

## Saulės elementų metilamonio švino halogenidų sugėriklių dielektrinis atsakas

### Dielectric Response of the Methylammonium Lead Halide Solar Cell Absorbers

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Hybrid organic–inorganic perovskites have recently attracted overwhelming attention due to their excellent photovoltaic performance yielding efficiencies well exceeding 20%. This has been related to properties such as long charge carrier lifetime, the exceptionally large diffusion length, large absorption coefficient, high carrier mobilities, large open-circuit voltages, and direct band gap. The organo-lead-trihalide perovskite compounds,  $\text{CH}_3\text{NH}_3\text{PbX}_3$ , are the forerunners in efficiency.

Among the most intriguing properties of  $\text{MAPbI}_3$  are the high charge carrier life times (up to 3 ms) and the diffusion length of up to hundreds of micrometers in single crystals, which are much longer than those in high-purity crystalline organic semiconductors. One of the reasons is the fast dissociation of excitons into free charge carrier pairs. It was argued that the low exciton binding energy is due to the relatively large dielectric permittivity at room temperature. The excitonic binding becomes significant only below the tetragonal-to-orthorhombic phase transition due to lowering of both dielectric permittivity and temperature. The long electron/hole diffusion length was attributed to rather weak trapping. Direct electron–hole recombination dominates over the indirect trap assisted decay regime associated with shallow levels of the defect states in the band gap.

The collective motion of the MA cations has been proposed to screen the electron–hole Coulomb potential and promote dissociation of excitons into free carriers, as well as to inhibit their recombination. It has further been suggested that the interaction between charge carriers and MA dipoles can result in the formation of polarons showing much reduced scattering by defects or phonons compared to free electrons or holes. Another mechanism is the interaction of defects with MA cations, which possess  $C_{3v}$  symmetry and their proper dipole moment. When the potential barrier for MA dipole rotation is smaller than the energy gain associated with the dipole trap interaction, the rearrangement of MA dipoles in the vicinity of defects will reduce the defect trapping cross section.

Although crucial information about ordering and dipolar dynamics of  $\text{MAPbX}_3$  can be obtained from dielectric spectroscopy, if measured across broad frequency and temperature ranges, only limited data exist. Earlier performed dielectric measurements for only a few discrete frequencies in the gigahertz range.

Similarly, characterization of thin polycrystalline films at frequencies below 100 kHz revealed an increase of dielectric permittivity at the decreasing frequency related to ionic transport and charge separation at grain boundaries. It have been reported dielectric measurements in the optical range (above 400 THz), however the frequency range between 1 MHz and 100 GHz remains unexplored.

We address the key role of the dynamical nature of MA dipoles by combining large frequency range and temperature-dependent dielectric measurements with ultrasonic. To do that, organolead trihalide perovskite samples,  $\text{CH}_3\text{NH}_3\text{PbX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ), were synthesized in two steps according to the procedure reported by Im et al. with small modifications. The phase purity and crystalline structure of the samples were analyzed by powder XRD using a Bruker Siemens D5000 diffractometer operating in reflection mode with  $\text{Cu K}_\alpha$  radiation. Relatively large crystallites of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  were chosen. Since the crystallites of the chloride compositions were too small, they were pressed to pellets and sintered at 120 °C for 2 h. Opposite faces of the samples were electroded with cold curing silver paste (Ferro GmbH).

Dielectric measurements were performed between temperatures 100 and 300 K and frequencies  $10^2$ – $10^{11}$  Hz. For frequencies from  $10^2$  to  $10^6$  Hz the complex impedance was measured using a HP 4284A precision LCR meter. For the higher frequency band ( $10^6$ – $10^9$  Hz) the samples were placed at the end of a coaxial line. Reflection and phase were measured using an Agilent 8714ET vector network analyzer. For highest frequencies, dielectric rods were made and measured in the rectangular waveguide system, then reflection and transmission were measured using an Elmika scalar network analyser R2400. All measurements were performed at a rate of  $1 \text{ K min}^{-1}$ .

We show that a sufficiently high dielectric constant exists across the entire frequency range allowing for efficient screening of charged entities, that is, carriers and defects. This is the fundamental effect facilitating the diffusion of photogenerated carriers.