

Crystal Structure Analysis of a Supramolecular Ferroelectric 55DMBP-H2ia at Low-temperature Phase

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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], in which the corrective proton motion should be playing an important role for the development of the ferroelectricity. Here, we report crystal structure of 55DMBP-H₂ia in a low-temperature phase obtained by the neutron diffraction in order to make clear the more precise hydrogen atom position.

Large single crystals of 55DMBP-H₂ia (3 x 1 x 10 mm³) were prepared by slow evaporation from methanol solution. The neutron diffraction experiments were performed at the T2-2 guide-hall of JRR-3M in JAEA, utilizing a four-circle diffractometer "FONDER" with 1.23960 Å neutron beam monochromized by a Ge(311) monochromator. We used the program SHELX-97 for the least-square fitting in order to refine the parameters. [2]

The crystal of 55DMBP-H₂ia consists of one-dimensional chain made from O...H...N type hydrogen bond between acid and base molecules. Figure 1a shows the hydrogen bonded chain structure of ferroelectric phase of 55DMBP-H₂ia (T = 50 K) obtained by a neutron crystal structure analysis. Lattice parameters, space group (P1), and atomic coordinates except for hydrogen atoms, consist with those obtained by the X-ray diffraction experiments. It can be

clearly observed that there are two types of hydrogen bonded site, a neutral O-H...N site and a ionic O-...H-N⁺ site, in the chain. From a comparison between ferroelectric structure and paraelectric structure (Fig. 1b), which was determined by the previous neutron diffraction study, one can find the corrective proton motion along the one-dimensional hydrogen bonded chain. The alternating O-H...N and O-...H-N⁺ constitute a polar chain and a polar three-dimensional structure. That is to say, the proton migration can be an origin of the polarization in this system.

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 P1, a = 9.996(5) Å, b = 8.729(2) Å, c = 12.650(3) Å, alpha = 66.54(2)°, beta = 67.57(2)°, gamma = 66.45(2)°, V = 895.1(5) Å³, R = 0.0433 for 3115 independent reflections (|Fo| > 4σ(|Fo|)).

Figure 1

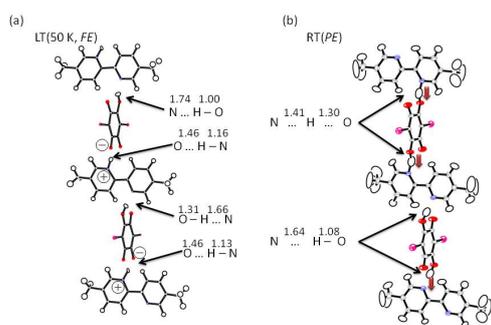


Fig. 1. Crystal Structure of 55DMBP-H2ia at (a) ferroelectric phase (50 K) and (b) paraelectric phase (room temperature).