

3 Molecular Crystal Project

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In this project, electronic correlation in molecular crystal systems is being investigated to elucidate novel phenomena such as superconductivity and charge ordering. We will analyze crystal structures of molecular crystals under high pressure and/or at low temperature to elucidate the origins of phase transitions.

3-1 Pressure-temperature phase diagram of hydrogen-bonded supramolecular ferroelectrics Phz-H₂xa

One of the targets of our investigation is the polarization origins of hydrogen-bonded supramolecular ferroelectrics. Recently, neutral-ionic valence instability has been found to vary on some acid-base supramolecular ferroelectrics [1]. In the neutral cocrystals of hydrogen-bonded phenazine (Phz, proton acceptor, A) and anilic acid (H₂xa, donor, D) [2], ferroelectricity arises from the chloranilic acid (H₂ca, X=Cl) and bromanilic acid (H₂ba, X=Br) but not from the less proton-donating fluoranilic acid (H₂fa, X=F) [3]. The paraelectric phase structure comprises nonpolar neutral molecules, which strengthen the partially ionic character below the Curie point T_c^I ; and the H₂xa releases one of the two protons toward the center position between the O and N atoms for spontaneous asymmetrization [4].

Analogous to the neutral-ionic transition of charge-transfer complexes, the cost of ionization of an acid-base pair would be replaced by that of proton transfer relevant to the proton affinities or acidic equilibrium constants pK_a of D and A molecules. Indeed, the pK_a values are nearly matched between the Phz (1.20) and H₂ca (0.73) or H₂ba (0.80) and could minimize the energy difference between the neutral and proton-transferred ionic forms. Meanwhile, contraction of the ionic crystal lattice under hydrostatic pressure would effectively change the electrostatic term.

The Phz and H₂xa molecules construct segregated π - π stacking along the crystallographic b -direction of a monoclinic lattice. Along the [110] or [1-10] direction, they are alternately linked side-by-side forming a linear chain by the intermolecular O-H...N bonds (Fig. 1). At ambient pressure, the Phz-H₂ca, Phz-H₂ba and their deuterated crystals exhibit incomplete proton displacement, which transforms the neutral molecules into semi-ionic molecules at low temperatures below the Curie point ($T_c^{IC} < T < T_c^I$). For the cocrystal of the less acidic H₂fa, the ferroelectric phase is induced only by applying hydrostatic pressure above ~ 0.6 GPa.

Synchrotron X-ray diffraction measurements have revealed that the low-temperature structure of Phz-H₂fa under high pressure is similar to that of Phz-H₂ca and Phz-H₂ba. According to temperature-dependent X-ray diffraction studies, the ferroelectric (FE-I) phase is always accompanied at lower temperatures by successive phase transitions to the lattice modulated phases with incommensurate periodicities (IC phase, $T_c^{II} < T < T_c^{IC}$) and with commensurate (twofold or threefold) periodicities (FE-II or FE-III phase, $T < T_c^{II}$). Whereas the ground-state structures at ambient pressure are different from one another among Phz-H₂ca (FE-II form), Phz-H₂ba (FE-III form), and Phz-H₂fa (paraelectric form), their systematic changes under pressure depict a universal pressure-temperature phase diagram (Fig. 2). The possible origins of structural changes are related to the valence instability and frustrated Coulomb interactions.

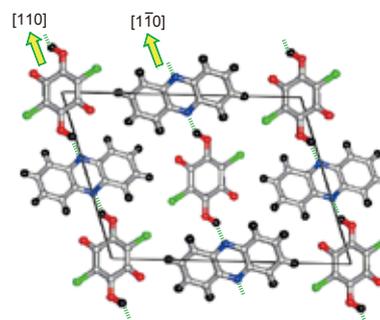


Fig. 1 Crystal structure of Phz-H₂xa.

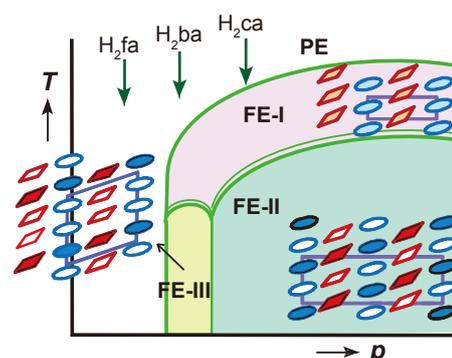


Fig. 2 Universal phase diagram of Phz-H₂xa.

3-2 Structural study of θ -(BEDT-TTF)₂CsZn(SCN)₄ under uniaxial strain

We performed structural studies of the quasi-2D organic conductor, θ -(BEDT-TTF)₂CsZn(SCN)₄ (CsZn-salt), under in-plane uniaxial strain. In the title organic conductor, multiple charge ordered (CO) patterns compete/coexist [5]. This phenomenon is considered to be a kind of charge frustration originating from the molecular arrangement (Fig. 3), which can be

regarded as an anisotropic triangular lattice from the viewpoint of nearest neighbor Coulomb interactions.

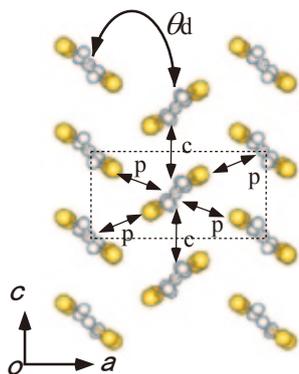


Fig. 3 θ -type Molecular arrangement.

Previously, we performed resistivity measurements of CsZn-salt under uniaxial strain to investigate the possibility of novel electronic phases in this type of material having such a frustration, by breaking up the frustration by applying uniaxial strain, and found some resistance anomalies such as a hump-like resistance anomaly under *c*-axial strain and a kink-like one under *a*-axial strain [6]. The purpose of our study at the BL-8A is to investigate the structural changes that are accompanied by resistance anomalies.

c-Axial strain induced insulating behavior in CsZn-salt, as shown in Fig. 4. Above 5 kbar, a unique hump-like anomaly was observed and the temperature at which it appeared gradually rose with increasing uniaxial strain. We examined the following three *c*-axial strain ranges:

Under 3 kbar: One genuine Bragg spot at room temperature is divided into four at low temperature. No superlattice spots are observed down to low temperature.

Under 6 kbar: We observe superlattices whose wave number is $(1/3, 0, 1/4)$ accompanied by the hump-like anomaly (upper panel of Fig. 5). The splitting of genuine Bragg spots is suppressed down to low temperature, indicating that a single phase having the superlattice is realized under 6 kbar. A structural fluctuation having the same wave number was observed in the high-temperature region of the isostructural θ -(BEDT-TTF)₂RbZn(SCN)₄ (RbZn-salt), which has a metal-insulator transition accompanied by a charge ordered transition below 190 K.

Under 8–10 kbar: New superlattices, whose wave number is $(0, 0, 1/2)$, appear in addition to the above-mentioned one $((1/3, 0, 1/4))$ (lower panel of Fig. 5). The superlattice spots $(0, 0, 1/2)$ were observed in RbZn-salt accompanied by the charge ordered transition. Genuine Bragg spots are divided into two

accompanied by the hump-like anomaly, indicating that one sample is constructed from two regions having these two kinds of superlattice spots, *i.e.*, that a phase separation occurs.

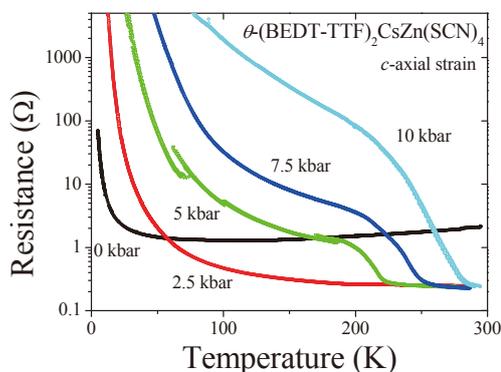


Fig. 4 Temperature dependence of resistance under various *c*-axial strains.

These results suggest that there exists an electronic phase with the superlattice spots $(1/3, 0, 1/4)$ between the charge frustrated metallic phase in CsZn-salt and the charge ordered insulating phase in RbZn-salt. A theoretical study proposed the possibility of a charge ordered metallic state (COM) in the vicinity of the charge ordered insulating phase; whether the newly observed electronic phase is a COM or not is left for future investigation.

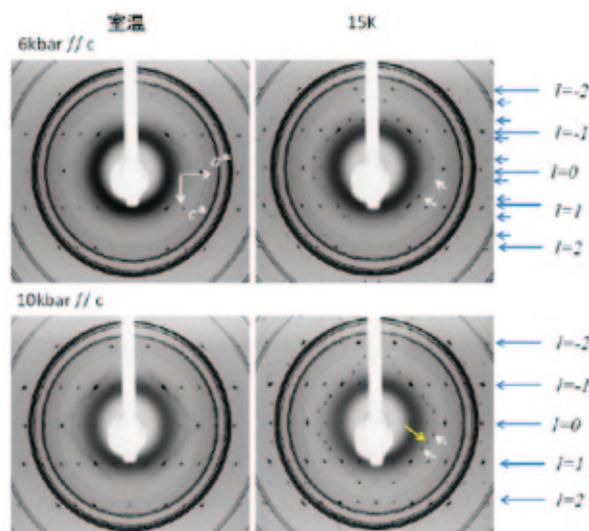


Fig. 5 Oscillation photograph of CsZn-salt under various *c*-axial strains.

a-Axial strain preserved the metallic state of CsZn-salt down to low temperature, and also suppressed the increase in resistance below 20 K, which was observed at atm. Under 7.5 kbar of *a*-axial strain, the kink anomaly was observed around 150 K. We found superlattices whose wave number is $(0, 0,$

1/2).

This result indicates that the kink-like anomaly is not a charge ordered transition but a structural transformation from θ -type to α -one, since the appearance of the superlattice is not accompanied by a metal-insulator transition and the α -type molecular arrangement can be regarded as the cell-doubling of θ -type one along the c -axis.

3-3 Structural analysis on an electric-field-induced metastable state of an organic conductor

Recently, nonlinear conduction such as giant nonlinear resistance, thyristor effect and electric-field-induced metastable states have been actively studied in organic conductors. In particular, charge ordered (CO) organic materials have attracted considerable interest because of fast switching at low voltage.

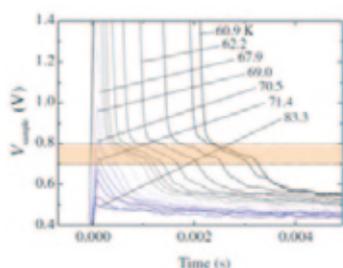


Fig. 6 Temperature dependence of time-resolved V_{sample} .

The CO conductor β -(meso-DMBEDT-TTF) $_2$ PF $_6$ undergoes the metal-insulator transition by the long-range checkerboard-type charge ordering (COO) below 70 K. In COO phase, a superlattice structure appears accompanied by unit cell doubling. Moreover, by applying an electric field below 70 K, two-step resistance drops were observed. The temperature dependence of the time-resolved sample voltage (V_{sample}) at the circuit voltage $V_{\text{circuit}} = 2.5$ V is shown in Fig. 6. The transient plateau between two drops indicates a metastable state induced by electric field. Raman spectra suggest that the metastable state is the homogeneous charge-fluctuated state. To clarify the metastable state, X-ray diffraction measurement under an electric field will be carried out.

Figure 7(a) shows a schematic representation of the time-resolved X-ray beam, pulsed source and a sample condition. The metastable state appears for about 1 ms under a pulsed source with pulse width of 2 ms, while the recovery period of the sample condition is 10 ms. First, we measured a standard sample, taurine, to evaluate the data quality for the structural analysis (Fig. 7(b)) using a chopped X-ray beam for the preliminary experiments. The total time of 22 hours for

collecting the intensity data was 4.4 times longer than that for a typical collection. The final R -factor was $R = 0.037$ for 4565 observed reflections. Compared with the data quality in a typical measurement condition, there was little deterioration. Next, we investigated the structural change under an electric field using the CO conductor β -(BEDT-TTF) $_2$ PF $_6$ whose single crystal does not easily deteriorate even when a voltage is repeatedly applied. In this material, the CO is known to melt when a low voltage is applied. The average intensities of superlattice reflections associated with the CO state under pulsed voltage were weaker than that when no voltage was applied. In future work, time-resolved experiments will be performed after synchronizing the pulse generator and the chopper shutter (Fig. 7(c)).

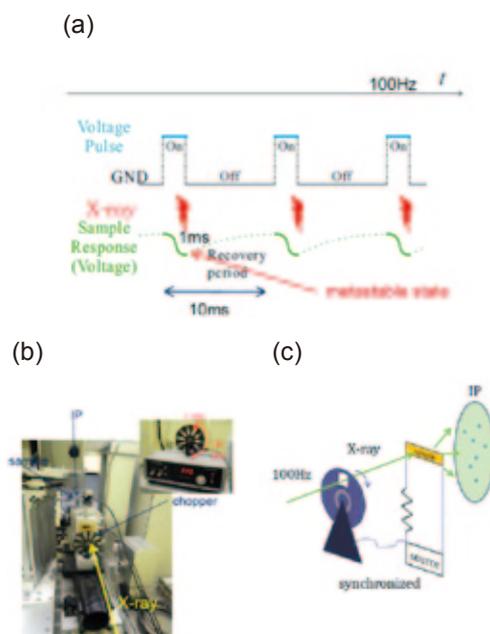


Fig. 7 Time-resolved X-ray diffraction and scattering with a resolution of the order of 1 ms.

3-4 Hydrogen-bonding molecular chains for high-temperature ferroelectricity

There is increasing demand for developing organic ferroelectrics in view of their advantages of light weight, flexibility, low cost, and environmentally benign characteristics, yet elaborate chemical designs of objective functions are required. Recently, croconic acid has been found to exhibit high polarization [7], and is the first single-component ferroelectric that is based on the cooperative proton tautomerism. In this study, by direct observation of the electric polarization - field hysteresis on molecular crystals with β -diketone enol or carboxylic unit, bistability of the hydrogen-bonding chains has been proved to functionalize the ferroelectricity of high polarization performance at room

temperature [8].

At the beginning, we explored the Cambridge Structural Database to seek polar crystal structures with the pseudo-symmetry. Among single-component molecules containing the β -diketone enol $O=C-C=C-OH$ moieties, several crystal structures can be selected as candidates as shown in Fig. 8:

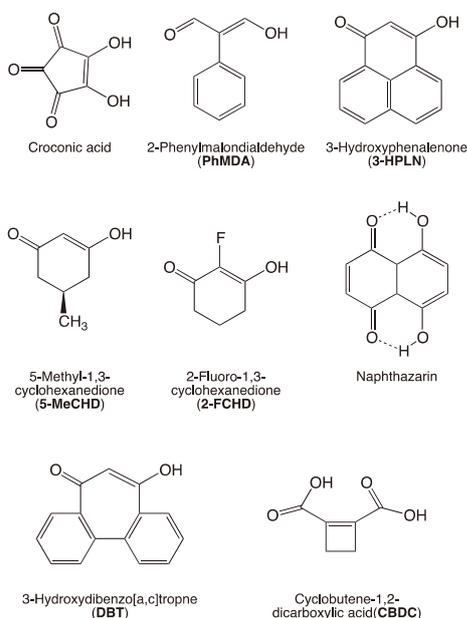


Fig. 8 Single-component organic ferroelectrics and prospective candidates.

We have successfully grown single crystals and examined the variation of crystal structures and ferroelectric properties with temperature for PhMDA, 3-HPLN, and CBDC crystals. In these crystals, the uniaxial polarity of the chain satisfies the primary condition of ferroelectricity.

The infinite sequence of hydrogen bonds (Fig. 9) involving the $C=O$ double bonds (and also $C=C$ bonds in PhMDA and 3-HPLN) is typical of π -cooperative hydrogen-bonding or resonance-assisted hydrogen bonding (RAHB), which can effectively strengthen the bonding through the resonance effect. Moreover, each chain can host the bistability necessary for ferroelectricity: all the hydrogen bonds switch from the $O-H...O$ to $O...H-O$ form at once, and simultaneously also the $O=C-C=C-O$ bond alternation occurs (*i.e.* the keto-enol transformation) without changing the chemical identity in the PhMDA and 3-HPLN crystals.

This study has revealed that high-performance ferroelectricity is not specific to only the croconic acid crystal but rather universally exists in many molecular crystals, which can be readily identified by scrutinizing the structural data and the P-E hysteresis (Fig. 9). Beyond the β -diketone enols, carboxylic acid, and the $O-H...O$ bonding-related system examined above, the

proton tautomerization represents one of the simplest design principles that can be adapted to diverse organic compounds including biomolecular systems and polymeric ones.

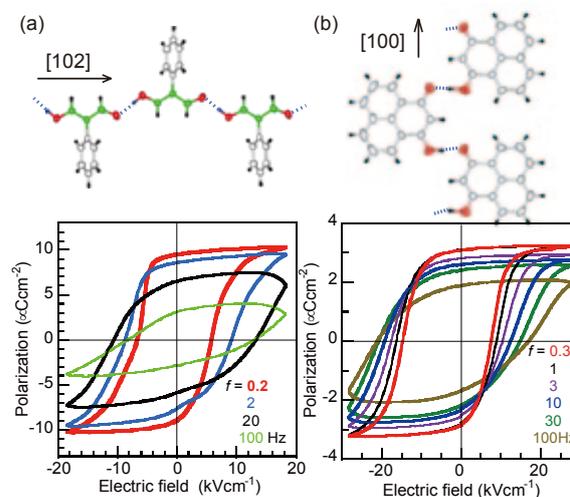


Fig. 9 Hydrogen-bonded chains and polarization hysteresis on (a) PhMDA and (b) 3-HPLN crystals.

References

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