High Pressure Phase Transition in Room Temperature Ionic Liquids

Hiroshi Abe\(^1,\ast\), Machiko Shigemi\(^2\), Takahiro Takekiyo\(^2\), Yukihiro Yoshimura\(^2\) and Nozomu Hamaya\(^3\)

\(^1\) Dept. of Mater. Sci. & Eng., National Defense Academy, Yokosuka 239-8686, Japan
\(^2\) Dept. of Appl. Chem., National Defense Academy, Yokosuka 239-8686, Japan
\(^3\) Graduate School of Hum. & Sci., Ochanomizu University, Tokyo 112-8610, Japan

1 Introduction
Room temperature ionic liquids (RTILs) are highlighted in nano-heterogeneity [1], water-mediated hierarchy structure [2] and confined water in the RTIL [3] even in the liquid. The RTIL simply consists of cation and anion. Under high pressure, simple molecular system crystallization [5] and metastable crystal with holding cation [6]. Degrees of freedom of cation conformers in the RTILs are a key to interpret the complicated phase transitions under high pressure.

2 Experiment
[\text{C}n\text{mim}][\text{PF}_6] (Kanto Chemical Co.) was selected as the ionic liquid in this study. High-pressure X-ray diffraction experiments were carried out by using a Mao-Bell type diamond anvil cell (DAC) in the BL-18C of the Photon Factory at the High Energy Accelerator Research Organization in Japan. For the high-pressure experiments, the maximum pressure used was 8.1 GPa. Two dimensional diffraction patterns were obtained using an Imaging-Plate system (BAS2000, Fuji-Film Co., Japan).

3 Results and Discussion
On compression process, \(\alpha\)-phase, which is the same crystal at low temperature and ambient pressure, appeared at around 0.3 GPa (Fig. 1). By further pressing, we can discover new high pressure crystal (\(\delta\)-phase, monoclinic) at 1GPa. Successively, \(\delta'\)-phase occurred. In the same manner with crystal polymorphs at low temperature, a series of phase transitions under high pressure is determined. A significant finding is that amorphous phase partially appeared above 6 GPa (=\(P_\text{c}\)). In Raman spectrum, new conformer of folding \(\text{C}4\text{mim}^+\) cation was induced above \(P_\text{c}\).

By structure analysis and simulations, the novel pressure-induced frustration–frustration process is clarified in one system only with a case of [\text{C}4\text{mim}][\text{PF}_6]. Under high pressure, a variety of \(\text{C}4\text{mim}^+\) conformations causes the successive frustrations, charge (scalar), orientation (vector), and coordination number (topology). On the basis of the results, we introduce “conformation glass” of the \(\text{C}4\text{mim}^+\) cation as a new concept. The potential impact of the findings presented in this study has an implication on the free-energy landscape at a nonequilibrium state and fills in gaps to the relation between degrees of freedom of motions and entropic stabilization in condensed matter physics.

**Fig. 1:** Schematic pressure–temperature diagram relating to the crystals combined with the previous studies. A stands for amorphous. The direct optical microscope images are provided as insets in the figure.

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References


* ab@nda.ac.jp