Probing Ferroelectricity in Lead Halide Perovskites Using Second Harmonic Generation Microscopy

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Crystalline materials are essential components of modern technology thanks to the specific properties (conductivity, piezoelectricity, birefringence, tensile strength, etc.) that depend on their periodic structure. Halide perovskites are solution-processable semiconductors that are widely studied as promising materials for building solar cells with high PCE, but their electro-optic properties make them also good candidates in other applications like LEDs, lasers and sensors.

Our research focuses on hybrid organic-inorganic metal halide perovskites (MHPs) and how to achieve control over their crystalline phase, as these materials' electro-optic properties strictly depend on their lattice structure. By tuning the experimental conditions (type of synthesis, solvent, temperature, capping agents, etc.) it is possible to favour the formation of specific polymorphs and to control the size and shape of the crystals [1]. In particular, we are interested in studying the presence of ferroelectricity (FE) in MHPs, which is still a matter of debate, and in the characterization of the crystal phase. We want not only to finally demonstrate the presence or absence of FE, but also to better understand how to induce or avoid its presence. For example, by doping the A- or X-sites of the typical ABX_3 structures (in our case A= methylammonium, formamidinium; B= Pb^{2+}; X= Cl^-, Br^-, I^-) of MHPs, non-centrosymmetry can be favored and the presence of FE and nonlinear optical properties potentially triggered [2,3].
The primary technique used to study FE is second harmonic generation (SHG) microscopy, which allows to characterize the point group symmetry in general and FE in particular, but at the same time to perform structural imaging of MHPs [4]. In essence, polarization controlled SHG microscopy consents to understand if the crystalline materials belong to one of the 10 polar point groups [5]. By combining this technique with other nonlinear optical probes, such as third harmonic generation and multiphoton microscopy, it's possible to obtain a structural characterization by optical means. The use of other techniques, like XRD, SEM, AFM, absorption and emission spectroscopies will help us to establish how the electro-optic properties relate to the crystal structure and to the presence of FE, so it will allow to determine how to better exploit MHPs in designing increasingly efficient devices.

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