Structural and conformational properties of 1-decyl-3-methylimidazolium tetrafluoroborate under high pressure

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Abstract

In situ crystallization of 1-decyl-3-methylimidazolium tetrafluoroborate ([C₁₀MIM][BF₄]) from melt has been investigated under high pressure up to 3.4 GPa at room temperature by using Raman spectroscopy and synchrotron X-ray diffraction measurement. Raman spectral analysis indicated that [C₁₀MIM][BF₄] experienced two successive phase transitions at about 0.3 GPa and 1.6 GPa. And the polymorphism was also discussed in view of the conformational isomerism of [C₁₀MIM]⁺ cation between gauche and trans conformers. Notably, liquid-crystal and crystal-crystal phase transitions were further confirmed by synchrotron X-ray diffraction

measurement. Moreover, it also indicated that high structural flexibility of the cations with long alkyl chain might have effect on the degree of disorder of pressure-induced crystallization for ionic liquids.

Keywords: ionic liquid, phase transition, high pressure, Raman spectra, X-ray diffraction

1. Introduction

Ionic liquids (ILs) have attracted extensive attention because of their unique properties, such as non-volatility, non-flammability, ionic conductivity, liquidity over a wide temperature range, and good dissolving properties [1-3]. The structures of ILs are flexible and can be designed according to the needs of specific applications, including novel electrolytes for energy applications and solvents for green processing of insoluble biomolecules [4]. And researchers also found facile and rapid methods for the estimation of fundamental physical properties of ionic liquids using a simple linear correlation between the given IL property and the residual volume of the nalkyl substituents [5]. Recently, studies on phase behaviors of ILs under high pressure have also led to growing interest [6-15], which may facilitate the search for their potential applications under extreme conditions.

In the case of imidazolium-based ILs, which is one of the most studied ILs, high-pressure phase behavior of some 1-alkyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_n\text{MIM}][\text{BF}_4]$) have been investigated in previous studies [16-19]. $[\text{C}_2\text{MIM}][\text{BF}_4]$ could be superpressed without crystallization up to 7 GPa, and behaved as a

superpressurized glass above 2.8 GPa. Interestingly, unusual crystallization was induced by decompression [16]. As to $[\text{C}_4\text{MIM}][\text{BF}_4]$, crystallization was not observed under high pressure up to 30 GPa at room temperature by using a high-pressure diamond anvil cell, and it was indicated that the structure change under high pressure might be associated with a conformational change in the butyl chain [17]. It was found that $[\text{C}_6\text{MIM}][\text{BF}_4]$ underwent two successive phase transitions at around 1.7 and 7.3 GPa. Further analysis of synchrotron XRD pattern and ruby fluorescence measurement indicated that the phase above the pressure 7.3 GPa is a kind of amorphous solid, while a compression-induced liquid to liquid phase transition in $[\text{C}_6\text{MIM}][\text{BF}_4]$ occurred at 1.7 GPa. The analysis of pressure effects on the conformational equilibrium of $[\text{C}_6\text{MIM}][\text{BF}_4]$ indicated that the conformational equilibrium was converted easily in liquid but difficultly in glassy state [18]. Recently, studies on phase behavior of a series of $[\text{C}_n\text{MIM}][\text{BF}_4]$ homologues with different alkyl chain lengths for $2 \leq n \leq 8$ up to about 7 GPa at room temperature had been conducted to investigate their stabilities under high pressure. $[\text{C}_n\text{MIM}][\text{BF}_4]$ for $2 \leq n \leq 8$ fell into superpressed state around 2–3 GPa, and ILs with longer alkyl chain exhibited more complicated phase behavior, which was likely due to the conformational flexibility in the alkyl chain [19].

For solidification of such kinds of ionic liquid, all of $[\text{C}_n\text{MIM}][\text{BF}_4]$ will be fall into superpressurized glass state upon compression? In order to gain more insight into the phase behavior of $[\text{C}_n\text{MIM}][\text{BF}_4]$ under extreme conditions, another $[\text{C}_n\text{MIM}][\text{BF}_4]$ homologue, 1-decyl-3-methylimidazolium tetrafluoroborate

([C₁₀MIM][BF₄]) was selected as the research object, the molecular structure of which was shown in Figure 1. In situ Raman spectroscopy and synchrotron X-ray diffraction had been conducted under high pressure up to 3.4 GPa at room temperature. Especially, the conformational changes of cations were also studied in relationship with the phase transitions.

2. Experimental section

1-decyl-3-methylimidazolium tetrafluoroborate ([C₁₀MIM][BF₄]) was gained from Lanzhou Institute of Chemical Physics, Chinese Academy of Science, whose purity was more than 99.5 %. Its molecular weight is 310.21 g/mol, and melting point is 269 K. Before all of the measurements, the sample was kept under a vacuum at a moderate temperature (353 K) for at least one day to reduce the moisture content.

A diamond anvil cell (DAC), with the diamond culet size of 0.4 mm, was used for generating high pressure. A droplet of the sample and few ruby chips was loaded in 0.12 mm diameter hole of a T301 gasket in the DAC, which was subsequently sealed when the opposite anvils were pushed toward one another. Two type-Ia diamonds were used for Raman measurements. The pressure was measured by the ruby-scale method [20].

Raman spectra were obtained using a Renishaw inVia Raman microscope (Renishaw, UK). The 532 nm line of laser (ca. 50 mW) was used as the excitation wavelength. Raman spectra were collected in a backscattering geometry with a 2400 gr/mm holographic grating, and the slit width was selected as 65 μ m corresponding to

a resolution of ca. 0.5 cm^{-1} . All high pressure spectra were taken at room temperature (297 K). The transparency of diamonds allows in situ observation for the sample under an optical microscope. The samples were held under each pressure for 15 min to establish the equilibrium, and then the data were determined. The obtained Raman spectra were fitted with Gaussian-Lorentzian mixing function using the WIRE 3.3 software (Renishaw, UK) for analyzing the spectral data.

High pressure XRD experiments were carried out at the 4W2 High-Pressure Station of Beijing Synchrotron Radiation Facility (BSRF) in China. The monochromatic $0.6199\text{ \AA}$ radiation with a $10 \times 31\text{ }\mu\text{m}^2$ spot was used for data collection. The scattered angle and the incident wavelength were calibrated by a standard CeO_2 polycrystalline. And the two-dimensional (2D) data were converted to one-dimensional intensity data versus 2θ by the software FIT2D [21].

3. Results and discussion

Pressure dependence of characteristic Raman bands of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ under high pressures at room temperature (297 K) were shown in Figure 2. Although specific assignments of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ had not been reported by quantum chemical calculation in the literature, some characteristic bands could be assigned according to previous studies about $[\text{C}_n\text{MIM}][\text{BF}_4]$ [22-24]. The Raman peaks at 763 and 1022 cm^{-1} are respectively assigned to BF symmetric stretching of the $[\text{BF}_4]^-$ anion and ring in-plane symmetric stretching of the $[\text{C}_{10}\text{MIM}]^+$ cation. Additionally, 2800-3050 cm^{-1} and 3050-3200 cm^{-1} spectral range are respectively attributed to CH stretching

of the alkyl chains and the imidazolium ring. As shown in Figure 2, the spectral profiles underwent dramatic changes as the pressure was elevated up to 0.3 GPa. A new peak at 740 cm^{-1} appeared abruptly. And the peak of ring in-plane symmetric stretching was red-shifted to lower frequencies. As a useful probe for structural changes, a sharp peak appeared at 2890 cm^{-1} , and CH stretching of the imidazolium ring split into five peaks. It could be inferred that $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ might undergo a phase transition leading to a new phase (designated as phase II, and the original phase was designated as phase I) around 0.3 GPa. Upon further compression up to about 1.6 GPa, Raman spectra showed different feature. The new peak at 740 cm^{-1} , the peak of BF symmetric stretching and the peak of ring in-plane symmetric stretching split into two peaks. The peaks of CH stretching of the imidazolium ring merged into two peaks. These results indicated that phase transition of phase II might occur leading to another new phase (designated as phase III) around 1.6 GPa.

Pressure-induced phase transitions were also discussed in relationship with the conformational changes of the cations. According to previous studies, $[\text{C}_{10}\text{MIM}]^+$ should have conformational equilibria between the trans and gauche conformers for the main long alkyl chain. For the cation $[\text{C}_{10}\text{MIM}]^+$, 599 cm^{-1} and 622 cm^{-1} peaks in the CH_2 rocking mode were assigned to be gauche and trans conformers relating to NCCC rotation [25]. As shown in Figure 2, two conformers coexisted in the liquid state under ambient temperature and pressure like other $[\text{C}_n\text{MIM}][\text{BF}_4]$ homologues with different alkyl chain lengths for $4 \leq n \leq 8$. With increasing pressure, Raman band at 622 cm^{-1} still existed, however, Raman band at 599 cm^{-1} disappeared abruptly

above about 0.3 GPa, which meant that the phase III showed trans conformers. Upon further compression, the peaks of 622 cm^{-1} splitted into two peaks, and two new peaks at 605 and 646 cm^{-1} appeared. Thus, it could be predicted that the phase III corresponded to distorted crystal containing the perturbed trans conformers.

The multi-peak fitting of characteristic bands for $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ with increasing pressure were summarized in Figure 3 in order to give an insight into the evolution of characteristic bands. The peak at 659 cm^{-1} and the new peak at 740 cm^{-1} which was initially observed at 0.3 GPa split into two peaks at the pressure of 1.6 GPa. And both of the peaks of BF symmetric stretching and ring in-plane symmetric stretching split into two peaks at the same pressure too. As a useful probe for structural changes, CH stretching of the imidazolium ring split into five peaks at 0.3 GPa and then merged into two peaks at the pressure of 1.6 GPa. Furthermore, the intensity ratio of some vibrational modes to BF_4 symmetric stretching (763 cm^{-1}) of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ as a function of pressure was shown in Figure 4. For clarity, F_1 , F_2 , F_3 and F_4 were used as the intensity ratio of Raman peak 659 cm^{-1} , 746 cm^{-1} , 3159 cm^{-1} and 3185 cm^{-1} to BF_4 symmetric stretching (763 cm^{-1}) respectively. It could be seen that the obvious discontinuous points occurred at the pressure of about 0.3 GPa and 1.6 GPa. These Raman spectral analysis indicated that $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ experienced two successive phase transitions under the pressure up to 3.4GPa.

To further illustrate the variations of the characteristic Raman peaks of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ with increasing pressure, Raman profiles of characteristic peaks with a combination of Gaussian and Lorentz functions were analyzed in detail [30]. Raman

shifts of some characteristic bands as a function of pressure are plotted in Figure 5. The peaks of the bands generally move to the higher wavenumber and display non-monotonic pressure-induced Raman shifts at about 0.3 and 1.6 GPa. In order to give an insight into the phase transitions, a linear fitting was introduced (red line, Figure 5). Most of the values of R^2 coefficient were close to 1, except the fitting of gauche conformer (the peak at 660cm^{-1}), which had a relative larger error (the R^2 coefficient was 0.46565). The slopes (i.e. change rates) of Raman shifts to pressure and R^2 coefficients in these three phases (I, II, III), extracted from Figure 5 by linear fitting, were shown in Table 1, which further elaborated the Raman shift discontinuities of the peaks at 599cm^{-1} , 622 cm^{-1} , 740 cm^{-1} , 1022 cm^{-1} , 3159cm^{-1} and 3176cm^{-1} of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ under different pressures. These results along with Raman spectral changes indicated that $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ underwent successive phase transitions up to 3.4 GPa. However, it was worth noting that peaks of CH stretching of the imidazolium ring moved to lower frequency when liquid to S1 phase transition occurred at about 0.3 GPa. This discontinuity in frequency shift might be related to the mechanism of C-H...F hydrogen bonding. This phenomenon was in agreement with C-H...O hydrogen bond stabilization under high pressure observed for 1, 3-dimethylimidazolium methyl sulfate, which showed non-monotonic pressure-induced frequency shifts and a red frequency shift of dominant imidazolium CH bands around 1 GPa [24]. Furthermore, the peak of ring in-plane symmetric stretching also shifted to lower frequency at about 0.3 GPa, which meant imidazolium ring elongated when liquid to S1 phase transition occurred. Therefore, it could be

inferred that hydrogen bonding and imidazolium ring changed dramatically when pressure-induced phase transition occurred.

[C₁₀MIM][BF₄] underwent pressure-induced successive phase transitions, which was concordant with in situ microscopic observation under high pressure, as shown in Figure 6. It could be obviously seen that the sample changed gradually from transparent liquid into translucent phase II around 0.3 GPa, then to translucent phase III around 1.6 GPa. When the pressure decreased to the atmospheric pressure, the sample became transparent liquid again, which indicated that pressure-induced phase transformations were reversible in the 0-3.4 GPa pressure range.

In order to give an further evidence for the high pressure phase transitions of [C₁₀MIM][BF₄], in situ synchrotron X-ray diffraction measurement was preformed, and the results were shown in Figure 7. The diffraction profile had a halo pattern under ambient pressure. With increasing pressure, sharp Bragg peaks were detected, and the phases of S1 and S2 showed completely different XRD patterns, which provided further evidence for the pressure-induced successive phase transitions of [C₁₀MIM][BF₄]. Moreover, it was interesting to point out that the Bragg peaks mainly present in the range below 8°, which suggested that lattice parameters of pressure-induced crystal phases of [C₁₀MIM][BF₄] were relatively large. As to another example of 1-alkyl-3-methylimidazolium tetrafluoroborates under high pressure, Yoshimura investigated the decompression-induced crystallization of [C₂MIM][BF₄] [26]. Without showing many sharp and small peaks like XRD patterns of [C₂MIM][BF₄], XRD patterns of [C₁₀MIM][BF₄] displayed relatively broad peaks.

Poor quality for XRD patterns might originate from the formation of disorder in the crystal. Therefore, it could be inferred that high structural flexibility of IL cations with long alkyl chain had effect on the degree of disorder of pressure-induced crystallization.

In the previous studies, Holbrey and Seddon investigated the phase behavior and thermal properties of $[C_n\text{MIM}][\text{BF}_4]$ homologues ($n=0-18$) under ambient pressure. It was interesting to point out that ionic liquids $[C_n\text{MIM}][\text{BF}_4]$ ($n=2-9$) exhibited a strong tendency to supercool, forming progressively more viscous liquids, and finally glasses, with no indication of crystallization even on slow cooling (1K min^{-1})[27]. However, the true melting point rised quite dramatically above $n=9$, and crystallization was observed for $[C_{10}\text{MIM}][\text{BF}_4]$ on cooling. As to the phase behavior of $[C_n\text{MIM}][\text{BF}_4]$ under high pressure, a series of $[C_n\text{MIM}][\text{BF}_4]$ ($n=2-8$) fall into the glassy state upon compression according to the previous the previous studies [16-19]. Intriguingly, $[C_{10}\text{MIM}][\text{BF}_4]$ showed crystal polymorphism upon compression in this study. Hence, it could be predicted that compression was equivalent to cooling to some extent for solidification of $[C_n\text{MIM}][\text{BF}_4]$ ($n=2-10$).

Furthermore, in the previous studies, experimental evidence of the existence of nanoscale heterogeneities in ILs was provided, such as 1-alkyl-3-methyl imidazolium-based salts with the alkyl tails longer than the butyl chain [28-29]. Besides, aggregation behavior played a vital part in IL-containing systems, such as ILs in aqueous solutions [30]. In the case of imidazolium-based IL, the increase in the alkyl chain length enhanced their nanostructural organization. Therefore, it could be

speculated that the size of the heterogeneities of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ was larger than that of $[\text{C}_n\text{MIM}][\text{BF}_4]$ homologues ($n=2-8$). In general, crystallization occurred step by step and could be divided into nucleation and crystal growth. The first step of crystallization might be formation of microscopic heterogeneities, aggregation and nucleation, which were still under intense scrutiny. For $[\text{C}_{10}\text{MIM}][\text{BF}_4]$, with larger heterogeneity size, an initial aggregation of the constituents of the crystalline phase might be more likely to occur. This might be the reason why crystallization was observed for $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ upon cooling at ambient pressure and upon compression at room temperature.

4. Conclusion

In summary, solidification behavior of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ under high pressure has been investigated up to 3.4 GPa using Raman spectroscopy and synchrotron X-ray diffraction measurement. Unlike the solidification behavior of other ionic liquid $[\text{C}_n\text{MIM}][\text{BF}_4]$ ($2 \leq n \leq 8$), which would be fall into superpressurized glass state upon compression, Raman spectral analysis along with synchrotron XRD result revealed that $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ underwent liquid-crystal phase transition at 0.3 GPa and crystal-crystal phase transition at 1.6 GPa. Upon compression, hydrogen bonding and imidazolium ring might change dramatically when liquid-crystal phase transition occurred. For conformational changes of $[\text{C}_{10}\text{MIM}]^+$, the crystalline phase of S1 showed trans conformers, and the crystalline phase of S2 might correspond to distorted crystal containing the perturbed trans conformers. Furthermore, XRD

patterns with relative poor quality for crystalline phases of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ under high pressure indicated that a certain degree of disorder was coupled with crystalline order, which might originate from high structural flexibility of IL cations with long alkyl chain. This study provided new insights into the phase behavior of $[\text{C}_n\text{MIM}][\text{BF}_4]$ homologue under extreme conditions and contributed to a better understanding of the influence of the conformational flexibility in the alkyl chain on high pressure phase behavior for ILs. These are of significant importance for a deeper understanding of solidification of this class of compounds.

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Figure Caption

Figure 1. Schematic diagram of 1-decyl-3-methylimidazolium tetrafluoroborate.

Figure 2. Raman spectra of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ under different pressures at room temperature (297 K).

Figure 3. Selected Raman spectra of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ upon compression at room temperature (297 K).

Figure 4. Intensity ratio of some vibrational modes to BF_4 symmetric stretching (763 cm^{-1}) of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ as a function of pressure. F_1 , F_2 , F_3 and F_4 indicate the intensity ratio of Raman peak 659 cm^{-1} , 756 cm^{-1} , 3159 cm^{-1} and 3158 cm^{-1} to 763 cm^{-1} , respectively.

Figure 5. Pressure dependence of the characteristic Raman bands of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ at room temperature (297 K).

Figure 6. Photomicrographs of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ in the sample chamber of the DAC under high pressures at room temperature (297 K).

Figure 7. Synchrotron radiation X-ray diffraction spectra of $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ under different pressures at room temperature (297 K).

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Table 1 The slopes of Raman shift to Pressure and R^2 coefficients for some vibrational modes of $[C_{10}MIM][BF_4]$ in Phases I, II and III, respectively.

Raman shift (cm^{-1})	$d\omega/dp$ (cm^{-1}/GPa)			R^2 coefficients			Approximate description
	I	II	III	I	II	III	
599	5.21 ± 0.74	—	—	0.96	—	—	Gauche
622	1.86 ± 0.49	3.14 ± 0.31	2.73 ± 0.29	0.91	0.95	0.96	Trans
740	—	3.85 ± 0.12	2.84 ± 0.38	—	0.99	0.93	BF_4 symmetric stretching
1022	3.02 ± 0.81	3.14 ± 0.16	3.11 ± 0.11	0.87	0.99	0.99	Cations symmetric stretching
3159	-4.96 ± 0.04	7.73 ± 0.39	—	0.99	0.98	—	C-H stretching
3176	8.37 ± 1.44	10.87 ± 0.68	4.94 ± 0.38	0.94	0.97	0.98	