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Large polaron evidence in the ultrafast THz response of Lead-Halide Perovskites

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Abstract. We unveil the large polaron fingerprints in the transient THz dielectric response of lead-halide perovskites. We clarify the mechanism underlying the physics of charge transport of full-inorganic lead-halide perovskites by combining ultrafast Thz spectroscopy with DFT calculations.

1 Introduction

Hybrid Organic-Inorganic Perovskites (HOIPs) represent a promising platform for emerging optoelectronics devices due to their exceptional physical properties. Although their low carrier mobility and the presence of static and dynamic disorder, HOIPs behave as defect-free semiconductors with long carrier lifetime and high diffusion length, hence promoting them as reliable candidates, for instance, for high efficiency solar cells [1].

Intriguingly, the formation of large polaron has been proposed as a possible explanation for the exceptional HOIPs dielectric response combined to their peculiar structure composed by a lead halide cage (PbX_3) and a disordered inorganic/organic cation sublattice (A^+) [2, 3]. To explain the relative moderate mobility of this class of materials, Zhu and Podzorov have proposed the presence of the large polarons formed due to the dielectric electron-phonon coupling combined with the light effective masses for bare carriers [4, 5]. Recently, Miyata *et al.* have provided a direct time domain view of phonon dynamics in the $CH_3NH_3PbBr_3$ and $CsPbBr_3$ single crystals using time-resolved optical Kerr effect

spectroscopy and demonstrated a phonon dressing of the photo-generated species in the fs-ps time regime [6].

To unveil the presence of large polarons, we studied all-inorganic $CsPbBr_3$ nanocrystals by means of Optical-Pump-THz probe spectroscopy that is capable to investigate excitations in the few meV range such as the carrier-lattice coupling.

2 Results and Discussion

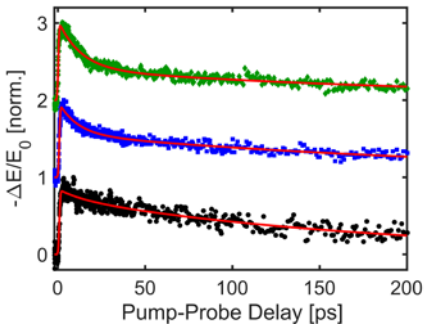

Figure 1 Normalized ΔE/E signal at 160, 80 and 20 μJ/cm^2 (green diamonds, blue squares and black circle respectively) together with the biexponential curves (continuous red line).

We excite the sample with a 400-nm, 25-fs 1-kHz laser pulses focused on the sample with a spot size diameter of 3 mm at different fluences, from 10 to 160 μJ/cm^2.

Figure 1 reports the transient electric field $\Delta E(t_p,0)$ at 20, 80 and 160 μJ/cm^2 respectively, where $\Delta E(t_p,0)$ is the change induced in the transmitted THz field detected at different pump-probe delays t_p in correspondence of the peak of the THz waveform. The dynamics probed up to 200 ps show an initial fast decay with a time constant of about τ_2=15 ps and a slower one of hundreds of ps. The slow component falls well in the band-to-band carrier recombination regime as probed by photoluminescence measurements and often reported in literature [7]. The fast decay component becomes dominant when the initial carrier density N_0 is larger than $0.5 \cdot 10^{18}$/cm^3. At these densities, traps states are saturated and many-body processes start to play a role, therefore we assign this fast dynamic to the increase of fast free carrier recombination and three-body processes.

To more deeply investigate the carriers transport mechanism in $CsPbBr_3$ NCs, we studied the frequency-resolved optical conductivity. Transient spectra at different pump probe delays reveal resonances that reflect the presence of electron-phonon coupling following the photoexcitation. Remarkably, the transient conductivity reported in Figure 2a) shows three main peaks in the 0.4-1.9 THz (15-60 cm^{-1}) region that bare almost the whole intensity at 3ps. Theory predicts that the formation of a large polaron is expected for $CsPbBr^-_3$ NCs after the carrier's photo-injection due to the coupling with lattice IR modes. The largest intensity is predicted for four Pb-Br-Pb bending modes at 0.75, 0.84, 1.35 and 1.88 Thz [6] that finely matches the experimental features (0.81, 1.26 and 1.74 THz). Figure 2b) shows the real part of the Lorentzian curves used for the fitting procedure. Remarkably, a redshift affects the curves at 200 ps. We rationalize this observation in terms of lattice shrinking and expansion: once the photoexcitation creates a hole in the top of the valence band, which is a Pb-Br anti-bonding, then the Pb-Br bonds shorten and the lattice shrinks with the resulting phonons blueshift; as the injected charge starts to relax, then the lattice can expand again with the consequent stretch of the Pb-Br bonds and phonons softening.

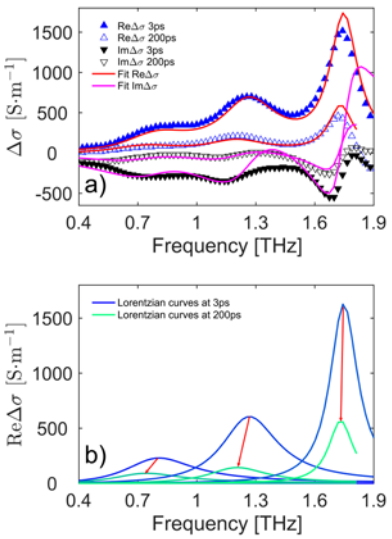

Figure 2 a) Drude-Lorentz fit of the optical conductivity at 3 (filled blue triangles and black down triangles) and at 200 ps (empty blue triangles and black down triangles); b) real part of the Lorentzian curves at 3 and 200 ps (blue and green lines respectively). Red arrows indicate the redshift of each component.

3 Conclusions

By combining Ultrafast THz spectroscopy with density-functional theory calculations we demonstrated the presence of large polaron in all-inorganic lead-halide Perovskites. We observed the fingerprints of the coupling between the photoinjected charge and the bending modes of the deformed PbBr lattice in the pump-induced conductivity spectra. Our findings agree with the recent results present in the literature [6] and explain the peculiar dielectric response that make lead halide perovskites the more intriguing playground for beyond the-state-of-the-art optoelectronics devices.

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