

# INTERNATIONAL SYMPOSIUM ON STRUCTURE-PROPERTY RELATIONSHIPS IN SOLID STATE MATERIALS

 NANTES

**SPSSM2016**  
from July 1<sup>st</sup> to 6<sup>th</sup>



Institut des Matériaux Jean Rouxel  
2 rue de la Houssinière - BP 32229  
44322 NANTES cedex 3 - FRANCE  
[www.cnrs-immn.fr](http://www.cnrs-immn.fr)



UNIVERSITÉ DE NANTES





# Program of oral presentations



**Thursday 30<sup>th</sup>**

**17:00** **Registration**

**Friday 1<sup>st</sup>**

<b>SESSION 1</b>	<b>Material prediction 1</b>	<b>Chairperson : Antoine VILLESUZANNE</b>
------------------	------------------------------	---

**Invited Talks**

- |              |             |  |
|--------------|-------------|--|
| <b>09:00</b> | <b>INV1</b> | <i>Understanding and designing novel materials for energy</i><br><b>Silvana BOTTI</b> , Friedrich-Schiller Universität Jena, Germany |
|--------------|-------------|--|
- |              |             |   |
|--------------|-------------|---|
| <b>09:35</b> | <b>INV2</b> | <i>Defect structure-property relationships in complex functional materials</i><br><b>Khang HOANG</b> , North Dakota State University, USA |
|--------------|-------------|---|

---

**10:10 COFFEE BREAK**

<b>SESSION 2</b>	<b>New materials (mixed anions)</b>	<b>Chairperson : Florent BOUCHER</b>
------------------	-------------------------------------	--

**Invited Talks**

- |              |             |  |
|--------------|-------------|--|
| <b>10:40</b> | <b>INV3</b> | <i>New developments in the chemistry of oxynitride materials</i><br><b>Amparo FUERTES</b> , Institut de Ciència de Materials de Barcelona, Spain |
|--------------|-------------|--|

**Oral Presentations**

- |              |           |  |
|--------------|-----------|--|
| <b>11:15</b> | <b>O1</b> | <i>Novel Oxyhydrides and Oxynitrides via High Pressure Synthesis</i><br><b>Cédric TASSEL</b> , Kyoto University, Japan |
|--------------|-----------|--|
- |              |           |  |
|--------------|-----------|--|
| <b>11:35</b> | <b>O2</b> | <i>Perovskite-related Oxynitride Materials for Visible-light Photocatalysis</i><br><b>François CHEVIRE</b> , Institut des Sciences Chimiques de Rennes, France |
|--------------|-----------|--|
- |              |           |  |
|--------------|-----------|--|
| <b>11:55</b> | <b>O3</b> | <i>Evidence of electrically charged crystal structures, balanced by pair</i><br><b>Olivier MENTRE</b> , Université Nord de France, Villeneuve d'Ascq, France |
|--------------|-----------|--|

---

**12:15 LUNCH**





<b>SESSION 3</b>	<b>Topological insulators and Metal-insulator transition</b>	<b>Chairperson : Roser VALENTI</b>
------------------	--	------------------------------------

#### Invited Talks

**14:00 INV4** *Topology – from the materials perspective*  
**Claudia FELSER**, Max Planck Institute of Chemical Physics for Solids, Germany

#### Oral Presentations

**14:35 O4** *New topological insulators in bismuth-halide systems*  
**Anna ISAEVA**, Dresden University of Technology, Germany

**14:55 O5** *Metal-insulator transition of quadruple perovskite  $\text{EuCu}_3\text{Fe}_4\text{O}_{12}$ . Optical spectroscopy and ab-initio calculations*  
**Benjamin BRIERE**, Université F. Rabelais, France

**15:15 O6** *Topological Property of Structure at Atomic and Electronic Length-scale*  
**Shuiquan DENG**, Chinese Academy of Sciences & Southwest Jiaotong University, China

**15:35 O7** *Interplay between localized and itinerant magnetism in EU-containing pnictides of the  $\text{ThCr}_2\text{Si}_2$  structure type*  
**Michaël SHATRUK**, Florida State University, USA

---

**15:55 COFFEE BREAK**

<b>SESSION 4</b>	<b>Chalcogenides</b>	<b>Chairperson : Stéphane JOBIC</b>
------------------	----------------------	-------------------------------------

#### Invited Talks

**16:25 INV5** *Optical and excitonic properties of 2D materials based on transition metal dichalcogenides*  
**Xavier MARIE**, Université de Toulouse, France

#### Oral Presentations

**17:00 O8** *Phase Change of SnTe Extreme Nano-Wires Encapsulated in Single-Walled Carbon Nanotube*  
**Andrij VASYLENKO**, University of Warwick, UK

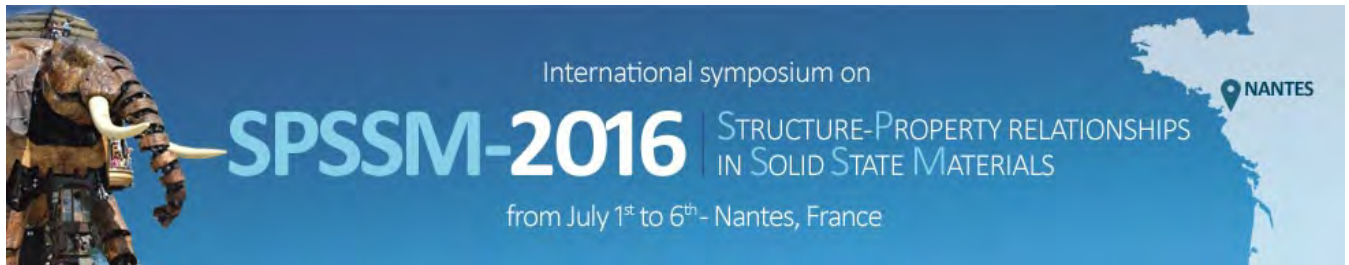
**17:20 O9** *Chemical bonding and reactivity of the layered intergrowth compound  $\text{Ba}_2\text{F}_2\text{S}_2$*   
**Dalel DRISS**, Université de Nantes, France

**17:40 O10** *A Theoretical and Experimental Investigation on Ge-Te-Se glasses by means of Solid-State NMR*  
**Lila BOUESSEL DU BOURG**, Université de Rennes 1, France

**18:00 O11** *Electronic structures of in-plane two-dimensional transition-metal dichalcogenides heterostructures*  
**Wei WEI**, Shandong University, China.

---

**18:30 POSTER SESSION**



**Saturday 2<sup>nd</sup>**

<b>SESSION 5</b>	<b>Magnetism and frustration</b>	<b>Chairperson : Mike WHANGBO</b>
------------------	----------------------------------	---------------------------------------

**Invited Talks**

08:30 INV6	<i>Prospects for topologically non-trivial electronic and magnetic states in correlated kagome lattice materials : an ab initio investigation</i> <b>Roser VALENTI</b> , Goethe-Universität Frankfurt, Germany
------------	---

**Oral Presentations**

09:05 O12	<i>Synthesis and structures of magnetic model systems with competing interactions</i> <b>Angela MOLLER</b> , Johannes Gutenberg-University Mainz, Germany
09:25 O13	<i>Tiny cause with huge impact: polar instability through strong magneto-electric-elastic coupling in bulk EuTiO<sub>3</sub></i> <b>Annette BUSSMANN-HOLDER</b> , Max-Planck-Institute, Germany
09:45 O14	<i>Magnetic frustration of Kagome lattices in M<sup>II</sup>M<sup>III</sup>F<sub>5</sub>(Htz) weberites</i> <b>Marjorie ALBINO</b> , Université du Maine, France

---

**10:05 COFFEE BREAK**

<b>SESSION 6</b>	<b>TCO, optoelectronics</b>	<b>Chairperson : Kazushige UEDA</b>
------------------	-----------------------------	---

**Invited Talks**

10:35 INV7	<i>Transparent conducting materials: insights from hybrid Hartree-Fock density functional calculations</i> <b>Antoine VILLESUZANNE</b> , Univ. Bordeaux, France & University of Bolton, UK
------------	---

**Oral Presentations**

11:10 O15	<i>Theoretical investigation of nitrogen defects in p-type ZnO</i> <b>Xavier ROCQUEFELTE</b> , Université de Rennes 1, France
11:30 O16	<i>Composition induced changes in optical response of Ti<sub>1-x</sub>Si<sub>x</sub>O<sub>2</sub> from first principles calculations</i> <b>Pavel ONDRACKA</b> , Masaryk University, Czech Republic
11:50 O17	<i>Structure – physicochemical property relationships in amorphous alumina</i> <b>Vanessa RIFFET</b> , IPVF & IRDEP, France
12:10 O18	<i>A Study by ab-initio calculation of structural and electronic properties of semiconductor nanostructures based on ZnSe</i> <b>Abderrahim RACHIDI</b> , Mohammedia University Hassan II Casablanca, Morocco

---

**12:30 LUNCH**



<b>SESSION 7</b>	<b>Emerging solar cells</b>	<b>Chairperson : Silvana BOTTI</b>
------------------	-----------------------------	--

#### Invited Talks

**14:00 INV8** *Physical properties of hybrid perovskites for photovoltaics and optoelectronics*  
**Jacky EVEN**, INSA Rennes, France

**14:35 INV9** *Development of mesoscopic p-type metal oxides for solar cell applications: challenges and opportunities*  
**Fabrice ODOBEL**, Université de Nantes, France.

#### Oral Presentations

**15:10 O19** *Inorganic Molybdenum Clusters as light-harvester in all inorganic solar cells : a proof of concept*  
**Adèle RENAUD**, Université de Rennes 1, France

---

**15:30 COFFEE BREAK**

<b>SESSION 8</b>	<b>Phosphors</b>	<b>Chairperson : Khang HOANG</b>
------------------	------------------	--------------------------------------

#### Oral Presentations

**16:00 O20** *Ce<sup>3+</sup>-doped Gd<sub>3</sub>Sc<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> : a new candidate as phosphor for LED-based lighting ?*  
**Géraldine DANTELLE**, Institut Néel, France

**16:20 O21** *Preparation and photo-/cathodo-luminescence of Ln doped CaZrO<sub>3</sub> films*  
**Kazushige UEDA**, Kyushu Institute of Technology, Japan

**16:40 O22** *Crystallographic localization of rare earth atoms by XRD and CTEM for the understanding of the luminescence of AlN:Er<sub>x</sub> (x= 0-6 %) films*  
**Valérie BRIEN**, Université de Lorraine, France

**17:00 O23** *Structural and luminescence properties of EU<sup>3+</sup> and TB<sup>3+</sup> rare earth fluorophosphates with general formula LiY<sub>1+x</sub>(PO<sub>4</sub>)<sub>x</sub>F<sub>4</sub> (x = 2, 3)*  
**Wahida LTAIEF**, Université de Sfax, Tunisie & Université Blaise Pascal, France

**Sunday 3<sup>rd</sup>**

**Sunday Tour**



**Monday 4<sup>th</sup>**

<b>SESSION 9</b>	<b>Material prediction and New materials</b>	<b>Chairperson : Xavier ROCQUEFELTE</b>
------------------	--	---

**Invited Talks**

**09:00 INV10** *Discovering materials with specific effective masses, band gaps and optical properties*  
**Xavier GONZE**, NAPS, Louvain-la-Neuve, Belgique

**Oral Presentations**

**09:35 O24** *Structure and composition of the 200 K-superconducting phase of H<sub>2</sub>S under ultrahigh pressure : the perovskite (SH)(H<sub>3</sub>S<sup>+</sup>)*  
**Juergen KOEHLER**, Max-Planck-Institut, Germany

**09:55 O25** *Towards the real structure of boron-carbide*  
**Karsten RASIM**, Max-Planck-Institut, Germany

**10:15 O26** *First spin-glass behavior of a ternary iron nitride: structure-property relationships in the solid solution Sn<sub>x</sub>Fe<sub>4-x</sub>N (0 ≤ x ≤ 0.9)*  
**Tanja SCHOLZ**, RWTH Aachen University, Germany

**10:35 O27** *Zigzag antiferromagnetic order and orbitally induced hierarchy of exchange interactions in honeycomb compounds A<sub>3</sub>M<sub>2</sub>SbO<sub>6</sub> (A=Li, Na, Ag; M=Ni, Co)*  
**Elena ZVEREVA**, Moscow State University, Russia

---

**10:55 COFFEE BREAK**

<b>SESSION 10</b>	<b>Information storage</b>	<b>Chairperson : Laurent CARIO</b>
-------------------	----------------------------	--

**Invited Talks**

**11:25 INV11** *A chemical (bonding) perspective on phase-change and related materials*  
**Richard DRONSKOWSKI**, RWTH Aachen University, Germany

**12:00 INV12** *From the structural characteristics of the Ge-rich GST phase change materials to the high reliability performances of the PCM devices*  
**Véronique SOUSA**, CEA-LETI, Grenoble, France

---

**12:35 LUNCH**





<b>SESSION 11</b>	<b>Magnetism and spin orbit coupling</b>	<b>Chairperson : Silvia PICOZZI</b>
-------------------	--	---

#### Invited Talks

**14:00 INV13** *Novel interplay of spin-orbit coupling and electron correlations in Ir<sup>4+</sup> complex oxides*  
**Hidenori TAKAGI**, Max-Planck-Institute, Germany & University of Tokyo, Japan

#### Oral Presentations

**14:35 O28** *Ba<sub>2</sub>NiOsO<sub>6</sub> : a possible spin-orbit coupling assisted ferromagnetic semiconductor*  
**Kazunari YAMAURA**, National Institute for Materials Science, Japan

**14:55 O29** *Thermodynamic properties, optical spectroscopy and underlying model in Franciste – type family of compounds Cu<sub>3</sub>RE(SeO<sub>3</sub>)<sub>2</sub>O<sub>2</sub>Cl*  
**Alexander VASILIEV**, M.V. Lomonosov Moscow State University & “MISiS”, Russia

**15:15 O30** *Magnetic state changes in the Co<sub>5-x</sub>Zn<sub>x</sub>TeO<sub>8</sub> spinel family*  
**Nicolas BARRIER**, ENSICAEN, France

**15:35 O31** *Motives of connectivity and spin-orbit interaction in kagome systems*  
**Peter LEMMENS**, TU Braunschweig, Germany

#### 15:55 COFFEE BREAK

<b>SESSION 12</b>	<b>Ferro and multiferroic compounds</b>	<b>Chairperson : Shuiquan DENG</b>
-------------------	---	--

#### Invited Talks

**16:25 INV14** *Soft Chemical Routes to Multiferroic Materials*  
**Mike HAYWARD**, University of Oxford, UK

#### Oral Presentations

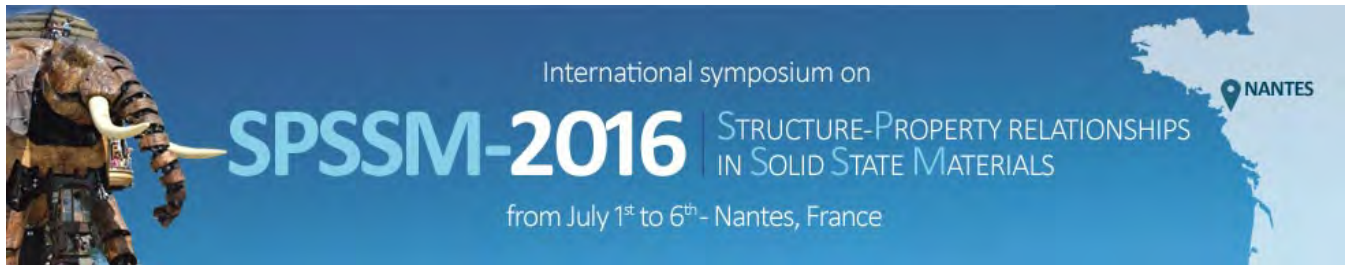
**17:00 O32** *Emergent chiral spin structure and unconventional electronic states in the stacked-kagomé-layered Co<sub>3</sub>Sn<sub>2-x</sub>In<sub>x</sub>S<sub>2</sub> shandites*  
**Mohamed A. KASSEM**, Kyoto University, Japan

**17:20 O33** *Epitaxially-strained GeTe as a prototype material for a microscopic understanding of bulk Rashba properties*  
**Emilie BRUYER**, Université de Rennes 1, France

**17:40 O34** *AMnGe<sub>2</sub>O<sub>6</sub> (A = Ca or Sr) : effect of the divalent cation in the pyroxene structure : how to induce multiferroicity ?*  
**Céline DARIE**, Institut Néel, France

**18:00 O35** *Persistent signature of type-II multiferroicity in nanostructured MnWO<sub>4</sub> ceramics prepared via spark plasma sintering*  
**Pascaline PATUREAU**, University of Bath, UK & IMN Nantes, France

#### 18:30 POSTER SESSION



**Tuesday 5<sup>th</sup>**

<b>SESSION 13</b>	<b>Modelling</b>	<b>Chairperson : Camille LATOUCHE</b>
-------------------	------------------	---

**Invited Talks**

**08:30 INV15** *Bridging first-principles calculations to Mössbauer spectra of defects in semiconductors*  
**José COUTINHO**, University of Aveiro, Portugal

**Oral Presentations**

**09:05 O36** *Describing the magnetic structure and origin of band gap on  $Ba_2CuOsO_6$  system ; density functional theory approach*  
**Changhoon LEE**, North Carolina State University, USA & Pohang University of Science and Technology, Korea

**09:25 O37** *Equation of state for solids*  
**Mike WHANGBO**, North Carolina State University, USA

**09:45 O38** *Structure and properties of mixed cobalt/manganese/iron tin clusters*  
**Tilo SOHNEL**, University of Auckland, New Zealand

---

**10:05 COFFEE BREAK**

<b>SESSION 14</b>	<b>Exotic electronic phenomena</b>	<b>Chairperson : Olivier MENTRE</b>
-------------------	------------------------------------	---

**Invited Talks**

**10:35 INV16** *Relativistic ferroelectrics : a novel class of multifunctional materials*  
**Sylvia PICOZZI**, Consiglio Nazionale delle Ricerche CNR-SPIN, Italy

**11:10 INV17** *High-Throughput Computational Design of Advanced Functional Materials : Topological Insulators and Two-Dimensional Electron Gas Systems*  
**Kesong YANG**, University of California San Diego, USA

**Oral Presentations**

**11:45 O39** *Electronic confinement in materials with artificial periodicity*  
**Ulrike LUDERS**, Ensicaen Université de Caen Normandie, France

---

**12:05 LUNCH**



<b>SESSION 15</b>	<b>New materials and magnetism</b>	<b>Chairperson : Romain GAUTIER</b>
-------------------	------------------------------------	---

#### Invited Talks

**14:00 INV18** *Fluoride-based  $S = \frac{1}{2}$  Kagome Magnets*  
**Philippe LIGHTFOOT**, University of St Andrews, UK

#### Oral Presentations

**14:35 O40** *New cation ordering in high pressure perovskites*  
**Angel M. AREVALO-LOPEZ**, University of Edinburgh, UK

**14:55 O41** *Hydrogen and carbon insertion into CeScSi-type systems*  
**Etienne GAUDIN**, Université de Bordeaux, France

**15:15 O42** *Bi lone-pair induced unusual charge disproportionation of A-site order perovskite  $\text{BiCu}_3\text{Cr}_4\text{O}_{12}$*   
**Masahiko ISOBE**, Max Planck Institute, Germany

**15:35 O43** *Basic properties of  $\alpha$ -,  $\beta$ '- and  $\gamma$ -modifications of  $\text{Mn}_3(\text{PO}_4)_2$*   
**Olga VOLKOVA**, "MISiS" & M.V. Lomonosov Moscow State University, Russia

---

**15:55 COFFEE BREAK**

<b>SESSION 16</b>	<b>Photocatalysis</b>	<b>Chairperson : Juergen KOEHLER</b>
-------------------	-----------------------	--

#### Invited Talks

**16:25 INV19** *"Soft" photocatalysis : 2D frameworks as platforms for light-driven hydrogen evolution*  
**Bettina LOTSCH**, Max Planck Institute Stuttgart & University of Munich, Germany

**17:00 INV20** *Nano-bio Photocatalyst for Hydrogen Evolution*  
**Peng WANG**, Shandong University, China & Argonne National Lab., USA

#### Oral Presentations

**17:35 O44** *Semiconductor heterojunctions for Enhanced Photocatalytic Activity*  
**Abdou LACHGAR**, Wake Forest University, USA

**17:55 O45** *Silver silicate photocatalysts with strong visible light absorption and high charge separation efficiencies*  
**Zeyan WANG**, Shandong University, China

---

**20:00 GALA DINNER**



**Wednesday 6<sup>th</sup>**

<b>SESSION 17</b>	<b>Energy 1</b>	<b>Chairperson : Baibiao HUANG</b>
-------------------	-----------------	--

**Invited Talks**

**08:30 INV21** *Proton conductors : from quantum to classical*  
**Gregory GENESTE**, CEA Arpajon, France

**Oral Presentations**

**09:05 O46** *Surface reactivity of layered lithium oxides used as cathode materials : a coupled experimental-theoretical study*  
**Germain VALLVERDU**, Université de Pau et des Pays de l'Adour, France

**09:25 O47** *Understanding paramagnetic battery materials through combined NMR/DFT studies*  
**Dany CARLIER**, Argonne National Laboratory, USA

**09:45 O48** *The  $\gamma/\gamma$  Cathode Materials in the  $\text{Li/V}_2\text{O}_5$  system : Spectroscopic and computational study of the lithiation-induced structure variations*  
**Rita BADDOUR-HADJEAN**, Université Paris Est-Créteil, France

---

**10:05 COFFEE BREAK**

<b>SESSION 18</b>	<b>Energy 2</b>	<b>Chairperson : Abdou LACHGAR</b>
-------------------	-----------------	--

**Invited Talks**

**10:35 INV22** *Thermoelectrics – a challenge for crystallography and solid-state chemistry*  
**Olivier OECKLER**, Leipzig University, Germany

**Oral Presentations**

**11:10 O49** *Structure and properties of pristine and iron-substituted thermoelectric tetrahedrites*  
**Andrei SHEVELKOV**, Lomonosov Moscow State University, Russia

**11:30 O50** *Iron oxalates as novel electrode materials for Li-ion and Na-ion batteries*  
**Wenjiao YAO**, University of St Andrews, UK

**11:50 O51** *Anode Materials Design for Lithium-Ion and Sodium-Ion Batteries*  
**Qilong SUN**, Shandong University, People's Republic of China

**12:10 O52** *Electronic Properties of Layered Materials and Phase Change in Lithium Ion Batteries*  
**Hong Seok KANG**, Jeonju University, South Korea



## Understanding and designing novel materials for energy

Silvana Botti<sup>a</sup>

<sup>a</sup> Friedrich-Schiller Universität Jena, Germany

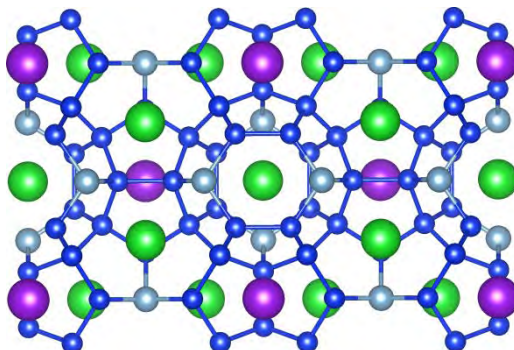
email address of the presenting author: silvana.botti@uni-jena.de

I will present an overview of our most recent theoretical and computational developments and some examples of their application to calculate from first-principles the structural and electronic properties of materials for energy production, storage, and saving.

The systems we are interested in are varied, ranging from thin-films absorbers and transparent conductive oxides for solar cells, to thermoelectrics, light-weight materials, and complex hydrides for on-board hydrogen storage.

Nowadays, *ab initio* approaches based on density functional theory ally accuracy and efficiency, which make them suitable for understanding the physics not only of simple bulk crystals, but also of nanostructures, crystals with defects, doped crystals, interfaces, alloys, etc. As a consequence, *ab initio* calculations are finally able to analyse the "real" samples measured in experiments, allowing accurate comparisons of both ground-state and excited-state properties.

Moreover, *ab initio* methods can be used together with structural prediction algorithms and evolutionary algorithms to solve the inverse problem, i.e. find the best material for a specific application, providing a precious guide for experimental search of novel materials.



- [1] *Stability and electronic properties of new inorganic perovskites from high-throughput ab initio calculations*, S. Körbel, M.A.L. Marques, and S. Botti, *J. Mater. Chem. C* **4**, 3157-3167 (2016).
- [2] *Prediction and synthesis of a non-Zintl silicon clathrate*, T.F.T. Cerqueira, S. Pailhès, R. Debord, V.M. Giordano, R. Viennois, J. Shi, S. Botti, and M.A.L. Marques, accepted in *Chem. Mater.* (2016).
- [3] *Low-density silicon allotropes for photovoltaic applications*, M. Amsler, S. Botti, M.A.L. Marques, T. J. Lenosky, and S. Goedecker, *Phys. Rev. B* **92**, 014101 (2015).
- [4] *Prediction of Stable Nitride Perovskites*, R. Sarmiento-Pérez, T.F.T. Cerqueira, S. Botti, and M.A.L. Marques, *Chem. Mater.* **27**, 5957-5963 (2015).
- [5] *Materials design on-the-fly*, T.F.T. Cerqueira, R. Sarmiento-Pérez, M. Amsler, F. Nogueira, S. Botti, and M.A.L. Marques, *J. Chem. Theory Comput.* **11**, 3955-3960 (2015).
- [6] *Identification of novel Cu, Ag, and Au ternary oxides from global structural prediction*, T.F.T. Cerqueira, S. Lin, M. Amsler, S. Goedecker, S. Botti, and M.A.L. Marques, *Chem. Mater.* **27**, 4562-4573 (2015).

# DEFECT-STRUCTURE-PROPERTY RELATIONSHIPS IN COMPLEX FUNCTIONAL MATERIALS

Khang Hoang

*Center for Computationally Assisted Science and Technology,  
North Dakota State University, Fargo, ND 58108, USA*

e-mail: khang.hoang@ndsu.edu

Functional materials such as those for energy-related and optoelectronic applications are often structurally and chemically complex compounds, where intrinsic point defects and impurities can be essential or detrimental to the materials' performance. A detailed understanding of the defect physics and chemistry in these materials is thus crucial for explaining, predicting, and optimizing their properties, and ultimately for rational design of materials. First-principles calculations have been proven to be an important tool in providing such an understanding.

In this talk, I will explore the relationship between defect structure and property in different functional materials, based on recent research results using first-principles defect calculations. Specific examples to be discussed involve delithiation and electronic conduction mechanisms in complex oxides for lithium-ion battery electrodes [1,2], optical rare-earth (RE) centers in RE-doped wide band-gap semiconductors for optoelectronics [3], and reaction products and pathways in the thermal decomposition of complex hydride hydrogen storage materials [4].

## References

- [1] K. Hoang, Phys. Rev. Appl. 3 (2015) 024013.
- [2] K. Hoang and M. Johannes, Chem. Mater. 28 (2016) 1325.
- [3] K. Hoang, Phys. Stat. Solidi RRL 9 (2015) 722.
- [4] K. Hoang, A. Janotti, and C. G. Van de Walle, Phys. Rev. B 85 (2012) 064115.

# NEW DEVELOPMENTS IN THE CHEMISTRY OF OXYNITRIDE MATERIALS

Amparo Fuertes

*Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain.*

amparo.fuertes@icmab.es

The introduction of nitrogen in oxidic compounds involves changes in the electronic structure affecting the physical properties. The lower electronegativity and higher polarizability of nitrogen increases the bond covalency decreasing the interelectronic repulsion. The larger electrical charge of nitride increases the crystal field splitting and the polarization. (1) Anion order may influence the physical properties and is driven by the different charge of oxide and nitride and by covalency. (2) In recent years new important oxynitride materials have been reported showing photocatalytic, dielectric and magnetic properties and orange-red luminescence. Nitrogen doping modifies the properties of oxides, for example tuning the bandgap of the photocatalyst CeO<sub>2</sub> from the UV to the visible range, and changing the redox properties and anion vacancies of ceria. (3) Nitride introduction in antiferromagnetic lanthanide chromites RCrO<sub>3</sub> induces the oxidation of Cr<sup>3+</sup> to Cr<sup>4+</sup> and decreases the Néel temperature but far less drastically than cation doping. This is a consequence of the greater covalency of Cr-N bonds showing that nitride enhances magnetic interaction strengths compensating for the reduction in T<sub>c</sub> due to hole doping. (4) Eu or Ce doped nitride-based silicates are important luminescent materials for applications in LED's. They show longer emission wavelengths than the oxysilicates because of larger covalency and crystal field splitting. The new family of oxynitridosilicates LnMSiO<sub>3</sub>N (Ln=Lanthanide, M=Alkaline earth, Eu) with beta-K<sub>2</sub>SO<sub>4</sub> structure show red luminescence under excitation in the UV-blue range and ferromagnetism at low temperatures (for M=Eu). (5, 6) They represent one of the few examples of oxynitride orthosilicates with isolated [SiO<sub>3</sub>N]<sup>5-</sup> groups and show partial anion order. This lecture will present different aspects of the research in functional oxynitrides focussing on the relationships between the synthesis conditions, the oxidation states of the cations, the nitrogen contents, the ordering of anions and the physical properties.

## References

- [1] A.Fuertes, Mat. Hor. 2 (2015) 453.
- [2] M.Yang, J.Oró-Solé, J.A. Rodgers, A. B. Jorge, A.Fuertes, and J. P.Attfield, Nat. Chem., 3 (2011), 47.
- [3] A. B. Jorge, Y.Sakatani, C.Boissière, C.Laberty-Roberts, G.Sauthier, J.Fraxedas, C.Sanchez, and A.Fuertes, J. Mat. Chem. 22 (2012), 3220.
- [4] A.P.Black, H.E.Johnston, J.Oró-Solé, B.Bozzo, C.Ritter, C.Frontera, J.P.Attfield and A.Fuertes, Chem. Comm. 52 (2016), 4317.
- [5] A.P. Black, K.A. Denault, J. Oró-Solé, A.R. Goñi and A.Fuertes, Chem. Comm. 51 (2015), 2166.
- [6] A.P. Black, K.A. Denault, C.Frontera, R.Seshadri, A.R. Goñi and A.Fuertes, J. Mat. Chem. C 3 (2015), 11471.

## Novel Oxyhydrides and Oxynitrides via High Pressure Synthesis

Cédric Tassel<sup>a</sup>, Yoshinori Kuno, Daichi Watabe, Hiroshi Kageyama

<sup>a</sup>Dept. of Energy & Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Email address of the presenting author: cedric@scl.kyoto-u.ac.jp

Mixed anionic perovskites containing the oxide anion and other elements such as F<sup>-</sup>, H<sup>-</sup>, N<sup>3-</sup>, S<sup>2-</sup>, Cl<sup>-</sup> or Br<sup>-</sup> are fascinating materials with numerous functional properties. These properties greatly differ from simple oxides as substituting O<sup>2-</sup> with different elements not only impacts the structure but also the band gap, the electronic properties, magnetic interactions and catalytic activities. And although these structures are worth of interest, numerous synthetic challenges exist which limits their development.

Our recent work has focused on using the high-pressure synthesis technique towards this aim. For instance, we used this approach to prepare a stoichiometric SrCrO<sub>2</sub>H structure (Fig. 1) that contains both the O<sup>2-</sup> and H<sup>-</sup> anions and cannot be obtained under ambient condition. This unexpected structure display one of the highest magnetic ordering temperature up to ~380 K, that is, higher than previously reported isoivalent ACrO<sub>3</sub> structures.

We further extended this research to oxynitride materials in order to prepare structures that cannot be obtained via classical high temperature ammonolysis and obtained MnTaO<sub>2</sub>N (Fig. 2). This compound crystallizes in a LiNbO<sub>3</sub>-type structure, previously unobserved in oxynitrides. Unlike most isostructural oxides (ScFeO<sub>3</sub>, MnTiO<sub>3</sub>, FeTiO<sub>3</sub>), which present weak ferromagnetic features, MnTaO<sub>2</sub>N exhibit an incommensurate magnetic ordering below 28K.

In this talk, we will discuss the synthesis and structure of these novel mixed anion phases prepared via the high-pressure and high-temperature technique and discuss the impact of the presence of H<sup>-</sup> and N<sup>3-</sup> on the superexchange interaction.

### Reference:

- [1] C. Tassel, et al. *Angew. Chemie Int. Ed.*, 53, 39 (2014), 10377–10380.  
 [2] C. Tassel, et al. *Angew. Chemie Int. Ed.*, 54, 2 (2015), 516–521.

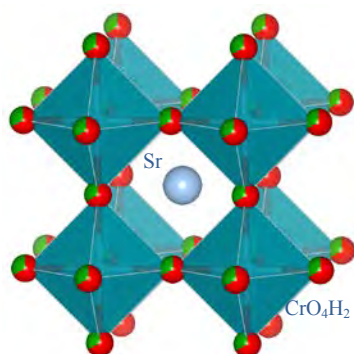


Figure 1. The structure of SrCrO<sub>2</sub>H.

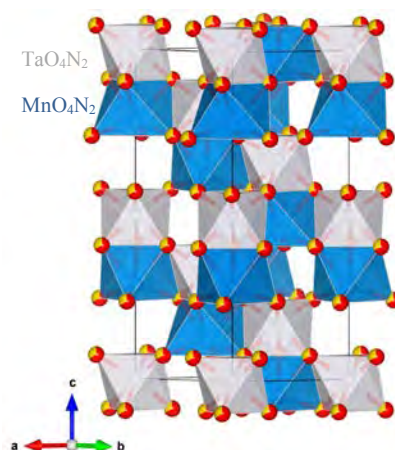


Figure 2. The structure of MnTaO<sub>2</sub>N.



## Perovskite-related Oxynitride Materials for Visible-light Photocatalysis

François Chevire, Ary Da Silva Maia\*

UMR CNRS 6226 Institut des Sciences Chimiques de Rennes (ISCR), Université de Rennes 1,  
35042 Rennes, France

\* LACOM - Departamento de Química, Universidade Federal da Paraíba, Cidade Universitária,  
João Pessoa, PB, CEP 58051-900, Brasil

francois.chevire@univ-rennes1.fr

Recently, much further attention has been paid to functional (oxy)nitrides as emerging material for environmental and energy applications considering the specific tuning properties offered by the nitrogen/oxygen substitution. For instance, as a less electronegative element than oxygen, insertion of nitrogen within the crystal structure of an oxide will greatly influence its covalency as well as its optoelectronic properties. In the case of photocatalytic materials, that would induce a redshift of the optical absorption into the visible range by tuning the optical gap and thus allowing harvesting of solar light to induce chemical reactions.  $\text{LaTiO}_2\text{N}$  or  $\text{BaTaO}_2\text{N}$  and their derivatives have been so far the most studied compounds among the  $d^0$  metal based oxynitride perovskites in order to improve both photoreduction and photooxidation activities under visible irradiation. On the other hand, while layered oxide materials have shown promising photocatalic behavior, very little is reported on layered oxynitrides materials. In the current work, we report the synthesis, characterizations and optical properties of novel B-site substituted  $\text{LaTiO}_2\text{N}$  perovskites - i.e.  $\text{La}(\text{M},\text{Ti})(\text{O},\text{N})_3$  where M is a  $d^{10}$  element (Zn or Ga) as well as of a new oxynitride Ruddlesden-Popper oxynitride ( $\text{K}_{1+x}\text{Ca}_2\text{Nb}_3\text{O}_{10-x}\text{N}_x$ ) and its protonated counterpart.

## EVIDENCE OF ELECTRICALLY CHARGED CRYSTAL STRUCTURES, BALANCED BY PAIR

Olivier Mentre<sup>a</sup>, Ignacio Blasquez-Alcover<sup>a</sup>, Marielle Huvé<sup>a</sup>, Susana Garcia-Martin<sup>b</sup>, Alain Wattiaux<sup>c</sup>, Mathieu Duttine<sup>c</sup>, Sylvie Daviero-Minaud<sup>a</sup>

<sup>a</sup> UCCS UMR CNRS 8181, Université Nord de France, Villeneuve d'Ascq, France

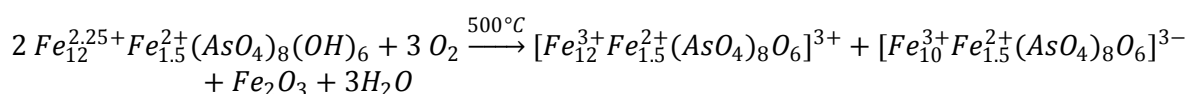
<sup>b</sup> Computense University of madrid, Spain

<sup>c</sup> ICMCB, UPR CNRS 9048, Université de Bordeaux, Pessac France

olivier.mentre@ensc-lille.fr

Following the discovery of the easy and reversible -Fe exsolution out of the 2D- $BaFe_2(PO_4)_2$  into a series of ordered iron-deficient  $BaFe_{2-x}(PO_4)_2$  (x up to 2/3) phases, we have continued our research for new adequate ferrous lattices for Fe-exsolution [1].

We have discovered the new phase  $Fe^{2+/3+}_{13.5}(AsO_4)_8(OH)_6$  with an original mixed valent framework phase intermediate between the lyonsite-type [2] and the  $M_{11}\square_1(HPO_3)_8(OH)_6$  phosphite compounds [3]. This phase, presents a topochemical structural transformation never reported before: upon mild oxidation, it transforms into a composite network made by two different 3D-charged phases  $A^{n+}$  (50%) and  $B^{n-}$  (50%) imbricated at the nanometric scale. The periodicity of each A and B sub-phases is preserved along the common hexagonal c-axis, due to strong cation-ion interactions but alternate in the (a,b) plane. The transformation consists of the deshydroxylation of the parent compound, and a partial Fe-exsolution written:



It results in an oxidation process where only common  $Fe^{2+}$  columns are preserved as templating units in both sub-phases. To our knowledge this observation is unique since it involves charged lattices that balance their charge by an intimate mixing. *In fine* we show here the existence of charged crystal structures, for the first time.

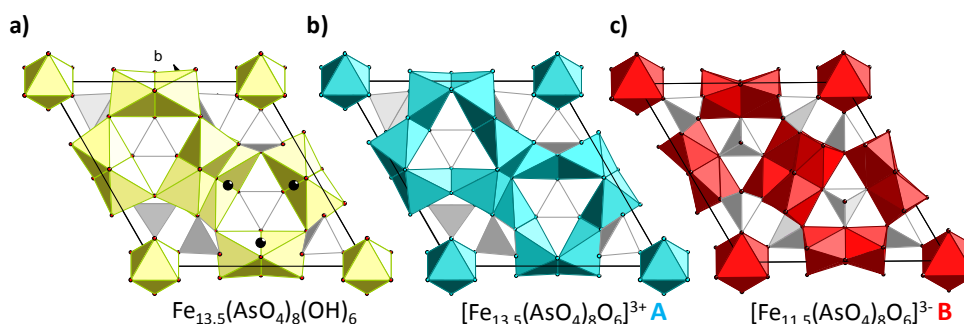


Figure 1 : Fragments of the crystal structure of the pristine (a) and imbricated charged products of reactions (b, c).

- [1] a) R. David, *et al.*, *Angew. Chem., Int. Ed.*, 53 (2014), 13365–13370. b) I. Blasquez-Alcover, *et al.*, *Cryst. Growth Des.* 15 (2015), 4237–4247. c) I. Blasquez-Alcover, *et al.*, *Inorg. Chem.*, 54 (2015), 8733–8743  
 [2] P. Jared. *et al.*, *Solid State Sciences*, 10 (2008) 396–400.  
 [3] J.P. Attfield *et al.*, *Acta Cryst. C*- 50 (1994) 981.

## TOPOLOGY – FROM THE MATERIALS PERSPECTIVE

Claudia Felser<sup>a</sup>, Binghai Yan<sup>a</sup>, Chandra Shekhar<sup>a</sup>

<sup>a</sup>Max Planck Institute of Chemical Physics for Solids, Dresden, 01187, Germany

email address of the presenting author: felser@cpfs.mpg.de

Topological insulators (TIs), Weyl and Dirac Semimetals are a new quantum state of matter, which have attracted interest of condensed matter science. Heusler compounds are a remarkable class of materials with more than 1,000 members and a wide range of extraordinary multifunctionalities [1] including tunable topological insulators (TI) [2]. Many of these ternary zero-gap semiconductors in Heusler compounds (LnAuPb, LnPdBi, LnPtSb and LnPtBi) contain the rare-earth element Ln, which can realize additional properties ranging from superconductivity (for example LaPtBi) to magnetism (for example GdPtBi) and heavy fermion behavior (for example YbPtBi). These properties can open new research directions in realizing the quantized anomalous Hall Effect and topological superconductors. C1b Heusler compounds have been grown as single crystals and as thin films. The control of the defects, the charge carriers and mobilities can be optimized [3]. The band inversion is proven by ARPES [4]. Dirac cones and Weyl points can occur at the critical points in the phase diagrams of TI, first Heusler compounds were identified [5]. GdPtBi and other magnetic topological family members break time reversal symmetry in an external magnetic field and develop Weyl points and show the corresponding transport properties [5].

Weyl points, a new class of topological phases was also predicted in NbP, NbAs and TaP [6-9]. The the magneto-transport properties of NbP show a large magnetoresistance of 850,000% at 1.85 K (250% at room temperature) in a magnetic field of up to 9 T, without any signs of saturation, and an ultrahigh carrier mobility of  $5 \cdot 10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  that accompanied by strong Shubnikov–de Haas (SdH) oscillations [6]. We founds also ultrahigh magneto resistance, mobilities and Fermi arcs in NbP TaAs and TaP [7-10]. Depending from the structure MoTe2 is a Weyl semimetal [11,12], which become superconducting under pressure [13]. More emerging quantum properties and potential applications will be discussed.

### References:

- [1] Tanja Graf, Stuart S. P. Parkin, and Claudia Felser, Progress in Solid State Chemistry 39 (2011) 1
- [2] S. Chadov, X. Qi, J. Kübler, G. H. Fecher, C. Felser, S.-C. Zhang, Nature Mater. 9 (2010) 541
- [3] C. Shekhar, S. Ouardi, A. K. Nayak, G. H. Fecher, W. Schnelle, C. Felser Phys. Rev. B 86 (2012) 155314
- [4] Z. K. Liu, L. X. Yang, S. -C. Wu, B. Zhou, Y. Zhang, S. -K. Mo, Z. Hussain, Z. X. Shen, B. H. Yan, Chandra Shekhar, C. Felser and Y. L. Chen, Nature Com. (2016) accepted preprint arXiv:1602.05633
- [5] C. Shekhar, et al. preprint: arXiv: 1604.01641
- [6] C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Wosnitza, W. Schnelle, H. Borrmann, W. Schnelle, J. Grin, C. Felser, B. Yan, Nature Physics 11 (2015) 645
- [7] Frank Arnold, C. Shekhar, et al., Nature Com. accepted preprint arXiv: 1506.0657
- [8] L. Yang, et al., Nature Physics 11 (2015) 728
- [9] Z. K. Liu, L. X. Yang, Y. Sun, T. Zhang, H. Peng, H. F. Yang, Y. Zhang, Y. F. Guo, P. Dharmalingam, Z. Hussain, S.-K. Mo, M. Schmidt, C. Felser, B. Yan and Y. L. Chen, Nature Materials 15 (2016) 27
- [10] J. Klotz, et al., Phys. Rev. B 93 (2016) 121105(R)
- [11] J. Jiang, et al., preprint: arXiv: 1604.00139
- [12] Yan Sun, et al., Physical Review B 92 (2015) 161107(R),
- [13] Yanpeng Qi, et al., Nature Com. 7 (2016) 11038

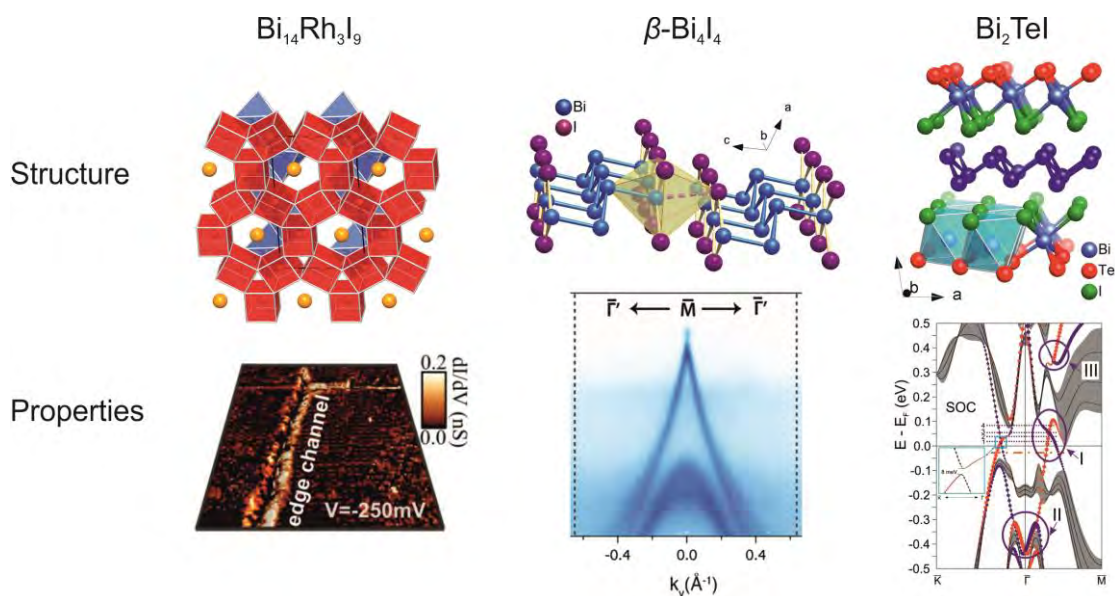
# NEW TOPOLOGICAL INSULATORS IN BISMUTH-HALIDE SYSTEMS

Anna Isaeva<sup>a</sup>, Bertold Rasche<sup>a</sup>, Thomas Doert<sup>a</sup>, Michael Ruck<sup>a</sup>  
<sup>a</sup> *Institute of Inorganic Chemistry II, Dresden University of Technology,  
 Bergstr. 66, D-01069, Dresden, Germany*

anna.isaeva@tu-dresden.de

Topological insulators (TI) are a new class of materials with peculiar surface properties that open new prospects for spin transport. These bulk semiconductors host metallic states at their surfaces that are immune to backscattering [1] due to the specific symmetries of the band-structure and could thus transmit information without dissipation. Topological insulators and related materials are envisioned as promising candidates for innovative data storage and quantum bits. Since 2009 the outmost explored pool of TI materials has been limited to  $\text{Bi}_2\text{Te}_3$  and related materials; therefore a task of finding new candidates is of great importance.

The present contribution reports some highlights of our quest for new topological materials among bismuth-rich halides. Employing the concept of “confined metals” we have established rough guidelines [2] toward the directed search of new topological insulators based on crystal-structure features. 3D topological insulators can have layered and quasi-one-dimensional crystal structures with 2D topological fragments interlaced by trivial spacers. This approach has by now yielded two 3D weak topological insulators ( $\text{Bi}_{14}\text{Rh}_3\text{I}_9$  [3–5],  $\text{Bi}_2\text{TeI}$  [6,7]) and a 3D strong topological insulator,  $\beta\text{-Bi}_4\text{I}_4$  [8].



## References:

- [1] M.Z. Hasan, C. L. Kane, *Rev. Mod. Phys.* 82 (2010), 3045–3067.
- [2] A. Isaeva, B. Rasche, M. Ruck, *Phys. Stat. Solidi RRL*, 1–2 (2013), 39–45.
- [3] B. Rasche, A. Isaeva, M. Ruck, S. Borisenko, V. Zabolotnyy, B. Büchner, K. Koepnick, C. Ortix, M. Richter, J. van den Brink, *Nat. Mater.* 12 (2013), 422–425.
- [4] B. Rasche, A. Isaeva, W. Van den Broek, M. Kaiser, A. Gerisch, U. Kaiser, Ch. Koch, M. Ruck, *Chem. Mater.* 25 (2013), 2359–2364.
- [5] C. Pauly et al., *Nat. Phys.* 11 (2015), 338–343.
- [6] P. Tang, B. Yan, W. Cao, S.-C. Wu, C. Felser, W. Duan, *Phys. Rev. B* 89 (2014), 041409.
- [7] I.P. Rusinov et al., *Sci. Rep.* 6 (2016), 20734.
- [8] G. Autès et al., *Nat. Mater.* 15 (2016) 154–158.



# Metal-insulator transition of quadruple perovskite $\text{EuCu}_3\text{Fe}_4\text{O}_{12}$

## Optical spectroscopy and *ab-initio* calculations.

B. Brière<sup>1</sup>, A. Kalinko<sup>2</sup>, I. Yamada<sup>3</sup>, P. Roy<sup>2</sup>, J.B. Brubach<sup>2</sup>, R. Sopracase<sup>1</sup>, M. Zaghrioui<sup>1</sup>, and V. Ta Phuoc<sup>1</sup>

<sup>1</sup> GREMAN, CNRS UMR 7347-CEA, Université F. Rabelais, UFR Sciences, Parc de Grandmont, Tours, 37200, France

<sup>2</sup> Synchrotron Soleil, Université Paris-Saclay, L'Orme des Merisiers, 91190 Saint-Aubin, France

<sup>3</sup> Nanoscience and Nanotechnology Research Center, Osaka Prefecture University Sakai, Osaka 599-8570, Japan

The unique structures and the great variety of composition of the quadruple perovskites  $\text{LnCu}_3\text{Fe}_4\text{O}_{12}$  (Ln = Lanthanides) provide them many intriguing functional properties. On one hand, small size rare earth ion compounds (Ln = Dy, Ho, Er, Tm, Yb and Lu) exhibit an iron charge-disproportionation accompanied by a paramagnetic-metal to a ferrimagnetic-semiconductor transition. On the other hand, large size rare earth ions family (Ln = La, Pr, Nd, Pm, Sm, Eu, Gd and Tb) undergoes an intermetallic charge transfer leading to a paramagnetic-metal to an AFM-insulator phase transition accompanied by a negative thermal expansion.

The optical properties of quadruple perovskite  $\text{EuCu}_3\text{Fe}_4\text{O}_{12}$  have been measured from 150K to room temperature. At 240K, the compound exhibits a metal to insulator transition (MIT) accompanied by an antiferromagnetic ordering and an abrupt augmentation of the unit cell volume without any lowering of symmetry. Above the MIT temperature, the optical conductivity shows a bad metal behavior whereas below, the compound has an insulating behavior with an electronic gap of 125 meV. In addition, we observed, at the transition, a large and abrupt spectral weight transfer toward an energy scale larger than 1 eV. *Ab-initio* calculations (DFT+U) shows that the evolution of the optical properties at the MIT is linked to a charge transfer between the  $3d$  orbitals of iron and the  $3d_{xy}$  orbitals of copper in good agreement with experimental results.

# Topological Property of Structure at Atomic and Electronic Length-scale

S. Deng,<sup>a,b\*</sup> Y. Zhang,<sup>b</sup> J. Köhler,<sup>c</sup>

<sup>a</sup>Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, China

<sup>b</sup>Key Laboratory of Advanced Technology of Materials, (Ministry of Education) Superconductivity and New Energy R&D Center (SRDC), Mail stop 165#, Southwest Jiaotong University, Chengdu, 610031, China

<sup>c</sup>Max-Planck Institute for Solid State Research, Heisenbergstr. 1, 70569, Stuttgart, Germany

S.Deng, Email: sdeng@fjirsm.ac.cn,

In the last few years, topology related properties such as quantum Hall effect and in particular topological insulators have been intensively and comprehensively studied in condensed matter sciences. Topological insulators(TI) have both gapless boundary states and fully gapped bulk states. This robust characteristic protected by time-reversal symmetry renders a number of potential applications in spintronics, quantum computing technology etc. On the other hand, these novel materials provide scientists with new platform for testing many new physical theories such as axions, magnetic monopoles, Majorana particles etc. Recently, we have studied a large gap insulator( $\sim 5.9$  eV),  $\text{BiYO}_3$ , which has a cubic fluorite structure [1] and a perovskite structural variant theoretically predicted as a TI [2]. In this work we show why this prediction is groundless. Length-scale dependent topological properties in other systems such as those for  $\text{Bi}_2\text{Se}_3$  etc. will also be discussed in this report.

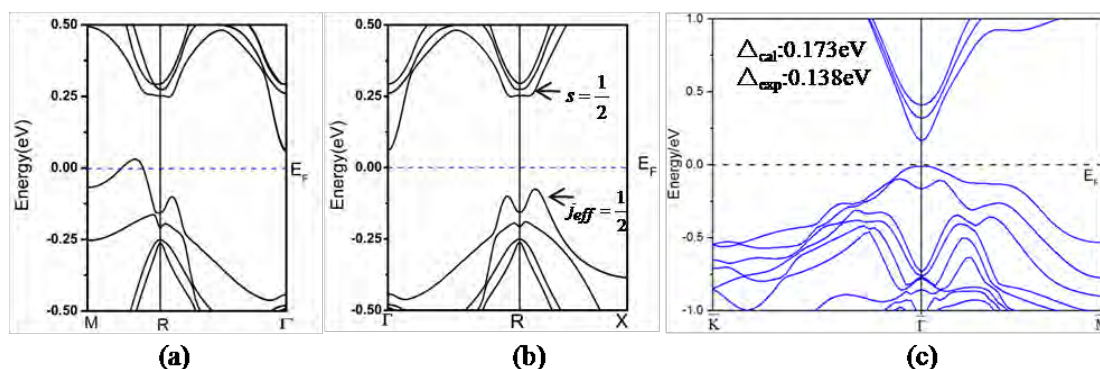


Fig. 1 (a) and (b) are the band structure of “perovskite”  $\text{YBiO}_3$  with spin-orbital coupling: along M-R- $\Gamma$  and  $\Gamma$ -R-X directions in the first Brillouin zone, respectively.(c) The band structure of  $\text{Bi}_2\text{Se}_3$  film with 3QLs (quintuple layer)

Keywords:  $\text{BiYO}_3$ , Perovskite, Topological property,  $\text{Bi}_2\text{Se}_3$

Aknowlegement: 973 program of MSTC(Grant No. 2014CB932101); 100 talents program of CAS & Fujian Province (Y5e6611ama); the Science Foundation for International Cooperation of Sichuan Province (2014HH0016)

Reference:

- [1] Y. Zhang, S. Deng, M. Pan, M. Lei, X. Kan, Y. Ding, Y. Zhao, J. Köhler, Phys. Chem. Chem. Phys. 18, 8205(2016).  
 [2] H.Jin, S. H.Rhim, J.Im and A. J. Freeman, Sci. Rep. 3 (2013) 1651.

## INTERPLAY BETWEEN LOCALIZED AND ITINERANT MAGNETISM IN EU-CONTAINING PnictIDES OF THE $\text{ThCr}_2\text{Si}_2$ STRUCTURE TYPE

Xiaoyan Tan<sup>a</sup>, Gilberto Fabbris<sup>b</sup>, Daniel Haskel<sup>b</sup>, Alexander A. Yaroslavtsev<sup>c,d</sup>, Alexey P. Menushenkov<sup>c</sup>, Roman V. Chernikov<sup>e</sup>, Michael Shatruk<sup>a</sup>

<sup>a</sup> *Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way, Tallahassee, FL 32306, USA*

<sup>b</sup> *Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

<sup>c</sup> *National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 115409, Moscow, Russia*

<sup>d</sup> *European XFEL GmbH, 22761 Hamburg, Germany*

<sup>e</sup> *DESY Photon Science, 22603 Hamburg, Germany*

shatruk@chem.fsu.edu

Itinerant magnets of the  $\text{ThCr}_2\text{Si}_2$  structure type exhibit strong correlations between their electronic structure and magnetic properties, which result in the magnetic behavior that is highly sensitive to such external perturbations as applied pressure or magnetic field. In particular,  $\text{ThCr}_2\text{Si}_2$ -type intermetallics have been shown to exhibit pressure-induced structural, magnetic, and electronic phase transitions. For example, pnictides  $\text{AFe}_2\text{As}_2$  ( $A = \text{Ca}, \text{Sr}, \text{Eu}$ ) exhibit antiferromagnetic (AFM) ordering under ambient conditions but become superconducting at high pressure [1-3].

We report a remarkable emergence of itinerant  $3d$  ferromagnetism (FM) caused by pressure-induced  $4f$  valence fluctuations in  $\text{EuCo}_2\text{As}_2$ . In striking contrast to high-pressure  $\text{EuCo}_2\text{P}_2$ , which contains mainly  $\text{Eu}^{3+}$  ions [4], high-pressure  $\text{EuCo}_2\text{As}_2$  exhibits the stabilization of a mixed-valent  $\text{Eu}^{2.25+}$  state that persists up to 12.6 GPa, the maximum pressure achieved in our experiments. Furthermore, we demonstrate the generality of this phenomenon in the present system by inducing valence changes via chemical compression in  $\text{Ca}_{0.9}\text{Eu}_{0.1}\text{Co}_2\text{As}_2$  and via direct electron doping in  $\text{Ca}_{0.9}\text{La}_{0.1}\text{Co}_2\text{As}_2$ .

We show the emergence of itinerant magnetism in  $\text{EuCo}_2\text{As}_2$  under pressure by using X-ray absorption near-edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) spectroscopy supported by the band structure calculations. The second-order structural phase transition around 4.7 GPa induces mixed valence in the Eu sublattice and breaks down the AFM ordering of the  $\text{Eu}^{2+}$  magnetic moments, as both Eu ( $4f$ ) and Co ( $3d$ ) moments become FM ordered with  $T_C = 125$  K. While the FM ordering of Eu  $4f$  moments was confirmed directly by XMCD experiment, the FM ordering of Co  $3d$  moments was established indirectly by electronic band structure calculations and by investigation of model compounds,  $\text{Ca}_{0.9}\text{R}'_{0.1}\text{Co}_2\text{As}_2$  ( $\text{R}' = \text{Eu}, \text{La}$ ). In the latter, the itinerant  $3d$  ferromagnetism in the Co sublattice is triggered by mixed valence of Eu induced by chemical compression and by direct electronic doping into the Co layer due to aliovalent substitution, respectively.

[1] S.-H. Baek, H. Lee, S. E. Brown, N. J. Curro, E. D. Bauer, F. Ronning, T. Park, and J. D. Thompson, *Phys. Rev. Lett.* 102 (2009) 227601.

[2] H. Lee, E. Park, T. Park, V. A. Sidorov, F. Ronning, E. D. Bauer, and J. D. Thompson, *Phys. Rev. B* 80 (2009) 024519.

[3] H. Kotegawa, H. Sugawara, and H. Tou, *J. Phys. Soc. Jpn.* 78 (2009) 013709.

[4] M. Chefki, M. M. Abd-Elmeguid, H. Micklitz, C. Huhnt, W. Schlabit, M. Reehuis, and W. Jeitschko, *Phys. Rev. Lett.* 80 (1998) 802.

# OPTICAL AND EXCITONIC PROPERTIES OF 2D MATERIALS BASED ON TRANSITION METAL DICHALCOGENIDES

Xavier Marie

*Université de Toulouse, INSA-CNRS-UPS, LPCNO*  
135 Avenue de Rangueil, 31077 Toulouse, France

[marie@insa-toulouse.fr](mailto:marie@insa-toulouse.fr)

The spectacular progress in controlling the electronic properties of graphene has triggered research in alternative atomically thin two-dimensional crystals. Monolayers (ML) of transition-metal dichalcogenides such as MoS<sub>2</sub> have emerged as very promising nanostructures for optical and electronic applications for mainly two reasons.

First, the indirect bulk semiconductor MoS<sub>2</sub> becomes direct when thinned to 1ML, resulting in efficient optical absorption and emission. Second, inversion symmetry breaking (usually absent in graphene) together with the large spin-orbit interaction leads to a coupling of carrier spin and  $k$ -space valley physics, *i.e.*, the circular polarization ( $\sigma^+$  or  $\sigma^-$ ) of the absorbed or emitted photon can be directly associated with selective carrier excitation in one of the two non-equivalent  $k$  valleys ( $K^+$  or  $K^-$ , respectively).

We have investigated the optical and valley properties for both neutral and charged excitons in transition metal dichalcogenide monolayers.

In this talk I will give an overview of the physical properties of 2D semiconductors based on Transition Metal Dichalcogenides (MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>, MoWSe<sub>2</sub>) : band structure, exciton effects, spin and valley dynamics...

## Phase Change of *SnTe* Extreme Nano-Wires Encapsulated in Single-Walled Carbon Nanotube

A.I. Vasylenko<sup>a</sup>, D. Quigley<sup>a</sup>, A.J. Morris<sup>b</sup>, J. Wynn<sup>b</sup>, P.V. Medeiros<sup>b</sup> and J. Sloan<sup>a</sup>

<sup>a</sup>*Department of Physics, University of Warwick, Coventry CV7 4AL, United Kingdom*

<sup>b</sup>*Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom*

email: a.vasylenko@warwick.ac.uk

The properties and structure of a material may undergo dramatic change under confinement [1-3]. In cases when confinement is extreme, crystals can form quasi-one-dimensional structures that are often unstable otherwise. Single-walled carbon nanotubes (SWCNT) with diameters ranging from 8Å to 14Å can be used as the confining environment for formation of such nano-wires from various compounds [4, 5]. The most stable stoichiometry and crystal structure of a compound can differ significantly under confinement.

In this work we study phases of crystalline *SnTe* structures embedded in SWCNT and the change of preferred stoichiometry under varying degrees of confinement. By means of *ab initio* random structure searching (AIRSS) approach for structure search and calculation of formation energy we demonstrate several competitive structures of *SnTe* that can be formed in SWCNT. We use a graphical representation of the Maxwell construction and the convex hull, which allows us to visualize the dependence of formation energy on stoichiometry. This also enables one to analyze relative stability as a function of SWCNT diameter. While constructing these diagrams, we consider several values of reference chemical potential for each species that allow us to draw conclusions regarding the most feasible routes to synthesis of these nano-wires in SWCNT.

Finally for the predicted *SnTe* nano-wires embedded in SWCNT we employ a multislice method [6] to construct a library of simulated conventional transmission electron microscope (TEM) images (See FIG 1) that can be used to unambiguously identify structures synthesized experimentally.



Figure 1. Simulated TEM image of *SnTe* nano-wire embedded in SWCNT

### References

- [1] Z. Li, S. Shao, N. Li, K. McCall, J. Wang, and S.X. Zhang, *Nano Lett.* 13 (11) (2013) 5443-5448.
- [2] X. Xiao, S.A. Yang, Z. Liu, H. Li and G. Zhou, *Scientific Reports* 5, (2015) 7898.
- [3] E.G. Barbaggiovanni, D.J. Lockwood, P.J.Simpson and L.V. Goncharova, *Appl. Phys. Rev.* 1 (2014) 011302.
- [4] J.H. Spencer, J.M. Nesbitt, H. Trehitt, R.J. Kashtiban, G. Bell, V.G. Ivanov, E. Faulques, J. Sloan, and D.C. Smith, *ACS Nano* 8 (9) (2014) 9044-9052.
- [5] R. Carter, M. Suetin, S. Lister *et al*, *Dalton Trans.* 3 (2014) 7391-7399.
- [6] E.J. Kirkland, *Advanced Computing in Electron Microscopy*, Springer, 2010.



## Chemical bonding and reactivity of the layered intergrowth compound $\text{Ba}_2\text{F}_2\text{S}_2$

D.Driss, Sylvian Cadars, Philippe Deniard, J.Y. Mevellec, Benoit Corraze, Etienne Janod, and Laurent Cario

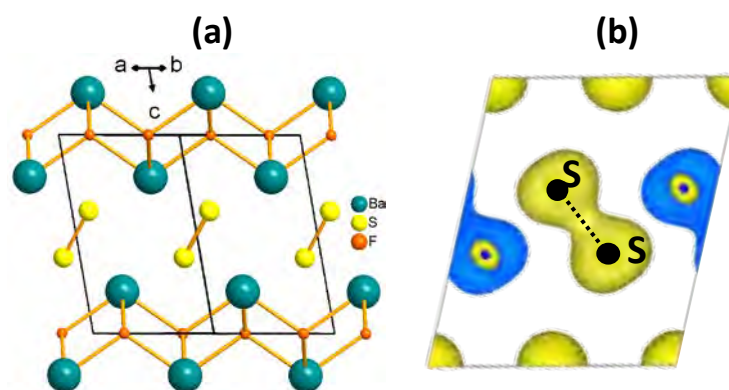
*Institut des Matériaux Jean Rouxel (IMN), CNRS Université de Nantes, UMR\_C 6502, 2 rue de la Houssinière 44322 Nantes cedex 3*

dalel.driss@cnrs-immn.fr

A great number of mixed anions systems such as oxychalcogenides<sup>1,2</sup> and oxypnictides<sup>3,4</sup> compounds show layered-type intergrowth structures. These compounds are built on an alternated stacking of few numbers of two-dimensional (2D) layers sometimes called secondary building units (SBU's). In turn these 2D SBU's can be assembled together to form new compounds provided that they have similar in-plane cell parameters, and lead to complementary electrons transfers.<sup>5</sup>

This work reports on the synthesis, the crystallographic structure and the electronic structure of the new compound  $\text{Ba}_2\text{F}_2\text{S}_2$ . In fact, this transparent yellow compound has an intergrowth structure built from the stacking of fluorite type layers and sulfur layers (see Figure 1). In this compound, the sulfur atoms form dimmers with interatomic distances as short as 2.1074(10) Å. The band structure calculations confirm that in this compound sulfur atoms are covalently bonded to form  $(\text{S}_2)^{2-}$  pairs. DFT calculations confirm also that this compound is a band insulator with the Fermi level lying in between the antibonding  $\pi^*$  and  $\sigma^*$  molecular orbital's of the sulfur dimmers.

The presence of this dimmers makes  $\text{Ba}_2\text{F}_2\text{S}_2$  an excellent precursor to form new compounds. In this study, we have explored the reactivity of  $\text{Ba}_2\text{F}_2\text{S}_2$  with copper to form quaternary phases.



*Figure 1 : Crystalline Structure of the compound  $\text{Ba}_2\text{F}_2\text{S}_2$  projected along the (110) direction (a) and isosurfaces of partial charge densities of sulfur pairs found in  $\text{Ba}_2\text{F}_2\text{S}_2$ (b).*

### References :

- [1] Palazzi, M. Comptes Rendus Acad. Sci. Ser. II Mec.-Phys. Chim. Sci. Terre Sci. 292 (1981) 789–791.
- [2] Cario, L.; Lafond, A.; Morvan, T.; Kabbour, H.; André, G.; Palvadeau, P. Solid State Sci.7 (2005) 936–944.
- [3] Quebe, P.; Terbüchte, L. J.; Jeitschko, W. J. Alloys Compd. 302 (2000) 70–74.
- [4] Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. J. Am. Chem. Soc.130 (2008) 3296–3297.
- [5] Kabbour, H.; Cario, L.; Danot, M.; Meerschaut, A. Inorg. Chem. 45 (2006) 917–922.

## A Theoretical and Experimental Investigation on Ge-Te-Se glasses by means of Solid-State NMR

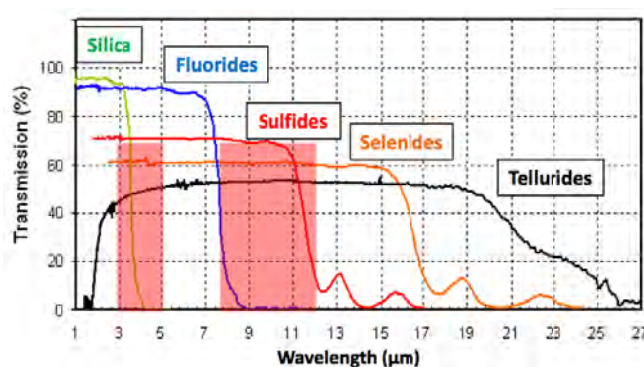
L. Bouëssel du Bourg<sup>a</sup>, L. Le Pollès<sup>a</sup>, C. Roiland<sup>a</sup>, M. Deschamps<sup>b</sup>, B. Bureau<sup>a</sup>, T. Bataille<sup>a</sup>,  
P. Florian<sup>b</sup>, C. Gonçalves<sup>a</sup>, C. Pickard<sup>c</sup>, E. Furet<sup>a</sup>

<sup>a</sup> ISCR - UMR 6226 – 11 allée de Beaulieu, 35708 Rennes Cedex 7, France

<sup>b</sup> CEMHTI, CNRS UPR 3079, 1D av. de la Recherche Scientifique, 45071 Orléans cedex 2, France

lila.bouesseldubourg@univ-rennes1.fr

Chalcogenide glasses have been widely studied over the past few decades to their manifold properties (high linear and non linear refraction indices, reversible crystal-amorphous transitions, thermoelectricity,...).<sup>1</sup> Among them, they possess large infrared transparency domain that covers the two atmospheric windows (3-5  $\mu\text{m}$  and 8-12  $\mu\text{m}$ ), as well as the vibrational signatures of most molecules. Additionally, their amorphous character allows them to be used for a lot of applications, such as lenses for thermal imaging or fibers for *in situ* spectroscopy.



licate,

The subset of tellurium materials are known to exhibit the largest transparency windows, for example, the prototypical  $\text{GeTe}_4$  glass transmits up to 20  $\mu\text{m}$ .<sup>2</sup> On the other hand, the synthesis is complicated because of demixing processes as well as possible recrystallization phenomena afterwards. Addition of selenium helps to avoid these problems, while preserving the large IR transparency window of the  $\text{GeTe}_4$  parent composition. In order to rationalize the impact of Se in these glasses, solid-state NMR is a helpful tool, being sensible to local order. However,  $^{77}\text{Se}$ ,  $^{73}\text{Ge}$  and  $^{125}\text{Te}$  are very challenging nuclei for NMR spectroscopy: low gyromagnetic coefficient ( $\gamma$ ) and natural abundance ( $\approx 7\%$ ), as well as strong quadrupolar coupling for  $^{73}\text{Ge}$ .

In this context, we wish to present results on crystals and Ge-Te-Se glasses by combining solid-state NMR, GIPAW calculations and *ab initio* molecular dynamics simulations.

[1] X. Zhang, B. Bureau, P. Lucas, C. Boussard-Plédel, J. Lucas, Chemistry European Journal 330 (2008) 1.

[2] B. Bureau, S. Danto, H.L. Ma, C. Boussard-Plédel, X.H. Zhang, J. Lucas, Solid State Sciences 14 (2008) 432.

[3] L. Bouëssel du Bourg, C. Roiland, L. Le Pollès, M. Deschamps, C. Boussard-Plédel, B. Bureau, C. J. Pickard, E. Furet, Phys. Chem. Chem. Phys. 17 (2015) 29020.

## **Electronic structures of in-plane two-dimensional transition-metal dichalcogenides heterostructures**

Wei Wei, Ying Dai, Baibiao Huang  
School of Physics, State Key Laboratory of Crystal Materials, Shandong University,  
Jinan 250100, China.

[weiw@sdu.edu.cn](mailto:weiw@sdu.edu.cn)

Electronic structures of in-plane two-dimensional transition-metal dichalcogenides (TMD) heterostructures have been studied on the basis of the first-principles density functional calculations. In contrast to vertically stacked TMD heterostructures, true type-II band alignment could be established in in-plane TMD heterostructures due to their coherent lattice and strong electronic coupling, and thus leads to the efficient separation of electrons and holes. In in-plane TMD heterostructures interfaced along the zigzag direction, electronic reconstruction causes band bending in constituent TMDs, unveiling the great potential in achieving high efficiency of water splitting and constructing Schottky barrier solar cells. In addition, type-I alignment could also be demonstrated in in-plane TMD heterostructures, enriching the photoluminescence features of TMD materials. In-plane TMD heterostructures with the ultimate thickness limit for semiconductor heterostructures will definitely spark a surge in research activity.

**Prospects for topologically non-trivial electronic  
and magnetic states in correlated kagome lattice materials:  
an ab initio investigation**

Roser Valenti<sup>a</sup>

<sup>a</sup>*Institut für Theoretische Physik, Goethe-Universität Frankfurt, 60438 Frankfurt am Main,  
Germany*

email: valenti@itp.uni-frankfurt.de

Electronic states with non-trivial topology host a number of novel phenomena with potential for revolutionizing information technology. The quantum anomalous Hall effect provides spin-polarized dissipation-free transport of electrons, while the quantum spin Hall effect in combination with superconductivity has been proposed as the basis for realizing decoherence-free quantum computing. Furthermore, there is a continuous interest in finding novel types of unconventional superconductivity. In this talk I will discuss some ab initio-based strategies we have been following for realizing these phenomena in correlated kagome lattice materials.[1,2]

[1] D. Guterding, H.O. Jeschke, R. Valenti, arXiv:1511.05686

[2] I.I. Mazin, H.O. Jeschke, F. Lechermann, H. Lee, M. Fink, R. Thomale, R. Valenti, Nature Comm. 5, 4216 (2014).

## Synthesis and structures of magnetic model systems with competing interactions

Angela Möller

*Johannes Gutenberg-University Mainz, Institute for Inorganic and Analytical Chemistry,  
Duesbergweg 10-14, 55128 Mainz – Germany*

*angela.moeller@uni-mainz.de*

Competing interactions may occur in magnetic materials with geometric frustration and thereby giving rise to non-trivial ground states. The triangular or kagome lattices are examples for such intriguing scenarios. From a chemist's point of view, a welcomed challenge is the development of classes of materials where the magnetic interactions (ferro- or antiferromagnetic) can be tuned by spin, charge, and size degrees of freedom. Moreover, by controlling the structural distortions examples for easy-axis, easy-plane Heisenberg, or collinear antiferromagnets on the triangular lattice can be obtained.<sup>1,2</sup> Here, we will discuss the structure-property relationships investigated of the  $A\text{Ag}_2\text{M}[\text{VO}_4]_2$  family of compounds with A = alkaline- / alkaline-earth and M = 3d transition metal cations. The recent investigations include neutron diffraction, magnetic and spectroscopic studies.

Support by the NSF (Grant 1149899), Oak-Ridge-National Laboratories, Texas Center for Superconductivity, University of Houston, (USA), and the Zeiss-Foundation (Germany) is gratefully acknowledged.

[1] N.E. Amuneke, J. Tapp, C. deLaCruz, A. Möller, *Chem. Mater.* 26 (2014) 5930–5935.

[2] M. Bratsch, A.P. Litvinchuk, J. Tapp, A. Möller; *Inorg. Chem.* 53 (2014) 4994–5001



## Tiny cause with huge impact: polar instability through strong magneto-electric-elastic coupling in bulk $\text{EuTiO}_3$

Annette Bussmann-Holder

*Max-Planck-Institute for Solid State Research, Heisenbergstr. 1, D-70569 Stuttgart, Germany*

[a.bussmann-holder@fkf.mpg.de](mailto:a.bussmann-holder@fkf.mpg.de)

Multiferroic materials with combined polar, magnetic, and elastic orderings are at the forefront of scientific research in view of their complex interactive couplings: magnetic order can be tuned by strain and an electric field, polar order can be triggered by a magnetic field and strain, and elastic properties are controlled by a magnetic and/or an electric field. Such materials are desirable for multiple applications. Even though the phenomenon of multiferroicity has been predicted long ago [1], its realization remains rare for rather simple reasons: typically polar order is achieved when a transition metal  $d^0$  configuration is combined with highly polarizable anions, whereas magnetic order relies on a finite  $d_n$  configuration. Obviously these two requirements yield a certain incompatibility for the coexistence of the two phenomena which have been tried to overcome by combining magnetic layers with polar ones, by growing composites, and via strain engineering [2, 3]. Even though a rather large number of materials have been shown to exhibit the desired properties, the coupling between magnetic and polar order is either very weak, or the spontaneous polarization/magnetization appears at low temperature only and remains too small to be of technological interest. Here we propose a new strategy to achieve strong magnetic-polar coupling by deriving the soft mode frequency of  $\text{EuTiO}_3$  as a function of its lattice parameter which exhibits unusual, yet very small temperature dependencies at high and low temperatures [4, 5]. Specifically we develop a route of how to induce ferroelectric order in bulk  $\text{EuTiO}_3$  (ETO) by combining experimental results with theoretical concepts. We show that marginal changes in the lattice parameter of the order of 0.01% have a more than 1000% effect on the transverse optic soft mode of ETO and thus easily induce a ferroelectric instability [6].

1. Smolenskii, G. A., Isupov, V. A., & Agronovskaya, A. I., *Sov. Phys Solid State*, **1** 149 (1959).
2. Erenstein, W., Mathur, N. D., & Scott, J. F., *Nature* **422**, 759-765 (2006).
3. Ramesh, R., & Spaldin, N. A., *Nature Materials* **6**, 21 (2007).
4. Reuvekamp, P. G., Kremer, R. K., Köhler, J., & Bussmann-Holder, A., *Phys. Rev. B* **90**, 094420 (2014).
5. Reuvekamp, P. G., Kremer, R. K., Köhler, J., & Bussmann-Holder, *Phys. Rev. B* **90**, 104105 (2014).
6. Reuvekamp P. G., Caslin K., Guguchia G., Keller H., Kremer R. K., Simon A., Köhler J., and Bussmann-Holder A., *J. Phys.: Cond. Mat.* **27**, 262201 (2015).

## Magnetic frustration of Kagome lattices in $M^{II}M^{III}F_5(Htaz)$ weberites

M. Albino<sup>a</sup>, L. Clark<sup>b</sup>, J. Lhoste<sup>a</sup>, V. Pimenta<sup>a</sup>, I. Da Silva<sup>c</sup>, M. Leblanc<sup>a</sup>, C. Payen<sup>d</sup>, J.-M. Grenèche<sup>a</sup>, P. Lightfoot<sup>b</sup>, and V. Maisonneuve<sup>a</sup>

<sup>a</sup> *IMMM, UMR 6283, Université du Maine, av. O. Messiaen, 72085 Le Mans, France*

<sup>b</sup> *School of Chemistry and EaStChem, University of St. Andrews, Fife, KY16 9ST, UK*

<sup>c</sup> *ISIS, Rutherford Appleton Laboratory Harwell Oxford, Didcot, OX11 0QX, UK*

<sup>d</sup> *IMN, UMR 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*

marjorie.albino@univ-lemans.fr

Magnetic frustration<sup>1</sup> generates unusual and potentially useful properties in hybrid organic-inorganic compounds based on various architectures with square, triangular, honeycomb or Kagome lattices. Giant negative magnetization for  $M^{II}$ - $M^{III}$  coupled systems<sup>2</sup> or quantum spin liquid ground states for  $S=1/2$  spins<sup>3</sup> are already reported and further theoretical and applied extensions are expected. Geometrically induced frustration of antiferromagnetic interactions is well established to occur in Hexagonal Tungsten Bronze (HTB) lattices<sup>4</sup>.

A series of eight  $M^{II}M^{III}F_5(Htaz)$  hybrid fluoride weberites ( $M^{2+} = Mn, Fe, Co, Zn$ ;  $M^{3+} = V, Fe, Ga$  and  $Htaz = 1,2,4$ -triazole), elaborated by solvothermal synthesis, is presented. The hybrid 3D structures consist of intersecting (101) and (10-1) HTB layers in which frustration occurs in the triangles of corner sharing octahedra (Figure 1). In  $Fe_2F_5(Htaz)$ , the  $Fe^{3+}$  magnetic moments sublattice is frustrated: the main components of  $Fe^{3+}$  magnetic moments are ferromagnetically aligned along  $b$  and antiferromagnetically coupled to  $Fe^{2+}$  moments (Figure 1). The magnetic modes are  $F_yG_z$  for  $Fe^{3+}$  and  $-F_y$  for  $Fe^{2+}$ . Such a  $F_y$  component of  $Fe^{3+}$  is not expected from Goodenough-Kanamori rules (antiferromagnetic interactions for  $Fe^{3+}$ - $F$ - $Fe^{3+}$  super-exchange at  $180^\circ$ ).

Neutron diffraction and Mössbauer experiments on iron phases together with magnetization measurements are reported. A negative magnetization is evidenced for  $Fe_2F_5(Htaz)$  (Figure 2) and  $CoFeF_5(Htaz)$ . All these hybrid fluoride weberites will be discussed in the light of magnetic ion anisotropy.

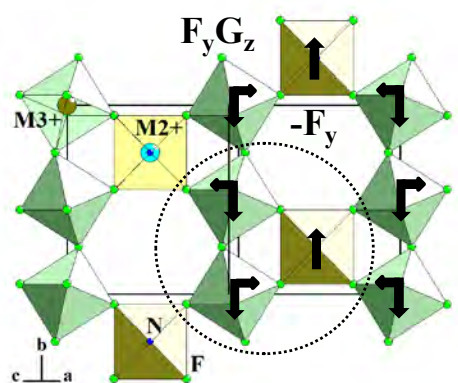


Figure 1. HTB layer of  $M^{II}M^{III}F_5(Htaz)$  weberite and orientation of magnetic moments in  $Fe_2F_5(Htaz)$

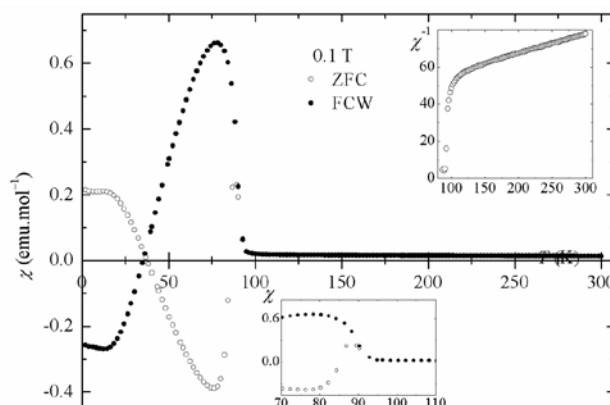


Figure 2. FCW and ZFC susceptibilities of  $Fe_2F_5(Htaz)$  measured in a 0.1 T field

[1] G. Toulouse, *Comm. Phys.* 2 (1977) 115.

[2] R. S. Fishman, F. A. Reboredo, *Phys. Rev. Lett.*, 99 (2007) 217203 1-4.

[3] F. H. Aidoudi, D. W. Aldous, R. J. Goff, A. M. Z. Slawin, J. P. Attfield, R. E. Morris, P. Lightfoot, *Nature Chemistry*, 3 (2011) 801-806.

[4] G. Férey, M. Leblanc, R. De Pape, J. Pannetier, *Inorganic Solid Fluorides*, ed. P. Hagenmuller, Academic Press, London, 1985, pp. 395-415.

## Transparent conducting materials: insights from hybrid Hartree-Fock density functional calculations

Antoine Villesuzanne<sup>a,b</sup>, Meilan Guo<sup>b</sup>, Xiaoping Han<sup>b</sup>, James Dutson<sup>c</sup>, Guosheng Shao<sup>b,d</sup>

<sup>a</sup> *Univ. Bordeaux, ICMCB, UPR 9048, 33600 Pessac, France*

<sup>b</sup> *Institute for Renewable Energy and Environmental Technologies, University of Bolton, Bolton BL3 5AB, United Kingdom*

<sup>c</sup> *Plasma Quest Ltd, Osborn Way, Hook RG27 9UT, United Kingdom*

<sup>d</sup> *International Centre for Design of Low-carbon and Environmental Materials, Zhengzhou University, 100 Kexue Road, Zhengzhou 450001, China*

email address of the presenting author: antoine.villesuzanne@icmcb.cnrs.fr

Two important challenges in the design of transparent conducting oxides (TCOs) are the replacement of tin-doped indium oxide (ITO) and the identification of p-type TCOs. In the case of p-type TCOs, the difficulties lie in compensating defects for charge carriers (holes) and in the high effective mass of holes. For n-type TCOs, doping SnO<sub>2</sub> either with fluorine or antimony allows achieving performances comparable to ITO; however, it is highly desirable to identify more environmental-friendly formulations, avoiding those elements as dopants.

We have first investigated the reliability of several exchange-correlation functional schemes within density functional theory (DFT), namely the generalized gradient approximation (GGA), the Tran-Blaha modified Becke-Johnson approach (TB-mBJ) and the so-called PBE0 and HSE06 hybrid schemes, for the calculation of effective masses in pristine SnO<sub>2</sub>. The DFT/PBE0 hybrid scheme allowed obtaining band gap and effective masses in excellent agreement with experimental values and was retained for the subsequent calculations on doped systems. The TB-mBJ scheme can be parametrized to fit the experimental band gap in SnO<sub>2</sub>, but the values for effective masses led to only qualitative agreement with experiment.

Hybrid DFT/PBE0 calculations were then performed to investigate the effect of transition metal (n-type) doping in SnO<sub>2</sub>, and p-type doping by trivalent elements. Non-oxide formulations were tested as well. The carrier mobility was estimated from the Bardeen-Shockley acoustic phonon-scattering model, which involves the calculation of bulk moduli and deformation potentials.

Depending on the nature of the transition metal involved for doping SnO<sub>2</sub>, either deep impurity levels are found in the band gap (impeding transparency), or efficient n-type doping can be expected when the transition metal d bands lie above the bottom of the Sn-character conduction band, while preserving both low effective masses and appropriate band gap for transparency in the visible spectrum. Promising results were found as well for candidates as p-type transparent conductors, in terms of low effective masses for doping holes.

Thin-film deposition and characterization of some proposed formulations are in progress; preliminary results will be presented.

## Theoretical investigation of nitrogen defects in p-type ZnO

Xavier Rocquefelte,<sup>1</sup> Camille Latouche,<sup>2</sup> François Cheviré,<sup>1</sup> Franck Tessier,<sup>1</sup> Fabien Grasset,<sup>1,3</sup> Laurent Cario<sup>2</sup> and Stéphane Jobic<sup>2</sup>

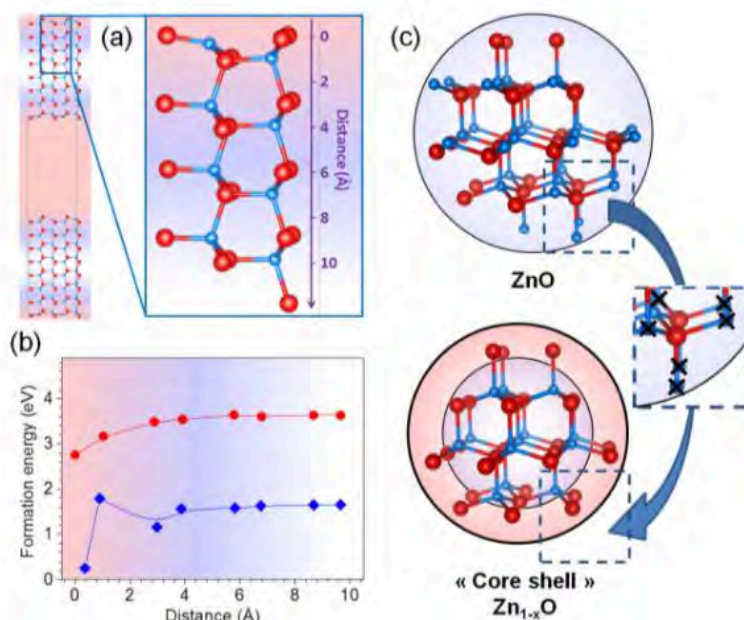
<sup>1</sup>*Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes, France*

<sup>2</sup>*Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, 2 rue de la Houssinière, 44322 Nantes cedex 3, France*

<sup>3</sup>*UMI 3629 CNRS - Saint Gobain - NIMS, Laboratory for Innovative Key Materials and Structures–LINK, National Institute for Materials Science, Tsukuba, Japan*

*Email address of the presenting author: xavier.rocquefelte@univ-rennes1.fr*

Zinc oxide is a material of paramount importance exhibiting pigmental, (photo)catalytic, piezoelectric, antibacterial, or varistor properties that are already developed in many fields of industry. Still novel applications emerge in various domains but they often require the preliminary stabilization of a p-type ZnO counterpart to the natural n-type ZnO to be stimulated. During the last few years many groups have invested on the understanding of the processes, which allow to obtain p-type ZnO. We have recently evidenced that the nanostructuration could be at the origin of the stabilisation of p-type charge carriers in nitrogen-doped ZnO nanoparticles (see figure). Here, we show our recent theoretical results dealing with the segregation of Zn-vacancies at the surface of the nanoparticles and the chemical nature of the nitrogen defects in ZnO.



[1] B. Chavillon, L. Cario, A. Renaud, F. Tessier, F. Cheviré, M. Boujtita, Y. Pellegrin, E. Blart, A. Smeigh, L. Hammarström, F. Odobel, and S. Jobic, JACS 134 (2012) 464.

[2] A. Renaud, L. Cario, X. Rocquefelte, P. Deniard, E. Gautron, E. Faulques, T. Das, F. Tessier, S. Jobic, Scientific Reports 5 (2015) 14592.

## Composition induced changes in optical response of $\text{Ti}_{1-x}\text{Si}_x\text{O}_2$ from first principles calculations

*Pavel Ondračka<sup>a,b</sup>, David Holec<sup>c</sup>, Eva Kedroňová<sup>a,b</sup>, Marek Eliáš<sup>a,b</sup>, Stéphane Elisabeth<sup>d</sup>, Antoine Goulet<sup>d</sup>, Lenka Zajíčková<sup>a,b</sup>*

<sup>a</sup> Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

<sup>b</sup> CEITEC - Central European Institute of Technology, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

<sup>c</sup> Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Franz-Josef-Straße 18, Leoben A-8700, Austria

<sup>d</sup> Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, UMR CNRS 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

email address of the presenting author: [pavel.ondracka@gmail.com](mailto:pavel.ondracka@gmail.com)

Mixed  $\text{Ti}_x\text{Si}_y\text{O}_2$  materials offer great potential for compositionally induced variation of their optical properties, due to the high difference of their refractive indices ( $\text{TiO}_2$ :  $\sim 2.5$ ,  $\text{SiO}_2$ :  $\sim 1.5$ ) and band gaps ( $\text{TiO}_2$ :  $\sim 3.2$  eV,  $\text{SiO}_2$ :  $\sim 8.5$  eV). This opens new possibilities for designing optical devices.

In the present work, the variation of  $\text{Ti}_{1-x}\text{Si}_x\text{O}_2$  optical constants caused by changed Si concentration is studied by employing Density Functional Theory. Special Quasi-random Structures method is used to generate structural models of  $\text{Ti}_{1-x}\text{Si}_x\text{O}_2$  disordered solid solutions based on various  $\text{TiO}_2$  and  $\text{SiO}_2$  phases. These initial supercells are fully structurally optimized (i.e., optimized with respect to the cell shape, size, and atomic positions) using the Vienna Ab initio Simulation Package. Ab initio Molecular Dynamics approach (“simulated annealing”) is used to generate structural models of the amorphous phase. Optical constants of the resulting structures are calculated using the linearized augmented plane wave method as implemented in the all-electron Wien2k code together with the modified Becke-Johnson exchange-correlation potential allowing for an accurate prediction of electronic structures and band gaps [1].

The calculated dielectric function and band gaps are compared with experimental data obtained by fitting the optical measurements (ellipsometry, spectrophotometry) carried out on  $\text{Ti}_{1-x}\text{Si}_x\text{O}_2$  films prepared by plasma enhanced chemical vapor deposition and atomic layer deposition.

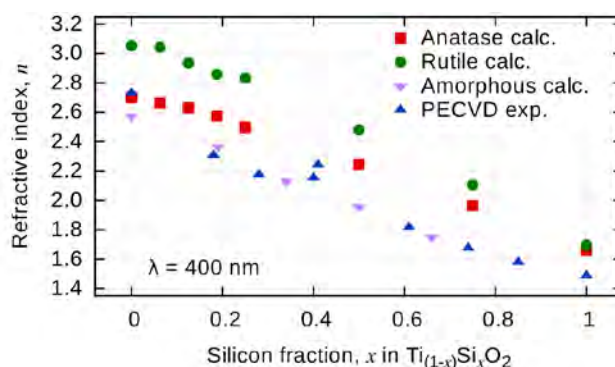


Figure 1: Predicted and measured evolution of refractive index of  $\text{Ti}_{1-x}\text{Si}_x\text{O}_2$

[1] F. Tran, P. Blaha, Phys. Rev. Lett. 102 (2009) 226401.



## Structure – physicochemical property relationships in amorphous alumina

Vanessa Riffet<sup>a,b</sup>, Julien Vidal<sup>b,a</sup>

<sup>a</sup> Institut Photovoltaïque d'Ile de France (IPVF), 8 rue de la Renaissance 92160 Antony, France

<sup>b</sup> Institut de Recherche et Développement sur l'Energie Photovoltaïque (IRDEP), UMR 7174-CNRS/EDF/Chimie Paristech, 6 quai Watier 78401 Chatou, France

Vanessa.riffet@ipvf.fr

Amorphous alumina ( $\text{AlO}_x$ ) is used in many technologically applications as (i) catalyst or (ii) photovoltaic insulation material due to its passivation potential and transparency. Thereby, a better understanding of the link between structural motives, chemical composition and optical or electrical properties is of considerable interest. In the case of photovoltaic industry,  $\text{AlO}_x$  is commonly used as passivation layer of the silicon surface and deposited by atomic layer (ALD).[1] By this process, impurities from precursors (as  $\text{H}_2\text{O}$ ) are incorporated within  $\text{AlO}_x$ , thereby changing its properties. Thus we decided to study computationally the properties of  $\text{AlO}_x\text{H}_y$  and to perform a statistical study. We analyzed inter alia the effect of the composition in oxygen and hydrogen.

In this context, we have developed a modeling protocol, based on the Melt and Quench technique to explore the potential energy surface.[2-4] As shown in Figure 1, for a given composition, we have identified a set of amorphous structures spanning wide region of density and energy. In our simulations, we showed that taking into account dispersion effects is important, while spin polarization is not. A ring analysis using the ANELLI program were used to describe the amorphous structures.[5] Bader charge analysis allow us to identify rapidly the defects [6] while optical properties were computed as bandgap and dielectric permittivity ( $\epsilon'$ ). Finally, some structure - property or property - property relationship will also be revealed.

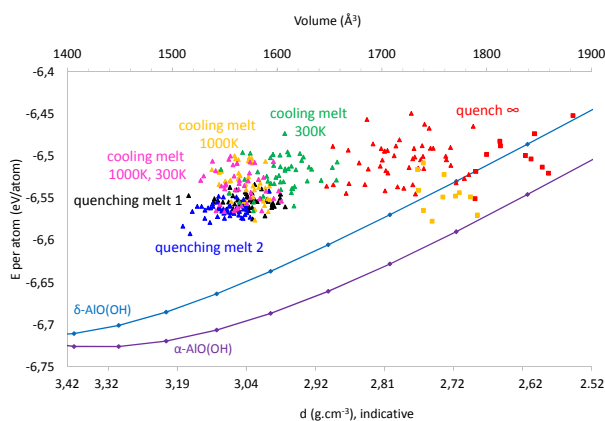


Figure 1: Energy per atom and volume of some amorphous structures  $\text{AlO}_x\text{H}_y$  ( $x=2$ ,  $y=1$ ).

This work was carried out in the framework of a project of IPVF (Institut Photovoltaïque d'Ile-de-France). This project has been supported by the French Government in the frame of the program of investment for the future (Programme d'Investissement d'Avenir – ANR-IEED-002-01).

Reference to a journal publication:

- [1] R.W. Johnson, A. Hultqvist, S.F. Bent, Mater. Today 17 (2014) 236-246.
- [2] J. Rosen, O. Warschkow, D.R. McKenzie, M.M. Bilek, J. Chem. Phys. 126 (2007) 204709.
- [3] H. Momida, T. Hamada, Y. Takagi, T. Yamamoto, T. Uda, T. Ohno, Phys. Rev. B 73 (2006) 054108.
- [4] R. Lizárraga, M. Ramzan, C.M. Araujo, A. Blomqvist, R. Ahuja, E. Holmström, EPL 99 (2012) 57010.
- [5] J. Rybicki, G. Bergmański, G. Mancini, J. Non-Cryst. Solids, 293-295 (2001) 758-763.
- [6] G. Henkelman, A. Arnaldsson, H. Jónsson, Comput. Mater. Sci. 36 (2006) 254-360.

## A Study by ab-initio calculation of structural and electronic properties of semiconductor nanostructures based on ZnSe.

<sup>△</sup> Rachidi<sup>a</sup>, E.H.Atmani<sup>a</sup>,N.Fazoune<sup>b</sup>

<sup>a</sup> *Laboratory Physics of Nanostructures and Advanced Materials, Department of Physics, Faculty of Science and Techniques Mohammedia University Hassan II Casablanca, Morocco.*

<sup>b</sup> *Laboratory of Physics of Materials and Mechanics, Department of Physics, Faculty of Science and Techniques, Sultan Moulay Slimane University, Beni Mellal, Morocco.*

rachidi.doc82@gmail.com

Our research is based on the technique of modelization and simulation Ab-initio that uses of the Density Functional Theory (DFT) [1] in order to optimize the structural and electronic properties of binary semiconductors  $II_b - VI_a$  based on ZnSe, because of their technological importance and their application in the development of a new opto-electronic devices. Our calculations are based on the Full - Potential Linearized Augmented Plane Waves (FP-LAPW) [2].method that requires a calculation process using approximations such as Local density (LDA) and Generalized Gradient (GGA) [3] developed in the modeling software of nanostructures WIEN2k [2]. Optimal ZnSe structure crystallizing in the complex phase of Zinc Blende (B3) was determined by studying the variation of energy depending on the volume of the elementary cell [4]. Then the electronic properties of the optimized state were analyzed such as the gap energy [5], the effective mass of the electrons, light and heavy holes [6], the total density of states (TDOS), the partial density of states (PDOS) and the repartition of the electronic charge density.

The obtained results were successful compared with other theoretical and experimental values reported in literature.

*Keywords:* ZnSe, Zinc Blende, Optimization, Ab-initio, DFT, FP-LAPW, LDA, GGA, Band gap energy, Effective mass,TDOS, PDOS, Electronic charge density.

Reference to a journal publication:

[1] P. Hohenberg, W. Kohn, Inhomogeneous Electron Gas ,Phys. Rev. B 136, 864 (1964).

[2] P. Blaha, K. Schwarz, G.K.H. Medsen, D. Kvasnicka J. Luitz, WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, Vienna UniversityTechnology, Vienna,Austria,(2001).

[3] K. Schwarz, P. Blaha, Comput. Mat. Sci. 28, 259 (2003).

[4] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 30, 244 (1944).

[5] J. A. Camargo-Martinez, R. Baquero , Detailed analysis of the performance of the modified Becke-Johnson potential, Phys. Rev. B 86, 195106 (2012).

[6] Ramos L. E. Ramos, L. K. Teles, L. M. R. Scolfaro, J. L. P.Castineira, A. L. Rosa, and J. R. Leite, Phys. Rev. B 63 ,165210 (2001).

## Physical properties of hybrid perovskites for photovoltaics and optoelectronics

Jacky Even<sup>a</sup>

<sup>a</sup> *FOTON CNRS UMR 6082, INSA, 20 avenue des buttes de Coësmes 35708 Rennes Cedex*

jacky.even@insa-rennes.fr

3D hybrid halide perovskites attract increasing attention of the scientific community for photovoltaics and light emission. Our scientific approach is based on solid-state physics concepts and group symmetry approaches originally developed for conventional semiconductors. Broad light-harvesting abilities and attractive transport properties of 3D metal-halide hybrid perovskites can be related to the multi-bandgap and multi-valley nature of their band structure, to band folding effects and a non-conventional huge spin-orbit coupling in the conduction band. The stochastic reorientations of the small organic cations in 3D hybrid perovskites, are important at room temperature [1-3]. Theoretical predictions will be compared to recent spectroscopy results on bulk materials [4,5]. However, achieving stability and reliability remains a critical challenge, which will determine the fate of perovskite cell technology. Advanced solar cell characterizations on the photo-degradation and fast self-healing of the photocurrent in perovskite solar cells under constant illumination were performed recently [6]. We attribute the photocurrent degradation to the formation of light-activated meta-stable trap states. Experimental characterization and theory suggest their origin to the formation of localized charged states strongly coupled with local structural lattice distortions and methyl ammonium (MA) quasistatic configurations. These seed the formation of macroscopic charged domains preventing efficient charge extraction.

The role of the organic cations for the quantum and dielectric confinements in layered hybrid perovskites will be first described theoretically, and compare to spectroscopy data [7-8]. We will also present a potential alternative for 3D perovskite cells in the form of layered perovskites with record photovoltaic efficiency of 11.2% (versus ~4% previously reported) showing excellent environmental and photostability with negligible degradation over more than 2000 hours [9]. The phenomenal increase in efficiency is attributed to the near single crystalline quality thin films with a preferential out of plane alignment of the inorganic perovskite component that facilitates efficient charge transport resulting in a dramatic increase in the photocurrent.

- [1] J. Even, L. Pedesseau, J.M. Jancu, C. Katan, *J. Phys. Chem. Lett.* 4 (2013) 2999-3005.
- [2] M. Kepenekian, R. Robles, C. Katan, D. Saponi, L. Pedesseau, J. Even, *ACS nano*, 9 (2015) 11557.
- [3] J. Even, M. Carignano, C. Katan, *Nanoscale* 8 (2016) 6222-6236
- [4] H.-H. Fang, R. Raissa, M. Abdu-Aguye, S. Adjokatse, G.R. Blake, J. Even, M. A. Loi, *Adv. Func. Mat.*, 25 (2015) 378.
- [5] H.-H. Fang, F. Wang, S. Adjokatse, N. Zhao, J. Even, M. A. Loi, *Light Sci. Appl. NPG* 5 (2016) e16056.
- [6] W. Nie, J.-C. Blancon, A. J. Neukirch, K. Appavoo, H. Tsai, M. Chhowalla, M. A. Alam, M. Y. Sfeir, C. Katan, J. Even, S. Tretiak, J. J. Crochet, G. Gupta, A. D. Mohite, *Nature Comm.* (2016) DOI : 10.1038/NCOMMS11574
- [7] J. Even, L. Pedesseau, M.A. Dupertuis, J.M. Jancu, C. Katan, *Phys. Rev. B* 86 (20), 20530
- [8] D. Saponi, M. Kepenekian, L. Pedesseau, C. Katan, J. Even, *Nanoscale* 8 (2016) 6369-6378.
- [9] H. Tsai, W. Nie, J.-C. Blancon, C. Stoumpos, R. Asadpour, B. Harutyunyan, R. Verduzco, J. J. Crochet, S. Tretiak, L. Pedesseau, J. Even, M. A. Alam, G. Gupta, J. Lou, P.M. Ajayan, M. J. Bedzyk, M. G. Kanatzidis, A. Mohite, *Nature* (2016) (in press)

## Development of mesoscopic p-type metal oxides for solar cell applications: challenges and opportunities

Fabrice Odobel,<sup>a</sup> Yoann Farré,<sup>a</sup> Tengfei Jiang,<sup>b</sup> Yann Pellegrin,<sup>a</sup> Laurent Cario,<sup>b</sup> Stéphane Jobic<sup>b</sup>

<sup>a</sup>*Chimie et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR 6230, Université de Nantes, 44322 Nantes cedex 3, France.*

<sup>b</sup>*Institut des Matériaux Jean Rouxel (IMN), CNRS, UMR 6502, Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes, Cedex 03, France*

Email address: [Fabrice.Odobel@univ-nantes.fr](mailto:Fabrice.Odobel@univ-nantes.fr)

Sensitization of p-type nanocrystalline semiconductors (p-SCs) have been much less investigated than classical Grätzel cells (dye-sensitized solar cells), but they have been receiving increasing attention, because they are the complementary photoelectrodes of conventional TiO<sub>2</sub>-based photoanodes to build tandem solar cells[1] and tandem photoelectrocatalytic devices for solar fuel production.[2] Tandem dye sensitized solar cells present the potential to achieve higher PCEs than conventional DSSCs, certainly above 15%. Contrary to conventional Grätzel cells (n-DSCs), whose operation principle is based on the photoinjection of electron into the conduction band of a n-type SC such as TiO<sub>2</sub>, in p-DSC the sensitizer excited-state decays by hole injection into the valence band of the p-SC. So far, NiO is the most investigated p-SC used in p-DSCs in spite of its majors intrinsic limitations (dark color, short hole diffusion length, shallow valence band potential), which prevent achieving high PCEs.[3] This contribution will be devoted to the preparation of new inorganic materials to build photocathodes for p-DSCs. More particularly, we will present the preparation and the properties of delafossites p-SC[4] and PbS quantum dots[5] for their uses as cathode material and sensitizer respectively for the fabrications of p-DSCs.

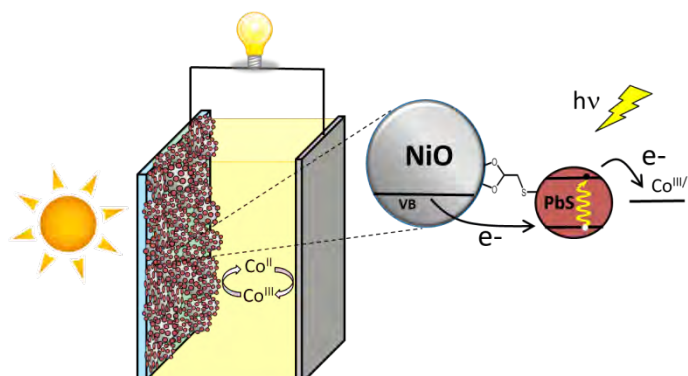


Figure. Schematic structure of a p-DSC sensitized with a PbS quantum dot.

### References

- [1](a) A. Nattestad, A. J. Mozer, M. K. R. Fischer, Y. B. Cheng, A. Mishra, P. Bäuerle, U. Bach, *Nat. Mater.* 9 (2010) 31-35; (b) E. A. Gibson, A. L. Smeigh, L. L. Pleux, J. Fortage, G. Boschloo, E. Blart, Y. Pellegrin, F. Odobel, A. Hagfeldt, L. Hammarström, *Angew. Chem. Int. Ed.* 48 (2009) 4402-4405.
- [2] F. Li, K. Fan, B. Xu, E. Gabrielsson, Q. Daniel, L. Li, L. Sun, *J. Am. Chem. Soc.* 137 (2015) 9153-9159.
- [3] F. Odobel, Y. Pellegrin, *J. Phys. Chem. Lett.* 4 (2013) 2551-2564
- [4] (a) T. Jiang, M. Bujoli-Doeuff, Y. Farre, E. Blart, Y. Pellegrin, E. Gautron, M. Boujtita, L. Cario, F. Odobel, S. Jobic, *RSC Adv.* 6 (2016) 1549-1553; (b) A. Renaud, L. Cario, Y. Pellegrin, E. Blart, M. Boujtita, F. Odobel, S. Jobic, *RSC Adv.* 5 (2015) 60148-60151; (c) A. Renaud, L. Cario, P. Deniard, E. Gautron, X. Rocquefelte, Y. Pellegrin, E. Blart, F. Odobel, S. Jobic, *J. Phys. Chem. C* 118 (2014) 54-59.
- [5] M. Raissi, Y. Pellegrin, S. Jobic, M. Boujtita, F. Odobel, *Sci. Rep.* 6 (2016) doi: 10.1038/srep24908.

## Inorganic Molybdenum Clusters as light-harvester in all inorganic solar cells: a proof of concept

Adèle Renaud<sup>a</sup>, Fabien Grasset<sup>b</sup>, Aurélien Planchat<sup>c</sup>, Benjamin Dierre<sup>b</sup>, Tetsuo Uchikoshi<sup>b,d</sup>, Naoki Ohashi<sup>b,d</sup>, Toshiaki Takei<sup>d</sup>, Laurent Cario<sup>e</sup>, Stéphane Jobic<sup>e</sup>, Fabrice Odobel<sup>c</sup> and Stéphane Cordier<sup>a</sup>

*a Institut des Sciences Chimiques de Rennes, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France*

*b CNRS-Saint Gobain, UMI 3629, Laboratory for Innovative Key Materials and Structures, National Institute of Material Science, 1-1 Namiki, Tsukuba 305-0044, Japan*  
*c Laboratoire de Chimie et Interdisciplinarité : Synthèse, Analyse, Modélisation (CEISAM), 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France*

*d National Institute of Material Science, 1-1 Namiki, Tsukuba 305-0044, Japan*

*e Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France*

E-mail: [adele.renaud@univ-rennes1.fr](mailto:adele.renaud@univ-rennes1.fr)

Functionalization of metal oxide semiconductors with transition metal clusters is a topic of growing interest because of its potential applications in several fields such as energy,<sup>[1]</sup> catalysis,<sup>[2]</sup> optical devices<sup>[3]</sup> or biotechnologies.<sup>[4]</sup> In this frame, we have investigated the functionalization of transparent conductive oxides, typically TiO<sub>2</sub> and NiO, by inorganic metal clusters presenting a richness of the crystal structures and properties in order to develop new types of photoelectronic devices and particularly new concept of photovoltaic cells namely cluster sensitized solar cell, directly inspired from dye solar cell and perovskite solar cell. They are based on the photoinjection of charges (electrons or holes) from the sun light harvester cluster to charge collectors consisting of mesoporous semiconductors (n- or p-type respectively) electrodes.

As preliminary studies, we focused our research on molybdenum octahedral cluster halides and particularly on [Mo<sub>6</sub>I<sub>14</sub>]<sup>2-</sup> units which presents a strong UV-Visible absorption with emission in the red-NIR region and we investigated the possibility to generate photoinduced charge transfers between molybdenum octahedral cluster iodide units and n- or p-type semiconductors (TiO<sub>2</sub>-based photoanode and NiO-based photocathode) by the design of the first cluster sensitized solar cells. After a carefully study of the morphology, the composition and the kinetic of cluster chemisorption of the photoelectrodes (TiO<sub>2</sub>-based photoanode and NiO-based photocathode), first cluster-based cells have been assembled and promising preliminary photovoltaic performances have been carried out.

This proof of concept paves the way of the use of transition metal clusters as a new class of inorganic solid state absorber in photovoltaic cells and photocatalytic systems too.

[1] a) D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* 407 (2000) 724–727 ; b) Y. Zhao , R. R. Lunt , *Adv. Energy Mater.* 3 (2013) 1143–1148.

[2] a) A. Barras, S. Cordier, R. Boukherroub, *Appl. Catal. B: Environ.* 123 (2012) 1–8 ; b) A. Barras, M. R. Das, R. R. Devarapalli, M. V. Shelke, S. Cordier, S. Szunerits, R. Boukherroub, *Appl. Catal. B: Environ.* 130 (2013) 270–276.

[3] a) P. S. Kuttipillai, Y. Zhao, C. J. Traverse, R. J. Staples, B. G. Levine, R. R. Lunt, *Adv. Mater.* 28 (2016) 320–326 ; b) S. Cordier, F. Grasset, Y. Molard, M. Amela-Cortes, R. Boukherroub, S. Ravaine, M. Mortier, N. Ohashi, N. Saito, H. Haneda, *J. Inorg. Organomet. Polym.* 25 (2015) 189–204.

[4] T. Aubert, F. Cabello Hurtado, M.A. Esnault, C. Neaime, D. Lebret-Chauvel, S. Jeanne, P. Pellen, C. Roiland, L. Le Polles, N. Saito, K. Kimoto, H. Haneda, N. Ohashi, F. Grasset, S. Cordier, *J. Phys. Chem. C* 117 (2013) 20154–20163.

## Ce<sup>3+</sup>-doped Gd<sub>3</sub>Sc<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: a new candidate as phosphor for LED-based lighting?

Géraldine Dantelle<sup>a</sup>, Lucie Devys<sup>b</sup>, Christophe Dujardin<sup>c</sup>, Ram Seshadri<sup>d</sup>, Thierry Gacoin<sup>b</sup>

<sup>a</sup> Institut Néel, 25 Avenue des Martyrs, BP166, 38042 Grenoble Cedex 09, France

<sup>b</sup> Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, Route de Saclay, 91128 Palaiseau Cedex, France

<sup>c</sup> Institut Lumière Matière, UMR5306 CNRS / Université Claude Bernard Lyon 1 Campus LyonTech- La Doua, 10 rue Ada Byron, 69622 Villeurbanne Cedex, France

<sup>d</sup> Materials Research Laboratory, University of California Santa Barbara, CA 93106-5121, USA

email address of the presenting author: [geraldine.dantelle@neel.cnrs.fr](mailto:geraldine.dantelle@neel.cnrs.fr)

Although widely used as phosphors for the generation of white light in LEDs, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) micro-crystals doped with Ce<sup>3+</sup> ions present two main intrinsic drawbacks : (1) a yellow emission band lacking from a red component, leading to a “cold white light” and (2) a limited cerium incorporation (~3 % at.), resulting in a weak yellow emission. We introduce here the Ce<sup>3+</sup>-doped Gd<sub>3</sub>Sc<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> (GSAG:Ce) phase and its potential as phosphors for white LEDs. Gd<sub>3</sub>(1-x)Ce<sub>3x</sub>Sc<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> micro-crystals were made by a solid-state microwave-assisted reaction, with  $x$  varying from 0 to 0.5. Ce<sup>3+</sup> ions can be incorporated into the GSAG matrix with a concentration up to 13 % at. without the formation of parasite phase. The maximum emission wavelength is situated at 573 nm for a doping concentration of 10 at.%, giving an orange feature to the emission. The luminescence quantum yield reaches 52 % for a doping concentration of 3 at.%. The figure of merit, composed by the product of the luminescence quantum yield by the Ce content, predicts a 50% increase of the luminescence intensity when using GSAG:10%Ce, with respect to YAG:3%Ce [1].

Nanoparticles of GSAG:Ce were synthesized by a solvothermal method, following the procedure developed for YAG:Ce [2]. The obtained colloidal solution was very stable and evidenced luminescence.

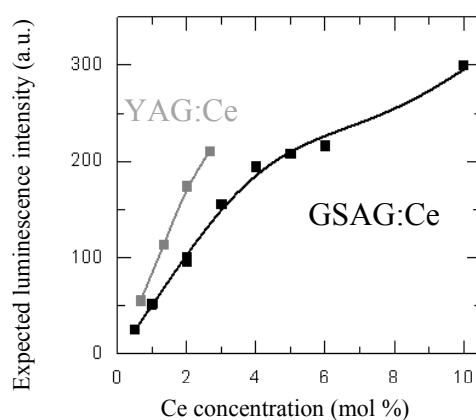


Figure 1: Evolution of the luminescence intensity of GSAG and YAG as a function of Ce concentration, calculated from the experimental values of luminescence quantum yield.

[1] L. Devys, G. Dantelle, C. Dujardin, G. Laurita-Plankis, R. Seshadri, T. Gacoin, in preparation

[2] A. Revaux, G. Dantelle, N. George, R. Seshadri, T. Gacoin, J.P. Boilot, *Nanoscale* 3 (2011) 2015-2022



## Preparation and photo-/cathodo-luminescence of Ln doped CaZrO<sub>3</sub> films

Kazushige Ueda<sup>a</sup>, Yuhei Shimizu<sup>a</sup>, Hiroshi Takashima<sup>b</sup>, Florian Massuyeau<sup>c</sup>, Stéphane Jobic<sup>c</sup>

<sup>a</sup> *Department of Materials Science, Graduate School of Engineering, Kyushu Institute of Technology, 1-1 Sensui, Tobata, Kitakyushu 804-8550, Japan*

<sup>b</sup> *Electronics Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*

<sup>c</sup> *Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France*

email address of the presenting author: kueda@che.kyutech.ac.jp

Perovskite-type CaZrO<sub>3</sub> doped with lanthanide ions show various luminescent colors. Eu<sup>3+</sup> doped CaZrO<sub>3</sub> shows red luminescence and Tb<sup>3+</sup> doped CaZrO<sub>3</sub> does green or blue luminescence depending on the Tb<sup>3+</sup> concentration [1]. This feature is largely different from similar Tb<sup>3+</sup> doped perovskite-type CaSnO<sub>3</sub> in which only green luminescence was observed [2]. Therefore, CaZrO<sub>3</sub> is one of rare host lattices that show RGB tricolor by just changing emission centers. To apply to optoelectronic devices, the preparation of high quality films of Eu<sup>3+</sup> or Tb<sup>3+</sup> doped CaZrO<sub>3</sub> is anticipated like other perovskite-type oxide phosphor thin films such as Pr<sup>3+</sup> doped titanates, Tm<sup>3+</sup> doped hafnates, Ln<sup>3+</sup> doped stannates, and Gd<sup>3+</sup> doped aluminates [3-7]. In this study, the Eu<sup>3+</sup> or Tb<sup>3+</sup> doped CaZrO<sub>3</sub> thin films were prepared on SrTiO<sub>3</sub>(STO) or LaAlO<sub>3</sub>(LAO) single crystal substrates by pulsed laser deposition and their photoluminescence(PL) and cathodoluminescence(CL) were examined.

The XRD patterns of the films indicated the obtained films were grown epitaxially on STO or LAO substrates. The film samples were transparent in visible region with transmittance as high as 70%. The RGB luminescence was observed from the Eu<sup>3+</sup> or Tb<sup>3+</sup> doped CaZrO<sub>3</sub> thin films in both PL and CL measurements. Brighter blue CL than PL was found in comparison between CL and PL implying differences in the relaxation processes.

### References:

- [1] Y. Shimizu, S. Sakagami, K. Goto, Y. Nakachi, K. Ueda, *Mater. Sci. Eng. B* 161 (2009) 100-103
- [2] K. Goto, Y. Nakachi, K. Ueda, *Thin Solid Films* 516 (2008) 5885-5889.
- [3] P. Boutinaud, E. Tomasella, A. Ennajdaoui, R.Mahiou, *Thin Solid Films* 515 (2006) 2316-2321.
- [4] H. Takashima, K. Ueda, M. Itoh, *Appl. Phys. Lett.* 89 (2006) 261915.1-3.
- [5] N. Arai, T.W. Kim, H. Kubota, Y. Matsumoto, H. Koinuma, *Appl. Surf. Sci.* 197–198 (2002) 402-405.
- [6] K. Ueda, T. Maeda, K. Nakayashiki, K. Goto, Y. Nakachi, H. Takashima, K. Nomura, K. Kajihara, H. Hosono, *Appl. Phys. Express* 1 (2008) 015003.1-3.
- [7] Y. Shimizu, K. Ueda, F. Massuyeau, S. Jobic, *Thin Solid Films* 571 (2014) 90-93.

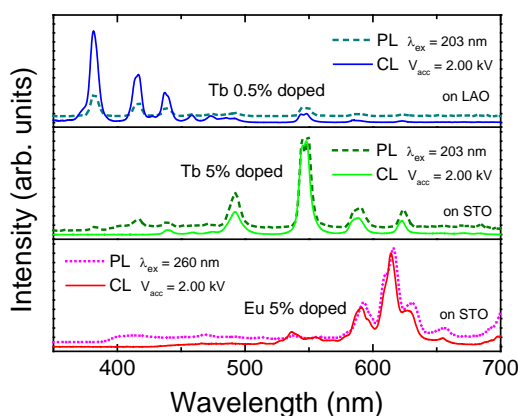


Fig. PL and CL spectra of Tb<sup>3+</sup> or Eu<sup>3+</sup> activated CaZrO<sub>3</sub> films.

# CRYSTALLOGRAPHIC LOCALIZATION OF RARE EARTH ATOMS BY XRD AND CTEM FOR THE UNDERSTANDING OF THE LUMINESCENCE OF $\text{AlN:Er}_x$ ( $x=0-6\%$ ) FILMS

V. Brien, P. Boulet

CNRS, Institut Jean Lamour, UMR 7198 CNRS – Université de Lorraine, Boulevard des Aiguillettes  
B.P. 239, F-54506 Vandœuvre lès Nancy, France

valerie.brien@univ-lorraine.fr

Rare earths (RE) are naturally not luminescent materials, however when adequately placed in specific matrices they can become optically active and lead to photo luminescent or electro luminescent phenomena. The associated modification of quantic selection rules is intimately related to the neighbourhood of the active centres. So, knowing where the optical centres are in the material is a key issue to progress in the understanding of their physical mechanisms. Nitrides (gallium, indium or aluminium based) doped with RE are known to exhibit a so called "*concentration quenching*" translating a saturation effect that is often mentioned to be due to precipitation of RE rich phases when increasing the doping of the luminescent element. The authors have used TEM and XRD to study the AlN system prepared by reactive magnetron R.F. sputtering on a doping range of Erbium from 0 to 6 atomic %. One will present the analysis of the data and stress on the specific XRD detexturation procedure achieved by the authors on the films. One will show that this process allows  $\text{AlN:Er}_x$  to be a solid solution even when  $x$  reaches 6 atomic %. One will also present the analysis of the XRD measurements thanks to intensity calculations based on atomic models confirming that the main location of Erbium in the AlN würtzite is the metal substitution site on the whole range. Results also authorize to think that both octahedral and tetrahedral sites of the würtzite do welcome Er ions over the [1.6 – 6 %] range. Finally, the localization of the atoms will be confronted to the diverse interpretations of literature concerning the concentration quenching luminescence, for instance to the model published by Benz [1] [2] [3].

- [1] F. Benz, A. Gonser, R. Völker, T. Walther, J.-T. Mosebach, B. Schwanda, N. Mayer, G. Richter, H.P. Strunk, *J. Lumin.* 145 (2014) 855–858.
- [2] F. Benz, J.A. Guerra, Y. Weng, A.R. Zanatta, R. Weingärtner, H.P. Strunk, *J. Lumin.* 137 (2013) 73–76.
- [3] F. Benz, M. Yang, Y. Weng, H.P. Strunk, *J. Lumin.* 132 (2012) 1493–1496.

**STRUCTURAL AND LUMINESCENCE PROPERTIES OF  $\text{Eu}^{3+}$  AND  $\text{Tb}^{3+}$   
RARE EARTH FLUOROPHOSPHATES WITH GENERAL FORMULA  
 $\text{LiY}_{1+x}(\text{PO}_4)_x\text{F}_4$  ( $x = 2, 3$ )**

Wahida Ltaief<sup>a,b</sup>, Aicha Mbarek<sup>a</sup>, Malika El-Ghozzi<sup>b</sup>, Daniel Zambon<sup>b</sup>, Houcine Naili<sup>c</sup>,  
Mohieddine Fourati<sup>a</sup>

<sup>a</sup> *Laboratoire de Chimie Industrielle, Ecole Nationale d'Ingénieurs de Sfax, Université de Sfax, BP W 3038, Sfax, Tunisie.*

<sup>b</sup> *Institut de Chimie de Clermont-Ferrand, UMR CNRS 6296, Université Blaise Pascal, 24 avenue Blaise Pascal, TSA 60026-CS 60026, 63178 Aubière Cedex, France.*

<sup>c</sup> *Laboratoire physico-chimique de l'état solide, Faculté des Sciences de Sfax, BP 802, 3018 Sfax, Tunisie.*

email address of the presenting author: ltaief.wahida@yahoo.fr

Rare earth orthophosphates have attracted much attention due to their wide range of applications, notably in the field of optics: plasma display panels, fluorescent lamps, solid state lasers, radiological screens, non-linear optics, biosensors and so on [1-5]. Such capabilities are mainly linked to their thermal stability and their excellent chemical behaviour. However, the cut-off phonon frequency of these materials is often high, sometimes more than  $1000 \text{ cm}^{-1}$ , leading to a disadvantageous luminescent efficiency. The phonon energy problem can be overcome through the addition of fluoride in the host matrix [6], leading to crystallized or glassy fluorophosphates materials. Moreover, fluoride materials are known for their optimal luminescent efficiencies.

In this work, we have developed a new family of fluorophosphates of general formula  $\text{LiY}_{1+x}(\text{PO}_4)_x\text{F}_4$  ( $x = 2, 3$ ), resulting from the combination of  $\text{LiYF}_4$  fluoride (scheelite structure) and  $\text{YPO}_4$  orthophosphate (zircon structure), selected in order to develop new opportunities in the aim of generation of new phosphors. The materials were elaborated using a conventional ceramic method, and characterized by XRD, NMR ( $^{31}\text{P}$ ,  $^7\text{Li}$  and  $^{19}\text{F}$ ) and Raman/IR spectroscopies. The luminescence properties of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions, the former being also used as an optical probe, are presented and discussed as a function of the host crystal structure.

### References :

- [1] A.I. Becerro, S. Rodríguez-Liviano, A.J. Fernández-Carrión, M. Ocana, *Cryst. Growth Des.* 13 (2013) 526–535.
- [2] K. Park, M.H. Heo, *J. Alloys Compd.* 509 (2011) 9111–9115.
- [3] Y.P. Fang, A.W. Xu, R.Q. Song, H.X. Zhang, L.P. You, J.C. Yu, H.Q. Liu, *J. Am. Chem. Soc.* 125 (2003) 16025–16034.
- [4] S.H. Lee, K. Teshima, S. Mori, M. Endo, S. Oishi, *Cryst. Growth Des.* 10 (2010) 1693–1698.
- [5] M.F. Dumont, C. Baligand, Y.C. Li, E.S. Knowles, M.W. Meisel, G.A. Walter, D.R. Talham, *Bioconjugate Chem.* 23 (2012) 951–957.
- [6] C. Ming, F. Song, Y. Qin, X. Ren, L. An, *Opt. Commun.* 321 (2014) 195–197.

## Discovering materials with specific effective masses, band gaps and optical properties.

Xavier Gonze

*NAPS - Chemin des Étoiles 8 bte L7.03.01 à 1348 Louvain-la-Neuve*

*xavier.gonze@uclouvain.be*

Many technologies require materials with specific effective masses, gaps and/or optical properties (e.g. photovoltaics, transparent conducting oxides, LED, phosphors, photocatalysis). In a high-throughput methodology, selected properties of several thousands of materials are computed from first principles, possibly with different degrees of accuracy, in order to constitute a database, from which one can select only a few candidates to be examined more closely by experimentalists. Sometimes, structure-property relationships emerge from such endeavour.

I will first describe our recent computational search for p-type transparent conducting oxide [1], in which not only several highly promising compounds displaying exceptionally low hole effective masses as well as wide band gaps have been identified, but a chemical rationalization of our findings has been made. One of the identified compounds indeed has recently shown impressive hole mobility [2]. Similarly, chemical rules yielding low electron effective masses in oxides have been identified [3].

The vast majority of high-throughput searches is based on Density Functional Theory with a (semi-)local exchange-correlation functionals (like GGA-PBE). In a second part of the presentation, I will describe our current efforts towards the inclusion of more accurate or more efficient formalisms, like many-body perturbation theory (GW or the Bethe-Salpeter equation, for accurate band gaps and optical properties), or density-functional perturbation theory (aiming at improved effective mass and phonon band structure calculations) in a high-throughput framework. I will also describe our search for a sufficiently lightweight procedure to select rare-earth activated phosphor materials in a high-throughput methodology.

[1] G. Hautier, A. Miglio, G. Ceder, G.-M. Rignanese and X. Gonze, *Nature Communications* 4, 2292 (2013)

[2] A. Bhatia et al, submitted.

[3] G. Hautier, A. Miglio, C. Waroquiers, G.-M. Rignanese and X. Gonze, *Chem. Mater.* 26, 5447 (2014).

## Structure and composition of the 200 K-superconducting phase of H<sub>2</sub>S under ultrahigh pressure: the perovskite (SH<sup>-</sup>)(H<sub>3</sub>S<sup>+</sup>)

Jürgen Köhler<sup>a</sup>, Elijah E. Gordon<sup>b</sup>, Ke Xu<sup>c</sup>, Hongjun Xiang<sup>c</sup>, Annette Bussmann-Holder<sup>a</sup>, Reinhard K. Kremer<sup>a</sup>, Arndt Simon<sup>a</sup>, Myung-Hwan Whangbo<sup>b</sup>

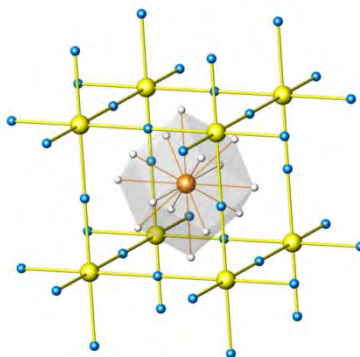
<sup>a</sup> Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany

<sup>b</sup> Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

<sup>c</sup> State Key Laboratory of Surface Physics, Collaborative Innovation Center of Advanced Microstructures and Department of Physics, Fudan University, Shanghai 200433, P. R. China

email address of the presenting author: j.koehler@fkf.mpg.de

H<sub>2</sub>S is converted under ultrahigh pressure (> 110 GPa) to a metallic phase that becomes superconducting with a record T<sub>c</sub> of ~200 K.<sup>[1]</sup> It has been proposed that the superconducting phase is body-centered cubic H<sub>3</sub>S (*Im* $\bar{3}$ *m*, a = 3.089 Å) resulting from a decomposition reaction 3H<sub>2</sub>S → 2H<sub>3</sub>S + S.<sup>[2,3]</sup> The analogy of H<sub>2</sub>S and H<sub>2</sub>O leads us to a very different conclusion. The well-known dissociation of water into H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> increases by orders of magnitude under pressure. An equivalent behavior of H<sub>2</sub>S is anticipated under pressure with the dissociation, 2H<sub>2</sub>S → H<sub>3</sub>S<sup>+</sup> + SH<sup>-</sup> forming a perovskite structure (SH<sup>-</sup>)(H<sub>3</sub>S<sup>+</sup>), which consists of corner-sharing SH<sub>6</sub> octahedra with SH<sup>-</sup> at each A-site (i.e., the center of each S<sub>8</sub> cube).<sup>[4]</sup> Our DFT calculations show that the perovskite (SH<sup>-</sup>)(H<sub>3</sub>S<sup>+</sup>) is thermodynamically more stable than the *Im* $\bar{3}$ *m* structure of H<sub>3</sub>S, and suggest that the A-site H atoms are most likely fluxional even at T<sub>c</sub>.



[1] A.P. Drozdov, M.I. Eremets, I.A. Troyan, V. Ksenofontov, S.I. Shylin, *Nature* **2015**, 525, 73.

[2] N. Bernstein, C.S. Hellberg, M.D. Johannes, I.I. Mazin, M.J. Mehl, *Phys. Rev. B* **2015**, 91, 060511.

[3] M. Einaga, M. Sakata, T. Ishikawa, K. Shimizu, M.I. Eremets, A.P. Drozdov, I.A. Troyan, N. Hirao, Y. Ohishi, arXiv: 1509.03156v1.

[4] E.E. Gordon, K. Xu, H. Xiang, A. Bussmann-Holder, R. K. Kremer, A. Simon, J. Köhler, M.-H. Whangbo, *Angew. Chem. Int. ed.* (2016), 55, 3682.

## Towards the real structure of boron-carbide

Karsten Rasim<sup>a</sup>, Christian Carbogno<sup>b</sup>, Matthias Schefler<sup>b</sup>, Juri Grin<sup>a</sup>

<sup>a</sup> *Max-Planck-Institute for Phys. Chemistry of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany*

<sup>b</sup> *Fritz-Haber-Institut of the Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany*

email address of the presenting author: karsten.rasim@cpfs.mpg.de

This investigation aims at a coherent and an as complete as possible understanding of boron carbide (BC) relating to its real structure and, closely linked to that, its electronic character.

BC, with its large homogeneity range from ~8 - ~20 at. % carbon is well known for displaying enormously high concentrations of deviations from the prototype structure that consists of B<sub>12</sub>-icosahedra and 3-atom chains of the C-B-C form.

A detailed computational study of the whole ensemble of possible kinds of “defects” throughout the whole phase width was carried out by means of DFT-modelling with the all-electron electronic structure code FHI-AIMS<sup>1</sup>.

The study, using large supercells of ~200 atoms, reveals that structural deviations from the prototype structure can, under certain conditions, become energetically stable ( $E_{\text{def}} < 0$ ) and hence structure-defining. Concerning that, attractive defect interactions were identified in a number of structural scenarios.

The corresponding electronic and vibrational features of the structural units are also under scrutiny and a combination of all this computational evidence is successful in unambiguously interpreting and rationalizing a large body of experimental findings. Those include, *e.g.*, structural imaging via HRTEM, IR/Raman data or information on the the predominant electronic p-type behavior.

[1] V. Blum et al, Computer Physics Communications, 180, (2009) 2175-2196.



# FIRST SPIN-GLASS BEHAVIOR OF A TERNARY IRON NITRIDE: STRUCTURE-PROPERTY RELATIONSHIPS IN THE SOLID SOLUTION $\text{Sn}_x\text{Fe}_{4-x}\text{N}$ ( $0 \leq x \leq 0.9$ )

Tanja Scholz, Richard Dronskowski  
Chair of Solid-State and Quantum Chemistry  
RWTH Aachen University, D-52056 Aachen, Germany

tanja.scholz@ac.rwth-aachen.de

Ferromagnetic  $\gamma'$ - $\text{Fe}_4\text{N}$  exhibits fascinating magnetic properties such as a large saturation magnetization and a low coercivity. Through systematically substituting iron atoms in the antiperovskite-like structure by other metal atoms, the magnetic properties of such ternary iron nitrides change drastically and can thus be tuned.

An ammonolytic synthesis with carefully controlled reaction conditions gave access to the solid solution  $\text{Sn}_x\text{Fe}_{4-x}\text{N}$ . Theoretical calculations showed that the incorporation of tin into  $\gamma'$ - $\text{Fe}_4\text{N}$  is energetically not preferred and that  $\text{Sn}_x\text{Fe}_{4-x}\text{N}$  is *metastable* with regard to  $\varepsilon$ - $\text{Fe}_3\text{N}$  and  $\gamma'$ - $\text{Fe}_4\text{N}$ . Using various experimental and theoretical methods, we concluded that tin exclusively substitutes the iron atoms on the larger unit-cell corners  $1a$  leading to a Vegard-type behavior of the lattice parameter over the compositional range while the center  $1b$  position is fully occupied by nitrogen as evident from PGAA [1].

Magnetic measurements proved that the gradual incorporation of tin is accompanied by a drastic weakening of the ferromagnetic interactions. AC magnetic measurements revealed the end member of the solid solution  $\text{Sn}_{0.9}\text{Fe}_{3.1}\text{N}$  as a canonical spin glass at low temperatures and as the first ternary iron nitride with a frustrated spin ground state. The time-dependent response of the magnetic spins to the external field was studied by extracting the distribution function of relaxation times  $g(\tau, T)$  up to the static glassy transition temperature from the complex plane of AC susceptibilities. To develop an understanding of the weakening of the ferromagnetic coupling, the Stoner criterion was considered and the exchange interactions were analyzed on the basis of electronic-structure calculations together with a quantum-theoretical bonding analysis [2].

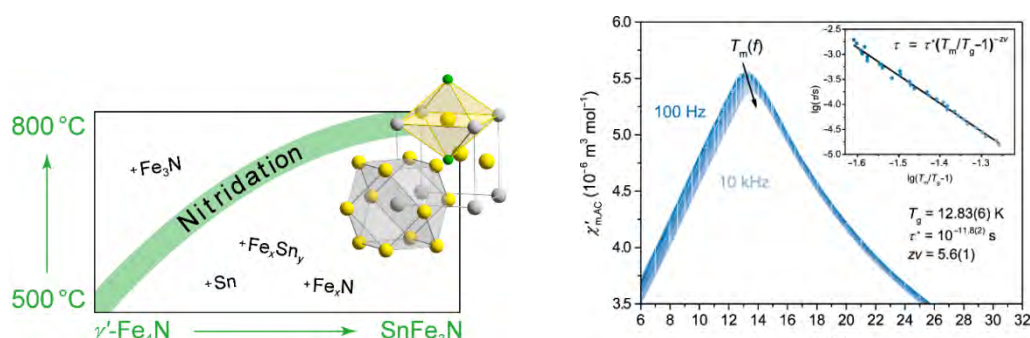


Figure: Temperature corridor for the nitriding reaction of the solid solution  $\text{Sn}_x\text{Fe}_{4-x}\text{N}$  (left) and temperature dependence of the real AC susceptibility component of  $\text{Sn}_{0.9}\text{Fe}_{3.1}\text{N}$  revealing the spin-glass behavior (right).

[1] T. Scholz, R. Dronskowski, Inorg. Chem. 54 (2015) 8800–8807.

[2] T. Scholz, R. Dronskowski, AIP Advances, *submitted*.

# ZIGZAG ANTIFERROMAGNETIC ORDER AND ORBITALLY INDUCED HIERARCHY OF EXCHANGE INTERACTIONS IN HONEYCOMB COMPOUNDS $A_3M_2SbO_6$ ( $A=Li, Na, Ag$ ; $M=Ni, Co$ )

Elena A. Zvereva<sup>a</sup>, Michail I. Stratan<sup>a</sup>, Alexey V. Ushakov<sup>b</sup>, Vladimir B. Nalbandyan<sup>c</sup>, Igor L. Shukaev<sup>c</sup>, Sergey V. Streltsov<sup>b</sup>, Alessandro Stroppa<sup>d</sup>, Silvia Picozzi<sup>d</sup>, Harald O. Jeschke<sup>e</sup>, Roser Valentí<sup>e</sup>, Alexander N. Vasiliev<sup>a</sup>

<sup>a</sup> Faculty of Physics, Moscow State University, 119991 Moscow, Russia

<sup>b</sup> Institute of Metal Physics, 620990 Ekaterinburg, Russia

<sup>c</sup> Chemistry Faculty, Southern Federal University, 344090 Rostov-on-Don, Russia

<sup>d</sup> Consiglio Nazionale delle Ricerche (CNR) SPIN, 67010 Coppito, L'Aquila, Italy

<sup>e</sup> Institut für Theoretische Physik, Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Germany

zvereva@mig.phys.msu.ru

We present a comprehensive experimental and theoretical study of the electronic and magnetic properties of three quasi-two-dimensional (2D) honeycomb-lattice monoclinic compounds  $A_3M_2SbO_6$  ( $A=Li, Na, Ag$ ;  $M=Ni, Co$ ). Magnetic susceptibility and specific heat data are consistent with the onset of antiferromagnetic (AFM) long range order, but *ab-initio* theoretical calculations reveal both antiferromagnetic and ferromagnetic intralayer spin exchange couplings between  $M^{2+}$  ions are present in the honeycomb planes supporting overall *zigzag* antiferromagnetic quantum ground state for all three compounds (Fig. 1). In addition, it was found that in contrast to  $A_3Ni_2SbO_6$  ( $A=Li, Na$ ) compounds where antiferro- and ferromagnetic couplings between  $Ni^{2+}$  ( $S=1$ ) ions occur at relatively equal strength, the ferromagnetic exchange between  $Co^{2+}$  ( $S=3/2$ ) ions is radically reduced in  $Ag_3Co_2SbO_6$ . Our GGA+U calculations show the importance of the orbital degrees of freedom, which maintain a specific hierarchy of exchange interaction for compound with Co. Thus, the strongest antiferromagnetic exchange coupling in  $Ag_3Co_2SbO_6$  was found in the shortest Co-Co pairs and is due to direct and superexchange interaction between the half-filled  $xz+yz$  orbitals pointing directly to each other (as shown on right part of Fig.1). The other four out of six nearest neighbor exchanges within the cobalt hexagon are suppressed, since for these bonds active half-filled orbitals turned out to be parallel and do not overlap. Based on the results of magnetic and thermodynamic studies in applied fields, we also propose the magnetic phase diagrams for all new honeycomb-lattice compounds.

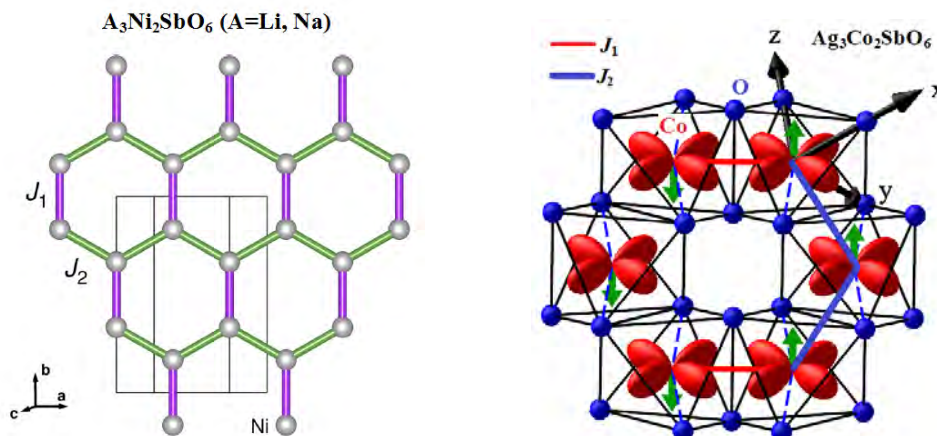


Fig. 1. Zigzag ferromagnetic chains coupled antiferromagnetically in honeycomb layer (left) of  $A_3Ni_2SbO_6$  ( $A=Li, Na$ ) and the orbital order within honeycomb cell with single half-filled  $t_{2g}$  orbital of Co as obtained in the LDA+U calculations (in the LMTO) (right).

## A CHEMICAL (BONDING) PERSPECTIVE ON PHASE-CHANGE AND RELATED MATERIALS

Richard Dronskowski  
*Chair of Solid-State and Quantum Chemistry*  
*RWTH Aachen University, D-52056 Aachen, Germany*

drons@HAL9000.ac.rwth-aachen.de

Phase-change materials (PCMs) are widely used for data storage and in other functional devices. Despite their often seemingly simple compositions, these materials exhibit intriguing microscopic complexity and a portfolio of fascinating physical properties. From a more chemical perspective, the technological success of PCMs is a simple consequence of the structural and electronic peculiarities on the atomic scale and, in particular, of their bonding nature [1]. In fact, the chemical bonding of crystalline and amorphous PCMs and also related materials is truly worth studying, now so easily done using state-of-the-art density-functional theory and properly chosen projection techniques (i.e., projected COHP) as implemented in the LOBSTER program suite [2]. In addition, finite-temperature properties of such solid-state materials are almost routinely accessible using quasiharmonic theoretical methods from first principles [3]. By doing so, structure-property relationships at zero Kelvin and beyond may be thoroughly analyzed for crystalline and amorphous bulk-like PCMs [4] as well as for surfaces structures [5], including their oxidation products [6] and chemically related chalcogenides [7].

- [1] M. Wuttig, D. Lüsebrink, D. Wamwangi, W. Welnic, M. Gillessen, R. Dronskowski, *Nature Mater.* 6 (2007) 122–128; T. Siegrist, P. Jost, H. Volker, M. Woda, P. Merkelbach, C. Schlockermann, M. Wuttig, *Nature Mater.* 10 (2011) 202–208; V. L. Deringer, R. Dronskowski, M. Wuttig, *Adv. Funct. Mater.* 25 (2015) 6343–6359; W. Zhang, V. L. Deringer, R. Dronskowski, R. Mazzarello, E. Ma, M. Wuttig, *MRS Bulletin* 40 (2015) 856–865.
- [2] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* 97 (1993) 8617–8624; V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Phys. Chem. A* 115 (2011) 5461–5466; S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Comput. Chem.* 34 (2013) 2557–2567; S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Comput. Chem.* 37 (2016) 1030–1035.
- [3] R. P. Stoffel, C. Wessel, M.-W. Lumey, R. Dronskowski, *Angew. Chem. Int. Ed.* 49 (2010) 5242–5266.
- [4] V. L. Deringer, W. Zhang, M. Lumeij, S. Maintz, M. Wuttig, R. Mazzarello, R. Dronskowski, *Angew. Chem. Int. Ed.* 53 (2014) 10817–10820
- [5] V. L. Deringer, R. Dronskowski, *J. Phys. Chem. C* 117 (2013) 15075–15089; V. L. Deringer, R. Dronskowski, *Chemical Science* 5 (2014) 894–903.
- [6] V. L. Deringer, R. Dronskowski, *J. Appl. Phys.* 116 (2014) 173703-1–8; V. L. Deringer, R. P. Stoffel, R. Dronskowski, *Cryst. Growth and Design* 14 (2014) 871–878.
- [7] V. L. Deringer, W. Zhang, P. Rausch, R. Mazzarello, R. Dronskowski, M. Wuttig, *J. Mater. Chem. C* 3 (2015) 9519–9523; V. L. Deringer, R. Dronskowski, *Angew. Chem. Int. Ed.* 54 (2015) 15334–15340.

## **FROM THE STRUCTURAL CHARACTERISTICS OF THE Ge-RICH GST PHASE CHANGE MATERIALS TO THE HIGH RELIABILITY PERFORMANCES OF THE PCM DEVICES**

V. Sousa<sup>a</sup>, G. Navarro<sup>a</sup>, N. Castellani<sup>a</sup>, M. Coué<sup>a</sup>, O. Cueto<sup>a</sup>, C. Sabbione<sup>a</sup>, V. Delaye<sup>a</sup>,  
F. Fillot<sup>a</sup>, P. Noé<sup>a</sup>, L. Perniola<sup>a</sup>, S. Blonkowski<sup>b</sup>, P. Zuliani<sup>c</sup>, R. Annunziata<sup>c</sup>

<sup>a</sup>CEA-LETI, Grenoble Cedex 9, 38054 France

<sup>b</sup>STMicroelectronics, Crolles, 38926 France

<sup>c</sup>STMicroelectronics, Agrate Brianza 2041, Italy

email address of the presenting author: veronique.sousa@cea.fr

Phase Change Memories (PCMs) are currently being developed as a possible solution for the future generations of non-volatile memories. In a PCM device, the storage element is a variable resistor comprising a small volume of phase change material. The binary information is encoded through the phase of the material, the latter being either amorphous or crystalline. One major challenge that drives the development of PCMs relates to improving the thermal stability of the programmed states. Indeed, the resistance of the two programmed states can be compromised at high temperature by two physical phenomena, which are the crystallization of the amorphous phase and the structural relaxation occurring within the polycrystalline phase. In our recent work, we have confirmed the high data retention performances of PCM devices based on Ge-rich GST materials [1]. In this presentation, we will focus on the understanding of the high thermal stability of the two programmed states, and show how it directly results from the structural characteristics of the Ge-rich GST materials at the core of the device [2].

Regarding the high resistance state which is based on the amorphous phase, we will demonstrate that the high thermal stability of the resistance relates to the non-uniform elemental distribution within the PCM layer. In fact, following the initial electrical activation of the device, the composition at the core of the storage element tends toward a Ge-rich GST alloy exhibiting a high crystallization temperature. For the low resistance state programmed under optimized conditions, we will show how the reduced drift of the resistance relates to the low number of grain boundaries formed along the conductive path in the phase change material layer. Finally, we will present the results of multi-physical simulations which account for the experimental observations, thus demonstrating how the segregation phenomena and the localization of the electronic switching of the amorphous material during programming impact both the elemental distribution and the formation of the crystalline structure at the core of the storage element.

### References:

- [1] G. Navarro, M. Coué, A. Kioussoglou, P. Noé, F. Fillot, V. Delaye, A. Persico, A. Roule, M. Bernard, C. Sabbione, D. Blachier, V. Sousa, L. Perniola, S. Maitrejean, A. Cabrini, G. Torelli, P. Zuliani, R. Annunziata, E. Palumbo, M. Borghi, G. Reimbold, B. De Salvo, « Trade-off Between SET and Data Retention Performance Thanks to Innovative Materials for Phase-Change Memory », Proceedings IEEE IEDM (2013)
- [2] V. Sousa, G. Navarro, N. Castellani, M. Coué, O. Cueto, C. Sabbione, P. Noé, L. Perniola, S. Blonkowski, P. Zuliani, R. Annunziata, « Operation Fundamentals in 12Mb Phase Change Memory Based on Innovative Ge-rich GST Materials Featuring High Reliability Performance », Proceedings IEEE VLSI (2015)

# Novel interplay of spin-orbit coupling and electron correlations in Ir<sup>4+</sup> complex oxides

Hidenori Takagi

*Max-Planck-Institute for solid state research, Stuttgart 70569, Germany*  
*Department of Physics, University of Tokyo, Tokyo 113-0033, Japan*

email address of the presenting author: h.takagi@fkf.mpg.de

Transition metal oxides with 3d elements have been a major playground for the science of strongly correlated electron systems (SCES). Recently, 5d transition metal oxides, in particular iridium oxides, emerged as a new paradigm of SCES research, where very strong spin orbit coupling meets with electron correlations. Spin-orbit coupling is a relativistic effect and relates the spin moment of an electron to its orbital momentum via a momentum-dependent effective magnetic field. In 3d oxides, spin-orbit coupling is of the order of tenth meV, which is small as compared with the other relevant electronic parameters, the band width, the Coulomb repulsion, and the crystal field splitting and can be treated as a perturbation. In contrast, spin-orbit coupling is as large as a half eV in 5d oxides represented by iridium oxides due to the strong relativistic effect in heavy elements. The spin orbit coupling in 5d oxides is comparable to the relevant parameters and therefore could modify the landscape of electronic structure [1,2]. In this talk, I would like to discuss the exotic ground states produced by the interplay of strong spin-orbit coupling with the electron correlations and the symmetry of lattice in Ir<sup>4+</sup> complex oxides. Topics include spin-orbital Mott insulating state and  $J_{\text{eff}}=1/2$  Heisenberg antiferromagnetism in the layered perovskite Sr<sub>2</sub>IrO<sub>4</sub> [1-4], Kitaev-type spin liquid state in the honeycomb Li<sub>2</sub>IrO<sub>3</sub> [4,5] and correlated Dirac semi-metallic state in the perovskite SrIrO<sub>3</sub> [6,7].

- [1] B. J. Kim *et al.*, *Phys. Rev. Lett.* **101**, 076402 (2008).
- [2] B. J. Kim *et al.*, *Science* **323**, 1329 (2009).
- [3] S. S. Fujiyama *et al.*, *Phys. Rev. Lett.* **108**, 247212 (2012).
- [4] G. Jackeli and G. Khaliullin, *Phys. Rev. Lett.* **102**, 017205 (2009).
- [5] T. Takayama, *et al.*, *Phys. Rev. Lett.* **114**, 077202 (2015).
- [6] Y. Chen *et al.*, *Nat. Commun.* **6**:6593 doi: 10.1038/ncomms7593 (2015).
- [7] J. Matsuno *et al.*, *Phys. Rev. Lett.* **114** 247209(2015).

## **Ba<sub>2</sub>NiOsO<sub>6</sub>: A POSSIBLE SPIN-ORBIT COUPLING ASSISTED FERROMAGNETIC SEMICONDUCTOR**

Kazunari Yamaura

<sup>a</sup> *Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

email address of the presenting author: yamaura.kazunari@nims.go.jp

Ba<sub>2</sub>NiOsO<sub>6</sub> was synthesized at 6 GPa and 1500 °C. It crystallized into a double perovskite structure [*Fm-3m*; *a* = 8.0428(1) Å], in which Ni<sup>2+</sup>/Os<sup>6+</sup> ions are perfectly ordered at the perovskite-B site. It is characterized as a semiconductor and we show that the spin-orbit coupling plays an essential role in opening the charge gap. A metamagnetic transition was discovered at 5 K. The magnetic state was investigated via density functional theory (DFT) calculations, as well as by neutron powder diffraction. The latter revealed that Ba<sub>2</sub>NiOsO<sub>6</sub> is in a helical magnetic state below ~32 K which transforms to a collinear ferromagnetic order in a certain magnetic field (>21 kOe at 5 K). Antiferromagnetic and ferromagnetic states are found to be almost degenerate by DFT calculations, which accounts for the metamagnetic transition. From these calculations we further conclude that Ba<sub>2</sub>NiOsO<sub>6</sub> is likely a Mott insulator, where both Coulomb and relativistic effects must be considered equally, similar to Sr<sub>2</sub>IrO<sub>4</sub>, α-RuCl<sub>3</sub>, and Ca<sub>3</sub>CoMO<sub>6</sub> (*M* = Co, Rh). Particularly, the field-induced ferromagnetic state offers the description of the compound as a “spin-orbit coupling assisted ferromagnetic semiconductor”, in qualitative distinction from a ferrimagnetic semiconductor. This finding might help to further develop the 3d/5d double perovskite oxides toward practical spintronic applications.

The study was conducted by Hai L. Feng,<sup>a,b</sup> Stuart Calder,<sup>c</sup> Madhav Prasad Ghimire,<sup>d,e</sup> Ya-Hua Yuan,<sup>a,f</sup> Yuichi Shirako,<sup>g</sup> Yoshihiro Tsujimoto,<sup>h</sup> Yoshitaka Matsushita,<sup>i</sup> Zhiwei Hu,<sup>b</sup> Chang-Yang Kuo,<sup>b</sup> Liu Hao Tjeng,<sup>b</sup> Tun-Wen Pi,<sup>j</sup> Yun-Liang Soo,<sup>j,k</sup> Jianfeng He,<sup>a,f</sup> Masahiko Tanaka,<sup>l</sup> Yoshio Katsuya,<sup>l</sup> Manuel Richter,<sup>d,m</sup>

<sup>a</sup> Superconducting Properties Unit, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan; <sup>b</sup> Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany; <sup>c</sup> Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA; <sup>d</sup> Leibniz Institute for Solid State and Materials Research, IFW Dresden, PO box 270116, D-01171 Dresden, Germany; <sup>e</sup> Condensed Matter Physics Research Center, Butwal-13, Rupandehi, Lumbini, Nepal; <sup>f</sup> Graduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan; <sup>g</sup> Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan; <sup>h</sup> Materials Processing Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan; <sup>i</sup> Materials Analysis Station, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan; <sup>j</sup> National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan; <sup>k</sup> Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan; <sup>l</sup> Synchrotron X-ray Station at SPring-8, National Institute for Materials Science, Kouto 1-1-1, Sayo-cho, Hyogo 679-5148, Japan; <sup>m</sup> Dresden Center for Computational Materials Science, DCMS, TU Dresden, D-01069 Dresden, Germany



# THERMODYNAMIC PROPERTIES, OPTICAL SPECTROSCOPY AND UNDERLYING MODEL IN FRANCISITE – TYPE FAMILY OF COMPOUNDS $\text{Cu}_3\text{RE}(\text{SeO}_3)_2\text{O}_2\text{Cl}$

K.V. Zakharov,<sup>a</sup> E.A. Zvereva,<sup>a</sup> P.S. Berdonosov,<sup>a</sup> E.S. Kuznetsova,<sup>a</sup> V.A. Dolgikh,<sup>a</sup>  
M.M. Markina,<sup>a</sup> O.S. Volkova,<sup>a,b</sup> S.A. Klimin,<sup>c</sup> Z.V. Pchelkina,<sup>d</sup> S.V. Streltsov,<sup>d</sup>  
A.N. Vasiliev<sup>a,b</sup>

<sup>a</sup>M.V. Lomonosov Moscow State University, Moscow 119991, Russia

<sup>b</sup>National University of Science and Technology "MISIS", Moscow 119049, Russia

<sup>c</sup>Institute of Spectroscopy, Russian Academy of Sciences, Troitsk 142190, Russia

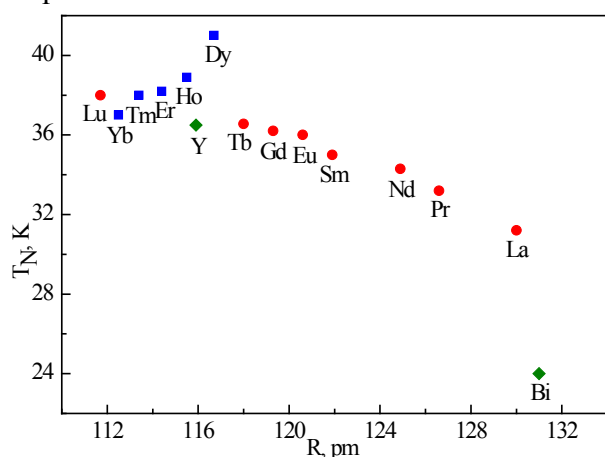
<sup>d</sup>Institute of Metal Physics, Russian Academy of Sciences, Ekaterinburg 620219, Russia

anvas2000@yahoo.com

The title compounds are the synthetic analogues of the mineral francisite  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ , which crystallizes in the orthorhombic space group  $Pm\bar{m}n$  with cell dimensions  $a = 6.354(1)$  Å,  $b = 9.630(1)$  Å,  $c = 7.220(2)$  Å and  $Z = 2$ . It consists of two-dimensional buckled kagome sheets of  $\text{Cu}^{2+}$  cations in the  $ab$ -plane, containing eight-coordinated  $\text{Bi}^{3+}$ , square-planar (or tetragonally distorted octahedra)  $\text{Cu}^{2+}$ , and three-coordinated  $\text{Se}^{4+}$ . The chloride ions and the selenium lone pair electrons occupy tunnels parallel to  $[001]$  crystal axis.<sup>1</sup>

At low temperatures, the francisite-type compounds develop an alternating antiferromagnetic order of the kagome layers, which individually exhibit a canted ferrimagnetic moment resulting from competing ferro- and antiferromagnetic intra-layer exchange interactions. An external magnetic field triggers a metamagnetic transition, where every second layer flips resulting in a ferrimagnetic structure.<sup>2</sup>

The presence of rare-earth ions in the francisite's structure adds new dimension to physics of this system. The Neel temperature  $T_N$  of Y-francisite is one and a half higher than that in Bi-francisite.<sup>3</sup> The radius of rare-earth ions  $R$  is not, however, the only factor which influences the ordering temperature. There are different trends in  $T_N$  vs.  $R$  dependence: with increasing radius the Neel temperature rises in a sequence from Yb to Dy and drops in a sequence from Tb to La.



Some of the rare-earth francisites, namely Nd-, Sm- and Yb-based ones, exhibit additional sharp transitions well below the Neel temperature evidenced in magnetization, specific heat and optical spectroscopy. These transitions are attributed to spin reorientation in the copper subsystem which realigns with the rare-earth magnetic moments. As a result, the magnetic anisotropy of rare-earth ions realizes resulting in an abrupt increase of the ground level splitting. The first principles calculations enable establishing the

underlying spin model for francisite-type family of compounds.<sup>3</sup>

## References

- [1] A. Pring, B.M. Gatehouse and W.D. Birch, Amer. Mineral. 75 (1990) 1421.
- [2] M. Pregelj, O. Zaharko, A. Günther, et al., Phys. Rev. B 86 (2012)144409.
- [3] K.V. Zakharov, E.A. Zvereva, P.S. Berdonosov, et al., Phys. Rev. B 90 (2014) 214417.

## Magnetic state changes in the $\text{Co}_{5-x}\text{Zn}_x\text{TeO}_8$ spinel family

Nicolas Barrier<sup>a</sup>, Alain Pautrat<sup>a</sup>, Morgane Poupon<sup>a</sup>, Gilles André<sup>b</sup>

<sup>a</sup>Laboratoire CRISMAT, UMR 6508 CNRS ENSICAEN, 6 bd Maréchal Juin, 14050 CAEN Cedex 4, France.

<sup>b</sup>Laboratoire Léon Brillouin, UMR12 CEA-CNRS, 91191 Gif sur Yvette Cedex, France

nicolas.barrier@ensicaen.fr

The  $\text{AB}_2\text{O}_4$  spinel phases are known for decades as a famous family in the field of magnetic oxides. More recently several spinel phases such as  $\text{CoCr}_2\text{O}_4$  have been intensively studied for their multiferroic properties. [1] In the spinel structure the A and B sites correspond to tetrahedral and octahedral environments, respectively. When both sites are occupied by magnetic cations the inter-sublattice exchange interaction  $J_{AB}$  is much stronger than the intra-sublattice ones  $J_{AA}$  and  $J_{BB}$ . These three exchange interactions are negatives leading to collinear ferrimagnetic order of Neel type. Nevertheless the two magnetic sublattices ( $J_{AA}$  and  $J_{BB}$ ) remain frustrated and short range magnetic order is also observed. The dilution with non-magnetic cations weakened the inter-sublattice interaction  $J_{AB}$  and the intra-sublattice interactions  $J_{AA}$  and  $J_{BB}$  are then strong enough to compete with the  $J_{AB}$  one. So, magnetic states such as re-entrant phase and pure spin glass are observed. [2,3,4] The magnetic dilution was extremely study on disordered spinel compounds but not so much on ordered ones, where two different octahedral sites B and B' are present.

In this context we will present our study on the spinel family  $\text{Co}_{5-x}\text{Zn}_x\text{TeO}_8$  ( $x = 0, 1, 2$ ). All crystal structures were refined from combined powder X-ray diffraction and neutron diffraction data. The magnetic properties were characterized from powder neutron diffraction data, small angle neutron scattering data as well as SQUID-based magnetometers measurements. We will compare the structures and magnetic properties of both phases  $\text{Co}_5\text{TeO}_8$  ordered and disordered, and we will discuss the presence of a possible magnetoelectric coupling. The effect on magnetic dilution on the A site will be presented through the results obtained on two ordered spinel phases  $\text{Co}_{5-x}\text{Zn}_x\text{TeO}_8$  ( $x = 1, 2$ ).

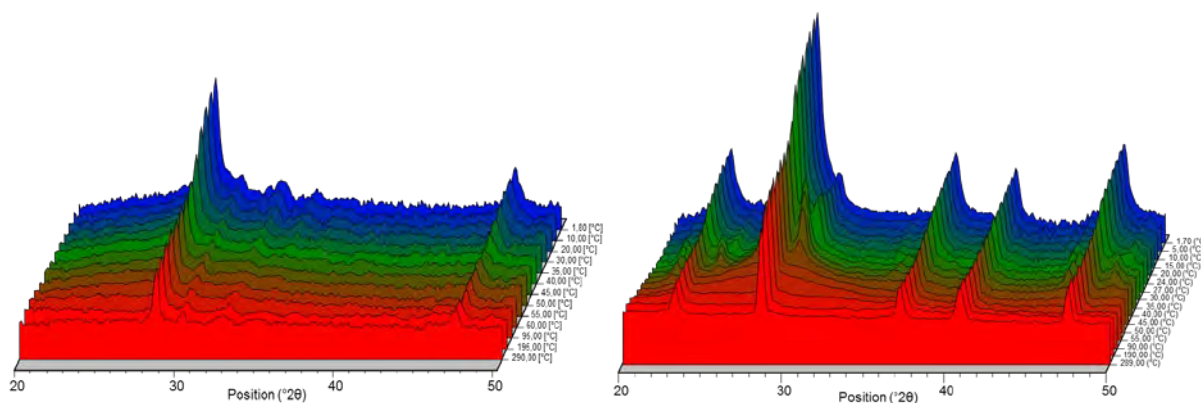


Figure 1. Powder neutron diffraction data versus temperature for  $\text{Co}_5\text{TeO}_8$  phases - disordered (left) and - ordered (right)

- [1] Y.Yamasaki, S. Miyasaka, Y. Kaneko, J.P. He, T. Arima and Y. Tokura, *Phys. Rev. Lett.* 96 (2006) 207204
- [2] J. Vilain, *Z. Physik B* 33 (1979) 31
- [3] C.P. Poole and H.A. Farach, *Z. Physik B* 47 (1982) 55
- [4] J.L. Dorman and M. Nogues, *J. Phys. : Condens. Matter.* 2 (1990) 1223

# MOTIVES OF CONNECTIVITY AND SPIN-ORBIT INTERACTION IN KAGOME SYSTEMS

P. Lemmens<sup>a</sup>

<sup>a</sup>*Inst. of Condensed Matter Physics, TU Braunschweig, D-38106 Braunschweig, Germany*

p.lemmens@tu-bs.de

Magnetism in layered compounds is related to an exceptional degree to motives of connectivity. This interplay of symmetry and magnetic interactions can even lead to a suppression of long range magnetic order. Here, we elaborate on the fact that this also shows up in dynamic effects of the lattice induced by spin-orbit interactions. We will compare different realizations of magnetic transition metal ions on a triangular or kagome lattice. Examples are synthetic minerals such as francisites, herbertsmithites, and kapellasites [1-4]. The role of spin-orbit interaction will be evaluated.

## Reference:

- [1] Structural and magnetic instabilities of the pseudo-Kagome francisites  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{X}$  with  $\text{X}=\text{Br}, \text{Cl}$ , V. Gnezdilov, Yu. Pashkevich, P. Lemmens, A. Vasiliev, P. Berdonosov, preprint (2016).
- [2] Tuning the spin dynamics of kagome systems, D. Wulferding, P. Lemmens, H. Yoshida, Y. Okamoto, and Z. Hiroi, *J. Phys.: Condens. Matter* **24**, 185602 (2012).
- [3] Interplay of thermal and quantum spin fluctuations in the kagome lattice compound Herbertsmithite, D. Wulferding, P. Lemmens, P. Scheib, J. Roeder, P. Mendels, Sh. Chu, T.-H. Han, Y. S. Lee, *Phys. Rev. B* **82**, 144412 (2010).
- [4] Magneto-structural transition in a frustrated magnet at high fields, V. Tsurkan, S. Zherlitsyn, V. Felea, S. Yasin, Yu. Skourski, J. Deisenhofer, H.-A. Krug von Nidda, P. Lemmens, J. Wosnitza, and A. Loidl, *Phys. Rev. Lett.* **106**, 247202 (2011).

## Soft Chemical Routes to Multiferroic Materials

Ronghuan Zhang, Michael Hayward

*Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, United Kingdom*

email address of the presenting author: michael.hayward@chem.ox.ac.uk

Magnetoelectric multiferroic materials – those which simultaneously exhibit both a spontaneous magnetic polarization (ferromagnetism) and a spontaneous electrical polarization (ferroelectricity) – are challenging to prepare. This is because the structural distortions which are usually responsible for the lifting of inversion symmetry (a prerequisite for ferroelectric behavior) are incompatible with magnetism.[1]

Recently there has been much interest in utilizing the cooperative tilting and twisting distortions of the networks of octahedra in layered perovskite phases to break inversion symmetry and induce ferroelectric behavior. For example if the  $a^-a^-c^+$  tilting scheme, observed in the  $GdFeO_3$  modification of the cubic perovskite structure, can be induced into an  $n = 2$  Ruddlesden-Popper framework then a non-centrosymmetric, potentially ferroelectric phase can be formed.[2]

We have been utilizing topochemical fluorine insertion reactions to modify the tilting schemes of  $n = 2$  Ruddlesden-Popper oxides so that we can better understand the factors that control the cooperative distortions in these phases and ultimately use this information to induce ferroelectric and magnetoelectric behavior.[3, 4]

[1] N.A. Hill, J. Phys. Chem. B 104 (2000) 6694.

[2] N.A. Benedek, J.M. Rondinelli, H. Djani, P. Ghosez, P. Lightfoot, Dalton Trans. 44 (2015) 10543.

[3] F. Denis Romero, P.A. Bingham, S.D. Forder, M.A. Hayward, Inorg. Chem. 52 (2013) 3388.

[4] R. Zhang, G. Read, F. Lang, T. Lancaster, S.J. Blundell, M.A. Hayward, Inorg. Chem. 55 (2016) 3169.

## Emergent chiral spin structure and unconventional electronic states in the stacked-kagomé-layered $\text{Co}_3\text{Sn}_{2-x}\text{In}_x\text{S}_2$ shandites.

M. A. Kassem<sup>1</sup>, K. Itou<sup>1</sup>, Y. Tabata<sup>1</sup>, T. Waki<sup>1</sup>, C. Michioka<sup>2</sup>, K. Yoshimura<sup>2</sup>, H. Nakamura<sup>1</sup>.

<sup>1</sup> Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan.

<sup>2</sup> Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan.

Email: kassem.ahmed.82s@st.kyoto-u.ac.jp

The Co-based shandites  $\text{Co}_3\text{Sn}_{2-x}\text{In}_x\text{S}_2$  have been attracting much interest because of their promising exotic magnetic and electronic properties: half metal ferromagnetism, magnetic instability, anisotropic conductivity and low gap semiconductivity with high thermoelectric properties [1-4]. The Co-based shandites has a stacked-kagomé-layered crystal structure with the space group  $R\bar{3}m$ . Metallic layers are arranged in the kagomé network of the Co atoms and triangular one of the intra-layer Sn/In atoms on  $3a$ -site. The S atoms and Sn/In atoms on  $3b$ -site locate at interlayer positions.

Here we present the structure-related magnetic and electronic properties observed using single crystals of  $\text{Co}_3\text{Sn}_{2-x}\text{In}_x\text{S}_2$  ( $0 < x \leq 2$ ) successfully grown out of Sn, In and Pb fluxes [5]. Magnetization measurements show a ferromagnetic-nonmagnetic quantum phase transition around  $x_c \sim 0.8$ . Through a combined work of magnetic and magneto-transport measurements, we found the topological Hall effect in the vicinity of the critical concentration,  $0.5 \leq x \leq 0.8$ , indicating presence of the chiral ordered state which should attribute to the geometry of the Co-kagomé sublattice (see Fig. 1(a)). A semimetallic, not semiconducting, transport behavior as well as a strong reduction of the electronic specific heat coefficient  $\gamma$  was observed around  $x \sim 1$ , which indicates an unconventional electronic state with anomalously small Fermi surface around  $x \sim 1$  (Fig. 1(b)). Moreover, the observed enhanced anisotropy in the electrical resistivity in the high In-concentration region indicates a quasi-two-dimensional (Q2D) electronic state due to the layered crystal structure of the Co-shandites.

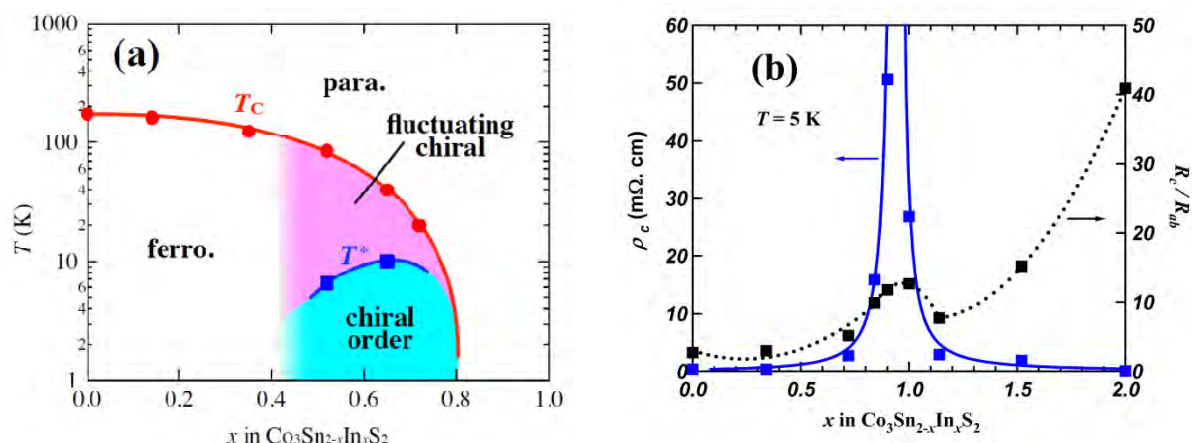


Fig. 1: (a) Magnetic phase diagram and (b)  $x$ -dependence of the electrical resistivity of  $\text{Co}_3\text{Sn}_{2-x}\text{In}_x\text{S}_2$ .

- [1] W. Schnelle, A. Leithe-Jasper, H. Rosner, F.M. Schappacher, R. Pöttgen, F. Pielhofer, R. Wehrich, Phys. Rev. B 88 (2013) 144404.
- [2] F. Pielhofer, J. Rothbaler, P. Peter, W. Yan, F.M. Schappacher, R. Pöttgen, R. Wehrich, Anorg. Allg. Chem. 640 (2014) 286–294.
- [3] R. Wehrich, I. Anusca, Z. Anorg. Allg. Chem. 632 (2006) 335–342.
- [4] J. Corps, P. Vaqueiro, A. Aziz, R. Grau-Crespo, W. Kockelmann, J.-C. Jumas, A. V. Powell, Chem. Mater. 27 (2015) 3946–3956.
- [5] M.A. Kassem, Y. Tabata, T. Waki, H. Nakamura, J. Cryst. Growth. 426 (2015) 208–213.

## Epitaxially-strained GeTe as a prototype material for a microscopic understanding of bulk Rashba properties

Emilie Bruyer<sup>a,c</sup>, Paolo Barone<sup>b</sup>, Domenico Di Sante<sup>b</sup>, Silvia Picozzi<sup>b</sup>

<sup>a</sup> *Institut des Sciences Chimiques de Rennes - UMR CNRS 6226, Rennes, France*

<sup>b</sup> *Consiglio Nazionale delle Ricerche (CNR-Spin), Via Vetoio, L'Aquila, Italy*

<sup>c</sup> [emilie.bruyer@univ-rennes1.fr](mailto:emilie.bruyer@univ-rennes1.fr)

Relativistic effects are increasingly seen as key ingredients in the burgeoning field of spintronics. Among them, the Rashba effect, in which the spin degeneracy is removed as a consequence of spin-orbit coupling (SOC) in noncentrosymmetric structures, plays a leading role. An interesting subclass of bulk materials lacking inversion symmetry is represented by ferroelectrics, which could in principle allow to bring in a novel functionality through the interplay between ferroelectricity and SOC-induced Rashba spin-splitting (RSS). For such materials, the coupling of RSS with electric polarization opens up a wide range of potential applications in the field of semiconductor spintronics, aiming at an all-electric control of spin transport in novel devices. In this context, many efforts are now given in the search for such multifunctional materials and strain engineering is nowadays regarded as a powerful tool to tune these highly desirable properties.

Using first-principles calculations, we simulated a (111) epitaxially-strained growth and computed the changes in the structural, electronic and magnetic behaviour of GeTe, a ferroelectric material known to also exhibit a wide bulk RSS. Interestingly, our results showed that RSS could not be driven by the sole modification of the ferroelectric polarization and the electronic band gap, as usually believed. Further DFT calculations and the elaboration of a tight-binding model lead to the identification of the main parameters entering the strength of RSS and identify their contribution. In particular, this study highlights that the RSS is not only strongly  $k$ -dependent, but also very sensitive to the orbital character of the bands around the Fermi level. Our findings demonstrate the decisive influence of the electronic structure on spin-orbital properties and the need of a deep understanding of these features for each multifunctional material.



## AMnGe<sub>2</sub>O<sub>6</sub> (A = Ca or Sr) : effect of the divalent cation in the pyroxene structure : how to induce multiferroicity ?

Lei Ding<sup>ab</sup>, Claire V. Colin<sup>ab</sup>, Céline Darie<sup>ab</sup>, J. Robert<sup>ab</sup>, F. Gay<sup>ab</sup>, Pierre Bordet<sup>ab</sup>

<sup>a</sup>Univ. Grenoble Alpes, Inst NEEL, F-38000 Grenoble, France

<sup>b</sup>CNRS, Inst NEEL, F-38000 Grenoble, France

celine.darie@neel.cnrs.fr

As a non-trivial magnetic system, pyroxenes with chemical formulas AMT<sub>2</sub>O<sub>6</sub> (A = mono- or divalent metal, M = di- or trivalent transition metal, T = Si or Ge) containing magnetic cations have recently attracted revitalized interest because of their intriguing quasi-one-dimensional magnetic [1,2] and multiferroic properties [3,4]. These properties are associated with the special arrangement of the pyroxene crystal structure, where almost isolated zig-zag chains of edge-sharing MO<sub>6</sub> octahedra are bridged by corner linked TO<sub>4</sub> tetrahedra chains. (fig1). However, the replacement of Ca<sup>2+</sup> by Sr<sup>2+</sup> may bring in new interesting results since the larger radius of Sr<sup>2+</sup> cations will certainly lead to modifications of the structure and hence of the magnetic interactions inside and between the magnetic cation chains. This would entail new invaluable information about the role of the different cations on the intriguing properties of this rich family of compounds. We present here the chemical synthesis and the investigation of crystal structure and magneto-electric properties of the two pyroxene compounds: AMnGe<sub>2</sub>O<sub>6</sub> (A = Ca, Sr), by means of neutron powder diffraction (NPD), heat capacity, magnetic and pyroelectric current measurements. For CaMnGe<sub>2</sub>O<sub>6</sub> these techniques coincidentally reveal the presence of 1D short range spin correlations appearing well above the long range antiferromagnetic order at T<sub>N</sub>=15 K. Consistent with the determination of the magnetic structure (C2'/c), the magnetic field dependence of the electrical polarization signals a clear linear magnetoelectric effect below T<sub>N</sub>. [5] A long range spin ordered state is found in SrMnGe<sub>2</sub>O<sub>6</sub> below 4.5 K and the relevant magnetic structure is determined to be cycloidal. The associated multiferroic properties (fig2) are experimentally observed and a spin-current model is used to explain the spontaneous polarization below T<sub>N</sub>. [6]

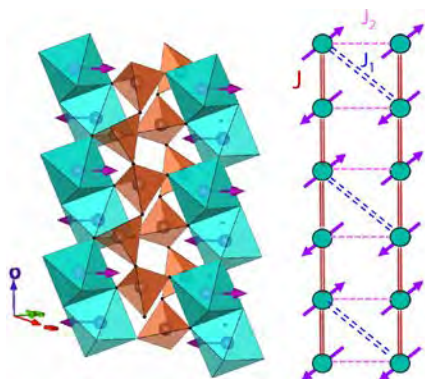


Fig. 1. (color online) (Left) Representation of the magnetic structure of CaMnGe<sub>2</sub>O<sub>6</sub>; (Right) the schematic drawing of exchange interactions

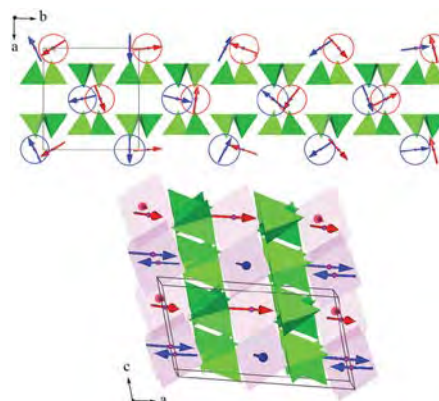


Fig. 2 Schematic of the cycloidal magnetic structure of SrMnGe<sub>2</sub>O<sub>6</sub> below T<sub>N</sub> projected onto the a–b plane (top) and the (a, c) plane (bottom)

[1] M. Isobe, E. Ninomiya, A. N. Vasil'ev and Y. Ueda, J. Phys.Soc. Jpn 71 (2002) 1423.

[2] S. V. Streltsov and D. I. Khomskii, Phys. Rev. B: Condens.Matter Mater. Phys 77 (2008) 064405.

[3] I. Kim, B. G. Jeon, D. Patil, S. Patil, G. Ne'ner and K. H. Kim, J. Phys.: Condens. Matter 24 (2012) 306001

[4] S. Jodlauk, P. Becker, J. A. Mydosh, D. I. Khomskii, T. Lorenz, S. V. Streltsov, D. C. Hezel and L. Bohaty', J. Phys.: Condens.Matter 19 (2007) 432201

[5] L. Ding, C.V. Colin, C. Darie, J. Robert, F. Gay and P. Bordet Phys. Rev. B: Condens.Matter Mater. Phys. 93 (2016) 064423

[6] L. Ding, C.V. Colin, C. Darie and P. Bordet J. of Mat. Chem. C, 2016, DOI: 10.1039/C6TC00149A



## Persistent signature of type-II multiferroicity in nanostructured MnWO<sub>4</sub> ceramics prepared via spark plasma sintering

Pascaline Patureau<sup>a</sup>, U-Chan Chung-Seu<sup>b</sup>, Dominique Michau<sup>b</sup>, Michaël Josse<sup>b</sup>,  
Rémi Dessapt<sup>a</sup>, Philippe Deniard<sup>a</sup>, Christophe Payen<sup>a</sup>, Mario Maglione<sup>b</sup>

<sup>a</sup> *Institut des Matériaux Jean Rouxel (IMN) – Université de Nantes, CNRS, 2 rue de la  
Houssinière, BP 32229, 44322 Nantes cedex 3, France*

<sup>b</sup> *Institut de Chimie de la Matière Condensée de Bordeaux, 87 Avenue du Dr Albert  
Schweitzer, 33600 Pessac, France*

Pascaline.patureau@gmail.com

Multiferroic materials have been intensively studied to develop sensors or new robust information storage hosts.<sup>[1]</sup> However, these application fields require miniaturisation of the materials down to the nanometric scale and this necessity has been proved to be challenging for the perovskite structures-based multiferroic materials. These so-called type I materials are nowadays the most promising ones for information storage due to their high polarization and transition temperatures. In these materials, the coupling between ferroelectric and magnetic properties is rather weak and the ferroelectric property is the first to degrade as the size decreases.<sup>[2,3]</sup> We thus chose to explore another type of magneto-electric multiferroic material; the spin-spiral type II multiferroic materials. Indeed, in these compounds, the polarization is directly induced by the spin alignment,<sup>[4]</sup> i.e., by the magnetic order which is expected to be much less sensitive to the size decrease than the ferroelectric one.

Nanoparticles of MnWO<sub>4</sub>, an archetypical spin-spiral type II multiferroic material,<sup>[5]</sup> were therefore synthesized by a hydrothermal route. This synthesis route allowed us tuning both the size and the morphology of the nano-objects.<sup>[6]</sup> Spark plasma sintering (SPS) process was then used to obtain dense pellets in which all the characteristics of the non-densified nanoparticles remained safe. The synthesis and densification of the MnWO<sub>4</sub> nanoparticles will be discussed in detail as well as their magneto-electric properties. These latter measurements showed a persistent signature of multiferroicity very similar to the bulk one regardless of both size and morphology of the nanoparticles.

[1] D. I. Khomskii, *J. Magn. Magn. Mater.* 306 (2006) 1–8.

[2] I. S. Golovina, S. P. Kolesnik, V. P. Bryksa, V. V. Strelchuk, I. B. Yanchuk, I. N. Geifman, S. A. Khainakov, S. V. Svechnikov, A. N. Morozovska, *Phys. B Condens. Matter* 407 (2012) 614–62

[3] Q. Jiang, H. Ning, Q. Zhang, M. Cain, M. J. Reece, H. Yan, *J. Mater. Chem. C* 1 (2013) 5628–5631.

[4] Y. Tokura, S. Seki, *Adv. Mater.* 22 (2010) 1554–1565.

[5] O. Heyer, N. Hollmann, I. Klassen, S. Jodlauk, L. Bohatý, P. Becker, J. A. Mydosh, T. Lorenz, D. Khomskii, *J. Phys. Condens. Matter* 18 (2006) L471.

[6] W. B. Hu, X. L. Nie, Y. Z. Mi, *Mater. Charact.* 61 (2010) 85–89

# BRIDGING FIRST-PRINCIPLES CALCULATIONS TO MÖSSBAUER SPECTRA OF DEFECTS IN SEMICONDUCTORS

José Coutinho<sup>a</sup>, Edgar Wright<sup>a</sup>, Sven Öberg<sup>b</sup> and Vitor J. B. Torres<sup>a</sup>

<sup>a</sup> *Department of Physics and I3N, University of Aveiro, Campus Santiago, 3810-193 Aveiro, Portugal*

<sup>b</sup> *Department of Engineering Sciences and Mathematics, Luleå University of Technology, Luleå S-97187, Sweden*

email address of the presenting author: jose.coutinho@ua.pt

A methodology combining pseudopotential and all-electron density functional calculations, to relate the structure of defects in supercells to the isomer shifts and quadrupole splittings observed by Mössbauer experiments, will be presented [1]. The method will be demonstrated to the technologically relevant case of iron-related defects in silicon, and to other group-IV hosts with less detail. Investigated defects include interstitial and substitutional iron, iron-boron pairs, iron-vacancy and iron-divacancy. We find that in general, agreement between the calculations and Mössbauer data is within a 10% error bar. Nonetheless, we show that the methodology can be used to make accurate assignments, including to separate peaks of similar defects in slightly different environments.

Reference to a journal publication:

[1] E. Wright, J. Coutinho, S. Öberg and V. J. B. Torres, to appear in *Journal of Applied Physics* (2016).

## Describing the magnetic structure and origin of band gap on $\text{Ba}_2\text{CuOsO}_6$ system; density functional theory approach

Changhoon Lee<sup>a,b,c</sup>, Jisook Hong<sup>b</sup>, Taewon Jin<sup>b</sup>,  
Ji Hoon Shim<sup>b,c</sup>, and Myung-Hwan Whangbo<sup>a</sup>

<sup>a</sup>*Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, USA*

<sup>b</sup>*Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea*

<sup>c</sup>*Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea*

email address of the presenting author: chlee0887@postech.ac.kr

We examine the magnetic structure and origin of band gap opening for  $\text{Ba}_2\text{CuOsO}_6$  by extracting spin exchange interaction and by adopting spin-orbit coupling effect. The ordered double-perovskites  $\text{Ba}_2\text{CuOsO}_6$  which consist of 3d and 5d transition-metal magnetic ions ( $\text{Cu}^{2+}$  and  $\text{Os}^{6+}$ , respectively) is magnetic insulators; the magnetic susceptibilities of  $\text{Ba}_2\text{CuOsO}_6$  obey the Curie-Weiss law with dominant antiferromagnetic interactions and the estimated Weiss temperature is -13.3 K. Solid-state osmium oxides can exhibit a variety of magnetic and electronic phenomena associated with their electron correlation. There are two important issues on solid-state osmium oxides; one is origin of band gap inducing metal to insulator transition. Other one is variety of oxidation state of Os ion. This wide spectrum of oxidation state of Os atom on osmium compounds is directly attributable to a large a spatial extension of Os 5d orbital. From the results of density functional study, the spin exchange interaction between Cu atoms is mainly responsible for antiferromagnetic ordering on  $\text{Ba}_2\text{CuOsO}_6$  system. To describe the magnetic insulating states of  $\text{Ba}_2\text{CuOsO}_6$ , it is necessary adopting an electron correlation effect as well as spin-orbit coupling effect.

## EQUATION OF STATE FOR SOLIDS

Elijah E. Gordon<sup>a</sup>, Jürgen Köhler<sup>b</sup>, M.-H. Whangbo<sup>a,\*</sup>

<sup>a</sup> *Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA*

<sup>b</sup> *Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany*

mike\_whangbo@ncsu.edu

For solids, the relationship between the atomic volume  $V$  and the applied pressure  $P$  is commonly described by the Birch-Murnaghan equation of state,<sup>[1]</sup>

$$P = \frac{3K_0}{2} \left[ \left( \frac{V}{V_0} \right)^{\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3(K'_0 - 4)}{4} \left[ \left( \frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right] \right\}, \quad (1)$$

which is derived by assuming that the bulk modulus,  $K = -V(\partial P / \partial V)_T$ , of a solid depends linearly on  $P$ , that is,  $K = K_0 + PK'_0$ . This equation of state is valid when the volume decrease under pressure is not large (typically, for  $V/V_0 \geq 0.8$ ). To find an equation of state applicable for a wide range of pressure, we examined the internal energy  $E$  and enthalpy  $H$  of elemental solids S, Se and Te as a function of  $P$  on the basis of DFT calculations. Our study reveals that, to a first approximation, both  $E$  and  $H$  depend linearly on  $P$ , thereby suggesting that the pressure  $P$  is a function of the energy term  $PV$ . Therefore, one might express  $P$  as a polynomial of  $PV$ ,

$$P = \alpha(PV) + \beta(PV)^2 + \gamma(PV)^3 + \dots, \quad (2)$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are constants. For the elemental solids S, Se and T, all known  $V$ . vs.  $P$  data for a wide range of pressure are well described by the quadratic equation,<sup>[2]</sup>

$$P = \alpha(PV) + \beta(PV)^2. \quad (3)$$

Implications of this observation will be discussed.

### References

[1] F. Birch, Phys. Rev. 71 (1947) 809–824.

[2] E. E. Gordon, J. Köhler, M.-H. Whangbo, to be submitted.

## STRUCTURE AND PROPERTIES OF MIXED COBALT/MANGANESE/IRON TIN CLUSTERS

Tilo Söhnel<sup>a</sup>, Morgan C. Allison<sup>a,b</sup>, Furitsu Suzuki<sup>a</sup>, Fritz. E. Wagner<sup>c</sup>, Glen Stewart<sup>d</sup>,  
Chris D. Ling<sup>e</sup>

<sup>a</sup> School of Chemical Sciences, University of Auckland, New Zealand

<sup>b</sup> School of Chemistry, The University of Sydney, Sydney, Australia

<sup>c</sup> Physics Department E15b, Technical University, Munich, Germany

<sup>d</sup> School of Physical, Environmental and Mathematical Sciences, UNSW@ADFA, Canberra, Australia

email address of the presenting author: t.sohnel@auckland.ac.nz

Layered oxides containing third row transition metals possess interesting crystal and electronic architectures, which may exhibit novel multiferroic properties such as ferroelectricity and giant magnetoresistance [1]. The parent compound for this presentation  $\text{Fe}_4\text{Si}_2\text{Sn}_7\text{O}_{16}$  [1] can be described as a layered composite of intermetallic ( $\text{FeSn}_6$ ) clusters and olivine-like  $(\text{SiO}_4)\text{-(FeO}_6\text{)/(SnO}_6\text{)}$  oxide layers within the one structure [2].  $\text{SiO}_4$  tetrahedra separate these layers which leads to electronic and magnetic isolation of the repeated layers by about 7 Å resulting in a nearly perfectly 2D oxide system comparable to a one layer thick oxide “thin film”. This combination of features therefore allows us a unique opportunity to study the electronic interaction of two materially independent features in the one material. In this study we have replaced iron positions with cobalt and/or manganese [3] in order to study the change in structure and material properties. Refinements of the structures on synchrotron and neutron diffraction data show the distinct different behaviour of Mn and Co replacement in  $\text{MSn}_6$  octahedral layer in these materials. Compounds containing both iron and cobalt resulting in the first 19 electron cluster seen in the tin system. The resulting electronic structure will be discussed based on DFT calculations and XANES measurements.

<sup>57</sup>Fe-Mössbauer spectra (Fig. 1) confirm the observation from neutron diffraction studies and show that Mn has a strong affinity for the oxide layer positions, whereas Co preferably occupies the of intermetallic Sn cluster layer.

The Fe/Mn cluster compounds show an antiferromagnetic ordering below 3 K. The magnetic structures could be solved using field dependent powder neutron diffraction.

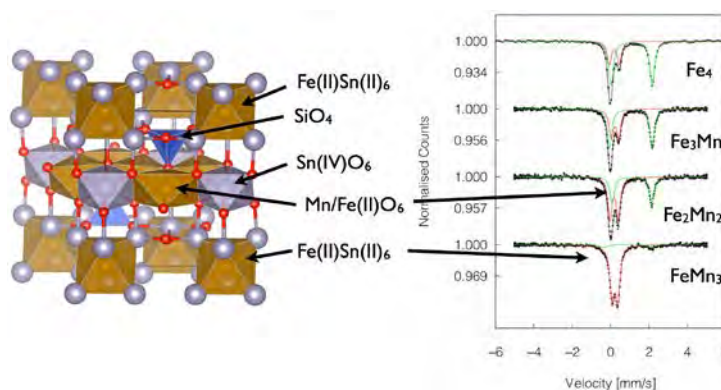


Figure 1: Crystal structure (left) and <sup>57</sup>Fe-Mössbauer spectra of  $\text{FeFe}_{3-x}\text{Mn}_x\text{Si}_2\text{Sn}_7\text{O}_{16}$ .

[1] S.W. Cheong, M. Mostovoy, *Nature Mater.* 6, (2007) 13.

[2] T. Söhnel, P. Böttcher, W. Reichelt, F. E. Wagner, *Z. Anorg. Allg. Chem.* 624 (1998) 708.

[3] M.C. Allison, M. Avdeev, S. Schmid, S. Liu, C.D. Ling, T. Söhnel, submitted.

**RELATIVISTIC FERROELECTRICS:  
A NOVEL CLASS OF MULTIFUNCTIONAL MATERIALS**

Silvia PICOZZI<sup>1</sup>,

<sup>1</sup> *Consiglio Nazionale delle Ricerche CNR-SPIN (67100 L'Aquila, Italy)*

The discovery of novel properties, effects or microscopic mechanisms in modern materials science is often driven by the quest for the coexistence and/or coupling of several functional properties into a single compound. Within this framework, by exploiting the interplay between spin and dipolar degrees of freedom via spin-orbit coupling in ferroelectric semiconductors, I will focus on the tight link between k-dependent spin-splitting in the electronic structure, spin-texture and electric polarization. Based on density functional simulations, I will show our theoretical predictions of a giant Rashba spin-splitting in “bulk” GeTe[1], prototype of novel multifunctional materials - labeled as Ferro-Electric Rashba Semi-Conductors (FERSC)[2] - where the chirality of the spin texture is one-to-one linked to polarization. As the latter can be induced/controlled/switched via an electric field in a non-volatile way, the integration of semiconductor spintronics with ferroelectricity is envisaged. In the second part of the talk, the connection between ferroelectricity and spin-degrees of freedom will be discussed by providing examples from different materials classes (oxides heterostructures,[3] halides perovskites,[4] chalcogenides, etc), all of them showing strong relativistic effects.

[1] D. Di Sante, P. Barone, R. Bertacco and S. Picozzi, *Adv. Mater.* **25**, 509 (2013); M. Liebmann et al, *Adv. Mater.* **28**, 560 (2016)

[2] S. Picozzi, *Front. Physics* **2**, 10 (2014)

[3] K. Yamauchi, P. Barone, T. Shishidou, T. Oguchi and S. Picozzi, *Phys. Rev. Lett.* **115**, 037602 (2015)

[4] A. Stroppa, D. Di Sante, P. Barone, M. Bokdam, G. Kresse, C. Franchini, M.-H. Whangbo, S. Picozzi, *Nature Communications*, **5**, 5900 (2014)

E-mail for corresponding author: [silvia.picozzi@spin.cnr.it](mailto:silvia.picozzi@spin.cnr.it)

# High-Throughput Computational Design of Advanced Functional Materials: Topological Insulators and Two-Dimensional Electron Gas Systems

Kesong Yang\*

Department of NanoEngineering, University of California San Diego, CA 92093, USA

Email: [kesong@ucsd.edu](mailto:kesong@ucsd.edu), web site: <http://materials.ucsd.edu>

As a rapidly growing area of materials science, high-throughput (HT) computational materials design is playing a crucial role in accelerating the discovery and development of novel functional materials. In this presentation, I will first introduce the strategy of HT computational materials design, and take the HT discovery of topological insulators (TIs) as a practical example to show the usage of such an approach. Topological insulators are one of the most studied classes of novel materials because of their great potential for applications ranging from spintronics to quantum computers. Here I will show that, by defining a reliable and accessible descriptor, which represents the topological robustness or feasibility of the candidate, and by searching the quantum materials repository [aflowlib.org](http://aflowlib.org), we have automatically discovered 28 TIs (some of them already known) in five different symmetry families.[1] Next, I will talk about our recent research work on the HT computational design of the perovskite-based two-dimensional electron gas (2DEG) systems. The 2DEG formed on the perovskite oxide heterostructure (HS) has potential applications in next-generation nanoelectronic devices. In order to achieve practical implementation of the 2DEG in the device design, desired physical properties such as high charge carrier density and mobility are necessary. Here I show that, using the same strategy with the HT discovery of TIs, by introducing a series of combinatorial descriptors, we have successfully identified a series of candidate 2DEG systems based on the perovskite oxides.[2] This work provides another exemplar of applying HT computational design approach for the discovery of advanced functional materials.

Reference to a journal publication:

1. K. Yang, W. Setyawan, S. Wang, M. Buongiorno Nardelli, and S. Curtarolo, A search model for topological insulators with high-throughput robustness descriptors. *Nat. Mater.*, **11**, 614-619 (2012).
2. K. Yang, S. Nazir, M. Behtash, and J. Cheng, High-throughput screening of two-dimensional electron gas systems based on perovskite oxide heterostructures. *submitted*, (2015).



## Electronic confinement in materials with artificial periodicity

Ulrike Lüders<sup>a</sup>

<sup>a</sup>*CRISMAT UMR 6508 CNRS Ensicaen Université de Caen Normandie, 6 bvd Maréchal Juin, 14050 Caen cedex 4, France*

email address of the presenting author: [ulrike.luders@ensicaen.fr](mailto:ulrike.luders@ensicaen.fr)

Thin film deposition techniques can be used to induce an artificial periodicity in the growth direction by the repetition of a bilayer of two materials, each of a thickness of some monolayers. If an insulating and a metallic or semi-conducting material are combined in such a way, the confinement of the mobile charges may have strong influences on the electronic properties of these materials. This can be used not only to synthesize new materials with 2D charge carriers, but also to trigger interesting functional properties.

Such an electronic confinement was achieved in superlattices of  $\text{LaXO}_3/\text{SrXO}_3$  where  $X = \text{V}, \text{Cr}$ . They exhibit metallic phases, which do not correspond to the properties of the bulk materials, as well as a magnetic phase in the vanadium case which is strongly dependent on the thickness of the La compound. X-ray diffraction studies and band structure calculations were used to assess the role of the structural mismatch in these superlattices, and especially structural distortions due to the octahedral rotations were shown to be crucial for the electronic confinement.

But artificial periodicities can also be induced in laminates made out of amorphous binary oxides. Here, the absence of crystal structure in the individual layers prevents any effects due to structural mismatch, and the only periodicity is given by the artificial periodicity along the growth direction. The dielectric properties of sub-nanometric laminates of  $\text{Al}_2\text{O}_3/\text{TiO}_2$  were studied, and a strong relationship with the artificial periodicity indicates again a successful confinement of the mobile charge carriers.

## Fluoride-based $S = \frac{1}{2}$ Kagome Magnets

Philip Lightfoot

*School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK*

pl@st-and.ac.uk

Frustrated magnetic systems present a continuing challenge in fundamental physics and also a significant ‘design-and-synthesis’ opportunity for the solid state chemist. A particularly sought-after phenomenon is a so-called ‘quantum spin liquid’ (QSL) state: a non-magnetic ground state in which electron spins are locally paired antiferromagnetically, but there is no long-range magnetic order, even at zero K [1]. For the solid-state chemist, the key ‘designable’ features of a QSL material include: (i) a geometrically frustrated crystalline lattice (typically triangular in nature) (ii) a layered crystal structure (iii) a ‘quantum’ spin state, ie.  $S = \frac{1}{2}$ . The kagome lattice fulfils these criteria, for example in the cases where the kagome nodes consist of  $\text{Cu}^{2+}$  or  $\text{V}^{4+}$  species. Prior to our work the only known examples of these systems were based on  $\text{Cu}^{2+}$ , for example in mineral analogues such as herbertsmithite,  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  [2]. Our partially serendipitous discovery of a  $\text{V}^{4+}$ -based kagome compound  $[\text{NH}_4]_2[\text{C}_7\text{H}_{14}\text{N}][\text{V}_7\text{O}_6\text{F}_{18}]$  [3] and its subsequent characterization as a QSL [4] demonstrated that there is a role for imaginative solid state chemistry in the pursuit of new QSLs. In particular, solvothermal chemistry of hybrid organic-inorganic vanadium (oxy)fluorides (VOFs) appears to be rich in potential for these systems. More recently, we have discovered several new variants on the  $\text{V}^{4+}$ -kagome theme, and these new materials also appear to show the essential hallmarks of QSL behavior [5]. In this talk I shall describe our work on these VOF-based QSLs, and also our search for further  $S = \frac{1}{2}$  kagome systems.

[1] L. Balents, *Nature*, 464 (2010) 199.

[2] M. P. Shores et al., *J. Amer. Chem. Soc.*, 127 (2005) 13462.

[3] F. Aidoudi et al., *Nature Chem.*, 3 (2011) 801.

[4] L. Clark et al., *Phys. Rev. Lett.*, 110 (2013) 207208.

[5] L. Clark et al., *Angew. Chem.*, 54 (2015) 15457.

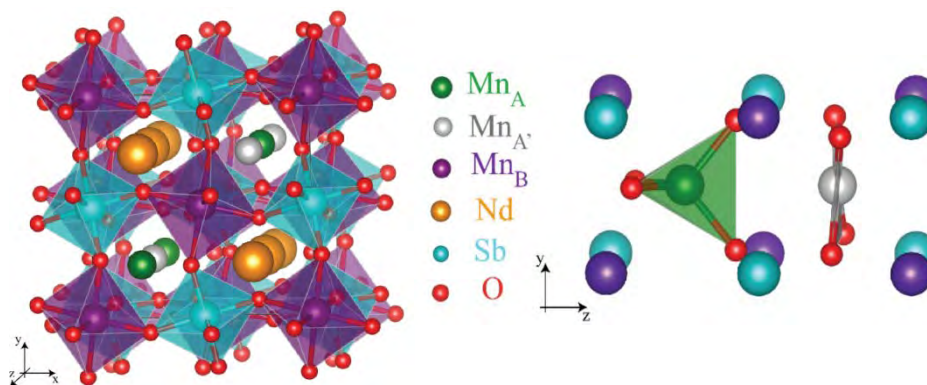
## NEW CATION ORDERING IN HIGH PRESSURE PEROVSKITES

Angel M. Arévalo-López<sup>a\*</sup>, Elena Solana-Madruga<sup>b</sup>,  
 Antonio J. Dos Santos-García<sup>c</sup>, Regino Sáez-Puche<sup>b</sup>, J. Paul Attfield<sup>a</sup>  
<sup>a</sup> CSEC & School of Chemistry, University of Edinburgh,  
 Mayfield Road, Edinburgh EH9 3JZ (UK)  
<sup>b</sup> Dpto. Química Inorgánica I, Fac. Químicas,  
 Universidad Complutense de Madrid, 28040, Madrid, Spain  
<sup>c</sup> Dpto. Ingeniería mecánica, química y diseño industrial.  
 ETSIDI. Universidad Politécnica de Madrid, 28012, Madrid, Spain.  
 \* aalopez@staffmail.ed.ac.uk

Cation order in ABO<sub>3</sub> perovskites adds to their chemical variety and can lead to properties such as ferrimagnetism and magnetoresistance in Sr<sub>2</sub>FeMoO<sub>6</sub>.<sup>[1]</sup> Through high pressure and temperature synthesis we have discovered a new type of ‘double double perovskite’ structure in the family MnRMnSbO<sub>6</sub> (R = La, Pr, Nd and Sm). This tetragonal structure has 1:1 order of cations on both A and B sites; A-site Mn<sup>2+</sup> and R<sup>3+</sup> cations are ordered in columns while Mn<sup>2+</sup> and Sb<sup>5+</sup> have rock salt order on the B sites.<sup>[2]</sup> The A-site Mn<sup>2+</sup> positions are further divided into tetrahedral and square planar environments as shown in Figure 1.

The MnRMnSbO<sub>6</sub> double double perovskites are ferrimagnetic at low temperatures with additional spin-reorientation transitions. The ordering direction of ferrimagnetic Mn spins in MnNdMnSbO<sub>6</sub> changes from parallel to [001] below T<sub>C</sub> = 76 K to perpendicular below the reorientation transition at 42 K at which Nd moments also order.

Smaller rare earths lead to conventional monoclinic double perovskites (MnR)MnSbO<sub>6</sub> for Eu and Gd, where Mn<sup>2+</sup> and R<sup>3+</sup> are disordered over the A sites while Mn<sup>2+</sup> and Sb<sup>5+</sup> have rock salt order at the B sites.



**Figure 1.** Double double perovskite structure of MnRMnSbO<sub>6</sub> oxides (R = La, Pr, Nd and Sm). B site MnO<sub>6</sub> and SbO<sub>6</sub> octahedra have a rocksalt type order while A site Mn and R are ordered in columns parallel to the unique z-axis. Mn A-sites are further split into Mn<sub>A</sub> and Mn<sub>A'</sub> environments with tetrahedral and square planar coordinations as shown on the right.

[1] D. Serrate, J.M. De Teresa, M.R. Ibarra, J. Phys. :Condens. Matter, 19 (200) 023201.

[2] E. Solana-Madruga, A.M. Arévalo-López, A.J. Dos Santos-García, E. Urones-Garrote, D. Ávila-Brandé, R. Sáez-Puche, J.P. Attfield, Angew. Chem. Int. Ed, 2016, submitted.

## HYDROGEN AND CARBON INSERTION INTO CeScSi-TYPE SYSTEMS

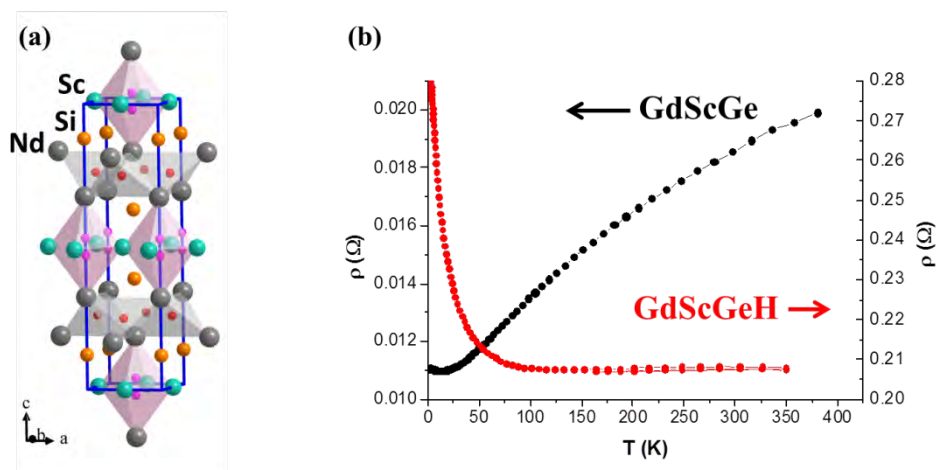
Etienne Gaudin, Tadhg Mahon, Bernard Chevalier, Sophie Tencé  
CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F33600 Pessac, France

etienne.gaudin@icmcb.cnrs.fr

Only a few intermetallics crystallize with the tetragonal CeScSi-type structure which is a derivative of the CeFeSi-type. In both structural types, layers of empty  $[Ce_4]$  tetrahedra are observed. It was shown in the past that, in the case of the CeFeSi-type structure, the  $[Ce_4]$  tetrahedra can be fully filled by hydrogen. This induces a very interesting modulation of the physical properties [1]. It is worth pointing out that these new hydrides  $RETXH$  ( $RE$  = rare-earth,  $T$  = transition metal,  $X$  = Si or Ge) adopt the ZrCuSiAs-type structure which is also observed for LaFePO [2], the first member of the new family of iron-based superconductors.

This work is devoted to the study of the insertion of hydrogen or carbon into the series of intermetallics  $RETX$  ( $RE$  = rare-earth,  $T$  = Sc or Ti,  $X$  = Si or Ge) crystallizing with the CeScSi-type structure (an ordered variant of the  $La_2Sb$  type).  $[RE_4]$  tetrahedral and  $[T_4RE_2]$  octahedral sites are available for the insertion of light element. According to the nature of the rare-earth and of the light element (i.e. H or C) different composition can be achieved. The examples of  $GdScGeH_{1.0}$ ,  $REScSiH_{1.5}$  and  $REScSiC_{0.5}$  ( $RE$  = Ce, Nd) will be presented.

The insertion of the light elements induces a strong modulation of the magnetic properties of the pristine compound. For instance, we evidenced that hydrogenation strongly reduces the Curie temperature of NdScSi from  $T_C = 175$  K to  $T_C = 4$  K in NdScSiH<sub>1.5</sub>, the H (or D) atoms being located in both interstitial sites (fig a) [3]. A significant change in the transport properties can be also induced. In the case of GdScGe, for instance, a transition from metallic to non-metallic behavior is observed (fig b).



(a) Structure of NdScSiD<sub>1.5</sub> with D atoms in Td and Oh sites.  
(b) Resistance measurements of GdScGe and GdScGeH.

- [1] Chevalier et al., Phys. Rev. B 77 (2008) 014414  
 [2] Kamihara et al., J. Am. Chem. Soc. 128 (2006) 10012  
 [3] S. Tencé et al., J. Solid State Chem. (2016), in press.

## Bi lone-pair induced unusual charge disproportionation of A-site order perovskite $\text{BiCu}_3\text{Cr}_4\text{O}_{12}$

Masahiko Isobe<sup>a</sup>, Martin Etter<sup>a</sup>, Hiroya Sakurai<sup>b</sup>, Robert E. Dinnebier<sup>a</sup> and Hidenori Takagi<sup>a</sup>

<sup>a</sup> Max Planck Institute for Solid State Research, Stuttgart, Germany

<sup>b</sup> National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan

email address of the presenting author: m.isobe@fkf.mpg.de

Many 3d transition metal oxides belong to a class of strongly correlated electron system. Among them, mixed-valent oxides show various interesting phenomena. Recently we have studied the novel metal-insulator transition in the mixed-valent chromium oxide,  $\text{K}_2\text{Cr}_8\text{O}_{16}$  [1-3]. In order to understand the physics and chemistry of the mixed-valent chromium oxide, we investigate another mixed-valent chromium oxide,  $A^{3+}\text{Cu}^{2+}_3\text{Cr}^{3.75+}_4\text{O}_{12}$  ( $A$  = rare-earth, Bi).

A-site-ordered perovskites with a chemical formula of  $AA'_3B_4\text{O}_{12}$  crystallize in an  $Im\bar{3}$  cubic lattice. The structure with cubic cell of  $2ap \times 2ap \times 2ap$  ( $ap$  is the simple perovskite lattice parameter) is a largely distorted variant of the perovskite structure in Fig. 1.  $A'$  site is of a pseudosquare planar coordination suited to Jahn-Teller active ions such as  $\text{Cu}^{2+}$  and  $\text{Mn}^{3+}$ , while  $A$  site is occupied by typical large A-site ions such as alkaline earth and rare earth metal ions. In this case,  $B$  site is occupied by a 3d-transition metal. They provide an opportunity for the mixed valence state of  $B$  site.  $B$  cations should be in the mixed valence state  $B^{+3.75}$ , when  $A$  and  $A'$  sites occupy 3+ cations and  $\text{Cu}^{2+}$  ions.

We have obtained new A-site ordered perovskite  $\text{BiCu}_3\text{Cr}_4\text{O}_{12}$  using high-pressure and high-temperature synthesis. Ferrimagnetic transition with a structural distortion was observed at around 185K. The resistivity exhibits an anomaly at the transition, but metallic behavior persists even in the magnetic phase. We have revealed an unusual charge disproportionation below the transition from the structural analysis in Fig. 1. It is considered that the origin of the transition is the local distortion of the  $\text{BiO}_{12}$  polyhedron for Bi 6s-O 2p-Bi 6p hybridization. The structural distortion stabilizes the Cr-O hybridization of the  $\text{Cr}^{4+}\text{O}_6$  octahedra. As the result, the two kinds of  $\text{Cr}^{3.5+}\text{O}_6$  and  $\text{Cr}^{4+}\text{O}_6$  chains ordered in a rocksalt-type substructure in ac plane in the low-temperature phase. This is the first observation of the charge disproportionation transition in the mixed-valent chromium oxides.

Leave one line blank

[1] K. Hasegawa, M. Isobe, et al., Phys. Rev. Lett. 103 (2009) 146403.

[2] T. Toriyama, et al., Phys. Rev. Lett. 107 (2011) 266402.

[3] P.A. Bhowe, et al., Phys. Rev. X 5 (2015) 041004.

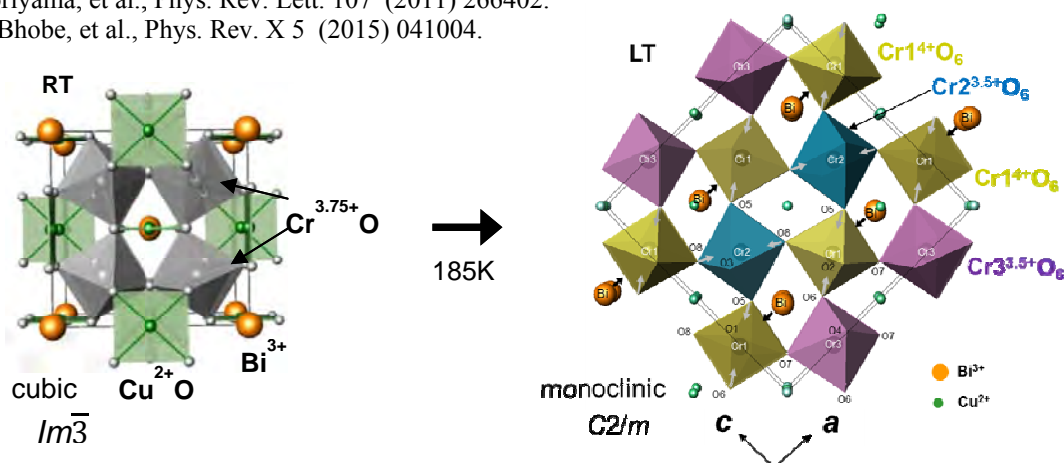


Figure 1: High-temperature phase and low-temperature charge-disproportionation phase in ordered perovskite  $\text{BiCu}_3\text{Cr}_4\text{O}_{12}$ . Large orange spheres and octahedral represent Bi cations and various  $\text{CrO}_6$  octahedral units.

## BASIC PROPERTIES OF $\alpha$ -, $\beta'$ - AND $\gamma$ -MODIFICATIONS OF $\text{Mn}_3(\text{PO}_4)_2$

O.S. Volkova<sup>a,b</sup>, L.V. Shvanskaya<sup>b</sup>, E.A. Zvereva<sup>b</sup>, E.A. Ovchenkov<sup>b</sup>, O.V. Dimitrova<sup>b</sup>, O.V. Yakubovich<sup>b</sup>, D.A. Charev<sup>c</sup>, B. Rahaman<sup>d</sup>, T. Saha-Dasgupta<sup>d</sup>, A.N. Vasiliev<sup>a,b</sup>

<sup>a</sup>National University of Science and Technology MISiS, 119991 Moscow, Russia

<sup>b</sup>M.V. Lomonosov Moscow State University, 119991 Moscow, Russia

<sup>c</sup>Institute of Experimental Mineralogy, Russian Academy of Sciences, 142432 Chernogolovka, Moscow District, Russia

<sup>d</sup>Department of Condensed Matter Physics and Materials Science, S.N. Bose National Centre for Basic Sciences, 700098 Kolkata, India

os.volkova@yahoo.com

The manganese (II) orthophosphate  $\text{Mn}_3(\text{PO}_4)_2$  belongs to the anhydrous phosphates family of divalent metals  $\text{M}_3(\text{PO}_4)_2$  with  $\text{M} = \text{Mg}, \text{Ca}, \text{Cr-Zn}$ . It stands out for multiple low symmetry crystal structures and limited amount of information about their properties. The  $\text{Mn}_3(\text{PO}_4)_2$  compound has been reported to exist in three polymorphs:  $\alpha$ - phase, a variety of grafonite structural type;  $\beta'$ - phase, characterized by superstructure to  $\beta$ - $\text{Zn}_3(\text{PO}_4)_2$  structure type [1, 2] and  $\gamma$ -phase [3], topologically close to the mixed (Zn,Mn) phosphate  $(\text{Zn}_{0.75}\text{Mn}_{0.25})_3(\text{PO}_4)_2$  with farringtonite  $\text{Mg}_3(\text{PO}_4)_2$  structure. All polymorphs adopt the same monoclinic space group of  $P2_1/n$  or  $P2_1/c$  (S.G. No. 14).

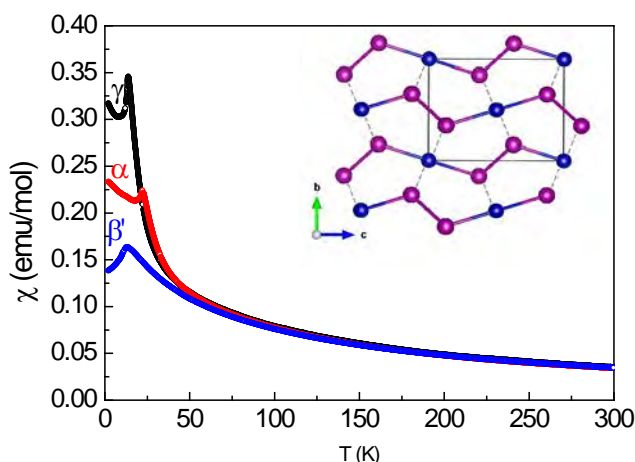


Fig. 1. The temperature dependencies of magnetic susceptibility of  $\alpha$ -,  $\beta'$  and  $\gamma$ - modifications of  $\text{Mn}_3(\text{PO}_4)_2$ . The inset represents the projection of exchange interactions network in  $\gamma$ - $\text{Mn}_3(\text{PO}_4)_2$ . Red and blue spheres denote Mn1 and Mn2. The strongest exchange interaction  $J_3$  is shown by bicolor lines, weaker  $J_1$  interaction is shown by unicolor lines, and the weakest  $J_2$  interaction is shown by dotted lines.

All compounds were characterized in measurements of thermodynamic and resonant properties in a wide temperature range and magnetic fields. Their magnetic exchange interactions were estimated from first principles calculations.

1. Nord A. and Eriksson T., Am. Mineral. 70 (1985) 624.
2. Kostiner E. and Rea J. R., Inorg. Chem. 13 (1974) 2876.
3. Glaum R. and Schmidt A., Z. Anorg. Allg. Chem. 623 (1997) 1672.

The temperature dependences of magnetic susceptibility  $\chi$  in  $\alpha$ -,  $\beta'$ - and  $\gamma$ - modifications of  $\text{Mn}_3(\text{PO}_4)_2$  are shown in Fig. 1. At elevated temperatures these dependences follow the Curie-Weiss law with addition of temperature independent term  $\chi = \chi_0 + C/(T-\Theta)$ . At low temperatures, these compounds demonstrate the peaks indicating formation of the long – range antiferromagnetic order. The  $\gamma$ -phase possessing trimerized fragments in magnetic structure shown in the Inset to Fig. 1 demonstrates 1/3 plateau in magnetization curve.



## "Soft" photocatalysis: 2D frameworks as platforms for light-driven hydrogen evolution

Bettina V. Lotsch<sup>a,b</sup>

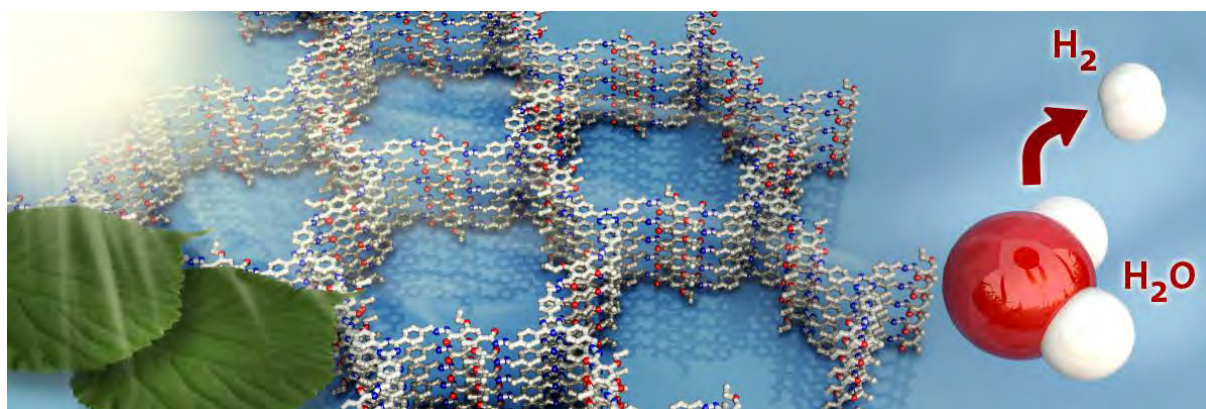
<sup>a</sup> Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart

<sup>b</sup> Department of Chemistry, University of Munich (LMU), Butenandtstraße 5-13, 81377 München, Germany

b.lotsch@fkf.mpg.de

The conversion of sunlight into storable chemical fuels through photocatalysis has been identified as a viable strategy to alleviate future energy shortage. Although a number of potent semiconductors for solar water splitting are at hand, key features such as earth-abundance, stability and low toxicity still need to be addressed, thus calling for new material solutions for sustainable photocatalysis. While heterogeneous systems excel through their stability, homogeneous catalysts offer the potential to tune every step in the photocatalytic mechanism through molecular engineering. Combining the best of both worlds opens up new possibilities for the design of tailor-made photocatalysts.

We have recently developed a class of “soft” photocatalysts based on 2D molecular frameworks, including covalent organic frameworks (COFs),<sup>1</sup> which are abundant and molecularly tunable organic semiconductors. Our recent progress in the rational design of triazine- and heptazine-based systems for hydrogen evolution will be discussed and possible catalyst optimization strategies will be highlighted – through doping,<sup>2</sup> exfoliation,<sup>3</sup> functionalization,<sup>4</sup> and active site engineering,<sup>5</sup> as well as hybridization with bio-inspired co-catalysts.<sup>6</sup>



- [1] L. Stegbauer, K. Schwinghammer, B. V. Lotsch, *Chem. Sci.* **2014**, *5*, 2789–2793;  
 [2] K. Schwinghammer, B. Tuffy, M. B. Mesch, E. Wirnhier, C. Martineau, F. Taulelle, W. Schnick, J. Senker, B. V. Lotsch, *Angew. Chem. Int. Ed.* **2013**, *52*, 2435–2439;  
 [3] K. Schwinghammer, M. B. Mesch, V. Duppel, C. Ziegler, J. Senker, B. V. Lotsch, *J. Am. Chem. Soc.* **2014**, *136*, 1730–1733;  
 [4] V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, *Nat. Commun.* **2015**, *6*, 8508, DOI: 10.1038/ncomms9508;  
 [5] V. W.-h. Lau, M. B. Mesch, V. Duppel, V. Blum, J. Senker, B. V. Lotsch, *J. Am. Chem. Soc.* **2015**, *137*, 1064–1072;  
 [6] C. A. Caputo, M. A. Gross, V. W. Lau, B. V. Lotsch, E. Reisner, *Angew. Chem. Int. Ed.* **2014**, *53*, 11538–11542.



## Nano-bio Photocatalyst for Hydrogen Evolution

Peng Wang<sup>a,b</sup>, Baibiao Huang<sup>a</sup>, Rozhkova Elena A<sup>b</sup>

<sup>a</sup>State Key Lab of Crystal Materials, Shandong University, Shanda Nanlu 27#, Jinan, Shandong, China, 250100

<sup>b</sup> Center for Nanoscale Materials, Argonne National Lab, Argonne, IL, US, 60439

email address of the presenting author: pengwangicm@sdu.edu.cn

Photocatalytic production of clean hydrogen fuels using water and sunlight has attracted remarkable attention due to the increasing global energy demand.<sup>1</sup> Nanophotocatalysis is one of the potentially efficient ways of capturing and storing solar energy. Biological energy systems that are intrinsically nano scaled can be employed as building blocks for engineering nanobiophotocatalysts with tunable properties.

The presentation shows two nano-bio photocatalysts for hydrogen evolution.<sup>2-3</sup> One is bacteriorhodopsin (bR) assembled on Pt/TiO<sub>2</sub>, another is bacteriorhodopsin (bR) assembled on Pt/TiO<sub>2</sub>-rGO. The hybrid system show high efficiency in hydrogen evolution. Photoelectrochemical and transient absorption studies indicate efficient charge transfer between bR protein molecules and TiO<sub>2</sub> nanoparticles. Electron paramagnetic resonance and transient absorption spectroscopy demonstrate an interfacial charge transfer from the photoexcited rGO to the semiconductor under visible light.

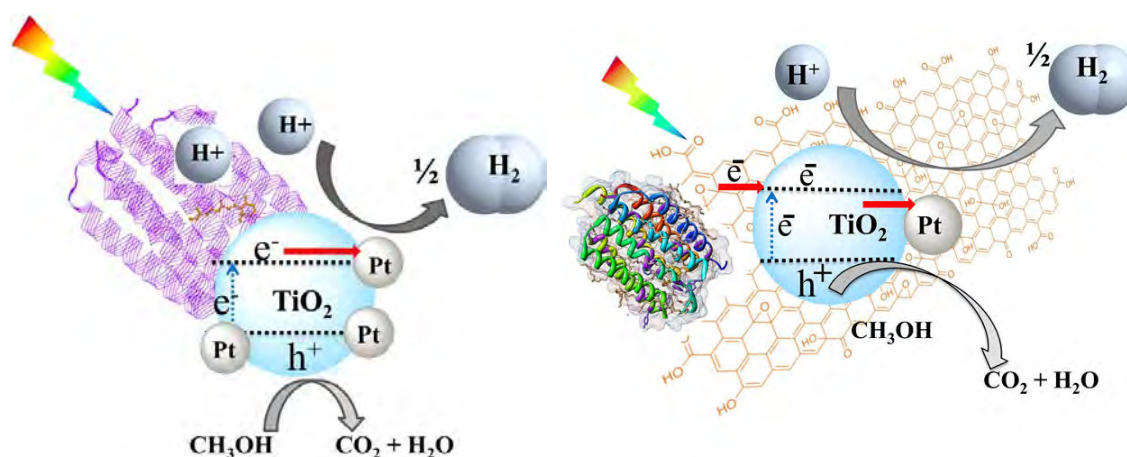


Figure 1: Nano-biophotocatalyst : the left one is bacteriorhodopsin (bR) assembled on Pt/TiO<sub>2</sub>, the right one is bacteriorhodopsin (bR) assembled on Pt/TiO<sub>2</sub>-rGO.

Reference to a journal publication:

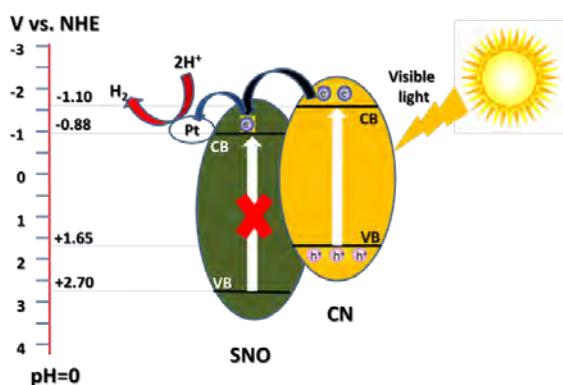
- [1] K. Maeda, K. Teramura, D. L. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, Nature 440 (2006) 295.
- [2] S. Balasubramanian, P. Wang, R. D. Schaller, T. Rajh and E. A. Rozhkova, Nano Lett. 13 (2013) 3365-3371.
- [3] P. Wang, N. M. Dimitrijevic, A. Y. Chang, R. D. Schaller, Y. Z. Liu, T. Rajh, E. A. Rozhkova, ACS Nano. 8 (2014) 7995-8002.

## Semiconductor heterojunctions for Enhanced Photocatalytic Activity

Abdou Lachgar and Shiba Adhikari

Department of Chemistry, and Center for Energy, Environment and Sustainability,  
Wake Forest University  
lachgar@wfu.edu

Semiconductor-based photocatalysis has received tremendous attention in the last few decades because of its potential for solving current energy and environmental problems. In a semiconductor photocatalytic system, photo-induced electron-hole pairs are produced when a photocatalyst is irradiated by light with frequencies larger than that of its band gap ( $h\nu > E_g$ ). The photo-generated charge carriers can either recombine, or migrate to the surface of the semiconductor, where they can be involved in electrochemical processes. High recombination rate of charge carriers and limited efficiency under visible light irradiation are two limiting factors in the development of efficient semiconductor-based photocatalysts. To overcome these drawbacks, a number of chemical and design strategies have been developed. Among these strategies, the design and formation of semiconductor heterojunctions using two or more semiconductors is a promising approach. Recently studied examples of these semiconductor heterojunctions will be presented to demonstrate that well designed heterojunctions can extend light absorption range and enhance the life time of photogenerated charge-carriers resulting in enhanced photocatalytic activity compared to their individual components. The plausible mechanism (Figure 1) for the enhanced photocatalytic activity for the heterostructured composites is proposed based on observed activity and band positions calculations.



**Figure 1.** Schematic diagram of separation and transfer of photogenerated carriers in  $g\text{-C}_3\text{N}_4/\text{Sr}_2\text{Nb}_2\text{O}_7$  heterojunction under visible light irradiation.

## Silver silicate photocatalysts with strong visible light absorption and high charge separation efficiencies

Zeyan Wang,<sup>a</sup> Baibiao Huang,<sup>a</sup> Ying Dai<sup>b</sup>

<sup>a</sup>State Key Laboratory of Crystal Materials and <sup>b</sup>School of Physics, Shandong University,  
250100, Jinan, China

Email address: [wangzeyan@sdu.edu.cn](mailto:wangzeyan@sdu.edu.cn)

Photocatalysis has attracted increasing interests owing to its potential applications on solving energy and environmental problems by directly utilizing solar energy. Although great efforts have been made in the last few decades. The photocatalytic efficiency is still far from the criteria for practical applications, which can be mainly attributed to the poor visible light response and the fast charge recombination during photocatalytic processes. Therefore, the exploration of new photocatalysts with both wide light absorption range and efficient charge separations are highly desirable.

Among the various photocatalysts, silver containing compounds are highly attractive due to their exceptional visible light absorption originated from the unique  $d^{10}$  electronic configurations of  $Ag^+$  ions and the localized surface plasmon resonance effects of Ag nanoparticles. Recently, we have fabricated several silver silicate photocatalysts, such as  $Ag_6Si_2O_7$ ,  $Ag_9(SiO_4)_2NO_3$  and amorphous silver silicates, and extensively investigated their photocatalytic properties.<sup>[1-3]</sup> And the relationship between photocatalytic properties and crystal structures have been extensively investigated. With the existence of Si, the internal electrostatic fields and different coordinated Ag can be easily formed in these silver silicates, which can facilitate the charge transportation and separation during photocatalytic processes and lead to enhanced photocatalytic activities. This could be beneficial for the design and exploration of high efficient photocatalysts with both strong visible light absorption and high charge separation efficiencies.

### References:

- [1] Z. Z. Lou, B. B. Huang, Z. Y. Wang et al., Chem. Mater., 2014, 26, 3873-3875.
- [2] Z. Z. Lou, Z. Y. Wang, B. B. Huang, Y. Dai et al., Chem. Eur. J., 2015, 21, 8706-8710.
- [3] X. L. Zhu, Z. Y. Wang, B. B. Huang, W. Wei, Y. Dai et al., APL Mater., 2015, 3, 104413 (6pp).

## PROTON CONDUCTORS: FROM QUANTUM TO CLASSICAL

G. Geneste<sup>a</sup>, J. Hermet<sup>a</sup>, B. Amadon<sup>a</sup>, F. Bottin<sup>a</sup>, G. Dezanneau<sup>b</sup>, M. Torrent<sup>a</sup>  
<sup>a</sup>CEA, DAM, DIF, F-91297, Arpajon, France

<sup>b</sup>Laboratoire Structures, Propriétés et Modélisation des Solides, UMR CNRS 8580, CentraleSupélec, Grande Voie des Vignes, 92295 Châtenay-Malabry Cedex, France

Email address of the presenting author: [gregory.geneste@cea.fr](mailto:gregory.geneste@cea.fr)

Recent advances in the modeling of proton conducting oxides -- to be used as electrolytes in Protonic Ceramic Fuel Cells -- are presented, with focus on two chemical processes: hydration and oxidation. The first chemical reaction is a necessary step to get **proton conductors**, while the second one, which occurs at high temperature, deteriorates the devices by making them **hole-type electronic conductors**. In order to fully understand these processes, it is mandatory to associate calculations at the microscopic scale, i.e. using density-functional theory (DFT) – we use the ABINIT code [1] -- to other techniques such as the Kinetic Monte Carlo method, to study transport [2], or the Path-Integral Molecular Dynamics, to take into account the large quantum fluctuations of the light H atoms [3]. Moreover, DFT in its local and semi-local approximations does not allow to treat correctly localized charges, especially the oxygen-type hole polarons appearing under oxidation at high temperature (Fig. 1), and more sophisticated methodologies have to be used.

Several aspects of these processes will be discussed: (i) behavior of protons in the classical and semi-classical regimes, in a low-symmetry compound such as BaCeO<sub>3</sub> [4], and a high-symmetry one such as BaSnO<sub>3</sub> [3], (ii) quantum effects affecting proton transport at low and intermediate temperatures [3], (iii) competition between elastic and chemical effects of dopants and its consequences upon hydration, oxidation and defect association, and (iv) physics of the **oxygen-type hole polarons** (Fig. 1) consecutive to the high-temperature oxidation process [5].

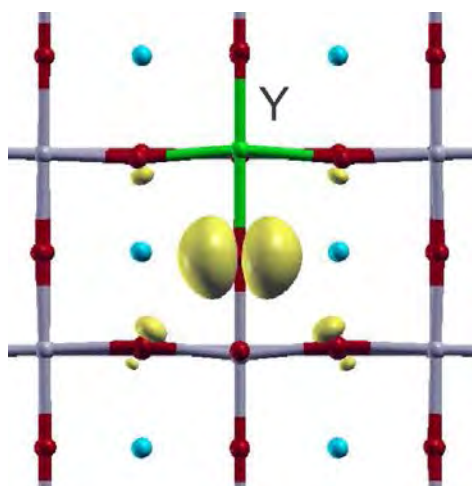


Fig. 1: Oxygen-type hole polaron bound to an Yttrium dopant in BaSnO<sub>3</sub>, simulated using DFT+U.

### References:

- [1] X. Gonze et al, Comput. Phys. Comm., in press (2016).
- [2] J. Hermet, F. Bottin, G. Dezanneau, G. Geneste, Solid State Ionics **252**, 48-55 (2013).
- [3] G. Geneste, A. Ottochian, J. Hermet, G. Dezanneau, Phys. Chem. Chem. Phys. **17**, 19104 (2015).
- [4] J. Hermet, M. Torrent, F. Bottin, G. Dezanneau, G. Geneste, Phys. Rev. B **87**, 104303 (2013).
- [5] G. Geneste, B. Amadon, G. Dezanneau, submitted.

## Surface reactivity of layered lithium oxides used as cathode materials: a coupled experimental-theoretical study

Ambroise Quesne Turin<sup>a</sup>, Germain Vallverdu<sup>a</sup>, Delphine Flahaut<sup>a</sup>, Laurence Croguenec<sup>b</sup>, Michel Ménétrier<sup>b</sup>, Isabelle Baraille<sup>a</sup>

<sup>a</sup> IPREM, Université de Pau et des Pays de l'Adour, UMR 5254, Technopole Hélioparc, 2 av. du Président Pierre Angot, 64053 Pau cedex 9, France

<sup>b</sup> ICMCB, Université de Bordeaux, ENSCBP, 33608 Pessac cedex, France

germain.vallverdu@univ-pau.fr

A large amount of chemical or physical processes take place at the surface or interface materials and are still difficult to investigate due to their low thickness or buried character. A technological challenge for which surface and interface phenomena are key factors is the electrochemical storage of energy through Lithium-ions batteries. Nowadays, these systems are widely used in mobile devices (smartphones, GPS...) and are among the best answers to the intermittent character of renewable energies. Safety and aging issues related to the degradation of the electrode material in contact with the electrolyte are the drawbacks of such systems. These phenomena are mainly due to parasite chemical reactions taking place at the interface between the electrode and the electrolyte. Thus, one of the main hurdles towards the improvement of lithium-ions batteries is the control of surface and interface phenomena.

In that scope we undertook a joined experimental and theoretical work in order to investigate the surface reactivity of layered lithium oxides which are largely used as cathode materials of lithium-ion systems. Our approach consists in a gas probe adsorption followed by XPS (X-ray Photoemission Spectroscopy) characterization which allow a clear identification and quantification of the adsorption sites at the surface of the materials. At the same time, the full electronic process of the gas probe adsorption is investigated through periodic DFT calculations. The both approaches give a complete view of the surface reactivity toward the gas probe and was applied with success to LiMO<sub>2</sub> compounds (M=Ni, Mn, Co or Al), LiCoO<sub>2</sub> being the most widely used cathode material in commercial cells. Recently, Li-rich materials appear as promising candidate to solve toxicity and cost issues due to the used of cobalt. We applied our approach to Li<sub>2</sub>MnO<sub>3</sub> as a model of Li-rich materials. It leads to a comparative study of the surface reactivity against the oxidation degree of the transition metal that is +III in LiMnO<sub>2</sub> and +IV in Li<sub>2</sub>MnO<sub>3</sub>.

[1] Vallverdu, G.; Minvielle, M.; Andreu, N.; Gonbeau, D.; Baraille, I. *Surface Science* **2016**, *649*, 46–55.

[2] Andreu, N.; Flahaut, D.; Dedryvère, R.; Minvielle, M.; Martinez, H.; Gonbeau, D. *ACS Appl. Mater. Interfaces* **2015**, *7* (12), 6629–6636.

[3] Andreu, N.; Baraille, I.; Martinez, H.; Dedryvère, R.; Loudet, M.; Gonbeau, D. *J. Phys. Chem. C* **2012**, *116* (38), 20332–20341.

## UNDERSTANDING PARAMAGNETIC BATTERY MATERIALS THROUGH COMBINED NMR/DFT STUDIES.

Dany Carlier<sup>a,b,\*</sup>, Tahya Bamine<sup>a,b</sup>, Michel Ménétrier<sup>a,b</sup>, Florent Boucher<sup>c</sup>

<sup>a</sup> *ICMCB-CNRS, UPR 9048, University of Bordeaux, Pessac, France*

<sup>b</sup> *Réseau Français sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, Amiens, France*

<sup>c</sup> *IMN-CNRS, UMR 6502, University of Nantes, Nantes France*

email address of the presenting author: dany.carlier@icmcb.cnrs.fr

Solid state Nuclear Magnetic Resonance (NMR) is a powerful tool to investigate the Li nucleus local environment in intercalation electrode materials for Li-ion battery application [1]; nevertheless the assignment of signals in paramagnetic materials is delicate, because it is dominated by the Fermi contact shift (due to the transfer of electron spin density from the transition metal ions to the Li nucleus), through delocalization or polarization mechanisms [2].

We recently developed a quantitative approach using the WIEN2k code (FLAPW and GGA or GGA+U approximations) and the experimental susceptibilities in order to reproduce closely the experimental Fermi contact shifts for several transition metal phosphates compounds [3-5]. In a first part, several results on combined NMR/DFT studies of several positive electrode materials will be presented, discussing the chemical bonds in the materials by analyzing the spin density transfer mechanism from  $M^{3+}$  ion to the probed nucleus. We will especially focus on tavorite-type  $AMPO_4X$  ( $A = Li, H; M = Fe, Mn, V; X = O, F, OH$ ) battery materials [6] and on layered  $Na_{1/2}VO_2$  oxides (using  $^{23}Na$  MAS NMR), which can exhibit peculiar V pairs or trimers and different Na/ vacancy orderings [7].

In a second part, we will address the use of combined NMR/DFT studies to understand defects in battery materials. As supercells considered to model defects are rather large, the use of the VASP code (PAW potentials) is preferred to that of the more computer-demanding “all electrons” WIEN2k code (FP-LAPW). Indeed, the latest version of VASP (5.3.12) now allows the computation of the spin density on the nuclei. After validation of such calculations, we will focus on the understanding of the defect in  $LiVPO_4F$ .

### References:

- [1] C. Grey and N. Dupré, *Chem. Rev.* 104 (2004) 4493.
- [2] D. Carlier, M. Ménétrier, C. P. Grey, C. Delmas and G. Ceder, *Phys. Rev. B.*, 67 (2003) 174103.
- [3] A. Castets, D. Carlier, Y. Zhang, F. Boucher, N. Marx, L. Croguennec, M. Ménétrier, *J. Phys. Chem. C*, 115 (2011) 16234-16241.
- [4] A. Castets, D. Carlier, Y. Zhang, F. Boucher, N. Marx, R. Gautier, E. Le Fur, L. Le Pollès, L. Croguennec, and M. Ménétrier, *Solid State NMR*, 42 (2012) 42–50.
- [5] Y. Zhang, A. Castets, D. Carlier, M. Ménétrier, and F. Boucher, *J. Phys. Chem. C*, 116 (2012) 17393–17402.
- [6] A. Castets, D. Carlier, Y. Zhang, F. Boucher and M. Ménétrier, *J. Phys. Chem. C*, 116 (2012) 18002-18014.
- [7] M. Guignard, D. Carlier, C. Didier, M.R. Suchomel, E. Elkaim, P. Bordet, J. Darriet and C. Delmas, *Chem. Mater.*, 26 (4) (2014) 1538-1548.

## The $\gamma'/\gamma$ Cathode Materials in the $\text{Li}/\text{V}_2\text{O}_5$ system: Spectroscopic and computational study of the lithiation-induced structure variations

Rita Baddour-Hadjean<sup>a</sup>, Mikhail Smirnov<sup>b</sup>, Konstantin Smirnov<sup>c</sup>, E. M. Roginskii<sup>d</sup>,  
V. Yu Kazimirov<sup>e</sup>, Jean-Pierre Pereira-Ramos<sup>a</sup>

<sup>a</sup> Institut de Chimie et des Matériaux Paris Est, ICMPE/GESMAT, UMR 7182 CNRS–Université Paris Est-Créteil, 2 rue Henri Dunant, 94320 Thiais, France

<sup>b</sup> Faculty of Physics, St. Petersburg State Univ., Petrodvorets, 194508 St. Petersburg, Russia

<sup>c</sup> Laboratoire de Spectrochimie Infrarouge et Raman, UMR 8516 CNRS – Université de Lille, Sciences et Technologies, 59655 Villeneuve d'Ascq, France

<sup>d</sup> Ioffe Physical Technical Institute, Polytekhnicheskaya 26, 194021 St. Petersburg, Russia

<sup>e</sup> Frank Lab. of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia

email address: baddour@icmpe.cnrs.fr

The present work reports results of a combined experimental and computational study of the structure, charge distribution and vibrational dynamics of the  $\gamma\text{-LiV}_2\text{O}_5$  material. Structure, electronic states, and vibrational dynamics of  $\gamma\text{-LiV}_2\text{O}_5$  were studied by combined use of the quantum chemical calculations and Raman spectroscopy.

The spin-polarized DFT+U calculations correctly mimic the structural changes induced by the Li intercalation into the  $\text{V}_2\text{O}_5$  framework. The analysis of the density of electronic states shows that the electrons of Li atoms are transferred to the Vb atoms and are aligned in ferromagnetic order. The charge distribution in the system reflects the change of valence state of the Vb atoms from 5+ to 4+ and it is in line with changes of Vb -O bond lengths.

The calculated Raman spectra of the  $\gamma\text{-LiV}_2\text{O}_5$  structure are in line with the experimental Raman spectrum that allows a reliable assignment of all prominent Raman peaks (figure 1). The comparison of the spectra of  $\gamma\text{-LiV}_2\text{O}_5$  and  $\gamma'\text{-V}_2\text{O}_5$  indicates spectral signatures of structural changes induced by the Li insertion into the  $\gamma'\text{-V}_2\text{O}_5$  lattice [1].

This work highlights the efficiency of the combined approach as a powerful tool for understanding the structural changes induced by Li insertion into the  $\gamma'\text{-V}_2\text{O}_5$  lattice at the atomic level.

### References

[1] M. Smirnov, E. Roginskii, V. Kazimirov, K. Smirnov, R. Baddour-Hadjean, J. P. Pereira-Ramos, V. Zhandun, J. Phys. Chem. C 119 (2015) 20801–20809

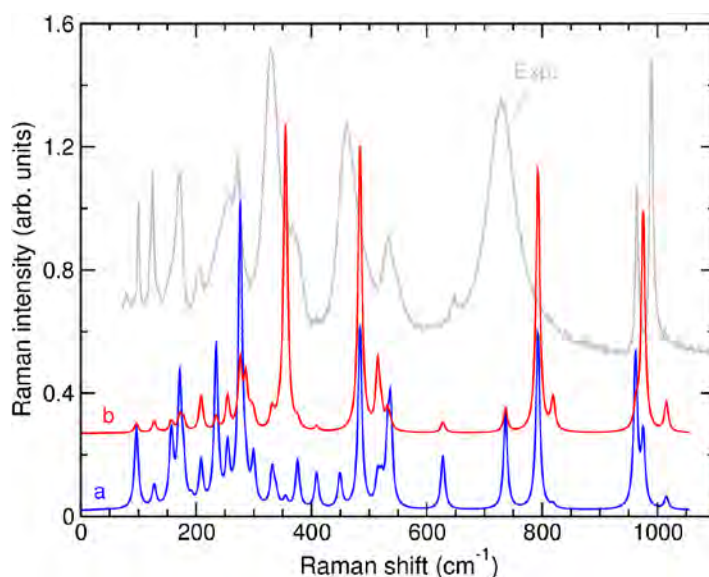


Figure 1. Experimental and calculated (a, b) Raman spectra of  $\gamma\text{-LiV}_2\text{O}_5$ . Theoretical spectra a and b were computed for  $\omega = 241.8$  THz and  $\omega = 604.5$  THz (1 and 2.5 eV), respectively.



# THERMOELECTRICS – A CHALLENGE FOR CRYSTALLOGRAPHY AND SOLID-STATE CHEMISTRY

Oliver Oeckler

*Institute of Mineralogy, Crystallography and Materials Science; Faculty of Chemistry and Mineralogy, Leipzig University, Scharnhorststr. 20, 04725 Leipzig, Germany*

oliver.oeckler@gmx.de

Thermoelectric materials can directly and reversibly interconvert heat into electricity and vice versa. Their application may become important for waste-heat recovery. However, the enhancement of their efficiency is an intriguing goal as fundamentally interrelated physical properties need to be decoupled and individually optimized. As this is almost impossible in ideal crystalline materials, new concepts involve heavily disordered and heterogeneous materials.

Nanostructured tellurides represent some of the most efficient material systems. Domain structures in chemically homogeneous systems can be obtained via incomplete diffusion-controlled phase transitions. Structural vacancies play a crucial role in such processes. As exemplified by germanium antimony tellurides (GST materials) and related compounds,<sup>[1]</sup> temperature-dependent structural changes involve complex ordering mechanisms but may still afford materials that are long-term stable. Approaches towards controlling defect concentrations and the distribution include substitution experiments which also influence phase transition temperatures and thus the nanostructures formed. Electronic properties can be modified by influencing the predominant features of chemical bonding. Many of these materials are a challenge for crystallographers. The disorder involves diffuse X-ray scattering which can be quantified using novel methods such as the 3D- $\Delta$ PDF<sup>[2]</sup> in combination with TEM imaging. Resonant X-ray scattering is an ideal method to determine the element distribution in multinary systems that contain several atom types with similar electron counts. A variety of synchrotron experiments further enables *in situ* studies, i.e. the direct observation of structural changes upon thermal treatment.<sup>[3]</sup> This is also essential for the analysis of dynamical disorder, i.e. highly mobile atoms in PLEC (phonon-liquid electron-crystal) materials.

Moreover, research increasingly focuses on chemically inhomogeneous systems. Ideally, these contain nanoscale precipitates endotaxially intergrown in a matrix that itself exhibits disorder and a domain structure. Skutterudite-type or cobalt germanide precipitates in GST materials demonstrate how nano- and microcrystallites significantly influence the thermoelectric properties.<sup>[4]</sup> In more complicated systems such as Cu-doped GST, mutual doping of matrix and precipitates needs to be considered. A new approach that exploits the advantages of both transmission electron microscopy and microfocused synchrotron radiation and enables the precise structure determination even of single sub-micron sized crystallites.<sup>[5]</sup>

[1] T. Rosenthal, P. Urban, K. Nimmrich, L. Schenk, J. de Boor, C. Stiewe, O. Oeckler, *Chem. Mater.* 26 (2014) 2567–2578; S. Welzmilller, F. Fahrnbauer, F. Hennersdorf, S. Dittmann, M. Liebau, C. Fraunhofer, W. G. Zeier, G. J. Snyder, O. Oeckler, *Adv. Electron. Mater.* 1 (2015) 1500266; T. Rosenthal, L. Neudert, P. Ganter, J. de Boor, C. Stiewe, O. Oeckler, *J. Solid State Chem.* 215 (2014) 231–240.

[2] P. Urban, A. Simonov, T. Weber, O. Oeckler, *J. Appl. Crystallogr.* 48 (2015) 200–211.

[3] M. N. Schneider, X. Biquard, C. Stiewe, T. Schröder, P. Urban, O. Oeckler, *Chem. Commun.* 48 (2012) 2192–2194; P. Urban, M. N. Schneider, O. Oeckler, *J. Solid State Chem.* 227 (2015) 223–231.

[4] F. Fahrnbauer, S. Maier, M. Grundei, N. Giesbrecht, M. Nentwig, T. Rosenthal, G. Wagner, G. J. Snyder, O. Oeckler, *J. Mater. Chem. C* 3 (2015) 10525–10533; F. Fahrnbauer, D. Souchay, G. Wagner, O. Oeckler, *J. Am. Chem. Soc.* 137 (2015) 12633–12638.

[5] F. Fahrnbauer, T. Rosenthal, T. Schmutzler, G. Wagner, G. B. M. Vaughan, J. P. Wright, O. Oeckler, *Angew. Chem. Int. Ed. Engl.* 54 (2015) 10020–10023.

## STRUCTURE AND PROPERTIES OF PRISTINE AND IRON-SUBSTITUTED THERMOELECTRIC TETRAHEDRITES

Andrei V. Shevelkov<sup>a</sup>, Daria I. Nasonova<sup>a</sup>, Igor A. Presniakov<sup>a</sup>, Alexey V. Sobolev<sup>a</sup>, Valeriy Yu. Verchenko<sup>a,b</sup>, Alexander A. Tsirlin<sup>c</sup>

<sup>a</sup> *Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia*

<sup>b</sup> *National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia*

<sup>c</sup> *Experimental Physics VI, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, 86135 Augsburg, Germany*

email: shev@inorg.chem.msu.ru

Synthetic and natural tetrahedrites of a general formula  $\text{Cu}_{12-x}\text{TM}_x\text{Sb}_4\text{S}_{13}$  are currently receiving great attention as potential thermoelectric materials for mid-temperature heat-to-power conversion. They consist of naturally abundant and non-toxic elements and demonstrate high thermoelectric figure-of-merit,  $ZT$ , exceeding 1.0 within the temperature range of 600-750 K. The origin of high thermoelectric efficiency in tetrahedrites is still the matter of debates in the literature; however, it is clear that tetrahedrites are different from conventional thermoelectric materials because they exhibit a unique combination of two important properties. The efficient charge transport is provided through the variable-range hopping mechanisms, whereas the low, glass-like, thermal conductivity stems from anharmonic interactions of lone e-pairs of antimony atoms with copper atoms shifted away of the triangle plane of three sulfur atoms.

In this work, we examine the low-temperature structure and thermoelectric properties of pristine and iron-substituted synthetic tetrahedrites,  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  and  $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ , by means of X-ray single crystal and synchrotron powder diffraction, Mössbauer spectroscopy, and thermodynamic and transport measurements. We will report on the details of the crystal structure near the metal-to-semiconductor transition in  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  and on its low-temperature thermoelectric properties as well as on the charge transfer in the iron-substituted tetrahedrites having different iron contents.

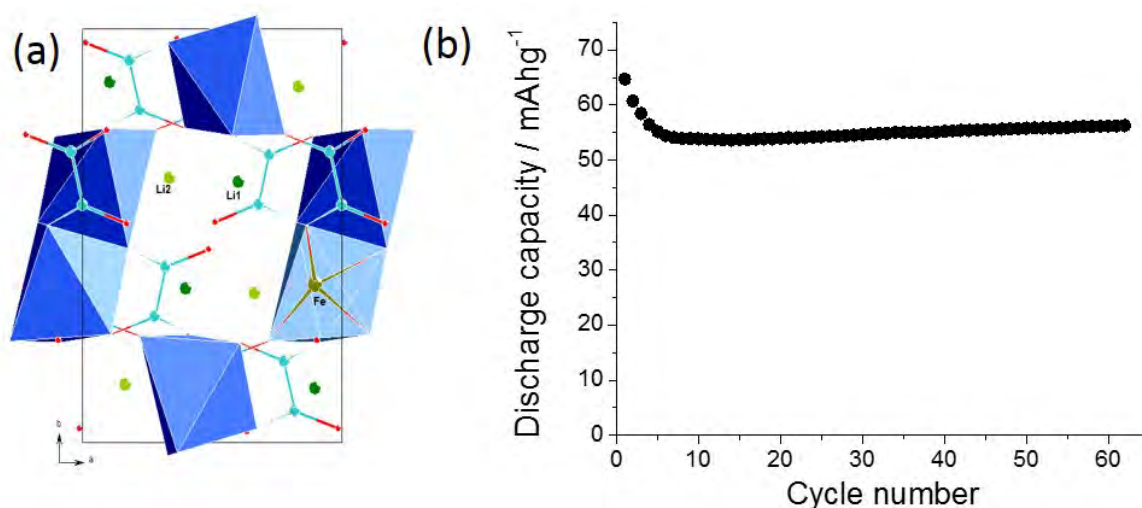
### References:

1. K. Suekuni, K. Tsuruta, M. Kunii, H. Nishiate, E. Nishibori, S. Maki, M. Ohta, A. Yamamoto, M. Koyano, *J. Appl. Phys.* 113 (2013) 043712.
2. J. Heo, G. Laurita, S. Muir, M.A. Subramanian, D.A. Keszler, *Chem. Mater.* 26 (2014) 2047–2051.
3. R. Chetty, P. Kumar, G. Rogl, P. Rogl, E. Bauer, H. Michor, S. Suwas, S. Puchegger, G. Giester, R.C. Mallik, *Phys. Chem. Chem. Phys.* 17 (2015) 1716–1727.
4. D.I. Nasonova, I.A. Presniakov, A.V. Sobolev, V.Yu. Verchenko, A.A. Tsirlin, Z. Wei, E.V. Dikarev, A.V. Shevelkov, *J. Solid. State Chem.* 235 (2016) 28-35

## Iron oxalates as novel electrode materials for Li-ion and Na-ion batteries

Wenjiao Yao, A. Robert Armstrong, Philip Lightfoot.  
School of Chemistry, University of St Andrews

There is intensive research activity targeted on developing new electrode materials for the next generation of rechargeable lithium batteries, particularly for large-scale use in future hybrid electric or pure electric vehicles and in stationary energy storage of solar/wind power [1-3]. Polyoxyanion compounds are receiving considerable interest as cathodes since the strong binding of the oxygen enhances stability and thus safety, compared with transition metal oxides. The electronic inductive effect shifts the d-states of the transition metal ions and hence the redox potentials, providing a means of tuning the latter. Phosphate materials, particularly  $\text{LiFePO}_4$ , have been extensively studied and continue to be important [2,3]. Recent work on oxalates by Tarascon and co-workers [4,5] has demonstrated the possible use of oxalate materials as a new class of polyoxyanion. Here we report the synthesis and characterization of hitherto-unknown alkali metal iron compounds in the oxalate system with new compositions and structures. The three dimensional framework structures were determined by single crystal X-ray diffraction, with an example shown in Fig. (a). All the materials displayed redox activity vs. either Li or Na, depending on the compound with stable cycling as shown in Fig. (b).



- (1) B. L. Ellis, K. T. Lee and L. F. Nazar, *Chem. Mater.*, 2010, 22, 691;
- (2) J. B. Goodenough and Y. Kim, *Chem. Mater.*, 2010, 22, 587.
- (3) A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.* 1997, 144, 1188.
- (4) H. Ahouari, G. Rousse, Y. Klein, J.N. Chotard, M.T. Sougrati, N. Recham, J.M. Tarascon. *Solid State Sci.* 2015, 42(6), 13.
- (5) H. Ahouari, G. Rousse, J.R. Carvajal, M.T. Sougrati, M. Saubanere, M. Courty, N. Recham, J.M. Tarascon. *Chem. Mater.*, 2015, 27, 1631.

## **Anode Materials Design for Lithium-Ion and Sodium-Ion Batteries**

Qilong Sun<sup>a</sup>, Ying Dai<sup>a</sup>, Baibiao Huang<sup>a</sup>

<sup>a</sup>*School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China*

Email: daiy60@sina.com

Identifying suitable electrodes materials with desirable electrochemical properties, which is mainly hindered by the limited choice of anodes, is urgently needed for the next generation of renewable energy technologies. For high capacities and extremely fast charging rates, two-dimensional (2D) materials have demonstrated the most promising applications as the anodes in the various metal-ion batteries. Here, we report an ideal candidate material, Mo<sub>2</sub>C monolayer, with not only required large capacity but also high stability and mobility by means of first-principles calculations. our results showed that the bare Mo<sub>2</sub>C monolayer exhibits minimal diffusion barriers of 0.035 and 0.015 eV for Li and Na atoms, respectively. This means Mo<sub>2</sub>C monolayer could exhibit a superior diffusion mobility and high charge and discharge rates for Li and Na atoms in the LIBs and NIBs. In addition, our work reveals high first cycle electrochemical capacity of 526 mAh·g<sup>-1</sup> with respect to total weight of the electrode with excellent cyclability of Li ions. Besides, we find that the relatively low capability of Na adsorbed on the Mo<sub>2</sub>C can attribute to the proposals competition mechanism. The results are encouraging, and provide a promising candidate for the next generation portable batteries.

# Electronic Properties of Layered Materials and Phase Change in Lithium Ion Batteries

Fazel Shojaei<sup>a</sup>, Hong Seok Kang<sup>b</sup>

<sup>a</sup> *laboratory name, full address* <sup>1</sup>*Department of Chemistry and Bioactive Material Sciences and Research Institute of Physics and Chemistry, Jeonbuk National University, Jeonju, Chonbuk 561-756, Republic of Korea*

<sup>b</sup> *Department of Nano & Advanced Materials, Jeonju University, Chonju, Chonbuk 560-759, SOUTH KOREA*

email: hsk@jj.ac.kr

Using first-principles calculations, we have investigated electronic structures of black ( $\alpha$ ) arsenic phosphoridene (AsP), which is a two-dimensional (2D) monolayer composed of equimolar mixture of phosphorus and arsenic. According to structure optimizations and phonon calculations,  $\alpha$  phase branches into three distinguished ones.[1] Second, our calculations in collaboration with photoluminescence measurement indicate that oxygen adsorption can cause the direct/indirect band gaps of GaS monolayer to converge, resulting in a strong emission.[2] Third, the I-V measurement of metal-semiconductor-metal (MSM) photodetectors involving multilayer nanobelts or monolayers of GaS and GaSe can be understood in terms of Fermi level alignment based on our HSE06 calculation.[3] Fourth, the bilayer nanoribbons of  $\alpha$ 1 AsP experiences cooperativity in the substitutional Si doping in such a way that Si-Si bonds are formed.[4] The doped bilayer exhibits an indirect band gap, which can be turned into a direct gap by Stone-Wales deformation.[4] Fifth, electronic and mechanical properties of recently synthesized 2D organometallic complexes of  $\pi$ -Conjugated M-Bis(dithiolene) ( $MC_4S_4$ ) (M= Ni, Pd) are shown to depend on the kind of metal ions. [5] Finally, band gap Tuning in mixed halide perovskite [6] and Phase evolution of Germanium and Tin Nanocrystals in Lithium Ion Batteries[7,8] will be also discussed.

- [1] F. Shojaei, H. S. Kang, J. Phyc. Chem. C 119 (2015) 20210-20216.
- [2] C. S. Jung et al. ACS Nano 9 (2015), 9585-9593.
- [3] Kang, H. S. et al. *in submission*.
- [4] F. Shojaei, H. S. Kang *in submission*.
- [5] F. Shojaei, J. R. Hahn, H. G. S. Kang, *Chem. Mater.* 26 (2014) 2967-2976
- [6] D. M. Jang et al. Nano Lett. 15 (2015), 5191-5199.
- [7] Y. J. Cho et al. ACS Nano 7 (2013) 9075-9084.
- [8] H. S. Im et al. ACS Nano 7 (2013) 11103-11111.



# POSTERS

## Study of structural, elastic and electronic properties of TbX (X=N, P, As, Sb) compounds using LSDA and LSDA+U approach.

B. Benbahi<sup>1</sup>, H. Bouafia<sup>1</sup>, B. Abidri<sup>2</sup>, S. Hiadsi<sup>1</sup>, D. Rached<sup>2</sup>, A. Akriche<sup>1</sup>.

- 1- Laboratoire de Microscope Electronique & Sciences des Matériaux USTO, département de physique, BP1505 El m'naouar, Oran, Algérie.
- 2- Laboratoire des matériaux magnétiques Université Djillali Liabbès 22000 Sidi Bel-Abbès, Algérie

### Abstract

Structural, elastic and electronic properties in the cubic TbX (X=N, P, As, Sb) compounds are derived from the full-potential linear muffin-tin orbital method, within the frame of density functional theory (DFT). The exchange correlation energy is described in the local spin density approximation LSDA+U approach, using the Perdew-Wang parameterization. The equilibrium lattice parameters, bulk modulus, transition pressure, elastic constants and their related parameters such as Poisson's ratio, Young modulus, shear modulus and Debye temperature were calculated. We compared our obtained results with available experimental and theoretical data. They are in reasonable agreement. The electronic properties are treated also with LSDA+U approach. Our results show that both compounds exhibit half metallic behaviour.

*Keywords: FP-LAPW, LSDA+u, ground state, elastic constants, electronic properties,*

---

\* Corresponding Author: [b\\_abidri@hotmail.com](mailto:b_abidri@hotmail.com) (Prof B. Abidri)



## SYNTHESIS, CRYSTAL STRUCTURE AND $\text{Eu}^{3+}$ OPTICAL STUDIES OF A NEW CADMIUM FLUOROPHOSPHATE WITH FORMULA $\text{Na}_2\text{CdPO}_4\text{F}$

**Mohamed Aboussatar<sup>1,2\*</sup>, Aïcha Mbarek<sup>3</sup>, Houcine Naili<sup>2</sup>, Malika El-Ghozzi<sup>1</sup>, Geneviève  
Chadeyron<sup>1</sup>, Daniel Avignant<sup>1</sup>, Daniel Zambon<sup>1</sup>**

<sup>1</sup> Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, UMR CNRS 6296, BP  
10448, F-63000 Clermont-Ferrand, France

<sup>2</sup> Laboratoire physico-chimie de l'Etat Solide, Faculté des Sciences de Sfax, Université de Sfax, BP 1171, 3000  
Sfax, Tunisie

<sup>3</sup> Laboratoire de Chimie Industrielle, Ecole Nationale d'Ingénieurs de Sfax,  
Université de Sfax, BP W3038, Sfax, Tunisie

\* med\_abau@yahoo.fr

During the two last past decades a growing interest has been devoted to the study of the fluorophosphates because of their potential applications in several fields such as electrode materials, ionic exchangers, molecular sieves, catalysis or optical properties[1,2]. In this context we have carried out the study of the  $\text{NaF-CdO-Na}_2\text{O-P}_2\text{O}_5$  system using X-ray powder diffraction.

In the course of the exploration of this  $\text{NaF-CdO-NaPO}_3$  pseudo-ternary phase diagram a new compound with the formula  $\text{Na}_2\text{CdPO}_4\text{F}$  was discovered. Its crystal structure was determined ab initio from powder X-ray diffraction data. It crystallizes in the orthorhombic system, space group  $\text{Pnma}$  ( $n^\circ 62$ ) with the lattice parameters  $a = 5.374(1) \text{ \AA}$ ,  $b = 6.854(1) \text{ \AA}$ ,  $c = 12.272(2) \text{ \AA}$ . In this structure the  $\text{Cd}^{2+}$  ions are octahedrally coordinated by 4 oxygen and 2 fluorine ions. Its crystal structure features one dimensional chains  $\infty [M^{II}O_4F]$  resulting from corner-sharing of  $\text{CdO}_4\text{F}_2$  octahedra linked through fluorine ions occupying cis positions in the equatorial plane of the octahedron. These chains are further linked through  $\text{PO}_4^{3-}$  groups to form the three-dimensional structure. The  $\text{Na}^+$  ions lie in hexagonally shaped channels and are coordinated by 5 oxygen and 2 fluorine ions.

Structural relationships with  $\text{Ca}_2\text{NaSiO}_4\text{F}$  and with other  $\text{Na}_2\text{MPO}_4\text{F}$  ( $M = \text{Fe, Mn, Co, Ni, Mg}$ ) will be presented and discussed. The observed long range cationic ordering between Na and Cd is corroborated by  $^{23}\text{Na}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  high resolution MAS NMR experiments and luminescence of the  $\text{Eu}^{3+}$  ion used as local structural probe.

The vibrational properties of  $\text{Na}_2\text{CdPO}_4\text{F}$  have been investigated by IR and RAMAN spectroscopies.

[1] B.L. Ellis, W.R.M. Makahnouk, W.N.Rowan-Weetaluktuk, D.H.Ryan, L. F. Nazar, *Chem. Mater.* 2010, **22**, 1059–1070.

[2] S.J. Dhoblea, V.B. Pawade, K.N. Shinde, *Eur. Phys. J. Appl. Phys.* **52**, 11104 (2010).

## SYNTHESIS AND STUDY OF PHOTOPHYSICAL PROPERTIES OF NEW SENSORS ON NITROAROMATICS COMPOUNDS BASED ON PYRIMIDINE AND DEVELOPMENT OF A PORTABLE DETECTOR OF EXPLOSIVES

Baranova A.A.<sup>2\*</sup>, Verbitskiy E.M.<sup>1,2\*</sup>, Khokhlov K.O.<sup>2</sup>,  
Rusinov G.L.<sup>1,2</sup>, Chupakhin O.N.<sup>1,2</sup>, Charushin V.N.<sup>1,2</sup>

<sup>1</sup>) Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, Yekaterinburg, Russia

<sup>2</sup>) Ural Federal University, Yekaterinburg, Russia

A number of push-pull dyes based on pyrimidines, bearing various electron-donating carbazole and triphenylamine fragments, have been studied as sensing fluorophores. Fluorescence studies demonstrated that the emission of all derivatives in acetonitrile is sensitive to the presence of some nitroaromatic explosives. A selective fluorescence quenching response, including a sharp color change under UV, makes these fluorophores promising fluorescence sensory materials for nitroaromatic explosives.

The design and synthesis of artificial sensors capable of rapidly detecting chemical explosives a prevalent and current research topics . The most common explosives are nitroaromatic compounds (NACs). NACs have received great attention in a last decades due to global terror threats and to their high toxicity to the environment. Various analytical methods have been developed for sensitive detection of nitroaromatic compounds . Among the physical methods, photoluminescence based chemosensors that exploit sensitive fluorescence quenching by nitroaromatic derivatives have been investigated extensively for both vapor and solution phases at low concentrations with high sensitivity and selectivity.

Using the reaction sequence of nucleophilic aromatic substitution of hydrogen (SNH) and the cross-coupling Suzuki-based pyrimidine (I) carried out the synthesis of 4-(het)arylpyrimidines (III), while 5-bromopyrimidine (II), were obtained the corresponding 4,5-di(het)arylpyrimidines (IV). On the basis of the fluorescence titration were determined by the constants of the stern-Folmer and detection limits of some model nitroaromatics explosives with the use of synthesized fluorophores. It is shown that the fluorophores monozameschennaya III had higher values of quenching constants and detection limits ( $10^{-5} \div 10^{-7}$  mol/l) than the corresponding disubstituted analogues of IV ( $10^{-3} \div 10^{-5}$  mol/l)

As a result the device was designed on the basis of this sensor material, sensitivity dependences of the sensor material in interaction with TNT vapors were revealed. The quantitative evaluation of luminescence intensity fall under the HE vapors influence was determined. This device was done in collaboration with the holding of the Plant "Promavtomatika" collaborating with his daughters firms "UralProektAvtomatika" (Ekaterinburg, Russia) and "Nitromolecular system of security" (Ekaterinburg, Russia).

## THEORETICAL STUDY OF $\text{CuCrZrSe}_4$ WITH AB INITIO METHODS

Karima BELAKROUM<sup>a</sup>, Radia BENECHIKH<sup>b</sup>, Zahia CHAFI<sup>c</sup>

<sup>a</sup> *Université Kasdi Merbah-Ouargla, Département de physique, laboratoire dynamique, interactions et réactivité des systèmes, route de Ghardaia, Ouargla 30000, Algeria*

<sup>b</sup> *Laboratoire de développement des énergies nouvelles et renouvelables dans les zones arides et sahariennes, route de Ghardaia, Ouargla 30000, Algeria*

<sup>c</sup> *Laboratoire de physico-chimie et catalyse, groupe de cristallographie et simulation. Université A. Mira. Bejaia, route Targua Ouzemour. Bejaia (06000) Algérie*

Email: radia.benechik@yahoo.fr

Inorganic compounds with the  $\text{AB}_2\text{X}_4$  spinel structure have been studied for many years and are in the focus of modern solidstate physics, because of their unusual physical properties, as there are heavy-fermion behaviour, complex spin order, spin dimerization, spin-orbital liquid, orbital glass, and multiferroicity [1-5]. In the crystallographic spinel structure, first solved by Bragg in 1915, the cations occupy 1/8 of the tetrahedral (A) and 1/2 of the octahedral (B) voids within the face-centred cubic (fcc)-lattice formed by the X anions. Interesting physics arises, when the B-site cations become mixed in valence. As the cations show different site preferences, by choosing the appropriate atoms it is possible to realize a selective magnetic dilution in one of the two sublattices. In the pseudo-binary systems  $\text{CuCrS}_2\text{-MS}_2$  ( $\text{M}=\text{Ti, Sn}$ ), spinel phases of the composition  $\text{Cu}_{2x}\text{Cr}_{2x}\text{M}_{2-2x}\text{S}_4$  have been discovered. The experimental evidence, to date, indicates that the  $\text{Cu}_{2x}\text{Cr}_{2x}\text{M}_{2-2x}\text{S}_4$  spinels are spin-glasses. These systems are very sensitive to the methods of preparation and deviations from stoichiometry. This effect was discussed with respect to a deficiency and excess of cations in tetrahedral or octahedral voids of the spinel structure. In this series, when the stoichiometric composition is passed through as  $2x$  increases, drastic changes occur in (i) the electric resistivity: the activation energy drops, (ii) magnetic susceptibility: the Curie-Weiss temperature  $\chi_p$  changes from negative to positive values, Contents lists available at which indicates that additional ferromagnetic couplings appear. Although there are numerous data available for powder materials, the studies of the effect of nonmagnetic  $\text{Zr}^{4+}$  substituted for  $\text{Cr}^{3+}$  atoms on the properties of the spinel structure are inconsistent. This raises the question about the proper location of the Zr ions and the metal excess of Cu in the spinel structure [6]. We focus on the corresponding selenide compound  $\text{CuCrZrSe}_4$  to study the influence of the larger Se anions on the crystallographic and magnetic properties by using a theoretical study. The approach followed in this work is based on the Hohenberg-Kohn density-functional theory (DFT). The exchange and correlation contributions to the total energy are treated in the local-density formalism. DFT describes the electronic ground-state of the solid: basically the electron density and the total energy per unit cell. Several interesting physical observables of the solid are derivatives of the total energy with respect to external perturbations.

### References:

- [1] J. Hemberger, P. Lunkenheimer, R. Fichtl, H.-A. Krug von Nidda, V. Tsurkan, A. Loidl, *Nature (London)* 434 (2005) 364.
- [2] S. Weber, P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, A. Loidl, *Physical Review Letters* 96 (2006) 157202.
- [3] Y. Yamasaki, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, Y. Tokura, *Physical Review Letters* 96 (2006) 207204.
- [4] T. Rudolf, Ch. Kant, F. Mayr, J. Hemberger, V. Tsurkan, A. Loidl, *New Journal of Physics* 9 (2007) 76.
- [5] J. Hemberger, T. Rudolf, H.-A. Krug von Nidda, F. Mayr, A. Pimenov, V. Tsurkan, A. Loidl, *Physical Review Letters* 97 (2006) 087204.
- [6] K. Belakroum, Z. Ouili, A. Leblanc-Soreau, M. Hemmida, H.-A. Krug von Nidda, *JMMM* 334 (2013) 130–135

## Electronic and optical properties of ternary alloy $B_xAl_{1-x}P$

**B, Settouf<sup>1</sup>, N.Benkhattou<sup>a,\*</sup>, D.Rached**

<sup>1</sup>Magnetic Materials Laboratory; Faculty of Exact Sciences; University  
Djillali Liabes of Sidi Bel Abbes, Algeria

### Abstract

In this work, we present a density-functional theory study of structural, electronic and optical properties of BAl, BP binary compounds and their ternary  $B_xAl_{1-x}P$  solid solutions. The calculations are done by using the linearized augmented plane wave method (FP-LAPW). For the exchange-correlation potential, local-density approximation (LDA) and generalized gradient approximation (GGA) have been used to calculate theoretical lattice parameters, bulk modulus, and its pressure derivative. The electronic band structure of these compounds have been calculated by using the above two approximations. We have also investigated in this work the density of state and the optical properties such as the dielectric function and the refractive index of BAl, BP and  $B_{0.25}Al_{0.75}P$  compounds by using the above method. The results obtained for structural and electronic properties are compared with experimental data and other computational work. It has been found that the energy bands with all these approximations are similar except the band gap values. It has also been found that our results with LDA and GGA are in good agreement with other computational work wherever these are available.

**Key words:** C. ab-initio calculations, A. Boride alloys; D. Electronic structure; D. Bowing parameter; D. Optical.

---

\* Corresponding authors: +213 .554192664

**E-mail address:** [noredine\\_bt@yahoo.com](mailto:noredine_bt@yahoo.com) (Prof. N. Benkhattou)

## First principle study of Strain effect on structural and dehydrogenation properties of complex hydride $\text{LiBH}_4$

Hind Benzidi

*University Mohammed V -faculty of sciences*  
*4 avenue Ibn Battouta B.P.1014 RP, Rabat-Maroc*  
[hind.benzidi@gmail.com](mailto:hind.benzidi@gmail.com)

Using the first principles calculations based on density functional theory (*DFT*), we have investigated the structure, stability, dehydrogenation thermodynamic and kinetic properties of complex hydride  $\text{LiBH}_4$  under different biaxial strains using *GGA* in the theoretically optimized crystal structure, the results show that biaxial tensile or compressive strain of complex hydride  $\text{LiBH}_4$  lowers its hydrogen desorption enthalpy and dehydrogenation temperature of complex hydride  $\text{LiBH}_4$ , further, the diffusion activation energy of hydrogen atom in  $\text{LiBH}_4$  is also decreased, which makes expected some improvements that could lead to use  $\text{LiBH}_4$  in hydrogen storage applications.

## First principal calculations of optical and electrical properties of Sc, Ti and V doped SnO<sub>2</sub> used in photovoltaic applications

M. Boujnah<sup>1,\*</sup>, A. Benyoussef<sup>1</sup>, A. El Kenz<sup>1</sup> and M. Loulidi<sup>1</sup>

<sup>1</sup> *Laboratory of Magnetism and Physics of High Energies, Department of Physics, B.P. 1014, Faculty of Sciences, Mohammed V- Agdal University, Rabat, Morocco*

\* *Corresponding author: boujnah.mourad@gmail.com*

### Abstract:

The full-potential linearized augmented plane wave method (FP-LAPW) based on the density functional theory (DFT) and Boltzmann's Transport theory, are employed to investigate theoretically the electronic structure, optical and electrical properties of Sc, Ti and V doped rutile SnO<sub>2</sub>. The FP-LAPW based on the new potential approximation known as the Tran–Blaha modified Becke–Johnson exchange potential approximation (mBJ). The calculated band structure and density of states (DOS) exhibit a band gap of pure SnO<sub>2</sub> (3.3 eV) closer to the experimental one. As well, our results indicate that the average transmittance in the 400 to 1000 nm wavelength region was 90%. The high transmittance and electrical conductivity indicate that hexagonal doped SnO<sub>2</sub> system is a potential as material for solar energy applications.

**Key words:** FP-LAPW, mBJ, transparent conductive oxide, electrical conductivity, Transmittance.

## SYNTHESIS AND CHARACTERIZATION OF A NOVEL COMPOSITE CLODRONATE-BIOGLASS

Salha Boulila<sup>a,b,c</sup>, Hassane Oudadesse<sup>a</sup>, Bertrand Lefevre<sup>a</sup>, Claire Roiland<sup>a</sup>, Abdelfattah Elfeki<sup>b</sup>, Hafed Elfeki<sup>c</sup>

<sup>a</sup> *University of Rennes 1, UMR CNRS 6226, Campus de Beaulieu, 35042 Rennes, France*

<sup>b</sup> *Laboratory of Animal Ecophysiology, Faculty of Sciences of Sfax, University of Sfax, P.O. Box 95, 3000 Sfax, Tunisia*

<sup>c</sup> *Laboratory of Sciences Material and environment, Faculty of Sciences of Sfax, B.P. 1171, 3000 Sfax, Tunisia*

email address of the presenting author: rima\_lina2008@yahoo.fr

In recent years, functional biomaterial research has been directed towards the development of improved biomaterials and new drug delivery systems. In this regard, both clodronate and bioactive glass are mostly used alone as treatment in various bone diseases. The object of this study was to define the optimal combination of clodronate (Clo) and bioactive glass (46S6) using lyophilisation technique. The evaluation of 46S6, Clo and 46S6-Clo17 (46S6 containing 17% wt% Clo) was based on X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Nuclear Magnetic Resonance spectroscopy (NMR) of <sup>31</sup>P. The results of DRX reveal that the composite 46S6-Clo17 maintains the amorphous structure assigned to the bioglass. FTIR analyses of 46S6-Clo17 shows that several characteristic bands, of pure bioactive glass and clodronate, which are appeared, disappeared or distorted. By the presence of clodronate in bioglass (46S6), the band at 463 cm<sup>-1</sup> (Si-O-Si) is observed on the spectrum of 46S6-clo17 but it is shifted towards smaller wavelengths. The band at 868 cm<sup>-1</sup> (P-C-P) and 730 cm<sup>-1</sup> (C-Cl) are also observed, but they are displaced slightly. As well, there are many bands that correspond to the PO group of two compounds with significant displacement. It is therefore noted several bands of clodronate and bioglass are distorted. Displacement, deformation or disappearance of characteristic bands observed in the spectrum of composite 46S6-clo17 illustrate the effects of clodronate in the glass matrix of bioactive glass. Presumably some of the hydrogen bonds are formed between the bioactive glass and clodronate as: - Si - O - clodronate, Si-OH ... O ... clodronate or complexes formed by OH<sup>-</sup> groups with Ca<sup>2+</sup> cations in the network bioactive glass. So, Based on these links, clodronate is combined with bioactive glass particles. The SEM studies show the adhesion of clodronate crystals to the particles of bioactive glass by encompassing effect. Finally, the solid state NMR results of 46S6-Clo17 shows a change in the chemical shifts of the bands related to phosphorus <sup>31</sup>P in comparison with those of 46S6 and Clo. This explains the apparent structural change in the glass matrix with the introduction of Clodronate. Therefore, we can conclude that these physicochemical changes in the glass matrix induced by the introduction of clodronate show the obtaining of a new composite 46S6-Clo17.



## **A general, environmentally synthesis procedure of self-assembled ZnO-based materials with multifunctional properties**

A.Stan<sup>a</sup>, P.Cucos<sup>a</sup>, C.Munteanu<sup>a</sup>, C.Chifiriuc<sup>b</sup>, D.Culita<sup>a</sup>, R. Birjega<sup>c</sup>, C.D.Ene<sup>a</sup>, O.Carp<sup>a</sup>

<sup>a</sup> *“Ilie Murgulescu” Institute of Physical Chemistry, Romanian Academy, Splaiul  
Independentei 202, 060021 Bucharest, Romania*

<sup>b</sup> *University of Bucharest, Faculty of Biology, Microbiology Department, 1–3  
Portocalilor Way, Bucharest, Romania*

<sup>c</sup> *National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor, POBox  
MG-36, 077125 Bucharest, Romania*

email address of the presenting author: ocarp@icf.ro

A bioinspired one-pot approach for the synthesis of ZnO - carbohydrate hierarchical architectures was developed. The synergy between a saccharide (mono, di- or polysaccharide) triethanolamine and or urea is the key parameter of the synthetic methodology.

The obtained materials were analyzed by help of IR, UV-Vis, Raman, room-temperature photoluminescence and X Ray photoelectron spectroscopy, X-Ray diffraction, scanning and transmission electron microscopy investigations.

The morphology of the ZnO composites is dictated by the used saccharide. Rod, spindle, solid and hollow spherical-like ZnO-based structures of different porosities are obtained varying the carbohydrate and the reaction conditions (temperature, time and raw materials concentrations). Moreover, the optical properties are dependent on the used synthetic parameters.

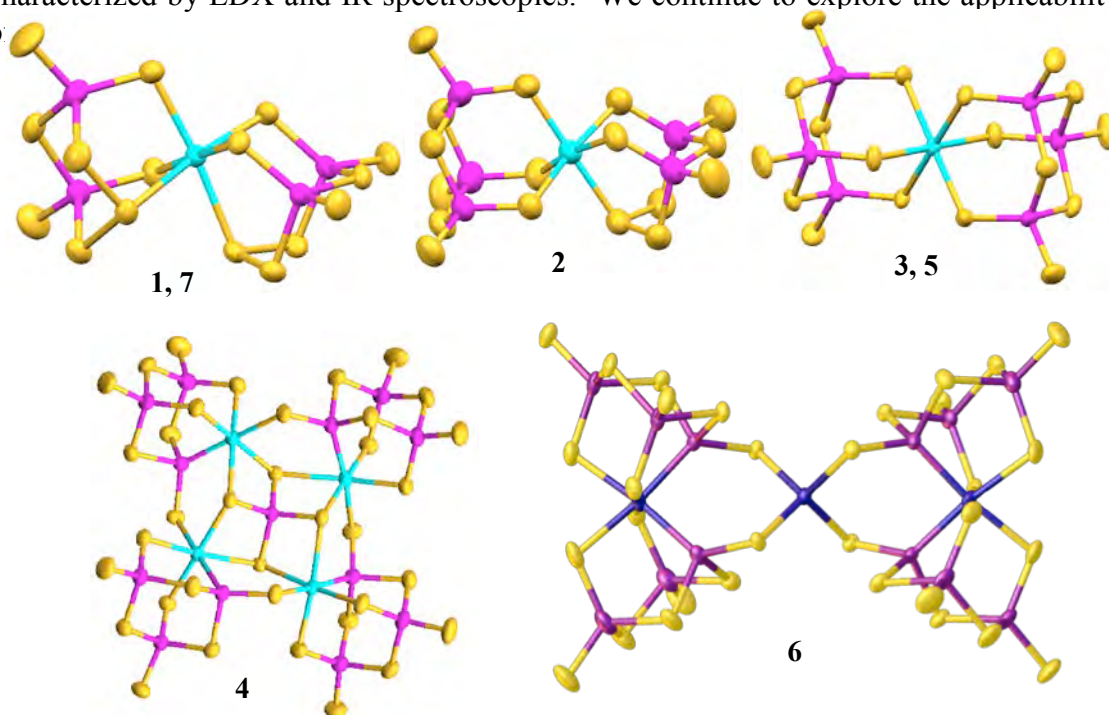
The synthesized composites present high photocatalytical toward different water pollutants (dyes, nitrates) and microbicidal and anti-biofilm activity against reference and clinical strains, highlighting their potential for the development of novel antimicrobial formulations.

## IONOTHERMAL SYNTHESIS OF METAL THIOPHOSPHATES

Lauren M. Dalecky, Christian A. Juillerat, Grant C. B. Alexander,  
 Gilbert J. Reynders, III, Kenneth B. Finch, and Jason A. Cody,  
 Department of Chemistry, Lake Forest College, 555 N. Sheridan Rd.  
 Lake Forest, IL, 60045, United States

email address of the presenting author: cody@lakeforest.edu

Seven new metal thiophosphate anions with five unique structures have been prepared as single crystals of EMIM (1-ethyl-3-methylimidazolium) salts (the anions are shown below): [EMIM]<sub>2</sub>[Ni(P<sub>2</sub>S<sub>8</sub>)<sub>2</sub>] (**1**), [EMIM]<sub>3</sub>[Ni(P<sub>3</sub>S<sub>9</sub>)(P<sub>2</sub>S<sub>8</sub>)] (**2**), [EMIM]<sub>4</sub>[Ni(P<sub>3</sub>S<sub>9</sub>)<sub>2</sub>] (**3**), [EMIM]<sub>7</sub>[(NiP<sub>3</sub>S<sub>8</sub>)<sub>4</sub>(PS<sub>4</sub>)] (**4**), [EMIM]<sub>3</sub>[Cr(P<sub>3</sub>S<sub>9</sub>)<sub>2</sub>] (**5**), [EMIM]<sub>4</sub>[Co(Co(P<sub>3</sub>S<sub>8</sub>)<sub>2</sub>)<sub>2</sub>] (**6**), and [EMIM]<sub>2</sub>[Mn(P<sub>2</sub>S<sub>8</sub>)<sub>2</sub>] (**7**). The crystals were prepared by ionothermal reaction of the elements in [EMIM][BF<sub>4</sub>] for compounds **1**, **2**, **3**, and **4** and in [EMIM][CF<sub>3</sub>SO<sub>3</sub>] for compounds **1**, **5**, **6**, and **7**. The ionic liquids used in all syntheses were prepared from N-ethylimidazole and the appropriate methylating agent relatively inexpensively and with high purity. In all of the anions, the P atoms are tetrahedrally coordinated; in all but **6**, the M atom is octahedrally coordinated. In the thiophosphate anions in **1** and **7**, two tridentate 1,3-P<sub>2</sub>S<sub>8</sub><sup>2-</sup> ligands are *cis* to each other on the metal atoms (M = Ni in **1**, Mn in **7**). The anion in **2** contains two different tridentate thiophosphate ligands, 1,3-P<sub>2</sub>S<sub>8</sub><sup>2-</sup> and P<sub>3</sub>S<sub>9</sub><sup>3-</sup> coordinated around the central Ni atom. The anions in **3** and **5** are structurally similar in that two P<sub>3</sub>S<sub>9</sub><sup>3-</sup> ligands coordinated around the central M atom (M = Ni in **3**, Cr in **5**). The anion in **4** consists of four NiP<sub>3</sub>S<sub>8</sub><sup>-</sup> clusters surrounding a central PS<sub>4</sub><sup>3-</sup> tetrahedron; within the NiP<sub>3</sub>S<sub>8</sub><sup>-</sup> groups, one P atom is directly bound to Ni. The anion in **6** has three cobalt ions in two different coordination environments and oxidation states, and has bridging, polydentate P<sub>3</sub>S<sub>8</sub><sup>3-</sup> groups that coordinate to the cobalt ions through both S and P atoms. The structures of all salts were determined by single-crystal X-ray diffraction and characterized by EDX and IR spectroscopies. We continue to explore the applicability of



## **Improvement of photocatalytic efficiency in plasmonic photocatalytic materials**

Ying Dai<sup>a</sup>, Xiangchao Ma<sup>a</sup>, Baibiao Huang<sup>a</sup>

<sup>a</sup>*School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China*

Email: daiy60@sina.com

In very recent years, many of novel photocatalytic materials developed, among them plasmonic photocatalytic system brings great potential to realize applications and becomes one of the most intensively investigated systems in photocatalysis field because of the high solar energy utilization efficiency. In the present poster, recent developments in plasmonic enhancement of photocatalysis are reviewed from the energy transfer mechanisms involved. Fundamental properties of localized surface plasmon resonance (LSPR), plasmon-induced hot electron injection and plasmon-induced direct electron injection from plasmonic metal to semiconductor, plasmon-induced resonance energy transfer, energy transfer through near-field enhancement, plasmon-induced radiative energy transfer are reviewed and some of guidances for optimizing plasmonic photocatalytic activity and an outlook for the future of the field are proposed.

### Reference:

[1] *Light: Science & Applications* (2016) 5, e16017; doi:10.1038/lssa.2016.17

## ATOMIC CONFINED NANOWIRES: STABILITY AND EXTREME PROPERTIES

Eric Faulques<sup>a</sup>, Victor Ivanov<sup>b</sup>, David C. Smith<sup>c</sup>, Jeremy Sloan<sup>d</sup>

<sup>a</sup> Institut des Matériaux Jean Rouxel, UMR 6502 CNRS - Université de Nantes,  
2 rue de la Houssinière, BP 32229, 44322 Nantes, France

<sup>b</sup> University of Sofia, Faculty of Physics, 5 James Bourchier blvd., 1164 Sofia, Bulgaria

<sup>c</sup> School of Physics and Astronomy, University of Southampton,  
Southampton SO17 1BJ, United Kingdom

<sup>d</sup> Dept. of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

*eric.faulques@cnrs-imn.fr*

Confinement and lower spatial dimensions results in substantial modification of the structure and electronic properties of materials, as compared to those in their bulk forms. In this context atomic nanowires can be elaborated on clean surfaces by self-assembly under ultra-high vacuum. Another method is to fill single walled carbon nanotubes (SWNT) which provide the unique possibility for 1-dimensional (1D) controlled crystal growth and synthesis of structures like alkali halides having no analogues in the 3D world. Inside their carbon walls these atomic nanowires are self-contained and do not interact with outer environment, they have extreme diameters, down to a single line of atoms, and thus extreme properties. Of particular interest is the synthesis of SnTe, SnSe, GeTe, HgTe nanowires encapsulated in SWNT for applications, e.g. in thermoelectrics, spintronics. Most of these compounds are topological insulators in bulk. We have performed density functional theory (DFT) calculation of the equilibrium structure and optical and vibrational properties of these nanowires after encapsulation. We confirm the stability of these 1D structures. For HgTe nanowires [1-2] we report the first calculation of optical transition energies and of the Raman spectrum. Our calculations confirm opening of an energy gap of  $\sim 1.35$  eV in the 1D electronic band structure in contrast to the gapless band structure of bulk HgTe (Fig. 1). The calculated frequencies of the  $\Gamma$ -point Raman-active modes are in fair correspondence to those obtained experimentally on HgTe@SWNT nanowires produced by melt infiltration into bundles of SWNT.

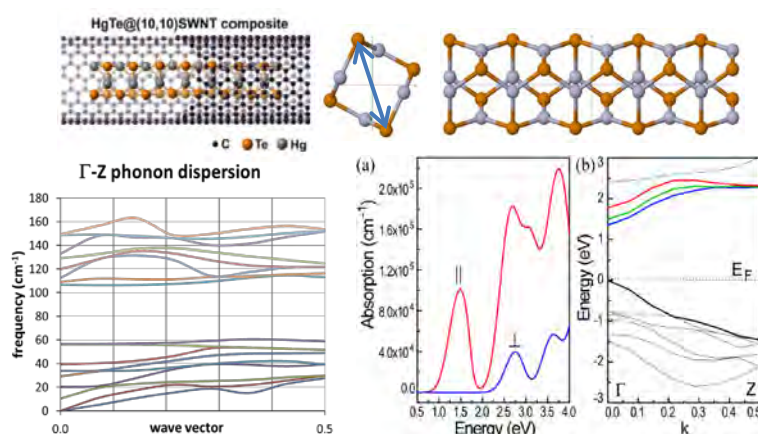


Figure 1 – HgTe nanowire. Top: fragment embedded in a (10,10) SWNT from high-resolution electron microscopy images [1] and corresponding optimized structure obtained with DFT package CASTEP. Bottom: PDOS, absorption and electronic structure [2].

[1] D. C. Smith, J. H. Spencer, J. Sloan, L. P. McDonnell, H. Trehwitt, R. J. Kashtiban, E. Faulques, *J. Vis. Exp.* 110 (2016), e53434, doi:10.3791/53434.

[2] J. Spencer, J. Nesbitt, H. Trehwitt, R. Kashtiban, G. Bell, V. Ivanov, E. Faulques, J. Sloan, D. C. Smith, *ACS Nano* 8 (2014), 9044.

## PIEZORESISTANCE STRAIN SENSING IN SINGLE CARBON FIBERS EPOXY COMPOSITES USING RAMAN MICROSCOPY

Nataliya Kalashnyk<sup>a</sup> Eric Faulques<sup>b</sup>, Jan Schjødt-Thomsen<sup>c</sup>, Lars R Jensen<sup>c</sup>, Jens Chr M Rauhe<sup>c</sup> and Ryszard Pyrz<sup>c</sup>

<sup>a</sup> Institut Jean Lamour, UMR 7198 CNRS - Université de Lorraine, Parc de Saurupt, 54011 Nancy, France

<sup>b</sup> Institut des Matériaux Jean Rouxel, UMR 6502 CNRS - Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes, France

<sup>c</sup> Department of Mechanical and Manufacturing Engineering, Aalborg University, Fibigerstræde 16, 9220 Aalborg East, Denmark

email: n.kalashnyk@yahoo.com

The change of electrical resistance in continuous single carbon fibers (CF) and single carbon fiber/epoxy model composites with applied strain [1-2] has been investigated by an electromechanical setup while the strain within CFs was measured with original *in-situ* Raman microscopy (Fig. 1). The study was performed using the facilities of Aalborg University. Raman spectra of sized and unsized 6.7  $\mu\text{m}$  diameter CFs embedded in epoxy matrix were obtained using a Renishaw inVia Raman Microscope at an excitation wavelength of 632.8 nm. The laser beam was focused to a spot of about 2  $\mu\text{m}$  on the fiber via a  $\times 50$  objective lens. The Raman setup was equipped with an electromechanical tensile testing machine. In all cases, a sudden increase to infinity of the piezoresistivity corresponds to fiber fracture. To insure statistical reliability in the results, each experimental point is the average of measurements carried out on 5 to 7 CF specimens of the same length and grade. It has been possible to determine the gage factors of the piezoresistance curves which are closely related to the dimensional change of the fiber under tension. Reinforcement/matrix interface are compared for bare and sized CFs. It is shown that, in principle, it is possible to correlate with Raman spectroscopy the fiber strain and the variation of electrical fibre resistance as a function of the applied strain for a single fiber embedded in epoxy. This study shows that carbon fibers embedded in epoxy matrix may serve as electrical strain sensors to detect both their own onset of damage and that of the composite under load, prior to specimen fracture.

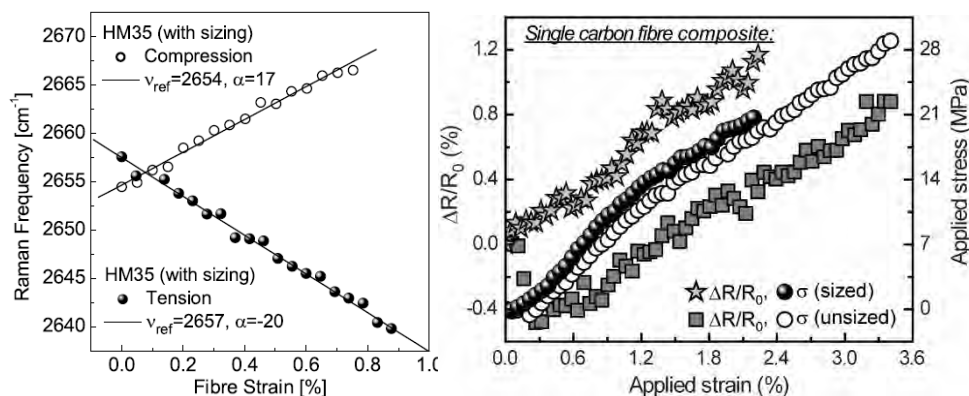


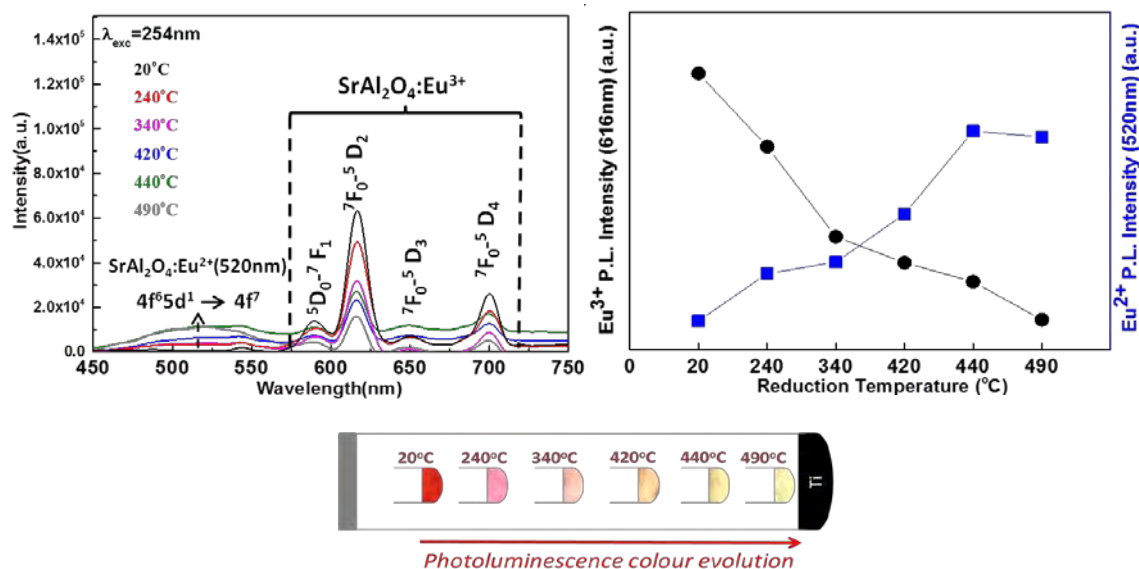
Figure 1- Left: strain compression and tension sensitivity of G' Raman band in a single carbon fiber. Right: piezoresistivity and applied stress of single carbon fiberspecimen embedded in epoxy versus applied strain.

- [1] P. C. Conon, C. N. Owston, Nature 223 (1969) 1146-1147.  
 [2] X. J. Wang, D. D. L. Chung, Carbon 35 (1997) 706-709.

## A Chemical Route Towards Single-Phase Materials with Controllable Photoluminescence

Gaganpreet Kaur Behrh, H el ene Serier-Brault, Romain Gautier, St ephane Jobic  
*Institut des Mat eriaux Jean Rouxel, CNRS, 2 Chemin de la Houssini ere, Nantes*  
 gaganpreet.behrh@cnsr-immn.fr

The oxidation states of dopants play an important role on the physical properties of many inorganic materials. For example, transition metal ion doped oxide compounds can exhibit different opto-electrical properties according to the oxidation states of the transition metals. In photoluminescent rare-earth metal ion doped materials, the photoemission differs according to the oxidation state of the dopant. Different techniques such as the redox reaction under controlled atmosphere or the co-doping with other cations allow targeting dopants in specific oxidation states but this control is usually poor or/and the addition of co-dopants may modify the properties. In this context, we realized a topotactic reduction of a well-known aluminate, namely  $\text{SrAl}_2\text{O}_4:\text{Eu}$ , by heating the material at low temperature with oxygen getters in sealed glass tubes. This soft chemistry route enables to control the ratio  $\text{Eu}^{3+}/\text{Eu}^{2+}$  in the host matrix and the optical properties are shown to be tunable according to this ratio. Indeed the photoemission corresponding to the 4f-4f transition of  $\text{Eu}^{3+}$  dopant (red emission) decreases and the photoemission corresponding to the 4f-5d transition of  $\text{Eu}^{2+}$  dopant (green emission) increases when the temperature of reduction increases. The mixing of red and green emissions in a controlled ratio could also be used to target yellow photoluminescent materials [1].



**Figure 1.** Evolution of emission color of  $\text{SrAl}_2\text{O}_4:\text{Eu}$  phosphors after reduction of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$  at different temperature with Ti as a getter.

### Reference

[1] G. Kaur Behrh, H. Serier-Brault, S. Jobic, R. Gautier, *Angew.Chem.* 127 (2015) 11663–11665.

## Interlayer interaction in the hetero-layered BiCuOS, BiCuOSe, and BiCuOTe compounds

Hyo Seok Ji<sup>a</sup> and Ji Hoon Shim<sup>a,b</sup>

<sup>a</sup> *Department of Chemistry, Pohang University of Science and Technology, Pohang, Korea*

<sup>b</sup> *Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang, Korea*

abcdef@postech.ac.kr

The *p*-type BiCuOSe (BiCuSeO or BiOCuSe) is a recent high-*ZT* thermoelectric material, i.e.,  $ZT = 1.4$  at 923 K<sup>[1]</sup>. Pristine compound exhibits intrinsically low thermal conductivity ( $< 1.0$  W/m-K), and its electrical conductivity is also small due to low hole mobility. By doping with cations such as Ba<sup>2+</sup> into Bi<sup>3+</sup> site, however, the electrical conductivity as well as its power factor are significantly increased. Further enhancement of the power factor through doping with light atoms increases both the carrier concentration and the mobility. Although its power factor is smaller than other high efficient thermoelectric materials, BiCuOSe can have high *ZT* values because of its very low phonon conductivity.

Combining the effect of layer mixing, and intrinsic defects, we have investigated the origin of very low phonon conductivity in thermoelectric BiCuO*Q* (*Q*: S, Se, Te) compounds. Based on the first-principles anharmonic lattice dynamics calculations<sup>[2, 3]</sup>, we use the single-mode relaxation time approximation of the linearized phonon Boltzmann equation, which shows good agreement with experiments. Here, we found that the most important parameter for the origin of low phonon conductivity is the interlayer interaction between BiO and Cu*Q* layers. By analyzing the phonon linewidth distribution, which indicates the phonon scattering, we propose that the interlayer interactions play crucial role on suppressing phonon conductivity, i.e., the hetero-layered crystal controls these interlayer interactions, achieving optimal phonon conductivity and also other TE properties.<sup>[4]</sup>

### References

- [1] J. Sui, J. Li, J. He, Y.-L. Pei, D. Berardan, H. Wu, N. Dragoe, W. Cai, and L.-D. Zhao, *Energy Environ. Sci.* 6 (2013) 2916.
- [2] A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* 78 (2008) 134106.
- [3] A. Togo, L. Chaput, and I. Tanaka, *Phys. Rev. B* 91 (2015) 094306.
- [4] C. Lee, J. Hong, M.-H. Whangbo, and J. H. Shim, *Chem. Mater.* 25 (2013) 3745.



## Tuning of the flat band potential of p-type $\text{CuCrO}_2$ nanoparticles by oxygen deinsertion via a soft chemical route

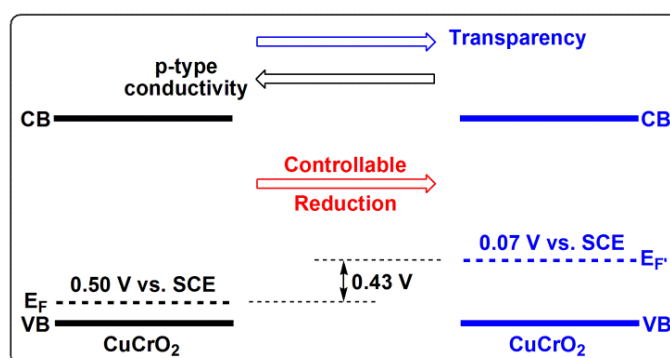
Tengfei Jiang<sup>\*</sup>, Xueyan Li, Martine Bujoli-Doeuff, Eric Gautron, Laurent Cario, Stéphane Jobic, and Romain Gautier

*Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes, Cedex 03, France.*

Email: tengfei.jiang@cns-immn.fr

Defects are the feature properties of the electronic structure of semiconductors.<sup>1</sup> They affect the optical, electrical, and magnetic properties of oxides.<sup>2</sup> Furthermore, their nature determines the performance in applications such as catalysis, sensor, and solar energy conversion.<sup>3</sup> Designing new approaches to engineer the concentration and spatial distribution of these defects, especially without extreme conditions, remains challenging. We propose a novel strategy to modulate the defects by using an oxygen getter, such as  $\text{CaH}_2$ , which promotes the capture of oxygen and lower the reduction temperature at the same time. Relatively low temperatures for reduction were selected to maintain the crystal structure of the materials, to result to the gradual release of oxygen, and thus to make the reduction more controllable.<sup>4</sup>

$\text{CuCrO}_2$  is a p-type semiconductor with a delafossite structure, which is widely used as transparent conduction oxide (TCO), catalysts, and p-type dye sensitized solar cell (p-DSSC).<sup>5</sup> Because of the non-stoichiometry, there is a slight amount of  $\text{Cu}^{\text{II}}$  in  $\text{CuCrO}_2$  which served as hole sources to supply excess carriers causing the p-type conductivity.<sup>6</sup> Herein, the reducing agent,  $\text{CaH}_2$ , acts as an oxygen getter to reduce the  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$ . More importantly, the reaction kinetics can be easily tuned by changing the temperature. The effect of the reduction temperature on the optical and electronic properties of  $\text{CuCrO}_2$  nanoparticles was investigated. As shown in Figure 1, the flat band potential, i.e. the Fermi level of  $\text{CuCrO}_2$  can be finely tuned by this new soft-chemistry route.



**Figure 1.** Graphical representation of the properties of  $\text{CuCrO}_2$  depending on the valence of Cu.

Reference to a journal publication:

- [1] G. Pacchioni, *ChemPhysChem*, 2003, 4, 1041–1047.
- [2] I. S. Cho, M. Logar, C. H. Lee, L. Cai, F. B. Prinz and X. Zheng, *Nano Lett.*, 2014, 14, 24–31.
- [3] F. Zuo, L. Wang, T. Wu, Z. Zhang, D. Borchardt and P. Feng, *J. Am. Chem. Soc.*, 2010, 132, 11856–11857.
- [4] G. Kaur Behrh, H. Serier-Brault, S. Jobic and R. Gautier, *Angew. Chem.*, 2015, 127, 11663–11665.
- [5] X. Xu, B. Zhang, J. Cui, D. Xiong, Y. Shen, W. Chen, L. Sun, Y. Cheng and M. Wang, *Nanoscale*, 2013, 5, 7963.
- [6] D. O. Scanlon and G. W. Watson, *J. Mater. Chem.*, 2011, 21, 3655.

## INTERCALATION ROUTE TO COMPLEX PEROVSKITES

### $AM_{0.2}Ta_{0.8}O_{3-x}N_x$ (A = Sr, Ba; M = Li, Na, Mg)

Young-Il Kim<sup>a</sup>, Jung-Mi Kim<sup>a</sup>, Maxim Avdeev<sup>b</sup>

<sup>a</sup> School of Chemistry and Biochemistry, Yeungnam University, Gyeongsan 38541, Republic of Korea

<sup>b</sup> Bragg Institute, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC NSW 2232, Australia

email address of the presenting author: yikim@ynu.ac.kr

New complex perovskite oxynitrides  $AM_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$  (A = Sr, Ba; M = Li, Na) and  $AMg_{0.2}Ta_{0.8}O_{2.6}N_{0.4}$  were synthesized by reacting  $A_5Ta_4O_{15}$  with  $M_2CO_3$  (M = Li, Na) or  $MgCl_2$  in flowing  $NH_3$ . The formation of above  $AM_{0.2}Ta_{0.8}O_{3-x}N_x$  can be described as the cooperative insertion of M cation and  $N^{3-}$  and the release of  $O^{2-}$  from the layered oxide,  $A_5Ta_4O_{15}$ .

A Rietveld refinement of the synchrotron X-ray and neutron powder diffraction patterns confirmed the complete structural transformation from a hexagonal layered-perovskite to a three-dimensional perovskite type, as well as the stabilization of M cations on the octahedral sites rather than on the dodecahedral sites in the latter. In all six compounds, M and Ta were disordered completely despite a charge difference of 3 or 4. The crystal symmetry of the average structure depended on the size of the dodecahedral cation; simple cubic for  $BaM_{0.2}Ta_{0.8}O_{3-x}N_x$ , and body-centered tetragonal for  $SrM_{0.2}Ta_{0.8}O_{3-x}N_x$ . This trend coincides with the symmetry transition from  $BaTaO_2N$  ( $Pm\bar{3}m$ ) to  $SrTaO_2N$  ( $I4/mcm$ ).

In both  $SrLi_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$  and  $SrNa_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$ , nitrogen atom preferentially occupied the *c*-axial  $4a$  site of the tetragonal cell. However, the nitrogen in  $SrMg_{0.2}Ta_{0.8}O_{2.6}N_{0.4}$  was partially ordered favoring the *c*-axial site over the *ab*-plane. Solid state magic angle spinning nuclear magnetic resonance spectroscopy showed that  $SrNa_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$  and  $ANa_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$  (A = Sr, Ba) exhibited marked downfield shifts of  $^{23}Na$ , manifesting an octahedral coordination. On the other hand, the  $^7Li$  NMR of  $SrLi_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$  and  $BaLi_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$  indicated a highly symmetrical coordination environment of Li.

The group of simple and complex perovskites,  $ATaO_2N$ ,  $ALi_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$ ,  $ANa_{0.2}Ta_{0.8}O_{2.8}N_{0.2}$ , and  $AMg_{0.2}Ta_{0.8}O_{2.6}N_{0.4}$  (A = Sr, Ba) cover the band gap range, 1.9~2.4 eV, and the color range from yellow to dark brown.

[1] Y.-I. Kim, Y. Paik, M. Avdeev, Cryst. Growth Des. 15 (2015) 53–61.

[2] K.H. Moon, J.-M. Kim, Y. Sohn, D.W. Cho, Y.-I. Kim, M. Aveev, Dalton Trans. 45 (2016) 5614–5621.

## COLOR TUNABLE MULTI-PHOTOLUMINESCENCE OF $\text{Ba}_{1.3}\text{Ca}_{0.7}\text{SiO}_4:\text{Eu}^{2+}/\text{Mn}^{2+}$ PREPARED BY A SOLUTION PROCESS

Jieun Park, Young Jin Kim\*

*Department of Advanced Materials Engineering, Kyonggi University, Suwon 443-760,  
Korea*

\*yjkim@kgu.ac.kr

Color-tunable phosphors with a single phase are suitable for the improvement of the luminous efficiency of white light-emitting diodes pumped by near ultraviolet chips. For this application,  $\text{Ba}_{1.3}\text{Ca}_{0.7}\text{SiO}_4:\text{Eu}^{2+},\text{Mn}^{2+}$  is one of the effective host materials, and the  $\text{Eu}^{2+}$  and  $\text{Mn}^{2+}$  ions are commonly used as sensitizers and activators, respectively.

In this study, we synthesized  $\text{Ba}_{1.3}\text{Ca}_{0.7}\text{SiO}_4:0.1\text{Eu}^{2+},x\text{Mn}^{2+}$  (BCSO: $\text{Eu}^{2+},x\text{Mn}^{2+}$ ) powders by a solution process. Precursors were prepared by a sol-gel-combustion process, and then they were fired at 1300 °C under an atmosphere of 5%  $\text{H}_2/95\% \text{N}_2$ . XRD data confirmed that for  $x = 0-0.06$ , the synthesized powders consisted of a BCSO single phase, indicating that the  $\text{Eu}^{2+}$  and  $\text{Mn}^{2+}$  ions were fully incorporated into BCSO lattices. Under 397 nm radiation, the photoluminescence spectra were composed of the green (~ 500 nm) and red emission bands (~ 600 nm), which were assigned to the  $\text{Eu}^{2+}$  and  $\text{Mn}^{2+}$  ions, respectively. The emission intensity ratio of green to red and the fluorescence decay time indicated that the red emission originated from the  $\text{Mn}^{2+}$  ions through an energy transfer process from  $\text{Eu}^{2+}$  to  $\text{Mn}^{2+}$ . The  $\text{Eu}^{2+}/\text{Mn}^{2+}$  ratio led to the variation of the green/red emission ratio, resulting in a color tunability of BCSO: $\text{Eu}^{2+},\text{Mn}^{2+}$  phosphors.

# FIRST-PRINCIPLES ANALYSIS OF LATTICE DYNAMICS AND PHONON CONDUCTIVITY OF $PbX$ ( $X=Te, Se$ and $S$ )

Sujee Kim<sup>a</sup>, Hyo Seok Ji<sup>b</sup>, Ji-Hoon Shim<sup>a,b</sup>

<sup>a</sup> *Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang, Korea*

<sup>b</sup> *Department of Chemistry, Pohang University of Science and Technology, Pohang, Korea*

kim77810@postech.ac.kr

The semiconducting lead chalcogenides have attracted much attention during last decades, in particular due to their high-temperature thermoelectric performance with low phonon conductivity. The thermoelectric materials can be used in the thermoelectric power generator to convert heat to electric power.<sup>[1]-[3]</sup> A number of recent investigations, both in experiment and theory, have aimed to gather insight on their unique lattice dynamics and electronic structures. While the electronic structures have been mainly studied using first-principles calculations,<sup>[4]</sup> the lattice properties have been studied using various theoretical methods such as empirical molecular dynamics and Boltzmann equation of lattice dynamics.<sup>[5]-[7]</sup> The detailed analysis of lattice dynamics have provided insights into the phonon properties and designing better thermoelectric materials.

In this study, we report phonon conductivity and lattice dynamics of the lead chalcogenides  $PbX$  ( $X=Te, Se, \text{ and } S$ ) using the combination of density functional theory calculation and Boltzmann transport equation with a direct force-constant method. Calculated lattice properties such as elastic moduli and phonon dispersions are compared with reported experimental results. Based on lattice properties, the thermal conductivities of  $PbX$  compounds are investigated. By analyzing anharmonic phonon scattering, we have found phonon modes determining the lattice thermal conductivity. Our results the lattice thermal conductivity of lead chalcogenide compounds can be further reduced by using phonon band engineering.

[1] H. J. Goldsmid, Introduction to Thermoelectricity, Springer, Berlin, 2009.

[2] G. J. Snyder and E. S. Toberer, Nat.Mater. 7 (2008) 105-114.

[3] J. R. Sootsman, D. Y. Chung, and M. G. Kanatzidis, Angew. Chem. Int. Ed. 48 (2009) 8616-8639.

[4] K. Hummer, A. Grüneis, and G. Kresse, Phys.Rev.B 75, (2007) 195211.

[5] Z. Tian, J. Garg, K. Esfarjani, T. Shiga, J. Shiomi, and G. Chen, Phys. Rev. B 85 (2012) 184303.

[6] O. Kilian, G. Allan, and L. Wirtz, Phys. Rev. B 80 (2009) 245208.

[7] T. Shiga, J. Shiomi, J. Ma, O. Delaire, T. Radzynski, A. Lusakowski, K. Esfarjani, and G. Chen, Phys. Rev. B 85 (2012) 155203.

## STRUCTURE-PROPERTY RELATIONSHIP IN (ZrO<sub>2</sub>)<sub>1-x-y</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>y</sub> SOLID SOLUTION CRYSTALS

Alexey V. Kulebyakin<sup>a</sup>, M.A. Borik<sup>a</sup>, S.I. Bredikhin<sup>b</sup>, V.T. Bublik<sup>c</sup>, I.E. Kuritsyna<sup>b</sup>,  
E.E. Lomonova<sup>a</sup>, F.O. Milovich<sup>c</sup>, V.A. Myzina<sup>a</sup>, V.V. Osiko<sup>a</sup>, P.A. Ryabochkina<sup>d</sup>,  
S.V. Seryakov<sup>c</sup>, N.Yu. Tabachkova<sup>c</sup>

<sup>a</sup> Prokhorov General Physics Institute RAS, Vavilov str. 38, Moscow, Russia

<sup>b</sup> Institute of Solid State Physics RAS, Institutskaya str. 2, Chernogolovka, Russia

<sup>c</sup> National University of Science and Technology «MISIS», Leninsky pr. 4, Moscow,  
Russia

<sup>d</sup> Ogarev Mordovia State University, Bolshevistskaya str. 68, Saransk, Russia

e-mail: kulebyakin@lst.gpi.ru

Scandia stabilized zirconia (ScZr) is a promising electrolyte for an application in solid oxide fuel cells (SOFC) that can operate at 800–850 °C. The material exhibits the highest ionic conductivity among the zirconia solid solutions. In practice solid electrolytes are mainly used as gas-tight ceramic membranes fabricated by various ceramics technologies. The functional properties of these ceramic membranes largely depend on their microstructure (grain size, grain boundaries, intergranular stresses, porosity etc.) which are in turn controlled by the synthesis process conditions. Another method of obtaining zirconia materials is the synthesis of crystalline materials using melt crystallization methods, in particular, skull melting technique. This approach facilitates the growing high density monolithic crystalline material with zero porosity and no grain structure.

There are two main issues limiting practical use of the (ScZr): transformation of the high conductivity cubic phase into the rhombohedral phase at about 500 – 600°C, and high aging rate (conductivity degradation during extended exposure at operating temperatures). One method to improve the properties of the electrolyte materials, such as to stabilize the cubic modification, to suppress conductivity degradation is the introduction of second dopant (co-dopant) in addition to Sc<sup>3+</sup> into the electrolyte structure.

For the first time crystals of solid solutions ( $x = 0.08 - 0.11$ ;  $y = 0.01 - 0.02$ ) have been grown by directional melt crystallization. We have determined the range of melt compositions for which growth from the melt produces of the (ZrO<sub>2</sub>)<sub>1-x-y</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>y</sub> solid solution single crystals. The single-phase optically transparent single crystals following composition were grown: (ZrO<sub>2</sub>)<sub>0.9</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>0.08</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.02</sub>;  
(ZrO<sub>2</sub>)<sub>0.89</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>0.09</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.02</sub>;  
(ZrO<sub>2</sub>)<sub>0.88</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>0.10</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.02</sub>;  
(ZrO<sub>2</sub>)<sub>0.89</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>0.10</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.01</sub>;

Comprehensive study of the crystal structure by using XRD, transmission electron microscopy, and Raman spectroscopy revealed that the all single crystals, which is identified by XRD data as cubic one, in fact have t<sup>z</sup> tetragonal structure, which forms by small displacement of oxygen ions along the c-axis. Data on the phase stability of the crystals during mechanical crushing were obtained. The electrical conductivity was measured as a function of temperature by electrochemical impedance spectroscopy. It is established that (ZrO<sub>2</sub>)<sub>0.89</sub>(Sc<sub>2</sub>O<sub>3</sub>)<sub>0.10</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.01</sub> crystals have the highest conductivity (0.168 S/cm at 1173 K).

The work was supported by research grants № 16-13-00056 of the Russian Science Foundation № 16-38-00521 mol\_a of the Russian foundation for basic research (RFBR)

## MAGNETIC ANISOTROPY AND MAGNETOELECTRIC COUPLING IN LiNbO<sub>3</sub>-TYPE InFeO<sub>3</sub>

William Lafargue-Dit-Hauret<sup>1</sup>, Koji Fujita<sup>2</sup>, Takahiro Kawamoto<sup>2</sup>, Olivier Hernandez<sup>1</sup>, Xavier Rocquefelte<sup>1</sup>, Pascal Manuel<sup>3</sup>

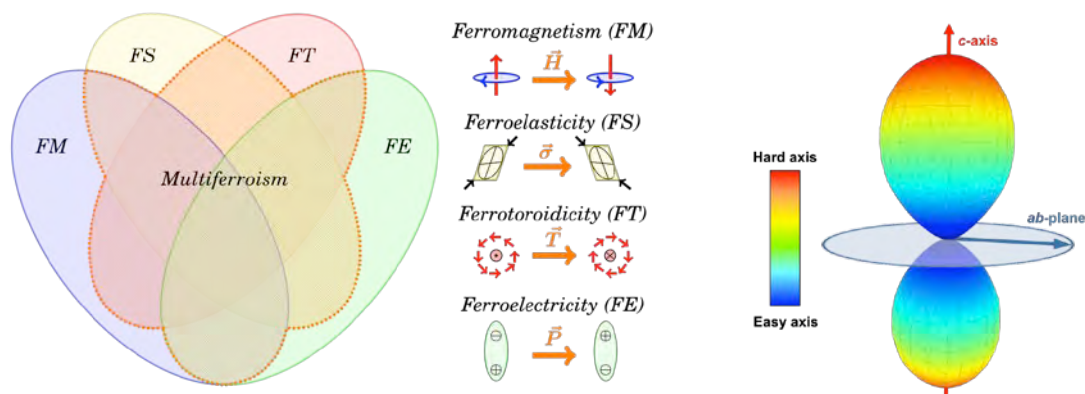
<sup>1</sup>*Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes, France*

<sup>2</sup>*Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

<sup>3</sup>*ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Oxon OX11 0QX, United Kingdom*

Email address of the presenting author: [william.lafargue-dit-hauret@univ-rennes1.fr](mailto:william.lafargue-dit-hauret@univ-rennes1.fr)

In the last few years, the field of multiferroics has greatly expanded with the idea to promote new technologies dealing with multi-states memory devices and spintronics [1,2]. Such materials exhibit simultaneously two ferroic properties. Here, we are interested by magnetoelectric materials, which combine ferroelectric and antiferromagnetic orders. Such properties have been evidenced in a wide range of perovskite compounds, such as BiFeO<sub>3</sub> [3,4]. One challenge in this field is to create room-temperature multiferroic materials with a large electric polarization, as observed in this compound. Following a recent report on a room-temperature magnetoelectric material, LiNbO<sub>3</sub> (LN)-type ScFeO<sub>3</sub> [5,6], this poster presentation will be focused on the theoretical investigation of a new LN-type InFeO<sub>3</sub>, exploiting experimental nuclear and magnetic models refined against time-of-flight neutron powder diffraction data measured at the WISH diffractometer, ISIS neutron facility.



Relationship between primary ferroic properties in multiferroic material (left) and magnetocrystalline anisotropy energy in perovskite LiNbO<sub>3</sub>-type InFeO<sub>3</sub> (right)

- [1] M. Bibes, A. Barthélémy, *Nature Mater.* 7 (2008) 425-426.  
 [2] Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T.-H. Arima, Y. Tokura, *Nature Mater.* 8 (2009) 558-562.  
 [3] C. Weingart, N. Spaldin, E. Bousquet, *Phys. Rev. B* 86 (2012) 094413.  
 [4] E. Bousquet, A. Cano, *J. Phys.: Condens. Matter* 28 (2016) 123001.  
 [5] T. Kawamoto, K. Fujita, I. Yamada, T. Matoba, S. J. Kim, P. Gao, X. Pan, S.D. Findlay, C. Tassel, H. Kageyama, A. J. Studer, J. Hester, T. Irifune, H. Akamatsu, K. Tanaka, *Journal of the American Chemical Society* 136 (2014) 15291-15299.  
 [6] K. Fujita, T. Kawamoto, I. Yamada, O. Hernandez, N. Hayashi, H. Akamatsu, W. Lafargue-Dit-Hauret, X. Rocquefelte, M. Fukuzumi, P. Manuel, A. J. Studer, C. Knee, K. Tanaka, *Journal of the American Chemical Society* (2016), *to be submitted*.

## Bismuth based metal organic frameworks as efficient photocatalysts

Yuanyuan Liu, Guanzhi Wang, Baibiao Huang

*State Key Laboratory of Crystal Materials, Shandong University, China*

[yliu@sdu.edu.cn](mailto:yliu@sdu.edu.cn)

Metal-organic frameworks (MOFs) are a class of crystalline-hybrid materials, consisting of metal ions as dots and organic molecules as linkers to form a 3D dimensional network. They have drawn more and more attention not only because of their unique properties, such as high specific surface areas, structural diversity, and tunable pore channels, but also because of the resulting wide applications in selective gas separation and adsorption, gas storage, optical materials, and also catalysis. The element of bismuth is of low toxicity and earth abundance. However, little attention has been paid on bismuth based MOFs.

We first synthesized a bismuth based MOFs composed of  $\text{Bi}^{3+}$  and  $\text{H}_2\text{mna}$  (2-mercaptopyridonic acid) using a solvothermal reaction, and the product was denoted as Bi-mna. Bi-mna is a highly efficient photocatalyst under visible light irradiation. A ligand to ligand charge transfer (LLCT) process is proposed to be responsible for its good photoelectric and photocatalytic performance. PL spectra suggests a much longer lifetime of photogenerated carriers compared with the organic ligand, which is believed to suppress electron-hole recombination and thus increase photocatalytic efficiency. <sup>[1]</sup>

Then, a novel topology structure of MOF based on bismuth and  $\text{H}_3\text{BTC}$  (Bi-BTC) was synthesized by a solvothermal method. Bi-BTC crystallizes in the  $\text{P}21/n$  space group, exhibits a novel 3D framework consisting of trimesic acid ( $\text{H}_3\text{BTC}$ ) linked with  $\{\text{Bi}_2\text{O}_{14}\}$  units and contains two helix chains which assemble regularly. In addition, Bi-BTC was found to show high photocatalytic activity of  $\text{O}_2$  production from water. <sup>[2]</sup>

Interestingly, an isomer of  $\text{BiO-BTC}_{\text{IE}}$  was synthesized after further investigation, which was denoted as  $\text{BiO-BTC}_{\text{IE}}$ .  $\text{BiO-BTC}_{\text{IE}}$  was obtained via an ion exchange reaction, between  $\text{BiOHCOO}$  and  $\text{H}_3\text{BTC}$ .  $\text{BiO-BTC}_{\text{IE}}$  displays layered structure consisting of  $\text{Bi}_2\text{O}_2^{2+}$  and BTC layers, which are stacked alternatively. The structure of  $\text{BiO-BTC}_{\text{IE}}$  was examined by XRD, EXAFS, FT-IR, TG/DTA, etc. By replacing the  $\text{HCOO}^-$  with BTC anions in the  $\text{Bi}_2\text{O}_2^{2+}$  interlayer, the  $\text{Bi}_2\text{O}_2^{2+}$  layer is distorted as revealed by the EXAFS, which lead to a longer life time of the photogenerated charge carriers and a higher photocatalytic activity of  $\text{BiO-BTC}_{\text{IE}}$  (more than 10 times). <sup>[3]</sup>

### Reference

- [1] G. Z. Wang, Q. L. Sun, Y.Y. Liu, B. B. Huang, Y. Dai, X. Y. Zhang, X. Y. Qin, *Chem. Eur. J.*, 21(2015), 2364-2367
- [2] G. Z. Wang, Y. Y. Liu, B. B. Huang, X.Y. Qin, X. Y. Zhang, Y. Dai, *Dalton Trans.*, 44 (2015), 16238-16241.
- [3] Y.Y. Liu, G. Z. Wang, J.C. Dong, Y. An, B. B. Huang, X. Y. Qin, X. Y. Zhang, Y. Dai, *J. Colloid Interf. Sci.* 469 (2016) 231-236.



## CALCULATION OF THE OPTICAL PROPERTIES IN SILICON CARBIDE BY MOLECULAR DYNAMICS

A. M. Mekeze<sup>a</sup>, G. Domingues<sup>a</sup>,  
B. Rousseau<sup>a</sup>

<sup>a</sup> *LTN, UMR CNRS 6607, Rue Christian Pauc, 44306 Nantes*  
E-mail: aubin.mekeze-monthe@univ-nantes.fr

Silicon carbide (SiC) is an interesting material due to its good thermal and mechanical properties and represents these last years a large subject of fundamental studies. From the point of view of industrial applications, SiC may be used under the shape of foams as absorber in concentrated solar power (CSP) to store thermal energy and to deliver this heat to a coolant fluid (air) which the role is to run a thermodynamic chain of conversion of mechanical energy into electrical energy. The correspondent Carnot efficiency is directly related to the efficiency of the absorber which increases when a maximum solar energy is absorbed in the visible range and a minimum thermal energy is lost in the far and mid infrared range. The spectral selectivity of SiC, hereafter defined, is a key element to optimize the efficiency of CSP. A way to reach this objective is to control the chemical doping in order to maximize the solar absorptivity in the visible range.

Precedent works of Guevelou *et al.*, based on the use of a Monte Carlo Ray Tracing code, have connected both the optical and the textural properties of SiC foams to their radiative properties [1]. Optical properties used for the solid struts parts are nevertheless considered at 300K, that is a temperature far from those required for the industrial utilization in CSP since temperatures can reach 1500K. So, we propose in this study to present an alternative way based on numerical simulations by mean of Molecular Dynamics (MD) for determining the temperature dependence of the optical properties of SiC crystalline samples with suitable chemical doping.

Numerical simulations is an interesting way to the determinate optical properties (index of refraction, index of absorption) of doped SiC at different temperature because one can control the rate of doping contrarily to experimental measures. Moreover, results issued from MD simulations are not affected by high temperature corrosion of the samples. The MD technique consists to generate a structure of SiC atoms and to follow the movement of each atom, by application of the fundamental principle of dynamics, in order to recreate the macroscopic behavior of a bulk system. Each atom is submitted to interaction forces which derive from an interaction potential. In our case, the chosen potential are the Vashista [2] and the Tersoff potentials [3]. The complex dielectric functions, which are the square root complex of the index of refraction, will be calculated via the linear response theory [4] applied to the electric dipole moment calculated in the SiC structure and stored during the simulation. We will simulate these dielectric functions for temperatures starting from 300 K to 1500 K and for different rates of doping. Theses results will be compared to experimental measures presented in the literature [5].

### References :

- [1] S. Guévelou, B. Rousseau, G. Domingues, J. Vicente, C. Caliot, IJHMT 93 (2016)
- [2] P. Vashista, R. K. Kalia, A. Nakano, J.P. Rino, J. of App. Phys. 101, 103515 (2007)
- [3] E. Halac, E. Burgos, H. Bonadeo, Phys. Rev. B 65,125202 (2002)
- [4] G. Domingues, S. Volz, K. Joulain, J. Greffet, Phys. Rev. Lett. 94, 085901 (2004)
- [5] K. Joulain, Y. Ezzahri, J. Drevillon, B. Rousseau, D.D.S. Meneses, Optics Express 243581 (2015)

## Enhancement of Ferromagnetic Ordering Curie Temperature in N-Doped MgO under Hydrostatic Pressure

<sup>a</sup>Mir Ali

<sup>a</sup> *Center University of Relizane, Algeria 48000*

mirali1205970@gmail.com

The all calculations have been performed within DFT implemented in the WIEN2k code [1]. Atoms were represented by hybrid full-potential (linear) augmented plane wave plus local orbitals (L/APW + lo) method [2]. The exchange-correlation energy was calculated using the Perdew-Wang local density approximations (LDA) [3]. We have explored the magnetic properties of Nitrogen doped cubic MgO using the full potential linearized augmented plane wave (FP-LAPW) method. The unit cell has 128 atoms, and two Nitrogen atoms are placed in the positions of oxygen sites. This corresponds to 3.125% doping concentration. Our calculations predict that the ferromagnetic state, with a magnetic moment of about 1.0  $\mu_B$  per Nitrogen-dopant, is more favorable in energy than the nonmagnetic state, and the ferromagnetic correlations are influenced by the impurity bound state. The magnetic moment mainly arises from p orbital of Nitrogen which substitutes the Oxygen atom, with a little contribution from the Oxygen atoms surrounding Nitrogen atom. The resulting band structure and densities of states agree well with the recent theoretical works. The ferromagnetic ordering temperatures obtained from DFT simulations have been given in detail. Our results show that the pressure enhances the temperature in MgO:N. Under hydrostatic pressure of N doped MgO has been conducted in order to understand the origin of magnetism. The MgO:N compound in which Oxygen is substituted by Nitrogen atoms is found to be ferromagnetic for all pressures estimated. The N atom forms a partially occupied gap state at the vicinity of the valence band edge which makes this material half metallic. It is found that the doping of N results a strong coupling between 2p states of dopant (N) and host (O). Finally, our calculations show that the Curie temperature  $T_C$  increases with hydrostatic pressure and it is found to be about 44 K for 250 GPa pressure.

Reference to a journal publication:

[1] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz, "WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties," 2th Edition, Vienna University of Technology, Vienna, 2001.

[2] E. Sjöstedt, L. Nordstrom and D. J. Singh, "An Alternative Way of Linearizing the Augmented Plane-Wave Method," Solid State Communication, Vol. 114, No. 1, 2000, pp. 15

[3] P. Perdew and Y. Wang, "Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy," Physical Review B, Vol. 45, No. 23, 1992, pp. 13244-13249.

## MAGNETISM OF ANTI-PEROVSKITE NITRIDE Cr<sub>3</sub>AsN

Kenta Takao<sup>a</sup>, Takeshi Waki<sup>a</sup>, Yoshikazu Tabata<sup>a</sup>, Hiroto Ohta<sup>b</sup>, Takeshi Yajima<sup>c</sup>, Zenji Hiroi<sup>c</sup>, Hiroyuki Nakamura<sup>a</sup>

<sup>a</sup> *Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*

<sup>b</sup> *Division of Advanced Applied Physics, Institute of Engineering, Tokyo University of Agriculture and Technology, Koganei 184-8588, Japan*

<sup>c</sup> *ISSP, The University of Tokyo, Kashiwa 277-8581, Japan*

email address of the presenting author: nakamura.hiroyuki.2w@kyoto-u.ac.jp

Anti-perovskite-type transition-metal compounds are known to show fascinating magnetic properties associated with the interplay between the high site symmetry and the orbital degeneracies of the transition-metal element. Ever-known Cr-based anti-perovskite materials are all nitrides and metallic, suggesting that they are categorized as itinerant-electron magnets. However their magnetism has been less investigated.

In this presentation, we pick up a particular material Cr<sub>3</sub>AsN, which forms the tetragonal structure (*I4/mcm*) at room temperature [1], and report for the first time the result on the magnetism. We found that Cr<sub>3</sub>AsN shows a ferromagnetic-like transition at ~260 K, below which the saturation magnetization reaches only 0.06 μ<sub>B</sub>/Cr. This value is anomalously small compared with the rather high transition temperature. We will discuss the nature of the transition on the basis of the results of <sup>75</sup>As NMR and low-temperature X-ray diffraction. The former show that the hyperfine field at the As site are uniform (a single As site) below the transition and the magnitude is ~1.0 T at the lowest temperature. The latter suggests the presence of tiny spontaneous volume magnetostriction below the transition, which mainly comes from the expansion in the lattice parameter *c*. These results indicate that the transition is of intrinsic itinerant-electron type but needs a particular model of the magnetic structure to explain the tiny moment.

[1] H. Boller, *Monatsh. Chem.* 99 (1968) 2444.

## Effect of the neutron and heavy-ion beam irradiation on the optical properties of beryllium oxide samples

Maxim D. Petrenko<sup>a</sup>, Igor N. Ogorodnikov<sup>a</sup>, Vladimir Yu. Ivanov<sup>a</sup>

<sup>a</sup> *Ural Federal University, Russian Federation, Ekaterinburg, Mira Street, 19*

Email: md.petrenko@urfu.ru

Since the discovery of intense ultraviolet (UV) emission from beryllium oxide (BeO) [1] and the development of the technology of growing large BeO single crystals [2], BeO has been the subject of numerous studies, see e.g. review [3]. Due its unique properties, such as a transparency in the wide spectral range of 121-7000 nm, a high melting temperature of  $T_m=2550^\circ\text{C}$ , an elevated radiation stability in optical properties, and a bright luminescence in the UV and vacuum UV spectral ranges, beryllium oxide are using in many application areas. In addition, it is a well-known optical material for use in solid state dosimetry using both the thermoluminescence (TL) and optically-stimulated luminescence (OSL) methodologies. Optical properties of beryllium oxide can be modified by various methods, such as thermochemical treatment or radiation action. The color centers in beryllium oxide can be created due to additive coloring in high-pressure beryllium vapor. They are in the form of the F-type color centers, which can significantly change optical properties, luminescence spectrum and TL-glow curves [4].

In present work we have comparatively examined beryllium oxide in the form of single crystals and hot-pressed ceramic samples. The BeO samples were subject to irradiation by either heavy ions ( $^{85}\text{Kr}$ ) with energy  $E=1,75\text{ MeV/nuc}$ l on DC-60 cyclotron, or thermal neutrons ( $F=10^{20}\text{ cm}^{-2}$ ). All experiments were carried out at Experimental Physics Department of Ural Federal University (Yekaterinburg) and in Interdisciplinary research complex (Astana).

The spectra of the optical absorption, x-ray-induced luminescence (XRL), and photoluminescence (PL), as well as TL glow curves were recorded for all BeO samples before and after irradiation. In addition, all spectra were obtained using step-by-step annealing of the samples (step of  $20^\circ\text{C}$ ). New PL emission band was revealed for the neutron-irradiated BeO crystals annealed at  $550^\circ\text{C}$ . The changes in absorption spectra for both the neutron and heavy-ion irradiated crystals were revealed and discussed. These results were compared with that for absorption spectra recorded for additively-colored BeO crystals.

In conclusion we discuss the origin of new luminescence centers created in beryllium oxide samples after neutron and heavy-ion beam irradiations. In addition, we have done a comparative discussion of the experimental absorption and luminescence spectra obtained for ion-beam irradiated and additively-coloured BeO samples. On the basis of this discussion we can speak about differences in the F and  $F^+$  centers created during the radiation and thermochemical treatment. Further development of this research work using optical spectroscopy methods and creation of the defects through an electron-beam bombardment, will bring new results to proof our models.

[1] H.O.Albrecht, C.E.Mandeville, Phys. Rev. 94 (1954) 776.

[2] S.B.Austerman, J.Amer. Ceram. Soc. 46 (1963) 6.

[3] I.N.Ogorodnikov, A.V.Kruzhalov, Material Science Forum, Vols. 239-241 (1997) 51.

[4] D.S.Tausenev, I.I.Milman, V.Yu.Ivanov, A.V.Kruzhalov, Radiation Measurements. 43 (2008) 349.

## P-type transition metal carbodiimides MNCN (M = Ni, Mn)

Baptiste Polteau<sup>a</sup>, Franck Tessier<sup>a</sup>, François Cheviré<sup>a</sup>, Adèle Renaud<sup>a</sup>, Laurent Cario<sup>b</sup>,  
Tengfei Jiang<sup>b</sup>, Stéphane Jobic<sup>b</sup>

<sup>a</sup> Institut des Sciences Chimiques de Rennes (UMR CNRS 6226), Université de Rennes 1, 263  
avenue du Général Leclerc, 35042 Rennes cedex, France

<sup>b</sup> Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, 2 rue de la Houssinière,  
44322 Nantes cedex 3, France

Over the last decade, p-type semiconductors (SC) have known a renewed interest. Indeed these materials may have potential applications for light-emitting diodes, transistors, solar cells, etc. Since the stabilization of the first p-type semi-conductor CuAlO<sub>2</sub> with a delafossite structure type (A<sup>+</sup>B<sup>3+</sup>O<sub>2</sub>) by H. Kawazoe in 1997<sup>[1]</sup>, many p-type semiconductors with the same structure have been reported such as CuGaO<sub>2</sub>, CuCrO<sub>2</sub>, CuScO<sub>2</sub>... Recently, X. Liu & *al* have reported the synthesis and the structure determination of a new family of materials: the transition metal carbodiimides MNCN (with M = Mn → Cu)<sup>[2,3]</sup>. These materials adopt a structure type related to the delafossite, formed by a divalent transition metal and NCN<sup>2-</sup> anion. We report here the synthesis and the microstructural characterization of two transition metal carbodiimides MnNCN and NiNCN. Impedance measurements demonstrate the p-type conductivity of these materials.

[1] Kawazoe, H.; Yasukawa, M.; Hyodo, H.; Kurita, M.; Yanagi, H.; Hosono, H. *Nature* **1997**, *389*, 939.

[2] Liu, X.; Krott, M.; Muller, P.; Hu, C.; Lueken, H.; Dronskowski, R. *Inorg. Chem.* **2005**, *44*, 3001.

[3] Krott, M.; Liu, X.; Fokwa, B. P.; Speldrich, M.; Lueken, H.; Dronskowski, R. *Inorg. Chem.* **2007**, *46*, 2204.

# Investigation of electronic structure, magnetic properties and thermal properties of the new half-metallic ferromagnetic full-Heusler alloys

## $\text{Cr}_2\text{NbGe}_{1-x}\text{Sn}_x$ : An ab-initio study.

I. Asfour<sup>1</sup>, D. Rached<sup>\*,1</sup>, H. Rached<sup>1,2</sup>, S. Benalia<sup>1</sup>

<sup>1</sup> Laboratoire des matériaux magnétiques, Département de physique, Faculté des Sciences, Université Djillali LIABES, Sidi-Bel-Abbès 22000, Algérie.

<sup>2</sup> Département de physique, Faculté des sciences, Université Hassiba BenBouali Chlef, Chlef 02000, Algérie.

### ABSTRACT

We have studied the structural, electronic, elastic, magnetic, thermal and thermodynamic properties of the quaternary Heusler alloys  $\text{Cr}_2\text{NbGe}_{1-x}\text{Sn}_x$  ( $x = 0, 0.25, 0.5, 0.75, 1$ ) with the linearized augmented plane wave method based on density functional theory and implemented in WIEN2K code. For exchange correlation potential, we have used the generalized gradient approximation (GGA) of Perdew et al. Our results provide a theoretical study for the mixed Heusler  $\text{Cr}_2\text{NbGe}_{1-x}\text{Sn}_x$  ( $0 < x < 1$ ) in which no experimental or theoretical data are currently available. In their equilibrium  $L2_1$  structure, all concentrations are magnetic and metallic. However, there is linear variation of the lattice parameter. The bulk modulus, the elastic constants and the Debye temperature was studied with variation of composition  $x$  of Ge. A regular solution model is used to investigate the thermodynamic stability, which is an essentially show a miscibility gap phase by calculating the critical temperatures for our alloys. In addition, the quasi-harmonic Debye model is applied to determine the thermal properties.

**Key words:** C. ab-initio calculations, A. Heusler alloys; D. Electronic structure; D. Magnetic properties. D. Thermodynamic properties.

---

\* Corresponding authors: +213 .554192664

**E-mail address:** [rachdj@yahoo.fr](mailto:rachdj@yahoo.fr) (Prof. D. Rached)

## Density-functional theory calculations of the structural magnetic and electronic properties for the Ferro-Spinel compounds $\text{AFe}_2\text{O}_4$

H. Rached<sup>1,2\*\*</sup>, N. Harichane<sup>1</sup>, D. Rached<sup>2</sup>, S. Benalia<sup>2</sup>

<sup>1</sup>*Hassiba BenBouali University, Faculty of sciences, Department of Physics, Chlef, 02000, Algeria*

<sup>2</sup>*Laboratoire des matériaux magnétique, université Djillali Liabes, Sidi Bel Abbès, 22000, Algérie*

### Abstract:

The aim of this paper is to study the structural stabilities, electronic and magnetic properties of  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  compounds by first-principles calculations. These compounds are among of the Ferri-spinel compounds, which are extensively reflected as one of the most important magnetic nanomaterials due to its significant potential applications, such as photocatalysis, information storage and electronic devices. All our calculations are carried out using the accurate ab-initio full-potential linearized augmented plane wave (FP-LAPW) method, in the framework of the density functional theory (DFT). The electronic exchange-correlation potential is treated with the generalized gradient approximation. The electronic structure and magnetic calculations show that our compounds exhibit half-metallic ferrimagnets and their magnetic moments are in agreement with the obtained one by the Slater-Pauling rule, which indicate the high spin polarization for these compounds. Consequently, our compounds are identified as probable candidates for information storage devices.

**KEYWORDS:** Magnetic materials; Ferro-spinel compounds; DFT; FP-LAPW

---

\*\*Corresponding authot. Tel: (+213) 661223197; E-mail:habib\_rached@yahoo.fr



## SHALLOW ACCEPTOR STATE IN ION IRRADIATED AND ANNEALED ZnO

S. Pal<sup>a</sup>, D. Jana<sup>a</sup>, T. Rakshit<sup>b</sup>, S. Dutta<sup>c</sup>, K. Asokan<sup>d</sup> and A. Sarkar<sup>e</sup>

<sup>a</sup>*Department of Physics, University of Calcutta, 92 A. P. C. Road, Kolkata 700009, India*

<sup>b</sup>*Department of Physics, Indian Institute of Technology, Kharagpur 721302, India*

<sup>c</sup>*Department of Physics, Rammohan College, 102/1, Raja Rammohan Sarani, Kolkata 700009, India.*

<sup>d</sup>*Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110067, India*

<sup>e</sup>*Dept. of Physics, Bangabasi Morning College, 19 R. C. Sarani, Kolkata 700009, India*

email address of the presenting author: sarkarcal@gmail.com

Activation of shallow acceptor state in n-type ZnO is one of the foremost debated topics for the last few decades [1-3]. In the present work, it has been realized in swift ion (96 MeV oxygen) irradiated and subsequently air annealed polycrystalline ZnO material [4]. Low temperature photoluminescence (PL) spectrum of the sample clearly exhibits acceptor bound exciton (ABX) emission at 3.360 eV, the intensity of which surpasses that of the dominant donor bound exciton emission (3.365 eV) at 40 K. The pristine or ion irradiated (not annealed) samples, however, do not show such acceptor related PL emission. Evolution of donor-acceptor pair (DAP) PL peak  $\sim$  3.229 eV is clearly observed in the spectrum. ABX and DAP peak energy positions confirm that the acceptor is nitrogen related [5]. The acceptor exciton binding energy can be estimated to be  $180 \pm 15$  meV. It is to be noted that there is no source of atomic nitrogen during the sample conditioning. The activation of shallow acceptors can only be possible through diffusion of molecular nitrogen inside the sample during annealing. The N<sub>2</sub> molecules get trapped at bulk defect sites incorporated by ion irradiation and subsequent annealing. The most probable defect sites, where N<sub>2</sub> molecules get chemically attached, can be presumed to be Zn-O di-vacancies. It has been found that oxygen ion irradiation is helpful for stabilizing acceptor states in ZnO [4]. Further annealing (at a relatively lower temperature  $\sim$  300 °C) in air reduces unwanted interstitial defects, creates small size vacancy agglomerates [6] and promotes diffusion of gaseous nitrogen in the sample. Rietveld analyses of the x-ray diffraction patterns of the samples support this contention. Results altogether provide a simple but controlled way of producing shallow acceptor state in ZnO. At the same time, generation of deep nitrogen related acceptors in ZnO, such as atomic nitrogen at vacant oxygen sites, can be avoided. If optimized through suitable choice of ion, its energy and fluence as well as the annealing temperature, this methodology can trigger further scope to fabricate devices using ZnO epitaxial thin films or nanowires. Details will be presented.

[1] J. Gutowski, N. Presser and I. Broser, Phys. Rev. B 38 (1988) 9746-9758.

[2] A. Zeuner, H. Alves, D. M. Hofmann, B. K. Meyer, A. Hoffmann, U. Haboeck, M. Strassburg and M. Dworzak, Phys. Stat. Sol. (b) 234 (2002) R7-R9.

[3] B. Chavillon, L. Cario, A. Renaud, F. Tessier, F. Chevire, M. Boujtita, Y. Pellegrin, E. Blart, A. Smeigh, L. Hammarstrom, F. Odobel, and S. Jobic, J. Am. Chem. Soc. 134 (2012) 464-470.

[4] S. Pal, D. Jana, T. Rakshit, S. S. Singha, K. Asokan, S. Dutta, and A. Sarkar, arXiv:1604.06653 (22.04.2016) and references therein.

[5] C. Ton-That, L. Zhu, M. N. Lockrey, M. R. Phillips, B. C. C. Cowie, A. Tadich, L. Thomsen, S. Khachadorian, S. Schlichting, N. Jankowski, and A. Hoffmann, Phys. Rev. B. 92 (2015) 024103-7pages.

[6] S. Dutta, S. Chattopadhyay, A. Sarkar, M. Chakrabarti, D. Sanyal and D. Jana, Prog. Mater. Sci. 54 (2009) 89-136.

# ORBITAL, NEMATIC ORDER, TOPOLOGICAL TRANSITION AND STRUCTURAL CORRELATION IN FE-BASED SUPERCONDUCTORS

Smritijit Sen and Haranath Ghosh

*Indus Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology, Indore - 452013, India.*

email address of the presenting author: smritijit.sen@gmail.com

Fe-based superconductors indicate several distinctly different physical properties, orbital physics, rich Fermiology, phase diagram, unconventional superconducting pairing mechanism (yet to be settled), that makes them overall a fundamentally different class ---superconductors with not only high  $T_c$  but also with technological applications. Various normal state characteristics (like structural transition, nematic phase, electronic topological transition etc.) of various 122 family of Fe-based superconductors will be presented from results of first principles simulations. We use experimentally determined structural parameters through out the phase diagrams of various 122 family of Fe-based superconductors as a function of doping and temperature as inputs of our simulation. Detailed electronic structures are extracted to examine temperature and doping dependence of orbital ordering. The electronic orbital ordering (between the  $d_{yz}$  and  $d_{xz}$  bands) takes place due to local breaking of in-plane symmetry that generates two non-equivalent a, b directions. It is comprehensively shown that the temperature and doping dependent 'orbital order' maps exactly to that of the experimentally determined 'orthorhombicity'. This indicates that the structural transition is dominantly an electronic transition and is determined by orbital ordering. Temperature/doping dependence of the orbital order is proportional to that of the nematic order ( $n_{d_{xz}} - n_{d_{yz}}$ ) and it sets in at a temperature where magnetic fluctuation starts building. Magnetic fluctuations in the orthorhombic phase is characterized through evolution of Stoner factor which reproduces experimental findings very accurately. Orbital ordering becomes strongly spin dependent in presence of magnetic interaction. The anion height plays a crucial role in establishing relationship among orbital, magnetic fluctuations, nematicity as well as Lifshitz transition in 122 family.

## **Effect of synthesis technique and micro structure on the carbon dioxide sensing properties of copper ferrite nanoparticles**

Sumangala T. P.<sup>a</sup>, L.Presmanes<sup>a</sup>, Y.Thimont<sup>a</sup>, V.Baco-Carles<sup>a</sup>, C. Bonningue<sup>a</sup>, A. Barnabe<sup>a</sup>

<sup>a</sup>*Institut Carnot CIRIMAT, Université de Toulouse, CNRS, Université Paul Sabatier, 118 Route de Narbonne, 31 062 Toulouse Cedex 9, France*

email address of the presenting author: [sumampoornima@gmail.com](mailto:sumampoornima@gmail.com)

Carbon dioxide is a non reactive gas and a constituent of atmospheric air. The monitoring of CO<sub>2</sub> in buildings and work places are essential for air quality control. CO<sub>2</sub> detectors can be helpful for detecting human proximity for introducing automation in air conditioners. This can lead to energy saving and cost effectiveness. This requires the CO<sub>2</sub> detectors to be installed in large numbers. This facilitates the need for cheap CO<sub>2</sub> detectors. In this paper, we report the development of new sensing layers of robust and cheap MOS (metal oxide semiconductor) CO<sub>2</sub> detectors.

Copper ferrite was chosen as the active material and was synthesized with co-precipitation using oxalate precursor. The powder was calcined at 780 °C to obtain a single phase. Room temperature Xray diffraction analysis of the powder showed that the sample was tetragonal phase copper ferrite. We have developed a novel method for fabricating a simple device with the synthesized powder on alumina substrate with silver electrodes. This method led to devices with high porosity and ensured that the morphology of the powder remained intact. The CO<sub>2</sub> sensing measurements were performed using Linkam cell with temperature control and the data acquisition was performed using Labview software. The response towards CO<sub>2</sub> (5000 ppm) was studied by noting the change in resistance of the device when CO<sub>2</sub> gas mixture and dry air was alternately passed to the test chamber. The sample was tested at temperatures varying from 200 – 350 °C. The experiment showed that the response of the sample was highest at an operating temperature of 350 °C. A response of 10% was obtained at this temperature. This was compared with the CO<sub>2</sub> sensing property of device made with sol gel combusted powder. It was seen that the response was less (3.6%) when compared to the co-precipitated powder. In order to understand the change in response with both the powder, a microstructure analysis was performed using scanning electron microscope (SEM). SEM microstructure analysis showed that sample synthesized using sol gel combustion had clusters with irregular shape and constituted of disconnected circular grains. The co-precipitated copper ferrite consisted of elongated grains with an open neck between the grains. The studies show that the CO<sub>2</sub> sensing property is related to the microstructure of the grains in the sample.

# COMPUTATIONAL AND EXPERIMENTAL STUDY OF THE x-DEPENDENT GRAIN BOUNDARY SEGREGATION IN THE CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

Polyxeni Tsoulka, Isabelle Braems, Nicolas Barreau, Sylvie Harel, Ludovic Arzel  
*Institut de Matériaux Jean Rouxel (IMN), University of Nantes, CNRS - UMR 6502*

Polyxeni.Tsoulka@cnrs-imn.fr

Polycrystalline CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (CIGSe) is one of the most promising materials for photovoltaic applications. Thin film solar cells based on CIGSe absorber layer have shown high conversion efficiency, since CIGSe possess the advantage of optimizing the optical band gap energy ( $E_g$ ) by tuning the Ga ratio,  $x = \frac{[Ga]}{[Ga]+[In]}$ . The lab scale conversion efficiency record reaches the 22% for  $x^* \approx 0.4$ , while theoretical predictions present a better performance for  $x$  between 0.7 and 0.8. ( $E_g \approx 1.4$  eV).

According to the recent results obtained by APT (Atom Probe Tomography)<sup>[1]</sup> on soda-lime (SLG) substrate, CIGSe present a chemical difference of the grain boundary segregating species for  $x < 0.4$  and  $x > 0.4$ , which could be a possible origin of the limitation at the electronic properties. In fact APT results demonstrate that for  $x > 0.4$  the GBs are Cu-enriched compared to the bulk while for  $x < 0.4$  the GBs are preferentially In-enriched, which is beneficial for the photovoltaic devices. Hence, to explain this selective segregation, we perform a computational and experimental study to understand the change at the GBs chemistry, occurring for different Ga ratios.

Based on the segregation theory for the binary alloys, we aim to comprehend the segregation driving forces in the CIGSe pseudo-binary system (CuInSe<sub>2</sub>-CuGaSe<sub>2</sub>). Therefore, we are first concerned by the alloy effect which is represented by the bulk phase diagram<sup>[2]</sup> and describes the tendency to phase separate or form an ideal solution. Thus, we implement first-principle calculations combined with thermodynamic modeling in order to obtain the bulk phase diagram of the pseudo-binary alloy, and have the first insights on the CIGSe homogeneity. Additionally, we compare the phase diagram obtained for a relaxed lattice<sup>[2]</sup> with one calculated for a rigid-lattice<sup>[3,4]</sup>, in order to observe the dependence of the phase diagram on the modeling method, when we take into account the elastic contributions.

As regards the experimental part of our study, we examine the crystallographic orientation dependence on the  $x$  and the effects of Na in the CIGSe structure. Hence, we are interested by the co-evaporation technique for the layer's growth and we perform compositional and structural analyses (RDX, EBSD, EDX) to carefully identify the crystallographic structure (texture, misorientation angles, grain sizes) of CIGSe, for different Ga ratios and for two different substrates (i) SLG and (ii) SLG containing a Na diffusion barrier.

## References:

- [1] M. Raghuvanshi, E. Cadel, P. Pareige, S. Duguay, F. Couzinie-Devy, L. Arzel, N. Barreau, Applied Physics Letters 105, 013902 (2014)
- [2] H. T. Xue, W. J. Lu, F. L. Tang, X. K. Li, Y. Zhang, Y. D. Feng, Journal of Applied Physics 116, 053512 (2014)
- [3] Y. Kumagai, Y. Soda, F. Oba, A. Seko, and I. Tanaka, Phys. Rev. B 85, 033203 (2012)
- [4] B. Huang, S. Y. Chen, H.-X. Deng, L.-W. Wang, M. A. Contreras, R. Noufi, and S.-H. Wei, IEEE J. Photovoltaics 4, 477 (2014)

## Fractional Kinetics in Photocatalytic Decomposition Process

WANG Chunlei

*School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan  
250100, P. R. China*

**Abstract** Fractional differential equation for photocatalytic decomposition process is proposed, with its solution as single parameter Mittag-Leffler function. Two groups experimental data are used to fit with the solution, one is from photo-degradation of methyl orange using  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nano-belts, and another is of Rhodamine B using tungsten trioxide assemblies of particle and fragments. The fitting results show that the derivative of the concentration with respect to time is not exactly first order, but a fractional order. That means that the photocatalytic decomposition process is of fractional first order chemical reaction. Therefore a characteristic time for photocatalytic decomposition process can be well defined in this sense. Possible relation between the order of derivative and the micro-structure is briefly addressed.

- [1] X Lin, Q F Guan, T T Liu, Y Zhang and C J Zou, Controllable Synthesis and Photocatalytic Activity of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  Particles with Different Morphologies, *Acta Phys. Chim. Sin* 2013, 29, 411-417
- [2] J G Yu and L F Qi, Template-free fabrication of hierarchically flower-like tungsten trioxide assemblies with enhanced visible-light-driven photocatalytic activity, *J. Hazardous Materials*, 169m (2009) 221-227

## First-Principles Structure Prediction for Nanowires Encapsulated in Carbon Nanotubes

Jamie Wynn<sup>a</sup>, Paulo Medeiros<sup>a</sup>, Jeremy Sloan<sup>b</sup>, David Quigley<sup>b</sup>, Andrew Morris<sup>a</sup>

<sup>a</sup> *Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, UK.*

<sup>b</sup> *Department of Physics, University of Warwick, UK.*

jw870@cam.ac.uk

The encapsulation of materials within single-walled carbon nanotubes affects their behaviour and structure dramatically relative to the bulk. In many cases, such encapsulated nanowires (ENWs) even exhibit long-range ordered one-dimensional phases that do not -- or cannot -- exist in three dimensions. Moreover, many are of considerable technological interest, especially in the case of the so-called nano phase-change materials, whose properties make them potential candidates for next-generation information storage technologies.

The *ab initio* random structure search (AIRSS) method has proved a powerful and effective tool in the prediction of both bulk materials [1] and defect complexes [2]. We have extended AIRSS for the prediction of the quasi-1D crystals formed by materials encapsulated within nanotubes, allowing us to perform the first truly *ab-initio* quantitative structure prediction calculations for ENWs.

To illustrate the capabilities of the method, we present results from AIRSS searches on encapsulated nanowires of germanium telluride. Our theoretical methodology allows us to map out the series of phase transitions occurring as the radius of the encapsulating nanotube is varied.

### References:

- [1] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. 97, 045504 (2006).
- [2] A. J. Morris, C. J. Pickard and R. J. Needs, Phys. Rev. B. 78, 184102 (2008).

## High-Throughput Computational Design of Advanced Functional Materials: Topological Insulators and Two-Dimensional Electron Gas Systems

Kesong Yang\*

*Department of NanoEngineering, University of California San Diego, CA 92093, USA*

*Email: [kesong@ucsd.edu](mailto:kesong@ucsd.edu), web site: <http://materials.ucsd.edu>*

As a rapidly growing area of materials science, high-throughput (HT) computational materials design is playing a crucial role in accelerating the discovery and development of novel functional materials. In this presentation, I will first introduce the strategy of HT computational materials design, and take the HT discovery of topological insulators (TIs) as a practical example to show the usage of such an approach. Topological insulators are one of the most studied classes of novel materials because of their great potential for applications ranging from spintronics to quantum computers. Here I will show that, by defining a reliable and accessible descriptor, which represents the topological robustness or feasibility of the candidate, and by searching the quantum materials repository [aflowlib.org](http://aflowlib.org), we have automatically discovered 28 TIs (some of them already known) in five different symmetry families.[1] Next, I will talk about our recent research work on the HT computational design of the perovskite-based two-dimensional electron gas (2DEG) systems. The 2DEG formed on the perovskite oxide heterostructure (HS) has potential applications in next-generation nanoelectronic devices. In order to achieve practical implementation of the 2DEG in the device design, desired physical properties such as high charge carrier density and mobility are necessary. Here I show that, using the same strategy with the HT discovery of TIs, by introducing a series of combinatorial descriptors, we have successfully identified a series of candidate 2DEG systems based on the perovskite oxides.[2] This work provides another exemplar of applying HT computational design approach for the discovery of advanced functional materials.

Reference to a journal publication:

1. K. Yang, W. Setyawan, S. Wang, M. Buongiorno Nardelli, and S. Curtarolo, A search model for topological insulators with high-throughput robustness descriptors. *Nat. Mater.*, **11**, 614-619 (2012).
2. K. Yang, S. Nazir, M. Behtash, and J. Cheng, High-throughput screening of two-dimensional electron gas systems based on perovskite oxide heterostructures. *submitted*, (2015).



## Direct evidence of stress-relaxed omega phase transformation accompanying deformation twinning in the metastable Ti-24Nb-4Zr-8Sn alloy

Y. Yang<sup>a,c</sup>, P. Castany<sup>a</sup>, M. Cornen<sup>a</sup>, Y.L. Hao<sup>b</sup>, L.Y. Sheng<sup>c</sup>, T. Gloriant<sup>a\*</sup>

<sup>a</sup>Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, INSA Rennes, 20 avenue des Buttes de Coësmes, 35708 Rennes cedex 07, France

<sup>b</sup>Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenhe District, 110016, Shenyang, China

<sup>c</sup>Shenzhen Institute, Peking University, W803, IER building, Gaoxin south seven street, 518057, Shenzhen, China

\*Corresponding author: thierry.gloriant@insa-rennes.fr

The  $\beta$  metastable Ti-based alloys are potential new materials for biomedical applications such as smart devices (stents, orthodontic wires, catheters, osteosynthesis staples...) due to their low modulus, high strength and superior biocompatibility. Depending on chemical composition and applied temperature, these alloys can be superelastic exhibiting a large recoverable strain due to a stress-induced martensitic transformation, or shape memory effect while a large residual deformation strain can be recovered after subsequent heating. At large deformation strain, this class of alloys is also frequently subject to mechanical twinning in order to accommodate the plastic deformation.

In this present case, a superelastic single crystal ( $\langle 110 \rangle // RD$ ) with composition of Ti-24Nb-4Zr-8Sn (wt.%) was used to investigate its plastic deformation mechanisms. TEM observations in Fig. 1 showed a typical deformation band consisting of primary twin with internal secondary twins as well as interfacial omega phase. Special attention was focused on the interfacial omega phase via the technique of *in situ* synchrotron X-ray diffraction (SXRD) in Fig. 2. Results reveal that two diffraction peaks indexed to be omega phase only appear under unloading condition at plastic deformation stage, while these omega-peaks disappear totally under the corresponding loading condition. These results clearly provide the direct evidence that interfacial omega phase at twinning boundaries was a stress-relaxed phase transformation and plays a role to accommodate the lattice distortion.

### References:

- [1] Hao Y.L., Li S.J., Sun B.B., Sui M.L., Yang R., Ductile titanium alloy with low Poisson's ratio, *Physical Review Letter*, 98(2007)216405.
- [2] Niinomi M., Recent research and development in titanium alloys for biomedical applications and healthcare. *Science and Technology of Advanced Materials*, 4(2003)445-454.
- [3] Geetha M., Singh A.K., Asokamani R., Gogia A.K., Ti based biomaterials, the ultimate choice for orthopaedic implants-A review. *Progress in Materials Science*, 54(2009)397-425.
- [4] P. Castany, A. Ramarolahy, F. Prima, P. Laheurte, C. Curfs, T. Gloriant, In situ synchrotron X-ray diffraction study of the martensitic transformation in superelastic Ti-24Nb-0.5N and Ti-24Nb-0.5O alloys, *Acta Materialia*, 88(2015)102-111.
- [5] Yang Y., Castany P., Cornen M., Prima F., Li S.J., Hao Y.L., Gloriant T., Characterization of the martensitic transformation in the superelastic Ti-24Nb-4Zr-8Sn alloy by in situ synchrotron X-ray diffraction and dynamic mechanical analysis, *Acta Materialia*, 88(2015) 25-33.

[6]Yang Y., Castany P., Cornen M., Thibon I., Prima F., Gloriant T., Texture investigation of the superelastic Ti-24Nb-4Zr-8Sn alloy, Journal of Alloys and Compounds, 591(2014) 85-90.

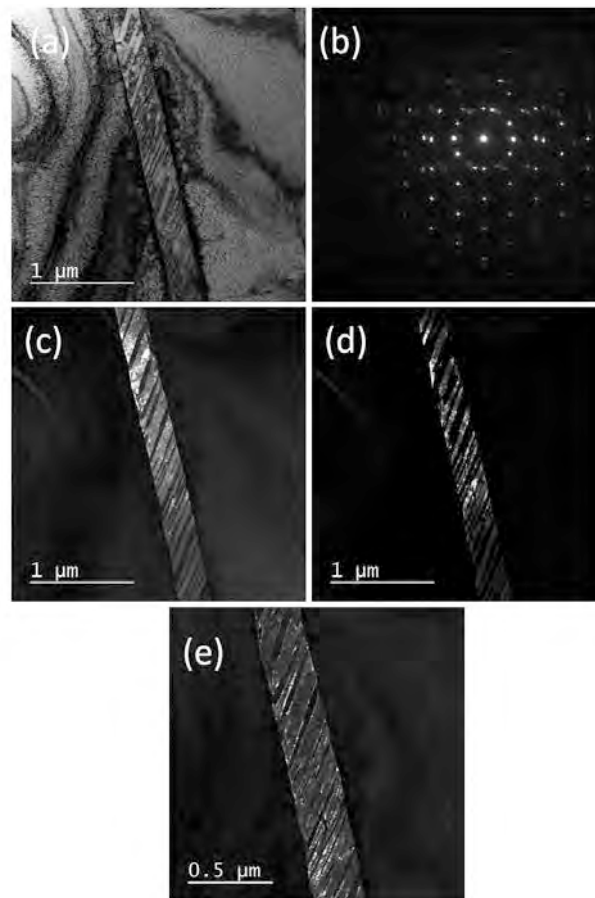


Fig. 1: hierarchy twinning morphology: (1) bright field image, (2) select area diffraction pattern, (3) dark field image of primary twin, (4) dark field image of secondary twin and (4) dark field image of interfacial omega phase.

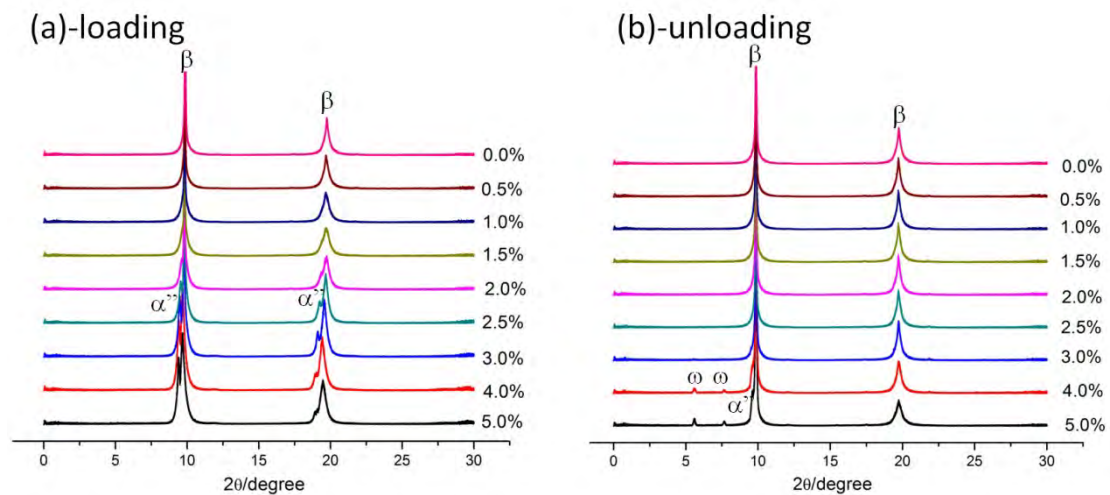


Fig. 2: In situ synchrotron X-ray diffraction profiles for single crystal Ti-24Nb-4Zr-8Sn under (a) loading conditions and (b) unloading conditions

## Synthesis and Characterization of Double Layer Perovskite NaLaCoWO<sub>6</sub> for Multiferroic Effect

Peng ZUO<sup>a, b</sup>, Céline DARIE<sup>a, b</sup>, Claire V. COLIN<sup>a, b</sup>, Holger KLEIN<sup>a, b</sup>  
<sup>a</sup>*Université Grenoble Alpes, Institut NEEL, F-38042 Grenoble, France*  
<sup>b</sup>*CNRS, Institut NEEL, F-38042 Grenoble, France*

email address of the presenting author: peng.zuo@neel.cnrs.fr

Multiferroics are materials where more than one of ferroelectric, ferromagnetic, ferrotoroidic, and ferroelastic properties are united in a single phase. [1] Magnetoelectric multiferroics attract intensive research interests, especially in the last 20 years, due to their promising applications like multiple states memory. However, in the known magnetoelectric multiferroics either the magnetoelectric coupling is weak [2] or the order transition takes place at low temperature and only with a small electric polarization [3]. They are therefore not interesting for real applications.

In this work, we pursue a different route searching for materials which have the potential to realize strong magnetoelectric coupling at high temperature. Double layer perovskites are such candidates since they could combine hybrid improper ferroelectricity and superexchange dominated magnetic ordering. Even though perovskites are one of the most interesting functional materials families for their diverse physical properties, double layer perovskites have been rather less explored. In this work we concentrate on one double layer perovskite, namely NaLaCoWO<sub>6</sub>.

The powder sample of NaLaCoWO<sub>6</sub> was synthesized by solid state reaction at 925 °C. Energy dispersive X-ray spectroscopy confirmed the right composition NaLaCoWO<sub>6</sub>. X-ray and neutron powder diffraction were combined with electron diffraction to investigate the structure and its temperature dependence. A structural phase transition was observed close to room temperature, probably between the space group  $P2_1$  and  $P2_1/m$ .

The magnetic ordering of Co<sup>2+</sup> is antiferromagnetic below its Néel temperature which is determined as 13 K by both magnetic and heat capacity measurements. The magnetic structure determined from NPD at 2 K can be indexed by the propagation vector (0.5 0 0.5). Dielectric measurements from 2.5 K to 330 K with or without magnetic field did not show any (anti)ferroelectric feature.

### References:

- [1] H. Schmid, *Ferroelectrics* 162 (1994) 317–338.
- [2] B. B. Van Aken, T. T. M. Palstra, *Phys. Rev. B* 69 (2004) 134113.
- [3] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, *Nature* 426 (2003) 55-58.



# List of Participants

NAME	First name	Affiliation	City	Country	Email
ABOUSSATAR	Mohamed	Institut de Chimie de Clermont Ferrand	Clermont Ferrand	France	med_abau@yahoo.fr
ALBINO	Marjorie	Institut des Molécules et Matériaux du Mans	Le Mans	France	marjorie.albino@univ-lemans.fr
AREVALO LOPEZ	Angel M	University of Edinburgh	Edinburgh	UK	aalopez@staffmail.ed.ac.uk
BADDOUR-HADJEAN	Rita	ICMPE-CNRS	Thiais	France	baddour@icmpe.cnrs.fr
BAIBIAO	Huang	Shandong University	Jinan	China	bbhuang@sdu.edu.cn
BARRIER	Nicolas	Laboratoire CRISMAT	Caen	France	nicolas.barrier@ensicaen.fr
BEHRH	Gaganpreet	Institut des Matériaux – Université de Nantes	Nantes	France	gaganpreet.behr@cnrs-imn.fr
BOTTI	Silvana	University of Jena	Jena	Germany	silvana.botti@uni-jena.de
BOUCHER	Florent	Institut des Matériaux – Université de Nantes	Nantes	France	florent.boucher@cnrs-imn.fr
BOUËSSEL DU BOURG	Lila	Institut des Sciences Chimiques de Rennes	Rennes	France	lila.bouesseldubourg@univ-rennes1.fr
BRIEN	Valérie	CNRS IJL	Vandœuvre lès Nancy	France	valerie.brien@univ-lorraine.fr
BRIERE	Benjamin	UFR des Sciences de Tours – Labo. GREMAN	Tours	France	benjamin.briere@etu.univ-tours.fr
BRUYER	Emilie	ISCR - CNRS - Université de Rennes 1	Rennes	France	emilie.bruyer@univ-rennes1.fr
BUSSMANN-HOLDER	Annette	Max-Planck-Institute for Solid State Research	Stuttgart	Germany	a.bussmann-holder@fkf.mpg.de
CARIO	Laurent	Institut des Matériaux – Université de Nantes	Nantes	France	laurent.cario@cnrs-imn.fr
CARLIER	Dany	ICMCB-CNRS	Pessac	France	dany.carlier@icmcb.cnrs.fr
CARP	Oana	Institute Physical Chemistry, Romanian Acad.	Bucharest	Romania	ocarp@icf.ro
CHEVIRE	François	ISCR - CNRS - Université de Rennes 1	Rennes	France	francois.chevire@univ-rennes1.fr
CODY	Jason	Lake Forest College	Lake Forest, IL	USA	cody@lakeforest.edu

CORRAZE	Benoit	Institut des Matériaux – Université de Nantes	Nantes	France	benoit.corraze@cnrs-immn.fr
COUTINHO	José	University of Aveiro	Aveiro	Portugal	jose.coutinho@ua.pt
DAI	Ying	Shandong University	jinan	China	daiy60@sdu.edu.cn
DALECKY	Lauren	Lake Forest College	Robins	USA	daleckylim@mx.lakeforest.edu
DANTELE	Géraldine	CNRS - Institut Néel	38042	France	geraldine.dantelle@neel.cnrs.fr
DARIE	Céline	Institut Néel CNRS UGA	Grenoble	France	celine.darie@neel.cnrs.fr
DENG	Shuiquan	Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences	Fuzhou	China	sdeng@fjirsm.ac.cn
DENIARD	Philippe	Institut des Matériaux – Université de Nantes	Nantes	France	philippe.deniard@cnrs-immn.fr
DRISS	Dalel	Institut des Matériaux – Université de Nantes	Nantes	France	dalel.driss@cnrs-immn.fr
DRONSKOWSKI	Richard	RWTH Aachen University	Aachen	Germany	drons@HAL9000.ac.rwth-aachen.de
EVEN	Jacky	INSA-Rennes	Rennes	France	jacky.even@insa-rennes.fr
FAULQUES	Eric	Institut des Matériaux – Université de Nantes	Nantes	France	eric.faulques@cnrs-immn.fr
FELSER	Claudia	MPI Dresden	Dresden	Germany	claudia.felsler@cpfs.mpg.de
FUERTES	Amparo	Institut de Ciència de Materials de Barcelona	Barcelona	Spain	amparo@icmab.es
GAUDIN	Etienne	ICMCB, CNRS, Université de Bordeaux	Pessac	France	etienne.gaudin@icmcb.cnrs.fr
GAUTIER	Romain	Institut des Matériaux – Université de Nantes	Nantes	France	romain.gautier@cnrs-immn.fr
GENESTE	Gregory	CEA DAM	Arpajon	France	gregory.geneste@cea.fr
GONZE	Xavier	Université Catholique de Louvain	Louvain-La-Neuve	Belgium	xavier.gonze@uclouvain.be
HAYWARD	Michael	University of Oxford	Oxford	UK	michael.hayward@chem.ox.ac.uk
HOANG	Khang	North Dakota State University	Fargo	USA	khang.hoang@ndsu.edu

ISAEVA	Anna	Dresden University of Technology	Dresden	Germany	anna.isaeva@tu-dresden.de
ISOBE	Masahiko	Max Planck Institute for Solid State Research	Stuttgart	Germany	m.isobe@fkf.mpg.de
JANOD	Etienne	Institut des Matériaux – Université de Nantes	Nantes	France	etienne.janod@cnrs-imn.fr
JI	Hyo Seok	POSTECH	Pohang	South Korea	abcdef@postech.ac.kr
JIANG	Tengfei	Institut des Matériaux – Université de Nantes	Nantes	France	tengfei.jiang@cnrs-imn.fr
JOBIC	Stéphane	Institut des Matériaux – Université de Nantes	Nantes	France	stephane.jobic@cnrs-imn.fr
KASSEM	Mohamed	Kyoto University	Kyoto	Japan	m.akareem11@gmail.com
KIM	Young-Il	Yeungnam University	Gyeongsan	South Korea	yikim@ynu.ac.kr
KIM	Young Jin	Kyonggi University	Suwon	South Korea	yjkim@kgu.ac.kr
KIM	Sujee	POSTECH	Pohang	South Korea	kim77810@postech.ac.kr
KOEHLER	Juergen	Max-Planck-Institute	Stuttgart	France	j.koehler@fkf.mpg.de
KULEBYAKIN	Alexey	General Physics Institute of the Russian Academy of Sciences (GPI RAS)	Moscow	Russia	kulebyakin@lst.gpi.ru
LACHGAR	Abdou	Wake Forest University	Winston Salem	USA	lachgar@wfu.edu
LAFARGUE-DIT-HAURET	William	ISCR - CNRS - Université de Rennes 1	Rennes	France	william.lafargue-dit-hauret@univ-rennes1.fr
LATOUCHE	Camille	Institut des Matériaux – Université de Nantes	Nantes	France	camille.latouche@univ-nantes.fr
LEE	Changhoon	Pohang University of Science and Technology	Pohang. Gyeongbuk.	South Korea	chlee0887@postech.ac.kr
LEMMENS	Peter	TU Braunschweig, Inst. Condensed Matter Physics	Braunschweig	Germany	p.lemmens@tu-bs.de
LIGHTFOOT	Phillip	University of St Andrews	St Andrews	UK	pl@st-andrews.ac.uk
LOTSCH	Bettina	MPI Stuttgart	Stuttgart	Germany	b.lotsch@fkf.mpg.de
LTAIEF	Wahida	Institut de chimie de Clermont Ferrand	Aubière	France	Itaief.wahida@yahoo.fr

LUDERS	Ulrike	CRISMAT	Caen	France	ulrike.luders@ensicaen.fr
MARIE	Xavier	INSA-Toulouse	Toulouse	France	marie@insa-toulouse.fr
MEKEZE MONTHE	Aubin	Laboratoire de thermocinétique de Nantes	Nantes	France	aubin.mekeze-monthe@univ-nantes.fr
MENTRE	Olivier	UCCS UMR CNRS 8181	Villeneuve d'Ascq	France	olivier.mentre@ensc-lille.fr
MÖLLER	Angela	JGU Mainz	Mainz	Germany	angela.moeller@uni-mainz.de
NAKAMURA	Hiroyuki	Kyoto University	Kyoto	Japan	nakamura.hiroyuki.2w@kyoto-u.ac.jp
ODOBEL	Fabrice	Université de Nantes	Nantes	France	Fabrice.Odobel@univ-nantes.fr
OECKLER	Oliver	Universität Leipzig	Leipzig	Germany	oliver.oeckler@gmx.de
ONDRACKA	Pavel	Masaryk University	Brno	Czech Republic	pavel.ondracka@email.cz
PATUREAU	Pascaline	Institut des Matériaux – Université de Nantes	Nantes	France	pascaline.patureau@gmail.com
PEAN	Emmanuel	Institut des Matériaux – Université de Nantes	Nantes	France	
PICOZZI	Silvia	Consiglio Nazionale delle Ricerche	L'Aquila	Italy	silvia.picozzi@spin.cnr.it
POLTEAU	Baptiste	ISCR - Université de Rennes 1	Rennes	France	baptiste.polteau@univ-rennes1.fr
RASIM	Karsten	Max-Planck-Institut fuer Chemische Physik fester Stoffe	Dresden	Germany	Karsten.Rasim@cpfs.mpg.de
RENAUD	Adèle	ISCR - CNRS - Université de Rennes 1	Rennes	France	adele.renaud@univ-rennes1.fr
RIFFET	Vanessa	Institut Photovoltaïque d'Ile De France	Antony	France	vanessa.riffet@ipvf.fr
ROCQUEFELTE	Xavier	ISCR - CNRS - Université de Rennes 1	Rennes	France	xavier.rocquefelte@univ-rennes1.fr
SCHOLZ	Tanja	Institute of Inorganic Chemistry, RWTH Aachen University	Aachen	Germany	tanja.scholz@ac.rwth-aachen.de
SHANG	Congcong	Institut des Matériaux – Université de Nantes	Nantes	France	congcong.shang@cnrs-immn.fr
SHATRUK	Michael	Florida State University	Tallahassee, FL	USA	shatruk@chem.fsu.edu



SÖHNEL	Tilo	University of Auckland	Auckland	New Zealand	t.soehnel@auckland.ac.nz
SUN	Qilong	Shandong University	Jinan	China	hsin.p.soh@hotmail.com
TAKAGI	Hidenori	MPI Stuttgart	Stuttgart	Germany	h.takagi@fkf.mpg.de
TAPHUOC	Vinh	UFR des Sciences de Tours – Labo. GREMAN	Tours	France	taphuoc@univ-tours.fr
TASSEL	Cédric	Kyoto University	Kyoto	Japan	cedric@scl.kyoto-u.ac.jp
THONDIYANOR PISHARAM	Sumangala	CIRIMAT, Université Paul Sabatier	Toulouse	France	sumampoornima@gmail.com
TSOULKA	Polyxeni	Institut des Matériaux – Université de Nantes	Nantes	France	polyxeni.tsoulka@cnrns-imn.fr
UEDA	Kazushige	Kyushu Institute of Technology	Kitakyushu	Japan	kueda@che.kyutech.ac.jp
VALENTI	Roser	Goethe Universität	Ffrankfurt	Germany	valenti@itp.uni-frankfurt.de
VALLVERDU	Germain	UPPA - IPREM	Pau	France	germain.vallverdu@univ-pau.fr
VASILIEV	Alexander	Moscow State University	Moscow	Russia	anas2000@yahoo.com
VASYLENKO	Andrij	University of Warwick	Coventry	UK	a.vasylenko@warwick.ac.uk
VILLESUZANNE	Antoine	ICMCB	Bordeaux	France	Antoine.Villesuzanne@icmcb.cnrs.fr
VOLKOVA	Olga	National University of Science and Technology	moscow	Russia	os.volkova@yahoo.com
WANG	Peng	Shandong University	Jinan	China	pengwangicm@sdu.edu.cn
WANG	Chunlei	Shandong University	Jinan	China	wangcl@sdu.edu.cn
WEI	Wei	Shandong University	Jinan	China	weiw@sdu.edu.cn
WENJIAO	Yao	School of Chemistry, University of St. Andrews	Fife	UK	yaowenjiao09@mails.ucas.ac.cn
WHANGBO	Myung-Hwan	NCSU	Raleigh	USA	whangbo@ncsu.edu
WYNN	Jamie	Cavendish Lab., University of Cambridge	Cambridge	UK	jw870@cam.ac.uk

YAMAURA	Kazunari	National Institute for Materials Science	Tsukuba	Japan	yamaura.kazunari@nims.go.jp
YANG	Kesong	University of California San Diego	La Jolla	USA	kesong@ucsd.edu
YANG	Yang	Shenzhen Institute, Peking University	Shenzhen	China	yy@alum.imr.ac.cn
YUANYUAN	Liu	Shandong University	Jinan	France	yyliu@sdu.edu.cn
ZEYAN	Wang	Shandong University	Jinan	China	wangzeyan@sdu.edu.cn
ZUO	Peng	Institut Néel CNRS	Grenoble	France	peng.zuo@neel.cnrs.fr