Bypassing the Soft Nature of Photovoltaic Halide-Perovskites to Prove its Ferroelectricity

Yevgeny Rakita[(1)]*, Omri Bar-Elli[(2)], Elena Meirzadeh[(1)], Hadar Kaslasi[(1)], Yagel Peleg[(1)], Gary Hodes[(1)], Igor Lubomirsky[(1)], Dan Oron[(2)], David Ehre[(1)]*, David Cahen[(1)]
Weizmann institute of Science, [(1)]Department of Materials and Interfaces and [(2)]Physics of Complex Systems, Rehovot, Israel, 7610001; *yevgeny.rakita@weizmann.ac.il ; david.ehre@weizmann.ac.il

Perovskites are a wide-ranging family of materials that often serve in switches, solid-state memory devices and other electronic components, and owe their properties to a characteristic crystalline structure. Until recently, the most commonly studied and used materials in this family were the hard and stable oxide perovskites. **Ferroelectricity** (the ability to change the spontaneous polarization in a material by an external electric field), which is well known for oxide perovskites, has been suggested as a possible reason for the outstanding solar-to-electrical energy conversion of halide perovskites - especially methylammonium lead iodide and bromide (abbr. $MAPbI_3$ and $MAPbBr_3$). Low carrier recombination rate, high voltage efficiencies and an efficient exciton separation are some of the possible benefits of ferroelectric domains to photovoltaic performance.

The relatively weaker interatomic bond nature of these halide perovskites[1] (in contrast to common ferroelectric materials) made the simple task of proving ferroelectricity by the straight-forward method of polarization measurement as a function of an applied DC electric field not so simple. The challenge for proving the existence of ferroelectricity occupied the scientific community for a couple of years with contradicting reports.

As polarity is a prerequisite condition for ferroelectricity, using the periodic temperature change (Chynoweth) method[2] under different surrounding temperature conditions, we show that the cubic phases of $MAPbI_3$ (>330K) and $MAPbBr_3$ (>236K) phase are clearly non-polar, which exclude any possible ferroelectric activity at these phases. However, the room-temperature (tetragonal $MAPbI_3$; 330K) phase shows clear pyroelectricity, which proves the **polar** nature of $MAPbI_3$ at room-temperature. Second harmonic generation - a proof for non-centrosymmetry that is a prerequisite condition for polarity - has been found to be consistent with the polarity results. When trying to find a final proof for ferroelectricity - a direct polarization measurement – it was found that **leakage** currents are very dominant and, therefore, must be taken into account when analyzing the polarization response, unlike the commonly analyzed capacitive currents. Together with cooling down to -70^{o}C (still at the tetragonal phase), to avoid decomposition of

1. Rakita et al. ; *MRS Comunications*, **5**, 623 (2015)
2. Lubomirsky, I. & Stafsudd, O. ; *Rev. Sci. Instrum.* **83,** 051101 (2012).
3. Rakita, Y, et al.; *PNAS* , E5504-E5512, (2017), ; doi: 10.1073/pnas.1702429114

the material under the applied electric field, we could clearly detect ferroelectric polarization response.[3]

1. Rakita et al. ; *MRS Comunications*, **5**, 623 (2015)
2. Lubomirsky, I. & Stafsudd, O. ; *Rev. Sci. Instrum.* **83,** 051101 (2012).
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