Low temperature and high pressure crystals of room temperature ionic liquid: \(N, N\)-diethyl-\(N\)-methyl-\(N\)-(2-methoxyethyl) ammonium tetrafluoroborate

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Abstract. Crystals of room temperature ionic liquid (RTIL) are obtained separately at low temperature or under high pressure. The RTIL is \(N, N\)-diethyl-\(N\)-methyl-\(N\)-(2-methoxyethyl) ammonium tetrafluoroborate, [DEME][BF\textsubscript{4}]. At ambient pressure, low-temperature (LT) crystals appeared on slow cooling. By simultaneous X-ray diffraction and differential scanning calorimetry (DSC) measurements, metastable monoclinic and stable orthorhombic phases coexist in pure [DEME][BF\textsubscript{4}]. Furthermore, the DSC thermal trace indicates that the metastable monoclinic phase was stabilized by adding water. In contrast, on compression process up to 7.6 GPa, crystallization is completely suppressed even upon slow compression. Direct observations using optical microscopy also support no crystal domain growth on compression process. High-pressure (HP) crystals at room temperature were seen only on decompression process, where two different kinds of crystals appeared subsequently. By crystal structure analysis, the LT crystal structures have no relation with the HP ones. Moreover, both metastable monoclinic phase at low temperature and higher pressure crystal has a folding molecular conformation and anti-parallel pairing of the [DEME] cation as the instability factors.

1. Introduction
Room temperature ionic liquids (RTILs) are highlighted in an electric double layer capacitor [1] and a CO\textsubscript{2} separation technique [2], and so on. On the other hand, nano-heterogeneity even in the liquid is a big topic on fundamental science [3]. In order to clarify the mysterious property of the RTILs, on molecular level, it is indispensable to investigate charge network and molecular orientational order based on the interaction between a cation and an anion. To remove the ambiguity in the liquid, a crystal structure of the RTILs provides a big insight to extract the molecular interactions from the molecular orientational order in crystal.

\(N, N\)-diethyl-\(N\)-methyl-\(N\)-(2-methoxyethyl) ammonium tetrafluoroborate, [DEME][BF\textsubscript{4}], is one of quaternary ammonium RTILs. Firstly, for an electrochemical device possessing a wide electrochemical windows, [DEME][BF\textsubscript{4}] was synthesized [4]. Tsuzuki et al. imply that oxygen of the [DEME] cation is electric negative part by density functional theory (DFT) [5]. It should be noticed...
that total charge of cation is plus one. Moreover, DFT calculation suggests that the [DEME] cation has a lot of degrees of freedom of molecular conformational stabilities [6]. More interestingly, the hydrophilic [DEME][BF$_4$] behaves more complicatedly by the hydrogen bonding of water. The complicated phase diagram in the [DEME][BF$_4$]-water system was determined by simultaneous X-ray diffraction and differential scanning calorimetry (DSC) measurements [7]. The attractive/repulsive interactions between them drastically change depending extensively on the water concentrations. At low temperature and ambient pressure, the crystal structures of pure [DEME][BF$_4$] [8] and its mixtures [9] were determined by X-ray diffraction. The crystal structures of pure [DEME][BF$_4$] and its mixtures were found to be monoclinic and orthorhombic phases. A significant point is that monoclinic a-axis corresponds to the diagonal length on a-b plane of orthorhombic lattice without the lattice mismatch.

Under high pressure and at room temperature, superpressurized phenomenon was observed by high-pressure X-ray diffraction [10, 11]. On compression process up to 7.6 GPa, there was no sharp Bragg reflections at all in [DEME][BF$_4$]. It’s very curious that crystallization is completely suppressed in the circumstance, where Coulomb force is much dominant in the shorter molecular distance under high pressure. On a contrary, on decompression process, subsequent crystallizations were detected both by in-situ optical microscopic observations and X-ray diffraction. The crystal structure at 0.8 GPa is monoclinic (Z=4), while that at 0.2 GPa is monoclinic (Z=2). Here, Z reveals the number of molecules per unit cell.

In this study, further crystal structure analysis and simulations of pure [DEME][BF$_4$] are carried out using ab-initio crystal determination method in order to distinguish the high-pressure (HP) crystals from the low-temperature (LT) ones. Molecular conformations and orientational order on the lattice sites of the HP and LT crystals reveal the intrinsic lattice stability/instability.

2. Experiments

As a sample of RTIL, hydrophilic [DEME][BF$_4$] (Kanto Chemical Co.) is selected. For H$_2$O mixtures, we used distilled water (Kanto Chemical Co.).

To determine LT crystal structures and investigate phase stabilities, in-situ observations were performed using a simultaneous X-ray diffraction and DSC (RINT-Ultima III, Rigaku Co.) [7], where the DSC is attached on a vertical goniometer. For in-situ observations of the liquids, the sample stage is fixed horizontally, since a sealed X-ray tube and a scintillation counter move simultaneously. Cu K $\alpha$ radiation ($\lambda=0.1542$ nm) was used for the simultaneous measurements. Temperature range in the simultaneous measurements was from 20 to $-80$ °C. The cooling and heating rate were 8 °C/min and 3 °C/min, respectively. During the simultaneous measurements, dry N$_2$ gas was flowing at 20 cc/min in order to reduce moisture.

High-pressure X-ray diffraction measurements were carried out with the diamond anvil cell (DAC) on beamline BL-18C of the Photon Factory at the High Energy Accelerator Research Organization in Japan, where an imaging plate system (BAS2000, Fuji-Film Co., Japan) was selected to obtain two-dimensional Debye rings [12]. The incident X-ray beam was collimated to be 100 $\mu$m in diameter. The incident wavelength was estimated to be 0.061872 nm calibrated with a standard CeO$_2$ polycrystalline. The pressure was monitored from the spectral shift of the $R_1$ fluorescence line of the ruby balls inside the DAC. The observed X-ray diffraction patterns both at low temperature and under high pressure were analysed by FOX, which is characterized by ab-initio crystal structure determinations [13].

3. Results and discussion

3.1. Low-temperature crystals on slow cooling

figure 1(a) shows the thermal traces both on cooling and heating of pure [DEME][BF$_4$]. Obviously, crystallization occurred at around -30 °C accompanying with the exothermal peak on the thermograph.
Figure 1. Thermal property of pure [DEME][BF₄] in (a) thermal traces on slow cooling and heating. Upon heating, two melting appeared. Two melting points are denoted by \( T_m^1 \) and \( T_m^2 \), respectively. Red curves reveal the calculated X-ray diffraction patterns at -80 °C of (b) monoclinic and (c) orthorhombic phases. The arrows in the figure indicate the Bragg peaks, which are not assigned by the calculations.

Figure 2. Low temperature crystals of (a) monoclinic and (b) orthorhombic phases in pure [DEME][BF₄].

and appearance of sharp Bragg reflections on X-ray diffraction. On the other hand, upon heating, we found two kinds of endothermic peaks in melting. Lower melting point is defined as \( T_m^1 \) and higher one is \( T_m^2 \). As seen in crystal polymorph of [bmmim][Cl] system [14, 15], monoclinic crystal is found to be metastable phase (\( T_m^1 \)), while orthorhombic one (\( T_m^2 \)) is much stabilized. The red curves in figures. 1(b) and 1(c) reveal the calculated diffraction patterns, while the black curves are the observed diffraction ones at -80 °C. By crystal structure analysis using FOX, two phases are determined to be \( P2_1/c \) (Monoclinic, \( Z=4 \)) and \( P2_12_12_1 \) (orthorhombic, \( Z=4 \)), respectively. The detailed crystallographic data are listed in Table 1. The arrows in figure 1(b) indicate the non-assigned peaks in the monoclinic phase. The Al sample container provides the additional Bragg reflection described by Al 111 in the figures. At least, two melting points and possible two crystal structures suggest that phase coexistence is realized at the lowest temperature (-80 °C). For a further understanding, we carried out the \textit{ab-initio} simulations, whose process is described by random molecular arrangement satisfying with the space group. Two LT crystal structures of pure [DEME][BF₄] are visualized in figures 2(a) and 2(b). Four carbons in the centre of nitrogen of a quaternary cation are described by the tetrahedron in the same manner with the green tetrahedral [BF₄] anion. Obviously, molecular orientational order of the thermally metastable monoclinic phase is quite different from that of the stable orthorhombic one. More importantly, we found that the thermally metastable monoclinic phase can coexist without the lattice

Table 1. Crystallographic data of the low-temperature phases at ambient pressure. The weighted reliability and conventional reliability factors are expressed as \( wR \) and \( R \), respectively.

| \( T \) (K) | Space group | \( a \) (nm) | \( b \) (nm) | \( c \) (nm) | \( \beta \) (°) | \( Z \) | \( \rho \) (g/cm³) | \( wR \) (%) | \( R \) (%) |
|-------|-------------|---------|---------|---------|---------|-------|-----------|---------|---------|
| 200   | \( P2_1/c \) | 1.6782  | 0.8926  | 1.0130  | 127.0   | 4     | 1.278     | 20.39   | 16.65   |
| 200   | \( P2_12_12_1 \) | 1.0128  | 1.3397  | 0.8926  | 90      | 4     | 1.278     | 19.18   | 15.42   |
mismatch; monoclinic $\beta$ angle is explained by the geometric relation as $a_{\text{monoc}} = \sqrt{a_{\text{ortho}}^2 + b_{\text{O}}^2}$, where $a_{\text{M}}, a_{\text{O}}$ and $b_{\text{O}}$ are lattice parameters of monoclinic $a$, orthorhombic $a$ and orthorhombic $b$ parameters, respectively.

Apart from the pure system, [DEME][BF$_4$]-water system was examined in order to clarify the hydrogen bonding nature of water inside the hydrophilic RTIL [4]. On the phase diagram, $T_{m1}$ is almost constant in the water poor region, while $T_{m2}$ decreases with increasing the water concentration. Thermodynamically, the stable orthorhombic phase in pure system became unstable by hydrogen of water. An interesting point is that metastable monoclinic phase is stabilized by additional water. For instance, a fraction of the metastable monoclinic phase, $f_{\text{monoc}}$, as a function of water concentration, $x$, is shown in figure 3. The $f_{\text{monoc}}$ is provided by,

$$f_{\text{monoc}} = \frac{I_{\text{monoc}}}{I_{\text{monoc}} + I_{\text{ortho}}}, \quad (1)$$

where $f_{\text{monoc}}$ and $f_{\text{ortho}}$ reveal the decomposed peak of monoclinic and orthorhombic phases from the DSC thermal trace in melting, respectively. Certainly, endothermic peak of the orthorhombic becomes larger proportionally to the water concentration by the simultaneous measurements. It is noteworthy that extraordinary increment of $f_{\text{monoc}}$ at around 1 mol% is caused by the specific superstructures of the [DEME][BF$_4$] at the water poor region [9]. The sublattice constant coincides with the average distance between water molecules at 1 mol%. Well arrayed water molecules over the medium-range could stabilize the monoclinic lattice so much. Another feature is that the lattice constant is almost the same as pure one in spite of water additive up to 20 mol% [9]. Water molecules might be intercalated into the [DEME][BF$_4$] crystal without the lattice expansion.

3.2. High-pressure crystals on decompression process

Upon compression process at room temperature, no crystallization occurred in pure [DEME][BF$_4$] and [C$_2$mim][BF$_4$], where the maximum pressure was around 8 GPa. On the other hand, on

![Figure 4. X-ray diffraction patterns of pure [DEME][BF$_4$] at (a) 0.8 GPa and (b) 0.2 GPa on decompression process at room temperature.](image)
decompression process, subsequent crystallizations were observed in the RTILs [10, 11]. The non-equilibrium freezing upon compression might be relating to the conformational-driven free energy landscape [16]. But, the superpressurized effect still remains unclear. figures 4(a) and 4(b) reveal X-ray diffraction patterns on decompression process at room temperature. Judging from sharp Bragg reflections on X-ray diffraction pattern, crystallization occurred below 1.3 GPa. Further decompression causes the solid-solid phase transition. The peak positions and intensities of the Bragg reflections are quite different each other. Therefore, it was found that two different kinds of crystals appeared subsequently by reducing pressure in pure [DEME][BF₄] system. The solid-solid phase transition was also observed in the optical microscope. At the phase transition pressure, crystal domain walls were moving distinctly. Here, the crystallographic data under high pressure are listed in Table 2. Based on the HP crystal data, the simulations of the HP phases were carried out in order to obtain the molecular orientations. The molecular arrangements and orientational order at 0.8 and 0.2 GPa are visualized as shown in figures 5(a) and 5(b), respectively. By losing c-glide, phase I (0.8 GPa) transforms to phase II (0.2 GPa) without varying the β angle. Consequently, b lattice parameter of phase II (Z=2) becomes the half value of phase I (Z=4).

Table 2. Crystallographic data of the high-pressure phases at room temperature.

| p (GPa) | Space group | a (nm) | b (nm) | c (nm) | β (°) | Z | ρ (g/cm³) | wR (%) | R (%) |
|--------|-------------|--------|--------|--------|------|---|-----------|-------|------|
| 0.8    | P2₁/c       | 0.791  | 1.081  | 1.342  | 107.9| 4 | 1.42      | 22.3  | 18.6 |
| 0.2    | P2₁        | 1.032  | 0.521  | 1.147  | 107.6| 2 | 1.32      | 27.9  | 23.9 |

3.3. Comparison between low-temperature and high-pressure crystals

In order to clarify thermal and pressure effects associating with the molecular interactions, we compare the crystal structures both of LT and HP phases. Two HP phases have no relation with the LT ones. Space group of the HP crystals was found to be monoclinic P2₁/c. Although the space group of the HP crystal (0.8 GPa) is the same as one of the LT crystals, lattice constants and β angle are entirely different as listed Tables 1 and 2. Therefore, we deduce that molecular-distance tunable pressure plays a different role, compared with the thermal effect. As another approach, degrees of freedom of cation conformations and molecular orientational order are a clue to obtain the molecular interactions at the each circumstance. From the viewpoint of molecular conformations, the cation conformations on the lattice sites are provided by the simulations. Conformations of [DEME] cation of metastable monoclinic (-80 °C), orthorhombic (-80 °C), monoclinic (0.8 GPa) and monoclinic (0.2 GPa) phases are shown in figures 6(a)-6(d), respectively. The peculiar feature is that cation foldings are demonstrated in metastable LT crystal (figure 6(a)) and highly packed HP one at 0.8 GPa (figure 6(c)). The characteristic folding cation is a key to understand the phase instability, since a zigzag sequence of cation is commonly preferred to minimize the electrostatic energy in the crystals of the conventional RTILs. In fact, the stable orthorhombic of the LT phase has no foldingconformer of cation (figure 6(b)).
In the charge-network preferred environment, a cation folding could be not formed for the well-arranged molecules in crystal. If we assume that the folding cation is regarded as the instability factor, instability might be induced in the higher pressure phase at 0.8 GPa. At 0.8 GPa, a packing efficiency has a priority against the electrostatic stabilization. In the same manner with the folding factor, molecular orientational order is a significant element considering the phase stability including a dipole-dipole interaction. For simplicity, [DEME] cation in crystal is represented only by oxygen and nitrogen in figures 7(a)-7(d). As theoretically predicted [5], oxygen (red circles) is electro negative part of cation, while nitrogen (silver circles) is located in the center of positive charge. Green circles are boron, which is central position of an anion. Surprisingly, anti-parallel pairing of the cation is seen clearly in the metastable LT phase (figure 7(a)). This means that charge network breaking occurs in the vicinity of the cation paring. On the other hand, a simple charge network is developed in the stable orthorhombic phase (figure 7(b)). Under high pressure, the specific cation pairing is also seen in the higher pressure phase at 0.8 GPa (figure 7(c)). It is clear that a cation-anion pair is interrupted by the cation pairing even under high pressure. At lower pressure (0.2 GPa), a cation and anion array such as a normal ionic crystal structure was obtained in figure 7(d). In addition to the folding conformation of cation, the anti-parallel pairing of cation is the second indicator of phase instability.

4. Concluding remarks
Crystal structures of LT and HP phases are distinguished by further structure analysis and simulations. Reflecting on the molecular interactions, the LT crystal structures are different from the HP ones. By
the detailed structure analysis, cation folding and anti-parallel pairing of cation appeared in unstable phases both at low temperature and under high pressure (instability factors). The intrinsic interactions provide an influence on the crystallization process. Normal crystallization occurs on slow cooling, although crystallization is completely suppressed on compression process (superpressurized phenomenon). The different structures, instability factors and superpressurized phenomenon are originated from a balancing among charge network, molecular orientational order, cation folding/unfolding and packing efficiency. Since pressure provides quite different results in pure [DEME][BF₄], pressure might be regarded as a significant external field to extract the inherent property of the RTILs.

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