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Science is not about believing; science is about logic, knowledge and questioning.

Second International Perovskite Workshop in Lund:

Toward fundamental understanding of optoelectronic properties of metal halide perovskite semiconductors.

May 10 – 11, 2023, Chemical Center, Lund University, Sölvegatan 39, Lund, Sweden

Organizers: **Ivan Scheblykin** (Lund University, Sweden),
Eva Unger (Helmholtz Center Berlin, Germany)

Sponsors:

- The Swedish Research Council (Vetenskapsrådet), Indo-Swedish joint network grant 2018-07064
- Lund University NanoLund
- Region Skåne.

Participation in the workshop is free of charge. Coffee and lunches will be provided.
Questions: ivan.scheblykin@chemphys.lu.se
Each invited talk has 40 min slot of which about 20 minutes are reserved for discussion.
Posters will be presented during the long coffee breaks.

May 10, 9.00 – 18.00

Phase segregation in mixed halide systems: matching theory and experiments.

1. **Eva Unger** (Helmholtz Center Berlin, Germany)
https://www.helmholtz-berlin.de/forschung/oe/se/hybrid-materials/index_en.html
Experimental evidence that light-induced defects causing meta-stability effects in halide perovskite semiconductors.
The existence and dynamic generation, migration, and annihilation of ionic defects in halide perovskite semiconductors give rise to a number of dynamic phenomena and meta-stabilities that have been observed early on in the community such as hysteresis (Unger et al.), light-induced phase-segregation (Hoke et al.) and PL enhancement (Tian et al.). Primarily an experimental annoyance, transient electronic/ionic phenomena raise concerns about the long-term operational stability of halide perovskite optoelectronics but also enable self-healing. This talk will provide a high-level summary of dynamic phenomena attributed to mobile ionic defects and set the stage for the topical discussions.

2. **Peter Bobbert** (Eindhoven University of Technology, The Netherlands)
https://www.tue.nl/en/research/researchers/peter-bobbert
Thermodynamic theory for light-induced halide segregation in mixed halide perovskites
Questions to discuss: How should the very initial stage of halide segregation be described microscopically? What defects are involved in halide segregation (halide vacancies, interstitials, …) and how do they determine the segregation dynamics? What can we learn from classical nucleation theory to understand the initial stage of halide segregation? Is there an illumination threshold for light-induced halide segregation and how can we estimate it? How can we suppress light-induced halide segregation? Can we use light-induced halide segregation to write patterns in perovskites for novel optical applications?

Coffee break

3. **Juan Galisteo** (Institute of Materials Science of Seville, Spain)
https://mom.icms.us-csic.es/dr-juangalisteo/

Iodide Nanodomain Formation in Mixed Halide Perovskites: Let's Discuss on the Role of Defects
The so-called "phase segregation" phenomenon in lead halide perovskites can be considered as part of a broader set of observations dealing with photo-induced processes (photo-brightening, photo-degradation, etc.). As such, it is strongly related with the defect structure of the material and thus sample morphology. Further, as with most photo-induced processes, the driving force is still an open (and hot) debate. In this presentation I want to introduce a discussion on what is the role of the defects in the phase segregation observed in thin films of mixed perovskites with the formulation MAPb(BrxI1-x)3. In particular, I would like to discuss the precise role played by vacancies and interstitials in the photo-induced formation of nano-domains with different composition and what the ultimate driving force for these structural changes is. Spectrally and time resolved photoluminescence confocal studies performed in our laboratory are used as a guide to the discussion and are put in context with literature on phase segregation and defect structure in lead halide perovskites.

4. **Feng Gao** (IFM, University of Linköping, Sweden).
https://liu.se/en/employee/fenga88
Phase segregation in blue LEDs based on mixed halide perovskites.
Questions discuss: what is the driving force for phase segregation? What is the difference between phase segregation in mixed Br/I perovskites and mixed Br/Cl perovskites? What are the approaches to minimize phase segregation for stable devices?

Lunch

5. **Rebecca Belisle** (Wellesly College, USA) https://www.wellesley.edu/physics/people/faculty/rbelisle
The relationship between defects and phase segregation.
Questions for discussion: What are the impacts of carrier induced defects on phase stability? What are sources of discrepancy in the halide segregation experimental data? What are potential pathways towards stability of wide bandgap perovskites?

6. **Masaru Kuno** (University of Notre Dame, USA),
https://chemistry.nd.edu/people/masaru-k-kuno/
A band gap model for mixed-halide photo segregation
Discussion topics: Photo segregation at moderated and remixing at high excitation intensities - how do we explain it? Is there a model that explains both concertedly? What is the origin of the x_terminal values close to 0.2 for many materials. Comparison between photosegregation in thin films and single crystals. Photosegregation in 2D and quasi 2D perovskites. Does the structure matter? Possible connection of the halide segregation with early colloidal growth models of LaMer and Sugimoto. Cations are also unstable. Are there any hints of concerted (or cooperative) cation and anion displacements during either photosegregation or biasing? We assume that cations remain still during anion segregation (and presumably remixing/photoremixing), is this a good assumption?

Coffee break

7. **Paul McIntyre** (Materials Science and Engineering, Stanford University, USA)
https://mse.stanford.edu/people/paul-mcintyre
Halide ion demixing during illumination of highly crystalline CsPbBr(1-x)Ix thin films: A combined cryo-EM, cathodoluminescence and phase field modelling study.
Questions to discuss: How can one account, both quantitatively and mechanistically, for the discrepancy between the "electronic" driving force for halide ion demixing, which can be estimated from the reported electronic structure of these materials, their reported photocarrier generation and recombination behaviour, etc., and that which is required for the observed phase separation?

8. **Michael Toney** (University of Colorado, USA).
https://www.colorado.edu/chbe/michael-f-toney

Perovskite lattice dynamics and the influence on halide diffusion.
I will discuss the importance of local structure and how this can be quantified and demonstrate this for organic-inorganic hybrid halide perovskites. While the importance of lattice dynamics and dynamical (dis)order have been recognized in these materials, their nature is poorly understood. We used X-ray and neutron diffuse scattering coupled with molecular dynamics to quantify the nature, size, and time scale associated with dynamical local order in CH3NH3PbI3 and CH3NH3PbBr3. We observe that the nominally cubic perovskite consists of dynamical, two-dimensional sheets of lower symmetry tetragonal regions of about 3 nm diameter with several picosecond lifetimes. The generality of these observations and their implications on halide perovskite properties will be discussed.

Dinner.

May 11, 9.00 – 18.00

Optical and electrical measurements to assess defect states and related topics.

9. **Thomas Kirchartz** (FZ Juelich, Institute for Energy and Climate Research, Germany).
https://www.fz-juelich.de/de/iek/iek-5/ueber-uns/ansprechpartner/t-kirchartz
Shallow Defects and Long Charge-Carrier Lifetimes in Lead-Halide Perovskites
Open questions to discuss: How to separate recombination from extraction processes? How to choose repetition rates? How to compare steady state and transient measurements? What can you learn from the differences between steady state and transient measurements?

10. **Dinesh Kabra** (Department of Physics, IIT Bombay)
https://www.phy.iitb.ac.in/en/employee-profile/dinesh-kabra
White light emission in low dimensional halide perovskites: Self-trapped Excitons (STE) vs Local Molecular triplets
Questions to discuss: STE is considered to have an origin of the distorted octahedral of PbX6. Hence, PLE spectra should show a sub-gap absorption related to broader emission peaks. If emission is from sub-gap localized states, it shows an increase in PL FWHM with an increase in temperature. Then why do we observe reverse characters? Localized excitons from distorted organic molecules adjacent to ordered in-organic lattice can't have an electronic coupling? Investigating lifetimes of these multi-peak emission and evolved spectral features can help to reveal interesting facts.

Coffee break + POSTERS

11. **Igal Levine** (Helmholtz Center Berlin, Germany)
https://www.helmholtz-berlin.de/pubbin/vkart.pl?v=nuqkq
Bridging the gap between optical and electrical characterization of Halide Perovskites using highly sensitive opto-electronic contactless characterization
Questions to discuss: Can we assess experimentally which defects are electronically-active? How do we fine-tune carrier extraction from the perovskite to the contact layers? PL vs. Surface PhotoVoltage (SPV) decay dynamics: what can we learn from the comparison? Can we find a single model that efficiently describes both PL and Surface PhotoVoltage (SPV) decay dynamics across a wide time range? What are the "correct" experimental conditions that need to be used in pulsed measurements in order to reliably predict the optoelectronic properties at steady-state operation?

Lunch

12. **Monojit Bag** (Department of Physics, IIT Roorkee, India).
https://iitr.ac.in/Departments/Physics%20Department/People/Faculty/100753.html
Halide perovskite materials beyond the photovoltaic applications: A tale of iontronics in energy storage and memory devices.

Most critical aspect of electronic-ionic transport phenomena in halide perovskites, its implication in energy storage, and memristor application will be discussed. I will present the transport phenomena in nanocrystals and the role of grain boundaries on the excitonic absorption in these systems. Some unusual behaviour in EIS measurement has been observed. I will discuss possible mechanisms to understand those. However, there will be an open discussion on how electron-ion coupling can lead to polarization or how grain boundaries can modulate the absorption spectrum.

13. **Thomas Unold**, (Helmholtz Center Berlin, Germany)

Inferring transport properties from transient-optical methods.

Questions to discuss: do optical and electrical methods lead to the same conclusions ? Transient vs steady-state characterization, what is the influence of nanostructures and grain boundaries. Are there differences between inorganic and hybrid halide perovskites?

Coffee break + POSTERS

14. **Arindam Chowdhuri** (Department of Chemistry, IIT Bombay)

https://www.chem.iitb.ac.in/~arindam/index.php

Spatiotemporal Correlations in Optical Instabilities of Hybrid Halide Perovskite Microcrystals

I will focus on an unusual light induced phenomenon, where entire micron-sized $MAPbBr_3$ crystals undergo multi-level, spatially-synchronous PL blinking (or flickering). Intriguingly, the extent of spatiotemporal correlations in PL flickering can often over space and time, implying some complex processes being operational. I will present a model which invokes the slow formation/annihilation of few meta-stable charged quenchers, coupled with correlated migration of charge carriers.

Question to discuss. However, the nature of the metastable traps (quenchers) responsible for the correlated flickering, as well as mechanisms of long-range communication between carriers within each crystal remains ambiguous. Moreover, the question remains whether such a phenomenon is unique for PL imaging on single crystals or similar meta-stability may also be observed for EL measurements. This raises another question on the (dis)similarity of the nature of defects generated by light and those created in EL devices.

15. **Ivan Scheblykin** (Chemical Physics, Lund University, Sweden)

www.chemphys.lu.se/research/groups/scheblykin-group/

Photosensitivity of metal halide perovskite semiconductors is a nightmare for laser spectroscopists. Does spectroscopy have any chance to tell us the "truth"?

I will discuss inherent light-controlled defect instability in MHPs and argue that every optical measurement using varying light conditions essentially reports on a different sample in terms of its defect concentration and dominant defect type even if the sample is physically the same. How should one interpret the data? Are we all searching for non-existing truth? The discussion will be supported by automatically recorded PLQY(f,P) maps (so-called "Horse" plots) of MAPI, MAPbBr3 and CsPbBr3.

Closing remarks