Photoconductivity of Pb-Sn Perovskite Induced by UV Pump and IR Push Pulses

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Organic-inorganic metal halide perovskite (MHP) has diversified into various fields, such as a solar cell and light-emitting diode. At the heart of the rich electronic behavior is the dielectric property associated with the permanent dipole of organic cation; however, knowledge on the charge-lattice interaction is still missing. We report an unusual complex photoconductive transient in MHPs composed of methylammonium cation (MA), mixture of lead-tin, and bromide (MA(Pb/Sn)Br₃). This anomaly found in the time-resolved microwave conductivity (TRMC) evaluation is rationalized by the charge traps and consequent orientation of MA dipoles insensitive to the microwave. The energetics of photogenerated charges are examined by a near-infrared (IR) push pulse exposed at a certain delay after the ultraviolet (UV) pump pulse. Contributions from a two-photon process and liberation of trapped charges upon the IR irradiation are separately discussed. The identified mechanism points to the utmost importance of dielectric behavior in the gigahertz region, which is usually hindered by mobile charge carriers in the inherent electronic property of MHP.

Keywords: Organic-inorganic perovskite, Dielectric permittivity, Pump-push TRMC

1. Introduction

Since the advent of the organic-inorganic metal halide perovskite (MHP) solar cells [1–3], MHPs represented by MAPbI₃ (MA: methyl ammonium cation, CH₃NH₃⁺) have gathered a great scientific interest [4–6]. The notable properties of a MHP are the long diffusion length of charge carrier [7], the large extinction coefficient associated with direct transition [8], and prompt charge separation owing to small exciton biding energy [9]. A part of these intriguing electronic properties may be related to the softness of the ionic lattice and liquid-like behavior of permanent dipole of A-site cation [10,11], which has a small rotational barrier less than the thermal energy [12,13]. The high dielectric permittivity (real part ε’ ≈ 50 and imaginary part ε” ≈ 30 at 300 K at 10 GHz)[10] of MAPbI₃ could screen the coulomb field between holes and electrons, thus facilitate the exciton dissociation and reduce the charge recombination with the help of ferroelectric[13] and Rashba-Dresselhaus effects [14,15].

Accordingly, dielectric property of MHP is of particular importance, which benefits the efficiency of a perovskite solar cell. The steady-state ε’ of MAPbI₃ in the kHz-MHz range is reportedly increased with a decrease of temperature [16], which follows Curie-Weiss law (∼(T–T_c)⁻¹, T_c: Curie temperature) [17]. At the lower temperature, the ε’ indicates a sudden drop at the phase transition from tetragonal to orthorhombic [16]. This is understood as the order-disorder transition into an antipolar state [11]. Characteristic frequency dispersions appear in the GHz and THz regions, which are attributed to the rotational relaxation of MA dipole and longitudinal optical (LO) phonon associated with the distortion of PbI₃ sublattice, respectively [10]. Giant photoinduced dielectric constant is another unique phenomenon observed in MHP [18,19]. Nonetheless, a research on the transient change of dielectric permittivity induced by photo excitation remains challenging, because photogenerated charge carriers dominate the
response to the external electromagnetic wave, owing to the large carrier mobility. Specifically, the mobile charge carriers in MHPs cause a large real (Δσ′) and imaginary (Δσ″) photoconductivity [20], which are proportional to the imaginary (Δε″) and real (Δε′) parts of the transient dielectric permittivity, respectively [21,22]. Therefore, dielectric behavior of MA dipole in the presence of photogenerated charge carriers are mostly hidden.

In this paper, we report the anomalous photoconductivity signals in Pb-Sn mixed MHP composed of MA as the A-site and Br as the X-site of an ABX₃ perovskite structure. Sn is one of the most plausible alternatives to the toxic Pb [23], while the incorporation of Sn degrades the device efficiency to a large extent, because of the instability of Sn²⁺ and resultant carrier traps [24]. However, we utilize the trap sites via cocktailing Sn to reduce the charge carrier mobility and to extract the dielectric behavior of MA dipole, which are observed by flash photolysis time-resolved microwave conductivity (TRMC) [20–22,25,26]. The second near-infrared (IR) push pulse in addition to the ultraviolet (UV) pump pulse is used to examine the energetics of the trapped states.

2. Experimental

2.1. Materials

PbBr₂ was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. MABr, SnBr₂, and SnF₂ were bought from Sigma-Aldrich Co., Llc. All chemicals were used without further purification. A 0.1 M precursor solution of Sn:Pb = 0.7:0.3 or 0:1 (molar fraction) was prepared in DMSO in a N₂-filled glovebox and drop-cast on a cleaned quartz substrate. The obtained films were subsequently annealed at 100 °C for 30 min. 10 mol% SnF₂ was mixed in the Sn-Pb cocktailed MHP to reduce the carrier doping [27], where the excessive doping is unfavorable in TRMC experiments [28,29]. The resultant films were MAPbBr₃ and MA(Pb₀.₃Sn₀.₇)Br₃ with 10 mol% SnF₂.

2.2. Pump-push TRMC

Figure 1 shows the schematic of a pump-push TRMC setup using continuous microwaves with the frequency of ~9 GHz (X-band). The third harmonic (THG, 355 nm) of a Nd:YAG laser (Spectra Physics Inc. GCR-100, pulse duration = 5–8 ns, 10 Hz) was used for UV pump. An idler light (~2 mJ cm⁻² pulse⁻¹) from an optical parametric oscillator (OPO, Continuum Inc., Panther) seeded by a Nd:YAG laser (Continuum Inc., Surelite II, pulse duration = 5–8 ns, 10 Hz) was used for IR push pulse [29]. The time interval of the pump and push pulses were controlled by synchronized digital pulse generators. The use of second pulse can be found in the studies on the reactivity of excited radical cation of a conjugated molecule [30] and the charge transfer states in organic photovoltaics [31]. The photoconductivity transient (Δσ) was measured using Δσ = A⁻¹ ΔP_r/P_r, where A is the sensitivity factor, P_r is the reflected microwave power and ΔP_r is the change in P_r upon exposure to the light. Δσ′ and Δσ″ were determined by fitting transient Q (quality) curves after exposure to the laser pulse as described elsewhere [21]. Coupling of a microwave circuit and a resonant cavity was tuned by an iris coupling, so as to perform the experiments at the under-coupling.

3. Results and discussion

Figures 2a and 2b display the Δσ′ and Δσ″ of MHP films upon exposure to an UV pulse, respectively. MAPbBr₃ indicates a large positive Δσ′ and a small negative Δσ″ (≈ –1/50 Δσ′), which is readily ascribed to the mobile charge carriers. The temperature dependence of Δσ′ reveals the band-like transport associated with acoustic phonon scattering (T⁻³/₂) in MAPbI₃ [20,25,32] and MAPbBr₃ [29]. Bonn et al. suggest involvement of dielectric drag in addition to phonon scattering in the charge transport mechanism [10], where the charges move by accompanying the oriented MA dipoles, forming a polaron [12,19] in crystal–liquid duality (Fig. 2c). The Δσ′ and Δσ″ of MAPbBr₃ decay at the same rate, evidencing the dominant, sole contribution of mobile charge carriers. In contrast, MA(Pb₀.₃Sn₀.₇)Br₃ exhibits an unusual Δσ′ that decays promptly within 0.2 μs and overshoots to the negative polarity. Note that the intensity of Δσ′ of MA(Pb₀.₃Sn₀.₇)Br₃ is small, since the excitation photon density is two orders of magnitudes larger than MAPbBr₃. A least-mean-square (LMS) fit of Δσ′ using two double stretched exponential functions (exp(–(kt)β)) yielded the rate constants of
the fast decay: \( k_1 = 1.7 \times 10^7 \text{ s}^{-1} \) and the slow decay: \( k_2 = 3.7 \times 10^5 \text{ s}^{-1} \). On the other hand, the \( \Delta \sigma'' \) showed a slow rise (~ 0.2 \( \mu \text{s} \)) and slow decay (~ tens of microseconds), the former of which was distinctly shorter than the instrumental response time (~ 40 ns). Of interest is the positive polarity of \( \Delta \sigma'' \), which is unusual and opposite to that observed in MAPbBr\(_3\). An LMS fit of \( \Delta \sigma'' \) using two double stretched exponential functions led to the slow rise: \( k_1 = 1.6 \times 10^7 \text{ s}^{-1} \) and the slow decay: \( k_2 = 3.6 \times 10^5 \text{ s}^{-1} \). Notably, these rate constants are coincident with those found in the \( \Delta \sigma' \), indicating that the same transient species are responsible for the unusual photoconductivity in the delayed time domain. Accordingly, the plausible mechanism is as follows: photogenerated mobile charge carriers that give the normal positive \( \Delta \sigma' \) and negative \( \Delta \sigma'' \) are trapped with the rate constant of \( k_1 \). The consequent trapped charges that give the negative \( \Delta \sigma' \) and positive \( \Delta \sigma'' \) disappear slowly with the rate constant of \( k_2 \). It should be noted that normal trapped charges cannot explain such an anomalous polarity in the Drude-Smith framework [21,33]. We have previously identified the trapped charges dressed with the rotation-frozen MA dipoles or fixed lattice displacement in ferroelectric materials (BaTiO\(_3\)) as the cause of the anomalous dielectric behavior [29]. This is well supported by the dependences on the temperature and microwave frequency, and comparative evaluation of trap density-controlled Pb-Sn MHPs. The energetics of the trapped charges (hole and electron) are illustrated in Fig. 2d. Based on this model, we envision that a low-energy IR push pulse corresponding to the trap depth may allow to liberate the trapped state, which induces a bleaching of the anomalous photoconductivity.

Figures 3a–3d exhibit the kinetic curves of...
MAPbBr₃ with the push, pump+push, and their difference. The push pulse was exposed at 1.3 μs after the UV pump pulse when the majority of the photogenerated charges in MA(Pb₀.₃Sn₀.₇)Br₃ were in trapped states. Despite the push pulse energy (939–1116 nm corresponding to 1.11–1.32 eV) lying far below the bandgap ($E_{th}$) of MAPbBr₃ (2.30 eV), the above pulse induced a large positive $\Delta \sigma'$ even in the absence of the pump pulse. This is ascribed to charge carrier generation via two-photon absorption and subsequent charge carrier generation, as previously reported for MAPbBr₃ (the details are discussed in the next paragraph) [34]. The kinetic curve obtained by subtracting the push from the pump+push was identical to the normal $\Delta \sigma'$ observed using only an UV pump. Therefore, no detrapping of charge carriers was observed in the defect-free MAPbBr₃ film. In stark contrast, a bleaching of unusual negative $\Delta \sigma'$ was observed in MA(Pb₀.₃Sn₀.₇)Br₃ (Figs. 3e–3h) upon IR push pulses (1000–1165 nm corresponding to 1.06–1.24 eV). A two-photon absorption process is still involved in MA(Pb₀.₃Sn₀.₇)Br₃, because an exposure to an IR pulse without an UV pulse generates a positive $\Delta \sigma'$ attributed to mobile charge carriers. Note that the kinetic difference between push and pump+push exhibits the bleaching of the negative $\Delta \sigma'$, which manifests the liberation of trapped charges by the IR push pulse. The intensity of the bleaching is decreased with decreasing the photon energy of the push pulse, consistent with the energetic landscape of trapped charges.

Figures 4a and 4b show the plots of $\Delta \sigma'$ maxima induced solely by IR pulse vs its photon energy observed in MAPbBr₃ and MA(Pb₀.₃Sn₀.₇)Br₃, respectively. Note that UV pulses are not exposed, and thus these plots reveal the dominant contribution from two-photon absorption (TPA). TPA is more pronounced for MAPbBr₃ (Fig. 4a) than for MA(Pb₀.₃Sn₀.₇)Br₃ (Fig. 4b), which is validated by the coincidence of threshold energy ($E_{th}$) with $E_{g}/2$ [29] ($E_{th} = 1.17$ eV and $E_{g}/2 = 1.15$ eV for MAPbBr₃; $E_{th} = 0.86$ eV and $E_{g}/2 = 0.95$ eV for MA(Pb₀.₃Sn₀.₇)Br₃).

The impact of the push pulse exposure on trapped charges is extracted as the $\Delta PP$ ($\Delta \sigma$)⁻¹, where $\Delta PP$ is the change in the $\Delta \sigma'$ between pump+push and push, and the $\Delta \sigma$ is the intensity at 1.3 μs (Fig. 4c). Thus, $\Delta PP$($\Delta \sigma$)⁻¹ is a measure of mobile charge liberation from trapped states by the push pulse, which excludes the contribution of the two-photon process (Fig. 4d). In the case of MAPbBr₃, no “pushed charges” were detected regardless of the push photon energy, whereas $\Delta PP$($\Delta \sigma$)⁻¹ of MA(Pb₀.₃Sn₀.₇)Br₃ increased with increasing the push photon energy. This means the deep trap states located in the mid-bandgap. The obtained results supported that the trapped charges (both hole and electron) dressed with oriented MA dipoles cause anomalous TRMC signals [29]. The freely-rotating MA dipoles contribute to the large dielectric constants of MHPs [10,34]. Therefore, the frozen MA dipoles oriented to the trapped charges lead to the decrease of real and imaginary dielectric constant, which corresponds to the observed anomalous TRMC signal. The pump-push TRMC can provide insight into the energetics of trapped states in MHPs, which plays an important role in the energy loss processes of MHP solar cells as well as emerging photo-energy conversion devices.

4. Conclusion

The real and imaginary parts of photoconductivity found in the TRMC kinetics of the MA(Pb₀.₃Sn₀.₇)Br₃ film exhibited anomalous polarity opposite to those of mobile/trapped charge carriers. The kinetic analysis revealed the rate constants of the fast decay of $\Delta \sigma'$ and the slow rise of $\Delta \sigma''$ were identical, and both $\Delta \sigma'$ and $\Delta \sigma''$ decayed slowly at the same rate. The phenomena were explained by trapped charges with oriented MA dipoles that are insensitive to the microwave.
Pump-push TRMC demonstrated the liberation of such a trapped state upon exposure to the IR pulse; however, this is a rare event compared to the charge generation via two-photon process of the IR pulses.

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