Rashba effect in halide-perovskite nanocrystal and bulk structures

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During the past few years, hybrid organic-inorganic perovskites have become one of the most promising materials in the photovoltaic field, when in less than four years, the efficiency of perovskite solar cells has quickly leapt from 3.81% to > 22.0%, rivaling the long-established inorganic photovoltaics, such as polycrystalline silicon (21.3%), cadmium telluride (22.1%) and copper indium gallium selenide (22.3%). The best performance was found in compounds with general chemical formula, ABX_3, when A is either organic or inorganic cation, like methylammonium (MA^+), formamidinium (FA^+) or Cs^+, B is a bivalent metal cation, such as Pb^{2+} and X is a halide, Cl^-, Br^-, or I^-. The amazing performance of ABX_3 perovskites is attributed to their direct band gap, high absorption coefficient, long carrier diffusion length, hot carrier bottleneck, an ambipolar carrier transport property and low production costs. A direct band gap and high absorption coefficient enables the full use of solar spectrum, while long carrier diffusion length guarantees complete collection of photo-generated carriers. Perovskites have also been demonstrated as suitable materials for detecting visible light, x-ray, or γ-ray. While remarkable observations were reported in recent years, there are still debated regarding the origin of the long diffusion length in such heterogeneous materials.

The present work describes a research that explored the band-edge properties of $CsPbBr_3$ perovskites, to elucidate the electronic origin for some of the unique phenomena. This compound was selected for the study due to its relative chemical and photochemical stability. The samples were supplied by the group of Prof. Maksym Kovelenko at ETH. The study focused on the investigation of single colloidal nanocrystals (NCs) as well as on bulk structures. The band-edge properties were examined by recording the linearly and circularly polarized micro-photoluminescence spectra in the presence of an external magnetic field up to 9 Tesla. The high resolution gained in the measure of a single NC enabled resolving fine split in the exciton emission at zero magnetic field, which grew gradually with the increase of the field strength. Representative example is shown in Figure 1. Surprisingly, the split energy grew nonlinearly with the increase of the magnetic field, a fact that indicated a deviation from a linear and from second order corrected Zeeman effects. Theoretical simulations, carried out by a collaborative work with the group of Prof. Andrew Rappe at University of Pennsylvania, revealed the existence of a Rashba effect predominantly at field strength < 4 Tesla, explaining the non-linear behavior. Further on, the circular polarized measurement showed an asymmetry between the $\sigma\pm$ components (see Figure 2), suggesting a partial mixing of one of them with higher electronic states. This point should be further explored in order to gain better understanding in the near future. The Rashba effect emanates in cases experiencing lack or breakage of inversion of symmetry and existence of spin-orbit coupling, both conditions presumably existing in the Perovskites materials, where the small cation A liability induces a crystal distortion and consequent inversion symmetry breaking.

Current observations on bulk $CsPbBr_3$ single crystal reflected similar observations for those viewed in analogous NCs, particularly when examined along unique crystallographic direction. Preliminary observations are shown in Figure 3. In addition, the observations found in the bulk samples indicate a plausible contribution of cubic Rashba effect, which may indicate a mixing of high lying states to the band-edge properties and may support also the asymmetry in the $\sigma\pm$ emission band patterns as was found in a single NC. This open question will be further investigated in the coming months. In any event, the Rashba effect split the band edge extrema to a $k\neq0$ a Brillouin point with momentum forbidden transitions, thus, extending the carriers lifetime at the excited state with a large benefit in photovoltaic devices and in x-ray, or γ-ray detectors.

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