Petersburg Perovskites – 2023

Book of Abstracts

St. Petersburg, Russia
29-30 June, 2023

Petersburg Perovskites – 2023
1st SPbU Summer School on Halide Perovskites

The international online summer school was dedicated to the novel photonics material – halide perovskites. At this two-day school, students and young scientists had the opportunity to hear lectures from the world's leading scientists involved in fundamental research on the physics and chemistry of halide perovskites and their low-dimensional analogues, as well as related technologies and their applications in various fields of optoelectronics and photonics. Participants also had the opportunity to present reports on their research.

The school was held online in Zoom for two days – **June 29 and 30, 2023**, with invited lectures and participants talks.

The school is organized by the Photonics of Crystals laboratory of St. Petersburg State University, Russia (crystal.spbu.ru) and supported by the Ministry of Science and Higher Education of the Russian Federation (Megagrant no. 075-15-2022-1112).

Program committee:

- Constantinos Stoumpos, SPbU and University of Crete (Greece)
- Alexei Emeline, SPbU
- Yury Kapitonov, SPbU

School secretary:
Aleksei Murzin, SPbU (a.murzin@2015.spbu.ru)
Web-site: https://crystal.spbu.ru/school.html

St. Petersburg State University

School program (Moscow time, GMT+3):

June 29, 2023

9:50-10:00		School opening
10:00-10:30	**Lingling Mao**, Southern University of Science and Technology, China	Hybrid low-dimensional perovskite and transition-metal halide phases
10:30-11:00	**Debajit Sarma**, Indian Institute of Technology Patna, India	Coordination Driven Frame-work Materials for Conversion of CO_2 to Value Added Chemicals
11:00-11:30	**Arief C. Wibowo**, Sultan Qaboos University, Oman	Lone pair containing compounds: MOF and perovskitoid coordination polymer
11:30-12:00		Coffee break
12:00-12:15	**Baeva Maria**, Alferov University, ITMO University, St. Petersburg, Russia	Dual-function Perovskite Light-emitting Electrochemical Cell on Silicon Substrate
12:15-12:30	**Xiaoyu He**, Huazhong University of Science and Technology, Wuhan, China	Universal Vapor-Phase Synthesis of Large-Area Ultrathin Two-Dimensional Halide Perovskites with Superior Stability
12:30-12:45	**Maniadi Maria**, University of Crete, Greece	2D Hybrid Double Halide Perovskites consisting of non-toxic elements
12:45-14:00		Lunch
14:00-14:30	**Tao Fan**, Skolkovo Institute of Science and Technology, Russia	AICON: A program for calculating thermoelectric transport properties quickly and accurately
14:30-15:00	**Daniel Sapori**, ITMO University, Russia	Organic-Perovskite 2T-Tandem Solar Cells in Parallel Connection
15:00-15:15	**Apostolos Pantousas**, University of Crete, Greece	Synthesis and Characterization of 2D Layered Halide Perovskite Quantum Wells
15:15-15:30	**Deribina Ekaterina**, St.Petersburg University, Russia	Optical Characterization of Low-dimensional GaAs/AlGaAs Structures Grown by Droplet Epitaxy

June 30, 2023

10:00-10:30	**Jing Zhao**, University of Science and Technology Beijing, China	Research Progress of Lead-Free Organic-Inorganic Hybrid Metal Halide Luminescent Materials
10:30-11:00	**Xianli Su**, Wuhan University of Technology, China	Oxygen induced transport behavior in Thermoelectric materials
11:00-11:30	**Leonidas Mouchliadis**, Institute of Electronic Structure and Laser, FORTH, Heraklion, Crete, Greece	Probing valley population imbalance in transition metal dichalcogenides via temperature-dependent second harmonic generation imaging
11:30-12:00		Coffee break
12:00-12:15	**Mikheleva Alena**, St. Petersburg University, Russia	Photoinduced Changes in IR Spectra of $MAPbBr_3$ Perovskite
12:15-12:30	**Alaelddin Michailids Barakat**, University of Crete, Hellenic Mediterranean University, Greece	Band gap prediction & data analysis of inorganic halide perovskites using machine learning
12:30-12:45	**Matthew Maksimov**, St. Petersburg University, Russia	Exciton spectroscopy from a wide quantum well of InGaAs/GaAs heterostructures.
12:45-14:00		Lunch
14:00-14:30	**Dmitry Shtarev**, Shenzhen MSU-BIT University, China	Alkyl diamine-based hybrid perovskites: Influence of carbon chain length on structural and optical properties
14:30-15:00	**Alexey Tarasov**, Moscow State University, Russia	Thin film encapsulation of perovskite solar cells: new tricks to withstand high temperature, long irradiation and light cycling
15:00-15:15	**Martynovich Mikhail**, St. Petersburg University, Russia	Photostimulated defect formation in $MAPbBr_3$
15:15-15:30	**Mamaeva Maria**, St. Petersburg University, Russia	Free exciton and defect-related states in $CH_3NH_3PbCl_3$ perovskite single crystal
15:30		School closing

Abstracts

Band gap prediction & data analysis of inorganic halide perovskites using machine learning

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Machine learning is a very prominent approach towards material discovery based on data mining and big data analysis. [1] This approach has been proven extremely successful in a wide range of research fields from medicine to artificial intelligence. In the field of solid-state chemistry, machine learning can provide us with a robust method of analyzing our experimental results and making predictions on the properties and synthesis of new materials. One such class of materials is Perovskites, an innovative class of semiconductor materials, which has spiked the interest of the scientific community for many years. In this project, we utilize machine learning in order to assist with the discovery of new materials combining a computational approach to identify the materials and a synthetic materials chemistry approach to attempt to verify the computational results. We ultimately seek to discover new compounds with desirable optoelectronic properties in the visible spectrum range for employment in photovoltaic research. [2] We use machine learning as an alternative method to other computational as well as test-and-trial methods, and we find that our machine learning methodology provides a higher accuracy in the prediction of photoactive perovskites. By employing machine learning on analyzing and predicting properties of perovskites, we have successfully surpassed the effectiveness hurdles of conventional theoretical methods, such as DFT.

References:
1. Lu Z., *MRE* **1** (3), 100047 (2021).
2. Stoumpos C.C. and Kanatzidis M.G., *Acc. Chem. Res.* **48** (10), 2791–2802 (2015).

Synthesis and Characterization of 2D Layered Halide Perovskite Quantum Wells

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Perovskites are a class of semiconducting materials with great interest in optoelectronic applications due to their high efficiency, high absorption coefficients and low cost. Two-dimensional (2D) perovskite structures provide the ability to further tune these properties and manufacture high-performance devices. In this work, we focus on the synthesis and characterization of a new homologous series of 2D layered lead halide perovskites based on the $CH_3NH_3PbBr_3$ bulk perovskite. The homologous series, with general formula $(CH_3(CH_2)_5NH_3)_2(CH_3NH_3)_{n-1}Pb_nBr_{3n+1}$, where n corresponds to the number of layers of the perovskite, produces a fertile ground for the study of quantum wells, since the alternating organic and inorganic layers generate a natural, periodic quantum well structure . By tuning the thickness, we control the degree of dielectric and quantum confinement of the photogenerated carriers inside the inorganic layers, thus creating a series of compounds with tunable optical properties in the visible spectrum range. The compounds were synthesized in pure form and their crystal structure was determined via single-crystal X-ray diffraction. The structural phase transitions were monitored via Differential Scanning Calorimetry (DSC) in the −80 – 120 °C temperature range while the optical properties were studied via steady-state and time-resolved photoluminescence (PL) spectroscopy in the −195 – 25 °C temperature range. The results suggest that the new compounds are excellent excitonic model systems and can be employed in specific applications like LEDs and lasers.

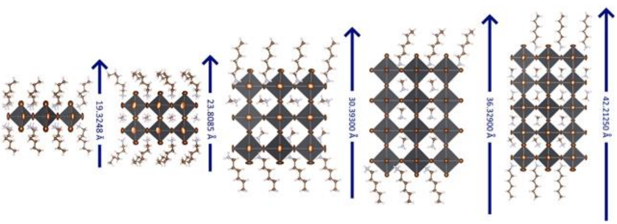

Fig. 1. The $(HA)_2(MA)_{n-1}Pb_nBr_{3n+1}$ (n = 1–5) homologous series at 393K.

References:
1. Stoumpos C.C. et al., *Chem. Mater.* **28** (8), 2852–2867 (2016).

Dual-function Perovskite Light-emitting Electrochemical Cell on Silicon Substrate

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Halide perovskite light-emitting electrochemical cells are a novel type of the perovskite optoelectronic devices that differs from the perovskite light-emitting diodes by a simple monolayered architecture. Here, we develop a perovskite electrochemical cell both for light emission and detection (Fig. 1), where the active layer consists of a composite material made of halide perovskite microcrystals, polymer support matrix, and added mobile ions. The perovskite electrochemical cell of $CsPbBr_3$:PEO:LiTFSI composition, emitting light at the wavelength of 523 nm, yields the luminance more than 7000 cd/m^2 and electroluminescence efficiency of $1.3 \cdot 10^5$ lm/W. The device fabricated on a silicon substrate with transparent single-walled carbon nanotube film as a top contact exhibits 40% lower Joule heating compared to the perovskite optoelectronic devices fabricated on conventional ITO/glass substrates. Moreover, the device operates as a photodetector with a sensitivity up to 0.75 A/W, specific detectivity of $8.56 \cdot 10^{11}$ Jones, and linear dynamic range of 48 dB. The technological potential of such a device is proven by demonstration of 24-pixel indicator display as well as by successful device miniaturization by creation of electroluminescent images with the smallest features less than 50 μm [1].

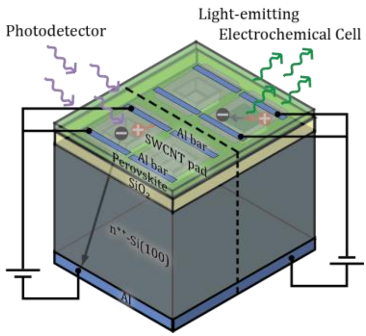

Fig. 1. Dual-function perovskite light-emitting electrochemical cell on silicon substrate.

References:
1. Baeva M. et al., *Opto-Electron Adv* **6**, 220154 (2023).

Optical Characterization of Low-dimensional GaAs/AlGaAs Structures Grown by Droplet Epitaxy

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GaAs/AlGaAs quantum dots (QDs) formed by filling nanoholes obtained by droplet epitaxy (NFDE method) have no stresses in the structure, in contrast to self-assembled InAs QDs. Therefore, they are of great interest for use in photonics devices, for example, for the manufacture of single-photon emitters, detectors, and solar cells [1].

In this work, we have grown a sample with GaAs/AlGaAs QDs: $Al_{0.47}Ga_{0.53}As$ – 7.3 nm; GaAs – 3.4 nm; $Al_{0.38}Ga_{0.72}As$ – 84.0 nm. Using micro-photoluminescence (µPL) and reflection spectroscopy, the optical properties of the sample were examined (Fig. 1). There are peaks associated with the emission of a quantum well (QW), QDs (A, B), as well as three-dimensional GaAs.

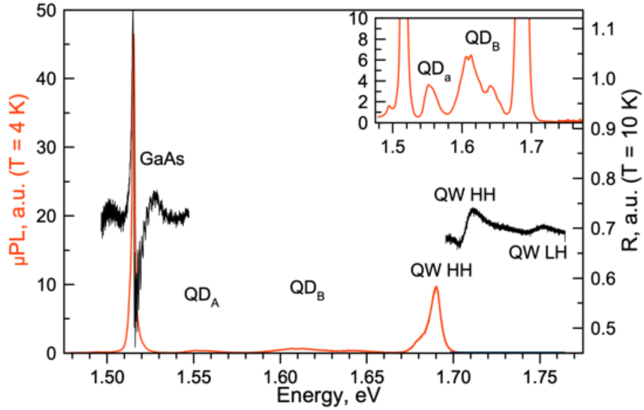

Fig. 1. µFL (50x) and reflection spectra of sample T874.

Acknowledgments: The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Megagrant no. 075-15-2022-1112) and the Russian Foundation for Basic Research (RFBR 19-52-12046). The work was performed on the equipment of the Resource Center of St. Petersburg State University "Nanophotonics".

References:
1. Gurioli M. et al., *Nat. Mater.* **18**, 799–810 (2019).

Free exciton and defect-related states in $CH_3NH_3PbCl_3$ perovskite single crystal

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Chloride perovskites are promising semiconductor materials for creating optoelectronic devices in the near ultraviolet range. This work presents an investigation of the photoluminescence and reflectivity of $MAPbCl_3$ ($MA^+ = CH_3NH_3^+$) halide perovskite single crystals at low-temperature orthorhombic phase in the T = 4–174 K temperature range. The position of the free exciton was determined, and defect-related states, which appeared as similarly polarized narrow emission lines up to 100 K, were analyzed in detail. The assumption that these states were phonon replicas was ruled out using photoluminescence excitation measurements (Fig. 1), and it was concluded that these narrow lines correspond to the emission of actual defect-related states that absorb light. This study provides new insights into the nature of defect-related states in perovskite single crystals, which could have important implications for the development of more efficient optoelectronic devices.

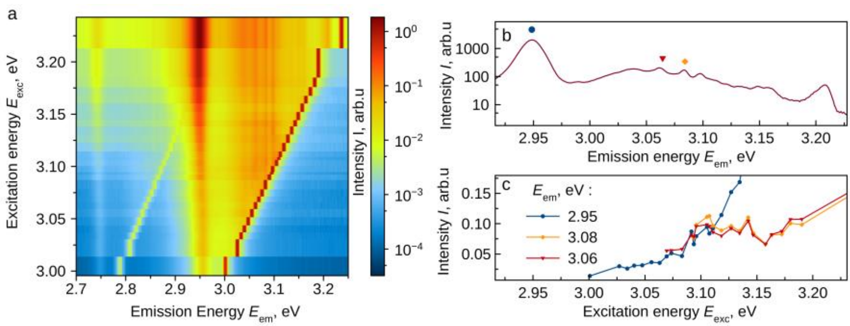

Fig. 1. (a) PLE measurements on $MAPbCl_3$ single crystal at T = 4 K (b) PL intensity dependency of lines on excitation energy. (c) PL spectrum of $MAPbCl_3$ single crystal captured at pump energy above PL, marks above lines correspond to line intensity plot (b).

Acknowledgments: The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Megagrant no. 075-15-2022-1112). The work was performed on the equipment of the Resource Center of St. Petersburg State University "Nanophotonics".

2D Hybrid Double Halide Perovskites consisting of non-toxic elements

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Lead halide perovskites AMX_3 (A^+ = Cs, CH_3NH_3 or HC $(NH_2)_2$, M^{+2} = Pb, Sn or Ge and X^- = Cl, Br or I) have become a notable research field. Two-dimensional perovskites show even greater development. Recent reports have shown that it is possible to stabilize double 2D perovskites consisting of two metal ions [1], making them a low toxicity alternative. In this work, we demonstrate that 2D hybrid double halide perovskites based on mixed metal Ag-In, Ag-Bi and Ag-Sb compositions, with a chemical formula $(4AMP)_2AgM^{III}Br_8.0.5H_2O$, ($M^{III}$ = In, Sb or Bi), can be obtained in high purity using low-temperature wet chemistry. The new compounds, have been characterized by single-crystal and powder X-ray diffraction and their optical properties at room temperature were determined (Fig. 1). The compounds possess a strong optical absorption in the visible. All compounds contain 0.5 H_2O molecules in the unit cell that can be removed by heating. Solid solutions with a combination of Ag-Sb-Bi, have also been obtained. These compounds are promising environmentally friendly semiconductors.

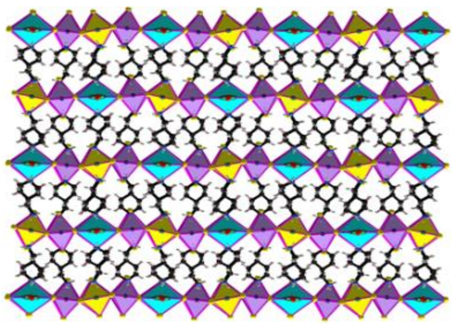

Fig. 1. The crystal structure of $(4AMP)_2AgM^{III}Br_8.0.5H_2O$.

References:
1. Li X. et al., *Chem. Mater.* **33** (15), 6206–6216 (2021).

Photostimulated defect formation in $MAPbBr_3$

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The work is devoted to the study of photostimulated defect formation in $MAPbBr_3$ perovskite using diffuse reflectance spectroscopy. In the course of the work, using a spectrophotometer with an integrating sphere, the diffuse reflectance spectra of a powdered $MAPbBr_3$ sample were measured before and after irradiation with a mercury lamp, from the spectrum of which the lines at 436, 546, and 572 nm were extracted. Subsequently, these spectra were recalculated into absorption spectra.

Difference spectra corresponding to the absorption of defects and a kinetic curve expressing the dependence of absorption on the irradiation time were plotted. Also in the work there is a comparison of the absorption spectra of defects and kinetic curves for $MAPbBr_3$ and $CsPbBr_3$, on the basis of which the following conclusions are made:

1. The studied $MAPbBr_3$ perovskite is characterized by photostimulated defect formation. The kinetics of defect formation indicates that this perovskite is a photoresistant material.
2. The absorption spectrum is a wide, weakly resolved absorption band, which indicates the inhomogeneity of the distribution over defective states.
3. Comparison with defect formation in $CsPbBr_3$ suggests that the observed defects are interstitial states of bromine.

Exciton spectroscopy from a wide quantum well of InGaAs/GaAs heterostructures.

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Studies on exciton spectroscopy of optical reflection in wide quantum wells is of current scientific interest as might be used to explore quantum beats – phenomena crucial to understand quantum entanglement, lasing without population inversion; and to create ultrafast optical devices.

In this paper we explore reflection from excitons in InGaAs/GaAs wide quantum well with continuous laser-pumping at a temperature of 11 K and at Brewster's angle. With the ability to perform measurements at a wide range of wavelengths (810–840 nm) it is possible to observe spectrums with characteristics representing transitions between energy levels associated with quantization of excitons' translational energy in a wide quantum well.

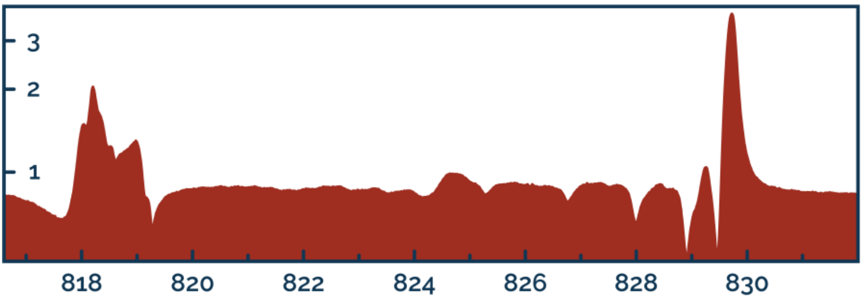

Fig. 1. Exciton reflection in InGaAs/GaAs quantum well. Intensity vs wavelength (in nm).

Obtained results confirm we've observed exciton reflection from a wide quantum well. Moreover, acquired spectrums are auspicious for further studies of quantum beats and photon echoes in this heterostructure [2].

Acknowledgments: The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Megagrant no. 075-15-2022-1112). The work was performed on the equipment of the Resource Center of St. Petersburg State University "Nanophotonics".

References:

1. Raiber S. et al., *Nat Commun* **13**, 4997 (2022).
2. Smirl A.L. et al. *Phys. Rev. B* **60**, 8267 (1999).

Photoinduced Changes in IR Spectra of $MAPbBr_3$ Perovskite

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In the last decade, hybid perovskites have attracted interest of materials scientists due to their great potential for fundamental and applied research. Methylammonium lead halides ($MAPbI_3$ and $MAPbBr_3$) are the most studied organic-inorganic hybrid perovskites [1]. However, new features of the behavior of these fascinating materials are still being discovered. In this work, $MAPbBr_3$ perovskite were studied at room temperature by *in situ* IR spectroscopy.

The photoinduced changes in IR spectra of this material were found. The dependences of the photoinduced band intensity alterations on spectral composition and the intensity of acting light were obtained. The temperature dependence was also presented.

The observed phenomenon is discussed in term of the material electric properties change and compared with literature data.

References:
1. Chen Y. et al., *Nat Commun* **7**, 12253 (2016).

Universal Vapor-Phase Synthesis of Large-Area Ultrathin Two-Dimensional Halide Perovskites with Superior Stability

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Halide perovskites with two-dimensional (2D) geometry have drawn tremendous attention in nano-micro electronic and optoelectronic devices due to their excellent compatibility with the current nanofabrication platforms. Unfortunately, it is highly challenging to obtain large-scale and chronically-stable ultrathin halide perovskites for practical application. To address the problem, we develop a self-limiting chemical vapor deposition (CVD) strategy to realize the universal growth of various longevity halide perovskites (*e.g.*, $MAPbBr_3$, $FAPbBr_3$, $MAPbI_3$, $FAPbI_3$, and Cs_4PbI_6), with the lateral size up to 1.5×1.5 cm^2. Attributing to the effective surface-capping effect, the $MAPbBr_3$ perovskite is found to maintain long-term stability without morphological change and performance degradation when exposed to the air environment for more than 180 days. The corresponding photodetectors also demonstrate ultrafast response time (< 10 μs) and outstanding photoelectric image sensing capability.

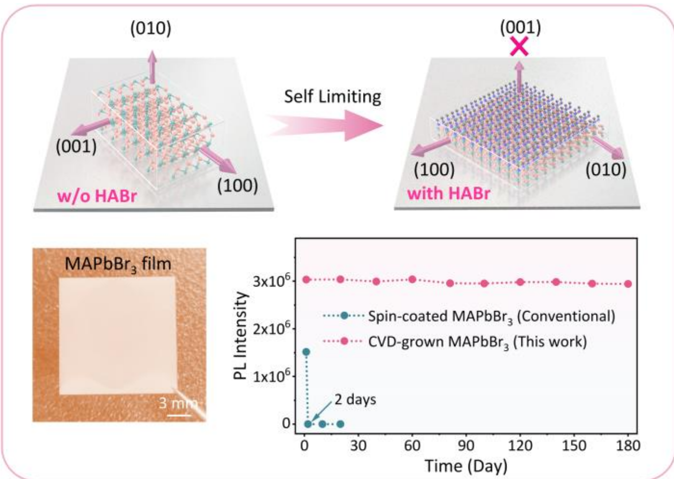

Fig. 1. Vapor-phase synthesis of large-scale and ultrathin halide perovskites with superior stability.

References:
1. He X. et al., *Adv. Mater.*, 2023 in revision.
2. He X. et al., *Chem. Rev.* **123** (4), 1207–1261 (2023).