institute, CNRS, UPR 3346, F-86360 Chasseneuil-du-Poitou, France*
[3] *CRISMAT, ENSICAEN, UMR 6508, F-14000 Caen, France*
[4] *Saint-Cyr Coëtquidan Military Academy, CReC, F-56380 Guer, France*
[5] *Nantes Université, CNRS, IMN Jean Rouxel, Nantes F–44000, France*
[6] *Graduate School of Pure and Applied Sciences, University of Tsukuba, 305-8671, Tsukuba, Japan*
[7] *National Institute for Materials Science (NIMS), MANA, University of Tsukuba, 305-0044, Tsukuba, Japan*
[8] *LINK, IRL 3629 CNRS – Saint Gobain – NIMS, Tsukuba, Japan*

vincent.pelletier@ensc-rennes.fr / regis.gautier@ensc-rennes.fr

Thermoelectric materials with potential industrial applications at very high temperature, from 600°C to 1000°C and possibly higher, are needed to harvest waste heat and convert it into usable energy. This particular temperature range targets the steel, non-ferrous, ceramics and glass industries that use a lot of energy, 50% of which being lost during the production process.

Materials based on the cubic structure Th$_3$P$_4$ are good candidates for applications at such high temperatures. Indeed, in this family of intermetallics, *n*-type La$_3$Te$_{4-x}$ is already known as a good thermoelectric material with ZT superior to unity above 1000°C [1-2]. These compounds have been developed by NASA for the past 10 years or so and will be implemented in their next generation radioisotope thermoelectric generators. There is a need to develop a *p*-type counterpart of the same structure type, e.g., rare-earth antimonides crystallizing in the anti-Th$_3$P$_4$ structure, making it easier to fabricate *p-n* thermoelectric couples. However, there is only scarce information about the *p*-type counterparts, even if a few reports have shown very promising thermoelectric properties and stability at high temperature, with, for instance a ZT of 0.75 reported for La$_{0.5}$Yb$_{3.5}$Sb$_3$ at 1000°C [3].

With the development of powerful methods to compute the electronic band structure of solids and the increasing complexity of the formulations of advanced thermoelectric materials, quantum chemical calculations based on density functional theory (DFT) are helpful tools for the optimization of thermoelectric material properties. To gain further information in the electronic transport properties, Boltzmann transport theory can be combined with band structure calculations assuming a constant relaxation time.

Theoretical and experimental investigations were carried out in order to better understand the differences in the transport properties of La$_4$Sb$_3$ and Yb$_4$Sb$_3$, and to improve the thermoelectric performance of these antimonides by doping Yb$_4$Sb$_3$ with various rare-earth and/or group 15 atoms.

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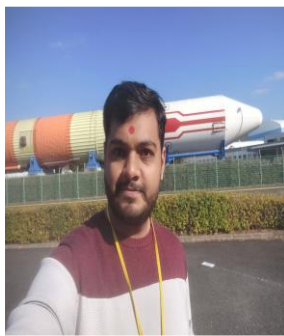
OPTIMIZATION OF THERMOELECTRIC PROPERTIES OF MISFIT LAYERED SULPHIDE $(LaS)_{1.14}(NbS_2)$ BY COMPOSITIONAL TUNING.

D. Parmar[1], C. Bourges[2], P. Deniard[1], O. Hernandez[1], C. Guillot-Deudon[1],
J.-C. Crivello[3], T. Mori[2,3], L. Cario[1], S. Jobic[1] and D. Berthebaud[1]

[1]*Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France.*
[2]*National Institute for Materials Science (NIMS), WPI-MANA, 1-1-1 Namiki, Tsukuba, 305-0044, Japan.*
[3]*CNRS-Saint-Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK), 1-1 Namiki, Tsukuba, 305-0044, Japan.*
divyesh.parmar@cnrs-imn.fr

Thermoelectric (TE) materials, which allow the conversion of heat into electricity, are promising candidates as one of the sustainable energy conversion technology. The conversion efficiency of the TE material as a function of temperature, known as the figure of merit ZT, depends on the Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ). In this work, we have optimized the thermoelectric performance of misfit layered sulfide, (LaS)1.14(NbS2), by tuning the composition of the system. The solid solution, (La1-xCexS)z(NbS2) " where x = 0, 0.1, 0.25, 0.5, " have been synthesized by sulfurization of a mixture of binary oxide under the flowing of H2S gas at high temperature (1000 °C) and later consolidated by Spark Plasma Sintering (SPS) process. The uniaxial load used during the sintering procedure induced a partial texturing of the natively anisotropic grain morphology of the misfit samples. Consequently, the TE properties have been measured in the perpendicular (in plane) and parallel (out-plane) direction to the pressing direction in order to confirm the texturing effect. The Seebeck coefficient and resistivity measurements showed a positive value indicating p-type semiconducting behaviour agreed with the hole as major charge carrier. Besides, the influence of the texturing has been highlighted through the high anisotropy in the electrical and thermal properties. In the in-plane direction, the increase in Ce concentration in the system yields lower lattice thermal conductivity in the system and the figure of merit (ZT) has been optimized from 0.102 (x = 0) to 0.133 (x = 1) at 773 K.

NOVEL INSIGHTS INTO COMPLEX HYDRIDES FROM GUIDED EVOLUTIONARY STRUCTURE PREDICTION

V. Baturin[1] and J.-C. Crivello[1,2]

[1]*ICMPE CNRS Thiais, France*

[2]*LINK CNRS Tsukuba Japan*

vladimir.baturin@cnrs.fr

One of the most well-studied families of complex hydrides, the borohydrides of alkaline earth metals, displays an impressive diversity of structures, some of which are extremely complex[1]. Given the significance of these and other complex hydrides (e.g., alanates, silanes, mixed anion hydrides) for hydrogen storage and other applications, a computational tool for designing such materials in silico is highly desirable. Existing crystal structure prediction (CSP) methods struggle to accomplish this, as the complexity increases exponentially with the number of degrees of freedom. For example, $Be(BH)_2$ contains over 200 atoms in the unit cell.

In this research, we address this problem by advancing the USPEX CSP algorithm[2] through the introduction of complex ions as building blocks. Specifically, we use well-known complex anions (BH_4, NH_4, SiH_4) and metal cations as elementary structural units. Additionally, to facilitate the discovery of possible reticular geometries, we propose a new method for generating candidate structures from Metal-Organic Framework (MOF) topologies.

Practically, this integrated strategy has predicted a number of complex hydrides as well as a novel two-dimensional polymorph in calcium borohydride. The layered morphology of this polymorph opens new possibilities for applications, particularly in hydrogen storage and catalysis. These findings underscore the potential of our approach, demonstrating its impact on the design of new materials.

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