PROGRAMUL DE COOPERARE ELVEȚIANO-ROMÂN
SWISS-ROMANIAN COOPERATION PROGRAMME

Small band-gap nanostructured perovskite materials for photovoltaic and photocatalytic hydrogen generation applications

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Thomas Lippert

Paul Scherrer Institut, Materials Group, Switzerland

Maria Dinescu

National Institute for Lasers, Plasma and Radiation Physics, Photonic Processing of Advanced Materials Group, Romania

PROIECT CO-FINANȚAT PRINTR-UN GRANT DIN PARTEA ELVEȚIEI PRIN INTERMEDIUL CONTRIBUȚIEI ELVEȚIENE PENTRU UNIUNEA EUROPEANĂ EXTINSĂ

The Teams

Markus Pichler,
the PhD student who
did most of the work
in CH

Daniele Pergolesi,
the direct supervisor
of Markus

XXX

Ruxandra Birjega,
researcher

Marius Dumitru,
PhD student

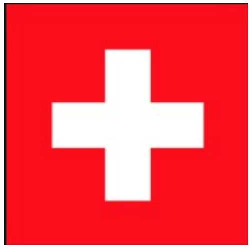
Nicu Doinel Scarisoreanu,
researcher

Maria Dinescu,
Romanian team
leader

Stefan Antohe,
Professor (PV)

The Project-Aim

The aim of this project was to explore the potential of combined photovoltaic and photocatalytic properties of perovskite-based materials which exhibit a small band gap. For these 2 different properties 2 different material classes have been selected:



Photocatalytic oxynitrides, such as $LaTiO_2N$, that can be used for water splitting using visible light.

Ferroelectric materials, such as $BiFeO_3$ (BFO), which exhibit a photovoltaic effect.

The ferroelectric materials are also exhibiting photocatalytic properties.

The Project-Approach

Each group will prepare one of the material classes in the form of thin films using the same deposition technique, i.e. pulsed laser deposition. The thin films are then characterized by standard methods, such as XRD, in each group, while techniques, which are only available in one group will be used also for the samples of the other group.

Deposition of oxynitrides, characterization by Rutherford backscattering (RBS) and ERDA (elastic recoil detection analysis). Building a setup for photocatalytic or photoelectrocatalytic characterization. Samples from both groups.

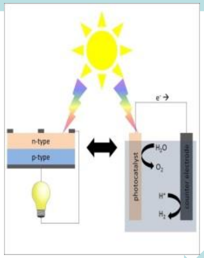
Deposition of ferroelectric materials, based on $BiFeO_3$ and cation doped $BiFeO_3$, characterization by XRD, spectroscopic ellipsometry and AFM. Photovoltaic characterization. Additionally, new oxynitride materials, such as $YGeO_2N$, which have been predicted to show photovoltaic and photocatalytic properties.

Scheme of Cooperation

Idea: new materials or new material's functionalities for sustainable energy harvesting

INFLPR, PPAM Group expertise:

- Radiofrequency assisted Pulsed Laser Deposition of thin films
- Properties characterization of thin films: optical, electrical, structural, stoichiometry.



PSI, Materials Group expertise:

- Pulsed Reactive Crossed-Beam Laser Ablation (PRCLA) for oxynitrides and nitrides.
- Photoelectrochemical characterization of thin films water-splitting efficiency.

New project: **Small band-gap nanostructured perovskite materials for photovoltaic and photo-catalytic hydrogen generation applications**

INFLPR, PPAM Group tasks in the project:

- Cation doped $BiFeO_3$, YGeON thin films for enhanced photovoltaic and photocatalytic properties.
- Tailoring the BFO thin films properties and integration into heterostructures for photo-voltaic and photocatalytic tests.

$LaTiO_{3-x}N_x$ to INFLPR for optical analysis.

Y-doped $BiFeO_3$ samples delivery for PEC measurements performed at PSI.
Thin film composition at PSI.

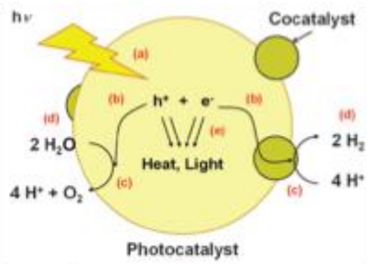
PSI, Materials Group tasks in the project:

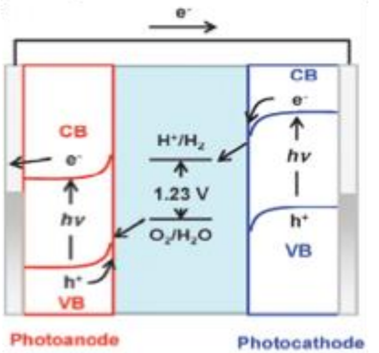
- $LaTiO_{3-x}N_x$ deposited with various N-content and test of photocatalytic photovoltaic activity.
- Analysis of the photo-electrochemical (water splitting) properties of the thin films.

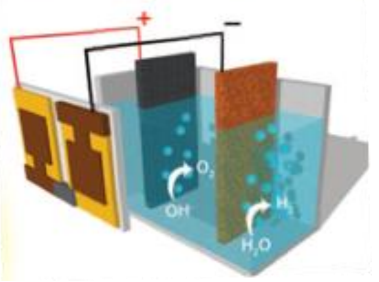
Oxynitrides for Photo(electro)catalysis

For solar driven water splitting:

- Photocatalysis: particulate samples-with co-catalysator.
- Photoelectrochemical (PEC), with electrodes (and co-catalysator).
- Photovoltaic (PV), solar cell + electrocatalyst.







Reactions:

- $4\ h^+ + H_2O \rightarrow O_2 + 4\ H^+$
- $2e^- + 2H^+ \rightarrow H_2$

1.23 eV per electron, 237 kJ/mol per H_2O molecular

O_2 evolution is the rate determining step during water splitting since it needs more charge carriers and has slower kinectic compared to H_2 evolution ➜ Photoanode: n-semiconductor: minority holes to the surface.

Fujishima, Honda, Nature, 1972, 238, 37-38
Hisatomi, *et al.,* Chem. Soc. Rev., 2014, 43, 7520—753
Graetzel, Nature, 2001, 414, 338-344
Graetzel, Science, 2014, 345, 1593-1596
Moniz, *et al.,* Energy Environ. Sci., 2015, 8, 731–759

Oxynitrides for Photo(electro)catalysis

- Most common photocatalyst-TiO_2: a band gap of 3.2 eV, only excited by UV light (3% of solar light), while visible light accounts for 44% ➜ visible-light responsive catalysts are needed.

- Requirements for photoelectrodes:
  1. Bandgap in the visible light range.
  2. Band edges straddling O_2 and H_2 evolution potentials.
  3. Reasonable chemical and structural stability.
  4. Appropriate surface reaction kinetics.
  5. High charge separation and mobility to avoid recombination.

- Oxynitride materials:
  - Tunable band gap in visible range due to N substitution of O.
  - Several unknown or very few studied promising candidates.

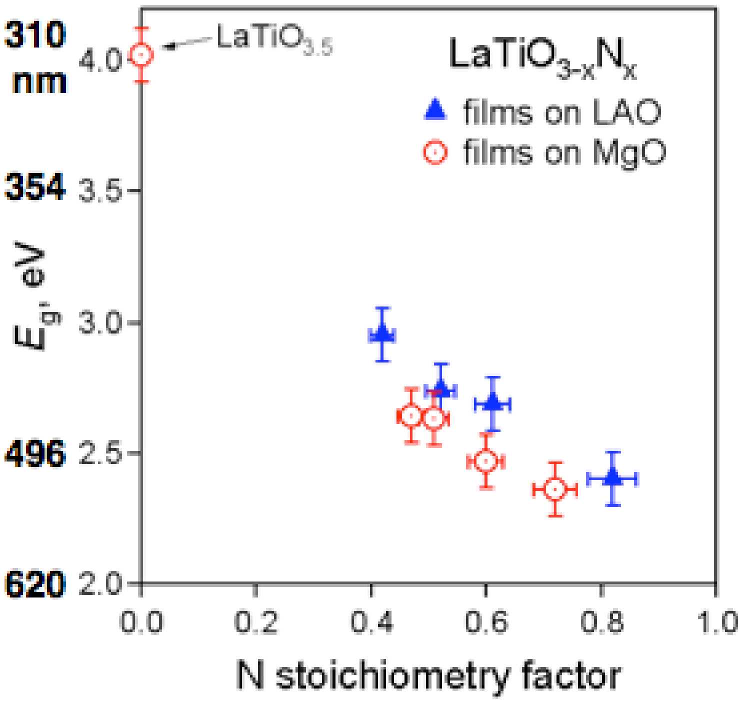
Moniz, *et al.,* Energy Environ. Sci., 2015, 8, 731–759; Xie, *et al.,* J. Am. Ceram. Soc., 2013, 96, 665–687

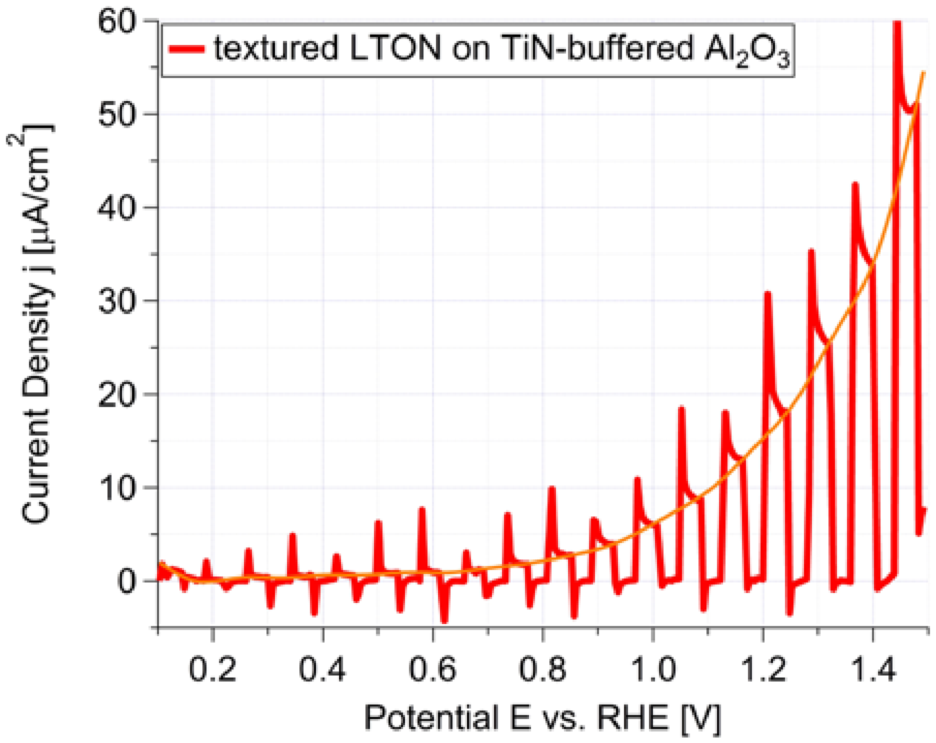
Oxynitrides Thin Films for Photo(electro)catalysis

- **Goals:**
  1. High quality crystals as model systems,
  2. With well defined surfaces and low defect number.
  3. Control over the crystallographic orientation.
  4. Compare to modeling.
- **Why the thin film approach**
  - "In any case, there are certainly some problems in the photocatalytic matrix. We are at the cusp not only of finding nitridation or post-treatment conditions which fulfill all the requirements (i.e., to reduce the defect density, enhance the crystallinity, and inhibit decomposition, at the same time), but also to target more aggressively a direct preparation method to obtain high-quality crystals of (oxy)nitrides"

    Y. Moriya, T. Takata, K. Domen, Coordination Chemistry Reviews 257, 19557 (2013)

Main Results: Oxynitrides





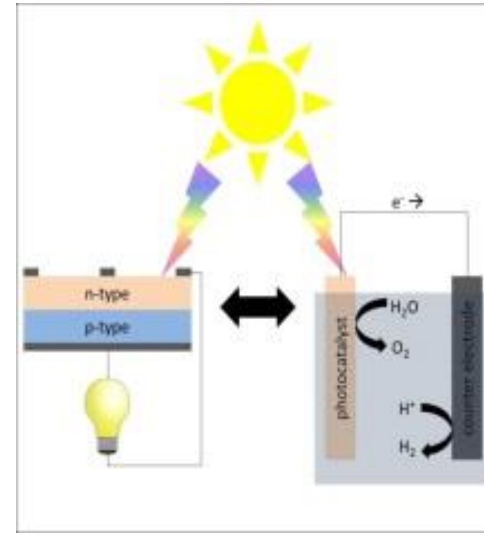
Shift of band gap: visible light will be absorbed

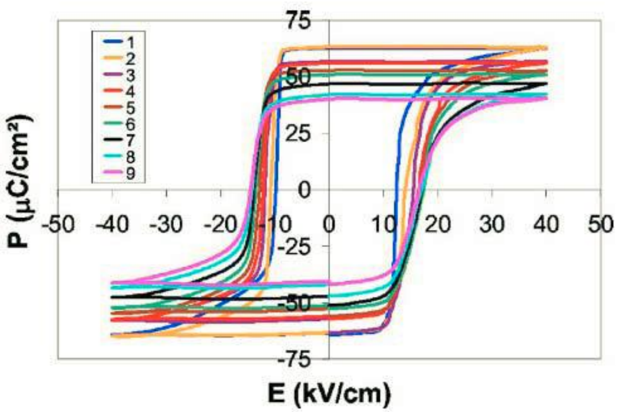
Photocurrent is observed: active for photoelectrocatalysis

Cation doped $BiFeO_3$ thin films

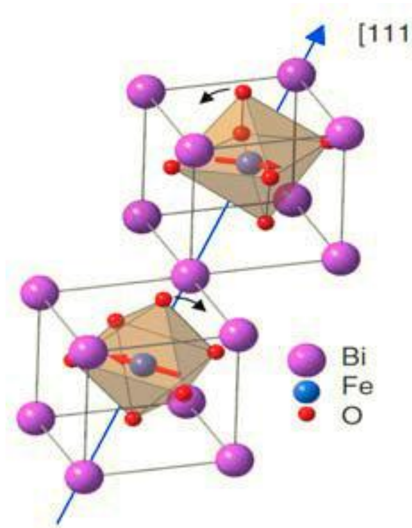
$BiFeO_3$ (BFO) summary:

- Rhombohedrally distorted ferroelectric perovskite**, R3c.**
- Antiferromagnetic Néel temperature of T_N=643° K.
- Ferroelectric Curie temperature of T_C=1103° K.
- The R3c symmetry permits the development of spontaneous polarization.
- (Ps) along the pseudocubic [111] direction.
- High remnant polarization in thin films form: 90 μ C/cm^2.

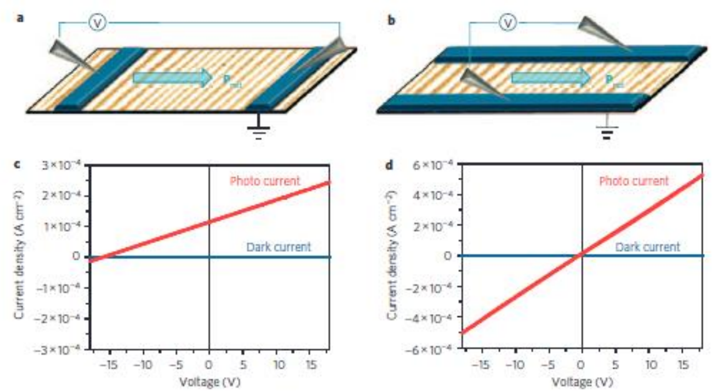




P-E hysteresis loops obtained from BiFeO3 /SrRuO3/SrTiO3 thin films
after: J. B. Neaton et al., Physical Review B Vol. 71, 014113 (2005).



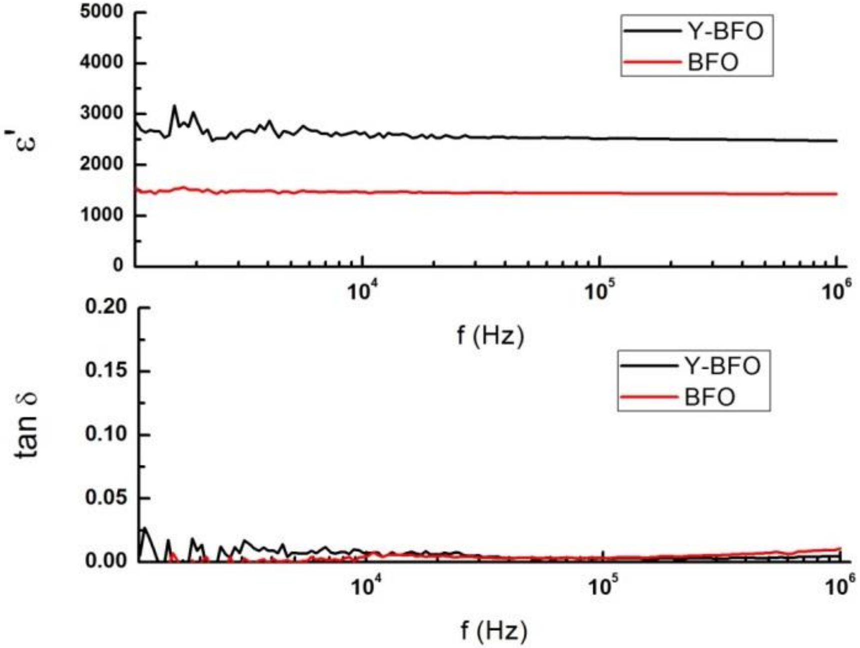
-bulk BFO crystal structure
after: Axel Lubk, S. Gemming, and N. A. Spaldin, Phys. Rev. B Vol. 80, 104110 (2009).



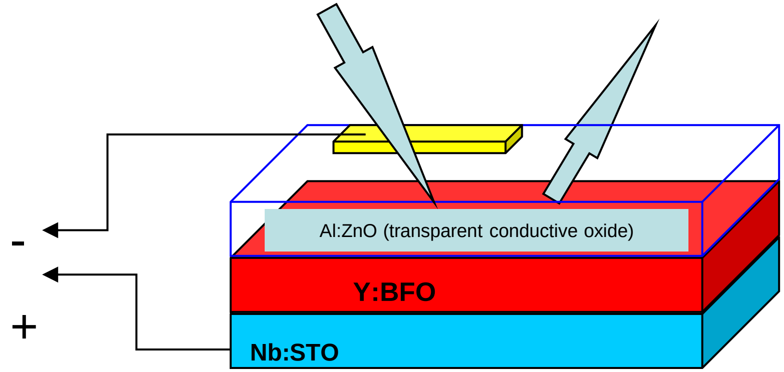
High photoinduced voltage- over 5-times the band gap of BFO
after S.Y.Yang et al, Nature Nanotechnology, 5, 2010

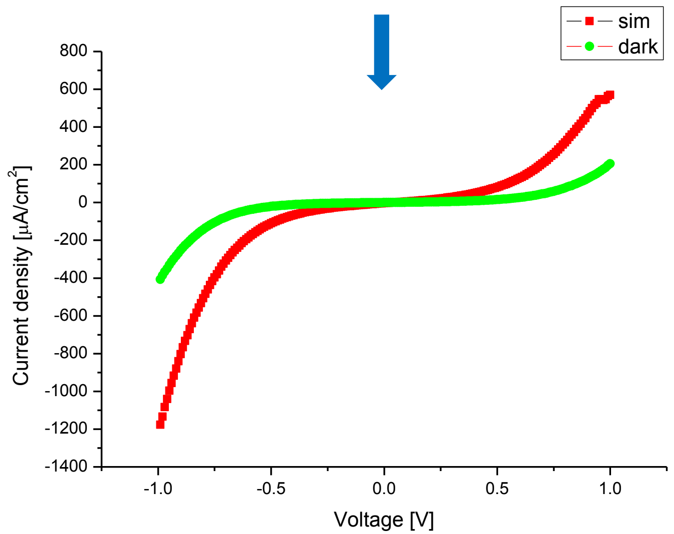
Main results: Y doped BFO thin films with-dielectric and photovoltaic

- Huge improvements on the dielectric response (low losses and high dielectric constant values) have been obtained for Y-doped BFO thin films



- Integration of Y doped BFO thin films in photovoltaic test hetero-structures.





Clear photovoltaic response

The Cooperation

What was the background of this cooperation? Why did we want to start this project?

- The groups were/are already in contact for more than 15 years with several previous projects (very good experience, over 20 joined paper).
- We had already a PhD student from the Romanian group in Switzerland (very good experience).
- Several researcher of the Romanian group visited Switzerland for experiments within the previous projects (very good experience).
- The equipment in the Romanian group is state of the art and complementary to our setups (I was several times visiting the laboratories and vice versa).
- The level of knowledge in the Romanian group is very high and complementary to us in many areas (in addition to common).
- We had a project idea, which would have the highest success rate if we would work on it together ➔ the cooperation program was the perfect tool.

The project was and is based on a true cooperation on equal basis.

The Cooperation

From our previous project we had already established a *modus operandi* for our project:

- Regular scheduled visits and exchange of samples and researcher in Switzerland and Romania (see later).
- Meet additionally at conferences of common interest, mainly the E- MRS Spring and Fall Meeting (yearly) and COLA (biannual).
- Direct communication between the involved researchers/PhD students (not necessarily through the project leaders). This type of contact has been established during the visits and at conferences.
- Regular critical discussions about the results and status of project (and this works easier if there is a well established contact = "trust").
- Agreement that we meet in Switzerland to prepare the scientific as well as financial reports together (with involvement of the PSI responsible for the finances within the project).
- Agreement that joint publications will be the one of our final goals (2 are in preparation).

The Cooperation-Examples

Planned cooperation:

- Photoelectrochemical (PEC) measurements of the $BiFeO_3$ (BFO) and doped BFO films produced in Romania. An example of the results is shown on the next slide (VERY PROMISING).

Not planned:

- During the project the following question came up for our oxynitride films: do they have a direct or indirect bandgap? Approach: spectroscopic ellipsometry in Romania-strong indication for indirect bandgap. For final confirmation experiments at the synchrotron are planned (SE was instrumental to get beam time).

Planned cooperation:

- Deposition of various BFO and doped BFO films on conducting substrates (required for PEC).
- Deposition of new materials.

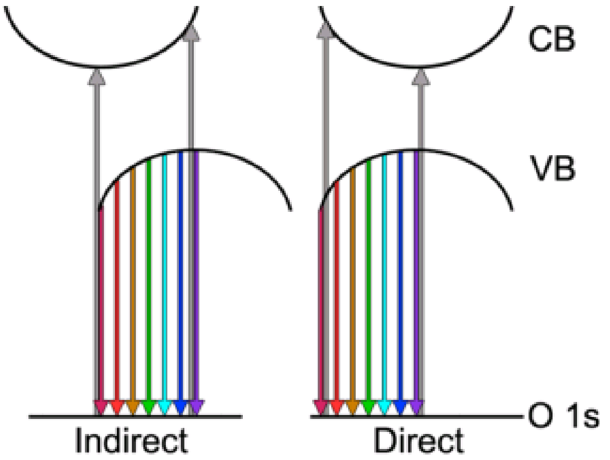
Not planned:

- Spectroscopic ellipsometry measurements on $LaTiO_xN_y$ films.

The Cooperation-Examples

- **Question came up, whether $LaTiO_xN_y$ has a direct or indirect bandgap, which is important for** absorption and recombination processes ➔ direct bandgap would be preferrable.
- UV-Vis measurements at PSI were unclear, suggesting it could be a direct or indirect bandgap.
- Samples were sent to INFLPR to perform spectroscopic ellipsometry (SE) measurements, which suggest strongly that it is an indirect bandgap.
- The SE data were used to apply successfully for beam-time at the Swiss Light Source for RIXS (resonant inelastic X-ray scattering) which can be used to determine the nature of the bandgap (indirect band gap leads to a **blue-shift** in emitted x-ray photons **with increasing excitation energy** (assuming transitions that are vertical in the energy-momentum plot, momentum of photon negligible).
- Measurements and analysis are ongoing.

Energy-momentum plot $BiVO_4$



Cooper et al., J. Phys. Chem. C 2015, 119, 2969−2974

Visits and Exchange of Knowledge

Visits at the project partner

- Maria Dinescu at PSI 27.02.2013- 01.03.2013
- Maria Dinescu and Stefan Antohe at PSI 23.10.2014- 26.10.2014
- Maria Dinescu at PSI 26.01.2014- 29.01.2014
- Maria Dinescu at PSI/ETH for PhD exam and final reports 16.05.2016- 19.05.2016
- Thomas Lippert at INFLPR 25.09.2013- 28.09.2013
- Thomas Lippert at INFLPR 25.03.2014- 29.03.2014
- Thomas Lippert at INFLPR 18.02.2015- 21.02.2015
- Thomas Lippert at INFLPR and here 25.05.2016- 27.05.2016
- Additional meetings at 2 annual conferences, where also the some of the other team members could meet, i.e. the annual E-MRS spring meeting in May/June and Fall meeting in September. Additional meeting took place at the 2013 and 2015 COLA conferences.
- Regular contact by email or telephone (when required for the project), but on average 1 per month.

Special outcome related of this project:

- One scientist from the Romanian group works now on a CTI project in the CH group (was a SCIEX fellow before and selected as “show case”).
- Another scientist form the Romanian group was as SCIEX fellow in the CH group.

VERY SUCCESSFUL projects and exchange beyond the project.

Challenges Met

What challenges could have been encountered in a bi-national project with "mixed" funding with different countries and different backgrounds?

- Scientific and/or organizational?
    1. Would there be open discussions about data, required measurements, etc., i.e. would the communication work well?
    2. Would an exchange of samples work?
    3. Would the measurements be performed "on-time" and carefully for samples of the other group?
    4. Etc.
- Administrative?
    1. Would the signing of the contracts go smooth?
    2. Would the required input to the scientific and financial reports be given on time and be well prepared?
    3. Would the "rules" for finances be followed?
    4. Etc.

- And ??????

Challenges Met

And now the great moment of truth ……

We encountered none of these problems at all:

- We had regular meetings and open discussions.
- The exchange of samples worked very well.
- The measurements from the other groups were performed on time and were well executed.
- The input for the scientific report came on time and was well prepared.
- The input for the financial report came on time, was well prepared, and a small minor problem was fixed fast and there were no problems for asking to get additional documents/signatures etc.

The only problems we had were purely related to science, e.g. the preparation of high quality thin films (oxynitrides, BFO and doped BFO) on conducting substrates for the PEC measurements was very difficult and time consuming for both groups.

Lessons Learnt

The only lesson to be learnt from our project is quite simple, why has it worked so well, i.e. without any problems (for me totally comparable or even better to projects with partners from a Swiss institutions)?

There is a long time cooperation between the two groups, i.e. we know each other for more than 15 years (I had a PhD students form the Romanian group and very often visiting scientists and was twice a reviewer of a PhD thesis from this group) and we had previously joint scientific projects, NATO SfP project (Romanian partner in charge) and we were both part in an EC FP7 project.

My explanation: Projects will most likely work well, if the partners know each for a longer time and have worked together before, meaning they have already for a long period common scientific interests.

For me, it was also a good opportunity to get/hire great and highly motivated coworkers from the Romanian group.

Follow up?

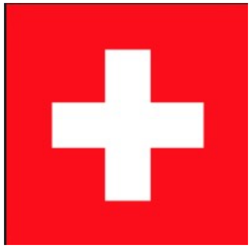
We would be very interested in any possibilities to continue this project and the collaboration.

- The topic of research which we started during this project is now established in both groups, and we are just now getting a lot of very promising data (e.g. first papers have just been published or submitted, and several are in preparation and more are envisioned).
- The setups for the characterizations have been built, and the required “experience” is now established.
- To be more specific, the data on the photoelectrochemical properties of the doped BFO were just obtained recently and are very promising.

In summary, we will continue this project and cooperations for sure in one or another form, but we would be very happy, if there would be an official project basis, e.g. based on a joint

Swiss- Romanian or Romanian- Swiss project.



Thank you very much for your attention

Any questions…