



## High Efficiency Lead-Free Perovskite Solar cells for indoor-outdoor Applications.

Paola De Padova,<sup>a</sup> Carlo Ottaviani,<sup>a</sup> Sofia Caretto,<sup>b</sup> Angelo De Paolis,<sup>b</sup> Paola Prete.<sup>c,\*</sup>

In 2009 Kojima et al.,<sup>1</sup> reported the first hybrid organometal halide perovskites as visible-light sensitizers for photovoltaic cells. They studied the photovoltaic function of the organic-inorganic lead halide perovskite compounds methylammonium ( $\text{CH}_3\text{NH}_3^+$ , MA)  $\text{PbBr}_3$  and  $\text{MAPbI}_3$  as visible-light sensitizers in photoelectrochemical cells, opening a fruitful worldwide field of research. Halide perovskites, generally are represented as  $\text{AMX}_3$ , where A is an alkyl ammonium cation, such as MA, dimethyl-ammonium ( $(\text{CH}_3)_2\text{NH}^+$ , DMA), formamidinium ( $\text{CH}_3(\text{NH}_2)_2^+$ , FA), or Cs; M is  $\text{Pb}^{2+}$ , and X is a halide ion ( $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ).

Although the efficiency of hybrid perovskite solar cells is today competitive with Si, achieving power conversion efficiencies exceeding 23%,<sup>2</sup> some drawbacks regarding these systems are the environmental toxicity of water-soluble Pb, and their air/humidity stability. In order to solve these disadvantages a fervent research is currently going on, and in 2016, materials with complete replacement of lead in the perovskite structure, by other cations such as nontoxic  $\text{Ag}^+$  and  $\text{Bi}^{3+}$ , leading to the double perovskite  $\text{Cs}_2\text{AgBiBr}_6(\text{Cl}_6)$  structure,<sup>3,4</sup> were synthesized. Amazingly, very soon, in 2019, these new perovskites exhibited increasing power conversion efficiencies up to 2.5%.<sup>5-7</sup>

This work aims to present the HELFO (High Efficiency Lead-Free Perovskite Solar cells for indoor-outdoor Applications) project and the preliminary results on fully-inorganic lead-free  $\text{Cs}_2\text{AgBiBr}_6(\text{Cl}_6)$  double-cations perovskites. HELFO is a challenging interdisciplinary project, which involves three Institutions of CNR from both fundamental condensed matter (CNR-ISM-Roma) and applied physics (CNR-IMM-Lecce) fields up to plant biology (CNR-ISPA-Lecce) field, aiming to combine different competences intrinsically belonging to CNR. Semitransparent lead-free  $\text{Cs}_2\text{AgBiBr}_6$  and  $\text{Cs}_2\text{AgBiCl}_6$  perovskites are synthesized by using both in-situ ultra-high vacuum molecular beam epitaxy deposition and ex-situ solution-processing, and investigated by XRD, SEM/AES/PL and UV-Visible optical techniques. Furthermore, these materials will be applied in green-houses for investigating, indoor-and-outdoor, the influence of solar light radiation shielding, through the  $\text{Cs}_2\text{AgBiBr}_6(\text{Cl}_6)$  perovskites, on seed germination and plant metabolic profiles at a molecular level of *Artemisia annua* and *Solanum lycopersicum* plant species. Photovoltaic devices will be assembled by matching the  $\text{Cs}_2\text{AgBiBr}_6(\text{Cl}_6)$  perovskites-based band alignment, with both electron- and hole-transporting layers.

**Acknowledgements.** This work has been funded through the Research Project @CNR “High Efficiency Lead-Free Perovskite Solar cells for indoor-outdoor Applications (HELFO)”.

## References

- 1 A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, *Journal of the American Chemical Society* 131 (17) (2009) 6050–6051.
- 2 D. Zhao, C. Wang, Z. Song, Y. Yu, C. Chen, X. Zhao, K. Zhu, Y. Yan, Four-terminal all-perovskite tandem solar cells achieving power conversion efficiencies exceeding 23%, *ACS Energy Letters* 3 (2) (2018) 305–306.
- 3 E. T. McClure, M. R. Ball, W. Windl, P. M. Woodward,  $\text{Cs}_2\text{AgBiX}_6$  (x = br, cl): new visible light absorbing, lead-free halide perovskite semiconductors, *Chemistry of Materials* 28 (5) (2016) 1348–1354.
- 4 A. H. Slavney, T. Hu, A. M. Lindenberg, H. I. Karunadasa, A bismuth-halide double perovskite with long carrier

<sup>a</sup> CNR - Istituto di Struttura della Materia, Roma, Italy

<sup>b</sup> CNR - Istituto di Scienze delle Produzioni Alimentari, Lecce, Italy

<sup>c</sup> CNR - Istituto per la Microelettronica e Microsistemi, Lecce, Italy

Creative Commons Attribution - Non commerciale - Condividi allo stesso modo 4.0 Internazionale

† poster at 4<sup>th</sup> Joint AIC-SILS Conference, (Trieste) 12-15/09/2022

- recombination lifetime for photovoltaic applications, *Journal of the American chemical society* 138 (7) (2016) 2138–2141.
- 5 M. R. Filip, S. Hillman, A. A. Haghghirad, H. J. Snaith, F. Giustino, Band gaps of the lead-free halide double perovskites  $\text{Cs}_2\text{BiAgCl}_6$  and  $\text{Cs}_2\text{BiAgBr}_6$  from theory and experiment, *The journal of physical chemistry letters* 7 (13) (2016) 2579–2585.
- 6 F. Igbari, R. Wang, Z.-K. Wang, X.-J. Ma, Q. Wang, K.-L. Wang, Y. Zhang, L.-S. Liao, Y. Yang, Composition stoichiometry of  $\text{Cs}_2\text{AgBiBr}_6$  films for highly efficient lead-free perovskite solar cells, *Nano letters* 19 (3) (2019) 2066–2073.
- 7 E. Greul, M. L. Petrus, A. Binek, P. Docampo, T. Bein, Highly stable, phase pure  $\text{Cs}_2\text{AgBiBr}_6$  double perovskite thin films for optoelectronic applications, *Journal of Materials Chemistry A* 5 (37) (2017) 19972–19981.