Ferroelectric Polarization in $\alpha$-(ET)$_2$I$_2$Br
Studied by Second-Harmonic Generation Microscopy

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Abstract. Raman spectrum and second-harmonic generation measurements have been performed for an organic conductor $\alpha$-(ET)$_2$I$_2$Br [ET: bis(ethylenedithio)tetrathiafulvalene]. The Raman spectrum showed splitting of a charge sensitive mode at low temperatures, illustrating that the metal-to-insulator transition of the compound is ascribed to charge ordering. Critical appearance of the second-order nonlinear optical signal below the transition temperature manifests that the inversion symmetry of the crystal is annihilated by the charge ordering to generate permanent electric polarization. This is the second example of the verification of ferroelectric transition in an organic conductor.

1. Introduction
Ferroelectric materials have been extensively studied for fundamental interests and potential applications related to permanent electric polarization. Usually, those polar dielectrics belong to highly insulating matter, e.g., ionic crystals or ceramics. However, we have recently found that an organic conductor $\alpha$-(ET)$_2$I$_3$ [ET: bis(ethylenedithio)tetrathiafulvalene] transforms to be a ferroelectric by measuring optical second-harmonic generation (SHG) [1].

The compound belongs to the group of charge-transfer complex, which has been investigated in terms of transport properties and magnetism associated with strongly correlated electrons. Based on the analysis of the photo-response of SHG, we argued that the ferroelectric polarization is attributed to the Wigner crystallization of electrons which is driven by repulsive Coulomb interactions between charge carriers. Hence, the spontaneous polarization in the complex is directly connected to the electron localization, which mechanism is distinct from the conventional one that depends on displacement of ions.

For understanding of the unconventional mechanism of ferroelectric transition, it is important to carry out a systematic investigation of the physical properties of relevant compounds. Thus, it is essential to expand the family of such ferroelectric compounds. In this study, we performed SHG measurement of $\alpha$-(ET)$_2$I$_2$Br, which is isostructural to $\alpha$-(ET)$_2$I$_3$, and investigated temperature dependence of the charge distribution by means of Raman spectroscopy.

2. Experimental

2.1. Materials
Single crystals of $\alpha$-(ET)$_2$I$_2$Br were prepared by the conventional electocrystallization from the benzonitrile solution of ET and tetrabutylammonium bromodiiodide. The donor and acceptor were
used after recrystallization of reagent-grade respective substances purchased from Tokyo Kasei. A bulk crystal (ca. 0.5x0.5x0.05 mm$^3$) and a filmy single crystal (thickness: ca. 3 µm) were selected for Raman spectrum and SHG measurement, respectively.

2.2. Optical Measurements
Raman spectrum was measured with a Renishaw Ramascope 1000 spectrometer using Ar$^+$ ion laser ($\lambda=514.5$ nm). The spectral region for the characteristic frequency of C=C stretching modes was concerned. Raman signal was collected in backscattering geometry from the single crystal mounted on a copper cold stage in a liquid-helium flowing cryostat.

SHG measurement was performed using an Er-doped fiber laser ($\lambda=1.55$ µm, pulse duration: 100 fs, repetition: 20 MHz). The collimated laser beam was converted to circularly polarized light with a quarter waveplate, and focused by a Mitsutoyo M Plan apo 5x objective lens (NA=0.14) into a spot (ϕ=ca. 20 µm) on the crystal $ab$ plane. The power density at the focus spot was ca. 500 W/cm$^2$, which is several times higher than that for the Raman measurement. In order to readily disperse the heat at the laser spot, the thin crystal was embedded in polymer matrix, afterwards sandwiched by a pair of two sapphire slides. Thus induced SHG signal ($\lambda=775$ nm) was collected by a Hamamatsu photonics R3896 photomultiplier after separated from the excitation light with optical filters. With the help of computer-controlled mirror-scanners, the laser spot was swept on the crystal. The SHG data was assembled in a contour map image by the signal acquisition synchronized with the mirror scanners.

3. Results and discussion
The crystal of $\alpha$-(ET)$_2$I$_2$Br is isostructural to $\alpha$-(ET)$_2$I$_3$ which belongs to triclinic system with P-1 symmetry [2]. Because of the smaller volume of the counterion I$_2$Br than I$_3^-$, the lattice constants of $\alpha$-(ET)$_2$I$_2$Br are contracted by 0.75 % along the $a$ axis, 0.29 % $b$ axis, and 0.67 % $c$ axis, respectively [2, 3]. It has been recognized that $\alpha$-(ET)$_2$I$_3$ undergoes a metal-to-insulator (MI) transition at 135 K—the ferroelectric transition we had identified by SHG measurements [1]. High pressure studies have demonstrated that the temperature of the MI transition has a tendency to decrease with the lattice contraction [4,5]. However, according to the conductivity measurement in [2], the MI transition of $\alpha$-(ET)$_2$I$_2$Br appeared at around 245-265, which is considerably higher than that of $\alpha$-(ET)$_2$I$_3$, in spite of the lattice contraction.

3.1. Raman spectrum
Figure 1 shows the Raman spectrum of $\alpha$-(BEDT-TTF)$_2$I$_2$Br measured at various temperatures. ($\lambda_{ex}=514.5$ nm)
assignment of the peaks as summarized in Table 1, with the assistance of the comprehensive analyses for the Raman spectrum of \(\alpha\)-(ET)\(_2\)I\(_3\) [7].

**Table 1.** Assignment of the Raman signal appearing in the C=C stretching region.

| Temperature (K) | Raman band | Frequency (cm\(^{-1}\)) | Assignment |
|----------------|------------|--------------------------|------------|
| 300            | a          | 1479                     | \(\nu_2(a_g)\) |
|                | b          | 1469                     | \(\nu_3(a_u)\) |
| 16             | c\(_1\)    | 1536                     | \(\nu_2(a_g)\) |
|                | c\(_2\)    | 1483                     | \(\nu_2(a_g)\) |
|                | d          | 1475                     | \(\nu_3(a_u)\) |
|                | c\(_3\)    | 1463                     | \(\nu_2(a_u)\) |

According to this assignment, the signal of \(\nu_2\) mode splits into three bands (c\(_1\), c\(_2\), and c\(_3\)) at low temperatures. The frequency of this mode obeys an approximate linear dependence to the ionicity of ET molecule [8]. Thus, the splitting of this mode illustrates that ET molecules are disproportionated at low temperatures to have different ionicity. It is therefore plausible to consider that the transition of \(\alpha\)-(ET)\(_2\)Br\(_2\)I originates from charge ordering similarly to \(\alpha\)-(ET)\(_2\)I\(_3\). In the case of \(\alpha\)-(ET)\(_2\)I\(_3\), the spectral variation due to charge ordering appeared at ca. 125 K, which was 10 K lower than the MI transition temperature. The small fall of the nominal transition temperature can be ascribed to heating of the sample due to the excitation light. For \(\alpha\)-(ET)\(_2\)Br, on the other hand, the appreciable variation of the spectrum started from ca. 140, which is largely lower than the reported transition temperature (around 245-265 K). The beginning of the spectral variation may be smeared due to the broad spectral profile, which makes difficult to compare the results of the present study to the conductivity data. However, the huge gap is too large to be ascribed to the smearing or overheating of the sample. It has been known that the charge ordering of \(\alpha\)-(ET)\(_2\)I\(_3\) occurs in the first order manner and there is no other transition at the ambient pressure. For the isostructural relative \(\alpha\)-(ET)\(_2\)Br, therefore, it is suggested that the charge disproportionation should occur simultaneously with the MI transition. The reason for the temperature gap between the splitting of the Raman band and the resistivity drop is being investigated.

### 3.2. SHG

To examine if ferroelectric polarization is generated in \(\alpha\)-(ET)\(_2\)Br, optical SHG measurement was carried out. By using a thin single crystal, the measurement was performed in transmission geometry to collect spatially-integrated nonlinear optical signal. In the present study, we adopted an Er-doped fiber laser (\(\lambda=1.55\) \(\mu\)m, pulse duration: 100 fs, repetition: 20 MHz) instead of an amplified Ti-sapphire laser used in [1]. The fiber laser provides us a stable and high quality beam, but the produced laser pulses are much weaker in peak power (pulse energy per pulse duration) than the amplified pulses. To enhance the intensity of SHG signal up to a sufficient level, the laser beam was focused with a microscope objective lens to gain the pulse irradiance (peak power per spot area).

The tightly focused beam enhances the peak power of the laser pulses, whereas it becomes difficult to suppress heating due to the high power density accumulated at the beam spot. To avoid the heating effect, we embedded the sample into a polymer resin, then sandwiched by sapphire slides for good thermal conductivity. One may concern that the matrix can cause undesirable influence to the sample such as inhomogeneous pressure [9,10]. Since some ferroelectrics are extraordinary structure sensitive, crystal strain caused by inhomogeneous pressure might lead to position dependence on ferroelectric polarization, which strongly affects the SHG intensity induced by the tightly focused beam.

In the present study, we carried out mapping collection of SHG and observed the spatial distribution of SHG signal to examine possible such matrix effect. The SHG image was obtained by point-by-point acquisition of SHG signal synchronized with a computer-controlled mirror-scanner which brought the excitation beam on the crystal.
Figure 2a shows the transmission image of the polymer-embedded specimen. It was observed that the thin crystal showed no SHG signal at high temperatures, whereas it emitted intensive SHG signal below the transition temperature as displayed in Figure 2b. Since the matrix is seen as black, it is certain that the SHG signal is not due to the polymer matrix but generated by the sample.

One can see in Figure 2a that the crystal (dark area) has a number of cracks. These cracks were developed with lowering temperature, indicating that these were caused by difference in thermal expansion coefficient between the sample and the polymer matrix fixed on sapphire substrates. Note that the signal in the SHG image is generated from the whole area of the crystal except the cracked region. The uniform SHG manifests that the bulk crystal transforms to ferroelectric state.

To investigate the temperature dependence of the SHG signal, we integrated the SHG signal in a square region of the sample, then plot it as a function of temperature. As shown in Figure 3, there was no SHG signal from 300 K down to 180 K. This is consistent with the reported crystal symmetry [2]. With further lowering, SHG signal emerged with a discontinuity then developed with temperature,
representing the occurrence of a first order transition. This behavior resembles the temperature dependence of SHG observed for α-(ET)$_2$I$_3$. Taking into account of the similarity in the crystal structure, we propose that the crystal of α-(ET)$_2$I$_2$Br generates ferroelectric polarization by the same mechanism as α-(ET)$_2$I$_3$.

4. Conclusion
We performed the Raman spectrum measurement and the SHG image observation for α-(ET)$_2$I$_2$Br. It was concluded that this compound undergoes charge ordering from the splitting of the Raman band of a charge sensitive mode. We succeeded in observing SHG image from the thin single crystal, which manifests that this charge transfer complex transforms to ferroelectric state by charge ordering as the isostructural compound α-(ET)$_2$I$_3$. This is the second example for the verification of ferroelectric transition in an organic conductor.

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