Ultrafast optical modulation of efficiently-generated terahertz-wave in charge ordered organic ferroelectrics

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Abstract: Terahertz-wave generation in organic ferroelectrics α-$(ET)_2I_3$ is over 70 times more efficient than prototypical ZnTe. Ultrafast (< 0.1 ps) and sensitive (~ 40 %) photoresponse of the terahertz wave results from strongly-correlated electrons therein.
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1. Introduction

Ferroelectrics have been mandatory for bright terahertz(THz)-wave sources toward a broad range of applications. Among them, the layered organic salt α-$(ET)_2I_3$ (ET: bis(ethylenedithio)-tetrathiafulvalene) illustrates the potentiality of the charge ordering (CO) formed by strong Coulomb repulsion[1]. Therein, spontaneous electric polarization ***P*** is peculiarly driven by the CO resulting in large nonlinear optical susceptibility[2]. Moreover, the strongly-correlated electrons host ultrafast (< 100 fs) 'melting' of the CO upon photoexcitation, and consequent insulator-to-metal transition, or quenching of ***P***[2-4]. Such characteristics, called as electronic ferroelectricity[5], should be promising for developing unprecedented THz-sources with brightness and ultrafast controllability.

α-$(ET)_2I_3$ is in the metallic phase above the CO transition temperature T_{CO} = 135 K. Below T_{CO}, charge disproportionation among ET molecules sets in to break spatial inversion symmetry [Fig. 1(a)]. Consequently, ***P*** as induced by the CO, but not by the structural deformation, shows up and hence it alternates the sign upon inversion of the CO pattern as confirmed by optical second harmonic generation experiments[2].

Here we show the THz-wave generation characteristics for α-$(ET)_2I_3$. The THz-wave generation by the well-known optical rectification process is over 70 times more efficient than prototypical ZnTe. We also observed ultrafast (< 0.1 ps) and sensitive (~ 40 %) response of the THz-wave generation upon photoexcitation.

2. Experiments

A single crystal of α-$(ET)_2I_3$ (*ab*-plane, typical size of 2 x 2 x 0.05 mm^3) was irradiated by a femtosecond laser pulse (1.55 eV, 25 fs, 1 kHz) with a spot of 3 mm in diameter as the fundamental light (parallel to the *a*-axis of the sample) for the THz-wave generation. The generated THz-wave (|| *a*) was detected via electro-optic sampling using ZnTe. A pump pulse (0.89 eV, || *b*) was generated in an optical parametric amplifier with time resolution of 150 fs.

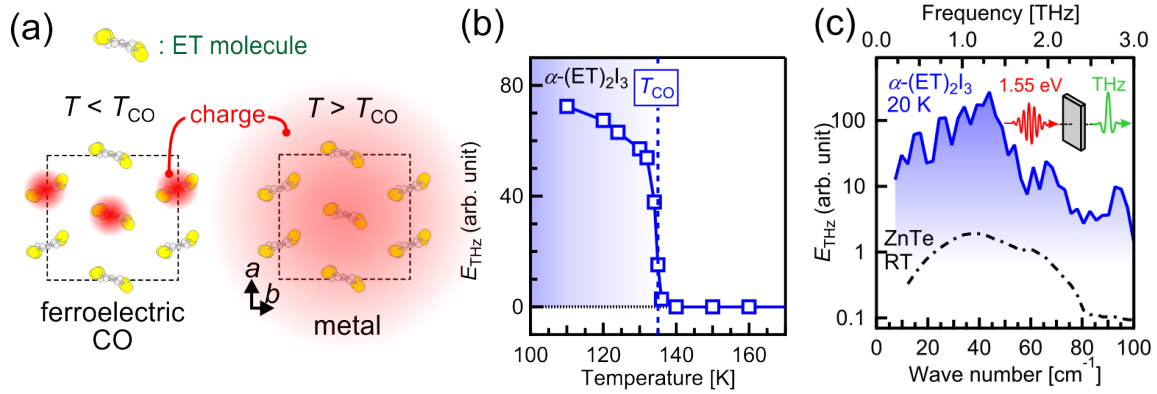

FIG. 1 (a) Schematics of arrangements of ET molecules and (ordered) charges in metallic and CO phases. (b) Temperature dependence of electric field amplitude E_{THz} (17-60 cm^{-1}) of the THz wave generated from α-$(ET)_2I_3$. (c) E_{THz} spectra for α-$(ET)_2I_3$ and ZnTe measured with a fundamental light fluence of 0.3 mJ/cm^2. The E_{THz} for ZnTe is normalized by penetration depth of α-$(ET)_2I_3$ at fundamental light energy.

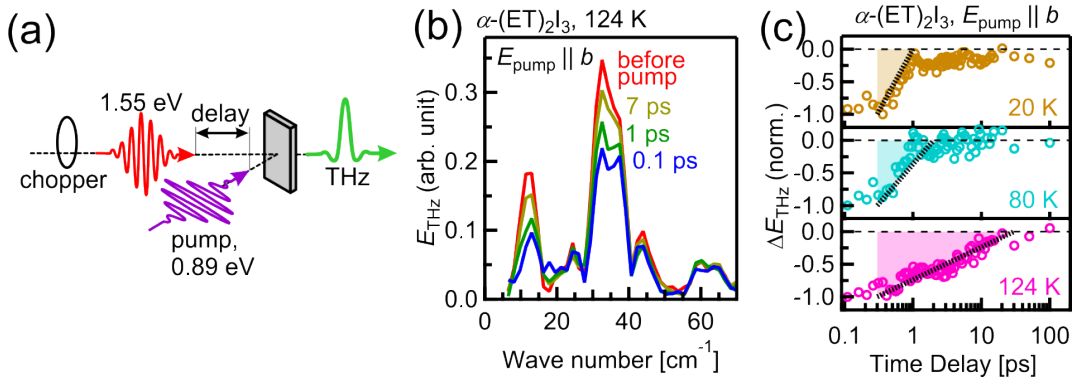

FIG. 2 (a) Schematics of the experimental setup for the time-resolved THz-wave-generation measurement. (b) Transient spectra of E_{THz} upon photoexcitation (0.3 mJ/cm^2) at 124 K. (c) Time evolutions of E_{THz} (10-13 cm^{-1}) at 20, 80 and 124 K. Broken lines are guides for the eyes.

3. Results and discussions

Figure 1(b) shows temperature dependence of the THz-wave generation in α-$(ET)_2I_3$, plotting electric field amplitude E_{THz} after Fourier transform of the observed temporal waveforms. It is clear that E_{THz} onsets at ferroelectric transition temperature T_{CO}, revealing that the THz-wave originates from the CO-induced ***P***.

Figure 1(c) shows the E_{THz} spectrum observed at 20 K. The spectrum has the bandwidths of up to 70 cm^{-1} below optical gap (~ 0.1 eV[6,7]), along with ripples or dips as a result of combined effects involving dispersion of (non)linear electric susceptibilities, absorption structures, and back reflection at the sample surface. It should be noted that E_{THz} was comparably large to that of (110)-oriented ZnTe (1 mm thick) observed with the same experimental setup. For comparison, we show the spectrum for ZnTe normalized by the penetration depth of α-$(ET)_2I_3$ at fundamental light energy (5 μm). It is obvious that the THz-wave generation is highly efficient.

Considering Fresnel loss, absorption, and the aforementioned penetration depth, nonlinear optical susceptibility $\chi^{(2)}(1\ \text{THz};\ \omega - \omega)$ for α-$(ET)_2I_3$ has been estimated to be l x 10^{-8} [m/V] by using ZnTe as a benchmark. Such a large value, which is more than 70 times larger than that of ZnTe, should be attributable to the polarization of electronic origin, or the CO, which is absent in ZnTe.

Another intriguing property of the electronic ferroelectricity is the ultrafast response upon photoexcitation. We have performed time-resolved THz-wave-generation measurements [Fig. 2(a)], using the pump light (0.89 eV) above the charge transfer band[3]. Figure 2(b) shows the transient spectra of E_{THz} upon photoexcitation at 124 K. While a double-peak-like lineshape might result from several origins as mentioned above, the amplitude works as a direct measure of ***P*** [Fig. 1(b)]. At the delay time $\tau = 0.1$ ps after the pump, E_{THz} showed a large decrease of approximately 40 %. The observed ***P*** quenching is not due to mere thermalization, but to the delocalization of correlated electrons upon photoexcitation and concomitant insulator(CO)-to-metal transition as reported previously[2-4]. Consequently, the photoinduced response of the THz-wave generation is instantaneous and sensitive revealing the capability of ultrafast photoswitching. In other words, the THz-wave generation works as a powerful probe for such transient ***P***.

The recovery of E_{THz} occurred in the order of picoseconds [Fig. 2(b)]. In Fig. 2(c) we show the time evolutions of the E_{THz} observed for several temperatures. As shown, the recovery rate clearly decreased with increasing temperature. This represents the diminishing stability of the ferroelectric CO in the vicinity of the transition temperature T_{CO}, which presumably corresponds to the stabilization of the photoinduced metal.

4. References

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