

## High Pressure Phase Transition in Room Temperature Ionic Liquids

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## 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 shows a superpressed liquid [4], decomposed 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

[C<sub>4</sub>mim][PF<sub>6</sub>] (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 ( $=P_g$ ). In Raman spectrum, new conformer of folding C<sub>4</sub>mim<sup>+</sup> cation was induced above  $P_g$ .

By structure analysis and simulations, the novel pressure-induced frustration–frustration process is clarified in one system only with a case of [C<sub>4</sub>mim][PF<sub>6</sub>]. Under high pressure, a variety of C<sub>4</sub>mim<sup>+</sup> 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 C<sub>4</sub>mim<sup>+</sup> 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.

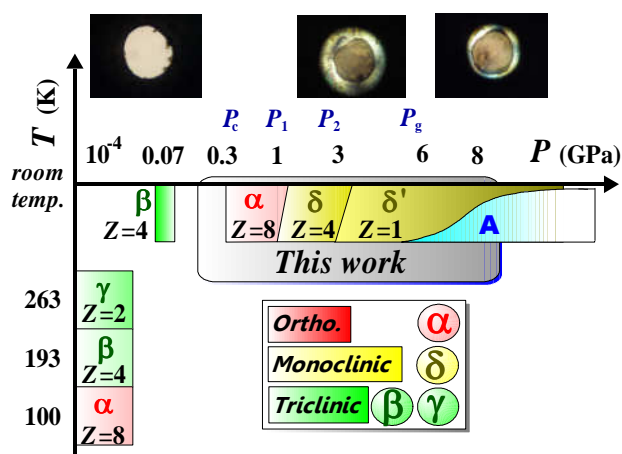


Fig. 1: Schematic pressure–temperature diagram relating to the crystals combined with the previous studies. A stands for amorphous. The direct optical microscope images are provided as insets in the figure.

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