# In Situ Crystallization of Low-Melting Ionic Liquid [BMIM][PF$_6$] under High Pressure up to 2 GPa

**Lei Su,**[†,‡] **Min Li,**[§] **Xiang Zhu,**[†] **Zheng Wang,**[†] **Zhenping Chen,**[†] **Fangfei Li,**[*,§] **Qiang Zhou,**[§] **and Shiming Hong**[‡]

*Department of Physics, Zhengzhou University of Light Industry, Zhengzhou 450002, China, Laboratory of High Pressure Physics, Southwest Jiaotong University, Chengdu 610031, China, and State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China*

To develop a new practical method of purifying and recycling ionic liquids, we performed direct microscopic observations and in situ crystallization of low-melting ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]), in detail by high pressure Raman spectroscopy. Compression of [BMIM][PF$_6$] was measured under pressures up to about 2.0 GPa at temperatures 293−353 K by using a high pressure diamond anvil cell (DAC). At room temperature, with pressure increasing, the characteristic bands of [BMIM][PF$_6$] displayed nonmonotonic pressure-induced frequency shifts, and [BMIM][PF$_6$] experienced the liquid−solid phase transition at about 0.50 GPa. In separate experiments, in situ crystallization of low-melting ionic liquid [BMIM][PF$_6$] were also measured at various *P*−*T* regions, in order to improve the understanding of its stability limits. Finally, the *T* versus *P* phase diagram of [BMIM][PF$_6$] was constructed, and it showed that the melting point was an increase function of pressure. It was also indicated that the structure changes in the crystalline and liquid states under high pressure might also be associated with conformational changes in the butyl chain. Pressure-released Raman spectra also showed that the phase transition of [BMIM][PF$_6$] was reversible.

## 1. Introduction

Ionic liquids (ILs) are liquids that are composed entirely of ions just like molten sodium chloride.[1,2] Applications of ionic liquids are being vigorously explored in various fields due to their unusual properties, which include electrolytes in batteries, lubricants, plasticizers, and solvents; catalysis in synthesis; matrices for mass spectroscopy; and solvents for the manufacture of nanomaterials, extraction, gas absorption agents, etc.[3−9] In the fundamental studies, researchers were mainly interested in their physical and chemical properties under ambient pressure such as melting point, density, viscosity, electrochemistry, and the relationship between anion and cation structure.[10−14] Voth et al. studied the structure and dynamics of the ionic liquids in detail by molecular dynamics simulations.[15−18] Gafurov et al. discussed the temperature effect on Raman bandwidth and peak position which was associated with temperature-induced phase changes in molten salts, and pointed out that a saturation of the rotary mobility of the anions in these salts occurred in the crystal phase.[19] From Raman studies of the ionic liquids, Nishikawa et al. studied the effects in a premelting region and the structural changes taking place during the crystallizing and melting processes for ionic liquids.[20] Triolo et al. described the effect of small amounts of water on the Raman spectrum of ionic liquids and provided clear experimental evidence of the prompt association between "free" water molecules and anions at very small water contents.[21] Lass'egues et al. and Umebayashi et al. investigated conformational behaviors of ionic liquids as a function of temperature by Raman spectroscopy and DFT calculations, and these studies indicated that the experimentally evaluated isomerization enthalpies in ionic liquids were in good agreement with those estimated by theoretical calculations.[22,23]

Although room temperature ionic liquids (RTILs) attract much attention of chemists,[24] there are still so many important fundamental questions which should be researched. It is well-known that, after the chemical reaction has taken place, this kind of industrial solvent as ionic liquid needs to be separated from the products, purified, and reused. At present, though, the potential for recovery is very dependent on the ionic liquid used, and there are no generic recovery methods. The "green" nature of ILs as solvent is difficult to evaporate, which prevents pollution in the environment. However, exactly because of this merit in ILs, distillation through evaporation, which is an important approach to recycle and purify common organic solvents, cannot be applied to ILs. It is also possible to use other solvents such as water to recycle ILs. If one has to recycle ILs many times by use of water, it may not be possible to name ILs as a "green solvent" anymore. Instead, crystallization may be the dominant method we have to choose. Winterton et al., a group from Liverpool University, used a novel method which was called "zone melting" for producing crystals and purifying ionic liquids.[25,26] For this method, they placed a small sample of an ionic liquid in a short glass capillary and cooled it to about 123 K in a stream of nitrogen to turn it into a solid, and then the team studied an in situ crystallization process of low-melting ionic liquids in detail using a pioneering combination of techniques involving a differential scanning calorimeter and an optical heating and crystallization device (OHCD). König et al. indeed presented the results of purification and ultrapurification of ionic liquid by melt crystallization, and in their paper, purification potential of ionic liquid was also discussed

* Author to whom correspondence should be addressed. E-mail: lifangfei@jlu.edu.cn.
† Zhengzhou University of Light Industry.
‡ Southwest Jiaotong University.
§ Jilin University.

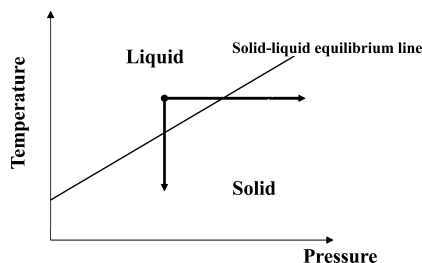**Figure 1.** Schematic drawing of compression and cooling.



**Figure 2.** Schematic diagram of 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM][PF$_6$]).

with respect to different crystallization techniques and different scales used for crystallization.[27]

Figure 1 shows a schematic drawing of compression and cooling, which implies that there are two ways about melt solidification. The conventional method is cooling; in fact, the other effective way is compression. In other words, compression is equivalent to cooling in the way of melt solidification, which can also overcome the limit of thermal conductivity. Moreover, in the compression process, whether the sample is crystal or glass, the pure end product will be compressed to a solid and then isolated from other solutions. Therefore, we believe that high pressure crystallization may be another effective way to recycle the room temperature ionic liquid. In the previous work, our group investigated the behavior of the phase transition of ionic liquids, [Cn-mim][PF$_6$], under pressures up to 1.0 GPa by using a high-pressure DTA (differential thermal analysis) apparatus. The structures of the recovered samples are also investigated by WAXS (wide-angle X-ray scattering).[28]

Spectra of high pressure experiments have proved that high pressure Raman spectroscopy is one of the most efficient high pressure probes to study pressure-induced structural phase transition of the material.[29] Kavitha et al. researched pressure-induced Raman spectroscopy on *n*-pentane up to 17 GPa at ambient temperature, and indicated that *n*-pentane underwent a liquid−solid transition around 3.0 GPa and a solid−solid transition around 12.3 GPa.[30] Hirai et al. studied solid methane using X-ray diffractometry and Raman spectroscopy in the pressure range 0.5−86 GPa, and the result suggested the existence of two new high pressure phases with a cubic symmetry above 35 GPa up to 86 GPa at room temperature, and also the existence of a metastable intermediate phase between phases A and B.[31] Under the high pressure conditions, the relative weights of the strong intramolecular interactions responsible for molecular bonding, and of the weaker intermolecular forces defining the aggregation state, are altered, and the repulsive side of the intermolecular potential is explored. Chang et al. investigated the rotational isomerism and the hydrogen bonding structures of 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride, respectively, and found that there were conformation changes of the butyl chain above a pressure of 0.3 GPa. Then, they investigated the behavior of 1-butyl-3-methylimidazolium chloride by high pressure Raman spectroscopy and found that there was a new high pressure phase formed above the pressure of 1.5 GPa.[32,33]

Although we have investigated the behavior of the phase transition of [Cn-mim][PF$_6$] under pressures up to 1.0 GPa by using a high-pressure DTA apparatus. It also can be inferred that these characteristic behaviors are due to the cooperative conformational changes of the butyl group linking to the melting and crystallizing processes. However, calorimetry does not provide information on exactly what the change is. So, in order to research the phase behavior of ionic liquids in detail, a low melting ionic liqu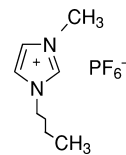id, [BMIM][PF$_6$], has been selected as objects because they have very stable physical properties and are easy to handle. By using a high-pressure DAC apparatus, the direct visual observations and in situ Raman measurements of [BMIM][PF$_6$] are presented in detail under pressures up to about 2.0 GPa. From the pressure dependence of Raman spectra and frequency shifts for the sample, the phase diagram of [BMIM][PF$_6$] at the temperature between 295 and 353 K is gained. Our aims are 2-fold: first, to establish whether high pressure crystallization could be a practical method of purifying and recycling ionic liquids, and second, to develop a sufficiently good understanding of ionic liquid structure and crystallization behavior under high pressure.

## 2. Experimental Section

1-Butyl-3-methyl imidazolium hexafluorophosphate (C$_8$H$_{15}$F$_6$N$_2$P), namely [BMIM][PF$_6$] (Henan Lihua Pharmaceutical Co. China), with purity above 99.9%, was used as starting material. Its molecular weight is 284.18 g/mol, and it is liquid under the ambient pressure and temperature. Figure 2 shows the schematic diagram of 1-butyl-3-methyl imidazolium hexafluorophosphate. It can be seen that the cation of the ionic liquid is composed of an imidazole ring, the 1,3 positions are replaced by butyl and methyl, and the anion is hexafluorophosphate. Because the ionic liquid was hygroscopic, it was dried under vacuum at 373 K for 3 h before the measurements were conducted.

A diamond anvil cell (DAC), with the diamond culet size of 0.5 mm, was used for generating pressures up to about 2 GPa. The sample was contained in a 0.2 mm diameter hole in a T301 gasket which was preindented to a thickness of about 90 $\mu$m and clamped between the two diamond anvils. Two type-Ia diamonds were used for Raman measurements. A droplet of a sample filled the empty space of the entire hole of the gasket in the DAC, which was subsequently sealed when the opposed anvils were pushed toward one another. The pressure was measured by the ruby-scale method.[34]

The temperature was measured by NiCr−NiSi thermocouples with a precision of ±1 K. The samples were held under each predetermined temperature and pressure for a long time, so that the equilibrium was established, and then the data were determined.

The Raman spectra were measured using an Acton SpctraPro500i spectrograph with a liquid nitrogen cooled CCD detector (Princeton Instrument, 1340 × 100). A solid-state diode-pumped, frequency-doubled Nd:vanadate laser ($\lambda$ = 532 nm) was used as excitation laser. The output power was set as 300 mW. Raman spectra were collected in a backscattering geometry with a 1800 gr/mm holographic grating, and the slit width was selected as 80 $\mu$m corresponding to a resolution of ca. 2 cm$^{-1}$. The sample image can be collected through an achromatic lens and then focused onto a CCD detector for visual monitoring during experiments.

## 3. Results and Discussion

Figure 3 displays the Raman spectra of [BMIM][PF$_6$] at room temperature under ambient pressure and 0.12, 0.29, 0.37, 0.49,
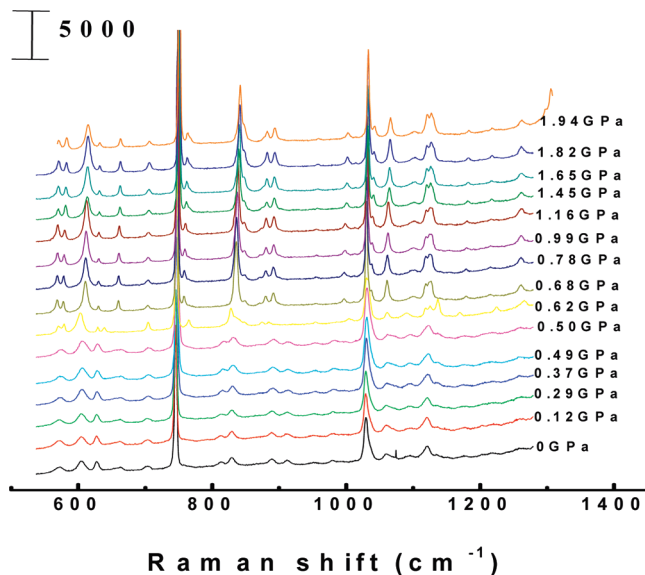
Low-Melting Ionic Liquid [BMIM][PF$_6$]

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**Figure 3.** Raman spectra of [BMIM][PF$_6$] under high pressures at room temperature (295 K).



**Figure 4.** Pressure dependence of the characteristic bands of [BMIM][PF$_6$] at room temperature.



**Figure 5.** Raman spectra of [BMIM][PF$_6$] under high pressures at room temperature.

0.50, 0.62, 0.68, 0.78, 0.99, 1.16, 1.45, 1.65, 1.82, and 1.94 GPa. In situ crystallization behavior of low-melting ionic liquid [BMIM][PF$_6$] has been investigated by Raman spectroscopy as a function of hydrostatic pressure. As the sample was compressed, Raman shifts in frequency for the modes were observed. The shift might originate from the combined effect of the overlap repulsion enhanced by hydrostatic pressure, phase transition, and so forth. From Figure 3, it could be seen that there was a monotonic frequency shift under the pressure below 0.50 GPa, which meant that the sample kept a thermodynamically stable form at the initial stage. When the pressure exceeded the sixth pressure point (0.50 GPa), the spectral profiles underwent dramatic changes as the pressure was elevated. Also, it could be seen that some old peaks disappeared and some new peaks appeared: namely, the bands at 663, 813, 911, and 1120 cm$^{-1}$, etc., observed in the liquid state disappeared abruptly in the crystalline state, while the bands at 639, 765, 847, 884, 1037, 1125, and 1169 cm$^{-1}$, etc., appeared abruptly in the crystalline state. It could indicate that a phase transition of the sample occurred under this condition. The conformations of imidazolium-based ILs have been widely reviewed in both their crystalline and liquid states. Hamaguchi et al. thought that the alkyl side chain of the ionic liquid existed in several conformations and might control the melting and solidification transition of these ionic salts.[35,36] So, in this work, the structure changes in the crystalline and liquid states under high pressure might also be associated with conformational changes in the butyl chain. Due to [BMIM][PF$_6$] being liquid under room temperature and at ambient pressure, it was speculated that the phase transition might be a liquid−solid phase transition. As the sample was further compressed, a monotonic frequency shift was observed again in frequency for the characteristic bands.

To further illustrate the frequency shift of [BMIM][PF$_6$] under high pressure, the pressure dependence of the characteristic bands of [BMIM][PF$_6$] at room temperature were plotted in Figure 4. With the pressure increasing, the main characteristic peaks of the bands moved to the high wavenumber. When the pressure was below 0.50 GPa, the pressure-induced frequency shifts of the characteristic bands are relatively small. However, while the pressure was elevated above 0.50 GPa, it could be seen that there was an inflection point at this pressure point; moreover, some new peaks appeared and some old peaks
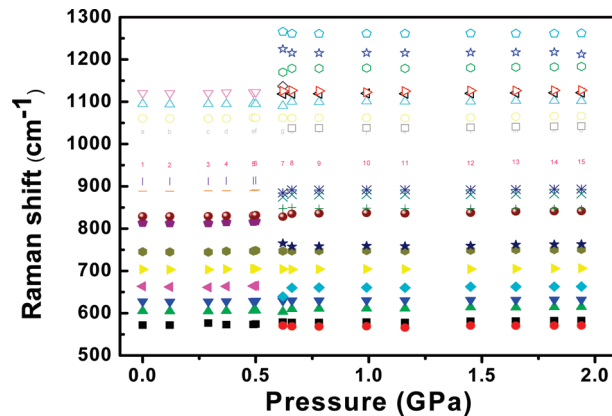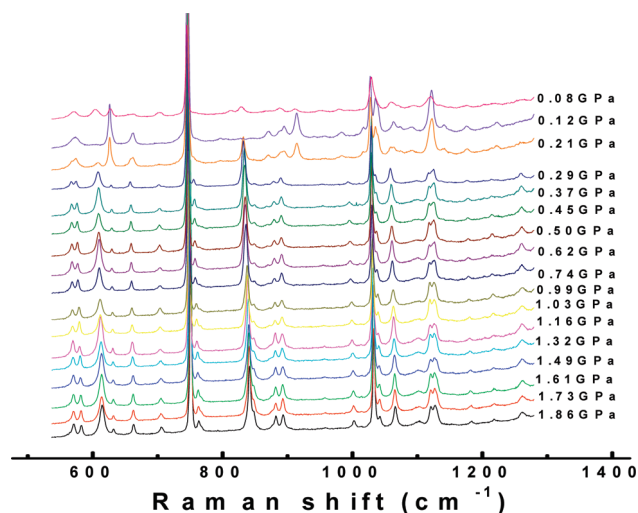
disappeared. This could indicate that a liquid−solid phase transition might occur under this condition. After that, the monotonic frequency shift was observed again for the characteristic bands up to a pressure of 1.94 GPa, which suggested that the sample seemed to be thermodynamically stable in the pressure range between 0.62 and 1.94 GPa.

Figure 5 shows the pressure-released Raman spectra, and the reversibility of the effects could be seen as pressure is reduced by a set of measurements. It also can be seen that some new peaks appeared and some old peaks disappeared, in contrast with the pressure-increased process. From Raman studies of the ionic liquids, Nishikawa et al. studied conformational changes of the cation of the ionic liquid during the crystallizing and melting processes.[20] As for the crystallizing process, conformational changes from the symmetric form to the asymmetric form are observed to occur instantaneously. In contrast, during the melting process, conformational changes from the asymmetric form to the symmetric form occur gradually with linking to melting. So it may be that, also for [BMIM][PF$_6$], this is a conclusive observation of the structural changes of ionic liquids. This demonstrates the conformational changes during the crystallizing and melting processes. It needs stating that the transition point of the solid−liquid transition of [BMIM][PF$_6$] during the pressure-released process is smaller than that during the pressure-increased process.

Microscopic observation of crystalline ionic liquid provides direct information on phase transformations. Figure 6 shows
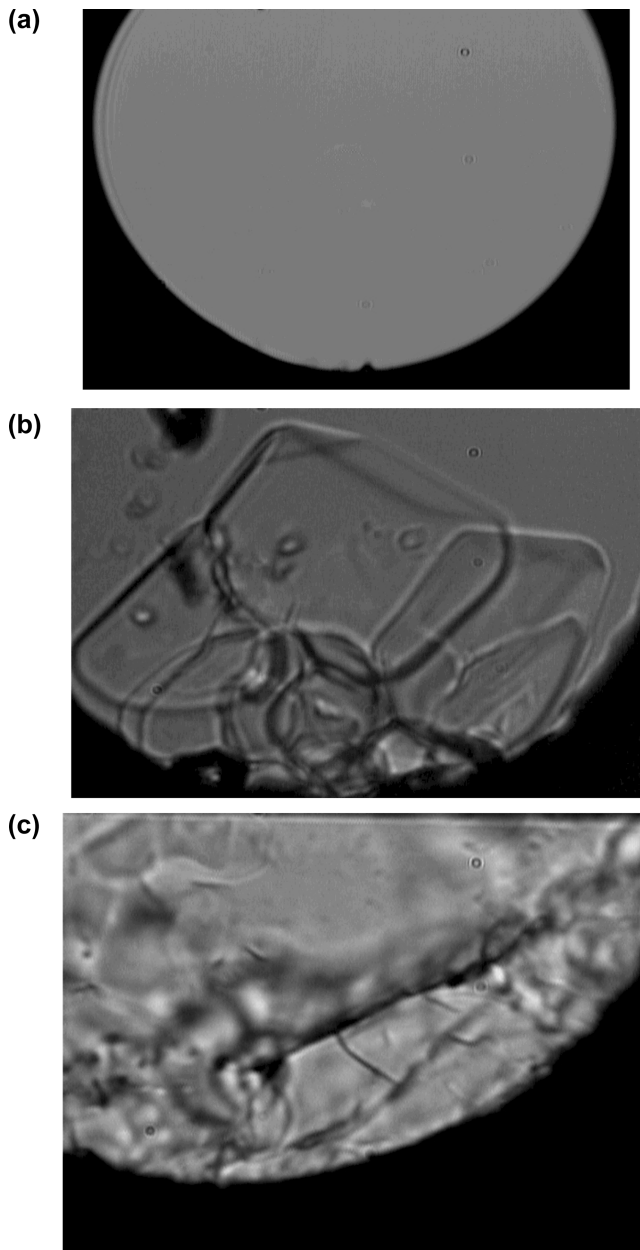
**(a)**



**(b)**



**(c)**



**Figure 6.** Photomicrographs of [BMIM][PF$_6$] in the sample chamber of DAC at the room temperature under high pressures: (a) 0.12, (b) 0.50, and (c) 0.62 GPa.

photomicrographs of [BMIM][PF$_6$] with increasing pressure at room temperature, which was visually observed by optical microscopy. It could be seen that the liquid phase of the sample disappeared and solidification formed gradually. In Figure 6a, [BMIM][PF$_6$] showed the property of the liquid at about $P = 0.12$ GPa. With the pressure increasing, the sample assembled, new crystals grew, and solidification began to form gradually. Some small bumps and pits on the surface occurred from the existence of some droplets of compressed ionic liquid on the growing processes. Then, the liquid phase of [BMIM][PF$_6$] changed to the solid phase completely at the pressure of 0.62 GPa. Additionally, comparing these three photomicrographs, we can see that the sample changed gradually from a transparent liquid into a translucent solid−liquid phase, and then into a still translucent solid with the pressure increasing. The transformation above is important for understanding the pressure-induced crystallizing process. As seen in Figure 6, in situ crystallization of room temperature ionic liquid [BMIM][PF$_6$] under high
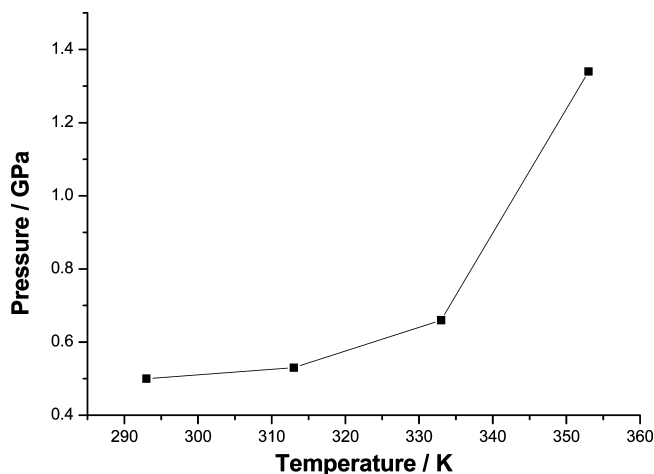


**Figure 7.** High pressure $T$ vs $P$ phase diagrams of [BMIM][PF$_6$].

pressure was observed in detail, which was coincident with the data determined by high pressure Raman analysis in Figures 3 and 4. That is, the Raman frequencies of characteristic bands of the ionic liquid showed a gradual increase at the initial state, while there was an inflection point at a pressure of 0.50 GPa, and some old peaks disappeared and some new peaks appeared above this pressure point.

Besides at the temperature of 295 K (room temperature), the behavior of the phase transition of [BMIM][PF$_6$] has also been investigated under pressures up to 2.0 GPa at temperatures of 313, 333, and 353 K by using high pressure Raman measurements. The visual observations and in situ crystallization of room temperature ionic liquid [BMIM][PF$_6$] have also been performed in detail under high pressures at each temperature. Figure 7 shows the $T$ versus $P$ phase diagram of [BMIM][PF$_6$] at temperatures between 295 and 353 K. From the S−L line it can be seen that the melting temperature increases with the pressure increasing, and it means that the thermal stability of the solid phase is enhanced as the high pressure increases under the given experimental conditions. It needs stating that the S−L line of the solid−liquid transition of [BMIM][PF$_6$] is different from that gained in the high pressure DTA measurements.[28] In these two kinds of methods, the temperatures of the phase transition observed in the DTA measurements are a little higher than these in this work. We think each result may have a certain degree of deviation. However, this method is better than the one which was used in the DTA measurement because the main deviation of the DTA measurements is the consequence of the high heating rate used in our previous work. In this study, we have given full consideration to this issue to decrease the deviation as much as possible. Once the $T$ versus $P$ phase diagram and crystallization behavior of ionic liquids are gained, high pressure technology might be applied to grow the crystal of melts of ionic liquids, and separate these ionic liquids from other impurities. Therefore, we believe that this method might be another new way to purify and recycle ionic liquids, besides the zone-melting technique which was used by Winterton et al. and König et al.[25−27]

In summary, in situ crystallization of room temperature ionic liquid [BMIM][PF$_6$] under high pressure up to 2 GPa was investigated by using the high pressure Raman apparatus. It was indicated that the structural changes in the crystalline and liquid states under high pressure might also be associated with conformational changes in the butyl chain. The $T$ versus $P$ phase diagram of [BMIM][PF$_6$] was constructed under the given experimental conditions. This work is an attempt to provide a

new method to purify and recycle room temperature ionic liquid using high pressure. Further work will be conducted in the future.

## References and Notes

(1) Rogers, R. D.; Seddon, K. R. *ACS Symp. Ser.* **2003**, *856*, 599.

(2) Rogers, R. D.; Seddon, K. R. *ACS Symp. Ser.* **2002**, *818*, 446.

(3) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459.

(4) Dupont, J.; De-Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.

(5) Huang, X. H.; Margulis, C. J.; Li, Y. H. *J. Am. Chem. Soc.* **2005**, *127*, 17842. Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 5300.

(6) Zhou, Y.; Antonietti, M. *J. Am. Chem. Soc.* **2003**, *125*, 14960. Kuang, D.; Bresesinski, T.; Smarsly, B. *J. Am. Chem. Soc.* **2004**, *126*, 10534. Nakashima, T.; Kimizuka, N. *J. Am. Chem. Soc.* **2003**, *125*, 6386. Wang, Y.; Yang, H. *J. Am. Chem. Soc.* **2005**, *127*, 5316. Cooper, E. R.; Andrews, C. D.; Wheatley, P. S. *Nature* **2004**, *430*, 1012.

(7) Jensen, M. P.; Neuefeind, J.; Beitz, J. V.; Skanthakumar, S.; Soderholm, L. *J. Am. Chem. Soc.* **2003**, *125*, 15466.

(8) Wang, Y. T.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, *127*, 12192.

(9) Eastoe, J.; Gold, S.; Rogers, S. E.; Paul, A.; Welton, T.; Heenan, R. K.; Grillo, I. *J. Am. Chem. Soc.* **2005**, *127*, 7302.

(10) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.

(11) Bowlas, C. J.; Bruce, D. W.; Seddon, K. R. *Chem Commun.* **1996**, *14*, 1625.

(12) Bonhote, P.; Dias, A. P.; Pageorigion, N. *Inorg. Chem.* **1996**, *35*, 1168.

(13) Mihkel, K. *Proc. Est. Acad. Sci., Chem.* **2000**, *49*, 145.

(14) Dullius, E. L.; Suarez Paulo, A. Z.; Einloft, S.; De Souza, R. F.; Dupont, J.; Fischer, J.; De Cian, A. *Organometallics* **1998**, *17*, 815.

(15) Wang, Y.; Voth, G. A. *J. Phys. Chem. B* **2006**, *110*, 18601.

(16) Del Pópolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 1744.

(17) Wang, Y.; Jiang, W.; Yan, T.; Voth, G. A. *Acc. Chem. Res.* **2007**, *40*, 1193–9.

(18) Jiang, W.; Yan, T.; Wang, Y.; Voth, G. A. *J. Phys. Chem. B* **2008**, *112*, 3121–31.

(19) Gafurov, M. M.; Aliev, A. R.; Akhmedov, I. R. *Spectrochim. Acta, Part A* **2002**, *58*, 2683.

(20) Endoand, T.; Nishikawa, K. *J. Phys. Chem. A* **2008**, *112*, 7543.

(21) Fazio, B.; Triolo, A.; Di Marco, G. *J. Raman Spectrosc.* **2008**, *39*, 233.

(22) Lass'egues, J. C.; Grondin, J.; Holomb, R.; Johansson, P. *J. Raman Spectrosc.* **2007**, *38*, 551.

(23) Umebayashi, Y.; Mitsugi, T.; Fujii, K.; Seki, S.; Chiba, K.; Yamamoto, H.; Canongia Lopes, J.; Pa'dua, A. H.; Takeuchi, M.; Kanzaki, R.; Ishiguro, S. *J. Phys. Chem. B* **2009**, *113*, 4338.

(24) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.

(25) Choudhury, A. R.; Winterton, N.; Steiner, A.; Cooper, A. I.; Johnson, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 16792.

(26) Choudhury, A. R.; Winterton, N.; Steiner, A.; Cooper, A. I.; Johnson, K. A. *CrystEngComm* **2006**, *8*, 742.

(27) König, A.; Stepanski, M.; Kuszlik, A.; Keil, P.; Weller, C. *Chem. Eng. Res. Des.* **2008**, *86*, 775.

(28) Su, L.; Li, L. B.; Hu, Y.; Yuan, C. S.; Shao, C. G.; Hong, S. M. *J. Chem. Phys.* **2009**, *130*, 184503.

(29) Edwards, C. M.; Butler, I. S. *Coord. Chem. Rev.* **2000**, *199*, 12153.

(30) Kavitha, G.; Narayana, C. *J. Phys. Chem. B* **2007**, *111*, 7003.

(31) Hirai, H.; Konagai, K.; Kawamura, T.; Yamamoto, Y.; Yagi, T. *Chem. Phys. Lett.* **2008**, *454*, 212.

(32) Chang, H. C.; Jiang, J. C.; Su, J. C.; Chang, C. Y.; Lin, S. H. *J. Phys. Chem. A* **2007**, *111*, 9201.

(33) Chang, H. C.; Chang, C. Y.; Su, J. C.; Chu, W. C.; Jiang, J. C.; Lin, S. H. *Int. J. Mol. Sci.* **2006**, *7*, 417.

(34) Mao, H. K.; Bell, P. M.; Shaner, J.; Steinberg, D. *J. Appl. Phys.* **1978**, *49*, 3276.

(35) Ozawa, R.; Hayashi, S.; Saha, S.; Kobayashi, A.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 948.

(36) Canongia Lopes, J. N. A.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 7485.