Final report
Project NN 127069
Pb-free perovskite solar cells with long-term stability

Participants:

Starting from the end of the first year, we employed Mehmet Derya Özeren. In the second half or the project, Bea Botka also joined the team. She is an experienced researcher and could effectively coordinate the methodology and the scientific activities.

Work plan:

Our role in the Korean-V4 consortium was the spectroscopic characterization of optoelectronic active layers and transport materials. In addition, we studied inorganic materials with optically active defect centers.
In the second half of the project, our experimental activities and international mobility were severely hindered by the COVID pandemic situation. Therefore, much of the equipment development and stability studies remained unfinished and the results are presented in the form of conference contributions and unpublished manuscripts.

Results

We present the results organized by topic and give the list of publications in the end, in order to be able to refer to them in the text. In case of unpublished work and work in progress (including unpublished conference posters and theses) we give a more detailed description.

Our activity was twofold: collaborative research on solar cell materials, and local experiments on the use of nanomaterials in optoelectronic applications.

On active solar cell materials, we demonstrated that the performance of tin-based perovskite solar cells can be enhanced by adding $Pb(SCN)_2$ to $CH(NH_2)_2SnI_3$. The optimal amount, based on morphology and power conversion efficiency, was found to be 0.25M $Pb(SCN)_2$, reducing the lead concentration to 0.08 g/mL compared to that of 0.37 g/mL in CH_3NHPbI_3 [A-1].

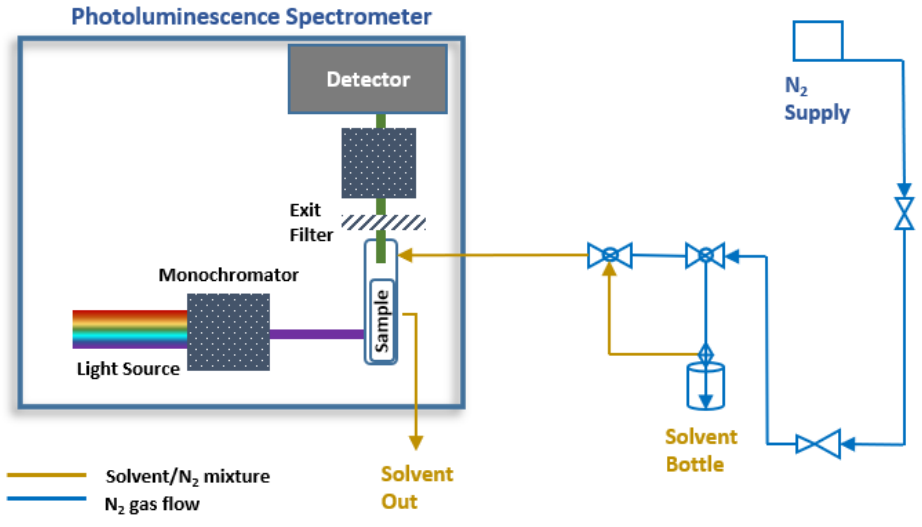
Planar perovskite solar cells were fabricated on F-doped SnO2 (FTO) coated glass substrates, with 4,4'-((1E,1'E)-((1,2,4-thiadiazole-3,5-diyl)bis(azaneylylidene))bis(methaneylylidene))bis(N,N-dip-tolylaniline) (bTAThDaz) as hole transport material. This imine was synthesized by our collaborators in Wroclaw in a one-step reaction, starting from commercially available and relatively inexpensive reagents. The material was fully characterized by electrochemical, optical, electrical, thermal and structural methods, and current-voltage measurements were performed on the full solar cell devices. Our research group determined the temperature- and time-dependent infrared spectra of the hole transport material and found that it remained stable up to 180 °C. The electrical behavior and photovoltaic performance of the perovskite solar cell was examined in a FTO/TiO_2/perovskite/bTAThDaz/Ag device architecture, yielding 14.4% solar conversion efficiency and good time and air stability together with quite small effect of hysteresis [A-2, C-1].

Lead-based perovskite materials can also be improved in order to increase their stability. Applying mixed halide anions is an efficient way of bandgap engineering, but these materials are prone to phase segregation. Potassium addition was found to be a promising way to overcome this segregation issue in mixed iodide-bromide lead perovskites, but the exact mechanism and best practices for achieving stability have not been explored in detail. We studied photoluminescence emission spectra of $MAPb(Br_{0.6}I_{0.4})_3$ films upon addition of KBr and KI while varying the atmosphere and the humidity, and found that the potassium addition does not passivate the surface. Oxygen and water absorption are possible, and the adsorbed water contributes significantly to the prevention of halide segregation [A-3, C-2, C-3].

Concerning other possible optoelectronic applications of nanomaterials, we detected near-infrared emission from divacancy centers in nanocrystalline SiC. These centers also show optically detected magnetic resonance, paving the way towards magnetic biosensors [A-4].

Work in progress

Organic lead halide solar cell materials still suffer from stability issues. We started a systematic study to correlate chemical composition with possible degradation and the role of additives in increasing stability. We performed a detailed investigation of post-treatment by various solvents on CH_3NHPbI_3, $CH_3NHPbBr_3$ and $CH_3NHPbI_xBr_{3-x}$ films deposited by the one-step method from solution [C-4, T-1, T-2]. For this purpose, we constructed a measurement chamber where solvent vapor and inert gas can be exchanged subsequently. Our efforts are centered on the influence of the environment on the stability of possible devices. We use infrared and photoluminescence spectroscopy, including temperature- and time-dependent measurements, to fully elucidate this problem. The spectroscopic data are compared to the chemical properties (electron donating and hydrogen-boning affinity) of the solvents [C-4]. We finished the data collection of this project and are working on preparing the results for publication.



Setup to measure photoluminescence during solvent exchange.

We also started to prepare carbon nanotube - perovskite and graphene - perovskite heterostructures by vacuum filtering, exfoliation and spin coating. In preparation for their photochemical investigation, we constructed various measurement setups for photoinduced measurements, to be used in our infrared spectrometer, with the infrared microscope or with the fluorometer, employing several lasers [C-5, C-6, C-7, C-8, T-3].

Two-dimensional perovskites

We also began to investigate the combination of three-dimensional perovskites and two-dimensional ones, based on organic ammonium ions and transition metal halides [C-9]. Building on previous work, where we characterized the 2D materials by x-ray diffraction and infrared and Raman spectroscopy, we started to build up a spectral library of 2D perovskite hybrid materials, including Pb, Cu, Co and Mn as central metal atoms, I, Br and Cl as halogen ingredients, and alkyl diammonium cations with varying length. We measured the infrared spectra and their temperature dependence. This database will be used to optimize surface layers of 2D perovskites to stabilize 3D perovskites.

Outlook

During this project, we established reliable protocols for hybrid perovskite preparation under inert atmosphere, constructed a measurement chamber for in-situ solvent exchange to perform post-treatment of hybrid perovskite surfaces by different solvents, and study the stability against defect formation or, in the case of mixed halides, segregation. We also built up equipment for photoinduced spectroscopic measurements. With this instrumentation, we will be able to go to the next step, use nanocarbon materials as transparent hole transport layers and combine them with stable perovskites. We hope to be able to contribute in this way to the solution of the most important issue of perovskite-based devices, long-term stability.

List of publications resulting from the project:

Articles in international journals:

A-1. D.Y. Heo, T.H. Lee, A. Iwan, L. Kavan, M. Omastova, E. Majkova, K. Kamarás, H.W. Jang, S.Y. Kim: **Effect of lead thiocyanate ions on performance of tin-based perovskite solar cells**
J. Power Sources **458,** 228067-1-8 (2020)

A-2. K.A. Bogdanowicz, B. Jewloszewicz, A. Iwan, K. Dysz, W. Przybyl, A. Januszko, M. Marzec, K. Cichy, K. Świerczek, L. Kavan, M. Zukalová, V. Nadazdy, R. Subair, E. Majkova, M. Micusik, M. Omastova, M.D. Özeren, K. Kamarás, D.Y. Heo, S.Y. Kim: **Selected electrochemical properties of 4,4'-((1E,1'E)-((1,2,4-thiadiazole-3,5-diyl)bis(azaneylylidene))bis(methaneylylidene))bis(N,N-di-p-tolylaniline) towards perovskite solar cells with 14.4% efficiency**
Materials **13,** 2440-1-17 (2020)

A-3. M.D. Özeren, B. Botka, Á. Pekker, K. Kamarás:
The role of potassium in the segregation of $MAPb(Br_{0.6}I_{0.4})_3$ mixed-halide perovskite in different environments
Phys. Stat. Sol.-R. **14,** 2000335 (2020)

A-4. D. Beke, J. Valenta, Gy. Károlyházy, S. Lenk, Zs. Czigány, B.G. Márkus, K. Kamarás, F. Simon, A. Gali: **Room temperature defect qubits in ultrasmall nanocrystals**
J. Phys. Chem. Lett. **11,** 1675-1681 (2020)

Conference presentations:

C-1. M.D. Özeren, B. Botka, Á. Pekker, K. Kamarás, M. Spina, B. Náfrádi, M. Kollár, L. Forró, E. Horváth, S. Kamal, A. Sabry: **Lead halide perovskites and PPL: Vibrational spectroscopy studies**
Korea-V4 project meeting, Bratislava, Dec 6, 2019, lecture

C-2. M.D. Özeren, B. Botka, Á. Pekker, K. Kamarás, M. Kollár, E. Horváth, L. Forró:
K^+ incorporation into methylammonium-based bromide rich mixed halide perovskites
XXXIVth International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2020), Kirchberg, Austria, March 7-14, 2020, poster

C-3. Á. Pekker, M.D. Özeren, B. Botka, K. Kamarás: **Effect of potassium addition on the segregation and degradation of $MAPb(Br_{0.6}I_{0.4})_3$ mixed halide perovskites**
Joint Conference of the Condensed Matter Divisions of EPS (CMD) and RSEF (GEFES), online, Aug. 31. - Sep. 4, 2020, lecture

C-4. M.D. Özeren, B. Botka, Á. Pekker, K. Kamarás: **In depth study of complex perovskite-solvent interactions by *in situ* photoluminescence spectroscopy**
Materials Research Society Fall Meeting&Exhibit, online, Dec. 6 - 8, 2021, lecture

C-5. K. Kamarás, M.D. Özeren, Á. Pekker, M. Spina, B. Náfrádi, L. Forró, E. Horváth, S. Kamal, A. Sabry: **Photochemical studies on perovskite – carbon nanotube hybrids**
EGNC Conference, Egypt Nano Technology Center, Cairo, Egypt, December 18, 2018, lecture

C-6. K. Kamarás, L. Badeeb, M.D. Özeren, Á. Pekker, S.K. Abdel-Aal, A.S. Abdel-Rahman, P. Andricevic, L. Forró, E. Horváth: **Investigation of charge dynamics and photoinduced charge transfer in metal halide perovskite/carbon nanotube composites by vibrational spectroscopy**
American Physical Society March Meeting, Boston, Massachusetts, March 4-8, 2019, V20.00013, lecture

C-7. B. Botka, Á. Pekker, M.D. Özeren, G. Németh, H.M. Tóháti, Zs. Szekrényes, P. Andricevic, B. Náfrádi, M. Kollár, E. Horváth, L. Forró, K. Kamarás: **Optical measurements on perovskite-carbon nanomaterial interfaces**
The XXXIII Conference "Materials Science and applications & Workshop on Graphene Applications", The Egyptian Materials Research Society, Hurgada, Egypt, Nov. 27-30, 2019, invited lecture

C-8. Á. Pekker, H.M. Tóháti, L. Badeeb, L. Bató, B. Botka, M.D. Özeren, K. Kamarás: **Fotofizikai vizsgálatok ólomhalogenid-perovszkit-szén nanoszerkezet hibrid rendszereken**
Magyar Fizikus Vándorgyűlés, Sopron, August 21-24, 2019, lecture

C-9. K. Kamarás, M.D. Özeren, Á. Pekker, M. Spina, B. Náfrádi, L. Forró, E. Horváth, S. Kamal, A. Sabry: **Photoinduced spectroscopic studies on perovskite-based solar cell materials**
Korea-V4 kickoff meeting, Prague, Nov 23, 2018, lecture

Student theses and works connected to the project:

T-1. Badeeb L.: **Infravörös spektroszkópiai vizsgálat a $CH_3NH_3PbI_3$ napelemanyagon**
TDK student conference,Eötvös Loránd University, 2018

T-2. Badeeb L.: **Infravörös spektroszkópiai vizsgálat a $CH_3NH_3PbI_3$ és $CH_3NH_3PbBr_3$ napelemanyagokon**
Eötvös Loránd University, 2018, B. Sc. thesis

T-3. Bató L.: **Alacsonydimenziós szénszerkezetek és perovszkit alapú napelemanyagok közötti kölcsönhatás vizsgálata infravörös és Raman-spektroszkópiával**
Eötvös Loránd University, 2019, B. Sc. thesis