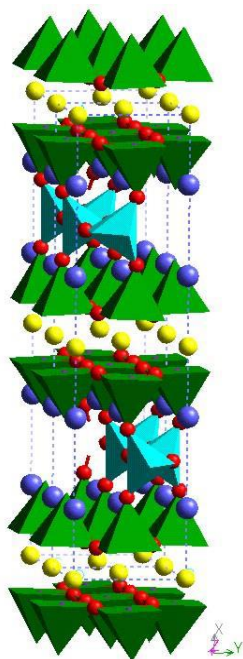


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6TH NATIONAL MEETING ON INORGANIC AND MATERIALS CHEMISTRY



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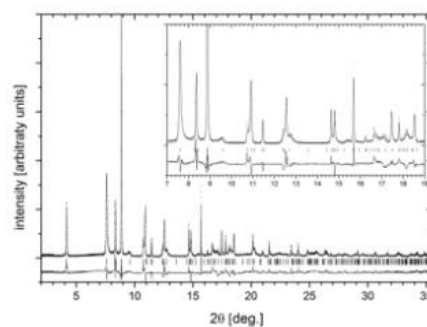
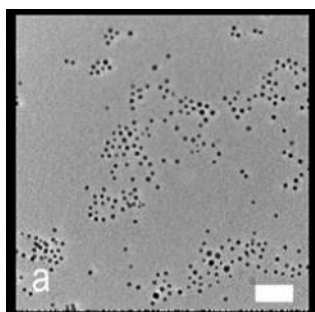
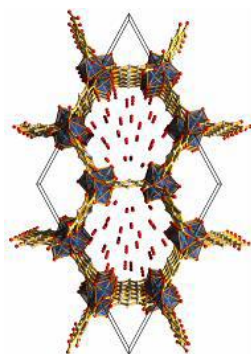
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2nd May 2017

6TH NATIONAL MEETING ON INORGANIC AND MATERIALS CHEMISTRY

10:00-10:45	Registration	
11:00-12:10	I Part of the meeting	
11:00-11:30	Truls Norby	"A complete model of protonic conduction in porous oxides"
11:30-11:50	Yang Hu	"Investigation of Li-Li(BH ₄) - Li ₂ S-P ₂ S ₅ system as solid electrolytes for all-solid-state Li-ion batteries"
11:50-12:10	Vegar Øygarden	"Synthesis of phase-pure τ -MnAlC using mechanical alloying and a single-step annealing route"
12:30-13:20	Lunch	
13:30-17:30	II Part of the meeting	
13:30-14:00	Santosh Pal	"Magnetocaloric Effect in Mn-based Intermetallic Compounds"
14:00-14:20	Antoine Dalod	"Simultaneous functionalization and controlled oriented attachment during hydrothermal synthesis of TiO ₂ nanoparticles"
14:20-14:40	Jian Zheng	"XPS and STM characterization of Pt(111) and PtRh/Pt(111) NH ₃ slip catalysts for NO _x abatement"
14:40-15:00	Abdel El Kharbachi	"Hydride Materials in All-Solid Li-Ion Cell Configuration"
15:00-15:20	Marit Norderhaug Getz	"Vibrational Defect Formation Entropy in Rutile and Anatase TiO ₂ by Ab-initio Phonon Calculations"
15:20-15:40	coffee- tea break	
15:40-16:00	Nils Wagner	"Optimisation studies of Li-ion batteries based on Si negative electrodes"
16:00-16:20	Andrey Bezrukov,	"Variation of network dimensionality and adsorption properties of metal-organic frameworks based on a series of phosphine containing linkers"
16:20-16:40	Mehdi Pishahang,	"Defect Chemistry in Grain Boundaries of Proton Conducting BaCeO ₃ "
16:40-17:00	Xin Liu	"Hydride migration in BaTiO ₃ -xH ₂ O oxyhydride"
17:00-17:30	Mari-Ann Einarsrud	"From aqueous solutions to oxide thin films and hierarchical structures"
17:30-19:00	Poster session (dinner follows at 20:00)	

6TH NATIONAL MEETING ON INORGANIC AND MATERIALS CHEMISTRY

3rd May 2017

I Part of the meeting	
09:00-12:00	
09:00-09:30	Per-Anders Hansen "Shining a new light on high efficiency solar cells"
09:30-09:50	Ragnar Strandbakke "Proton Ceramic Electrolyzers; operation, challenges and developments"
09:50-10:10	Federico Bianchini "First-principles study of structural stability and electro-chemical properties of Na ₂ M SiO ₄ (M = Mn, Fe, Co and Ni) polymorphs"
10:10-10:30	Didrik René Småbråten "A first principles study of charged domain walls in improper ferroelectric hexagonal YMnO ₃ , InMnO ₃ , and YGaO ₃ "
10:30-10:50	coffee- tea break
10:50-11:10	Matylda N. Guzik "Half-Heusler Phase Formation and Ni atom distribution in M-Ni-Sn (M = Hf, Ti, Zr) System"
11:10-11:30	Katherine Inzani "Electronic and optical properties of Cr-N Co-doped TiO ₂ for use as an Intermediate Band Material"
11:30-11:50	Tarjei Bondevik "Space charge layers in interfaces of BZY investigated by advanced microscopy, theoretical calculations, and electrical measurements"
12:00-12:50	Lunch
13:00-14:30	II Part of the meeting
13:00-13:30	Koji Amezawa "Electrode reaction path in mixed ionic and electronic conducting cathodes for solid oxide fuel cells"
13:30-13:50	Georgios Kalantzopoulos "Sub-unit cell structural transformations during template-removal and hydration of SAPO-37 microporous catalysts"
13:50-14:10	Anders Bank Blichfeld "Thermoelectric and Structural Study of Zinc-Antimony Thin Films Grown by Sputtering Deposition"
14:10-14:30	Mustafa Balci "Single Crystal Phosphors for High-Power Lightning and Display Technologies"
14:30-14:50	Summing up; venue for next meeting
14:50-15:30	FUM-NKS; Inorganic Chemistry group at NKS; general assembly
15:30-	End of the meeting. Departure
Legend	5 key note lectures (25 min + 5 min) 19 general talks (15 min + 5 min)

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A complete model of protonic conduction in porous oxides

Sindre. Ø. Stub,¹ Einar Vøllestad,¹ Per Martin Rørvik,² Truls Norby,^{1*}

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Many oxides dissolve interstitial protons in the form of hydroxide groups in the presence of water vapour even at elevated temperatures. This gives rise to proton conduction by jumps of free protons between the oxide ions hosts. In certain cases this can be dominating and used as proton ceramic electrolytes for fuel cells, electrolyzers, hydrogen pumps.

At lower temperatures, water starts also to adsorb on external and internal surfaces, and eventually – at high relative humidities – gives rise to considerable protonic conduction in sufficiently porous oxides. The physics and chemistry behind this has however not been well understood. In the NaProCs projects we have explored this over the last years, and reached a general model for the conductivity behaviour over a large range of conditions (high to low temperatures, dry to wet conditions, different oxides, AC or DC frequency). This is now being published,¹⁻⁴ and the main findings are summarised in the present contribution.

At intermediate temperatures, surfaces are easily covered by a layer of chemisorbed water, and the conductivity in porous ceramics gets a protonic contribution, resulting from jumps of protons between terminating -O^{2-} , -OH^- , and -OH_2 groups. The activation energy consists of defect formation and mobility, and makes the conductivity decrease with decreasing temperature, varying with the chemical properties of the surface of the oxide.⁴

As the relative humidity increases by decreasing temperature, the water layer starts to increase beyond the first layer, entering into the region called physisorption, where water molecules are bonded mainly by van der Waals hydrogen bonding forces. This decreases the enthalpy of dissociation (defect formation) and mobility, and increases the thickness of the layer, causing the conductivity to start to increase with decreasing temperature.^{1,4}

At about 60% relative humidity, the water layer is thick enough to change from being “ice-like” to being “water-like”, causing a shift in dissociation and mobility parameters. Eventually, most oxides show similar area-specific protonic conductivities. EMF-type transport-number and isotope shift studies show that the conduction mechanism changes from free proton H^+ Grotthuss-type at high temperatures and chemisorbed or “ice-like” physisorbed water, to vehicle-type H_3O^+ in “water-like physisorbed water”.³

Impedance spectroscopy shows two time constants (two different capacitances) in protonic surface conduction, as also indicated for proton diffusion by NMR in zeolites and MOFs, allowing for the first time to attribute this to the space charge of grain boundaries intersecting the surfaces of the ceramic.²

Acknowledgement: This work has been supported by the Research Council of Norway (RCN) through the RENERGI NaProCs (216039) project.

¹ S.Ø. Stub, E. Vøllestad, P.M. Rørvik, T. Norby, “On the interaction of grain boundaries and protonic surface transport in porous oxides”, to be submitted.

² S.Ø. Stub, E. Vøllestad, T. Norby, “Protonic surface conduction controlled by space charge of intersecting grain boundaries in porous ceramics”, submitted.

³ S.Ø. Stub, E. Vøllestad, T. Norby, “Protonic surface transport mechanism in porous oxides”, submitted.

⁴ S.Ø. Stub, K. Thorshaug, P.M. Rørvik, E. Vøllestad, T. Norby, “Influence of acceptor and donor doping on protonic surface conduction of TiO_2 ”, to be submitted.

Magnetocaloric Effect in Mn-based Intermetallic Compounds

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Abstract: Serious environmental consequences of the traditional vapor-compression cooling techniques have turned the research efforts towards development of alternative cooling techniques, and the search for materials showing large caloric effect. Magnetic cooling technology is a rapidly growing technology with a potential of becoming more economic, energy efficient and environmental friendly cooling technology. The search of new or improving the existing magnetic materials exhibiting large magnetocaloric effect near room temperature but with the use of none or negligibly small amount of critical/toxic elements is a field of intense research for magnetic cooling technology.

The magnetocaloric effect of a material can be significantly improved by combining the lattice degree of freedom with the magnetic one. This produces a first-order magnetostructural transition which in turn leads to a gigantic magnetocaloric effect. Intermetallic alloy MnCoGe is an interesting compound which experiences a martensitic structural transformation and a magnetic transition separated by around 100 K. Both of the transitions can be tuned *via* physical and/or chemical pressure which can lead to a magnetostructural coupling resulting in a first-order transition and thus a giant magnetocaloric effect.

In this presentation, the magnetostructural coupling and giant magnetocaloric effect *via* tuning of the structural and magnetic transitions of MnCoGe compound through partial substitution of Co and Mn by Cu will be discussed. A giant maximum isothermal entropy change of $\sim 40 \text{ J Kg}^{-1} \text{ K}^{-1}$ (for $\Delta H = 5 \text{ T}$) has been obtained for 10 at.% Mn substitution by Cu. The Mn-substituted samples show a normal paramagnetic to ferromagnetic transitions. Interestingly, in addition to paramagnetic to ferromagnetic transitions, the Co-substituted samples show ferromagnetic to antiferromagnetic (FM to AFM) and then AFM to FM transitions with decreasing the temperature. The presence of antiferromagnetic phase and complex magnetic transitions can be possibly due to the varying Mn-Mn distances during the martensitic transition. A comparative study of the Mn- and Co-substituted samples and a correlation of the magnetic and structural properties will be presented and discussed.

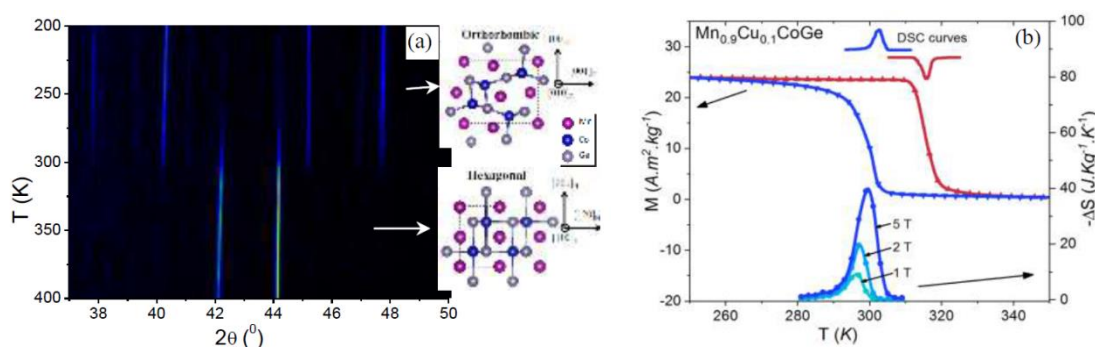


Fig. 1 (a) XRD contour plot showing the martensitic structural transformation at around 300 K and (b) magnetization (M), entropy change ($-\Delta S$) vs temperature (T) and DSC curves for Mn_{0.9}Cu_{0.1}CoGe sample.

References:

1. K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Tsokol, Recent developments in magnetocaloric materials, Rep. Prog. Phys. 68 (2005) 1479.
2. V. Johnson, Diffusionless Orthorhombic to Hexagonal Transitions in Ternary Silicides and Germanides, Inorganic chemistry 14 (1975) 1117.
3. F. Guillou, F. Wilhelm, O. Tegus, *et al.*, Microscopic mechanism of the giant magnetocaloric effect in MnCoGe alloys probed by XMCD, Appl. Phys. Lett. 108 (2016) 122405.
4. K. Koyama, M. Sakai, T. Kanomata, K. Watanabe, Field-Induced Martensitic Transformation in New Ferromagnetic Shape Memory Compound Mn_{1.07}Co_{0.92}Ge, Jpn. J. Appl. Phys. 43 (2004) 8036.
5. D. Choudhury, T. Suzuki, Y. Tokura and Y. Taguchi, Tuning structural instability toward enhanced magnetocaloric effect around room temperature in MnCo_{1-x}Zn_xGe, Scientific reports 4 (2014) 7544.

From aqueous solutions to oxide thin films and hierarcical structures

Mari-Ann Einarsrud, Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology

Nanoscale engineering is a fascinating research field spawning extraordinary materials possessing at least one dimension in the nm range, which revolutionizes microelectronics, medicine as well as energy production and utilization. Reproducible and robust fabrication of these nanoscale materials in an environmental friendly and cheap way is challenging and needs to be realized in order to fully exploit the potential of these materials. In a recently started Toppforsk project, we aim to develop an aqueous synthesis platform for thin films and hierarchical structures based on an *in situ* characterization toolbox, which combined with theoretical principles and models, will enable precise control of nucleation and growth of the oxide nanomaterials and replace current empirical approaches. Aqueous chemical synthesis methods are environmental friendly and highly flexible routes to tailored nanostructures and will serve as the basis for this project focusing on lead-free piezo- and ferroelectric materials. The knowledge emerging from the project will be the basis for providing general guidelines for the reproducible fabrication of nanostructured materials and thin films, in addition to give generic guidelines for the design of novel lead-free piezo- and ferroelectric oxide materials. Here we will give a presentation of the project and present the first data on using *in situ* X-ray diffraction techniques to reveal information about nucleation and growth of nanostructures with different structures like lead-free piezoelectrics, AgCuO_2 and TiO_2 . In the figure below, we can see how an *in situ* X-ray diffraction technique can reveal the formation of several very short-lived intermediate phases during the hydrothermal formation of NaNbO_3 .

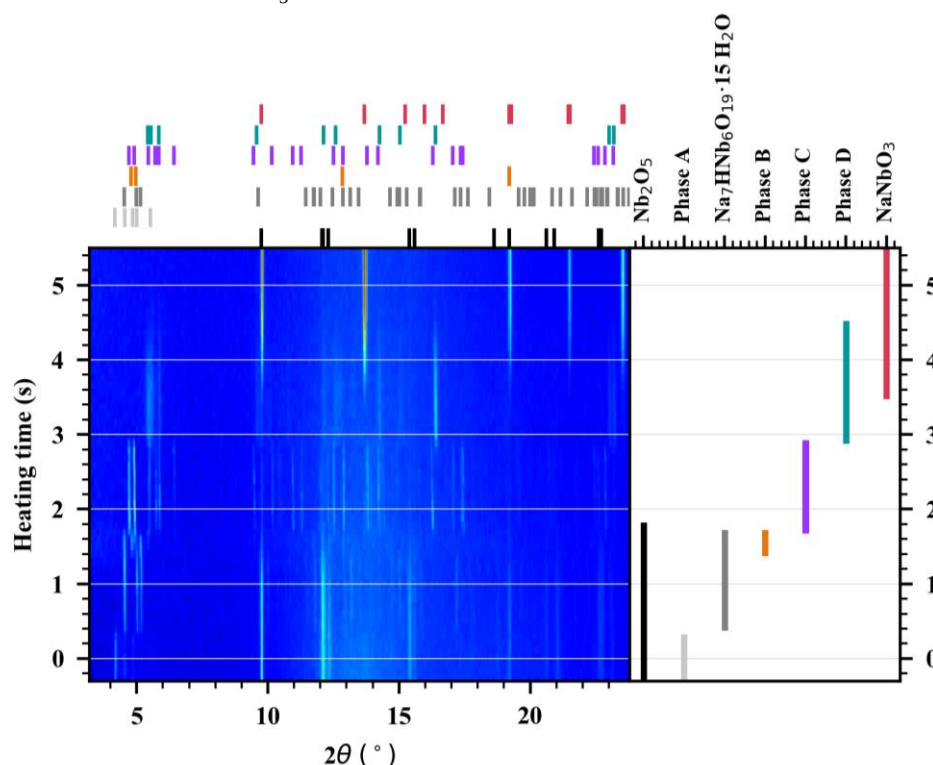


Figure. 2D X-ray contour plot of the fast evolution of phases in the Na-Nb-O system during hydrothermal synthesis at 423 °C and 250 bar including a schematics showing the phase development (S. Skjærvø et al.).

Shining a new light on high efficiency solar cells

Per-Anders Hansen, Nafuma, Department of Chemistry, UiO

Around a decade ago, Nafuma took its first steps into the field of luminescent materials. Today, our work has grown counting several PhD's, international collaboration, a major grant and participation in two FME centers on solar cell technologies. Our major focus is to use luminescence to increase the efficiency of silicon solar cells, mainly through down conversion where a UV photon is split into two NIR photons.

Having the potential to double the quantum efficiency of solar cells in the UV/blue range, this has been investigated for many years now, in particular after close to 200 % luminescence efficiency was discovered in $\text{LiGdF}_4:\text{Eu}^{3+}$. In order to obtain efficient down conversion, 3 parts must be solved: (1) Strong absorption of UV/blue light, (2) Efficient splitting of one photon into two excited states, (3) emission at around 900-1000 nm. Several groups around the world have managed to combine 2 of these in different ways, but combining all 3 is still elusive.

In this talk, I will explain how the competences and infrastructures at Nafuma gives a unique angle for combining all 3 parts into an efficient material that down converts solar UV for solar cells.

References:

1. R. T. Wegh, H. Donker, K. D. Oskam and A. Meijerink, *J. Lumin.*, **1999**, **82**, 93-104.

Electrode reaction path in mixed ionic and electronic conducting cathodes for solid oxide fuel cells

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Mixed ionic and electronic conducting (MIEC) oxides, such as $(\text{La,Sr})\text{CoO}_{3-\delta}$ and $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$, are typically used as the cathode materials for solid oxide fuel cells (SOFCs). In an MIEC SOFC cathode, it is believed that the electrode reaction, *i.e.* electrochemical reduction of oxygen gas, takes place on the oxide surfaces (gas/electrode interface, double phase boundary, DPB) and the contribution of the reaction at the electrode/electrolyte/gas interface (triple phase boundary, TPB) is insignificant. Most of investigations on the electrode kinetics for an MIEC SOFC cathode, therefore, concerns the surface reaction on the electrode. However, the contribution of TPB reaction to the total electrode reaction is not clearly understood yet.

For the quantitative evaluation of the contribution of TPB reaction, in this work, we proposed to use patterned thin film electrodes as model electrodes. The schematic illustration of the proposed electrodes is given in Fig.1. The patterned thin film electrodes are kinds of a columnar electrode simplifying the microstructures of a porous electrode. We fabricated patterned thin film electrodes with or without TPBs, as shown in Fig. 1(A) and (B), respectively, by helps of lithographic techniques. Electrochemical measurements, such as DC polarization and electrochemical impedance spectroscopy, were performed with the prepared model electrodes to evaluate the contribution of TPB reaction distinctively from that of DPB reaction. *Operando* micro X-ray absorption spectroscopy was applied to directly observe how the reaction distribution depends on the presence of TPB. It was demonstrated that the reaction at TPBs significantly contributes to the SOFC cathodic reaction even on an electrode having mixed ionic and electronic conduction.

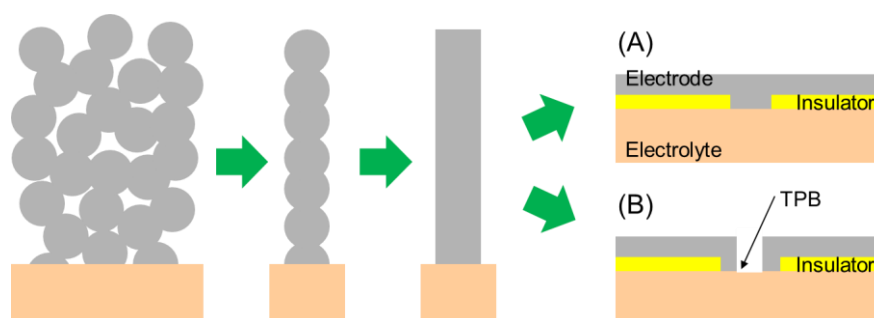


Fig. 1. Schematic illustration of the patterned thin film electrodes: (A) without and (B) with triple phase boundary.

Investigation of LiI-Li(BH₄) - Li₂S-P₂S₅ system as solid electrolytes for all-solid-state Li-ion batteries

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The development of all-solid-state batteries lies on the exploration of suitable solid electrolytes which can provide adequate Li-ion conductivities as well as good chemical/electrochemical stability. Among the bulk-type solid electrolytes, several glassy sulfides have been reported to exhibit room-temperature conductivities which are comparable to those of conventional aqueous-based/organic electrolytes ($\sim 10^{-3} \text{ Scm}^{-1}$). In order to compromise their stability issues ^[1], lithium halides has been introduced as additives to improve the ionic conductivities and contacting at electrode/electrolyte interface ^[2]. Recently, considerable scientific interests haven been drawn to hydride materials, including LiBH₄-Li₂S-P₂S₅ system ^[3,4] and high-*T* stabilized Li(BH₄)_{0.75}I_{0.25} ^[5] towards the potentials for solid electrolytes due to their interesting ionic properties, good thermal and structural stability and stable electrolyte/electrode interface.

The current work is aiming to combine these two aforementioned systems by embedding Li(BH₄)_{0.75}I_{0.25} in a 0.75Li₂S·0.25P₂S₅ amorphous matrix to form composite electrolytes using different preparation methods. The ionic conductivity was characterized by impedance spectroscopy from room temperature to above 100 °C. An enhancement of conductivity was achieved with the compositional variation, and one composition with the best room-temperature conductivity (close to 10^{-3} Scm^{-1}) was chosen for further battery tests. The chemical/electrochemical stability was investigated by cyclic voltammetry. Galvanotactic cycling was performed on half-cell using Li and TiS₂ electrodes. The Li/electrolyte and electrolyte/TiS₂ interfaces after cycling at different charge states were examined by XRD to investigate the structural changes, interface stability and the fading mechanism.

Acknowledgements

This work is financially supported by Research Council of Norway under the program EnergiX via the Project no. 244054, LiMBAT - "Metal hydrides for Li-ion battery anodes". We acknowledge use of the Norwegian national infrastructure for X-ray diffraction and Scattering (RECX).

References

- [1] M. Tatsumisago, S. Hama, A. Hayashi, H. Morimoto, T. Minami, *Solid State Ionics* **154–155** (2002) 635.
- [2] S. Ujiie, A. Hayashi, M. Tatsumisago, *Solid State Ionics* **211** (2012) 42.
- [3] A. Yamauchi, A. Sakuda, A. Hayashi, M. Tatsumisago, *Journal of Power Sources* **244** (2013) 707.
- [4] A. Unemoto, H. Wu, T.J. Udovic, M. Matsuo, T. Ikeshoji, S.-i. Orimo, *Chemical Communications* **52** (2016) (3) 564.
- [5] R. Miyazaki, T. Karahashi, N. Kumatani, Y. Noda, M. Ando, H. Takamura, M. Matsuo, S. Orimo, H. Maekawa, *Solid State Ionics* **192** (2011) (1) 143.

Synthesis of phase-pure τ -MnAlC using mechanical alloying and a single-step annealing route

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ABSTRACT

Permanent magnets (PMs) play an important role in the continuous technological development of the modern world.¹ Rare-earth (RE) magnets, such as Nd₂Fe₁₄B with an energy density $(BH)_{max}$ up to 59.1 MGOe (470 kJ m⁻³), are used for applications where high magnetic energy-density values are needed.² For applications where lower energy-density suffice, ferrites such as (Sr,Ba)Fe₁₂O₁₉, dominate the market with an energy density $(BH)_{max}$ up to 5.0 MGOe (40 kJ m⁻³).³

The rising cost and exposed supply-chain of rare-earth magnets have spawned a global search for rare-earth free alternatives that are able to plug the gap between the rare-earth based and ferrite-based permanent magnets that currently dominate the market. τ -MnAlC has long been investigated as a promising candidate due to its high potential energy density, low weight, and readily available resources, but development has been slowed down by challenging synthesis conditions and issues with phase purity.

This study presents a simplified, up-scalable and reliable synthesis-route to produce 100 % phase-pure τ -MnAlC, using mechanical alloying combined with a single annealing step. The resulting synthesis-route is of high interest to the permanent magnet community as a streamlined and repeatable route to phase-pure τ -MnAlC, avoiding needs for more complicated synthesis techniques such as drop synthesis, melt spinning and induction melting. The importance of the cooling rate of the annealing step is highlighted and discussed in detail. Rietveld-refinements of synchrotron x-ray and neutron diffraction data is used to demonstrate the phase-purity, as well as the magnetic structure and the magnetic moments of the Mn-site. We also provide a description of the magnetic properties of the phase-pure τ -MnAlC which showed promising magnetization and energy product. Finally, the stabilizing role of interstitial carbon is discussed.

REFERENCES

- ¹ O. Gutfleisch, M. A. Willard, E. Bruck, C. H. Chen, S. G. Sankar, and J. P. Liu, Adv. Mater. **23** (7), 821 (2011).
- ² J.F. Herbst, Rev Mod Phys **63** (4), 819 (1991).
- ³ J. M. D. Coey, J Phys-Condens Mat **26** (6) (2014).

Simultaneous functionalization and controlled oriented attachment during hydrothermal synthesis of TiO₂ nanoparticles

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Control of the particle size, morphology, and crystallinity (including the phase) of titanium dioxide (TiO₂) has attracted a lot of interest with respect to more efficient materials dedicated to applications such as photocatalysis, solar cells, lithium ion batteries, or in the biomedical field [1-2]. Surface functionalization of TiO₂ nanoparticles can bring additional properties to new applications such as biosensors and diagnostics [3], and better dispersibility in organic solvent and polymer, in the aim of synthesizing polymer nanocomposites, but it has the disadvantage to be mainly a multistep process [4].

We recently reported an *in situ* hydrothermal synthesis route to surface functionalized TiO₂ nanoparticles using selected silane coupling agents; a synthesis leading to [001] oriented rod-like nanostructures, in addition to spherical nanoparticles, when performed with aminosilanes [5].

Here, we describe the growth mechanism and the effect of hydrothermal synthesis parameters (pH, time and precursor/functionalization agent ratio) during *in situ* functionalization of anatase TiO₂ nanoparticles with 3-aminopropyltriethoxysilane. Elongated crystallographically oriented TiO₂ nanoparticles were formed by oriented attachment mechanism. The growth mechanism was determined by a combination of *ex situ* techniques such as high-resolution transmission electron microscopy combined with *in situ* synchrotron X-ray diffraction and density functional theory calculations. Oriented attachment induced by the aminosilane agent was shown to be the origin of the elongation of the nanoparticles, as only spherical nanoparticles were formed in the absence of surface functionalization or with decyltriethoxysilane. Finally, it was shown that the amount and the size of the elongated nanoparticles can be tuned by adjusting pH.

- [1] Liu, G. *et al.*, *Chem. Rev.*, **114** (2014) 9559–9612.
- [2] Zhang, Y. *et al.*, *RSC Adv.*, **5** (2015) 79479–79510.
- [3] Zhuo, Y. *et al.*, *Biosens. Bioelectron.*, **26** (2011) 3838–3844.
- [4] Kango, S., *et al.*, *Prog. Polym. Sci.*, **38** (2013) 1232–1261.
- [5] Dalod, A.R.M. *et al.*, *Beilstein J. Nanotechnol.*, **8** (2017) 304–312.

XPS and STM characterization of Pt(111) and PtRh/Pt(111)***NH₃ slip catalysts for NO_x abatement***

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Abstract

In this presentation, we describe the role of converter catalyst in the auto vehicle and the performance of PtRh on the selective catalytic oxidation (SCO). To investigate the function of Rh in the PtRh catalyst, a Rh deposited Pt(111) were used to model the catalyst and characterized with scanning tunneling microscope (STM) and X-ray photoemission spectra (XPS). STM images of the sample deposited with Rh (<1ML) at room temperature indicate the initial cluster shape of the deposited Rh are mostly triangles with two monolayers. After annealing, the shape transforms from triangle to hexagonal at about 600K, while the coverage start decrement at ~500K. XPS results imply that the ratio of Rh/Pt of the sample reduce with from 450K as function of annealing temperatures. The obtained results confirmed a preferable condition for sample preparation for the operando measurements under real working conditions.

Hydride Materials in All-Solid Li-Ion Cell Configuration

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Solid-state electrolytes have the potential to improve the safety of Li-ion batteries. Many different materials have been proposed over the years. However, especially at lower temperatures, most solid-state electrolytes display lithium ion conductivities lower than the one of conventional organic liquid electrolytes (about 3-5 mS.cm⁻¹ at room temperature). Several sulfides are among the compounds reported which display Li-ion conductivities in or above this range. However, issues regarding costs and/or electrochemical stability of sulfide electrolytes still remain [1]. The addition of lithium halides to the glass electrolyte Li₂S-P₂S₅ has been shown to improve the ionic conductivities and form favorable interface contacts [2]. Recently, the LiBH₄-Li₂S-P₂S₅ system has attracted attention owing to its interesting ionic properties [3,4]. LiBH₄ is a good Li-ion conductor only above its phase transition temperature (110°C). However, the high-*T* phase can be stabilized by partly substituting BH₄⁻ with halides, Li(BH₄)_{0.75}I_{0.25}, thus preserving high ionic conductivity on cooling down to room temperature.

The present work deals with the investigation of the Li-ion conduction properties of the Li(BH₄)_{0.75}I_{0.25} phase embedded in a 0.75Li₂S·0.25P₂S₅ amorphous matrix. The temperature dependence of the ionic conductivities for the glass system 0.75Li₂S·0.25P₂S₅ before and after addition of the Li(BH₄)_{0.75}I_{0.25} phase were derived from EIS analysis and compared to previous data for the single components. The study is supplemented by electrochemical stability (*I-E*) measurements and battery tests, first using a standard conversion type TiS₂ electrode and then with high-capacity MgH₂ based anodes (2037 mAh.g⁻¹), paving the way for high-power lithium solid-state batteries at moderate temperatures.

Acknowledgements

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References

- [1] M. Tatsumisago, S. Hama, A. Hayashi, H. Morimoto, T. Minami, *Solid State Ionics* **154–155** (2002) 635.
- [2] S. Ujiie, A. Hayashi, M. Tatsumisago, *Solid State Ionics* **211** (2012) 42.
- [3] A. Yamauchi, A. Sakuda, A. Hayashi, M. Tatsumisago, *J. Power Sources* **244** (2013) 707.
- [4] A. Unemoto, H. Wu, T.J. Udovic, M. Matsuo, T. Ikeshoji, S.-i. Orimo, *Chem. Commun.* **52** (2016) (3) 564.

Vibrational Defect Formation Entropy in Rutile and Anatase TiO₂ by Ab-initio Phonon Calculations

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Abstract

As part of the ongoing effort on explaining and improving the photocatalytic properties of TiO₂, there have been several studies on the formation of point defects by ab-initio calculations¹⁻⁴. The most extensive prior works are based on the rutile polymorph¹⁻³, even though anatase is considered a more promising material for photocatalysis⁵. In addition, the obtained formation energies at 0 K are usually extrapolated to finite temperatures by considering only the thermodynamics of the change in chemical potential¹, thereby ignoring the change in entropy from lattice vibrations. In the present work, we investigate the defect properties of anatase and rutile TiO₂ with focus on the phonon contribution to the defect thermodynamics from first principles phonon calculations. We found that the entropy change depends heavily on the volume change upon defect formation, i.e. the defect induced chemical expansion, and is more pronounced for rutile compared to anatase, as shown in Figure 1. The phonon contribution to the formation entropy for anion and cation vacancies in rutile was found to be approximately -1 and +1 eV at 1000 K, respectively, and as such leads to significant contributions to the defect formation energies. The formation entropies of vacancies differs more between anatase and rutile compared to interstitials. This is likely due to the larger volume changes of the vacancies, as rutile is the denser structure, and the relative change in volume would differ more between the polymorphs for defects with larger relaxation volumes.

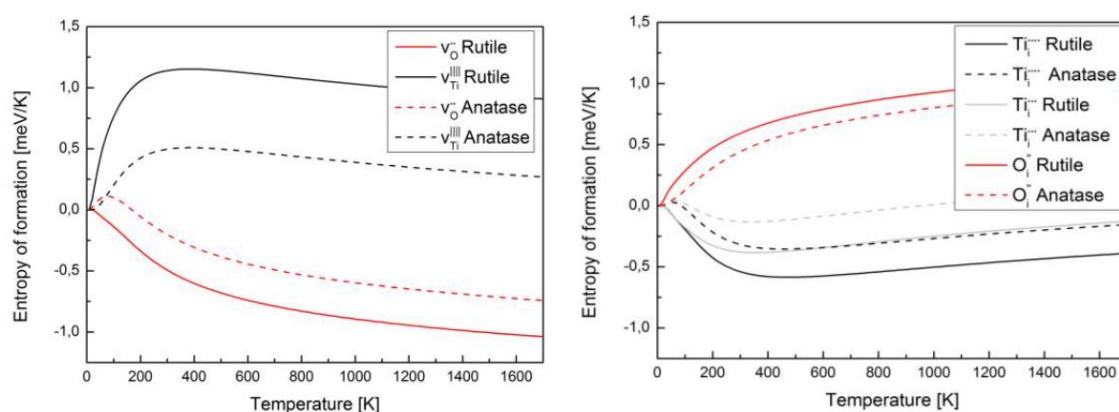


Fig. 1: Vibrational entropy change of rutile (dashed line) and anatase (solid line) TiO₂ upon formation of cation and anion vacancies (left) and interstitials (right).

References

1. Bjørheim, T. S., et al., *The Journal of Physical Chemistry C* (2013) **117** (11), 5919
2. Stausholm-Møller, J., et al., *The Journal of chemical physics* (2010) **133** (14), 144708
3. Zhu, H. X., et al., *Physics Letters A* (2014) **378** (36), 2719
4. Morgan, B. J., and Watson, G. W., *The Journal of Physical Chemistry C* (2010) **114** (5), 2321
5. Luttrell, T., et al., *Scientific Reports* (2014) **4**, 4043

Optimisation studies of Li-ion batteries based on Si negative electrodes

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As lithium based chemistry is on the forefront of battery technology, many efforts are done to optimise Li batteries in terms of lifetime and energy density. During the last decade many alternative Li chemistries arose which could potentially replace classical rocking chair Li batteries. As today, most of these technologies, such as Li-air, Li sulphur or reaction electrodes based on M_nX_m (M = transition metal, X = O, N, P...), are still in their infancy and it cannot be foreseen if the ascending challenges will be solved. Today's Li-ion batteries rely on intercalation host materials and the capacity is limited by the positive host materials delivering a specific charge of around 100-200 mAh/g. Graphite is the state of the art negative electrode in commercial cells and delivers a moderate capacity of 370 mAh/g. A two to three fold increase in specific capacity of the negative electrode would have a profound effect on the specific capacity of a full Li-ion cell.

Lately, Si was described as a negative electrode in Li batteries forming a Li-Si alloy when cathodically polarised to low potentials. Upon full lithiation, a Si negative electrode can deliver a specific charge of about 3600 mAh/g corresponding to a Li:Si ratio of 4:1. This heavy lithiation causes enormous volume changes, which come with the price of electrode detachment or pulverisation and an instable SEI layer, which cannot keep intimate contact with the Si surface upon these volume changes. Hence, Si negative electrodes suffer from severe inefficiencies and charge fade. These issues have been partly mitigated by adding SEI promoting additives such fluoroethylene carbonate to the electrolyte. Furthermore, nanostructuring and limiting the specific charge to about a third of the theoretical value has improved the cycleability of Si based negative electrodes. In addition, different water-soluble binders have been proposed to accommodate and withstand volume changes upon lithiation. The production of Li-ion batteries could be arranged in a much more environmentally benign manner if these water soluble binders could replace PVDF also for the positive electrode.

The focus of this study lies on the cycleability full cell Li-ion batteries based on Si negative electrodes and the processing of both electrode sides with water-soluble biopolymers as binder material. Full cells with a cycle life of more than a hundred cycles and increased specific energy are presented and discussed.

Variation of network dimensionality and adsorption properties of metal-organic frameworks based on a series of phosphine containing linkers.

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Metal-Organic Frameworks (MOFs) are porous materials based on coordination bonds between metal ion or metal cluster and organic linker. The flexibility in choice of the linker makes MOFs attractive for design of functional materials with tailored properties for application in adsorption and separation, catalysis, sensors and conductivity. Linkers with several functional groups of widely differing chemical affinity may be used to obtain frameworks with functional groups that are uncoordinated and accessible from the pore. These sites can serve as anchors for immobilization of catalytically active organometallic complexes.

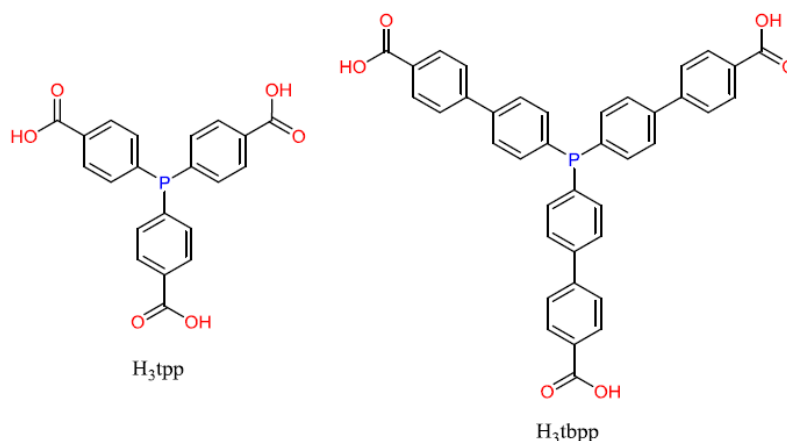


Figure 1. Bifunctional phosphine based linker molecules used in the synthesis of **1-5**.

Triphenylphosphine (PPh_3) is widely used as the ligand in catalytic systems, for example for hydrogenation or C–C cross-coupling. Therefore there is a strong interest in incorporation of PPh_3 functionality into the structure of MOFs.^[1] The triphenyl phosphine derivatives H_3tpp ^[2] and H_3tbpp ^[3] linkers (Figure 1) were used for the MOF synthesis.

Here, we present five new porous metal-organic frameworks containing the PPh_3 moiety, namely $[\text{Zn}_3(\text{tpp})_2(\text{DMF})_2] \cdot n\text{DMF}$ (**1**), $[\text{Zn}_3(\text{tpp})_2(4,4'\text{-bipy})_2] \cdot n\text{DMF}$ (**2**), $[\text{Zn}_3(\text{tpp})_2(3,3'\text{-bipy})] \cdot n\text{DMF}$ (**3**), $[\text{Y}(\text{tpp})(\text{DMF})] \cdot n\text{DMF}$ (**4**) and $[\text{Y}(\text{tbpp})] \cdot n\text{DMF}$ (**5**).

- [1] a) A. M. Bohnsack, I. A. Ibarra, V. I. Bakhmutov, V. M. Lynch, S. M. Humphrey, *J. Am. Chem. Soc.* **2013**, *135*, 16038-16041; b) X. Xu, S. M. Rummelt, F. L. Morel, M. Ranocchiari, J. A. van Bokhoven, *Chem. - Eur. J.* **2014**, *20*, 15467-15472; c) A. B. Redondo, F. L. Morel, M. Ranocchiari, J. A. van Bokhoven, *Acs Catalysis* **2015**, *5*, 7099-7103.
- [2] a) S. M. Humphrey, P. K. Allan, S. E. Oungoulain, M. S. Ironside, E. R. Wise, *Dalton Trans.* **2009**, 2298-2305; b) A. J. Nunez, L. N. Shear, N. Dahal, I. A. Ibarra, J. Yoon, Y. K. Hwang, J.-S. Chang, S. M. Humphrey, *Chem. Commun.* **2011**, *47*, 11855-11857.
- [3] T. Sawano, Z. Lin, D. Boures, B. An, C. Wang, W. Lin, *J. Am. Chem. Soc.* **2016**, *138*, 9783-9786.

Defect Chemistry in Grain Boundaries of Proton Conducting BaCeO₃

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In this work, first-principles calculations are utilized to study the grain boundaries and defect energetics in bulk and interfaces of proton conducting BaCeO₃. Several geometrically possible grain boundaries are constructed and analyzed energetically. BaCeO₃ (102) surface proves to exhibit surface energies compared to those experimentally reported. Defect calculations are performed for this interface with focus on protons, oxygen vacancies and Y-acceptor dopants. Especially in case of oxygen vacancies, some interesting new relaxed structures emerge upon structural relaxation, thus strong tendency to segregate to the surface. The most notable one is face sharing octahedra at interface, which creates low energy states, and.

Hydride migration in $\text{BaTiO}_{3-x}\text{H}_x$ oxyhydride

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Abstract

Several oxyhydrides have recently been demonstrated to exhibit significant hydride ion (H^-) diffusion with potential applications in novel energy technologies. However, the transport mechanism is unclear, especially for the electron dominated transition-metal oxyhydrides. In this contribution, we elaborate on the migration behavior of hydride ions in $\text{BaTiO}_{3-x}\text{H}_x$ by means of mass spectrometry (MS), secondary ion mass spectrometry (SIMS) and first principles calculations. $\text{BaTiO}_{3-x}\text{H}_x$ powder with different hydride contents ($x=0.35$ and 0.51) is used to measure the hydrogen release and H/D isotopic exchange rate between 300 to 500 °C by mass spectrometry. Hydride evolution and isotopic exchange rates are used to interpret hydride ion migration mechanism in $\text{BaTiO}_{3-x}\text{H}_x$. Further, the hydride tracer diffusion coefficient is measured by annealing $\text{BaTiO}_{3-x}\text{H}_x$ oxyhydride single crystals in D_2 . DFT is employed to calculate hydride ion's possible migration trajectories in $\text{BaTiO}_{3-x}\text{H}_x$, which will be compared with experimental data from MS and SIMS. We hope some further QENS and NMR studies could provide quantitative information on mobility of hydride ions.

Proton Ceramic Electrolysers; operation, challenges and developments

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The Electra project focuses on development of tubular proton ceramic electrolyzers (PCE's) for intermediate temperature electrolysis of steam. Lowering operation temperature of high temperature electrolyzers is a targeted aim to mitigate challenges with respect to materials limitations and operation complexity. [1] PCEs face challenges with respect to slow kinetics and high polarization resistance in the steam electrode (anode) at lower temperatures. In addition, partial conduction of electron holes through the electrolyte at high temperatures and pO_2 's makes the optimal operation temperature window narrower. At low temperatures, the polarization resistance is too high, and at high temperatures the p-type leakage current is too high, both causing lowered faradaic efficiency. The series connected ionic resistances from electrolyte and electrodes determine the fraction of charge transported by protons versus electrons, and the temperature and cell potential affects the electronic transference number. Hence, lowering anode resistance is vital for efficient operation. The Electra project has focused on anode development and cell manufacturing. Both single phase and composite electrodes are tested under operation, and tubular single cells with high faradaic efficiency at intermediate temperatures are developed and tested. Furthermore, infiltration procedures of the active electrode phase $Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ (BGLC) in BZCY backbones are developed, and the effects of enhanced microstructure are investigated. Based on the findings, performance of a "perfect" steam anode is modelled, [2] and the results are used to foresee power inputs and thermo-neutral operation for BZCY-based PCEs with different electrode performances.

Acknowledgements

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References

1. Wachsman, E.D. and K.T. Lee, *Lowering the Temperature of Solid Oxide Fuel Cells*. Science, 2011. **334**(6058): p. 935-939.
2. Strandbakke, R., et al., *Ba_{0.5}Gd_{0.8}La_{0.7}Co₂O_{6-δ} Infiltrated in Porous BaZr_{0.7}Ce_{0.2}Y_{0.1}O₃ Backbones as Electrode Material for Proton Ceramic Electrolytes*. Journal of The Electrochemical Society, 2017. **164**(4): p. F196-F202.

First-principles study of structural stability and electro-chemical properties of Na_2MSiO_4 ($M = \text{Mn, Fe, Co and Ni}$) polymorphs

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The family of lithium orthosilicates Li_2MSiO_4 ($M = \text{Mn, Fe, Co, Ni}$) is a promising cathode material due to the possibility of exchanging two electrons per formula unit, corresponding to theoretical capacities in excess of 300 mA h g^{-1} . However, these materials exhibit a complex polymorphism, and a phase transition occurring upon cycling significantly decreases the initial capacity. The analogous Na_2MSiO_4 compounds have been recently recognised as more promising candidates due to a lower deintercalation voltage plateau and to a significantly higher diffusivity with respect to the Li case. The latter can be attributed to the larger equilibrium volumes predicted for the Na-based compounds and to the corresponding weaker interaction between atomic layers.

In this talk I will discuss the polymorphism of this materials class on the base of Density Functional theory calculations. I will provide a physical-chemical insight on the bonding between Na, Si, Fe and the neighbouring O atoms, followed by a study of the average voltage of sodium deintercalation/intercalation and of conductivity of Na atoms. The dependence of these properties on the transition metal atom M is analysed, suggesting that the voltage and the ionic conductivity of $\text{Na}_2\text{FeSiO}_4$, a good candidate for battery electrode due to the natural abundance of both Fe and Na, can be enhanced by Ni-doping.

Keywords: density functional theory, electronic structure, Na-based battery materials

A first principles study of charged domain walls in improper ferroelectric hexagonal YMnO_3 , InMnO_3 , and YGaO_3

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Ferroic oxide materials display a variety of properties of current and future technological interest, and understanding and controlling interfaces is imperative to the development of oxide based electronics. In ferroelectrics, all dipoles within a *domain* align in the same direction. These domains are separated by internal interfaces known as domain walls. Hexagonal RMnO_3 ($R=\text{Dy to Lu, Sc, In}$) is multiferroic, showing antiferromagnetic behavior below 75 K [1] and improper ferroelectricity below 1260 K [2]. Since polarization is not the primary order parameter in an improper ferroelectric, charged 180° head-to-head and tail-to-tail ferroelectric domain walls may form. These charged domain walls can attract mobile charge carriers and become conducting [3], and can be switched reversibly from resistive to conducting by an electric field [2]. RMnO_3 is robust with respect to cation [5,6] and anion stoichiometry [7,8], where intrinsic oxygen is shown to be a source for *p*-type conductivity [9]. Thus, RMnO_3 is a suitable material class for tailoring the local crystal and electronic structure at and close to the domain walls by electric field, heat treatment, and heterovalent doping.

In this study, we investigate and characterize charged domain wall structures in isostructural hexagonal YMnO_3 , InMnO_3 , and YGaO_3 by density functional theory. We raise and discuss three important questions. First, can we define the local structure at the domain walls, and is the calculated energy landscape for different structures in agreement with experimental work? Secondly, how does the local crystal structure evolve across the domain walls, and can we from this predict the domain wall width with respect to host material? And finally, how does the electronic structure and electrostatic potential change across the charged domain walls?

- [1] M. Fiebig, T. Lottermoser, D. Fröhlich, A. V. Goltsev and R. V. Pisarev, *Nature* **419**, 818 (2002).
- [2] M. Lilienblum, T. Lottermoser, S. Manz, S. M. Selbach, A. Cano and M. Fiebig, *Nat. Phys.* **11**, 1070 (2015).
- [3] D. Meier, J. Seidel, A. Cano, K. Delaney, Y. Kumagai, M. Mostovoy, N. A. Spaldin, R. Ramesh and M. Fiebig, *Nat. Mat.* **11**, 284 (2012).
- [4] J. A. Mundy, J. Schaab, Y. Kumagai, A. Cano, M. Stengel, I. P. Krug, D. M. Gottlob, H. Doğanay, M. E. Holtz, R. Held, Z. Yan, E. Bourret, C. M. Schneider, D. G. Schlom, D. A. Muller, R. Ramesh, N. A. Spaldin, and D. Meier, *Nat. Mater.* **advance online publication** DOI: 10.1038/nmat4878 (2017).
- [5] T. Shimura, N. Fujimura, S. Yamamori, T. Yoshimura and T. Ito, *Jpn. J. Appl. Phys.*, **37**, 5280 (1998).
- [6] I. Gelard, N. Jehanathan, H. Roussel, S. Gariglio, O. I. Lebedev, G. Van Tendeloo and C. Dubourdieu, *Chem. Mater.* **23**, 1232 (2011).
- [7] S. Remsen and B. Dabrowski, *Chem. Mater.* **23**, 3818 (2011).
- [8] A. J. Overton, J. L. Best, I. Saratovsky and M. A. Hayward, *Chem. Mater.* **21**, 4940 (2009).
- [9] S. H. Skjærvø, E. T. Wefring, S. K. Nesdal, N. H. Gaukås, G. H. Olsen, J. Glaum, T. Tybell, and S. M. Selbach, *Nat. Commun.* **7**, 13745 (2016).

Half-Heusler Phase Formation and Ni atom distribution in M-Ni-Sn (M = Hf, Ti, Zr) System

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Half-Heusler (HH) compounds are among the most promising thermoelectric (TE) materials being investigated for automotive and industrial waste heat recovery applications. These cost-effective phases, consisting of abundant constituents, reveal excellent chemical stability at relatively high temperatures. Apart from that, they are environmentally friendly compared to their Pb-based alternatives. Though, it has been shown that TE properties of HH-alloys drastically depend on their modifications at micro- and nanoscales (e.g. sample composition, particle size, lattice strain, grain boundaries, etc.), systematic studies that relate TE performance with structural and morphological aspects are still missing.

To partly fill this gap, we have already initiated comprehensive structural analysis on selected HH-phases. For this reason, a number of (Ti,Zr,Hf)NiSn-based phases were synthesized and studied by high-resolution synchrotron powder X-ray diffraction. The obtained results revealed segregation of the nominally stoichiometric ZrNiSn into two Zr-based HH phases with very similar lattice parameters (Figure 1). Though, the observed multiphase nature of HH compounds has been already reported, the coexistence of HH-phases in the unsubstituted ternary compositions (Hf/Ti/ZrNiSn) has not been confirmed experimentally before.

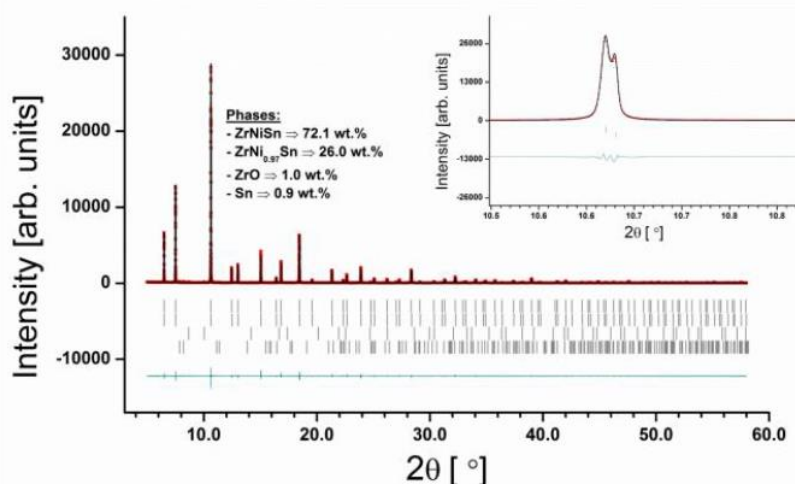


Figure 1. Observed (red line), calculated (black line) and difference (blue line) high resolution SR-PXD pattern ($\lambda = 0.40000$ Å) obtained for ZrNiSn (space group: $P-43m$). Vertical bars indicate Bragg peaks positions of the crystalline phases.

The Research Council of Norway, under NANO2021 program (Project THELMA, No. 228854), is acknowledged for financial support.

Electronic and optical properties of Cr-N Co-doped TiO₂ for use as an Intermediate Band Material

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A density functional theory (DFT) study is presented on the effect of chromium and nitrogen co-doping on the electronic and optical properties of TiO₂. Anatase is a promising candidate host material for an intermediate band solar absorber due to its wide-band gap and high photocatalytic response. In order to form a mid-gap band for increased absorption, a suitable dopant and high doping concentration is required. In this work a co-doping strategy is explored by substitution of both Cr and N in anatase TiO₂ to increase the thermodynamic solubility and form an intermediate band. In addition, the co-doping scheme provides passivation of recombination centres, which is required for an efficient photovoltaic device.

Here we have used DFT to calculate the effect of Cr and N substitution on the anatase and rutile phases of TiO₂. The electronic structure is calculated for a range of dopant concentrations, using hybrid exchange correlation functionals to give accurate band gaps. Optical properties are evaluated by calculation of the dielectric function and absorption spectra. These results allow an assessment of effective dopant levels in order to advise experimental studies and synthesis of an intermediate band material. In addition, this work provides optical constants for input to device level models for solar cell design.

Space charge layers in interfaces of BZY investigated by advanced microscopy, theoretical calculations, and electrical measurements

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Y-substituted BaZrO₃ (BZY) exhibits high grain interior proton conductivity¹, but grain boundaries have large resistances attributed to charge carrier depletion in space charge layers next to positively charged grain boundary cores^{2,3}. The same may affect electrodes and surfaces. We are interested in methods of direct verification and extension of the positive charge, comparison with theory, and quantitative prediction of effects on electrical properties. For this purpose, grain boundaries and surfaces will be examined with TEM inline electron holography; by measuring the electrostatic potential across grain boundaries as a function of specimen thickness, one may succeed in dividing between surface effects and grain boundary volume effects. The results will be compared with DFT calculations of bulk and model interfaces. Models will be developed for the DC and AC impedance across grain boundaries and compared with impedance spectroscopy results, with the intention to develop useful approximate functions beyond constant phase elements (CPEs).

Acknowledgement: This work is part of the nationally coordinated project Functional OXides for Clean Energy Technologies (FOX CET, RCN, 102006684-1), with SINTEF, NTNU and UiO as active partners.

¹ E. Fabbri, D. Pergolesi, and E. Traversa, "Materials challenges toward proton-conducting oxide fuel cells: a critical review," *Chemical Society Reviews*, vol. 39, pp. 4355–4369, 2010.

² X. Guo and R. Wasser, "Electrical properties of the grain boundaries of oxygen ion conductors: Acceptor-doped zirconia and ceria," *Progress in Materials Science*, vol. 51, pp. 151–210, 2006.

³ J. Nowotny, *The CRC Handbook of Solid State Electrochemistry*, CRC Press, 1997.

Sub-unit cell structural transformations during template-removal and hydration of SAPO-37 microporous catalysts

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Zeolites are important materials for catalysis; however, long term stability can be a problem. Although the materials have been used since the 1980s, the effect of different activation parameters on their long-term stability remains unclear. By studying the structural changes in SAPO-37 during template removal¹ and consecutive low-temperature hydration with high time-resolution, we gathered information that helps us understand the stability of the materials. The recent upgrades at BM01 at the ESRF, with the significant improvement in time-resolution, give us a new level of information about fundamental procedures such as template removal and hydration, revealing details previously impossible to see.

We have studied the structural behavior of SAPO-37 during calcination and consecutive hydration at close to ambient conditions. *In-situ* powder-XRD revealed that the **FAU** cages and **SOD** cages have different thermal response to the combustion of each template. The **FAU** cages are mainly responsible for the unit cell volume expansion observed after the template combustion. This expansion seems to be related with residual coke from template combustion. We could differentiate between the thermal response of oxygen and T-atoms. The T-O-T angle between two double 6-rings and a neighboring T-O-T linkage shared by **SOD** and **FAU** had different response to the thermal events. Furthermore, we were able to monitor the changes in the positions of oxygen and T-atoms during the removal of TPA⁺ and TMA⁺.

A critical parameter that promotes structural changes in SAPOs during real-life applications is the presence of humidity. Template-free SAPO-37 is known to have poor structural stability in contact with humidity below 345 K². Although the loss of SAPO-37 crystallinity has been known since the early 1990s³, the mechanism governing this long-range order loss still remains to be experimentally revealed. By making complimentary use of the RECX lab and SNBL we could identify the sub-unit cell structural transformations that lead to the SAPO-37 unit cell rupture and consecutive loss of long-range order under humid conditions. High time-resolution *in-situ* XRD helped us identify preferential positions where H₂O molecules locate themselves within the SAPO-37 framework. Long-term *in-situ* experiments at the RECX lab combined with high time-resolution XRD at SNBL showed the effect on the material crystallinity loss at above and below 345 K, the critical temperature at which framework decomposition under humid conditions is significantly accelerated.

- (1) Kalantzopoulos G.N., Lundvall F., *et al.* SAPO-37 microporous catalysts: revealing the structural transformations during template removal. *Catalysis, Structure & Reactivity*, **2017**, 3, p. 79-88.
- (2) Briend M., Shikholeslami A., *et al.* Thermal and hydrothermal stability of SAPO-5 and SAPO-37 molecular sieves. *Journal of the Chemical Society, Dalton Transactions*, **1989**, p. 1361-2.
- (3) Briend M., Lamy A., *et al.* Thermal stability of tetrapropylammonium (TPA) and tetramethylammonium (TMA) cations occluded in SAPO-37 molecular sieves. *Zeolites*, **1993**, 13, p. 201-11.

Thermoelectric and Structural Study of Zinc-Antimony Thin Films Grown by Sputtering Deposition

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Zinc antimonides are highly interesting as thermoelectric materials, because of the relative good thermoelectric properties as well as for the price and non-toxic constituent elements.[1, 2] This material system has been studied over the last 20 years, with β -Zn₄Sb₃ and ZnSb as the most investigated phases, which are also the better thermoelectric phases, but the complex binding scheme in the binary system opens up for a variety of different phases with only slight changes in stoichiometry obtainable by ordinary solid state routes.

We have shown how to upscale the production of bulk pellets of β -Zn₄Sb₃ and ZnSb and shorten the processing time to a diameter of 1 inch and 45 minutes, respectively.[3, 4] The pellets can directly be used as sputtering targets for sputtering deposition. Preparing intermetallic thin films by a bottom up approach, typically amorphous films can be prepared. Heat treatment of the as-deposited films can reveal metastable phases otherwise unobtainable.

Here results on thin films of varying zinc-antimony compositions, prepared by single-target sputtering deposition and studied for their thermoelectric properties, will be presented. The recent advances in analyzing the structure of thin films by total scattering and pair distribution function (tfPDF) method has been applied to selected samples.[5, 6] In this presentation the use of tfPDF will be taken to the next step, by performing *in-situ* tfPDF on Zn_xSb_{1-x} thin films. The as-sputtered films show amorphous or metastable phases that undergo various phase transitions in the studied temperature range, and eventually become thermodynamically stable phases.

1. Iversen, B.B., *Fulfilling thermoelectric promises: β -Zn₄Sb₃ from materials research to power generation*. Journal of Materials Chemistry, 2010. **20**(48): p. 10778-10787.
2. Fedorov, M.I., et al., *Thermoelectric Efficiency of Intermetallic Compound ZnSb*. Semiconductors, 2014. **48**(4): p. 432-437.
3. Yin, H., et al., *Fast Direct Synthesis and Compaction of Homogenous Phase-Pure Thermoelectric Zn₄Sb₃*. ACS applied materials & interfaces, 2014. **6**(13): p. 10542–10548.
4. Blichfeld, A.B. and B.B. Iversen, *Fast direct synthesis and compaction of phase pure thermoelectric ZnSb*. Journal of Materials Chemistry C, 2015. **3**(40): p. 10543-10553.
5. Jensen, K.M.O., et al., *Demonstration of thin film pair distribution function analysis (tfPDF) for the study of local structure in amorphous and crystalline thin films*. IUCrJ, 2015. **2**(5): p. 481-489.
6. Bauers, S.R., et al., *Structural Evolution of Iron Antimonides from Amorphous Precursors to Crystalline Products Studied by Total Scattering Techniques*. Journal of the American Chemical Society, 2015. **137**(30): p. 9652-9658.

Single Crystal Phosphors for High-Power Lightning and Display Technologies

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Abstract:

Laser diodes (LDs) are replacing the conventional lightning and display technologies rapidly due to their long lifetime and high conversion efficiencies. Phosphor materials excited by LDs provide high brightness and low cost solution for better color quality in display technologies. Since LDs deliver much higher light intensities than LEDs, phosphor efficiency and thermal quenching properties are very crucial for the future of blue laser diode (LD) driven lightning and display technologies. We have characterized Ce doped single crystals as stationary phosphor candidates for blue laser driven solid lighting without heatsink. The luminous properties of the single crystals are improved when compared to the commercial phosphor wheels ($\text{Ce}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$). The high-power blue diode laser driven temperature increase versus quantum efficiency is discussed. The results indicate that Gd and Ga doping decreases the luminescence quenching temperature.

Poster Session Abstracts

- P1** “Gadolinium cobaltites as Ammonia Slip Catalysts: synthesis, characterization and testing”
- P2** “Tantalum oxynitride nanotubes for photoelectrochemical water splitting”
- P3** “A comprehensive structural study of the CO₂ adsorption process in the CPO-27 family”
- P4** “Effect of ligand substitution on breathing mode of MOFs with MIL-53 type crystal structure”
- P5** “In situ X-ray diffraction studies of hydrothermal synthesis”
- P6** “Evaluating Dawsonite as sorbent for the SEWGS process”
- P7** “Functionalisation of silica aerogels with cobalt and rhenium.”
- P8** “Operando Investigation of Surfaces for NO_x Catalysis”
- P9** “Synthesis, characterization and thermal stability of the hydride conducting oxyhydride La_{2-x}Nd_xLiHO₃”
- P10** “Nucleation and growth mechanisms during aqueous chemical solution deposition of oxide thin films”
- P11** “Lanthanum cobaltite as a novel conducting oxide interconnect in thermoelectrics”
- P12** “NcNeutron – Norwegian center for Neutron research”
- P13** “PHOTOCATHODE FOR SOLID-STATE PHOTOELECTROCHEMICAL CELL”
- P14 (no title)**
- P15** “Exploring the Surface chemistry of Y-doped Barium Zirconate Proton Conducting ceramics”
- P16** “Black Titania Nanotube arrays with high capacitive energy”
- P17** “Thin films of Amino-functionalized metal-organic frameworks”
- P18** “Magnetic properties and structure correlations of novel double perovskite oxides”
- P19** “Positive and negative magneto-resistance effects in layered perovskite Ca₄Mn₃O₁₀”
- P20** “Sb₂MoO₆ as possible anode for lithium and sodium ion batteries”
- P21** “New synthetic strategies for novel oxyhydrides”

Gadolinium cobaltites as Ammonia Slip Catalysts: synthesis, characterization and testing

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A majority of catalysts used in industry are based on mixed metal oxide structures. Among them, rare-earth-transition metal perovskite materials appear as a serious alternative for platinum-group metals (PGMs) in the ammonia slip reaction. Internal tests performed at the Yara Technology Center have shown that despite their excellent catalytic activity¹, Lanthanum perovskite catalysts suffer from a low mechanical stability towards long-term water vapour exposure. Based on this observation, other systems, such as Gadolinium or Yttrium perovskites, are now being studied and tested as catalysts for the ammonia slip reaction.

The application of perovskites in the field of heterogeneous catalysis requires materials with a large accessible surface area. A typical surface area of 0.5-10 m² g⁻¹ is obtained using classical synthesis routes (ceramic, coprecipitation)². Using other preparation routes (mechanosynthesis, sol-gel, combustion, nanocasting) allows to form perovskites with higher surface areas. In this project the combination of polymerization (modified sol gel route) followed by a post mechanical treatment has been done to obtain five single-phase Gadolinium cobaltite catalysts. The temperature of calcination has been reduced from 900 to 700 °C.

All the compositions have been characterized by X-ray powder diffraction at the RECX Center, and by BET at the Yara Technology Center with the help of Siri-Mette Olsen. The BET results show an increase of surface area when the catalysts are subject to a post-mechanical treatment. A maximum of 18.5 m² g⁻¹ has been obtained for the GdCo_{0.6}Mn_{0.4}O₃ composition.

Catalyst testing has been performed in March 2017 at the Yara Technology Center by Karl Isak Skau. The results will be sent before the conference, and will represent a large part of the poster.

¹ V. A. Sadykov et al., Applied Catalysis A: General, 204, 59-87, 2000

² S. Royer et al., Chemical Reviews, 114, 10292-10368, 2014

TANTALUM OXYNITRIDE NANOTUBES FOR PHOTOELECTROCHEMICAL WATER SPLITTING

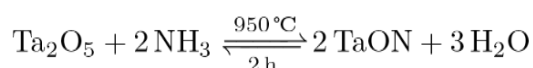
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TaON is a potential semiconductor that can be used as a photoanode for photoelectrochemical (PEC) water splitting and fuel production [1]. Its low bandgap [2] makes it possible to utilize the visible light, hence to increase the solar-to-hydrogen conversion efficiency, which can be further enhanced by nano morphology modifications, e.g. nanotubes [3].

In this work Ta₂O₅ nanotubes were grown by anodization, which was adapted from a well-developed method for growing TiO₂ nanotubes [4], followed by the annealing in an NH₃ atmosphere at 950 °C in order to convert the oxide into oxynitride:



The obtained TaON nanotubes, with an average length of 18 μm, are covered by a porous layer on the top (Fig. a). Its photoelectrochemical performance was tested by linear voltage sweep under AM 1.5G solar illumination (Fig. b).

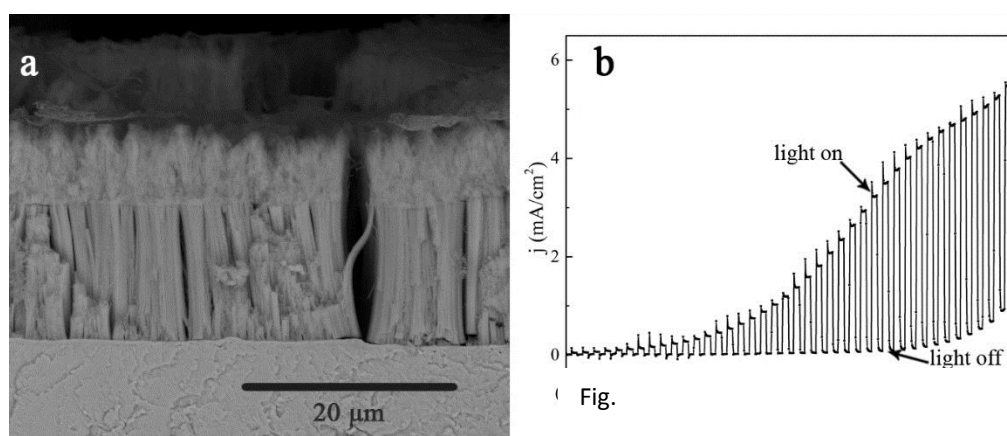


Fig.a, cross-section SEM image of TaON after annealing in NH₃ at 950 °C for 2 hours; b, current-potential curve under AM 1.5G chopped solar light with Pt-C as the counter electrode, within 0.5 M Na₂SO₄ electrolyte.

Acknowledgement: this work is funded by the Research Council of Norway under the NANO2021 program, project CO2BioPEC (250261).

References

- [1] M. Hara, G. Hitoki, T. Takata, J.N. Kondo, H. Kobayashi, K. Domen, *Catal. Today*, 78 (2003) 555-560.
- [2] L. Yuan, Y.-J. Xu, *Appl. Surf. Sci.*, 342 (2015) 154-167.
- [3] X. Feng, T.J. LaTempa, J.I. Basham, G.K. Mor, O.K. Varghese, C.A. Grimes, *Nano Lett.*, 10 (2010) 948-952.
- [4] A. Chatzitakis, M. Grandcolas, K. Xu, S. Mei, J. Yang, I.J.T. Jensen, C. Simon, T. Norby, *Catal. Today*.

A comprehensive structural study of the CO₂ adsorption process in the CPO-27 family

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Among metal-organic frameworks, the isostructural series CPO-27-M, (CPO: Coordination Polymer of Oslo) or M-MOF-74, where M is a divalent cation, is potentially one of the most interesting families for application in adsorption and separation processes due to their high concentration of open metal sites, combined with a stable and rigid open framework structure. The results presented here are focused on the use of CPO-27 as solid adsorbent for carbon dioxide (CO₂). The CPO-27-M materials have a high capacity for CO₂ adsorption at relative low partial pressures, and they might be eminently suitable for use in temperature or pressure swing processes for carbon capture.

The CO₂ adsorption process in CPO-27-M (M=Mg, Mn, Co, Ni, Cu, and Zn) was studied by variable-temperature powder synchrotron X-ray diffraction under isobaric conditions. The Rietveld analysis of the data provided a time-lapse view of the adsorption process on CPO-27-M. The results confirm the temperature-dependent order of occupation of the three adsorption sites in the pores of the CPO-27-M materials. In CPO-27-M (M=Mg, Mn, Co, Ni, and Zn), the adsorption sites are occupied in sequential order, primarily because of the high affinity of CO₂ for the open metal sites. CPO-27-Cu deviates from this stepwise mechanism, and the adsorption sites at the metal cation and the second site are occupied in parallel. The temperature dependence of the site occupancy of the individual CO₂ adsorption sites derived from the diffraction data is reflected in the shape of the volumetric sorption isotherms. The fast kinetics and high reversibility observed in these experiments support the suitability of these materials for use in temperature- or pressure-swing processes for carbon capture.

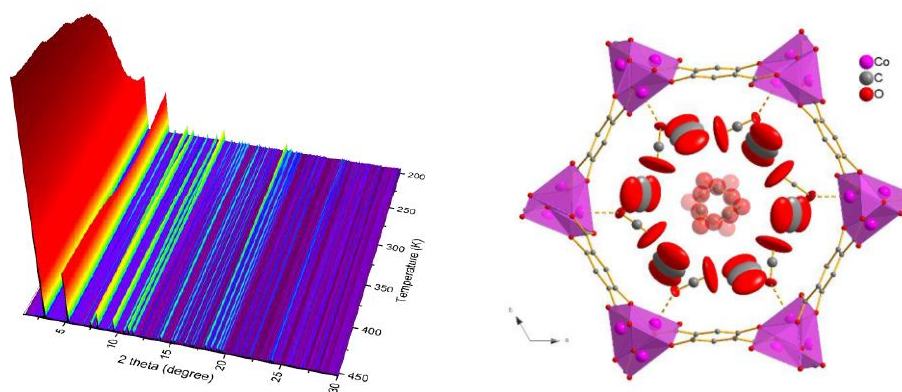


Figure 1. Left: Variable temperature X-ray powder pattern of CPO-27-Co at 1 bar of CO₂ pressure. Right: Partial view of the CPO-27-Co (1 bar of CO₂ pressure) crystallographic unit cell to highlight the 3 different adsorption sites inside the hexagonal pores.

[1] B. Pato-Doldán, M. H. Rosnes, P. D. C. Dietzel, "An In-Depth Structural Study of the Carbon Dioxide Adsorption Process in the Porous Metal–Organic Frameworks CPO-27-M", *ChemSusChem* **2017**, doi: 10.1002/cssc.201601752.

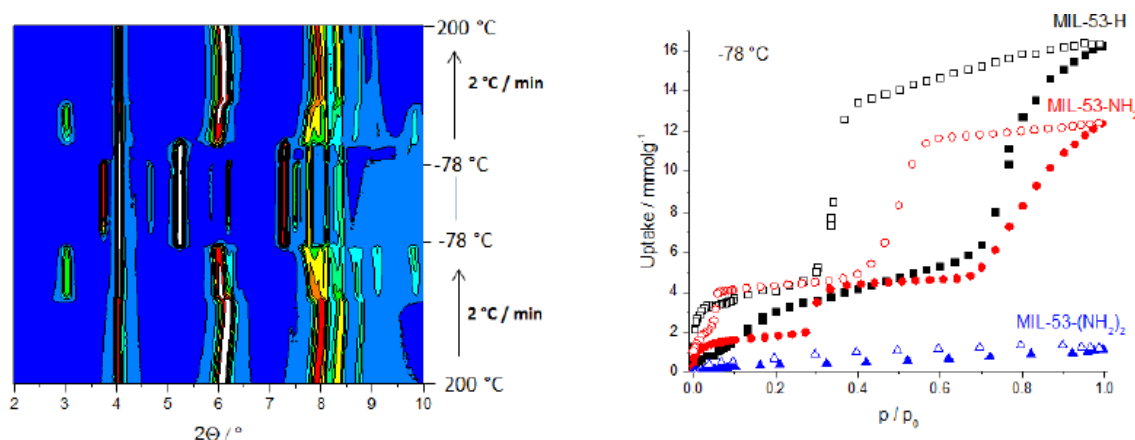
Effect of ligand substitution on breathing mode of MOFs with MIL-53 type crystal structure

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The MOF MIL-53 is known to exhibit a dramatic breathing effect, shown by a change in lattice parameters, upon solvent removal and/or incorporation of alternative guest molecules in the pore volume.^[1] We have synthesized a series of scandium MIL-53 compounds with terephthalate^[2], 2-aminoterephthalate and 2,5-diaminoterephthalate as the organic linker in the MOF structure.



1

Figure 1. Contour plot of a variable temperature powder diffraction experiment of MIL-53(Sc)-NH₂ in CO₂ atmosphere (left) and CO₂ adsorption isotherm measurements of MIL-53(Sc)-(NH₂)_x ($x = 0-2$) at 195 K (right).

In order to investigate the breathing behavior of these series we performed time resolved powder diffraction experiments at variable temperature and/or variable pressure. All three “as synthesized” scandium MIL-53 compounds exhibit phase transitions from an open- to a closed-pore form with significant changes in the lattice constants, due to the desolvation process.

In addition, variable temperature powder diffraction using CO₂ shows that the pore-opening of the closed “guest free” MIL-53(Sc)-NH₂ is fully reversible and proceeds in two steps via an intermediate phase. Complementary low temperature (195K) CO₂ adsorption measurements confirm the reversible two step pore-opening for MIL-53(Sc)-NH₂ and the existence of the intermediate phase at different temperature/pressure conditions. Furthermore, the CO₂ gas adsorption experiments showed that the gate pressure, the pressure at which the pore fully opens up, is shifted to higher values with increasing number of amino groups.

[1] C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, G. Férey, *Adv. Mater.* **2007**, *19*, 2246-2251.

[2] J. P. S. Mowat, V. R. Seymour, J. M. Griffin, S. P. Thompson, A. M. Z. Slawin, D. Fairen-Jimenez, T. Düren, S. E. Ashbrook, P. A. Wright, *DaltonTrans.*, **2012**, *41*, 3937–3941.

In situ X-ray diffraction studies of hydrothermal synthesis

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Abstract

Production of 1D nanostructured ferroelectric materials have gained an increased interest in the later years because of possible applications in Random Access Memory, sensors, energy harvesting devices and NEMS technology. Hydrothermal synthesis, being a versatile synthesis method, stands out as a promising method for the production of 1D nanostructured ferroelectric materials.[1] However, for full control over the hydrothermal method and production of 1D nanostructured ferroelectric oxide, a better understanding is needed on the nucleation and growth mechanism under hydrothermal conditions.[2]

On this poster, we present our experimental setup for use at synchrotron facilities that is used for doing *in situ* X-ray diffraction experiments under hydrothermal conditions. Combining synchrotron radiation, our experimental setup and Rietveld refinement have shown to be a very powerful tool for a better understanding of the hydrothermal synthesis. This is presented by two examples; the fast nucleation pathway of NaNbO₃ through a set of short lived intermediate phases[3] and an oriented attachment mechanism of TiO₂ nanoparticles under certain hydrothermal reaction conditions.[4] Both of these observations was made possible by *in situ* X-ray diffraction measurements.

References

- [1] P. M. Rørvik, T. Grande, and M.-A. Einarsrud, "One-Dimensional Nanostructures of Ferroelectric Perovskites," *Advanced Materials*, vol. 23, no. 35, pp. 4007-4034, 2011.
- [2] M. Niederberger and H. Colfen, "Oriented attachment and mesocrystals: Non-classical crystallization mechanisms based on nanoparticle assembly," *Physical Chemistry Chemical Physics*, 10.1039/B604589H vol. 8, no. 28, pp. 3271-3287, 2006.
- [3] S. L. Skjærvø *et al.*, "*In situ* time-resolved synchrotron X-ray diffraction during hydrothermal syntethesis of NaNbO₃," ed, 2017.
- [4] A. R. M. Dalod *et al.*, "Oriented attachment and *in situ* functionalization of TiO₂ nanoparticles during hydrothermal syntethesis with APTES," ed, 2017.

Evaluating Dawsonite as sorbent for the SEWGS process

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The sorbent enhanced water-gas shift (SEWGS) process is an emerging technology for pre-combustion CO₂ capture. In pre-combustion CO₂ capture processes, the fuel is reformed to give a syngas rich (H₂ + CO) gas mixture. This gas mixture can be shifted towards higher H₂ yields through the water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$). *In-situ* absorption of CO₂ shifts the equilibrium of the WGS reaction towards the desired product H₂. During sorbent regeneration, the carbon from the original fuel source is captured in the form of CO₂ and processed for storing. This results in a clean, decarbonized fuel for e.g. gas turbines (Figure 1).

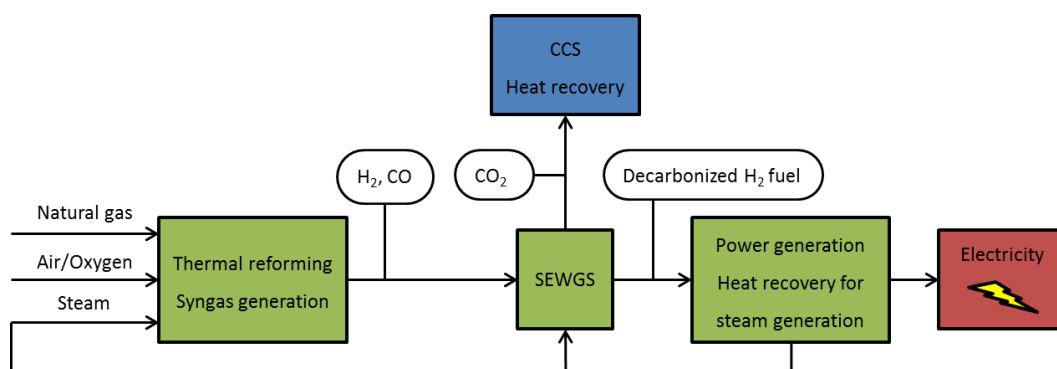


Figure 1: Schematic drawing of the SEWGS process

SEWGS has already reached a technology readiness level sufficient for upscaling to pilot plant scale. However, some issues remain before commercialization is feasible. In particular, the cost for SEWGS is closely associated with the cyclic CO₂ absorption capacity of the sorbent. Hence, next generation high stability materials with good cyclic CO₂ absorption capacity will play a major role in reducing the process's operating cost, making it competitive with existing amine-technologies.

Here we evaluate synthetic Dawsonite ($\text{MAl}(\text{CO}_3)(\text{OH})_2$, $M = \text{K}, \text{Na}$) as a sorbent for the SEWGS process. Studies have demonstrated that Dawsonite can form when potassium promoted alumina is subjected to SEWGS-like conditions¹. Hence we wanted to investigate if synthetic Dawsonite can absorb/desorb CO₂ cyclically at SEWGS relevant temperatures. In addition we wanted to monitor any physical changes to the material during CO₂ sorption in detail. The results include variable temperature cyclic CO₂ sorption,² *in-situ* synchrotron XRD during activation and CO₂ sorption as well as *ex-situ* TG-MS-DSC data. The results show reasonable cyclic sorption properties at relatively low temperatures (~280-300 °C) for SEWGS. Furthermore, the XRD and TG-MS data show that the active phase is a poorly ordered material that forms as the as-synthesized Dawsonite is activated.

- (1) Walspurger, S.; Cobden, P. D.; Haije, W. G.; Westerwaal, R.; Elzinga, G. D.; Safonova, O. V., *Eur. J. Inorg. Chem.* **2010**, 2010, 2461-2464.
- (2) Lundvall, F.; Kalantzopoulos, G. N.; Wragg, D. S.; Arstad, B.; Blom, R.; Olafsen Sjøstad, A.; Fjellvåg, H., *Energy Procedia* **2017**, in press.

Functionalisation of silica aerogels with cobalt and rhenium.

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Abstract

Silica aerogels are amorphous, low density and highly porous materials. The structure consists of interconnected silica particles that form both mesopores and micropores. Other properties are high surface area, low thermal conductivity and hydrophobicity. Preparation of an active phase within this 3D carrier has several benefits affecting both reactivity and economy. High dispersion is often obtained on functional inner surfaces, and imposed growth limitations can prevent sintering which can greatly affect both reducibility and reversibility of the metal phase. (1)(2)

Cobalt rhenium nitride systems are catalytically active towards ammonia synthesis (3) and cobalt rhenium particles towards Fischer-Tropsch (4). Due to economic reasons a supported, well dispersed phase would be more beneficial. The aim of this work is to functionalise silica aerogels with cobalt and rhenium nanoparticles.

Functionalised silica aerogels with copper and rhenium have been prepared through a sol-gel route with ambient pressure drying. XRD reveals that the rhenium phase exists as ammonium perrhenate in the as-prepared gels. XAS recorded at the Swiss-Norwegian beamlines at the ESRF in Grenoble, France reveals that during reduction of the functionalised silica aerogels there is a phase forming that is similar, but not identical to a metallic phase.

References:

1. de Graaf J, van Dillen AJ, de Jong KP, Koningsberger DC. Preparation of Highly Dispersed Pt Particles in Zeolite Y with a Narrow Particle Size Distribution: Characterization by Hydrogen chemisorption, TEM, EXAFS Spectroscopy, and Particle Modelling. *Journal of Catalysis*. 2001;203(2):307-21.
2. Akolekar DB, Bhargava SK. Investigations on gold nanoparticles in mesoporous and microporous materials. *Journal of Molecular Catalysis A: Chemical*. 2005;236(1-2):77-86.
3. Kojima R, Aika KI. Rhenium containing binary catalysts for ammonia synthesis. *Applied Catalysis A: General*. 2001;209(1-2):317-25.
4. Voronov A, Tsakoumis NE, Hammer N, van Beek W, Emerich H, Rønning M. The state and location of Re in Co-Re/Al₂O₃ catalysts during Fischer-Tropsch synthesis: Exploring high-energy XAFS for in situ catalysts characterisation. *Catalysis Today*. 2014;229:23-33.

Operando Investigation of Surfaces for NO_x Catalysis

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For better understanding of a mechanism of catalytic reactions and nanoscale interactions at the surface of a catalyst, a combination of “*operando*” spectroscopy and microscopy is presented. Several model catalysts (PtRh/Pt, V₂O₅/WO₃/TiO₂) are studied using Scanning Tunneling Microscopy and X-ray photoelectron spectroscopy at Ultrahigh Vacuum and in high pressure and temperature to obtain atomic morphology and surface composition at realistic process conditions.

Synthesis, characterization and thermal stability of the hydride conducting oxyhydride $\text{La}_{2-x}\text{Nd}_x\text{LiHO}_3$

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Complex oxides exhibit a wide range of properties that may give rise to a number of applications within future energy and electrochemical devices. A new category of such materials are oxyhydrides, mixed anion compounds containing hydride- and oxide anions. Only a handful number of oxyhydrides are so far reported, amongst others La_2LiHO_3 ^{1,2}, $\text{LaSrCoH}_{0.7}\text{O}_3$ ³ and SrCrHO_2 ⁴. These compounds have received attention due to their exotic chemistry, magnetic and electronic properties, and recently the oxide hydride La_2LiHO_3 was reported to exhibit conductivity of hydride anions².

Here we have studied the structure, thermal stability and conditions for synthesis of the solid solution $\text{La}_{2-x}\text{Nd}_x\text{LiHO}_3$ in a halide flux, all with an anion orthorhombic ordered version of the K_2NiF_4 structure. As synthesized the samples consists of single crystals with an average size around $10 \times 10 \times 10 \text{ } \mu\text{m}$, figure 1a. The La_2LiHO_3 and LaNdLiHO_3 can be synthesized phase pure in between $600 \text{ } ^\circ\text{C}$ and $750 \text{ } ^\circ\text{C}$ without any impurity phases, for Nd_2LiHO_3 we observe the presence of NdHO and Nd_2O_3 . The compounds are thermally stable in oxygen gas up to $450 \text{ } ^\circ\text{C}$ before oxidizes to the oxidized derivatives, $\text{La}_{2-x}\text{Nd}_x\text{LiO}_{3.5}$, figure 1b.

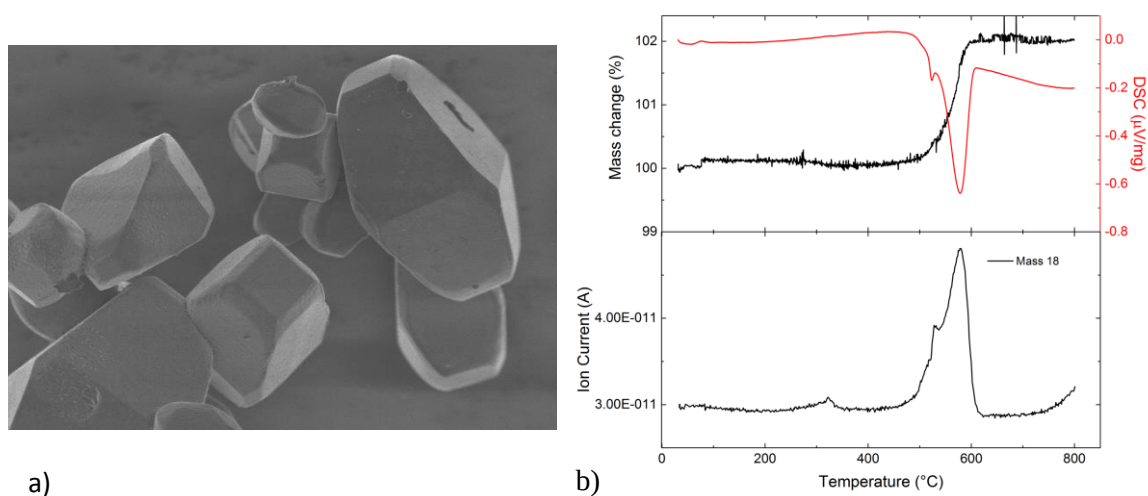


Figure 2: SEM image of single crystals of La_2LiHO_3 and b) MS/DSC and MS of La_2LiHO_3 under O_2 -flow heated at 5 K min^{-1} .

References:

1. H. Schwarz, *Neuartige Hydrid-Oxide der Seltenen Erden: Ln_2LiHO_3 mit $\text{Ln} = \text{La, Ce, Pr}$ und Nd* , Karlsruhe, 1991.
2. G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science*, 2016, **351**, 1314-1317.
3. M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer, M. J. Rosseinsky, C. J. Kiely, S. J. Blundell, I. M. Marshall and F. L. Pratt, *Science*, 2002, **295**, 1882-1884.
4. C. Tassel, Y. Goto, Y. Kuno, J. Hester, M. Green, Y. Kobayashi and H. Kageyama, *Angewandte Chemie International Edition*, 2014, 10377-10380.

Nucleation and growth mechanisms during aqueous chemical solution deposition of oxide thin films

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This poster presents the experimental approach of the FASTS project. *In situ* XRD and *in situ* diffuse reflectance infrared spectroscopy (DRIFTS) is used to determine the nucleation and growth mechanisms during aqueous chemical solution deposition of oxide thin films.

Chemical solution deposition is a well-suited, inexpensive and flexible method to produce oxide thin films on an industrial scale. Additionally, the use of aqueous precursors makes this fabrication method an environmentally friendly choice. The focus of this project is aqueous chemical solution deposition of piezoelectric oxides, and barium titanate (BaTiO_3) is used as a model system to develop the *in situ* methods. The phase development of barium titanate by chemical solution deposition have some distinct features, the precursor develop into the crystalline perovskite phase through the formation of an intermediate oxycarbonate phase[1-3], which is easily observed in both XRD and DRIFTS.

1. Durán, P., et al., *On the formation of an oxycarbonate intermediate phase in the synthesis of BaTiO_3 from (Ba,Ti)-polymeric organic precursors*. Journal of the European Ceramic Society, 2002. **22**(6): p. 797-807.
2. Gablenz, S., et al., *New evidence for an oxycarbonate phase as an intermediate step in BaTiO_3 preparation*. Journal of the European Ceramic Society, 2000. **20**(8): p. 1053-1060.
3. Ischenko, V., et al., *Formation of metastable calcite-type barium carbonate during low-temperature decomposition of (Ba,Ti)-precursor complexes*. Solid State Sciences, 2007. **9**(3-4): p. 303-309.

Lanthanum cobaltite as a novel conducting oxide interconnect in thermoelectrics

Process of extracting energy from different sources and converting it into consumable electrical energy can address most of the energy crises across the world. Use of thermoelectric generators to transform thermal waste energy from furnaces and heaters into electrical energy was known for almost two eras. Metal oxides are potential candidates for thermoelectric applications because of low thermal conductivity, good electrical conductivity, and, high thermal and chemical stability in air. ZT is generally inferior oxide TE, but the stability is better and the negative environmental impact is less. We can improve the ZT value by reducing the thermal conductivity and enhancements in the power factor but the serious drawbacks currently in constructing modules with oxide materials are the high contact resistance at the junction of oxide/metal electrode, cracking/ evaporation during operation cycles and high cost. In order to reduce the cost, to overcome the morphological instability and evaporation in air of the metal interconnect, in this point of view conducting oxides are highly promising candidates, because of their high thermal stability, high resistance to chemical corrosion, good integration with TE oxide and favorable electrical conductivity. Lanthanum cobaltite (LaCoO_3) is a very good example for conducting oxides, with high thermal stability, low cost and catalytic activity close to the noble metal. It is found that alkaline earth doped LaCoO_3 has improved conductivity and it is maximum for LaSrCoO_3 . In addition, due to their high conductivity strontium substituted lanthanum cobaltites LaSrCoO_3 (LSC) have several potential applications as conducting oxide in various fields. So it is very important to study the interaction at the interfaces of thermoelectric module with conducting oxide to produce an outstanding thermoelectric performance.

References

1. Chalasani, S. and J.M. Conrad. *A survey of energy harvesting sources for embedded systems*. in *Southeastcon, 2008. IEEE*. 2008. IEEE
2. Liu, W., et al., *Current progress and future challenges in thermoelectric power generation: From materials to devices*. *Acta Materialia*, 2015. **87**: p. 357-376.
3. Petrov, A.N., et al., *Crystal structure, electrical and magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$* . *Solid State Ionics*, 1995. **80**(3): p. 189-199.

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NcNeutron – Norwegian center for Neutron research

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The neutron scattering facilities at the JEEP II reactor at IFE, Kjeller got the status as National Infrastructure and was granted 31 MNOK by RCN for upgrading in 2015.

NcNeutron currently consists of the powder neutron diffractometers PUS, ODIN and DIFF as well as small-angle neutron scattering instrument SANS. The upgrade program has four major tasks:

- Install a new cold moderator with a optimized design (finished 2019)
- Build a neutron reflectometer, FREJYA (finished 2020)
- Build a neutron imaging/tomography instrument, NIMRA (finished 2019)
- Rebuild the PUS diffractometer to a residual stress scanner, NEST (finished 2020)

The poster presents the status and plans of the upgrade in more detail as well as the new scientific possibilities offered by the upgraded NcNeutron infrastructure.

PHOTOCATHODE FOR SOLID-STATE PHOTOELECTROCHEMICAL CELL

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The need for cheap and environmentally friendly hydrogen production is steadily increasing as the world witness huge investments in e.g. hydrogen-fueled transportation and infrastructure. Several promising hydrogen production technologies are already under development, but are typically immature and further research is needed to obtain viable alternatives to fossil-based fuel production [1].

This project aims to produce a Cu₂O photocathode for use in tandem with a titanium dioxide photoanode to achieve a stand-alone photoelectrocatalytic water vapour-splitting/hydrogen-producing cell. A well-known problem with Cu₂O is its reductive decomposition in illuminated aqueous environments, but by replacing the aqueous electrolytes with solid, proton-conducting polymer membranes we hope to i) separate the anode and cathode compartments, ii) keep the Cu₂O cathode dry, and thereby stable, while at the same facilitating H₂ production.

Deposition and formation of cuprous oxide are achieved by electrodeposition from a 0.2 M CuSO₄ electrolyte on webbed carbon paper in a two-electrode set-up with a constant current of -0.1 mA (galvanostatic) for 3 hours at 30°C. Post-deposition SEM and XRD were used to investigate surface coverage and Cu₂O phase confirmation. Initial electrochemical characterization by linear sweep voltammetry was done in a three-electrode set-up, with a 0.5 M Na₂SO₄ solution, in order to confirm the degrading nature of Cu₂O in aqueous electrolytes.

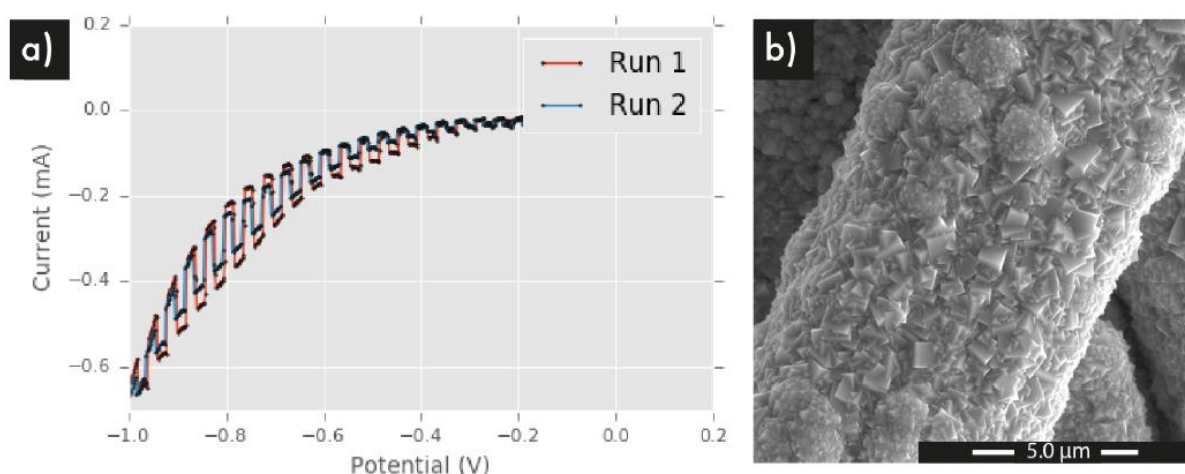


Figure 1: SEM images of deposited Cu₂O on carbon paper. a) Subsequent linear sweep voltammetry runs showing the reductive decomposition of Cu₂O. b) Showing the crystalline nature of the deposited sample.

[1] Dincer, I. Acar, C. Int. J. Hydrogen Energy 40 (2015) 11094–11111.

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Abstract:

Development of new deNO_x technology is still highly topical, as seen from both the “Volkswagen-scandal” in 2015 and ban of diesel-driven vehicles in Oslo winter 2017 due to NO_x emissions during periods of high level of air pollution¹⁻². Copper containing, microporous SAPO-34 has shown great activity concerning selective reduction of NO_x (NH₃-SCR and HC-SCR) and may be thought of as a new possible engine catalyst for NO_x removal³⁻⁷. These catalysts are known to suffer from instability concerning copper addition and deactivation due to coking. The goal of this project is to solve these challenges by developing micro- and mesoporous, copper incorporated SAPO-34 to relieve the mass transfer issues and stabilise copper in the specified zeotype. The developed materials are meant for use in HC-SCR deNO_x, in which copper is a part of the framework, and the mesopores may work as highways for the exhaust.

A hydrothermal synthesis route for copper incorporated, hierarchical SAPO-34 is under development, and preliminary results will be presented. Preliminary results from XRD shows that phase pure CuSAPO-34 has been synthesised with no additional phases. Furthermore the BET surface area and BJH pore size distribution measurements shows that the SAPO-34 contains mesopores, but this must be further investigated and optimised. ICP-MS has been conducted and the copper content is found to be 1.5 wt% and 2.2 wt% in the samples. Ex-Situ XAS has been recorded at the Swiss-Norwegian Beam Line at the ESRF in Grenoble, France in order to obtain information about the local environment of the copper species in the sample.

1. Misje, S. a., Dieselforbud i Oslo fra tirsdag. VG 15.01.2017, 2017.
2. Hotten, R., Volkswagen: The scandal explained. *BBC News* 10.12.2015, 2015.
3. Deka, U.; Lezcano-Gonzalez, I.; Warrender, S. J.; Lorena Picone, A.; Wright, P. A.; Weckhuysen, B. M.; Beale, A. M., Changing active sites in Cu-CHA catalysts: deNO_x selectivity as a function of the preparation method. *Microporous and Mesoporous Materials* **2013**, 166, 144-152.
4. Jakobsen, T. Master Thesis, NTNU, 2014.
5. Lomachenko, K. A.; Borfecchia, E.; Negri, C.; Berlier, G.; Lamberti, C.; Beato, P.; Falsig, H.; Bordiga, S., The Cu-CHA deNO_x Catalyst in Action: Temperature-Dependent NH₃-Assisted Selective Catalytic Reduction Monitored by Operando XAS and XES. *Journal of the American Chemical Society* **2016**, 138 (37), 12025-12028.
6. Moliner, M.; Martínez, C.; Corma, A., Synthesis Strategies for Preparing Useful Small Pore Zeolites and Zeotypes for Gas Separations and Catalysis. *Chemistry of Materials* 2014, 26 (1), 246-258.
7. Wang, D.; Zhang, L.; Kamasamudram, K.; Epling, W. S., In Situ-DRIFTS Study of Selective Catalytic Reduction of NO_x by NH₃ over Cu-Exchanged SAPO-34. *ACS Catalysis* 2013, 3 (5), 871-881.

Exploring the Surface chemistry of Y-doped Barium Zirconate Proton Conducting ceramics

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Segregation of aliovalent dopants on pervovskite oxide (ABO_3) surfaces are crucial to the performance of solid oxide fuel / electrolysis cells. ^[1] In this study, the surface chemistry of a solid proton conductor $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZY10) was investigated using the low energy ion scattering (LEIS) and X-ray photoelectron spectroscopy for proton ceramic electrochemical cell (PCEC) applications. An ~ 5 nm thin layer with Ba and Y segregation was estimated on the surface of BZY10 ceramics. The key reason behind the Y segregation is suggested to be the electrostatic attraction of the negatively charged A-site dopants (Y'_{Zr}) by the positively charged oxygen vacancies and protons enriched at the surface, corresponding to a space charge layer (SCL).

Acknowledgements

The research leading to these results has received funding from Research Council of Norway through the FOXCET (228355) project.

References

[1] N. Tsvetkov, Q. Lu, L. Sun, E.J. Crumlin, B. Yildiz, Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface, *Nature Materials*, 15 (2016) 1010-1016.

BLACK TITANIA NANOTUBE ARRAYS WITH HIGH CAPACITIVE ENERGY STORAGE

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Electrochemical capacitors represent energy storage devices that can act complementarily to rechargeable batteries, with the difference that they can be charged and discharged within seconds. Pseudocapacitors made of metal oxides have higher specific capacitance compared to electrical double-layer capacitors (EDLC), but they suffer from poor conductivity and irreversibility of Faradaic surface reactions [1, 2]. TiO_2 is an extensively studied photocatalyst with poor electrical conductivity under dark conditions, but its electrochemical properties can be remarkably altered by annealing conditions [2].

In this study, thermally reduced TiO_2 nanotubes (Black Titania) were used as electrodes for supercapacitors. UiO's single component hydrogenated TiO_2 nanotubes show metallic-like behavior with high energy and power densities, which are comparable to the state-of-the-art metal oxide composites (Fig. 1 left). They also show very good cycling stability with only 12% reduction in capacitance after 10000 cycles at high current densities (2 mA cm^{-2}).

These findings together with the easiness in controlling the surface area of the TiO_2 nanotube arrays can lead to the development of tunable, high-performance and highly stable supercapacitors.

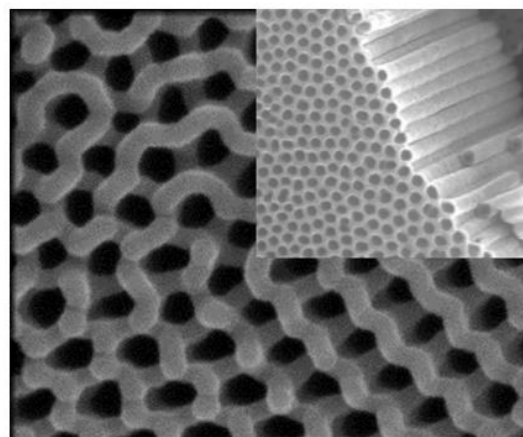
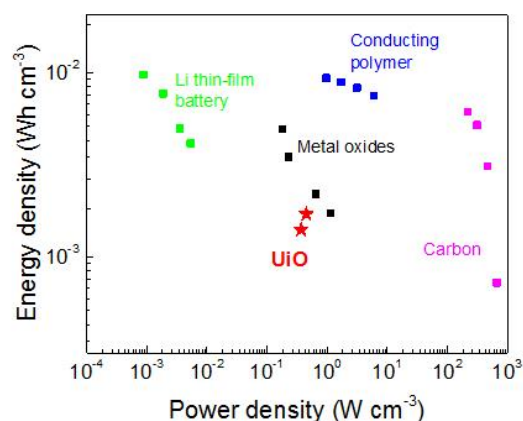


Figure 1: Ragone plot of the state-of-the-art supercapacitors of different materials (left). The UiO single component metal oxide electrodes for supercapacitors are given in red (left). Hydrogenated TiO_2 nanotubes (right).

This project is funded by the Research Council of Norway under the NANO2021 program, project number 239211, “PH2BioCat”.

References

- [1] P. Simon, Y. Gogotsi Nat. Mater. 7 (2008) 845.
- [2] X. Lu, G. Wang, T. Zhai, M. Yu, J. Gan, Y. Tong, Y. Li Nano Lett. 12 (2012) 1690.

Thin films of Amino-functionalized metal-organic frameworks

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Metal-organic frameworks (MOFs) are a class of micro-porous materials with many possible applications. They are traditionally made as powders through solvothermal synthesis. Recently, we have shown that synthesis of MOF thin films is possible through atomic layer deposition (ALD). This has the potential to enable further applications for MOFs for instance in microelectronics where thin films are required, and where solvothermal synthesis is a disadvantage. In order to achieve the full potential of MOF thin films by ALD, we need to be able to functionalize the MOF thin films in a variety of ways similar to what is possible in the bulk form of MOFs. We here present a technique for formation of amino functionalized crystalline MOF thin films through ALD followed by a post deposition crystallization step.

Magnetic properties and structure correlations of novel double perovskite oxides

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The perovskite is a very interesting structure type due to its large flexibility in atomic combinations, permitting a mix of several different oxidation states, and allows structure variations decided by atomic content. In this work, several new Yttrium-based double perovskites has been synthesized, characterized, and investigated for magnetic properties. The La- and Nd-based equivalents of these perovskites have also been investigated to see how properties change as a function of octahedral tilting and bond distances in the perovskite structure.

The perovskite oxides $A_2BB'O_6$ ($A = Y, Nd, La, B = Fe, Co, Ni$) has been synthesized by a wet chemical route, producing products of high homogeneity. For instance, the interesting composition Y_2CoFeO_6 shows a ferro/ferri magnetic like transition just below room-temperature, see figure 1. By comparing properties of several compositions, and considering the electronic states, the mechanism for interaction may be understood to a larger extent than currently done in literature.

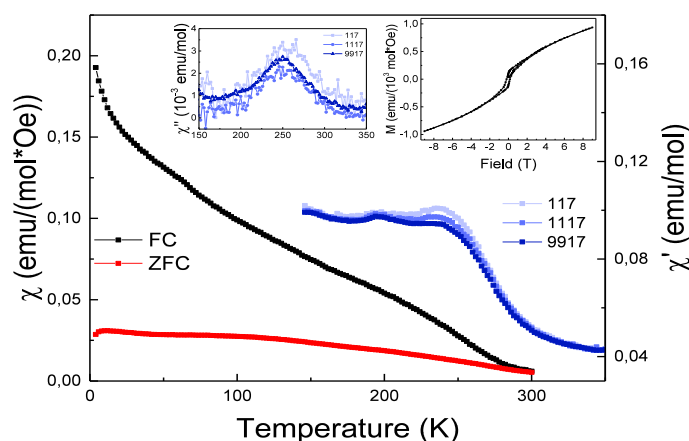
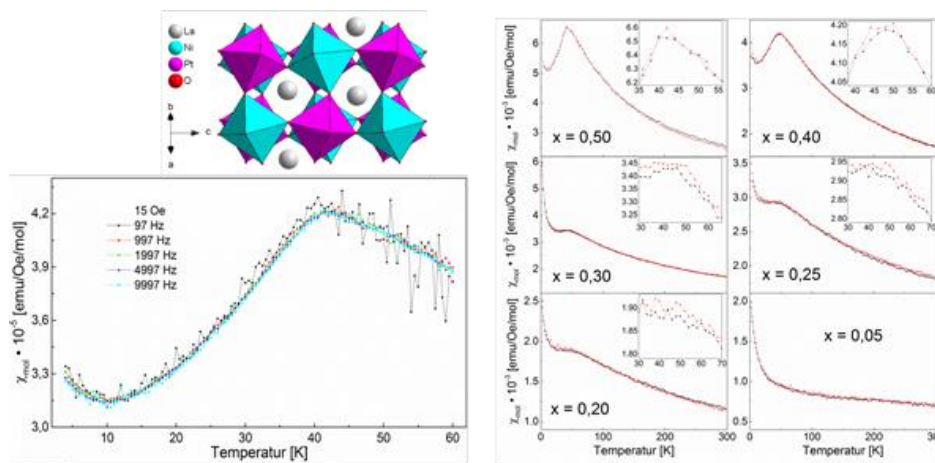


Figure 1.

Magnetic measurements of Y_2CoFeO_6 . ZFC/FC is plotted on the left Y-axis, AC magnetization is on the right Y-axis (real component) and in the inset (imaginary component). Hysteresis at 4K is in the right hand inset.

The stoichiometric material La_2NiPtO_6 is a B-site ordered orthorhombic double perovskite, with an antiferromagnetic transition at 40 K, see figure 2. When the relative amount of Ni is increased, as in $LaNi_{1-x}Pt_xO_3$, the Néel point is approx. the same, but the significance of the transition is lowered, see figure 2. This is due to the thinning of the structurally ordered and magnetic sub-lattice, and we find that the formula $La_2Ni_x^{II}Ni_{1-x}^{III}Pt_x^{IV}O_6$ better describes the real composition of the system.

Figure 2.



Top left: the structure of La_2NiPtO_6 . Bottom left: AC-magnetization measurement of La_2NiPtO_6 .

Right: DC-magnetization measurements of $LaNi_{1-x}Pt_xO_3$.

Positive and negative magneto-resistance effects in layered perovskite $\text{Ca}_4\text{Mn}_3\text{O}_{10}$

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ABSTRACT: $\text{Ca}_4\text{Mn}_3\text{O}_{10}$ belongs to Ruddlesden-popper class and is synthesized by citric acid method. Structural refinement of this phase exhibits orthorhombic layered perovskite structure in space group $Pbca$, with the cell dimensions of $a = 5.255(4) \text{ \AA}$, $b = 5.255(3) \text{ \AA}$, $c = 26.951(8) \text{ \AA}$. Our study indicates that $\text{Ca}_4\text{Mn}_3\text{O}_{10-\delta}$ exhibits a weak ferromagnetic behavior below $T_N = 115 \text{ K}$, which is due to the canting of anti-ferromagnetic sublattice. Moreover, a metal-to-insulator transition at 70 K is observed in the temperature dependent electrical resistivity study. The different electrical resistivity behaviors (metallic; $d\rho/dT > 0$ and insulator; $d\rho/dT < 0$) with respect to temperature depending on their different magnetic spin states. An electric resistivity anomaly (derivative plot) at the magnetic ordering temperature establishes a direct correlation between magnetic and electric order parameters. Interestingly, a positive magneto-resistance effect in the metallic region ($< 70 \text{ K}$) and negative magneto-resistance effect in the insulating region ($> 70 \text{ K}$) are observed. The positive magneto-resistance effect in this system may be attributed to the spin-dependent carrier localization. The negative magneto-resistance effect is due to the minimization of spin-dependent scattering by applied magnetic field. This appears to be a new form of magneto-resistance, differing from previous reports in that it occurs in an undoped, layered bulk perovskite. This unique magneto-resistance switching phenomena observed in $\text{Ca}_4\text{Mn}_3\text{O}_{10-\delta}$ is originated from Mn in non-integral oxidation state i.e, Mn^{3+} and Mn^{4+} induced by the charge compensation effect associated with oxygen vacancies and offers a promising future in various potential applications.

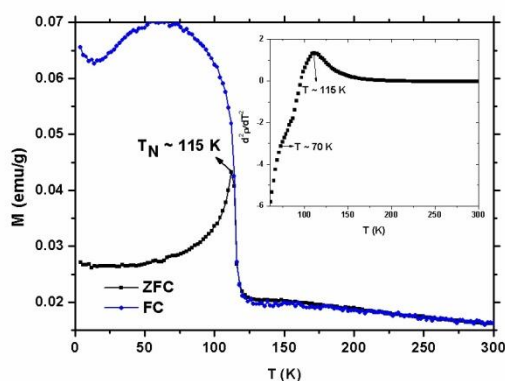


FIG 1. Electrical resistivity anomaly at T_N establishes a direct correlation between magnetic and electric order parameters.

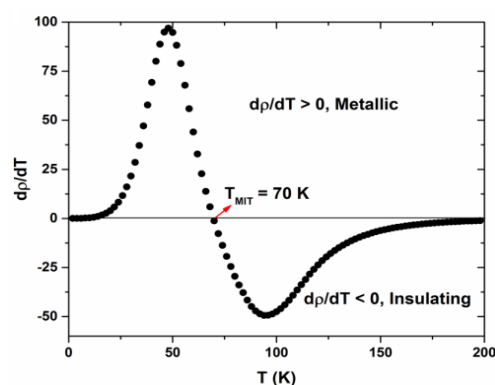


FIG 2. Temperature derivative of electrical resistivity showing MIT transition at 70 K .

References

- [1] P. D. Battle et al., *Chem. Mater.*, vol. 10, pp. 658-664, Jan. 1998.
- [2] P. Manimuthu et al., *Phys. Chem. Chem. Phys.*, vol. 17(27), pp. 17688-17698, Jul. 2015.
- [3] X. X. Zhang et al., *Europhys. Lett.*, vol. 47(4), pp. 487-493, Jun. 1999.

Sb₂MoO₆ as possible anode for lithium and sodium ion batteries

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Mixed metal oxides such as Sb₂MoO₆ and Bi₂(MoO₄)₃ are promising anodes in lithium and sodium ion batteries respectively [1, 2]. Here we investigate Sb₂MoO₆ as a possible anode material for lithium ion batteries. Sb₂MoO₆ was synthesized via solid state reaction by mixing of α-MoO₃ and Sb₂O₃ and heating for 96 h at 650 °C in vacuum. This yielded large crystallites of Sb₂MoO₆, see figure 1 left picture. Furthermore Sb₂MoO₆ was ball milled for 24 h in a 7:3 ration with carbon creating a Sb₂MoO₆:C composite, see figure 1 right. Bulk Sb₂MoO₆ was found crystalline by x-ray diffraction whereas the Sb₂MoO₆:C composite was amorphous. Furthermore we have investigated these materials as anodes in both lithium and sodium batteries.

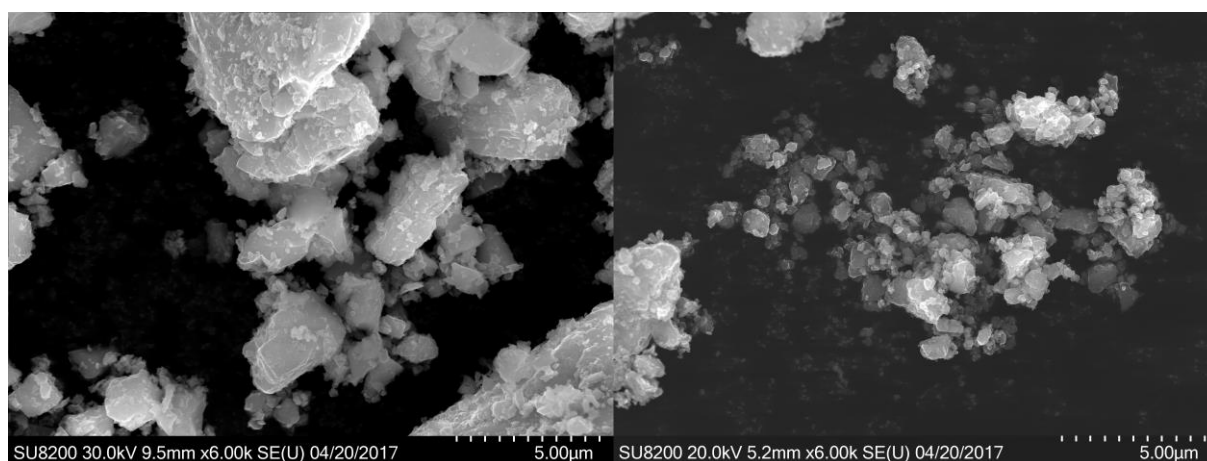


Figure 3: SEM pictures of bulk Sb₂MoO₆, left, and Sb₂MoO₆:C composite, right, magnified 6000 times.

The main goal of this project is to see if there is any benefit with regards to specific capacity and cycling stability by making a Sb₂MoO₆:C composite. Furthermore we would like to understand the mechanisms during dis-/charge of Sb₂MoO₆.

References

1. Sottmann, J., et al., *Bismuth vanadate and molybdate: Stable alloying anodes for sodium-ion batteries*. Chemistry of Materials, 2017.
2. Lu, X., et al., *Synthesis of Hierarchical Sb₂MoO₆ Architectures and Their Electrochemical Behaviors as Anode Materials for Li-Ion Batteries*. Inorganic Chemistry, 2016. 55(14): p. 7012-7019.

New synthetic strategies for novel oxyhydrides

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Oxyhydrides have attracted considerable attention since the first such system was discovered in 2002[1]. The class exhibits a rich structural variability and instances of promising transport properties[2], interesting magnetic and electronic properties. About ten structures have been found, spanning a little more than thirty different compositions containing significant amounts of both oxygen and hydrogen anions intimately mixed in a pure phase. The hunt is on for more of these materials.

An interesting approach is using intercalation of hydride into oxygen vacancies - with compensating anionic or cationic defects - to obtain an oxyhydride from a precursor oxide. Similar approaches have been successful in a precursor defect structure deposited as a thin film[3] and in a bulk structure with crystallographic cage-like features[4]. We will present defect structures that have been tested and more being considered.

1. Hayward, M.A., et al., *The Hydride Anion in an Extended Transition Metal Oxide Array: LaSrCoO₃H_{0.7}*. Science, 2002. **295**(5561): p. 1882-1884.
2. Kobayashi, G., et al., *Pure H⁻ conduction in oxyhydrides*. Science, 2016. **351**(6279): p. 1314-1317.
3. Katayama, T., et al., *Topotactic synthesis of strontium cobalt oxyhydride thin film with perovskite structure*. AIP Advances, 2015. **5**(10): p. 107147.
4. Hayashi, K., et al., *Light-induced conversion of an insulating refractory oxide into a persistent electronic conductor*. Nature, 2002. **419**(6906): p. 462-465.

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