

Structural Study of Organic Ferroelectrics TTF-CA

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Ferroelectricity is one of the most fundamental issues in both condensed matter physics and applied materials science. In the displacive-type ferroelectrics, based on the traditional point charge model, a macroscopic polarization is estimated as a product of relative displacement and charge of the ions. Recently, first-principles calculations based on the Berry phase approach, which is correctly represented the macroscopic polarization of oxides, predicted that a large spontaneous polarization more than 20 times of point charge model exists in the organic charge-transfer complex, TTF-CA [1,2].

TTF-CA is a well known prototypical material which shows neutral-to-ionic phase transition (NIT). The crystal structure comprises alternating stacks of an electron donor (*D*), tetrathiafulvalene (TTF) and an acceptor (*A*), *p*-chloranil (CA) along the *a*-axis and one-dimensional nature along this chain brings structural instability of Peierls or spin-Peierls type. Therefore, below $T_c = 81$ K, *D* and *A* molecules are displacing to the dimerized *DA* pairs. As a result, the crystal structure is symmetry-broken to a polar space group of *Pn* at NIT. To clarify the direction of polarization and molecular displacement in the ionic phase, we carried out x-ray diffraction experiments under electric field at BL-8A, PF, KEK.

The bulk symmetry-breaking of TTF-CA crystal structure under electric field was probed by the intensity difference between Bijvoet pair (*hkl* versus $\bar{h}\bar{k}\bar{l}$) reflections. Just below T_c , the observed normalized integrated intensities readily approach the full polarization values according to the simulation. The polarity was interchanged by inverting the electric field direction due to polarization switching at 61 K. Based on these results, we will discuss the absolute configuration of ferroelectric phase under electric field.

[1] G. Giovannetti *et al.*, PRL **103**, 266401 (2009).

[2] S. Ishibashi *et al.*, Physica B **405**, S338 (2010).