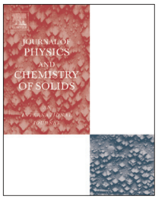
Journal of Physics and Chemistry of Solids 84 (2015) 13–16

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Heterogeneity of propyl-ammonium nitrate solid phases obtained under high pressure

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ARTICLE INFO

Article history:
Received 29 June 2014
Received in revised form
10 October 2014
Accepted 18 December 2014
Available online 19 December 2014

Keywords:
Organic compounds
Raman spectroscopy
Phase transitions
Microstructure

ABSTRACT

A recent work reported on different solid phases obtained on the protic ionic liquid propyl-ammonium nitrate (PAN) under a pressure up to 2 GPa. However, the experimental parameters and measurement protocols driving the solidification process were not clarified. Here, we report on and discuss three different Raman measurements on PAN carried out over different pressure ranges (up to 4 GPa). Exploiting different pressure increasing rates for each measurement we obtained a variety of solid phases. The differences between these phases are highlighted by visual inspection, by different solidification pressure values and by the Raman spectroscopic features relative to the anion stretching mode and to the cation alkyl chain vibration. Our results indicate different local structures surrounding the ionic couple in the solid phase and the capability of pressure to lock the cation alkyl chain in conformations different from those of the liquid state. These evidences also suggest the use of systematic and careful measurement protocols in order to reproduce a particular solid phase of PAN under pressure.

1. Introduction

In recent years, ionic liquids (ILs) have triggered the attention of the scientific community because of their promising physical and chemical properties for applications ranging from fuel cells to green chemistry [1]. ILs are formed by ionic couples with an organic/inorganic anion and an organic cation characterized by a large steric hindrance, which makes possible a liquid phase at room temperature. ILs present a high versality, as it is possible to design an ionic liquid with the desired physical–chemical properties by changing the molecular structure of the constituents [2].

The delicate balance between the several kinds of intermolecular interactions (Coulombian, hydrogen bonding, Van der Waals) acting on ILs is responsible for the formation of nanoscaled structured polar and nonpolar domains [3]. In particular, the driving force for molecular ordering in nonpolar domains is the Van der Waals interaction, whereas it is the ionic interaction in polar domains.

This has been verified also for protic ionic liquids (PILs) [4–6], an important subclass of ILs characterized by the presence of proton donors and acceptor sites, which gives rise to a network of hydrogen-bonds. This network strongly influences the physical–chemical properties of the system [7–11] and can also induce several phase transitions and polymorphism upon a temperature or pressure change [12–14].

Exploiting high pressure, it is possible to reduce the intermolecular distances and thus to modify the balance between the various interactions. With this purpose, aprotic ILs have been studied under high pressure for several years [15–20]. On the contrary, studies about the effect of high pressure on PILs started to appear in the literature only a few years ago [12–14,21]. A very recent work is the one of Faria et al. [14], who performed a Raman study on the effect of temperature and pressure on propyl-ammonium nitrate (PAN). Vibrational micro-spectroscopy represents a simple way to gain insight on intra- and inter-molecular structures and to probe sample homogeneity under pressure. Indeed, Faria et al. observed strongly inhomogeneous PAN solid phases induced by pressure which are marked by spectroscopic signatures of a H-bonding distorted network in polar domains and of different cation alkyl chain conformations in nonpolar domains. However, it is not clear which parameters drive the solidification process and how to experimentally reproduce a solid phase with a specific local structure. Considered the high viscosity of ILs and the

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http://dx.doi.org/10.1016/j.jpcs.2014.12.006
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steric hindrance of the ionic couples, the pressure increasing rate could play a prominent role in the solidification process. However, in the work of Faria et al. this is only addressed qualitatively, with a “quick” or “slow” definition of the used rate.

In this work, we investigate several pressure induced PAN solid phases by means of Raman micro-spectroscopy. High pressure Raman measurements were carried out from ambient pressure up to 4 GPa. Raman spectroscopy was correlated over the whole experiment with the visual analysis of the samples inside the DAC, by monitoring the possible inhomogeneities. We obtained unreported solid phases, characterized by different Raman signatures, pointing out several kinds of microstructures for the local ionic couples' arrangement. First indications on the role of the pressure increasing rate on the obtained solid phases are also addressed.

2. Experimental methods

The PAN samples investigated in this work were acquired from IoLiTec (Ionic Liquids Technologies).

Raman spectra were collected in the spectral region between 300 and 3300 cm^{-1} using LabRam Infinity confocal-micro-spectrometer (Horiba-Jobin Yvon) in back-scattering geometry equipped with a long-working-distance 50 × objective. The 632.8 nm line of a He–Ne laser was used for excitation and the Raman signal was analyzed with a 1800 lines/mm grating and recorded via a CCD detector. The estimated spectral resolution was better than 3 cm^{-1}.

Thin-walled quartz cuvettes were used to contain samples at ambient pressure, whereas a membrane diamond anvil cell (DAC) was used for pressure dependent measurements (for further details on the experimental setup see Ref. [22]). The DAC was equipped with a couple of IIa type, low fluorescence diamonds with culets of about 400 μm diameter. The sample was loaded in a 150 μm diameter hole, drilled in a molybdenum gasket (55 μm thick under working conditions). The fluorescence of a ruby nanosphere loaded together with the sample was exploited for the well-established *in situ* measurement of the pressure [23] with an uncertainty of 0.1 GPa.

The microscope coupled to the spectrometer was capable of collecting Raman signal from small size areas (about 4 $\mu\mathrm{m}^2$). This allowed for testing the sample homogeneity under pressure, thanks to several measurements collected from different points of the sample inside the DAC. At the same time, a careful visual inspection of the sample was possible. The optical observation of the samples was useful to draw further information on the state of the samples investigated with Raman spectroscopy.

3. Results and discussion

Three different series of Raman measurements on PAN at room temperature as a function of the applied pressure were performed. For each run, a different measurement protocol was adopted in order to investigate the link between the properties of a particular PAN solid phase and the specific experimental procedure leading to the solidification. In particular, we changed the pressure increasing rate, the stabilization time after the pressure raise, the size of the pressure step and the overall pressure range. The parameters used for each measurement will be specified in the following presentation of the results. For all the three series of measurements, after the run increasing the pressure, we also collected data during the release of the pressure (data not shown). All the observed phase transitions were always found to be reversible and the sample came back to the pristine liquid phase at 0 GPa.

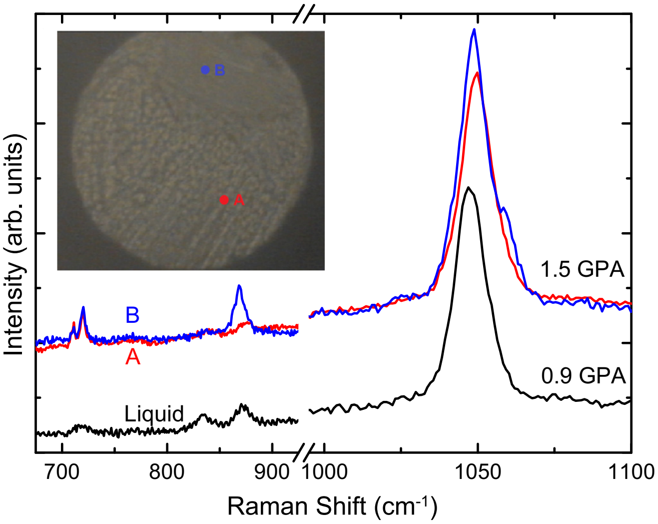

Fig. 1. Measurement 1. Raman spectra of PAN in the spectral range 700–1100 cm^{-1} around the liquid–solid phase transition, which occurs between 0.9 and 1.5 GPa. In the liquid state, interference fringes due to the diamond culets are present. In the solid phase at 1.5 GPa, Raman spectra have been collected from two different points, indicated in the photograph of the sample shown in the inset. The corresponding spectra have the same color assigned to the measure point. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

In the first series of measurement, a pressure of 1.5 GPa was reached in two steps (we collected only another pressure point at 0.9 GPa). The time employed to reach 1.5 GPa, starting from ambient pressure, was 2 h. Raman spectra of PAN in the spectral range 700–1100 cm^{-1} collected at 0.9 GPa (liquid phase) and in two positions at 1.5 GPa (different solid phases) are shown in Fig. 1, where a photograph of the sample is also reported. The liquid–solid phase transition thus occurs between 0.9 and 1.5 GPa (actually, can be assumed to be around 1.3 GPa, as will be clear in the following) and it is marked by both visual inspection of the sample (see the sample image in the inset of Fig. 1) and spectroscopic signatures (compare the spectra collected from points A and B with the one in the liquid phase). At the same time it is quite clear that the rather fast pressure increase gives rise to two distinct solid phases: one apparently spatially homogeneous (B) and the other one looking like a “polycrystalline/glassy” phase. The shape of the Raman peak at about 1045 cm^{-1}, assigned to the anion symmetric stretching mode, does not show any remarkable differences by comparing the spectra collected from the inhomogeneous solid phase (A) and from the liquid phase. On the other hand, the two peaks at about 830 and 870 cm^{-1}, assigned to the *gauche* and *anti* conformation of the cation alkyl chain respectively [14], have a much lower intensity than in the liquid. In the Raman spectrum collected in the homogeneous phase (B), the peak around 1045 cm^{-1} has a clear shoulder on the high frequency side whereas the peak at about 870 cm^{-1} is enhanced and redshifted if compared to both the liquid phase and the inhomogeneous solid (A). The only common spectral features between the two solid phases are the sharp peaks replacing the broad and low intensity peak at 720 cm^{-1} of the liquid phase, assigned to the anion bending mode.

Bearing this in mind we can try to depict the scenario of the two observed solid phases. In the homogeneous phase (B), all the propyl-ammonium cations have been led in the *anti* conformation during the crystallization process, as should be expected considering that the *anti* conformer has a lower energy than that of the *gauche* one [24]. Moreover, the nitrate anions experience a different polar domain compared to the liquid phase, as witnessed by the high frequency shoulder appeared on the peak around