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The Crystal to Plastic Crystal Phase Transition of Tetraethylammonium Difluorophosphate and Tetrafluoroborate

Kazuhiko Matsumoto,* Takeshi Okawa, and Rika Hagiwara
Graduate School of Energy Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501

(Received November 14, 2011; CL-111105; E-mail: k-matsumoto@energy.kyoto-u.ac.jp)

Ion configuration in the crystal structure of tetraethylammonium difluorophosphate ([TEA][PO_2F_2]) is highly related to that in tetraethylammonium tetrafluoroborate ([TEA][BF_4]). Both [TEA][PO_2F_2] and [TEA][BF_4] exhibit a crystal–plastic crystal phase transition above room temperature (323 and 340 K, respectively), and the plastic crystal phase has a NaCl-type structure. The TEA^+ cation in both the salts adopts a *trans–gauche* conformer in the crystal structure, whereas the *trans–trans* conformer is dominant in the plastic crystal structure.

Thermal, structural, and spectroscopic properties of tetraalkylammonium salts in the solid state were studied and presented in a number of papers.[1–8] Many tetraalkylammonium salts exhibit a first-order solid–solid phase transition below their melting points. Recent studies revealed that the high-temperature solid phase is often ionic plastic crystal. Plastic crystal is a mesophase observed between crystal and liquid phases, and constituent molecules (or ions in the case of ionic compounds) rotate in this phase, giving an expanded crystal lattice.[9] Recent progress in the studies of ionic liquids extended the chemistry of ionic plastic crystals as well. Bulky and spherical organic cations tend to give an ionic plastic crystal phase at relatively low temperature (sometimes below room temperature).[10–12] Application of ionic plastic crystals as solid electrolytes with high safety is widely studied because of their negligible vapor pressure and flammability, which is in contrast to organic molecular plastic crystals.[13,14]

Organic difluorophosphate salts exhibit low melting points, and sometimes form room-temperature ionic liquids as reported in our recent study,[15] whereas tetra(*n*-alkyl)ammonium salts based on $PO_2F_2^-$ are not known. This study reports thermal properties and structural changes at the crystal to plastic crystal phase transition for [TEA][PO_2F_2] (TEA: tetraethylammonium) in comparison with the well-known [TEA][BF_4] salt. Tetraethylammonium salts have been extensively studied as supporting electrolytes in electrochemical devices because of their high electrochemical and chemical stabilities.[16,17] Although thermal and structural properties of some tetraethylammonium salts were studied by several methods and their plastic crystal behavior was investigated,[1,5,18] the structural change of [TEA][BF_4] at the crystal to plastic crystal phase transition was not sufficiently studied. Understanding of such a structural change and related conformational changes of the cations is important for applications of plastic crystals as electrolytes. Effects of anionic structures on plastic crystal structures are also examined in this study.

Experimental details are given in Supporting Information; SI.[19] Differential scanning calorimetry (DSC) revealed that [TEA][PO_2F_2] and [TEA][BF_4] show an endothermic peak at 323 and 340 K, respectively (Figure S1[19] for DSC curves). Neither compound showed a melting point below the thermal decomposition temperature (568 K for [TEA][PO_2F_2] and 613 K for [TEA][BF_4] at the temperature of 5% weight loss, see Figure S2[19] for thermogravimetric curves). This thermal behavior of [TEA][BF_4] agrees with a previous report.[18] As described below, the endothermic peak observed for [TEA][PO_2F_2] and [TEA][BF_4] is ascribed to the first-order phase transition from crystal to plastic crystal. It is noteworthy that the transition temperatures are not significantly different in the two cases in spite of the difference in symmetry between the two anions. Strong effects of the cationic structure on the solid–solid transition may be responsible for this behavior. Enthalpy changes of the solid–solid transition ($\Delta H_{\text{s–s}}$) are 9.6 kJ mol^{-1} for [TEA][PO_2F_2] and 11.0 kJ mol^{-1} for [TEA][BF_4], the latter being in good agreement with the literature value (11.7 kJ mol^{-1}). The corresponding entropy changes ($\Delta S_{\text{s–s}}$) are 30 J K^{-1} mol^{-1} for [TEA][PO_2F_2] and 32 J K^{-1} mol^{-1} for [TEA][BF_4]. The relatively large entropy values suggest that the plastic crystal phase has a highly disordered structure. The transition from plastic crystal to crystal is also observed in the cooling process.

Crystal structure of [TEA][PO_2F_2] was determined at 100 K using single-crystal X-ray diffraction.[20] The asymmetric unit contains two pairs of ions as shown in Figure 1. The TEA^+ cation is known to be fluctional and adopts two major conformations (Figure 2), the *TT*-conformer (*trans–trans* and *trans–trans* in D_{2d}) and *TG*-conformer (*trans–gauche* and *trans–gauche* in S_4) (see SI[19] for optimized structures and vibrational frequencies of TEA^+ by HF, B3LYP, PBE1PBE, MPW1PW91, and MP2 calculations combined with the cc-pVTZ basis set and see the references[4,6,8] for crystallographic and spectroscopic examples). In the [TEA][PO_2F_2] structure, both the crystallographically independent cations have a *trans–gauche* conformation with nearly S_4 symmetry. This crystal structure is highly related to the previously known [TEA][BF_4] structure,[21] and the cation–anion configurations in the two unit cells are essentially the same, although the space groups of these two lattices are different (*Pc* for [TEA][PO_2F_2] and *Cc* for [TEA][BF_4]) because of the difference in orientation of the anions. The difference in unit cell volume reflects the larger molecular volume of $PO_2F_2^-$ than that of BF_4^- (e.g., 86 Å^3 for $PO_2F_2^-$ and 73 Å^3 BF_4^- at MP2/aug-cc-pVTZ.[19,22] Comparison of cell parameters at 298 K is shown in Table S1[19]).

X-ray diffraction patterns of [TEA][PO_2F_2] and [TEA][BF_4] at 273, 343, 373, and 423 K are shown in Figure 3. The diffraction patterns of these compounds at 273 K (crystal phase) resemble each other, reflecting their structural similarity. At temperatures above the phase transition, the diffraction patterns became simple and only five peaks are observed at low angles regardless of the measuring temperature. This high-temperature phase can be indexed as a cubic lattice with the indices (111),

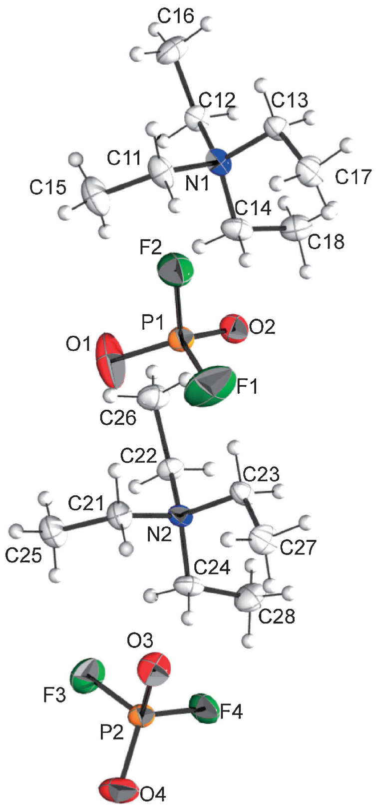

Figure 1. X-ray crystal structure of [TEA][PO_2F_2] at 100 K; thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (degree): N–C, 1.506(6)–1.530(5) [1.512]; C–C, 1.507(7)–1.538(7) [1.516]; P–O, 1.443(3)–1.470(3) [1.490]; P–F, 1.539(4)–1.558(3) [1.608]; C–N–C (small), 107.9(3)–109.4(3) [108.7]; C–N–C (large), 111.0(3)–112.0(4) [111.0]; N–C–C, 114.0(4)–116.1(4) [115.3]; O–P–O, 122.3(2) and 123.0(3) [125.6]; O–P–F, 105.7(3)–111.3(2) [108.0]; F–P–F, 97.8(2) and 95.8(2) [94.9]. The values in brackets are the bond lengths and angles in the optimized geometries at MP2/cc-pVTZ for TEA^+ and MP2/aug-cc-pVTZ for $PO_2F_2^-$. See SI[19] for the details on calculated geometric parameters of TEA^+ and the reference[15] for those of $PO_2F_2^-$.

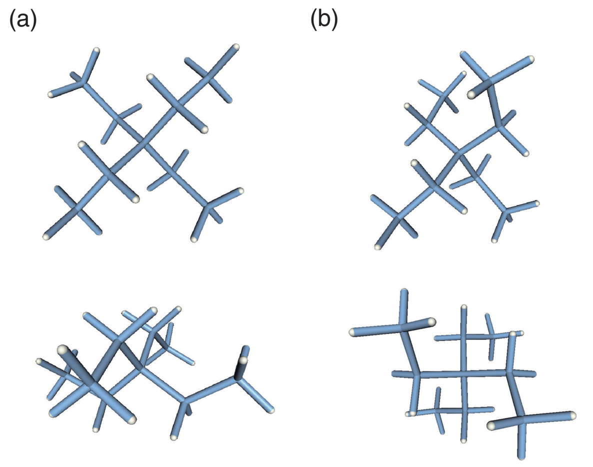

Figure 2. Molecular structures of TEA^+ conformers: (a) *TT*-conformer (D_{2d}) and (b) *TG*-conformer (S_4).

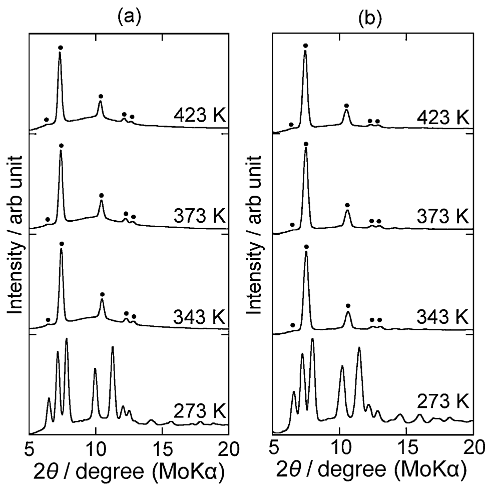

Figure 3. X-ray diffraction patterns of (a) [TEA][PO_2F_2] and (b) [TEA][BF_4] at 273, 343, 373, and 423 K. Solid circles denote the diffraction peaks assigned to the plastic crystal phases of [TEA][PO_2F_2] and [TEA][BF_4] with the NaCl-type structure.

Table 1. Powder X-ray diffraction data for [TEA][BF_4] and [TEA][PO_2F_2] at 373 K

hkl	2θ/degree	Intensity	d_{obs}/Å	d_{calc}/Å
[TEA][PO_2F_2][a]				
111	6.53	w	6.24	6.38
200	7.38	s	5.52	5.53
220	10.44	m	3.91	3.91
113	12.24	w	3.33	3.33
222	12.74	w	3.20	3.19
[TEA][BF_4][b]				
111	6.61	w	6.17	6.27
200	7.52	s	5.42	5.43
220	10.62	m	3.84	3.84
113	12.42	w	3.29	3.27
222	12.96	w	3.15	3.13

a) $a = 11.05$ Å (determined from the d_{obs} values of (200) and (220)), $V = 1349$ Å^3. b) $a = 10.85$ Å (determined from the d_{obs} values of (200) and (220)), $V = 1277$ Å^3.

(200), (220), (113), and (222), as shown in Table 1. The systematic extinction observed suggests five possible space groups, $Fm\bar{3}m$, $F432$, $F\bar{4}3m$, $Fm3$, or $F23$, whereas the assumption that each ion rotates three-dimensionally leads to the NaCl-type structure under $Fm\bar{3}m$. Several ionic plastic crystals of alkylammonium salts are known to have the NaCl- and CsCl-type crystal structures.[23] Disappearance of diffraction peaks at high angles is caused by large thermal motions of each ion in the plastic crystal phases. The a and V lattice parameters at 373 K for [TEA][PO_2F_2] ($a = 11.05$ Å and $V = 1349$ Å^3) are larger than those for [TEA][BF_4] ($a = 10.85$ Å and $V = 1277$ Å^3) as in the case of crystal phase. According to a previous study,[24] the radius-ratio rule[25] can be applied to ionic plastic crystals. In the present case, the radius ratios (R_-/R_+, where R_- and R_+ are radii of anion and cation, respectively) are

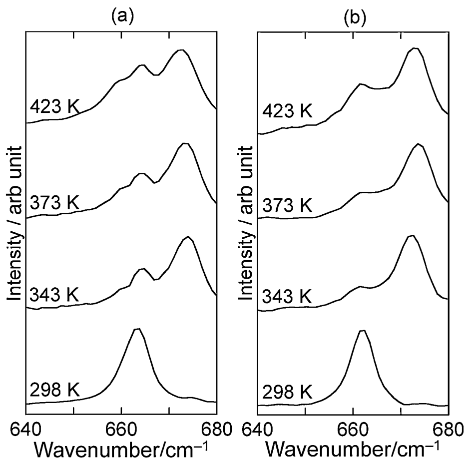

Figure 4. Raman spectra of (a) [TEA][PO_2F_2] and (b) [TEA][BF_4] at 298, 343, 373, and 423 K. The peaks observed in this region are assigned to the $\nu_s(NC_4)$ mode of TEA^+.

0.73 and 0.70 for [TEA][PO_2F_2] and [TEA][BF_4], respectively, based on the results of quantum mechanical calculations (MP2/cc-pVTZ and MP2/aug-cc-pVTZ, see SI[19]). Although both [TEA][PO_2F_2] and [TEA][BF_4] have the NaCl-type structure, the R_-/R_+ values are located around the boundary between the NaCl-type (0.414–0.732) and CsCl-type (0.732–1.000) structures. The cell volumes of the crystal phases determined at 298 K are 1245.54(16) $Å^3$ for [TEA][PO_2F_2] and 1178(1) $Å^3$ for [TEA][BF_4]. The ratio of the volumes at 373 K (plastic crystal phase) and 298 K (crystal phase) is 1.08 for both [TEA][PO_2F_2] and [TEA][BF_4], which demonstrates significant lattice expansion at the crystal–plastic crystal phase transition.

Raman spectra of [TEA][PO_2F_2] and [TEA][BF_4] in the region between 640 and 680 cm^{-1} are shown in Figure 4. Although peaks appearing in this region are assigned to the $\nu_s(NC_4)$ mode of TEA^+, the frequency for the *TG*-conformer is slightly smaller than that for the *TT*-conformer according to previous reports (e.g., 664 cm^{-1} for the *TG*-conformer in [TEA][ClO_4] and 675 cm^{-1} for the *TT*-conformer in [TEA][SCN]).[4,6,7] Our calculation at MP2/cc-pVTZ also gives the same trend (674 cm^{-1} for the *TG*-conformer and 684 cm^{-1} for the *TT*-conformer). The peak position at 298 K is 664 cm^{-1} for [TEA][PO_2F_2] and 662 cm^{-1} for [TEA][BF_4] and agree with the value for the *TG*-conformer as was shown by crystallographic work. Above the crystal–plastic crystal phase-transition temperature, another peak around 674 cm^{-1} for [TEA][PO_2F_2] and 673 cm^{-1} for [TEA][BF_4] corresponding to the *TT*-conformer appears in both the cases although the low-frequency peak is still observed, which suggests that both the conformers exist in the plastic crystal lattices of [TEA][PO_2F_2] and [TEA][BF_4] and that the *TT*-conformer is dominant. The ratio of the *TT*-conformer to the *TG*-conformer decreases with increase in temperature. The weak cation–anion interaction and rotation of each ion lead to a variation in conformation in the plastic crystal phase as was reported in a previous work.[4] The shoulder around 660 cm^{-1} in the plastic crystal phase of [TEA][PO_2F_2] becomes more and more prominent with increase in temperature, which might suggest that another conformer exists at these temperatures. The vibrational modes for the anions also exhibit some shifts at the crystal–plastic crystal transition (Figure S5[19]). Both the XRD patterns and Raman spectra of the [TEA][PO_2F_2] and [TEA][BF_4] below the plastic crystal to crystal transition temperature in the cooling process are the same as those in the heating process; that is, the structural change at the phase transition (monoclinic–cubic) is reversible.

In summary, the present study reports thermal properties and structural changes at the crystal–plastic crystal transition for [TEA][PO_2F_2] and [TEA][BF_4]. These two compounds have a similar structure in the crystal phases which turns into a NaCl-type structure at the transition. The TEA^+ cation adopts the *TG*-conformer in the crystal structure, whereas the *TT*-conformer is dominant in the plastic crystal structure.

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19 Supporting information is available electronically on the CSJ-Journal Web site, http://www.csj.jp.journals/chem-lett/index.html.
20 Crystal data for [TEA][PO_2F_2]: $C_8H_{20}NPO_2F_2$, $M_r = 231.22$ monoclinic, space group *Pc*, $a = 12.400(3)$, $b = 7.5654(16)$, $c = 13.677(3)$ Å, $\beta = 113.939(6)°$, $V = 1172.7(5)$ $Å^3$, $Z = 4$, $T = 100$ K, $\mu = 0.239$ mm^{-1}. 8750 reflections measured, 3755 reflections independent ($R_{int} = 0.0615$). $R_1 = 0.0641$ ($I > 2\sigma(I)$), $wR_2 = 0.1698$ ($I > 2\sigma(I)$). CCDC-853437 contains the supplementary crystallographic data for this paper. Copy of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi.
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