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Interfacial electrical property of ionic liquid on polarization field formed by TGS single crystal

Takuya Kishimoto, Tatsuya Fukushima, Yasuko Koshiba, Shohei Horike, and Kenji Ishida

Department of Chemical Science & Engineering, Kobe University,
1-1 Rokkodai, Nada, Kobe,
Hyogo, 657-8501, Japan
Phone: +81-78-803-6150 E-mail: kishida@crystal.kobe-u.ac.jp

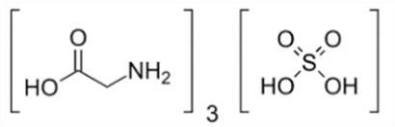
Abstract

In this study, we have investigated interfacial electric property change at ionic liquid (IL) / ferroelectric with liquid-solid phase transition behavior of ionic liquid, trimethylhexylammonium bis(trifluoromethanesulfonyl)imide ([TMHA][TFSI]), by utilizing polarization field in ferroelectric triglycine sulfate (TGS) single crystal. The properties of stacked device, with the structure of indium-tin-oxide (ITO) / IL / TGS single crystal / silver paste, greatly changed when IL transited from solid to liquid phase. Also, electric double layer (EDL) in IL was affected and pinned by remnant polarization in TGS.

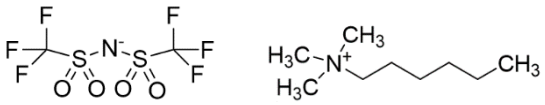
1. Introduction

The ionic liquid which is a room temperature molten salt has been studied for its application to green solvents [1, 2] and electric double layer capacitors [3, 4] because of its low volatility [5] and high ionic conductivity [6]. A more detail understanding of the interface state of the EDL formed at the interface of different materials is particularly important in the development of new electronic properties and control of existing devices.

In this study, we have investigated the electric properties in an IL / solid interface by utilizing polarized field of TGS (Fig. 1(a)) single crystal with ferroelectricity. To reveal the interfacial electric properties, we fabricated an IL / TGS stacked device using a polarization-controlled TGS [7]. In electrical measurements, we observed the change in physical properties at the solid-liquid phase transition phenomenon of [TMHA][TFSI] (Fig. 1(b)) that has a melting point near 302 K [8].



(a) TGS



(b) [TMHA][TFSI]

Fig. 1. Chemical structures used in this study.

2. Experiments

TGS single crystals were prepared by the evaporation method [9]. The TGS plate crystals of approximately 1 mm thickness were obtained by cleaving along the polarization plane and polishing. We fabricated TGS single crystal thin plate / IL stacked devices as shown in Fig. 2. [TMHA][TFSI] was injected a gap between a glass substrate with ITO and TGS. Silver paste was coated as top electrode. After the stacked device cooled 173 K, ferroelectric and dielectric characteristics were measured at each set temperature during controlling the temperature. For the electrical measurements, we prepared the devices with two different conditions. One device was that IL was solidified without TGS polarizing (Method A, Fig. 3 (a)). The other device was that with TGS polarizing (Method B, Fig. 3 (b)).

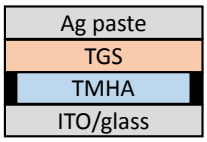


Fig. 2. Device structure of IL / TGS stacked device.

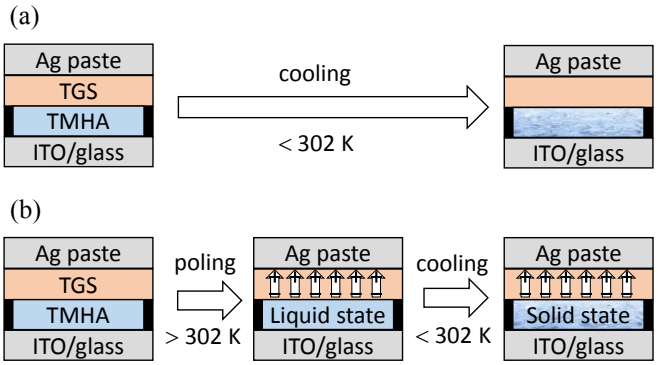


Fig. 3. Two cooling conditions for Method A and B.

3. Results and discussions

Fig. 4 shows the frequency dependence of the electric displacement (D) – applied electric field (E) hysteresis at 275.4 K in which [TMHA][TFSI] is in the solid phase, and 307.7 K in which is in the liquid phase. Polarization reversal of TGS was confirmed at 10 Hz or less when [TMHA][TFSI] was in the solid phase and at 100 Hz or less in the liquid phase. This

results are considered to be caused by different dielectric constants of the [TMHA][TFSI] in liquid and solid states. The dielectric constant of solid [TMHA][TFSI] is very small compared to the liquid state (ε_{solid}: ~10 and ε_{liquid}: ~10^7). Thus, the divided voltage applied to TGS is less than the coercive electric field, resulting that polarization inversion is prevented.

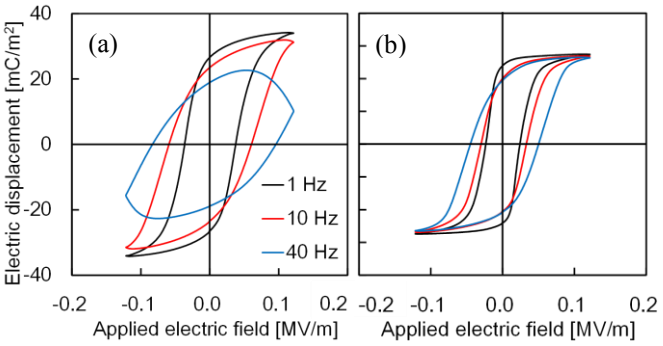


Fig. 4. Frequency dependences of *D*-*E* hysteresis measured at (a) 275.4 K and (b) 307.7 K for Method A.

To understand the dynamics of IL and TGS, impedance measurements were performed. Fig. 5 shows the frequency dependence of dielectric loss with various temperatures. It can be seen that the response of 10 to 1000 Hz at the low temperature is shifted to the high frequency region by increasing temperature. This shift is considered to originate from the formation of electric double layer in the IL / TGS interface. Also, the complex frequency response around 323 K suggests significant interaction change between polarization field and electric double layer, accompanying ferroelectric-paraelectric phase transition (Curie point of TGS is 323 K [10]) of TGS and solid-liquid phase transition (melting point of [TMHA][THFI] is 302 K) of IL.

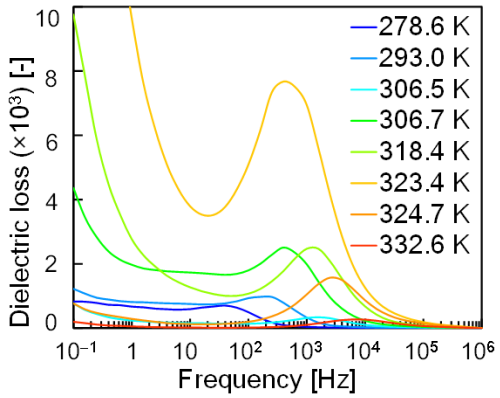


Fig. 5. Frequency dependence of dielectric loss of the IL / TGS device for Method A at various temperatures.

Fig. 6 shows the electric displacement (*D*) – applied electric field (*E*) hysteresis of Method B at 275.5, 301.2, and 314.2 K. Here, liquid and solid phases of [TMHA][TFSI] coexist at 301.2 K, whereas liquid phase exists at 314.2 K in IL. Polarization reversals of TGS were confirmed at 301.2, and 314.2 K. However, that of TGS did not be observed at 275.5 K when [TMHA][TFSI] becomes solid phase, originating from dipole in TGS single crystal pinned by the EDL in IL layer.

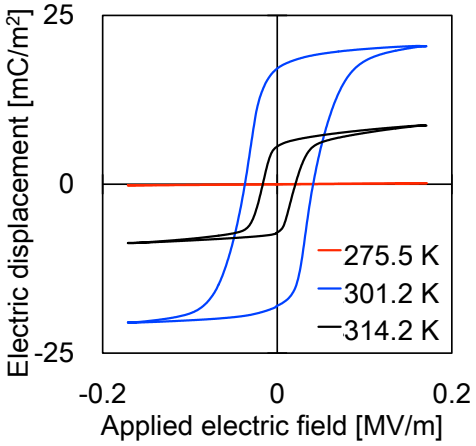


Fig. 6. Temperature dependence of *D*-*E* hysteresis of the IL / TGS device for Method B.

3. Conclusions

We carried out the various electrical measurements to understand the interfacial electrical properties at the IL / TGS stacked device. The ions in [TMHA][TFSI] and the polarization in the ferroelectric interact strongly and polarization reversal in TGS is disturbed by EDL in [TMHA][TFSI]. Dielectric loss was drastically change by dynamics in [TMHA][TFSI] and TGS at the melting of the ionic liquid and ferroelectric-paraelectric phase transition, respectively. Our findings would help to understand the driving mechanisms of ionic liquid-based electronic devices with phase transitions.

Acknowledgements

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