

Ultrafast infrared spectroscopy reveals intragap states in methylammonium lead iodide perovskite materials

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ABSTRACT

Organic-inorganic hybrid materials have recently attracted a lot of attention for optoelectronic applications as they allow combining the flexibility and processibility of organic molecular systems with the good stability and charge-transport properties of inorganic crystalline materials. In this contribution, we report on the use of ultrafast vis-pump / infrared(IR)-probe spectroscopy to investigate the optical signature of charge carrier dynamics in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films. We observed that this perovskite shows a complex response which involves strong ground-state bleach contribution. This behaviour differs from most inorganic semiconductors and quantum dot materials that show strong photoinduced absorption in IR upon carrier generation. The bleaching probably results from a partial filling of intragap states next to the conduction band edge. It may also indicate the existence of a Burstein–Moss type effect in perovskite materials.

Keywords: ultrafast spectroscopy, methylammonium lead iodide perovskite, charge dynamics, charge trapping.

1. INTRODUCTION

Organic-inorganic hybrid materials have recently attracted a lot of attention for optoelectronic applications as they allow combining the flexibility and processibility of molecular systems with the good stability and charge-transport properties of inorganic crystalline materials.[1] Particularly, the recent introduction of methylammonium lead halogenide perovskites for photovoltaic applications have stimulated a number of ground-breaking developments in the field, holding the promise of a cheap and scalable renewable energy source.[2]

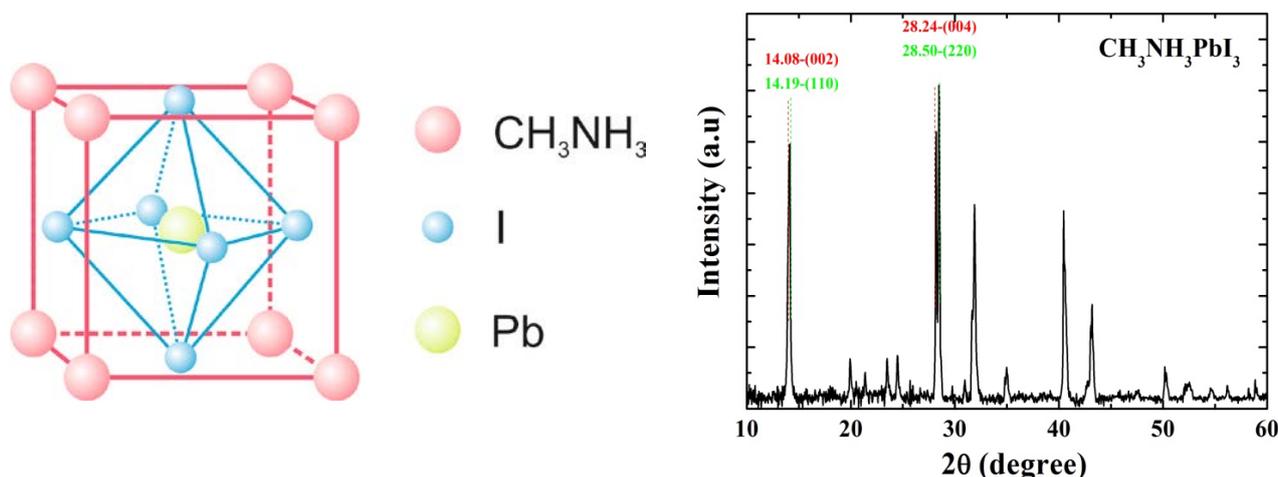


Figure 1. (a) The structure of perovskite crystal structure and (b) its XRD characterization.

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The use of perovskite for light-harvesting was initially demonstrated in a dye-sensitised solar cell configuration. These photovoltaic devices were composed of a porous nanostructured TiO_2 or Al_2O_3 layer, a perovskite sensitizer and a hole-transporter layer. Subsequently, perovskite photovoltaic devices have been realized in a variety of structures, including planar thin film p-i-n cells, using various chemical or physical deposition and preparation procedures. These developments have quickly led to promising results, reaching efficiencies of $\sim 12\%$ at solar illumination. Within the last year even more promising results have been obtained with energy conversion efficiencies up to 19.3% .

In spite of the impressive progress in perovskite device development, many aspects regarding the nature of the electronic states in perovskite materials are still unclear. The very nature of the primary excited states, excitons or charge pairs, has been and still is a subject of intense discussion.[3] Even less is known about the valence and conduction band structures as well as about the electron, hole, or exciton intraband dynamics. This knowledge is crucial for understanding charge transport in perovskite materials. It would also assess the potential of perovskite materials in exploiting hot-carrier extraction and carrier multiplication to further boost photovoltaic device efficiency.

In this contribution, we use ultrafast vis-pump / IR-probe spectroscopy [4] to investigate the optical signature of charge dynamics in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. We observed that this perovskite shows a multi-component response which indicates the presence of populated states inside the material band gap. This behaviour contrasts with that of most inorganic semiconductors and quantum dot materials that show strong photoinduced absorption in IR upon carrier generation,

2. METHODS

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ was synthesized according to a previously reported procedure.[5] Typically, the $\text{CH}_3\text{NH}_3\text{I}$ precursor was synthesized from CH_3NH_2 and HI and then purified. $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 were mixed and dissolved in degassed γ -butyrolactone with 1:1 molar ratio, reaching to a solution of 40 wt%. The solution was stirred overnight at 60°C , and filtered twice with PTFE $0.2\mu\text{m}$ filters. Samples were prepared by spin-coating the stock solution on CaF_2 substrates with a rotation speed of 2000rpm for 1 min. During the spinning process, visual colour change could be observed from yellow to black. Subsequently the sample was annealed at 100°C for 1 hour in an Ar filling golvebox.

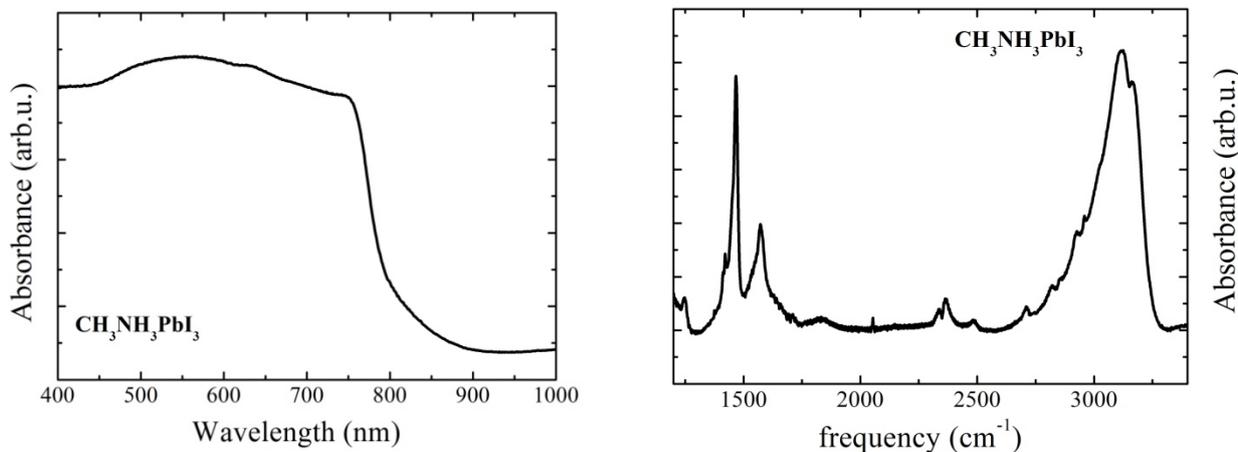


Figure 2. (a) Visible and (b) IR absorption spectra of the perovskite films under study.

The pulses for the pump-probe experiments are generated using the output of a regenerative 1 kHz Ti:Sapphire amplifier system (Coherent, Legend Elite Duo, 800 nm, 40 fs pulse duration, 7 mJ per pulse). The pulses were split into two parts.[6] One part was used generate 400nm visible pump pulses via frequency doubling (~ 100 fs pulse duration). Another part was used to generate mid-IR probe pulses using a parametric amplifier combined with a difference frequency generation stage (HE TOPAS, 80 fs, 1900 cm^{-1}). The beams were focused to a $\sim 100\mu\text{m}$ spot on the perovskite film deposited a CaF_2 substrate. After the sample the transmitted probe beam was dispersed with a spectrograph and detected with a mercury-cadmium-telluride (MCT) infrared detector array. All the measurements were performed at room temperature under nitrogen atmosphere.

3. RESULTS

Figure 1 shows the crystal structure of the perovskite material involved (a) and its characterization by X-ray diffraction (XRD) (b). The peaks at 14.08, 14.19, 28.24 and 28.508 degrees correspond to the (002), (110), (004) and (220) planes, respectively, and demonstrate the presence of a tetragonal perovskite structure with lattice parameters of $a=b= 8.88 \text{ \AA}$ and $c= 12.68 \text{ \AA}$. Figure 2 presents the visible and IR absorption spectra of the sample. There is a strong well-defined electronic absorption band at energies below 800 nm; optical excitation of this band has been shown to lead to a strong photovoltaic effect. In the IR, the absorption consists of narrow vibrational lines, probably associated with CH_3NH_3 molecular vibrations, on top of a broadband background absorption of comparable amplitude. The origin of this latter absorption is not exactly known, but, in analogy with other inorganic semiconductors, it is likely associated either with intraband transitions within the conduction or valence band manifolds, or with transitions between in-gap ‘defect’ states and one of the bands.

To investigate the carrier dynamics and to identify the nature of the IR absorption, we performed time-resolved optical experiments with a 70 fs IR probe pulse around 1900 cm^{-1} , where vibrational lines are absent and only electronic transitions contribute to the response. The charge carriers are excited with a visible 400-nm, 50-fs pump light pulse. All measurements were performed in transmission geometry at room temperature in nitrogen-flow atmosphere.

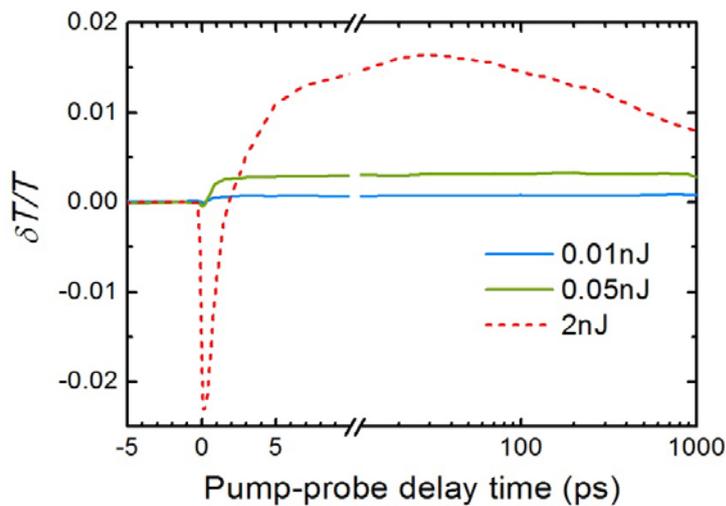


Figure 3. Vis-pump IR-probe characterization of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film measured at pump pulse energies of 0.01, 0.05 and 2 nJ.

Figure 3 shows the pump-induced change in transmission of the probe as a function of delay for a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, measured at different pump pulse energies. At low pump pulse energy the observed dynamics consist of a minor prompt initial photoinduced absorption which rapidly evolves to a bleaching signal. The conversion rate is clearly longer than 100 fs, which implies that the observed dynamics are not due to a coherent artefact response. The prompt induced absorption response after carrier photogeneration is a well-known phenomena observed in inorganic crystals, amorphous films, quantum dots[7] and conjugated macromolecules.[8] It is usually associated with pump-excited charge carriers showing low-energy transitions within the conduction or valence band manifolds. The observation of an IR broadband photoinduced bleaching is very unusual for semiconducting systems and is probably associated with intermediate subgap states, as we will discuss below in more detail. The bleaching signal shows little change on a sub-ns timescale, suggesting very slow geminate recombination dynamics of the associated carriers.

At a high pump power of $\sim 2 \text{ nJ/pulse}$ the dynamics change dramatically. The prompt induced absorption feature becomes larger in amplitude. The induced absorption rises linear with the pump power, supporting the interpretation that this absorption is due to carriers in the conduction and valence band showing low-energy intraband transitions. The decay of the absorption signal is observed to become faster with increasing pump energy, which indicates the presence of bimolecular, probably Auger-recombination effects.[9]

The bleaching signal at longer delays also increases with increasing pump energy, but its dependence on the pump energy pointing at a saturation effect. The saturation suggests that the bleaching is associated with a finite and relatively

small sub-ensemble of states. In figure 4, we show a relaxation model which can explain the observed phenomena. It roughly resembles the Burstein–Moss effect which has been reported before for inorganic semiconductor materials.[10] The figure is designed for electrons and conduction band related transitions, but a similar model can be made for holes and valence band transitions. We propose that the perovskite material possesses partly filled intragap defect states giving rise to the background IR absorption due to defect-to-conduction-band transitions. Upon visible excitation, a number of electrons is transferred to high-energy states in the conduction band, giving rise to an induced IR absorption associated with intraband transitions. Relaxation of these carriers to the bottom of the conduction band decreases the difference in population between the defect states and the lower energy states of the conduction band, thus inducing a bleach of the previously existing IR absorption of the defect states. The bleaching response saturates at high pump energies because the defect states have a limited number density.

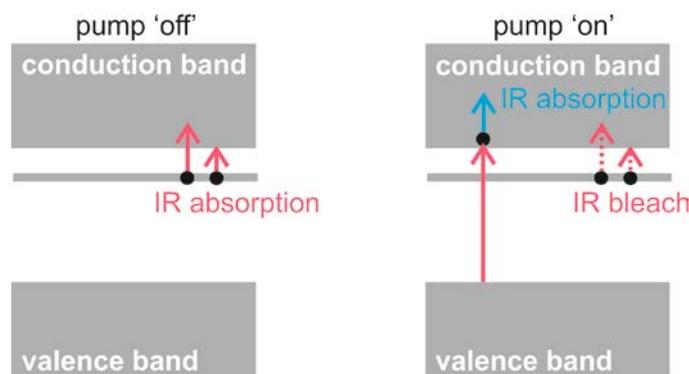


Figure 4. Transition model explaining the interplay between bleaching and photoinduced absorption using filling intragap states and associated electronic IR transitions.

4. CONCLUSIONS

In conclusion, we have investigated the early-time charge carrier dynamics in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films using ultrafast IR transient absorption spectroscopy. Our measurements reveal that the perovskite material shows a complex response in the infrared, consisting of an instantaneous induced absorption followed by a bleaching effect. We propose that the bleaching is associated with partially populated intragap defect states located $<0.2\text{eV}$ above/below the edge of conduction or/and valence band. Those states may play an important role in charge carrier recombination as well as in electron and hole transport in perovskite-based electronic devices.

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