EPJ Web of Conferences **41**, 03020 (2013)
DOI: 10.1051/epjconf/20134103020

Photoinduced Growth of Ferroelectric Charge Order in Organic Dimer-Mott insulator

K. Itoh[1], H. Itoh[1, 2], S. Iwai*[1, 2], M. Naka[1], S. Ishihara[1, 2], S. Saito[3], N. Yoneyama[2, 4], and T. Sasaki[2, 4]

[1]Department of Physics, Tohoku University, Sendai 980-8578, Japan
*Email: s-iwai@m.tohoku.ac.jp
[2]JST, CREST, Sendai 980-8578, Japan
[3]National Institute of Information and Communications Technology, Koganei, 184-8795, Japan
[4]Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

Layered triangular organic dimer Mott (DM) insulator κ-$(ET)_2Cu_2(CN)_3$ was shown to exhibit a relaxor-like dielectric anomaly below 40 K with strong dispersion relation, reflecting its electric dipole glass (ferroelectric charge order; FCO) nature[1, 2]. The dielectric anomaly in κ-$(ET)_2Cu_2(CN)_3$ indicates that this compound is located in the vicinity of the DM-FCO phase boundary, where ferroelectric fluctuation such as the electric dipole glass state or the polar cluster is formed in the DM phase. Optical excitation of the DM-FCO competing state by an ultrashort light pulse enables us to achieve dramatic responses, such as photoinduced ferroelectricity, photoinduced growth of the electric dipole glass or the polar clusters.

1 Introduction

In strongly correlated electron systems, the dipole field induced by the Coulomb repulsion interaction sometimes shows ferroelectricity and ferroelectric fluctuation such as the electric dipole glass state or a polar nano region (PNR) if the electronic inversion symmetry is broken [3, 4]. Such a new class of ferroelectric behavior with an electronic origin could have applications in the ultrafast (Tb/s) modulation of ferroelectric memory and other dielectric devices. The Layered triangular organic dimer-Mott (DM) insulator κ-$(ET)_2Cu_2(CN)_3$ (ET; bis[ehtylenedithio]-tetrathiafulvelene) is recognized as a spin-liquid system.

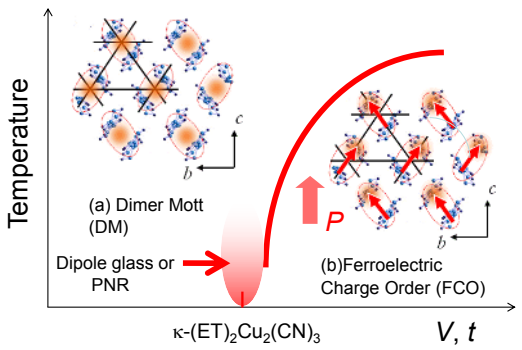

Fig. 1. Schematic illustration of the theoretically predicted phase diagram of a dimer Mott insulator k-ET salt [4]. Molecular arrangement and charge distribution of DM phase (a) and FCO phase (b) are shown.

Very recently, an origin of the spin-liquid phase has been reconsidered, i.e., this compound was shown to exhibit a relaxer-like dielectric anomaly below 40

K with strong dispersion relation, reflecting its electric dipole glass nature[1-2, 4]. In DM insulator, adjacent ET molecules are dimerized and a charge is localized on each dimer, as shown in Fig. 1(a). However, the DM phase is unstable with regard to the ferroelectric charge order (FCO) that is formed by the intra-dimer charge disproportionation for large intermolecular Coulomb energy V or inter dimer transfer integral t [Fig. 1(b)][2].

The dielectric anomaly in κ-$(ET)_2Cu_2(CN)_3$ indicates that this compound is located in the vicinity of the DM-FCO phase boundary (red area in Fig. 1), where the electric dipole glass state or the PNR is formed in the DM phase. In such a DM-FCO competing state, optical excitation of the DM-FCO competing state by an ultrashort light pulse enables us to achieve dramatic responses, such as photoinduced ferroelecricity, photoinduced growth of the electric dipole glass or the PNR.

2 Experiment

Single crystals of κ-$(ET)_2Cu_2(CN)_3$ (average size: 1 × 1 × 0.5 mm^3) were prepared using a previously reported procedure. Near-infrared (NIR) pump (0.89 eV)-THz-probe spectroscopy was performed using a 1-kHz Ti:Al_2O_3 regenerative amplifier system (Legend Elite USX; Coherent) as the light source. The NIR pump pulses was generated in an optical parametric amplifier, and the THz probe pulses was emitted in a ZnTe crystal; they were focused on a single crystal of κ-$(ET)_2Cu_2(CN)_3$ in a 1.5-mm-diameter region excited by the pump beam.

3 Results and discussions

Fig. 2(a) shows the steady state optical conductivity σ_1 (ω) spectra at 6, 10, and 20 K for E//c. We detected the broad spectrum at ~31 cm^{-1} for E//c. We will refer to this band as "1 THz band". A prominent dip at the center of this band is attributable to the Fano interference between the electronic and the phonon excitations. The 1 THz band grows markedly below 40 K. The dielectric relaxation with large dispersion observed below 40 K [1, 2], that is widely seen in disordered systems such as relaxer ferroelectrics, reminds us the emergence of the dipole glass or the PNR in the DM phase.

Considering that, the marked increase in the 1 THz band at <40 K is associated with the growth of such ferroelectric fluctuations. Furthermore, the theoretical calculation also indicates that the 1THz band is attributable to the collective excitation of the intra-dimer electric dimer dipole. Fig. 2(c) shows the photoinduced changes of optical conductivity $\Delta\sigma_1$ at t_d (delay time between the pump

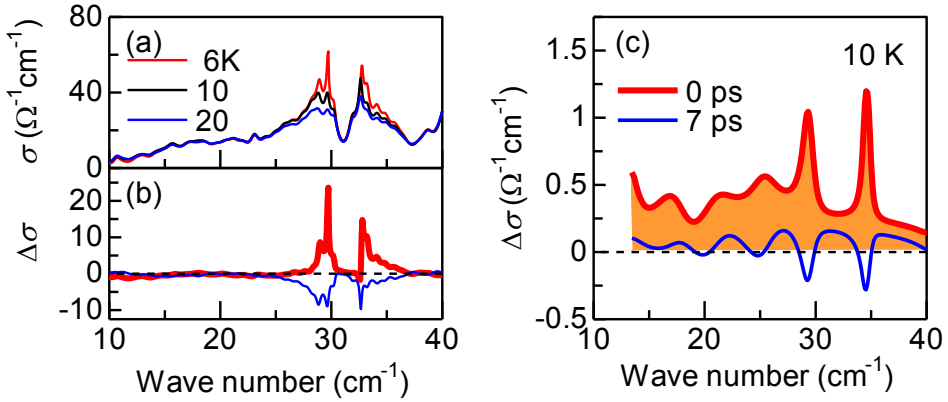

Fig. 2. (a) Steady state σ_1 spectra (b) spectral differences σ_1(6 K)-σ_1(10 K) (blue curve) (c) photoinduced changes of optical conductivity $\Delta\sigma_1$ at t_d = 0.1 ps (red curve) and 7 ps (blue curve). Excitation energy and intensity are 0.89 ev and 0.01 mJ/cm^2.

and THz probe pulses) =0.1 ps (red curve) after the excitation at 0.89 eV, corresponding to the intra-dimer excitation of the DM state (excitation intensity I_{ex}=0.01 mJ/cm^2). The spectral features of $\Delta\sigma_1$ at t_d =0.1 ps, showing peaks at 29 and 34 cm-1, are quite analogous to those of the spectral difference between 6 K and 10 K (σ_1(6 K)-σ_1(10 K); red curve in Fig. 2(b)). The positive signal of $\Delta\sigma_1$ at 29 and 34 cm-1, reflecting the increase in the 1 THz band clearly indicates the photoinduced change from the high temperature state to the low temperature state, i.e., the growth of the dipole glass or the PNR in DM phase. There are few studies of such photoinduced enhancement of the ferroelectric fluctuation, although the optical melting of the FCO has been investigated [5, 6].

Fig. 3 shows the time evolution of $\Delta\sigma_1$ observed at 30 cm^{-1} , which can be reproduced using the equation:

$$\Delta\sigma_1(t) = \int_{-\infty}^{t} \left[Ae^{-\tau/\tau_{decay}} + Be^{-\tau/\tau_{decay}} \cos(\omega t - \varphi) \right] g(t-\tau) d\tau, \quad g(t) = \frac{1}{\sqrt{\pi}} e^{-\left(4\ln 2/\Gamma^2\right)t^2}$$

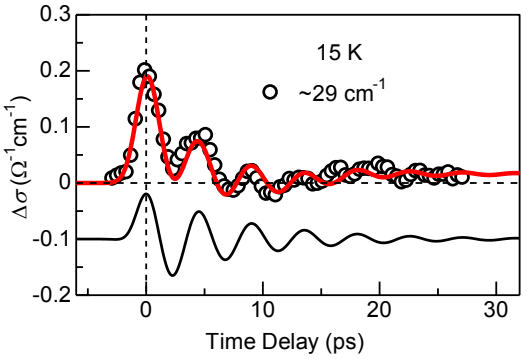

Fig. 3. Time evolution of $\Delta\sigma_1$ observed at 29 cm^{-1} (open circles) and fitting curve (red curve). The solid curve shows the oscillating component.

where the time constant of the decay, τ_{damp} = 2.6 ps, the oscillating period, $2\pi/\omega$ = 4.6 ps, the oscillating damping time τ_{damp} = 8 ps, the initial phase of cosine function, ϕ = 0 and the FWHM of the response function g(t), Γ= 1 ps. The Coefficients A = 0.017 and B = 0.014. The oscillating energy $\hbar\omega$= 0.9 meV does not correspond to that of the intermolecular optical phonon (5-10 meV). A possible candidate for the origin of this oscillation is the coherent domain wall motion, reflecting the critical nature in the vicinity of the DMFCO boundary.

4 Summary

In summary, optical pump-THz probe measurement in κ-$(ET)_2Cu_2(CN)_3$ showed that the THz response was increased by the photoexcitation, demonstrating the photoinduced growth of the electric dipole glass or the PNR, as a result of the photoinduced collapse of the DM phase.

References

1. M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, Phys. Rev. B, **82**, 125119 (2010)
2. M. Naka, and S. Ishihara, J. Phys. Soc. Jpn., **79**, 063707 (2010)
3. P. Monceau, F. Ya. Nad, and S. Brazovskii, Phys. Rev. Lett., **86**, 4080 (2001)
4. S. Ishihara, J. Phys. Soc. Jpn., **79**, 011010 (2010)
5. Y. Kawakami, T. Fukatsu, Y. Sakurai, H. Unno, H. Itoh, S. Iwai, T. Sasaki, K. Yamamoto, K. Yakushi, and K. Yonemitsu, Phys. Rev. Lett., **105**, 246402 (2010)
6. Y. Kawakami, S. Iwai, T. Fukatsu, M. Miura, N. Yoneyama, T. Sasaki, and N. Kobayashi, Phys. Rev. Lett., **103**, 066403 (2009)