# In Situ Observation of Multiple Phase Transitions in Low-Melting Ionic Liquid [BMIM][BF₄] under High Pressure up to 30 GPa

Lei Su,[†,*] Xiang Zhu,[†] Zheng Wang,[†] Xuerui Cheng,[†] Yongqiang Wang,[†] Chaosheng Yuan,[†] Zhenping Chen,[†] Chunli Ma,[‡] Fangfei Li,[‡] Qiang Zhou,[‡] and Qiliang Cui[‡]

[†]The High Pressure Research Center of Science and Technology, Zhengzhou University of Light Industry, Zhengzhou 450002, China
[‡]National Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

ABSTRACT: In situ characterization of phase transitions and direct microscopic observations of a low-melting ionic liquid, 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM]-[BF₄]), has been performed in detail by Raman spectroscopy. Compression of [BMIM][BF₄] was measured under hydrostatic pressure up to ∼30.0 GPa at room temperature by using a high-pressure diamond anvil cell. With pressure increasing, the characteristic bands of [BMIM][BF₄] displayed non-monotonic pressure-induced frequency shifts, and it is found to undergo four successive phase transitions at around 2.25, 6.10, 14.00, and 21.26 GPa. Especially, above a pressure of 21.26 GPa, luminescence of the sample occurs, which is connected with the most significant phase transition at around this pressure. It was indicated that the structure change under high pressure might be associated with a conformational change in the butyl chain. Upon releasing pressure, the spectrum was not recovered under a pressure up to 1.16 GPa, thereby indicating that this high-pressure phase remains stable over a large pressure range between 30 and 1.16 GPa in low-melting ionic liquid [BMIM][BF₄]. Although the sample was kept under the normal pressure for 24 h, the spectrum was recovered, and it showed that the phase transition of [BMIM][BF₄] was reversible. In other words, such a low-melting ionic liquid [BMIM][BF₄] remains stable even after being treated under so a high pressure of up to 30 GPa.
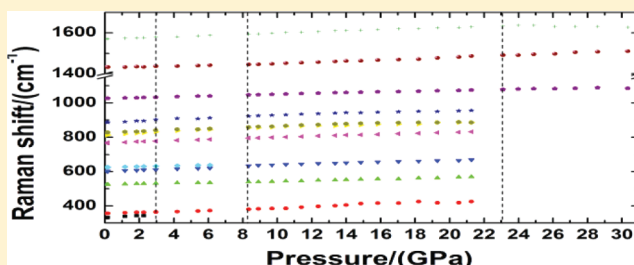
1. INTRODUCTION

Room temperature ionic liquids (RTILs) are a class of organic salts that consist entirely of ions at conditions around room temperature in their pure state. They have been used especially as green solvents and exhibit attractive properties, including negligible vapor pressure, nonflammability, extraordinarily high chemical and thermal stability, good conductivity, and controllable hydrophobicity.[1−6] The need for a better understanding of physicochemical processes in RTILs has stimulated many studies on the structure and the solvation mechanisms of molecular solutes in these systems.[7−13]

The l-butyl-3-methylimidazolium cation, [BMIM]⁺ (Figure 1), makes a number of ionic liquids (ILs) with varying
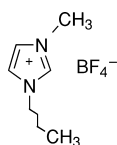

Figure 1. Schematic diagram of 1-butyl-3-methyl imidazolium tetrafluoroborate.

properties when combined with different anions. These salts are most extensively used in basic IL investigations as well as in practical applications. Therefore, determination of the structure of the [BMIM]⁺ cation in these RTILs will be an important first step for the elucidation of the microscopic liquid structure of

ionic liquids in general. The imidazolium cation can be sketched as a polar head (the ring) with an apolar tail (the alkyl chain, Cₙ). The alkyl tails will tend to aggregate when they exceed some critical length, in analogy with other amphiphilic systems. Understanding the complex interplay among these factors represents an intriguing structural problem. For [BMIM]⁺, the conformers can be obtained with rotations around both NCCC and CCCC dihedral angles of the butyl group.

Ozawa et al. studied rotational isomerism of the [BMIM]⁺, the TT (trans−trans) and GT (gauche−trans) forms, and the Raman spectra of liquid [BMIM][BF₄] indicated that at least two rotational isomers of the [BMIM]⁺ cation coexist in the ionic liquid state.[14] Holomb et al. studied the conformational isomerism in [BMIM][BF₄] by infrared (IR), Raman spectroscopy, and ab initio calculations. The result showed that the coexistence of at least four [BMIM]⁺ conformers (GG, GT, TG, and TT) at room temperature was established through unique spectral responses. To assess the total spectral behavior of the ionic liquid, both the contributions of different [BMIM]⁺ conformers and the interactions of cation and anion in the vibrational spectra are discussed.[15] Berg et al. described the vibrational frequencies of [BMIM]⁺ in TT and GT
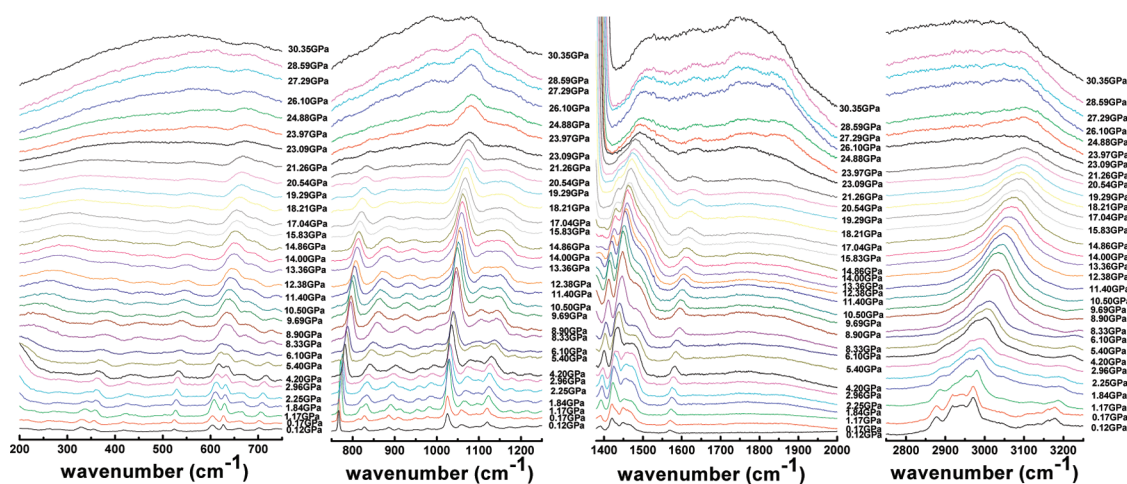
Figure 2. Raman spectra of [BMIM][BF$_4$] under high pressures up to 30 GPa at room temperature (the increasing process of pressure).

conformation using ab initio MP2 calculations, and Raman spectra of [BMIM][BF$_4$] were characteristic for different conformers.[16]

Although room-temperature ionic liquids have attracted much attention from scientists, studies at elevated pressure are very limited, and there still remain some important fundamental questions to be answered. 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 conformational changes of the butyl chain above a pressure of 0.3 GPa, and 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 a pressure of 1.5 GPa.[17,18] In 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, and the structures of the recovered samples were also investigated by WAXS (wide-angle X-ray scattering).[19] 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.

To research the phase behavior of ionic liquids in detail, a low-melting ionic liquid, [BMIM][PF$_6$], has been selected as the object. By using a high-pressure diamond anvil cell (DAC) apparatus, direct visual observations and in situ Raman measurements of [BMIM][PF$_6$] are presented in detail under pressures up to ~2.0 GPa.[20] In relation to the above, using Raman spectroscopy, Takekiyo et al. reported pressure-induced conformational change in [BMIM]$^+$ of [BMIM][PF$_6$] up to 0.8 GPa. It showed that the high-pressure, solid phase of [BMIM][PF$_6$] preferred the GT conformer of [BMIM]$^{+}$.[21] Furthermore, in a subsequent paper, they investigated the conformational stabilities of [BMIM][BF$_4$] at high pressures by Raman spectroscopy and determined the difference in the partial molar volume between the conformers of the imidazolium cations. The results indicated that the GT conformer of the [BMIM]$^+$ became predominant at high pressures.[22]

Recently, to continue to develop the new practical method of purifying and recycling ionic liquids, we tried to investigate the crystallization behavior of a low-melting ionic liquid, [BMIM]-[BF$_4$]. Unfortunately, the crystal of the ionic liquid was not found under high pressure. On the contrary, pressure-induced amorphization appeared under a pressure of up to 30 GPa. Furthermore, we found that the phase transition of the ionic liquid under high pressure was very complicated. The result showed that the sample underwent four successive phase transitions at around 2.25, 6.10, 14.00, and 21.26 GPa. Especially, above a pressure of 21.26 GPa, the luminescence of the sample occurs, which is connected with a most significant phase transition at around this pressure. It was indicated that the structure changes under high pressure might be associated with conformational changes in the butyl chain.

2. EXPERIMENTAL DETAILS

1-Butyl-3-methyl imidazolium tetrafluoroborate ([BMIM]-[BF$_4$]) was purchased from Henan Lihua Pharmaceutical Co. Ltd., whose purity was more than 98%. To reduce the water content and volatile compounds to negligible values, a vacuum at a moderate temperature (333.15 K) was applied to the samples for at least 3 days prior to use. Its molecular weight is 225.89 g/mol, and it presents a melting temperature (T_m) at −75 °C,[23] so it is liquid under ambient pressure and temperature.

A DAC, with a diamond culet size of 0.5 mm, was used for generating pressures up to ~30 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 μm and clamped between the two diamond anvils. Type Ia diamonds with low photoluminescence 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.[24] The samples were held under each pressure for 20 min so that equilibrium was established, and then their data were determined.

The Raman spectra were measured using an Acton SpctraPro500i spectrograph with a liquid-nitrogen-cooled CCD detector (Princeton Instruments, 1340 × 100). A solid-state, diode-pumped, frequency-doubled Nd:vanadate laser (λ = 532 nm) was used as the excitation laser. The output power was set as 300 mW. Raman spectra were collected in a backscattering geometry with an 1800 gr/mm holographic grating, and the slit width was selected as 80 μm, corresponding to a resolution of ~2 cm^{-1}. The sample image can be collected
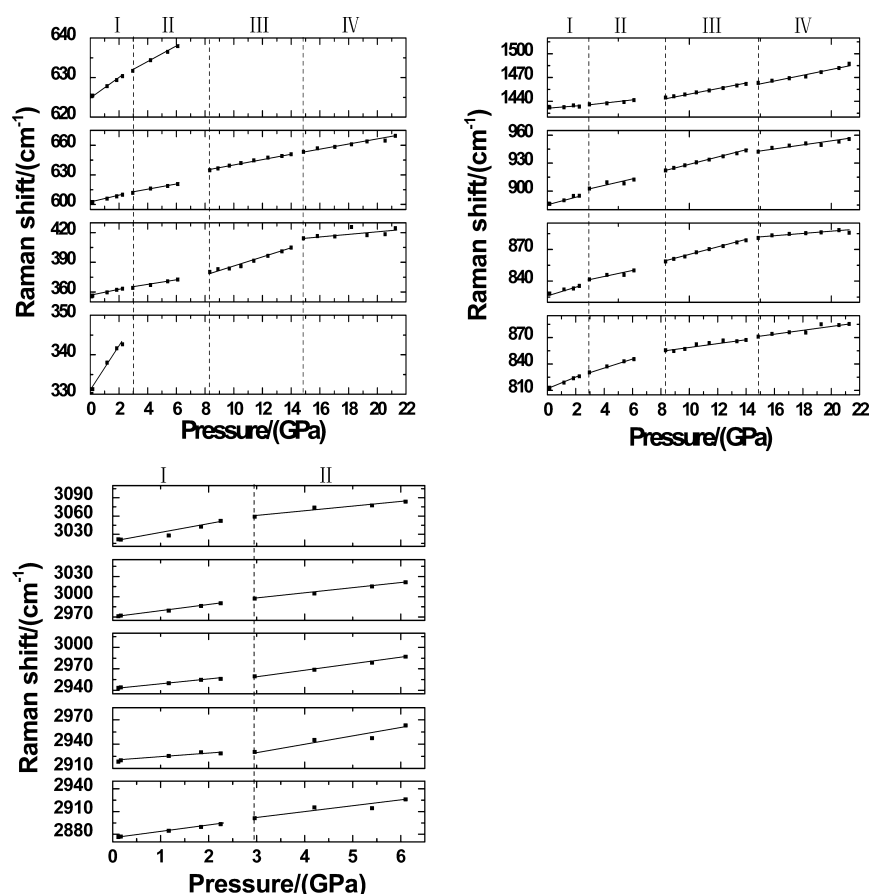
Figure 3. Raman shift discontinuities of some vibrational modes of [BMIM][BF$_4$] at the different pressures.

through an achromatic lens and then focused onto a CCD detector for visual monitoring during experiments.

3. RESULTS AND DISCUSSION

Raman scattering experiments for [BMIM][BF$_4$] were conducted at room temperature (295 K) and pressures up to about 30 GPa. Figure 2 displays the Raman spectra of [BMIM][BF$_4$] under different pressures. As the sample was compressed, it could be seen that some peaks disappeared and some peaks widened: namely, the bands at 330, 602, and 827 cm^{-1}, etc., observed under low pressure, disappeared abruptly under high pressure, but the full width at half-maximum (fwhm) of the bands at 524, 766, 1037, and 1032 cm^{-1}, etc., widened abruptly with the increasing pressure. Especially above the pressure of 21.26 GPa, the width of the Raman peak increases significantly, and the luminescence of the sample occurs, which is connected with the most significant phase transition at around this pressure.

To further illustrate the frequency shift of [BMIM][BF$_4$] under high pressure, Raman shifts discontinuities of some vibrational modes of [BMIM][BF$_4$] at the different pressures are shown in Figure 3. With the pressure increasing, the main characteristic peaks of the bands moved to the high wavenumber. However, in the increasing course of pressure, some sharp breaks exist in the plot of Raman frequency versus pressure. It can be seen that there are four discontinuous points in Raman shifts as a function of pressure at about 2.25, 6.10, 14.00, and 21.26 GPa. Therefore, it is concluded that [BMIM][BF$_4$] experiences four phase transitions in the increasing course of pressure up to 30 GPa at room

temperature. The slopes of the frequency to pressure in these phases, extracted from Figure 3 by linear fitting, are shown in Table 1, which further elaborated Raman shift discontinuities of

Table 1. The Slopes of the Frequency to Pressure for Some Vibrational Modes of [BMIM][BF4] in Phases I, II, III, and IV

Raman shift (cm^{-1})	dω/dP (cm^{-1}/GPa)			
	I	II	III	IV
330	5.97 ± 0.48			
356	3.49 ± 0.14	2.74 ± 0.15	4.35 ± 0.28	1.14 ± 0.64
602	3.43 ± 0.08	2.79 ± 0.17	2.86 ± 0.10	2.22 ± 0.19
625	2.36 ± 0.03	1.96 ± 0.06		
812	6.43 ± 0.14	4.82 ± 0.27	2.36 ± 0.32	2.33 ± 0.38
827	3.32 ± 0.30	2.29 ± 0.64	3.52 ± 0.08	0.86 ± 0.21
886	4.39 ± 0.43	2.55 ± 0.96	3.66 ± 0.07	1.77 ± 0.26
1433	0.71 ± 0.47	1.58 ± 0.29	3.02 ± 0.03	3.60 ± 0.32
2876	7.86 ± 0.15	6.82 ± 2.09		
2918	5.06 ± 0.82	9.20 ± 2.15		
2943	6.02 ± 0.29	8.60 ± 0.63		
2971	8.84 ± 0.36	7.77 ± 0.54		
3021	13.69 ± 2.17	7.43 ± 1.31		

some vibrational modes of [BMIM][BF$_4$] under different pressures.

The pressure dependence of the characteristic bands of [BMIM][BF$_4$] at room temperature are plotted in Figure 4. It
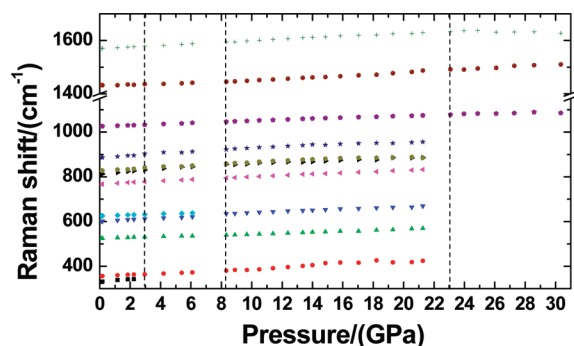
Figure 4. Pressure dependence of the characteristic bands of [BMIM][BF$_4$] at room temperature.

can be seen that there were some inflection points with increasing pressure. Obviously, some peaks observed under the low pressure disappeared abruptly when the pressure was elevated above 21.26 GPa. To further study the multiple phase transitions in low-melting ionic liquid [BMIM][BF$_4$], the relationship between pressure and fwhm of some vibrational modes of [BMIM][BF$_4$] is analyzed in detail in Figure 5. As a contrast, the relationship between pressure and Raman shifts of some vibrational modes of [BMIM][BF$_4$] is also shown in this figure. From this figure, the fwhm of some vibrational modes of [BMIM][BF$_4$] increased with increasing pressure, and it can be seen that there were some inflection points in the increasing course of pressure, which was coincident with the data determined by high-pressure Raman analysis in Figures 3 and 4.

The conformations of imidazolium-based ILs have been widely reviewed in both their crystalline and liquid states. In this work, the structure changes in this ionic liquid under high pressure might also be associated with conformational changes in the butyl chain. Holomb et al. described four [BMIM]$^+$ conformers at room temperature, which were firmly established by four unique Raman modes at 808, 825, 883, 905 cm^{-1}, characteristic of the GG, GT, TG, and TT conformers, respectively. In addition, the GT and TT are the two most stable conformers at low temperature.[15] Furthermore, Takekiyo et al. investigated the Raman bands at 600 and 624 cm^{-1} assigned to the GT and TT conformers under a pressure up to 1.0 GPa, and the results showed the GT conformer of the [BMIM]$^+$ became predominant at high pressures.[22] In this work, four [BMIM]$^+$ conformers (GG, GT, TG, and TT)

coexisted under high pressure. To elaborate the conformational change in the [BMIM]$^+$, the intensity fraction of the conformers was determined by

$$ f_{ij} = \frac{I_{ij}}{\sum_{i,j} I_{ij}} \qquad i, j = \text{T, G} \tag{1} $$

Figure 6 shows the intensity fraction changes in f_{TT}, f_{TG}, f_{GT}, and f_{GG} of the four different conformers as a function of
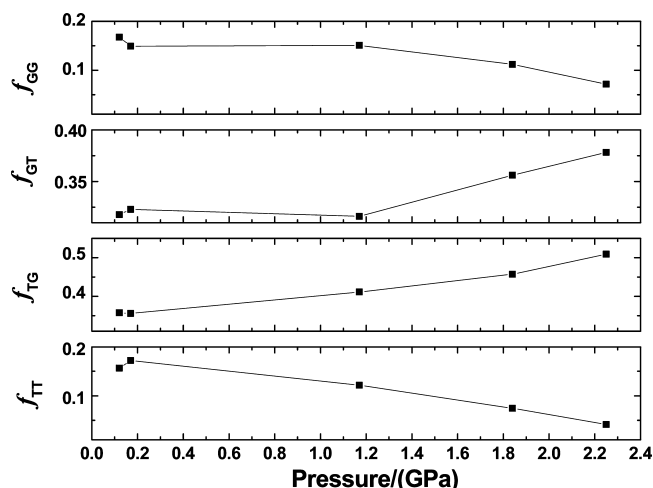

Figure 6. Intensity fractions of the conformers TT, TG, GT, and GG of [BMIM]$^+$ as a function of pressure.

pressure. The GT and TG conformers increased with a pressure up to 2.25 GPa, and the TT and GG conformers decreased with increasing pressure. The conformational behavior [BMIM][BF$_4$] at high pressure showed the higher stability of the GT and TG conformer of [BMIM]$^+$ as the pressure increased.

Figure 7 shows the pressure-released Raman spectra of [BMIM][BF$_4$] at room temperature. Upon releasing pressure, we could not find any evident change present in the Raman spectra of [BMIM][BF$_4$] under a pressure up to 1.16 GPa, in contrast with the increased pressure process. Namely, the spectrum was not recovered, thereby indicating that this high-pressure phase remains stable when released over a large pressure range between 30 and 1.16 GPa in [BMIM][BF$_4$].
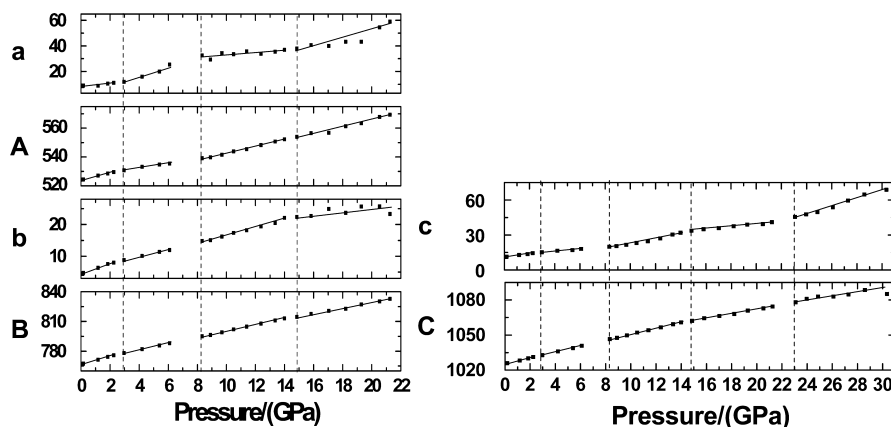

Figure 5. Full width at half maximum of some vibrational modes of [BMIM][BF4] at different pressures (A, relationship between pressure and Raman shifts of some vibrational modes of [BMIM][BF$_4$]; a, relationship between pressure and fwhm of some vibrational modes of [BMIM][BF$_4$]).
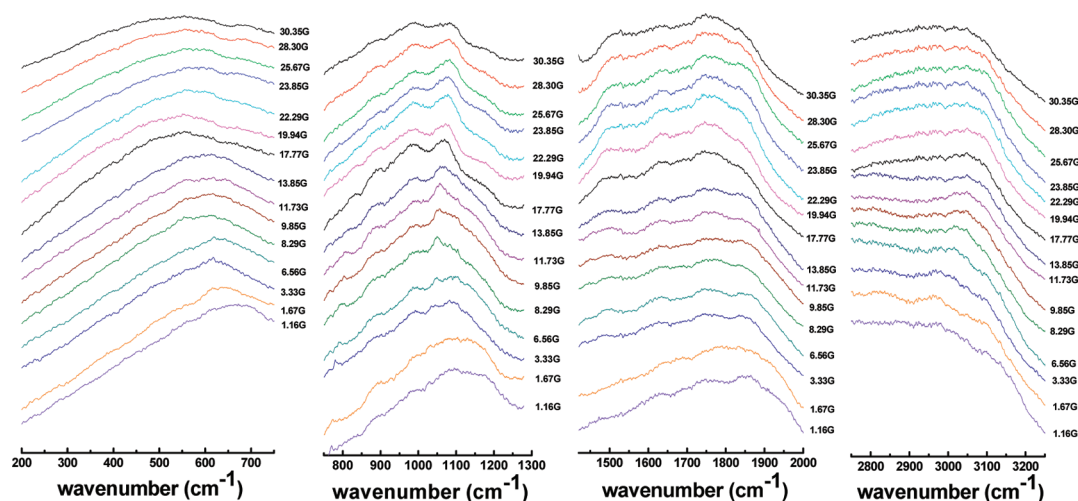
Figure 7. Raman spectra of [BMIM][BF$_4$] under high pressures at room temperature (the decreasing process of pressure).
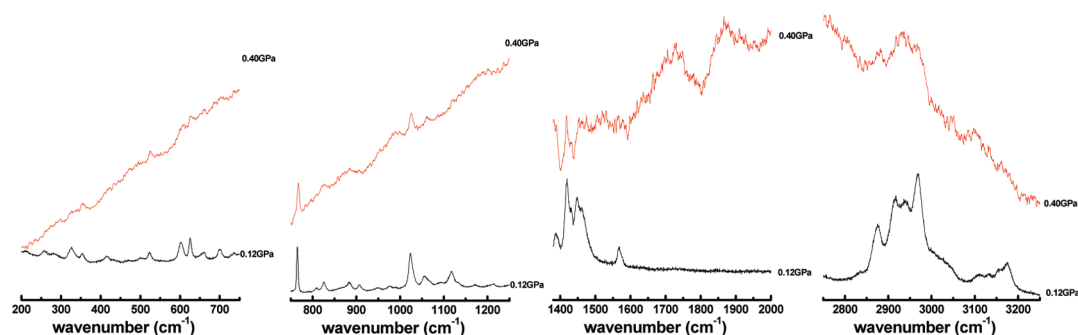

Figure 8. Raman spectra of [BMIM][BF$_4$] under low pressure (about normal pressure: 0.12 GPa) and release to low pressure (0.40 GPa) from a pressure of 30 GPa at room temperature.

Although the sample was kept under the low pressure (about normal pressure) for 24 h, it was surprisingly found that the spectrum was recovered; therefore, it showed that the phase transition of [BMIM][BF$_4$] was reversible. In other words, such a low-melting ionic liquid [BMIM][BF$_4$] remains stable even after being treated under so high a pressure of up to 30 GPa. This kind of phenomenon can be seen from Figure 8. It needs stating that because it is difficult for us to decrease the pressure to normal pressure exactly, there is a little difference in these two Raman spectra.

Figure 9 shows photomicrographs of [BMIM][BF$_4$] with increasing pressure at room temperature, which was visually observed by optical microscopy. Interestingly, all of the photomicrographs of [BMIM][BF$_4$] are mostly the same in the sample chamber of DAC under different pressures. This phenomenon is different from that in the previous study,[20] from which we could see that the sample changed gradually from a transparent liquid into a translucent solid−liquid phase and then into a still translucent solid with increasing pressure. Microscopic observation of the ionic liquid provides direct information on phase transformations, and it could be seen that the liquid phase of the sample disappeared and solidification happened gradually. However, in this study, from all of the photomicrographs of [BMIM][BF$_4$], we could not draw a conclusion of direct information on phase transformations.

How does one make sure that the phases of [BMIM][BF$_4$] below the pressure of 30 GPa are solid or liquid? From the Raman spectra of [BMIM][PF$_6$] of a previous study,[20] it could be seen that some new peaks appeared with increasing pressure, and in situ crystallization of room temperature ionic liquid [BMIM][PF$_6$] under high pressure was investigated by using the high-pressure Raman apparatus. In contrast, in this study, with increasing pressure, it could only be seen that some old peaks disappeared and no new peaks appeared. It was speculated that crystallization of the ionic liquid did not occur in this increasing course of pressure, so it was granted that the phases of [BMIM][BF$_4$] below the pressure of 21.26 GPa may be liquid. Especially, above a pressure of 21.26 GPa, the width of the Raman peak increases significantly and some peaks observed under the low pressure disappeared abruptly, and the luminescence of the sample occured simultaneously, which is connected with the most significant phase transition at around this pressure. It was granted that the phases of [BMIM][BF$_4$] above a pressure of 21.26 GPa might be a kind of amorphous solid. Of course, there should be a series of high-pressure experiments in situ, such as in situ high-pressure Brillouin scattering experiments, etc., to make certain the fact above. Additional work will be conducted in the future.

In summary, in situ characterization of phase transitions and direct microscopic observations of a low-melting ionic liquid, [BMIM][BF$_4$], have been performed in detail by Raman spectroscopy. The phase transition of the ionic liquid under high pressure is very complicated, and four successive phase transitions are reported in the 0−30 GPa range. It was indicated that the structure changes under high pressure might also be associated with conformational changes in the butyl chain. From Raman spectra of [BMIM][BF$_4$], it was granted that the phases of [BMIM][BF$_4$] below the pressure of 21.26 GPa
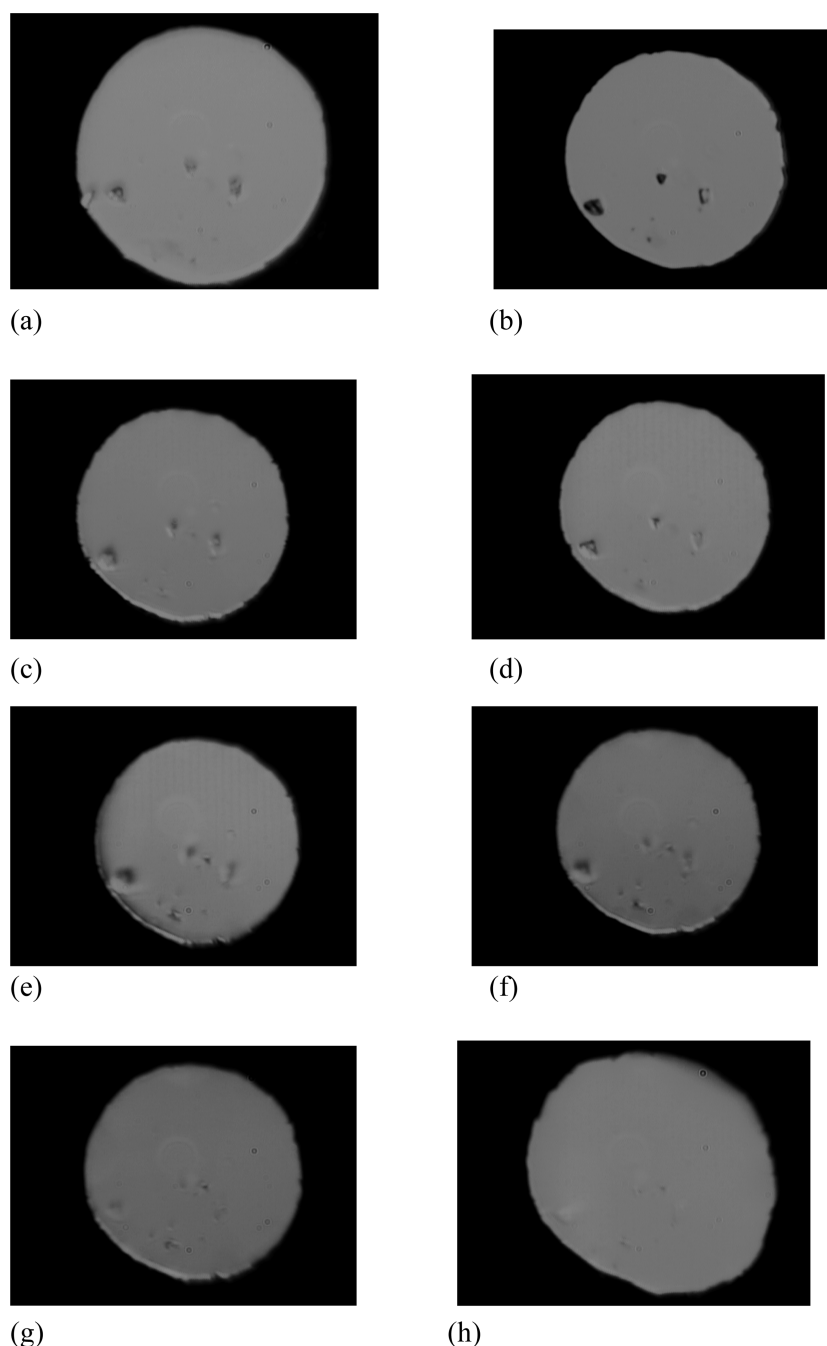
Figure 9. Photomicrographs of [BMIM][BF$_4$] in the sample chamber of the DAC at room temperature under high pressures: (a) 0.12, (b) 2.25, (c) 5.40, (d) 9.69, (e) 13.36, (f) 17.04, (g) 23.97, and (h) 30.35 GPa.

might be liquid and the phase above the pressure 21.26 GPa might be a kind of amorphous solid. Observed multiple phase transitions under high pressure are not present in other room temperature ionic liquids investigated by us in previous studies.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: zz_sulei@zzuli.edu.cn.

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