Importance of molecular dipole alignment and surface compensation in *P-V* hysteresis of $MAPbBr_3$(001)

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Metalorganic halide perovskites attracted extraordinary attention as low-cost photovoltaic materials, due to their rapid increase of the conversion efficiency within a few years only. However, it is unclear to what degree the reported conversion efficiencies extracted from current density versus voltage (*J-V*) curves are accurate, since *J-V* hystereses are known to make "bad cells look good". It is thus of paramount importance to unravel the physical mechanisms inducing hysteresis, but no consent has been achieved yet. We demonstrate the presence of a hysteresis in tunneling spectra acquired at 4.3 K on cleaved MA-Br terminated (001) surfaces of $MAPbBr_3$ single crystals. Simulations of the tunneling spectra reveal an underlying polarization-voltage (*P-V*) hysteresis, caused by an interplay of field-induced rotation and alignment of the MA molecules, stabilized by dipole-dipole interactions, and an ion-lattice relaxation. The field-induced, ferroelectric polarization in the bulk is compensated at the surface by an oppositely oriented, counteracting out-of-plane polarization component of the otherwise in-plane antiferroelectrically ordered surface dipole arrangement. This suggests that at low temperatures only ferroelectric effects govern the hysteresis in $MAPbBr_3$ and its related compounds, whereas at high temperatures thermally activated processes such as ion migration and charge trapping-detrapping dominate.[1]

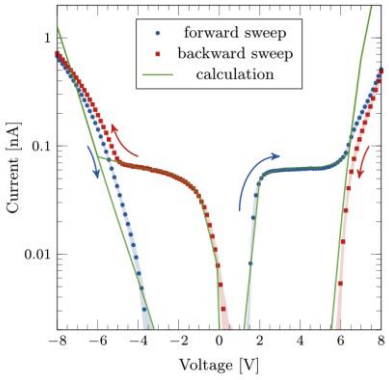

Figure 1 Scanning tunneling spectroscopy of the cleaved $MAPbBr_3$ single crystal (001) surface

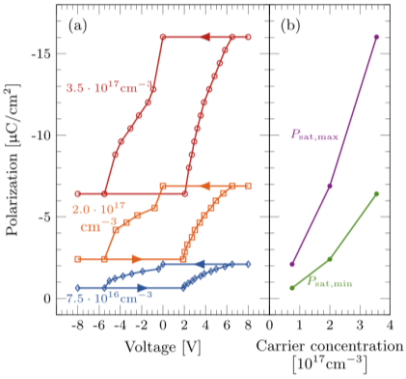

Figure 2 Extracted spontaneous polarization vs. applied voltage (*P-V*) hysteresis, assuming different carrier concentrations

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