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# Study of Thermal Phase Behavior for an Ionic Liquid by High Sensitive DSC


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## Introduction

Ionic liquids have attracted much attention in recent years because they have some unique properties that molecular liquids do not show, e.g., negligible vapor pressure, high thermal stability, extremely low flammability, high ionic conductivity, unique solubility and so on. Application of ionic liquids to electrolytes, biotechnology, novel reaction media and separation/extraction processes has been widely studied. Investigation of basic physical properties of ionic liquids, especially thermal phase behavior, is important for not only obtaining ionic liquids having desirable properties for the applications but also their basic understanding.

1-butyl-3-methylimidazolium hexafluorophosphate ([$C_4$mim] $PF_6$) is one of the most typical ionic liquids composed of a representative cation and anion. It shows three crystal polymorphs and complex thermal phase behaviors [1-3]. We have reported the thermal phase behavior at the slow scanning rate of 0.3 K $min^{-1}$ [1] using a lab-made calorimeter [4]. [$C_4$mim] $PF_6$ shows a cold crystallization (226.5 K), then it has two endothermic peaks at 250 K and 276 K before melting (285 K) in the heating process [1]. Since the peak at 276 K is very small and close to the melting point, it was not observed clearly in the previous work performing the measurement at the heating rate of 10 K $min^{-1}$ using a conventional DSC [3].

Here we focus on the behavior of the peak at 276 K in a variety of scanning rates using a commercial high sensitive DSC.

## Experiments

### Material

1-butyl-3-methylimidazolium hexafluorophosphate ( [$C_4$mim] $PF_6$ )

### Preparations

[$C_4$mim] $PF_6$ was prepared by metathesis of 1-butyl-3-methylimidazolium chloride with sodium hexafluorophosphate. It was purified by washing with distilled water and using activated charcoal.

### Measurements

DSC: X-DSC7000 (SII NanoTechnology Inc.)

Measurement range: 173 to 283 K

Heating rate: 0.5, 1, 5, 10, and 20 K $min^{-1}$

Sample weight: 10 mg

Sample pan: Aluminum sealed pan


## Results

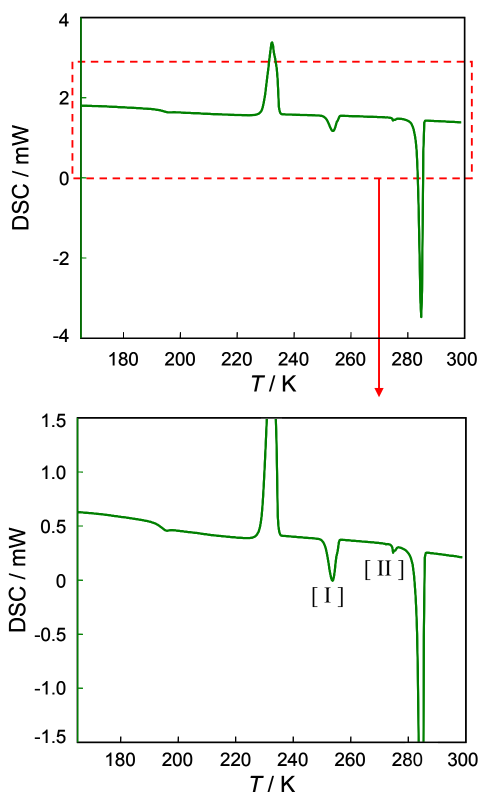


Figure 1 DSC curve of [$C_4$mim]$PF_6$ at 1 K $min^{-1}$

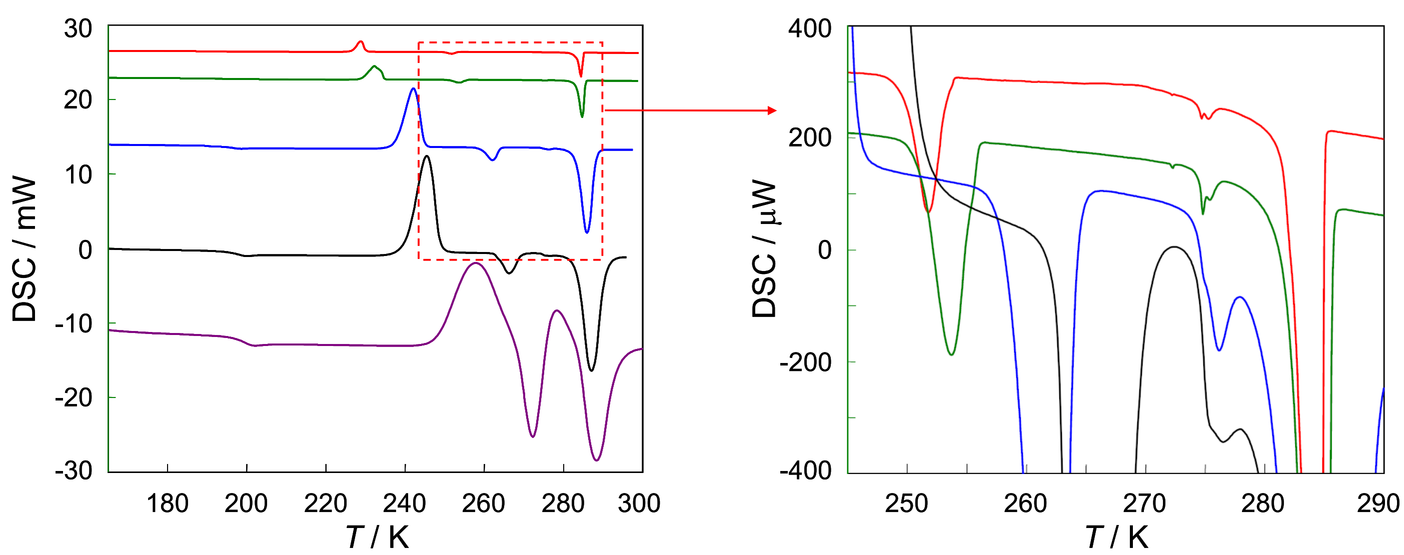


Figure 2 DSC curves of [$C_4$mim]$PF_6$

Heating rate
- : 0.5 K $min^{-1}$
- : 1 K $min^{-1}$
- : 5 K $min^{-1}$
- : 10 K $min^{-1}$
- : 20 K $min^{-1}$

[$C_4$mim]$PF_6$ shows the glass transition at 190 to 200 K, cold crystallization at 235 to 245 K, and melting at 280 to 290 K. In addition, two crystal – crystal phase changes at 250 K [ I ] and 276 K [ II ] were observed.

The heating rate dependency is observed in the cold crystallization and the crystal – crystal phase change [ I ]. On the other hand, heating rate dependency is not observed in the crystal – crystal phase change [ II ] and the melting. Furthermore, the crystal – crystal phase change [ II ] is observed a double peak in heating rate less than 1 K $min^{-1}$.

## Conclusions

Thermal changes of [$C_4$mim] $PF_6$ were measured by commercial high sensitivity DSC. The peak at 276 K was clearly distinguished from the melting peak at the heating rate of 1 K $min^{-1}$. In addition, the subtle peak at 276 K was ascertained to be a double peak.
As can be seen from the data above, the peak at 276 K is quite weak. When it comes to analyzing Ionic liquids, a highly sensitive DSC is required in order to capture the weakest thermal effects.

## References


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