

Phase transition and ionic transport mechanism of $(C_4H_9)_4NI$

Ryou Asayama ^{a,*}, Junichi Kawamura ^a, Takeshi Hattori ^b

^a *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aobaku, 980-8577 Sendai, Japan*

^b *Department of Applied Physics, Tokyo University of Science, 162-8601 Tokyo, Japan*

Received 8 July 2005; in final form 11 August 2005

Available online 6 September 2005

Abstract

Phase transition and ionic transport in tetrabutylammoniumiodide $(C_4H_9)_4NI$ (TBAI) was investigated using X-ray diffraction, DSC, ionic conductivity and high resolution proton NMR spectroscopy. The TBAI exhibited a solid state phase transition at 391 K of $\Delta S = 95.2$ J/mol K from an ordered phase I to a rotationally disordered plastic phase II. Ionic conductivity in phase I increased gradually near the phase transition point. On the other hand, proton NMR diffusion coefficients showed decrease with raising temperature. The observed fast diffusion of the TBA cation has significant contribution to the observed ionic conductivity of this material.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Recent progress in advanced batteries strongly demands the use of fast ion transport in organic liquids and even in solids [1]. Recently, the glasses containing AgI and alkylammonium salts were reported to show very high ionic conductivity even at room temperature, and is called as organic–inorganic hybrid superionic conductor glasses [2,3]. The alkylammonium halides have also been studied as a class of plastic crystals with rotational disorder [4,5]. MacFarlane et al. [6–10] have recently reported a number of plastic crystals exhibiting high ion conductivity around room temperature. The diffusion coefficient of organic molecules in the plastic crystal was reported to be significant in plastic phases [10].

From these observations, it is necessary to investigate in detail the ionic transport in alkylammonium halide, especially the alkylammoniumiodide which is the major component of the organic–inorganic superionic conductor glasses. Although a number of tetraalkylammonium halides has been studied by DSC, NMR and X-ray diffraction [11–13], there was little work on ionic conductivity or diffusion on these materials. In this work, phase

transition dynamics and ionic transport of tetrabutylammonium iodide (TBAI) were investigated by X-ray diffraction, a differential scanning calorimetry (DSC), impedance spectroscopy and a high resolution proton NMR spectroscopy. The diffusion coefficients of the TBA cation were first measured by Pulse Field Gradient-Spin-Echo (PFG-SE) method in liquid, plastic crystal and in low temperature phases.

2. Experimental

Tetrabutylammonium iodide (TBAI) was purchased from Aldrich Co. (99.9%). X-ray diffraction was measured by using Rint H diffractometer by Rigaku in the temperature ranging from 293 to 400 K; in the system Cu K α line was used. Thermal analysis of the sample was carried out by using SEIKO DSC6200 in temperature range from 213 to 473 K with scanning rate at 10 K/min.

The ionic conductivity of the sample was measured between 371 and 473 K in increasing temperature by using a Solartron SI-1260 impedance analyzer. The complex impedance spectra of the pressed sample were measured in the frequency range from 1 Hz to 1 MHz. The observed impedance data were analyzed as the conventional way to evaluate the bulk ionic conductivity from the so-called Cole–Cole plot.

* Corresponding author. Fax: +81 22 217 5344.

E-mail address: asayama@mail.tagen.tohoku.ac.jp (R. Asayama).

The proton NMR spectra and the diffusion coefficients were measured by a Bruker Avance 400WB spectrometer in the temperature range from 300 to 434 K. The measurements were repeated two times for different samples. The diffusion coefficients of the TBA cations were measured by the Pulse Field Gradient-Spin-Echo (PFG-SE) method for the proton NMR signal of the sample. The pulse sequence of the PFG-SE method was used ($\pi/2 - \tau - \pi - \tau$) with a $\pi/2$ pulse of 7 μs and a π of 14 μs . The gradient strengths G ranged from 0 to 1500 G/cm and the diffusion time Δ was 5.26 ms. The echo amplitudes were measured by varied the gradient strengths and were fitted to the following equation [14]:

$$A(g) = A(0) \exp[-\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)], \quad (1)$$

where A is the echo amplitude, γ is the gyromagnetic ratio, g is the gradient strength, δ is the duration of the gradient pulse, Δ is time between gradient pulses and D is the diffusion coefficient.

3. Results

3.1. X-ray diffraction

Fig. 1 is the powder X-ray diffraction patterns of TBAI at 307 K (a) and (b) at 400 K. The diffraction pattern at room temperature is in good agreement with those reported by Wang et al. [12], which can be attributed to the space group $C2$ monoclinic structure. The atom reported in [12] reproduced the observed diffraction pattern. Although the diffraction pattern at high-temperature phase II was not found in literature, it was described to be cubic structure of $a = 14.78 \text{ \AA}$ with a random rotating TBA and an iodide anion.

It is interesting to point out that the sample rapidly quenched from the phase II to room temperature showed

a little different pattern at room temperature as shown in Fig. 1c, where no peak is seen corresponding to the (002) reflection although other peaks from phase I is seen. The (002) reflection of phase I corresponds to a superlattice reflection from the two unit cells of phase II. This results suggest that the quenched sample of phase II is not completely ordered monoclinic structure but has a randomly oriented TBA ions in the one force of the monoclinic cell which corresponds to the cubic unit cell of phase II.

3.2. Thermal analysis

There are observed two endothermic signals in DSC measurements. A lower temperature phase transition at 391 K has an entropy change of $\Delta S = 95.2 \text{ J/mol K}$, corresponding to the rotational disorder in phase II. The other higher temperature phase transition at 420 K is due to the melting of the TBAI with an entropy change of $\Delta S = 28.3 \text{ J/mol K}$. The values of the transition temperatures and transition entropies are listed in Table 1; they are in good agreement with those reported by Xenopoulos et al. [11]. The very large value of the entropy change at the solid–solid phase transition at 391 K is an indication of the transition from an ordered crystal to a plastic crystal phase, where both the rotational motion of the whole cation and the conformation disorder of the $\text{CH}_2\text{--CH}_3$ bonds take place [11,12].

3.3. Ionic conductivity

Ionic conductivity of the sample was determined from the impedance analysis; the temperature dependence of the conductivity is shown in Fig. 2. The conductivity is increasing with raising temperature and obvious discontinuities were observed at 391 K corresponding to a solid–solid phase transition from I to II as well as at 420 K of the melting temperature. Ionic conductivity in the plastic phase is $2 \times 10^{-6} \text{ S/cm}$ at 393 K and increased gradually near the melting point up to 10^{-2} S/cm similar to other plastic crystals [8]. The conductivity in the ordered phase I is lower but is still 10^{-8} S/cm at 388 K with strong temperature dependence. The activation energy of the conductivity was estimated to be 0.85 eV in the phase II, which is about one third of the value of 2.96 eV for the low temperature phase I. These results imply the fast ion diffusion in the plastic phase II and somewhat less but considerable diffusion of ions in the ordered phase I.

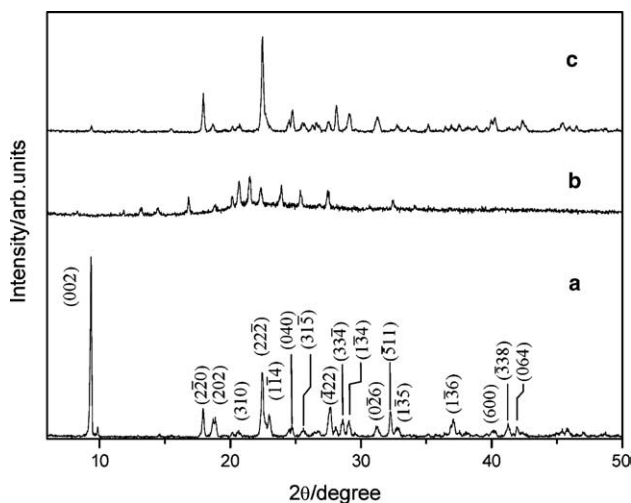


Fig. 1. Powder X-ray diffraction patterns of tetrabutylammonium iodide (TBAI) at 307 K (a) and at 400 K (b). The pattern of the sample quenched from 400 K to room temperature is also shown in (c).

Table 1

Thermodynamic phase transition temperatures and the entropy changes at the phase transition from the ordered phase I to the plastic phase II and phase II to the melt

TBAI	T (K)	ΔS (J/mol K)
I \rightarrow II (T_r)	391 (394 [11])	95.2 (71.2 [11])
II \rightarrow melt (T_m)	420 (421 [11])	28.3 (21.3 [11])

The data reported by A. Xenopoulos is also shown in the parenthesis.

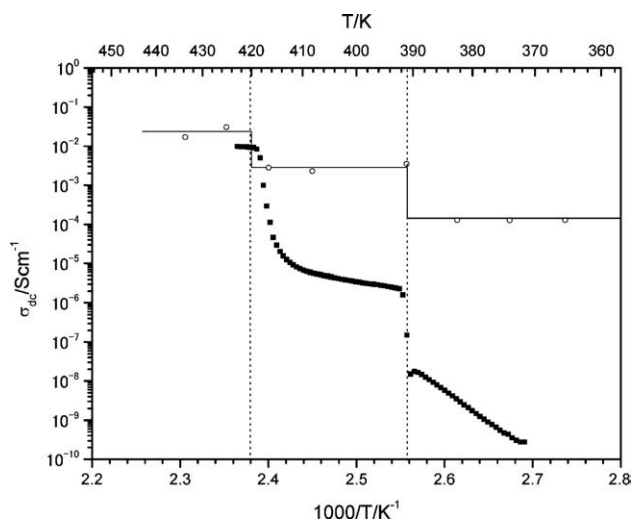


Fig. 2. Arrhenius plot of the ionic conductivity of TBAI (○, from NMR; ■, from impedance analyzer). The solid curve indicates calculated values by using Eq. (2).

3.4. NMR spectra

The temperature dependence of the proton NMR spectra of TBAI is shown in Fig. 3. The spectrum consists of a very broad large component of FWHM 50 ppm (20 kHz) and an overlapping small narrow component of about 400 Hz. The spectrum width of this broad component is in good agreement with those reported previously by Szafranska and Pajak [13] using a wide-line spectrometer, where the observed 2nd moment $M_2 \sim 16 \text{ G}^2$ was attributed to the ^1H – ^1H dipolar interactions in TBA cations. The narrow component observed here suggests the existence of a small amount of faster mobile cations even in phase I, whose spectrum is much sharper than those of phase II and similar to that of in liquid state. With raising

the temperature the signal intensity of this sharp component increased, and at the temperature of the phase transition I–II, the both narrow and broad components merged into a single fairly narrow spectrum of FWHM 10 ppm (4 kHz). This narrowing of the spectrum in phase II was also reported in the previous wide-line measurements to show the M_2 value of 0.2 G^2 , which was explained as the result of the averaging of the dipole–dipole interactions by the total cation tumbling in phase II [13].

Above the melting point 420 K, four narrower lines were observed corresponding to CH_3 , two $-\text{CH}_2-$ and $-\text{CH}_2-\text{N}$ groups in a TBA cation, which is in good agreement with those of a solution spectrum (not shown) of TBAI in D_2O .

In order to estimate the quantity of the narrow component in phase I, the total NMR spectra in phase I were deconvoluted into a narrow and a broad component, from which the relative intensity of the narrower component was evaluated by the integration of the each component, as shown in Fig. 4. This relative intensity of this narrow component is about 0.2% at 293 K up to 6% at 383 K of the total intensity.

3.5. Diffusion coefficients

The Diffusion coefficient of the TBA ions was evaluated from the analysis of PFG-SE signal. The echo intensity obeyed Eq. (1) to give a unique value of diffusion coefficient of $D = 1.9 \times 10^{-10} \text{ m}^2/\text{s}$ at 434 K at high temperature in liquid phase. On the other hand, the echo intensity deviated from the single Gaussian dependence in the solid states at phases I and II as shown in Fig. 5a. The echo signal was analyzed by assuming two diffusion components, one is fast diffusing and the other is non-diffusing. The fitting result is also shown in Fig. 5a. Temperature dependence of diffusion coefficient of the fast component was shown in Fig. 5b. Interestingly, the diffusion coefficient of the TBA

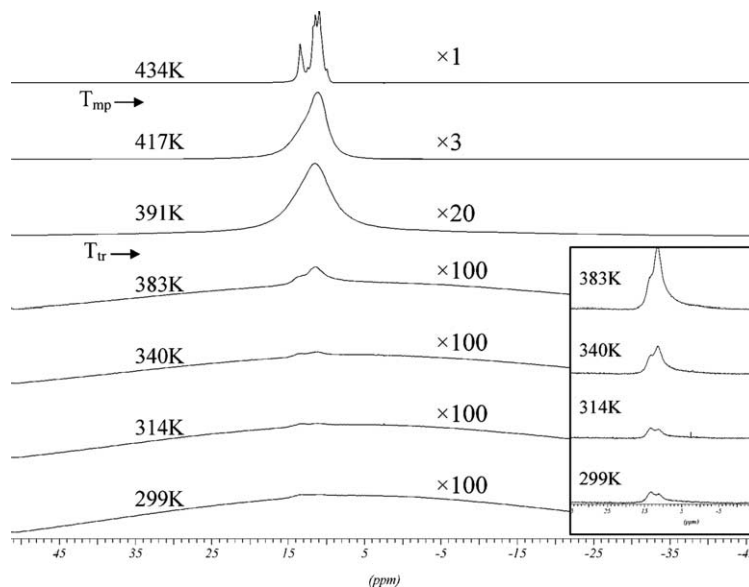


Fig. 3. Temperature dependence of the proton NMR spectra. The inset represents the spectra of narrow line below 391 K.

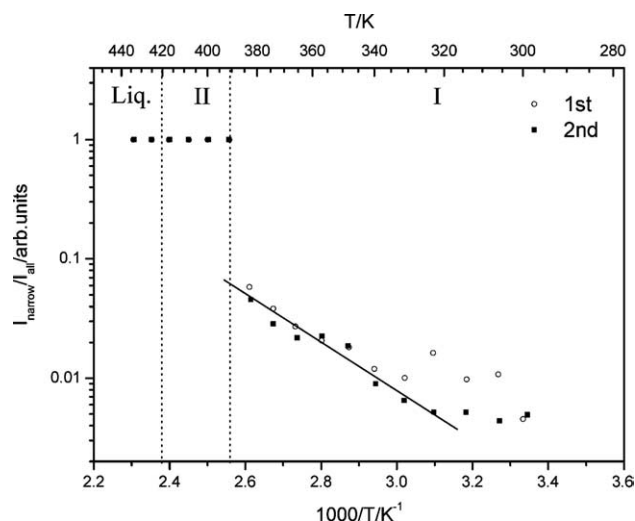


Fig. 4. The relative intensity of the narrow component of the proton NMR signal of TBAI plotted as a function of the reciprocal temperature. Temperature region of phase I, II and liquid states are indicated by dashed lines determined from DSC measurements. The line represents guide line.

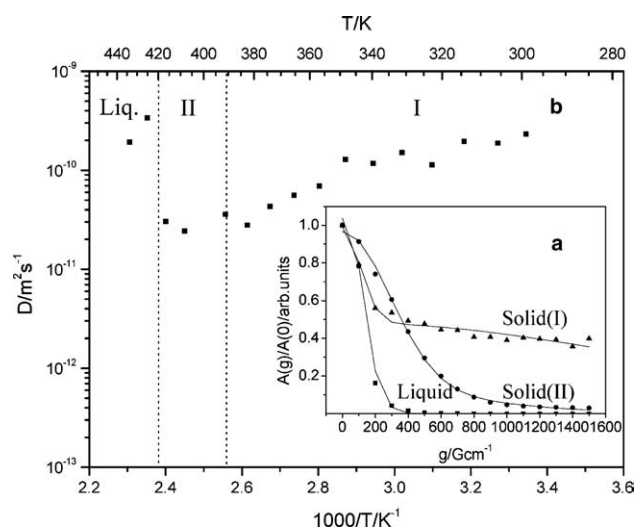


Fig. 5. Temperature dependence of the diffusion coefficient of the fast component of the proton NMR spectra of TBAI (b) and spin-echo attenuation versus gradient intensity of phase I, II and liquid states (a). The lines of (a) represent best fit.

cations at room temperature is around $2.3 \times 10^{-10} \text{ m}^2/\text{s}$, which is almost equivalent to that at liquid state. This result supports the above speculation from the spectrum width that a small amount of TBA cations is mobile even in the ordered phase I. Upon heating a steady decrease in the diffusion coefficient of these cations was observed in phase I approaching to the phase II. However, the diffusion coefficient was found almost constant in phase I about $D = 3.0 \times 10^{-11} \text{ m}^2/\text{s}$.

4. Discussion

Fast ionic diffusion in plastic crystals has been reported recently by MacFarlane's group [6–10]. In their extensive

work, it is pointed out that not only the anions but also organic molecular ions such as imidazolium ions can diffuse in the plastic crystals [10]. TBA ion studied here has much simpler structure than those imidazolium ions, however the possibility of its translational diffusion was also suggested by Szafranska and Pajak [13] from the broad line proton NMR spectra. The present results of the diffusion coefficient in the plastic phase II is the evidence of such conjecture. Moreover the appearance of the fast diffusing TBA ions even in the low temperature ordered phase I is beyond the expectation. These observations will enforce us to reconsider the origin of the ionic conductivity in the organo-ionic crystals, where the bulky organic ions were assumed to be immobile and fixed at their lattice positions.

Taking into account the contribution from both cation σ_+ and anions σ_- , the total ionic conductivity σ is described by the following Nernst–Einstein form:

$$\sigma = \sigma_+ + \sigma_- = (D_+ N_+ q_+^2 + D_- N_- q_-^2) / kT, \quad (2)$$

where D_+ and D_- are the diffusion coefficients of the cation and the anion, N_+ and N_- are their concentrations, q_+ and q_- are the charges, k is the Boltzmann constant and T is the absolute temperature. We can estimate the mobile cation number N_+ from the narrow component in proton NMR spectra as well as the diffusion coefficient D_+ of them. Thus, the contribution of the TBA cation to the conductivity can be estimated from these quantities.

The result of this calculation is shown as $\sigma_+(\text{cal})$ by the solid curve in Fig. 2. The calculated value is almost equal to the observed conductivity in liquid state, where both TBA^+ and I^- have translational freedom. On the other hand, the calculated value is three to four orders larger than the observed conductivity in phases II and I. If one takes into account the contribution from iodide anion, the discrepancy will be larger.

This discrepancy may be due to the over estimation of the concentration of mobile TBA cations from the narrow component of the NMR signal. Probably, not all the TBA ions are translationally mobile even in the plastic phase II, but only a few percentage of them contribute the macroscopic diffusion. Actually, the NMR spin-echo signal in the diffusion measurements consists of two components, i.e., fast decaying signal and slow one. This suggests that even the narrow component should be further separated into two or more components corresponding to the diffusing ions and the only rotating ones. It is difficult to do the quantitative separation of the spin-echo signal at this moment, since the slowly decaying component is very noisy. Anyway, the considerations above exhibited that some part of the TBA cations are diffusing in the plastic phase II and even in the low temperature ordered phase I, which may contribute significantly to the observed total ionic conductivity.

It is necessary to discuss the observation of diffusing TBA even in the ordered phase I. Translational motion of the imidazolium ions in the plastic phase is discussed

by MacFarlane et al. [10] and attributed to some complex defects such as pipe diffusion or diffusion through dislocations. In our measurements, the diffusion is observed not only the plastic phase but also in the low temperature ordered phase. The NMR signal shape and the diffusion coefficient value in the low temperature phase suggest that only a few percentage of TBA are very mobile like in the liquid state. Actually, the sample quenched from the liquid or phase II to room temperature showed larger amount of the narrow NMR signals. Also, the disappearance of the (002) reflection in XRD pattern of the quenched sample suggests that the lattice mismatch may also relate to this problem. We are now considering these experimental results by assuming the residual plastic domains remaining even in phase I, whose interface to phase I is disordered configuration like supercooled liquid state. Apparent decrease in diffusion coefficient with the increasing temperature as shown in Fig. 5b is probably due to the shrink of the interface contributions. The detailed of the model and further experimental evidences will be presented elsewhere.

References

- [1] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [2] J. Kawamura, S. Hiyama, *Solid State Ionics* 53–56 (1992) 1227.
- [3] J. Kawamura, H. Itoigawa, T. Kamiyama, Y. Nakamura, *Solid State Ionics* 121 (1999) 37.
- [4] T. Shimizu, S. Tanaka, N. Onoda-Yamamuro, S. Ishimaru, R. Ikeda, *J. Chem. Soc., Faraday Trans.* 93 (2) (1997) 321.
- [5] S. Iwai, M. Hattori, D. Nakamura, R. Ikeda, *J. Chem. Soc., Faraday Trans.* 89 (5) (1993) 827.
- [6] J. Sun, D.R. MacFarlane, M. Forsyth, *Solid State Ionics* 148 (2002) 145.
- [7] J. Efthimiadis, S.J. Pas, J. Sun, M. Forsyth, D.R. MacFarlane, *Solid State Ionics*. 154–155 (2002) 279.
- [8] S. Long, M. Forsyth, D.R. MacFarlane, *Solid State Ionics* 161 (2003) 105.
- [9] M. Forsyth, J. Haug, D.R. MacFarlane, *Nature* 412 (1999) 792.
- [10] H.A. Every, A.G. Bishop, D.R. MacFarlane, G. Oradd, M. Forsyth, *J. Mater. Chem.* 11 (2001) 3031.
- [11] A. Xenopoulos, J. Cheng, M. Yasunuma, B. Wunderlich, *Mol. Cryst. Liq. Cryst.* 214 (1992) 63.
- [12] Q. Wang, A. Habenschuss, A. Xenopoulos, B. Wunderlich, *Mol. Cryst. Liq. Cryst.* 264 (1995) 115.
- [13] B. Szafranska, Z. Pajak, *Z. Naturforsch.* 42a (1986) 253.
- [14] E.O. Stejskal, J.E. Tanner, *J. Chem. Phys.* 42 (1965) 288.