Time-resolved measurement of photocarrier generation in CH₃NH₃PbI₃ single crystals

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Abstract. A giant microwave response is transiently observed in CH₃NH₃PbI₃ single crystals under pulsed laser excitation at temperatures in both structural phases across the transition at 161 K. The response is caused by photocarriers generated in the specimen mounted in a microwave cavity. This detection technique is capable of measuring the carrier dynamics with a time-resolution of a few nanoseconds. Based on the time-resolved excitation spectrum near the absorption edge, we unveil that the photocarriers are generated by long-lived excitons as well as by fast band-to-band transition.

1. Introduction
Organo-metal halide perovskite systems have attracted increasing attention as light absorbers in solar cells [1]. Remarkable device performances [2] are originated form characteristic properties of these materials, such as a high optical absorption coefficient, free carrier generation, low trapping rate, a large carrier diffusion length, and photon recycling [3]. Regarding the structural phase transition, the rotational motion of organic cation comes to be restricted at the low temperature phase, affecting the dielectric constant significantly [4]. Dielectric fluctuation due to a collective orientational motion of cation is considered to be important to set up a low-trap platform for carrier transport in the high temperature phase [5]. The role of excitons for the device function has been a hot topic under investigation. The binding energy of free exciton in CH₃NH₃PbI₃ was figured out to be c.a. 13 meV in the low-temperature phase from the temperature dependence of steady-state photocurrent (PC) and photoluminescence (PL) with a single crystal [6] and the transient-absorption with a thin film [7].

In this study, we investigate photocarrier generation mechanisms in CH₃NH₃PbI₃ single crystals by a newly developed transient microwave response measurement. Microwave at the frequency of 9.6 GHz can probe overall photocarriers generated inside a crystal without electrodes and wire connection, in contrast to the ordinary surface-current measurements. Observed excitation spectrum of the signals is changed drastically across the phase transition temperature of $T_c = 161$ K in iodide, in accordance with the previous steady-state PC measurement [6]. From time-resolved excitation spectra, we unveil that the photocarriers are generated by long-lived excitons as well as by fast band-to-band transition in both structural phases.

2. Experiment
Single crystals of CH₃NH₃PbI₃ were synthesized in solution via inverse temperature recrystallization [8]. We confirmed that XRD peaks appeared at the expected angles for this material [8]. A crystal of typical size of 2.5×2.5×1.0 mm³ was mounted in a microwave cavity (Bruker, MD5W1) which is capable of adjusting the value of the quality factor (Q). The crystal was exposed to continuous
microwave and laser light pulses in the temperature range of 10 - 300 K. A transient microwave response was measured by an oscilloscope (Bruker, SpecJet in ELEXSYS E580) synchronized to the laser pulse. Wavelength of excitation light was selected near the absorption edge from a linearly-polarized tunable pulse laser (Spectra Physics, MOPO). Incident pulse energy was controlled in the range of 1 - 3 μJ. Temperature of sample was monitored by a K-type thermocouple on the cavity with assistance by a Cernox resistor mounted on the cryostat under cooling with liquid helium or nitrogen.

It is known that dielectric constant of the specimen is very large in the tetragonal phase above $T_c$ and drastically decreases in the orthorhombic phase below $T_c$ [4]. When a small sized dielectric material is installed in a microwave cavity, a loaded Q-value is influenced by the dielectric constant of the material. Actually the value monitored at a critical coupling was varied with temperatures reflecting the change of dielectric constant. Therefore, we measured a transient microwave response by adjusting the Q-value as low as of 800 (a time-resolution of 13 ns) at each temperature in order to perform measurement under the same condition.

3. Results and Discussion

A giant microwave response was observed under pulsed laser excitation depending on the excitation photon energy and temperature. Figure 1 shows the temporal profile of the microwave power response after the excitation laser pulse at various photon energies near the absorption edge, measured at temperatures, (a) 92 K in the orthorhombic phase and (b) 284 K in the tetragonal phase. Each time profile consists of the fast and slow decay components. The fast decay component within 0.1 μs changes sharply at the low energy side. Overall characteristics of the response are shown in coloured contour maps (Fig. 2) at (a) 92 K and (b) 284 K, as functions of time after a pulsed excitation and excitation wavelength. Besides the fast component at the high intensity (red-yellow) parts, a long-lived component continued over 1 μs is remarkably recognized as a broad peak around 1.64 eV at 92 K or around 1.52 eV at 284 K.

These signals appeared irrelevantly to an applied magnetic field, in contrast to the signals in the cyclotron resonance [9]. Present signals can be attributed to the transient carriers injected by optical excitation as follows. In general, a loaded Q-value of a microwave cavity depends on a dielectric property of an inserted specimen. If the real or imaginary part of the dielectric constant of the specimen is changed, the loaded Q-value is modified [10]. When the optical conductivity, which is directly relating to the imaginary part of the dielectric constant, instantaneously increases by photocarrier generation in the specimen, the Q-value suddenly decreases and then a part of irradiated microwave power cannot enter the cavity at the moment. As a result, a transient response of microwave power in a balanced detector is observed. Therefore, a dynamical photocarrier generation in the specimen can be monitored as a transient microwave power response in present method.
Figure 2. A contour map of the transient microwave power response at (a) 92 K and (b) 284 K, as functions of time after a pulsed excitation and excitation wavelength. The excitation photon energy was indicated in the upper horizontal axis.

Figure 3. Microwave power responses as a function of the excitation photon energy at various temperatures of 90, 120, 150, 180, and 290 K, averaged in time window (a) 0 - 8 ns, (b) 16 - 38 ns, and (c) 3 - 4 μs. The curves at 284 K were magnified two times. The vertical broken lines indicate the photon energies of (i) absorption edge in the orthorhombic phase, (ii) absorption edge in the tetragonal phase, and (iii) edge of photocurrent at room temperature, where the values were taken from ref. [6].

Time-resolved excitation spectrum provides dynamical and spectroscopic aspects of the carrier generation. Figure 3 shows the excitation spectra as a function of the excitation photon energy at various temperatures averaged in three time-windows, (a) 0 - 8 ns, (b) 16-38 ns, and (c) 3-4 μs. The vertical broken lines indicate the energies of (i) absorption edge in the orthorhombic phase (1.640 eV), (ii) absorption edge in the tetragonal phase (1.575 eV), and (iii) PC edge at room temperature (1.459 eV), where the values were taken from ref. [6]. At the time immediately after the excitation pulse (Fig. 3a), the excitation spectra at 92, 118, and 144 K correspond to the intrinsic absorption of the specimen in the low temperature phase. Those at 182 and 284 K indicate responses to the excitation photon energy covering the absorption in the high temperature phase. At the temporal peak (Fig. 3b) and the later delay (Fig. 3c) times, the excitation spectra in the low temperature phase exhibited peaks at 1.646 eV and at 1.635 eV, respectively, indicating peak shift depending on the delay time. Each spectrum appears as a superposition of an isolated band and a continuum, referring to the dull-shaped edge of absorption spectrum which was resolved into an exciton band and band-to-band transition in literatures [7, 11]. The energies at half of maximum of spectrum in Fig. 3a and at peak in Fig. 3c were plotted in Fig. 4 as a function of temperature, including peaks at 1.535 eV at 182 K and 1.492 eV at 284 K (Fig. 3c) in the high temperature phase. These
characteristic photon energies exhibit a significant jump of values across the $T_c$, which is qualitatively in agreement with previous reports on the energies of exciton and band gap [11, 12]. The energy difference of 13.5 meV at 10 K was in consistent with previously reported exciton binding energy in the orthorhombic phase [6, 7]. Therefore, the long-lived isolated band is attributed to carriers generated by dissociation of long-lived excitons. The lifetime longer than 0.5 μs may indicate a carrier dynamics dominated by exciton recombination process [13] or a contribution of delayed excitons due to shallow traps as discussed in colloidal quantum dot system of CsPbBr$_3$ [14]. The long-lived responses extended to the lower energy side below absorption edge in the tetragonal phase (Fig.3a-c) are probably related to recent report of a circular photogalvanic effect due to Rashba spin splitting [15].

![Excitation Spectra](https://www.nrel.gov/pv/assets/images/efficiency_chart-20180716.jpg)

**Figure 4.** Temperature dependence of characteristic photon energies, the photon energy at half maximum of excitation spectra (open circles) extracted from Fig. 3a and the photon energy at the peak of the excitation spectra (open squares) extracted from Fig. 3c.

4. Conclusion
We investigated the photocarrier generation in a CH$_3$NH$_3$PbI$_3$ single crystal by measuring a transient microwave response. Time-resolved excitation spectra at different time windows unveiled that the photocarriers are generated through long-lived excitons as well as fast band-to-band transition. Such microwave detection is highly sensitive to study a photocarrier generation without wire connection, involving carrier dynamics measurement with a time-resolution of a few nanoseconds.

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