

Perovskite solar cells - in pursuit of their stability

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Organic-inorganic perovskites are regarded among the most promising materials for the next-generation solar cells. Over the last 5 years, a number of breakthroughs have led to a rapid evolution of this technology and high efficiencies. At 22.7% of efficiency, they are comparable to state-of-the-art inorganic photovoltaics, such as CdTe or crystalline silicon, technologies that have been around for decades[1]. Perovskite layers can be fabricated using a relatively easy and low-cost method and on flexible substrates, which opens the possibility for a wide range of applications. However, there are still significant challenges; The lack of the stability being the most important that need to be overcome for the practical use and commercialization of this technology. State-of-the-art perovskite solar cells are based on methylammonium (CH₃NH₃) lead iodide (MAPbI₃). It has been observed that they undergo a rapid degradation when exposed to oxygen and light. Recent experimental studies supported by *ab initio* simulations have shown that oxygen diffusion into perovskite is accompanied by a photo-induced formation of the highly reactive superoxide (O₂⁻). This is critical for the degradation process, and the preferential site of such a form of oxygen in a perovskite lattice is iodine vacancy[2]. On the other hand, it has been reported that perovskite films are more stable if precursors contain chlorine besides of iodine[3], but the origin of this superior stability remains unclear.

We prepared and studied a series of 4 perovskite samples based on MAI, PbI₂, PbCl₂, with different relative amount of iodine and chlorine, starting from a pure MAPbI₃, through mixed materials with a PbI₂ to PbCl₂ ratio in solution 2:1, 1:1 and 1:2, respectively. Scanning electron microscopy measurements revealed that for the lowest concentrations of chlorine homogenous films were obtained, with an uniform distribution of all elements, in particular I and Cl. For a higher Cl content, a phase separation into MAPbI₃ and MAPbCl₃ was observed, suggesting, contrary to common belief, that it is not possible to obtain mixed MAPbI_{3-x}Cl_x in a whole range of I and Cl compositions. This is most likely due to large difference in I and Cl ion radii. Electron diffraction and high resolution transmission electron microscope imaging confirmed perovskite crystallization after annealing at 100⁰C at atmospheric pressure, as well as at room temperature under high vacuum conditions (~10⁻⁴ Pa). X-ray photoelectron spectroscopy analysis helped to identify the optimal chlorine content that lower an oxygen diffusion into perovskite layer. It seems possible that such a small amount of chlorine can accommodate into MAPbI₃ lattice substituting in iodine sites. As a result there is no phase separation, and more importantly, some iodine vacancies are “blocked” by chlorine, what makes oxygen diffusion less efficient and boosts stability of perovskite layers.

The research was financed by the National Centre for Research and Development (Poland) under the project TECHMATSTRATEG1/347431/14/NCBR/2018.

[1] <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>, [2] N. Aristidou et al., Nature Comm. 8, 15218 (2017), [3] S. Colella et al., Chem. Mater. 25, 4613 (2013)