

The importance of proton chemistry in halide perovskites.

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The widely used Methylammonium (MA⁺) and Formamidinium (FA⁺) cations are relatively acidic compounds, with the potential to dissociate in the halide perovskites, giving a proton (H⁺) and the corresponding ammine. Despite the fact that they were considered not to do so, I will bring new evidence that the dissociation does happen and that H⁺ can migrate, associate with eventual water molecules internalized in the perovskite, be absorbed by basic hole transporting layers and other related phenomena. I will also comment on the chemistry of H⁺ in solution and show how it influences the final state of a perovskite layer after the coating.

As it happens in general, in the perovskites the chemistry of protons is reversible and is characterized by chemical equilibria, which are modified by a large number of factors. I will provide indications on how temperature, illumination intensity, electronic doping of the perovskite material and the presence of other molecules pushes the acid-base equilibrium towards the dissociation or the association. The complexity of these equilibria is at the base of a series of phenomena that have been observed in halide perovskites like fast ion-migration, light-soaking and reversible damage repair (self-healing).

In this talk, I will provide proof of the migration of protons in the perovskites as obtained by exchange of H⁺ with deuterons (D⁺) and discuss their diffusion coefficient in halide perovskite single crystals. Through optical microscopy (confocal, hyperspectral, fluorescence lifetime imaging spectroscopy), I will also provide proof on how the proton chemistry influences the photoluminescence of the perovskites showing how proton deficient perovskites have better optoelectronic properties. In particular, I will analyze how the positive effects of methylamine treatment in the perovskites can be related to proton chemistry and how light might locally originate methylamine causing the effect of light soaking in the perovskites. I will also show that H⁺ acts as an oxidizer when the perovskite is put into contact with metals and its influence should be considered when depositing contacts directly on the perovskite material.

I will also analyze the chemistry of protons in the perovskite precursor solutions showing how their presence influences which particular lead complexes are actually in solution during crystallization. I will show how the electrochemical potential of the precursor solution (and therefore of the perovskite material) is partially determined by the presence of protons with consequences on the quality and quantity of defects in the perovskite materials.

To conclude, the aim of this talk is to provide the listener a wide view on proton chemistry in halide perovskites providing the theoretical tools to understand the influences that proton chemistry has on the optoelectronic properties and the stability of the perovskites. This talk will be rich in chemical knowledge but it will be adapted to an audience working on halide perovskite devices with more engineering or physics background.