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超広帯域可視−近赤外フェムト秒過渡吸収分光による$CH_3NH_3PbI_3$ペロブスカイト薄膜の励起状態ダイナミクスの観測

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Ultra-broadband Vis-NIR femtosecond transient absorption spectroscopy of $CH_3NH_3PbI_3$ perovskite thin films

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[Abstract] We studied the ultrafast dynamics of methylammonium ($CH_3NH_3^+$; MA) lead iodide perovskite ($MAPbI_3$) thin films and examined the nature of photo-generated species by ultra-broadband (650-1470 nm) femtosecond time-resolved absorption spectroscopy to obtain key information for designing high-efficiency solar cells. On the basis of the observed transient absorption spectral shapes and pump-fluence-dependent dynamics, we concluded that the photo-generated species are free carriers, instead of excitons.

[Introduction] The $MAPbI_3$ perovskite has emerged as one of the most promising light absorbers for low-cost, high-efficiency solar cells due to the unprecedentedly rapid improvement in power conversion efficiency. Despite the excellence in device performance, understanding of the fundamental photophysics behind the thin film $MAPbI_3$ absorber still remains scarce. One question under debate is the branching ratio of the initial photo-generated species between free carriers and excitons, which is a crucial issue for designing the proper device structure realizing the maximum performance. Transient absorption spectroscopy is a powerful tool to clarify this problem. However, the reported interpretations and assignments on transient absorption vary due to the limited spectral range of each measurement. In the reported transient absorption spectra of thin film $MAPbI_3$, the ground-state bleaching (GSB) at the band edge has been attributed to the band filling effect [1] and the pump-fluence-dependent relaxation dynamics are explained in terms of the second-order recombination of free carriers [2]. Recently, Sheng *et al.* reported a new excited-state absorption (ESA) band in the near-infrared (NIR) region [3]. Since its temporal behavior and anisotropy decay are different from those of the GSB signal, they assigned this ESA band to photo-generated excitons. However, their GSB and ESA dynamics were measured with different laser systems and pulse energies, so that the present assignment needs to be verified. Here, we report the transient absorption spectra of the $MAPbI_3$ thin film in the ultra-broad spectral range (650-1470 nm) and their pump-fluence-dependent dynamics (1-150 $\mu J/cm^2$). These data were obtained under the same optical configuration, which enables us to make consistent assignments and discussions.

[Methods] The $MAPbI_3$ thin film with ~300 nm thickness was prepared with spin-coating on a glass substrate by the antisolvent method [4]. Then, the $MAPbI_3$ thin film was sandwiched

by another thin coverslip and sealed by the optically transparent glue to prevent contact with moisture. The transient absorption measurements were carried out using a setup based on a Ti:sapphire regenerative amplifier. The pump beam (623 nm, 65 fs) was generated by a non-collinear optical parametric amplifier. The broadband white light probe was obtained by focusing the 1800-nm idler from another optical parametric amplifier into a sapphire plate. The pump polarization was set at the magic angle. The transmitted probe beam is spectrally dispersed and detected by a CCD (650-1000 nm) or an InGaAs array (980-1470 nm).

[Results and Discussion] Figure 1a shows a steady-state absorption spectrum of the $MAPbI_3$ thin film. The broad weak absorption band peaked at around 1100 nm is likely attributable to trap absorption related to I^- vacancy [5]. The transient absorption spectra in Figure 1b show a prominent GSB band around the band edge region, which grows in intensity and narrows within ~2 ps, indicating thermalization of the hot carriers. On the other hand, a broad ESA was observed across the whole NIR region. A previous study reported the existence of a narrow ESA band in NIR which was assigned to the exciton [3]. However, we notice that the spectral shape of ESA has a shallow dip at around 1200 nm, which is likely attributable to the bleaching of the trap absorption band which is seen in the steady-state absorption spectrum. By comparing the temporal dynamics of ESA and GSB in Figure 2, we find that the decay dynamics of the ESA is a mirror image of the dynamics of the higher energy GSB (red curve, Figure 2). Therefore, the ESA in the NIR region is not attributed to the exciton but assignable to the intraband absorption of free carriers well above the band gap.

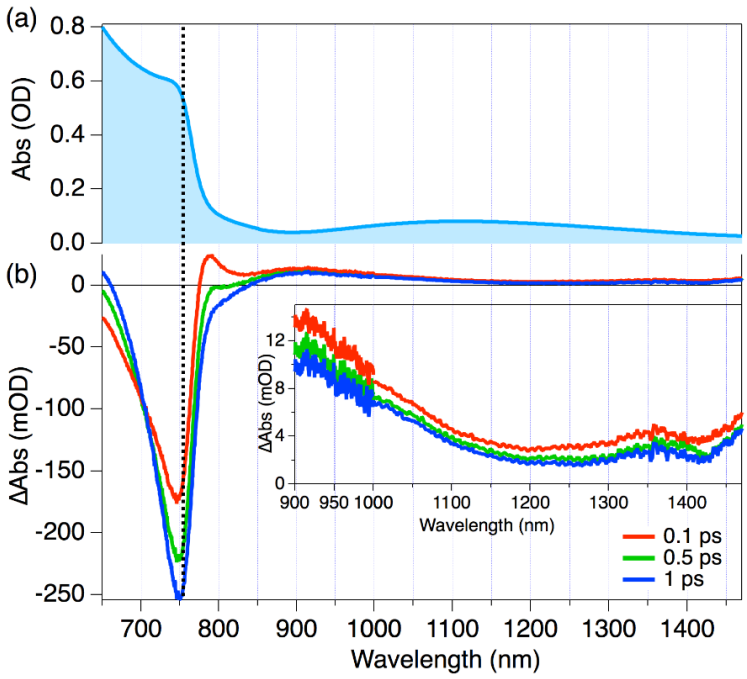

Fig. 1 (a) Steady-state absorption spectrum and **(b)** transient absorption spectra of $MAPbI_3$ thin film measured with 100 $\mu J/cm^2$ pump fluence. (Inset shows the enlarged spectra of ESA in NIR) The black dotted line indicates the band gap of $MAPbI_3$ at 756 nm.

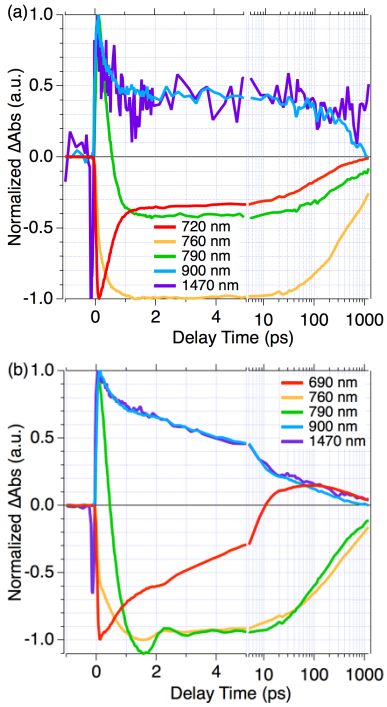

Fig. 2 Selected temporal dynamics measured with **(a)** 10 $\mu J/cm^2$ and **(b)** 100 $\mu J/cm^2$ pump fluence. Note that the delay time region longer than 5 ps is plotted in log scale.

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