

Crystal Structure Analysis of a Supramolecular Ferroelectric 55DMBP-H₂ia

R. Kumai(A), D. Okuyama(B), S. Horiuchi(A), T. Arima(C), M. Watanabe(C), Y. Noda(C), and Y. Tokura(A,B,D)

(A)CERC AIST, (B)Multiferroic Project, ERATO, JST, (C)IMRAM, Tohoku Univ. (D)Dept. Appl. Phys., Univ. Tokyo

Ferroelectrics have been motivated not only by basic science but also by application because of those various utilizations for electronics. Recently Horiuchi et al. have reported a new ferroelectric realized by proton dynamics in a hydrogen-bonded chain with supramolecular structure, the cocrystal of 5,5'-dimethyl-2,2'-bipyridine (55DMBP, C₁₂H₁₂N₂) and iodanilic acid (H₂ia, C₆H₂O₄I₂). [1] The previous X-ray crystal structure analysis work suggests that the proton transfer occurs at Curie temperature ($T_C = 268$ K on cooling) and the corrective proton motion should be playing an important role for the development of the ferroelectricity in this material. Here, we report the crystal structure of 55DMBP-H₂ia obtained by the neutron diffraction in order to make clear the more precise hydrogen atom position.

Large single crystals of 55DMBP-H₂ia ($3 \times 1 \times 10$ mm³) were prepared by slow evaporation from methanol solution. Neutron diffraction experiments were performed by utilizing a four-circle diffractometer FONDER with 1.245 Å neutron beam monochromized by a Ge(311) monochromator. We used the program DABEX for the absorption correction and the calculation of the diffraction path length which was used for extinction corrections. Using the corrected data sets, we used the program SHELX-97 for the least-square fitting in order to refine the parameters. [2]

Figure 1a shows the crystal structure of paraelectric phase of 55DMBP-H₂ia at $T = 300$ K obtained by a neutron crystal structure analysis. Lattice parameters, space group ($P - 1$), and atomic coordinates except for hydrogen atoms agree with those obtained by the X-ray diffraction exper-

iments. It can be clearly observed that there are two types of hydrogen bonded site in the crystal. The significantly elongated thermal ellipsoid of hydrogen atom in the methyl group shows the rotational disordering of the methyl group. One can find the slightly elongated thermal ellipsoid of one hydrogen nuclei (H2), which indicates a broadly distributed hydrogen atom. From the interatomic distance table (inset of Fig. 1a), the migration of hydrogen atom of H2 site toward the center of the N···O hydrogen bond can be found. The situation can be also observed in the nuclear density distribution obtained by the maximum entropy method (MEM) analysis of the diffraction data. Figure 1b shows the nuclear density distribution between N···O hydrogen bond. The broadly distributed nuclear density at H2 site indicates the proton disorder in the short N···O (2.58Å) hydrogen bonded site. In the low-temperature phase, we can be observed proton transfer at both H1 and H2 sites from the X-ray structure analysis. Neutron diffraction study of the ferroelectric phase of the 55DMBP-H₂ia, which is planned in near future, can provide us for more precisely information of the proton dynamics and the origin of polarization in the crystal.

References and notes [1] S. Horiuchi, R. Kumai, Y. Tokura, *Angew. Chem. Int. Ed.*, 46, 3497 (2007). [2] 55DMBP-H₂ia 300K: C₁₈H₁₄N₂O₄I₂, $Z = 2$, Triclinic $P - 1$, $a = 10.14(3)$ Å, $b = 8.81(5)$ Å, $c = 12.782(15)$ Å, $\alpha = 67.05(7)^\circ$, $\beta = 67.80(12)^\circ$, $\gamma = 67.06(10)^\circ$, $V = 933(3)$ Å³, $R = 0.0343$ for 1527 independent reflections ($|F_o| > 4\sigma(|F_o|)$).

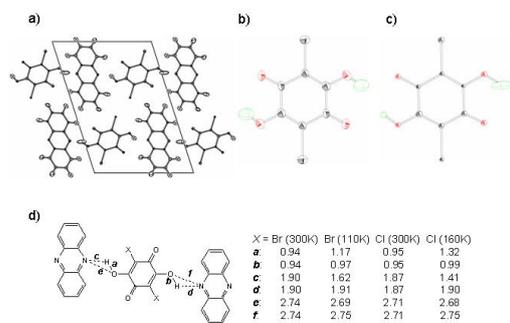


Fig. 1. (a) Crystal Structure, (b) nuclear density distribution map, and nuclear densities of hydrogen atom in the hydrogen bond for paraelectric phase (room temperature) obtained by the present neutron diffraction study.