

## Abstract

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**Thesis Title:** Structure, Dynamics and Optical Properties of Organic-Inorganic Hybrid Perovskites

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Organic-inorganic hybrid perovskites have emerged as promising photovoltaic materials in the last few years, with the possibility of easy, solution synthesis. In this thesis, we have investigated some intrinsic material properties of the hybrid lead halide perovskites in an attempt to understand factors responsible for the excellent photovoltaic behaviour. The presence of the  $(\text{CH}_3\text{NH}_3)^+$  or methylammonium (MA) ion with a permanent dipole moment in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  gives rise to the possibility of ferroelectricity. In view of the continued controversy concerning the ferroelectric/non-ferroelectric nature of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , we have addressed the more basic question of whether it is polar or not. We have measured the Second Harmonic Generation (SHG) efficiency, which is a sensitive probe to the presence of centre of inversion in the system and show that SHG efficiency of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , if non-zero, is below the detection limit, strongly indicative of a nonpolar structure; consistent with P-E loop and single crystal XRD measurements. This nonpolar structure is a time-averaged description of the MA dipoles, consistent with many different dynamic behaviours, such as MA units rotating freely or in a correlated manner or frozen randomly. A comparison of temperature dependent dielectric constants of  $\text{MAPbX}_3$  and  $\text{CsPbBr}_3$  (without dipolar units) suggests that the  $\text{MA}^+$  dipoles are rotating freely with time scales much faster than  $\mu\text{s}$ . *Ab initio* molecular dynamics simulations show that these dipoles are randomly oriented with no net dipole moment when averaged over even a few unit cells, with a rotational time scale of  $\sim 7$  ps at 300 K for these dipoles. Further, using pump-probe SHG efficiency measurements in  $\text{MAPbX}_3$  we have ruled out the possibility of a transient ferroelectric state in presence of photoexcitation. Further, we have carried out detailed investigation of dielectric properties of a larger class of hybrid lead halide perovskites, specifically the formamidinium lead halides ( $\text{FAPbX}_3$ ). Although the behaviour of dielectric constants of  $\text{FAPbCl}_3$  and  $\text{FAPbBr}_3$  in the low temperature resemble that of the  $\text{MAPbX}_3$  system, the absence of its strong temperature dependence in contrast to  $\text{MAPbX}_3$  lead us to conclude that the formamidinium (FA) dipoles are frozen in a glassy state. This is supported by the temperature dependent single crystal XRD results, which reveal disordered FA ions in the room temperature as well as at 100 K.

Exciton binding energy is an important parameter in a photovoltaic material since it determines whether the mechanism is dominated by free charge carriers or excitons at room temperature. The exciton binding energy reported for  $\text{MAPbI}_3$  in the literature varies over a wide range of values. From careful experiments to measure temperature dependent PL spectra of  $\text{MAPbI}_3$  and  $\text{MAPbBr}_3$  we have estimated the exciton binding energy. PL intensity of  $\text{MAPbBr}_3$  films is observed to be sensitive to vacuum, environmental conditions and illumination. Since the penetration depth of the excitation wavelength, 405 nm, is very small in the sample, most part of the PL intensity observed can be considered to be from the near-surface region of the sample. We propose that defects are created at the surface of  $\text{MAPbBr}_3$  by the evaporative loss of  $\text{MABr}$  due to dynamic pumping. Considering all these factors, we have obtained the binding energy of  $\text{MAPbBr}_3$  film to be 79 meV, which corresponds to the intrinsic nature of the surface of  $\text{MAPbBr}_3$  film in vacuum.