

Chemical solutions for the working and environmental issues in mixed organic-inorganic perovskites: a theoretical analysis

Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656 & CREST-JST, 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan.

○ Giacomo Giorgi, Koichi Yamashita

[Introduction] Mixed organic-inorganic halide perovskites (OIHP) with formula ABX_3 , (A=organic cation; B=Pb, Sn, Ge; X=halide) [1] are a class of revolutionary materials that are nowadays changing the scenario of photovoltaics. They are characterized by very unique features, like the very long diffusion lengths of the carriers [2, 3] along with their ambipolar nature [4] that have lead to unprecedented photoconversion efficiencies (PCEs) when employed as light harvesters in solar cells. Most of the obtained results focus on methylammonium ion usage because $MAPbX_3$ shows high compatibility with solution-based processing, good efficiencies because of its high absorption coefficient, and a value for the band gap that matches the optimal value for single-junction solar cells (1.1–1.4 eV). Different procedures are followed in order to assemble such perovskite based devices, among the others, the sensitization [5] and the thin-film heterojunction architecture [6]. Anyway, regardless the architecture, the final device is always affected by a noticeable hysteresis in the J - V efficiency measurement curves that depends on several parameters (i.e., scan rate and perovskite deposition process play a primary role [7]). Despite efforts spent to understand the origin of this drawback, no conclusive reasons for this detrimental behaviour have been provided so far. A further not secondary issue associated to the usage of such perovskites in PV is that the most performing ones contain lead, their usage representing a serious environmental risk.

[Results and Discussion] We have performed an *ab-initio* campaign of calculations [8] to predict possible chemical solutions to the two issues based on the replacement of the two cations, the organic (A-site) and the inorganic (B-site). In the former case we considered other cations, i.e. guanidinium (GA) and formamidinium (FA) (See Fig. 1) and their intermediate alloys, that being characterized by a reduced dipole moment result less sensitive to any applied external bias, and thus able to (at least partly) alleviate the devices from the hysteresis.

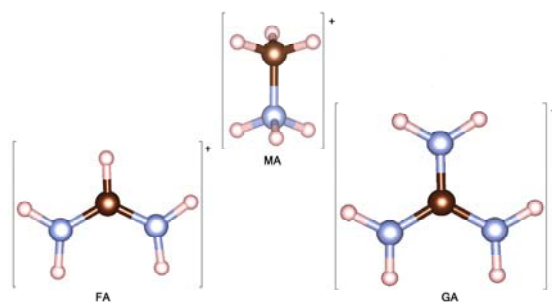


Figure 1: Methylammonium (MA, top), Formamidinium (FA, bottom left), Guanidinium (GA, bottom right) cations.

Concerning the latter, we have considered the possible reduction of Pb concentration as possible alternative to reduce the environmental risks.

We here discuss the role of several A- and B-site cations in mixed organic-inorganic perovskites, mainly focusing on the structural and electronic properties of the resulting species and on their potential applicability in PV devices.

- [1] A. Kojima *et al.*, *J. Am. Chem. Soc.*, 2009, 131, 6050.
- [2] G. Xing *et al.*, *Science* 2013, 342, 344.
- [3] S. D. Stranks *et al.*, *Science* 2013, 342, 341.
- [4] G. Giorgi & K. Yamashita, *J. Mater. Chem. A*, 2015, 3, 8981.
- [5] H.-S. Kim *et al.*, *Sci. Rep.* 2012, 2, 591. J. Burschka *et al.*, *Nature* 2013, 499, 316
- [6] M. Liu *et al.* *Nature*, 2013, 501, 395.
- [7] see among the others: (a) H. J. Snaith, *et al.*, *J. Phys. Chem. Lett.*, 2014, 5, 1511. (b) R. S. Sanchez *et al.*, *J. Phys. Chem. Lett.*, 2014, 5, 2357.
- [8] <http://www.vasp.at>