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High-pressure phase behavior of the room temperature ionic liquid 1-ethyl-3-methylimidazolium nitrate

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ABSTRACT

The phase behavior of 1-ethyl-3-methylimidazolium nitrate ([emim][NO_3]) was investigated at 298 K under high pressures, reaching 8.6 GPa, by Raman spectroscopy. This compound was found to crystallize at 0.4 GPa. The crystalline state of [emim][NO_3] seems to undergo, at least, three more phase changes under the present experimental conditions. The conformational isomerism of the $[emim]^+$ cation between *planar* and *nonplanar* forms was also investigated. Remarkably, these crystals showed drastic conformational changes upon phase changes, concomitant with the appearance of a new Raman peak attributable to the *planar* $[emim]^+$ cation. This behavior contrasts markedly with previous results obtained for 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), which showed pressure-induced amorphization at 2.8 GPa.

1. Introduction

Room temperature ionic liquids (RTILs), which typically consist of organic cations and inorganic anions exhibit many attractive properties [1,2] and unique phase behaviors [3–5]. RTILs remain liquid over a wide temperature range at ambient pressure but readily achieve their glassy state when supercooled below their melting points [6–8]. Therefore, investigating their stabilities under high pressure as another extreme variable is intriguing. Previous studies [9] showed that the common RTIL, 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), could be superpressurized without crystallization at elevated pressures reaching 8.6 GPa and behaved as a superpressurized glass above 2.8 GPa. This suggests that RTILs are useful materials for the study of glass transition [10].

So far, few studies have been conducted to understand the behavior of [emim]-based RTILs at high pressure [9,11–14]. For example, Su et al. [11] investigated the solid to liquid phase transition of 1-ethyl-3-methylimidazolium hexafluorophosphate ([emim][PF_6]) up to ~1 GPa by high pressure differential thermal analysis and found that another crystalline phase exists between solid and liquid [emim][PF_6]. Umebayashi et al. [12] evaluated the microscopic structural changes of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([emim][TFSA]) and bis(fluorosulfonyl)amide ([emim][FSA]) up to 2.5 GPa by infrared spectroscopy. They suggested that [emim][TFSA] may undergo a pressure-induced solidification above 0.3 GPa in view of the pressure-induced frequency shifts of the imidazolium C–H bands. When [emim][FSA] was compressed, the structural equilibrium between the network, comprising ion pairs or larger ion clusters, and isolated species, consisting of free ions or smaller ion clusters, in the RTIL shifted in favor of the network configuration. Then it is intriguing to know high-pressure phase behavior of 1-ethyl-3-methylimidazolium nitrate ([emim][NO_3]), which is also the common RTIL.

In addition, the $[emim]^+$ cation exhibits a conformational equilibrium between the *planar* (*P*) and *nonplanar* (*Np*) conformers for its C2N1C7C8 dihedral angle [15]. Energy optimized structures of *P*- and *Np*-conformer geometries are shown in Fig. 1. The local structural changes of the $[emim]^+$ cation may be evaluated according to phase change.

In this study, the pressure-induced Raman spectral changes of [emim][NO_3] were investigated up to 8.6 GPa to gain more insight into the phase behavior of RTILs at high pressure. This spectroscopic analysis suggests that [emim][NO_3] crystallizes at 0.4 GPa and presents crystal–crystal phase transitions upon further compression. Remarkably, the $[emim]^+$ cation underwent a drastic conformational change that generated a new conformer at high pressure.

2. Experiments

Commercially available high purity [emim][NO_3] (Sigma-Aldrich, ≥99%) was used as received. Because the as-received sample may contain a small amount of water, we checked that its water concentration was below 150–170 ppm by Karl–Fischer titration.

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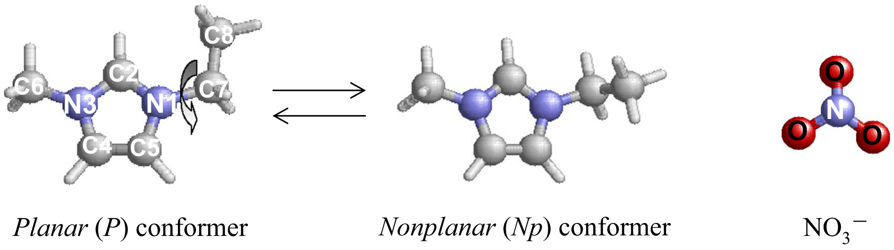

Fig. 1. B3LYP/6-311G+(d) optimized *planar* (*P*) and *non-planar* (*Np*) conformers of $[emim]^+$ cation and $[NO_3]^-$ anion, along with the atom numbering scheme.

Phase changes were monitored by Raman spectroscopy, which provides information on local structure. High-pressure Raman spectra were typically measured at room temperature (298 K) using a JASCO NR-1800 Raman spectrophotometer equipped with a single monochromator and charge-coupled device detector combined with a diamond anvil cell (DAC). The 514.5 nm line of an argon ion laser (ca. 350 mW) was used as the excitation wavelength.

All Raman data were collected during the stepwise sample compression up to ca. 8.6 GPa. The pressure was increased at a compression rate of roughly 1 GPa/h. Pressures were determined from the spectral shift of the R_1 fluorescence line of the ruby ball in the DAC sample chamber [16,17]. Samples were prepared in a dry box to avoid exposure to atmospheric moisture and CO_2.

To identify the newly discovered conformer, density functional theory (DFT) calculations were performed using the Gaussian 03 program [18]. Becke's three-parameter (B3) exchange function [19] was combined with the Lee–Yang–Parr correlation function (B3LYP) for DFT calculations of the $[emim]^+$ cation [20]. All geometry optimizations and normal frequency analyses were conducted in the gas phase using the 6-311G(d) basis set.

3. Results and discussion

3.1. Pressure-induced phase transitions of [emim][NO_3]

To gain insight into the local structure of the $[emim]^+$ cation, the C–H stretching vibration frequently served as a useful probe for structural changes [21] such as crystallization. Fig. 2a shows the Raman C–H stretching spectra of $[emim]^+$ as a function of pressure together with optical images of the transformations. These Raman C–H stretching bands were established by Heimer et al. [22]. For convenience, typical assignments are indicated on the spectrum recorded at 0.1 MPa. Basically, the frequency region spanning from 2800 to 3050 cm^{-1} corresponds to the C–H stretching (ν_{CH}) mode of the alkyl chains, whereas the 3050–3200 cm^{-1} range is attributed to the ν_{CH} of the imidazolium ring. All compression-induced frequency changes are shown in Fig. 3. The crystallization (designated as S1), which occurred around 0.4 GPa, resulted in the appearance of new peaks (open triangles, Fig. 3). All C–H stretching frequencies increased with increasing pressure, in agreement with the high-pressure behavior of 1-ethyl-3-methylimidazolium hydrogen sulfate

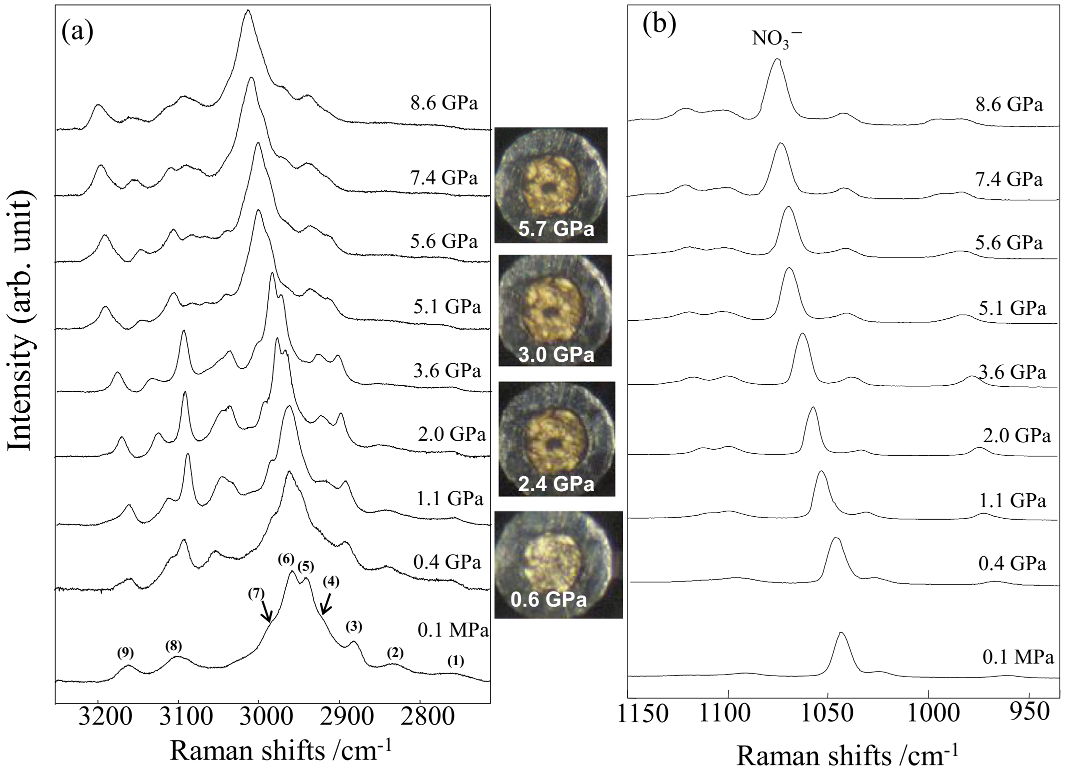

Fig. 2. (a) Raman C–H stretching (ν_{CH}) spectra of [emim][NO_3] as a function of pressure and optical images obtained with increasing pressure. Numbers represent the spectral assignments of the C–H stretching modes of the alkyl chain (C6, C7, and C8) and the imidazolium ring (C2, C4, and C5): (1) unknown; (2) C8; (3) C6–C8; (4) C7 and C8; (5) C8; (6) C6; (7) C6; (8) C4 and C5; (9) C2, C4, and C5. Pressures ranged from 0.1 MPa to 8.6 GPa, and the temperature was set at 298 K. (b) Raman spectra between 930 and 1150 cm^{-1} showing the symmetric stretching (ν_1) of NO_3^- as a function of pressure.