Spectroscopic Studies on Electronic Ferroelectricity in Organic Conductors

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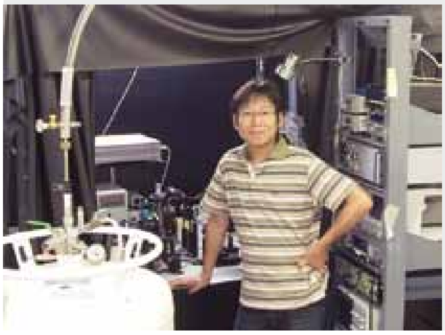
Division of Electronic Properties



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Organic conductors exhibit unusual physical properties due to the critical nature of valence electrons fluctuating under localizing and delocalizing regime. Recently, we discovered that an organic superconductor, α-$(BEDT\text{-}TTF)_2I_3$ [BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene], induces optical second-harmonic generation (SHG) along with charge-ordering driven by the repulsive electron-electron interactions.[1)] The SHG activity proves that the organic complex induces macroscopic electric polarization by the electronic transition. To understand the fundamental and functional properties of such "electronic ferroelectrics," we are engaged in the material research and development of experimental technique dedicated for low-temperature SHG microscopy of tiny organic crystals.

1. SHG Microscopy of Ferroelectric Organic Conductor Using Hydrostatic Pressure Apparatus with Argon as a Heat Transfer Medium[2)]

To perform nonlinear microscopy at low-temperatures, one has to dissipate the excessive heat from the photo-irradiated spot of the sample without affecting the physical properties. In the present study, we designed a sapphire-anvil cell, which is usually adopted for high-pressure measurements, as a cooling apparatus used along with liquid-argon as heat-transfer medium. The cryogenic performance of the argon-loaded sapphire cell was examined by the observation of SHG of an organic conductor α'-$(BEDT\text{-}TTF)_2IBr_2$ at low temperatures.

This α-type compound is unusually susceptible to mechanical stress. In a previous study, we have embedded the single crystals of the compound into a polymer resin and sandwiched them by sapphire plates, and observed the SHG at low temperatures. Because of the difference in thermal shrinkage between the samples and the sapphire plates, the crystals were fragmented with decreasing temperature. The observed image of SHG showed distinct inhomogeneity; the nonlinear optical signal was generated only from limited areas of the crystals, suggesting that the single crystals were divided into ferroelectric and antiferroelectric regions, presumably due to the mechanical stress.

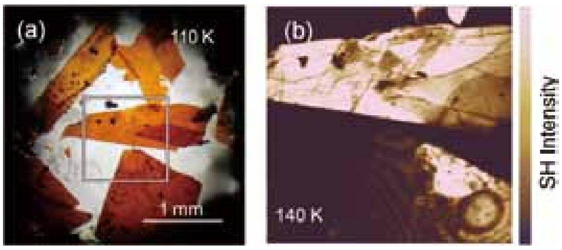

Figure 1. (a) Thin crystals of α'-$(BEDT\text{-}TTF)_2IBr_2$ in a sapphire-anvil cell loaded with liquid argon. (b) SHG image in the square region of (a) (T = 140 K).

Figure 1(a) shows the transmission image of the filmy thin crystals of the complex mounted in the sapphire cell loaded with liquid argon. The crystals cooled via the heat transfer medium were not completely intact, but the pieces of the cleaved crystals were much larger than the above mentioned fragmented crystals. As shown by the SHG image [Figure 1(b)], the cleaved crystals generated SHG from their whole region. This fact proves that the compound is a bulk ferroelectric matter, and at the same time, indicates that the heat at the irradiated spot was efficiently dissipated via the heat transfer medium without applying severe mechanical stress to the sample.

The successful SHG observation demonstrates that the cooling technique is helpful for low-temperature measurements of nonlinear optical microscopy requiring high-density photo-excitations.

References

1) K. Yamamoto, *et al.*, *J. Phys. Soc. Jpn.* **77**, 074709 (2008).
2) K. Yamamoto, *et al.*, *Phys. Status Solidi C* **9**, 1189 (2012).