A077-04-240823

Crystal polymorphs and multiple pathways of phase transitions in ionic liquids

H. Abe

National Defense Academy, Yokosuka 239-8686, Japan

ab@nda.ac.jp

Keywords: Keyword Crystal polymorph, Multiple pathways, Ionic liquids

Ionic liquids consist simply of a cation and an anion. The representative cation is 1-alkyl-3-methylimidazolium, $[Cnmim]^+$, where n reveals the alkyl chain length. Even in the simple molecular system, complicated phase transitions were observed at low temperature (LT) and high pressure (HP) [1-5]. The complicated phase behaviours were caused by a competition between molecular conformational polymorph and packing polymorph.

At LT, simultaneous X-ray diffraction and differential scanning calorimetry measurements were carried out using a vertical goniometer (SmartLab Rigaku Co.). A one-dimensional detector (D/teX, Rigaku Co.) was integrated into the diffractometer for rapid scanning. The X-ray incident wavelength was Cu Kα (λ = 0.1542 nm). HP X-ray diffraction experiments were performed using a Mao-Bell type diamond anvil cell (DAC) in the BL-18C of the Photon Factory (KEK in Japan). In a glovebox with dry flowing helium, the sample and ruby balls were loaded into DAC. A microbeam with a diameter of 35 m was obtained using double collimators. Two-dimensional (2D) diffraction patterns were obtained using an imaging plate system (BAS2500, Fuji-Film Co., Japan). Subsequently, the 2D data were converted into 1D intensity data to minimize the preferred orientation on the Debye rings. To eliminate air scattering, a vacuum chamber was used. The incident wavelength (0.08293 nm) was calibrated by using a standard CeO2 polycrystalline.

Figure 1 reveals the complicate phase behaviours of 1-butyl-3-methylimidazolium perfluorobutanesulfonate, [C4mim][PFBS]. Both cation and anion have conformational degrees of freedom (Fig. 1) [3]. The crystal structures of [C4mim][PFBS] are characterized by the long lattice constants, which are derived from the lattice modulations. At LT and HP, different kinds of crystal polymorphs were distinguished by X-ray diffraction. Particularly under HP, the HP crystal polymorph was irreversible upon compression and decompression. The hybrid layered structure, which is different from the liquid crystal-like layered structure, was formed. Moreover, gauche conformers both of cation and anion were preferred for the high packing efficiency. The HP-crystal polymorph based on the cationic and anionic conformational varieties supports a concept of the crystal energy landscape [6].

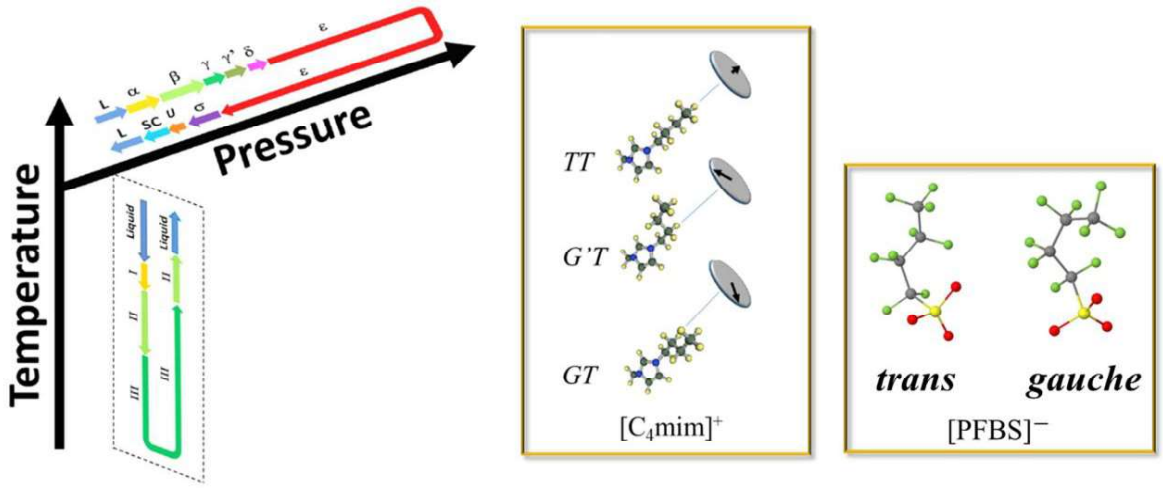

Figure 1. Schematic crystal polymorphs of [C4mim][PFBS] at LT and HP and their molecular conformers.

1 Koyama, Y., Shimono, S., Abe, H. & Matsuishi, K. (2020) J. Mol. Liq., 317, 113908.
2 Abe, H., Koyama, Y., Kishimura, H. & Matsuishi, K. (2020) J. Mol. Liq., 318, 113959.
3 Koyama, Y., Shimono, S., Kishimura, H., Takekiyo, T., Yoshimura, Y., Abe, H. & Matsuishi, K. (2021) J. Mol. Liq., 335, 116415.
4 Abe, H. & Kishimura, H. (2022) J. Mol. Liq., 352, 118695.
5 Abe, H., Koyama, Y., Shimono, S., Kishimura, H. & Matsuishi, K. (2022) Chem. Phys. 557, 111479.
6 Price, S. L. (2008) Phys. Chem. Chem. Phys., 10, 1996.