First-principles calculation of bulk photovoltaic effect in CH₃NH₃PbI₃ and CH₃NH₃PbI_{3-x}Cl_x

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The power conversion efficiency (PCE) of organometallic halide perovskites photovoltaic has soared from around 9% to 20% within two years.^{1,2} A great deal of studies have been done to understand the reason of such high efficiency. Methylammonium lead halide perovskite (MAPbI₃) as the one with relatively high PCE has been studied intensively. This material has the perovskite structure ABX_3 (X=Cl, Br, I) with corner-sharing PbI_3 octahedral cages forming the inorganic frame. Small organic molecule methylammonium (MA) occupies A site to balance the charge. Besides its outstanding properties such as appropriate band gap, high light absorption coefficient, fast electron-hole pair generation and long carrier life time, MAPbI₃ shows very high open-circuit voltage.³ Various *I/V* hysteresis loops are also observed. Since bulk photovoltaic effect (BPVE) can provide high open-circuit voltage, it is possible that the ferroelectricity and BPVE in this material play an important role. In this work, we focus on its ferroelectric properties induced by different orientations of organic molecules. Shift current as the dominant mechanism for BPVE has been calculated for this material. By using Density Function Theory, we found that for the configurations with dipole moments aligned in parallel, the inorganic PbI₃ frame are more significantly distorted than configurations with near net zero dipole. And this distorted configuration also yields a larger shift current response. This can further explain the measured high open-circuit voltage as well as I/V hysteresis. Furthermore, we explore the effect of Cl substitution of I, as MAPbI_{3-x}Cl_x has been observed to have the highest PCE. We find that Cl substitution at the equatorial site induces a larger response than does substitution at the apical site. But its effect to the total polarization becomes less significant.

Acknowledgements

The authors were supported by the Department of Energy Office of Basic Energy Sciences, the Office of Naval Research, the Roy & Diana Vagelos Scholars Program in the Molecular Life Sciences, and the National Science Foundation. Computational support was provided by the High-Performance Computing Modernization Office of the Department of Defense and the National Energy Research Scientific Computing Center.

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