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# Polymorphs in Room Temperature Ionic Liquids under High Pressure

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## 1 Introduction

Room temperature ionic liquids (RTILs) are recently known as novel solvent in green chemistry. We have already reported outstanding liquid hierarchy, nanoheterogeneity of liquid structures, crystal polymorphs, and multiple glass transition, and so on. The topics are summarized in the recently published paper [1].

Focusing on pressure-induced phase changes, we are investigating high pressure (HP) phases in Table 1. For a comparison, low temperature (LT) phases are also denoted. Red colored phases were determined by our group. In Table 1, cc and dc represent cold crystallization and decompression crystallization, respectively. A variety of solid phases are results in the inherent properties of cation and anion.

To fill the solid phases in Table 1 is necessary to distinguish the pressure effect from thermal one relating with characteristic cation and anion.

## 2 Experiment

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. Data were collected at room temperature. Two dimensional diffraction patterns were obtained using an Imaging-Plate system (FLA 7000,GE Healthcare Life Sciences Co.).

[DEME][$BF_4$] (*N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate) [2, 3], [$C_2$mim][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate) [4], [$C_4$mim][$PF_6$] (1-butyl-3-methylimidazolium hexafluorophosphate) [5], [$C_2$mim][$NO_3$] (1-ethyl-3-methylimidazolium nitrate) [6], and a series of [$C_n$mim][$BF_4$] (1-alkyl-3-methyl imidazolium tetrafluoroborate) [7] are selected in this study.

## 3 Results and Discussion

The intrinsic features of anions in Table 1 are described as follows; (i) $NO_3^-$ anion possesses the property of proton capturing, (ii) $BF_4^-$ anion is identified by geometrical freezing factor, (iii) $PF_6^-$ anion causes rotational disorder, (iv) $TFMS^-$ anion is chemically stable acid, and (v) $TFSI^-$ has two stable conformers.

$PF_6^-$ anion is a clue to interpret the HP effect in solidifications. For instance, HP crystals of [$C_4$mim][$PF_6$] below 1 GPa are the same as LT ones [5]. Above 1 GPa, entirely different crystal structures appeared. Thus, LT crystal polymorphs are not equal to HP ones. Orientational disorder of $PF_6^-$ anion plays an important role with molecular packing efficiency under high pressure. Furthermore, in [DEME][$PF_6$], different kind of HP crystal polymorph was observed on decompression process. Crystal structure analysis is now in progress. The result will provide cation effect in HP crystal polymorphs in the RTILs.

| | $C_2mim^+$ | $C_3mim^+$ | $C_1mim^+$ | $DEME^+$ | $MEMP^+$ |
|---|---|---|---|---|---|
| $NO_3^-$ | LT: Cryst. | LT: - | LT: cc | LT: Amor. | LT: cc |
| | HP: Cryst. | HP: - | HP: Amor. | HP: Amor. | HP: ? |
| $BF_4^-$ | LT: Cryst. | LT: Amor. | LT: Glass | LT: Cryst. | LT: cc |
| | HP: dc | HP: ? | HP: Amor. | HP: dc | HP: Amor. |
| $PF_6^-$ | LT: Cryst. | LT: Cryst. | LT: cc | LT: Cryst+cc | LT: Cryst. |
| | HP: Cryst. | HP: ? | HP: Cryst. | HP: Cryst. | HP: ? |
| $TFMS^-$ | LT: Cryst. | LT: - | LT: Cryst. | LT: Amor. | LT: Cryst. |
| | HP: ? | HP: - | HP: Cryst. | HP: Amor. | HP: ? |
| $TFSI^-$ | LT: cc | LT: Amor. | LT: cc | LT: Amor. | LT: Amor. |
| | HP: Cryst. | HP: ? | HP: ? | HP: Amor. | HP: ? |

Table 1. Low-temperature (LT) and high pressure (HP) phases of RTILs.

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