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Melting and Crystallization Behaviors of Alkali Metal (Fluorosulfonyl)(trifluoromethylsulfonyl)amides

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Asymmetric perfluoroamides with Li^+ and Rb^+ exhibited unusual phase transition behaviors such as very slow crystallization and a large shift in melting point of the melt-crystallized salts, which have not been reported in alkali metal salts so far. Considering that corresponding symmetric amides do not exhibit such unique phenomena, the structural asymmetry in anions serves an important role in these phase-transition behaviors.

Perfluoroamide anions such as $[(CF_3SO_2)_2N]^-$ ($TFSA^-$) have been the most valuable perfluoroanion as raw material for ionic liquids (ILs) melting below room temperature.[1] The significant ability to form low melting ILs with various cations has been explained by their low charge density due to the relatively large size and the high flexibility of the amide structure compared to other conventional anions such as monoatomic halides and spherical BF_4^-.[2] Such structural feature of perfluoroamide is also exhibited in their alkali metal salts. Conventional alkali metal halides have high melting points (T_m), (450–1000 °C) due to the closed crystal packing of monoatomic alkali metal cations and halides; however, alkali metal salts containing flexible $TFSA^-$ exhibit much lower T_m (100–250 °C).[3] Recently, we reported that asymmetric amide anions, such as $[(FSO_2)(CF_3SO_2)N]^-$ (FTA^-), reduce T_m in not only ILs composed of aliphatic ammonium cations[4] but also alkali metal salts[5] compared to the corresponding symmetric amide anions such as $TFSA^-$ and $[(FSO_2)_2N]^-$ (FSA^-) (Figure 1). These results pointed out that the structural asymmetry enhances the potential ability of amide anions to reduce T_m. In this paper, we show that the FTA^- induces unusual phase-transition behaviors, which have not been observed in alkali metal salts containing conventional anions and other perfluoroanions.

Alkali metal FTA salts were synthesized by ion exchange from potassium salts according to a previous study.[4] The phase-transition behaviors of these salts were investigated by DSC (Perkin-Elmer, Pyris 1) using an Al seal pan under a helium gas purge. The transition temperature and enthalpy were determined by onset and area of peak in the DSC curve, respectively. The melting and crystallizing behaviors displayed in the DSC curves were also visually confirmed by samples sealed in a test tube upon heating in an oil bath. We selected Li[FTA] and Rb[FTA] as typical examples for summarizing the unusual phase-transition behaviors of alkali metal FTA salts.

The prepared Li[FTA] melted (**S** → **L**) at 100 °C (Figure 2a) during the first heating cycle as in our previous study.[5] The liquid phase of Li[FTA] (**L**) which melted once showed a glass transition upon cooling (Figure 2b). The glass state (**G**) also displayed neither crystallizing nor melting but only a glass transition (**G** → **L**) during the second heating (Figure 2c). Subsequently, the glass transition was observed upon repetitive heating and cooling cycles. Only the glass transition is observed at slower scans (2 and 10 °C min^{-1}) and visually confirmed in a test tube. Thus, the melted Li[FTA] remains in the supercooled state and requires a long relaxation time at temperatures between T_g and T_m to crystallize. After holding this Li[FTA] for at least 7 days at room temperature, the melting (**S** → **L**) was observed again upon heating at the same T_m and enthalpy as observed during the first heating without the glass transition (Figure 2d), which indicates that the crystallization (**L** → **S**) occurred during the holding time. After that, the liquid phase, which melted again, was also glass-forming liquid, and the crystallization required a long holding time. The crystallization of Li[FTA] was also caused by applying ultrasonic waves to the supercooled sample in an ultrasonic bath. This indicated that the unforced crystallization of Li[FTA] was reversible but very slow. Generally, the liquid phases of alkali metal salts, especially in the lithium salts such as Li[FSA] and Li[TFSA], promptly crystallized below their T_m as shown for Na[FTA] (Figure S1).[10] Such a very slow crystallization of Li[FTA] melt must be caused by the structural asymmetry of FTA^-. A similar thermal behavior, as shown in Figures 2a and

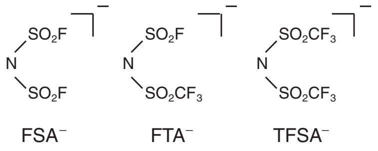

Figure 1. Structures of perfluoroamide anions.

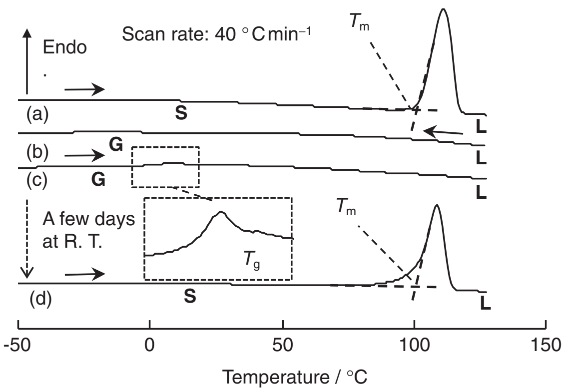

Figure 2. DSC curve for Li[FTA] of (a) the first heating, (b) the first cooling, (c) the second heating, and (d) heating after holding for a few days at room temperature.

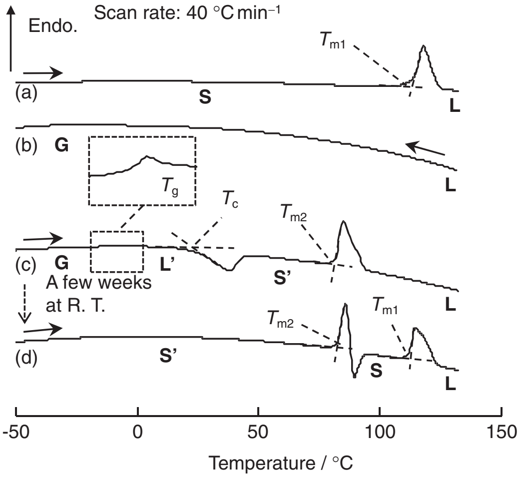

Figure 3. DSC curve for Rb[FTA] of (a) the first heating, (b) the first cooling, (c) the second heating, and (d) heating after holding for a few weeks at room temperature.

2b was reported for triflate salts containing 4,5-dibromo-1-butyl-3-methylimidazolium.[6] The authors pointed out that a minor difference in the chemical structure of the asymmetric imidazolium cation strongly affects the phase transition, melting point, glass-transition temperature, and crystal structure of the triflate salts. Considering that the FTA salts studied here contain simple monoatomic cations, the observed slow crystallization must be due to the small difference in the chemical structure of FTA$^-$.

On the other hand, another quite unique thermal behavior, such as metastable polymorphism, was observed in Rb[FTA] as shown in Figure 3. After the Rb[FTA] melted (**S** → **L**) at $T_{\rm m1}$ upon the first heating (Figure 3a), the liquid phase showed a glass transition (**L** → **G**) upon cooling (Figure 3b) as in the case of Li[FTA]. However, crystallization of the melt occurred at $T_{\rm c}$ during the second heating, and the crystallized Rb[FTA] (**S′**) melted again upon the second heating at over a 30 °C lower temperature ($T_{\rm m2}$) than the first melting ($T_{\rm m1}$) (Figure 3c). These unique behaviors were not observed in the corresponding rubidium amides, such as Rb[FSA] and Rb[TFSA]. These thermal behaviors observed at 40 °C min^{-1} were substantially unchanged at slower scans (2 and 10 °C min^{-1}). Crystallization was observed upon cooling without a glass transition whereas the melting transitions at $T_{\rm m1}$ and $T_{\rm m2}$ were independent of the scan rates. Furthermore, based on a visual observation, Rb[FTA] sealed in a test tube melted at $T_{\rm m1}$ once in the oil bath, and the melt-crystallized sample melted at $T_{\rm m2}$ again, which corresponds to the DSC results (Figures 3a and 3c). The shift in the $T_{\rm m}$ even in the same compounds indicated that a metastable solid phase (**S′**) emerged from the melt (**S** → **L** → **S′**). It is noted that the stable solid phase (**S**) could be reproduced by grinding the metastable solid (**S′**) in a mortar. Therefore, these observed unusual behaviors were not caused by sample degradation during the DSC measurements. On the other hand, the glass transition and the melting at $T_{\rm m2}$ as shown Figures 3b and 3c were repeatedly observed during the heating and cooling cycles, which indicated that the metastable solid phase (**S′**) is difficult to directly revert back to the stable one (**S**). However, after holding the supercooled liquid phase (**L′**) for a few weeks at room temperature, the metastable solid phase (**S′**), which crystallized during the holding time, melted at $T_{\rm m2}$, but the liquid phase (**L**) immediately crystallized to the stable solid phase (**S**) (Figure 3d). Subsequently, the crystallized solid phase melted at $T_{\rm m1}$ as well as the first heating as shown in Figure 3a (**S** → **L**). Thus, the transition from the metastable solid phase (**S′**) to the stable one (**S**) occurs through the liquid phase (**S′** → **L** → **S**).

To the best of our knowledge, such a shift in $T_{\rm m}$ of a melt-crystallized solid caused by metastable polymorphism has not been observed in conventional alkali metal salts except when applying a very high pressure.[7] Similar results were usually observed in a relatively large molecule with many conformational isomers such as drug substances.[8] As stated above,[6] a tiny conformational difference in imidazolium cations leads to a large effect on the phase transition, and the polymorphism derived from the molecular structure of cation was reported in 1-butyl-3-methylimidazolium ($\mathrm{C_4mim^+}$) chloride.[8] The presence of two polymorphs, such as orthorhombic and monoclinic, was caused by the small difference in the conformation of the butyl group.[9] In the case of FTA salts with monoatomic alkali metal cations, the conformation of FTA$^-$, which might be the trans and cis forms, may lead to the two polymorphs. Moreover, the asymmetry of FTA$^-$ might contribute to producing the metastable polymorph since Rb[TFSA] and Rb[FSA] did not exhibit these phenomena. The shift in $T_{\rm m}$ was also slightly observed in K[FTA] (Figure S2[10]), furthermore, Cs[FTA] exhibited both a slow crystallization and polymorphism (Figure S3).[10]

In conclusion, the two unusual behaviors, the slow crystallization, and the shift in $T_{\rm m}$, were observed in alkali metal FTA salts. These phenomena might result from the asymmetric structure of FTA$^-$; however, the observed behaviors are different depending on the included cations. The effect of interaction between each alkali metal cation and FTA$^-$ needs to be investigated. In order to identify the polymorphs of Rb[FTA] and Cs[FTA], X-ray diffraction measurements are now underway. In particular, this measurement at different temperatures can be used to investigate the phase-transition behaviors between the two polymorphs and the liquid phase.

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References and Notes

1 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168.
2 Z.-B. Zhou, H. Matsumoto, K. Tatsumi, *Chem.—Eur. J.* **2005**, *11*, 752.
3 R. Hagiwara, K. Tamaki, K. Kubota, T. Goto, T. Nohira, *J. Chem. Eng. Data* **2008**, *53*, 355.
4 H. Matsumoto, N. Terasawa, T. Umecky, S. Tsuzuki, H. Sakaebe, K. Asaka, K. Tatsumi, *Chem. Lett.* **2008**, *37*, 1020.
5 K. Kubota, T. Nohira, R. Hagiwara, H. Matsumoto, *Chem. Lett.* **2010**, *39*, 1303.
6 T. Mukai, K. Nishikawa, *Solid State Sci.* **2010**, *12*, 783.
7 S. K. Charabarti, *Phys. Status Solidi B* **1977**, *82*, 557.
8 D. Giron, *Thermochim. Acta* **1995**, *248*, 1.
9 J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, S. Johnson, K. R. Seddon, R. D. Rogers, *Chem. Commun.* **2003**, 1636.
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