

High Pressure Phase Transition in Room Temperature Ionic Liquids

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Under high pressure, room temperature ionic liquid (RTIL) shows the superpressurized effect on compression process. The RTIL is *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate ([DEME][BF₄]). On the other hand, on decompression process, crystal polymorphism was observed. The crystal structures at high pressure are different from those at low temperature.

1 Introduction

[DEME][BF₄] is one of quaternary ammonium RTILs (Fig. 1). At low temperature and ambient pressure, two kinds of crystal structures of [DEME][BF₄] were determined by X-ray diffraction [1]. When crystallization occurred on cooling, monoclinic and orthorhombic structures coexist without a lattice mismatch.

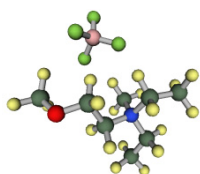


Fig. 1: [DEME][BF₄].

2 Experiment

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. The incident X-ray beam was collimated to be 100 μm in diameter. The incident wavelength was estimated to be 0.061872 nm calibrated with a CeO₂ standard polycrystalline. The pressure was monitored by the spectral shift of the *R*₁ fluorescence line of the ruby balls. The observed X-ray diffraction patterns were analyzed by *FOX*, which is characterized by *ab initio* crystal structure determinations.

3 Results and Discussion

On compression at room temperature, no crystallization were observed up to 7.6 GPa as shown in Fig. 2(a) [2]. Superpressurized phenomenon was found even under Coulomb interaction dominant circumstance. On decompression process, crystal appeared at 0.8 GPa (Fig. 2(b)). Closed circles reveal the observed intensity, while red curves are obtained by *FOX*. Further decompression

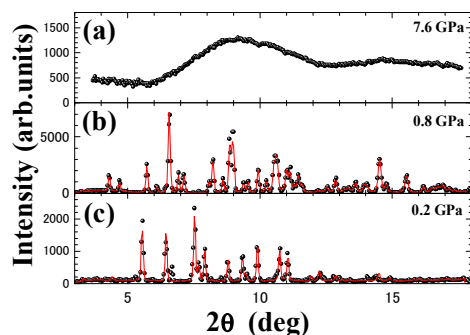


Fig. 2 Observed X-ray diffraction patterns at (a) 7.6 GPa, (b) 0.8 GPa and (c) 0.2 GPa.

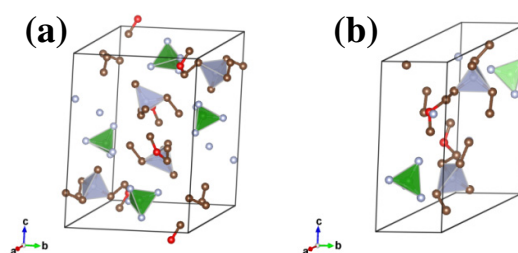


Fig. 3 Crystal structure at (a) 0.8 GPa and (b) 0.2 GPa.

causes the solid-solid phase transition judging from the different X-ray diffraction pattern (Fig. 2(c)). The crystallographic data of both crystals are summarized in Table 1. 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 becomes the half value of phase I. Since high pressure crystals are not the same as the low temperature ones, pressure effect is entirely different from thermal one in the [DEME][BF₄].

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Table 1: Crystallographic data.

<i>P</i> (GPa)	Space group	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	β (°)	<i>Z</i>	ρ (g/cm ³)
0.8	<i>P</i> 2 ₁ / <i>c</i>	0.791	1.081	1.342	107.9	4	1.42
0.2	<i>P</i> 2 ₁	1.032	0.521	1.147	107.6	2	1.32

References

- [1] Y. Imai, H. Abe and Y. Yoshimura, *J. Phys. Chem. B* **113**, 2013 (2009).
 [2] Y. Yoshimura, H. Abe, Y. Imai, T. Takekiyo and N. Hamaya, *J. Phys. Chem. B* **117**, 3264 (2013).

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