Calorimetric Study of Polymorphism in 1-Butyl-3-methylimidazolium Hexafluorophosphate

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Abstract

Stable and metastable crystal phases of 1-butyl-3-methylimidazolium hexafluorophosphate were obtained in an adiabatic calorimeter providing precise temperature control during crystallization. Heat capacities, as well as temperatures and enthalpies of phase transitions, including fusion, were determined for three polymorphic sequences (I, II, and III). Structures of the crystal phases were assigned using crystallographic studies from the literature. The standard entropy for each sequence was the same at $T = 0 \text{ K}$ within the uncertainty of the measurements. This, in combination with the crystallographic results, implies that the lowest-temperature crystal form is ordered for all sequences. The complete pattern of phase transformations in this ionic liquid at ambient pressure is described, and results show that the relative stability of Sequences II and III invert at $T \approx 281 \text{ K}$.

1. Introduction

Room-temperature ionic liquids (ILs) are salts that typically incorporate bulky cations and, sometimes, bulky anions. As a result, the energy of interaction between the ions is lower than that of typical salts, favoring a low temperature of fusion. This effect is further enhanced due to the asymmetry of the cations typically used in ILs. Those two factors result in the possibility of multiple crystal packings with little difference in lattice energy and polymorphism. Multiple crystal phases have been reported for various ILs (cf., [C$_n$mim]NTf$_2$, [C$_4$mim]An (An = Cl, NO$_3$), [Et$_4$N]NTf$_2$. [1–5]).

1-butyl-3-methylimidazolium hexafluorophosphate [C$_4$mim]PF$_6$ is probably the most studied polymorphic IL [6–26], though its behavior in the crystal state is not understood completely. Due to precise temperature control and the ability to observe subtle heat effects associated with crystal transformations, adiabatic calorimetry can be a powerful tool in determining relative phase stabilities, as well as temperatures and enthalpies of phase transitions. An assignment of the crystal phases for [C$_4$mim]PF$_6$ has been proposed by Saouane et al. [6] as a part of an X-ray study. It is impractical to monitor slow or complex phase changes by X-ray diffraction, and we will show that
assignments made require some revision. Similarly, interpretations based on spectroscopy or
differential scanning calorimetry can also be misleading due to the inability to carefully monitor
the solid-state transformations. As demonstrated below, different phases were sometimes obtained
from the same sample placed in a calorimeter, an X-ray diffractometer, or a spectrometer.

In this work, we combine experimental data obtained by adiabatic calorimetry with structural and
calorimetric data available in the literature to identify crystal phases of \([\text{C}_4\text{mim}]\text{PF}_6\) and determine
relative stability and thermodynamic properties for various polymorphs of this compound from 0 K to the corresponding triple-point temperatures \(T_{\text{fus}}\).

2. Experimental Section

A commercial sample of \([\text{C}_4\text{mim}]\text{PF}_6\) (Merck) with the stated purity of 99 mass percent was
exposed to a vacuum of approximately 1 kPa at room temperature with constant stirring. The mole
fraction purity of the sample was determined to be 99.68 % by fractional melting analysis of two
distinct polymorphs in the adiabatic calorimeter (Figure 4).

Heat capacities of the sample in the temperature range (5 to 370) K were measured in a TAU-10
adiabatic calorimeter (Termis, Moscow, Russia) [29]. The experimental procedures have been
previously described [30]. Each heat-capacity determination involved initial measurement of
temperature and its drift rate, as well as the electrical heating of the sample cell, which was
followed by an equilibration period and measurement of the final temperature, adjusted for the
background drift rate. This procedure is typical for adiabatic calorimetry [31]. Temperatures were
measured with an Fe/Rh resistance thermometer \((R_0 = 50 \ \Omega)\) calibrated on ITS-90 by VNIIFTRI
(Moscow). The heat capacity of the sample contributed about 80% of the total heat capacity of the
system near 5 K, about 40% near 100 K, and 54% near 370 K. The equilibration times were close
to 100 s at the lowest temperatures. At higher temperatures the typical equilibration times were
300 s. The expanded uncertainty (0.95 confidence interval) in the heat capacity measurements was
determined to be 0.4 % above $T = 20$ K and 2 % near $T = 5$ K [30]. Sample masses were corrected for buoyancy.

The Fe/Rh thermometer is placed on an adiabatic shield and the temperature difference between the shield and the container is measured with a differential thermocouple [30]. Normally, the thermocouple works at small $\Delta T$. To make the temperature calibration at the large temperature differences (up to 30 K) occurring on cooling, the temperatures of peaks $T = (176.4$ and $216.8)$ K were used. The expanded uncertainty after this calibration was estimated to be $u(T) = 1$ K.

The heat capacity was derived from the cooling curve with the following differential equation:

$$
\left(C_p(s) + C_p(\text{cont})\right) \frac{dT}{d\tau} + k_1(T - T_0) + k_2(T_s - T_0) = 0
$$

(1)

where $C_p(s)$ and $C_p(\text{cont})$ are the heat capacities of the sample and the container, respectively; $T$, $T_s$, and $T_0$ are the temperatures of the container, the adiabatic shield, and the liquid nitrogen bath. The empirical parameters $k_1$ and $k_2$ were found using the experimental heat capacity of Sequence II obtained during regular measurements in the temperature range of $T = (150$ to $225)$ K. The relative expanded uncertainty in the derived heat capacity was estimated to be $U_r(C_P) = 20\%$.

The reported uncertainties correspond to the 95 % confidence interval for the normal distribution (coverage factor $k = 2$) unless specified otherwise.

3. Results

3.1 Calorimetry

The experimental heat capacities for the studied IL are presented in Figures 1–3 and in Table S1. On cooling, the liquid supercooled and formed glass. Crystallization occurred when the glass devitrified and then was heated to $T = 213$ K. Three sequences of crystalline phases were obtained. These sequences are designated as Sequence I, Sequence II, and Sequence III in order of their appearance on continuous heating. Solid phases within a given sequence are distinguished by
numeric indices starting with the lowest temperature phase. For example, crII₁ is the lowest temperature phase observed in Sequence II, crII₂ is the next higher temperature phase, etc. Sequence III has only one crystal phase crIII. One crystal phase crI was also observed in Sequence I. However, during the measurements, the sequence became unstable significantly below $T_{\text{fus}}$ and other polymorphs may be missing.

**Liquid.** Heat capacities for the liquid phase obtained in this work (Figure 3) were combined with the literature data considered in the review by Paulechka [27] and a general equation was obtained for the temperature range (191 to 370) K:

$$
C_{P,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 326.94 - 26.201(T / 100 \text{ K}) + 26.149(T / 100 \text{ K})^2 - 2.7848(T / 100 \text{ K})^3 \quad (2)
$$

**Sequence I (crI).** Phase crI was first formed (Figure 1) when crystallization was initiated near $T = 213$ K. The sample warmed spontaneously to about $T = 234$ K. Annealing at this temperature would finally result in formation of crII₃, so measurements for the quenched crystals are reported here for crI. This crystal contained $(0.6 \pm 0.1)\%$ of the phases belonging to Sequence II, as estimated from the area of the very small peak with $T_{\text{max}} = 176$ K, which is characteristic of Sequence II. The heat capacity curve had a hump with a maximum at $T \approx 190$ K. As demonstrated in the Results section, this hump is related to disordering in the crystal phase.

An endothermic peak with a maximum at $T = (250 \pm 1) \text{ K}$ and with a standard molar enthalpy $\Delta_{\text{crI}}^{\text{fus}} H_{\text{m}} = 1.50 \pm 0.11 \text{ kJ} \cdot \text{mol}^{-1}$ was observed. These parameters were obtained in three series of measurements with the freshly obtained quenched crystals (Table S2). The observed decrease of heat capacity just before the peak is an artifact caused by incomplete equilibration. This artifact has no effect on the enthalpy of transition reported above. The equilibration time was not increased since it would favor transformation into crIII before this solid-phase transition. This phenomenon is similar to the transformations reported earlier [18], [6] and should be assigned to the irreversible transition to crII₄, the stable phase of Sequence II above $T = 250$ K.
Upon continued heating (~7 K·h⁻¹), the transition near $T = 250$ K was followed by an exothermic transformation of crII₄ into crIII (Figure 1). With freshly obtained quenched crystals, the initial rate of this exothermic process was significantly less than that for the annealed crystal or the crystal cooled to $T = 80$ K before the measurements. The maximum heat evolution rate was observed at $T \approx 265$ K, as determined from the temperature drifts observed in the calorimetric experiments.

![Figure 1](image-url)

**FIGURE 1.** Experimental heat capacities and temperature drifts during calorimetric measurements (——) for crI: Blue circles, heat capacities in the region of kinetic stability; ⋅⋅⋅⋅⋅⋅, baseline used for extrapolation of heat capacity; −−−−−−, temperature of phase transition. Heat capacities near $T = 250$ K (red circles) have large uncertainties, as discussed in the text. Above $T = 252$ K (red line), the experiments were continued to track changes in temperature drifts; heat capacities in that range could not be determined. The temperature drifts were measured at 300 s after the end of heating.

The measurements were continued until the sample liquefied completely to determine the enthalpy change $H_m^\circ(l; 286$ K) $– H_m^\circ($crI, 230 K) $= (31.00 \pm 0.12)$ kJ·mol⁻¹ (Table S3). This value in combination with $H_m^\circ($crI; 230 K) $– H_m^\circ($crI, 0 K) $= (39.46 \pm 0.16)$ kJ·mol⁻¹ obtained in this work yields the enthalpy for crI between 0 K and the liquid at $T = 286$ K. With the analogous enthalpy change for Sequence III ($H_m^\circ(l; 286$ K) $– H_m^\circ($crIII, 0 K) $= (75.39 \pm 0.30)$ kJ·mol⁻¹) [21], we
calculate the enthalpy of crI relative to crIII to be $H^\circ_m(\text{crI}; 0 \text{ K}) - H^\circ_m(\text{crIII}, 0 \text{ K}) = (4.93 \pm 0.36)$ kJ∙mol$^{-1}$.

Although not measured directly, it is possible to approximate the melting temperature and enthalpy of fusion for crI using the following reasoning. The heat capacity curve in Figure 1 shows no evidence of positive curvature that would indicate pre-melting. Pre-melting for crIII was detected ~20 K below $T_{\text{fus}}$. Based on this, the melting temperature for crI should be greater than 267 K. In addition, Sequence I has the lowest thermodynamic stability relative to the other sequences, so its melting point would also be the lowest. As demonstrated below, it means $T_{\text{fus}} < 283.6$ K. These two criteria allow one to make estimates: $T_{\text{fus}}(\text{crI}) = (275 \pm 8)$ K and $\Delta_{\text{fus}}^\circ H_m = (12.85 \pm 0.60)$ kJ∙mol$^{-1}$.

**Sequence II.** If a mixture of crII$_4$ + crIII is heated a few tenths of a Kelvin above the melting temperature of crIII, the sample will contain only the phase belonging to Sequence II in equilibrium with liquid.

Fractional melting of this crystal (Figure 4) allowed us to determine its triple-point temperature to be $T_{\text{fus}} = (284.55 \pm 0.06)$ K. If the (crII$_3$ + liquid) mixture is cooled at an initial rate of 20 mK∙s$^{-1}$, a sample suitable for measurements can be obtained. The heat capacity curve for Sequence II is distinguished by two non-isothermal phase transitions with maxima at $T = (176.4 \pm 0.7)$ K and $T = (216.8 \pm 0.4)$ K (Figure 2) determined in three experiments and averaged. The corresponding enthalpies of phase transitions were $\Delta_{\text{crII}_1^2}^\circ H_m = (0.75 \pm 0.05)$ kJ∙mol$^{-1}$ and $\Delta_{\text{crII}_2^3}^\circ H_m = (0.89 \pm 0.06)$ kJ∙mol$^{-1}$. 
FIGURE 2. Experimental heat capacities and temperature drifts during calorimetric measurements (—) for Sequence II: Blue circles, heat capacity in the region of kinetic stability; – – – – – –, baseline used for extrapolation of heat capacity to \( T_{\text{fus}} \); ; – – – –, peak temperatures of phase transitions; —, heat capacity derived from the cooling curve. Above \( T = 252 \) K (red line), the experiments were continued to track changes in temperature drifts; heat capacities in that range could not be determined. The temperature drifts were measured at 300 s after the end of heating.

Polymorph crII_3 became unstable at \( T = 220 \) K and transformed into crIII. The large and positive temperature drifts for \( T > 200 \) K are evidence of this transformation (Figure 2).

To obtain more information about Sequence II, the heat capacity was derived from the cooling curve in the calorimeter (Figure 2). In addition to the transitions observed during regular measurements, the peak with a maximum at \( T = (250 \pm 1) \) K was detected. The enthalpy of this phase transition was estimated to be \( \Delta_{\text{crII}_3} H_m^\circ = (0.5 \pm 0.1) \) kJ·mol\(^{-1} \) based on cooling-curve analysis.

To determine the enthalpy of fusion for crII_3, the enthalpy change \( H_m^\circ(\text{l}; 286 \) K) – \( H_m^\circ(\text{crII}_3, 220 \) K) = \( (33.15 \pm 0.13) \) kJ·mol\(^{-1} \) was measured (Table S4) and the contributions from the heating of
crII3 and the liquid were subtracted. The following equation, based on the experimental data in the range (220.1 to 224.0) K, was used to estimate the crystal-phase heat capacity in the calculation of the enthalpy of fusion.

\[ C^{\circ}_{P, m} / J\cdot K^{-1}\cdot mol^{-1} = 194.18 + 0.41657(T / K) \]  

(3)

At \( T = 0 \) K, crII1 is less stable than crIII by \( H^\circ_m(\text{crII}; 0 \text{ K}) - H^\circ_m(\text{crIII}, 0 \text{ K}) = (4.02 \pm 0.42) \text{ kJ} \cdot \text{mol}^{-1} \).

**Sequence III (crIII).** Heat capacities (Figure 3) as well as temperature and enthalpy of fusion (Table 1) were reported in our previous publication [21]. This crystal had a smooth heat capacity curve with no solid-phase transitions.

In this work, spontaneous crystallization of crI resulted in formation of crII4. Crystal crIII could be obtained with a negligible content of other phases by heating crystals belonging to Sequence II if they were first cooled to \( T = 80 \) K. The enthalpy change \( H^\circ_m(\text{l}; 286 \text{ K}) - H^\circ_m(\text{crIII}, 260 \text{ K}) = (28.53 \pm 0.11) \text{ kJ} \cdot \text{mol}^{-1} \) obtained in this work (Table S5) is in a very good agreement with the value (28.63 ± 0.11) kJ·mol⁻¹ reported earlier [21].

The triple-point temperature for crIII determined in this work by fractional-melting (Figure 4) was 0.05 K higher than the value reported in our previous work [21]. Since the reliability of the earlier measurements is comparable to that of this work, we estimate the expanded uncertainty for this value to be \( U(T_{\text{fus}}) = 0.03 \) K (for 0.95 confidence interval).
FIGURE 3. Experimental heat capacities of crIII [21] (blue circles) and liquid (red circles)
**FIGURE 4.** Fractional melting curves for (a) crystal III, (b) crystal II₄. Various symbols are used for different measurement series, and $f$ is the fraction melted at temperature $T$. Crystal phase designations are described in the first paragraph of the *Results* section of the text.

At temperatures a few tenths of a kelvin below the temperature of fusion of crIII, heat evolution due to the formation of crII₄ was observed. Further heating of the sample resulted in formation of the (crII₄ + liquid) mixture. In all series of measurements, the heat capacity curve in the melting region had the melting peak of crIII followed by the melting peak of crII₄ (Figure 5). The relative peak heights differed in various series of measurements.
FIGURE 5. Typical melting curve for the studied sample, the first peak was assigned to melting of crIII, the second one was assigned to crII₄. — — are corresponding triple points. The line is a guide for the eye. Uncertainties for the heat capacities are large due to long equilibration times that precluded high-precision measurements in this region.

The observed phase transformations are summarized in Figure 6.

FIGURE 6. Observed phase transformations of [C₄mim]PF₆, black arrows are used for equilibrium transitions, red arrows designate non-equilibrium transformations

3.2 Thermodynamic functions and relative stability of polymorphs
Calculation of the absolute entropy of a polymorph requires heat capacities from the temperature of interest to 0 K. Extrapolation of heat capacities for the crystals from 5 K to 0 K were performed with the use of the empirical function:

\[ C_{P,m} = D_3(\theta_D/T) + E(\theta_E/T) \]  \( (4) \)

where \( D_3(\theta_D/T) \) is the Debye heat-capacity function for three degrees of freedom and \( E(\theta_E/T) \) is the Einstein heat capacity function for one degree of freedom. The parameters \( \theta_D \) and \( \theta_E \) were 47.3 K and 52.1 K for crI and 58.2 K and 46.0 K for crII. They were determined from the experimental data in the temperature range (5.1 to 7.1) K and (5.4 to 7.9) K, respectively.

The experimental heat capacities were smoothed with polynomials. The thermodynamic functions (Table S8), including those in the non-isothermal phase transition regions (except crII₃–crII₄), were calculated using the smoothed heat capacities. In narrow ranges where the heat capacities changed abruptly, numerical integration of the experimental heat capacities was applied. The baselines were used for calculations of the thermodynamic functions only in the pre-melting ranges.

The relative thermodynamic stability of the polymorphs is demonstrated in Figure 7. Sequence I remains metastable at all temperatures. At temperatures below \( T = 281 \) K, crIII is the stable phase, while above this temperature, crII₄ becomes the thermodynamically stable phase.

The entropies of the crystals for Sequences I and II are higher than that of Sequence III at all temperatures above \( T = 0 \) K. At \( T > 150 \) K, the differences exceed 12 J·K⁻¹·mol⁻¹ (Figure 8). Moreover, at \( T = 200 \) K, the entropy difference becomes approximately half of the entropy of fusion for crIII. This implies that the crystals for Sequences I and II are characterized by higher disorder relative to crIII at \( T > 150 \) K. This is also confirmed by structural studies discussed below.

The entropies for the liquid phase at \( T = 298.15 \) K determined with the experimental data for Sequences I, II, and III are \( (490.6 \pm 2.3) \) J·K⁻¹·mol⁻¹, \( (492.3 \pm 2.1) \) J·K⁻¹·mol⁻¹, and \( (493.0 \pm 2.1) \) J·K⁻¹·mol⁻¹ [21], respectively. Differences in these values are not statistically significant.
Therefore, the entropy at $T = 0$ K for all sequences is the same. It is equal to zero, as follows from the X-ray results considered below.

The low-temperature heat capacities of crI and crII are significantly higher than that of crIII (Figure 9). Moreover, $C_{p,m}(crI)$ is higher than the heat capacity of the glass reported by Kabo et al. [21]. While this phenomenon has previously been observed for some ILs [28], it is still relatively rare.

**FIGURE 7.** Relative Gibbs energy of [C$_4$ mim]PF$_6$ phases: blue, Sequence I; green, Sequence II; black, Sequence III [21]; red, liquid [21].
FIGURE 8. Comparison of entropies for various [C₄mim]PF₆ phases: blue, Sequence I; green, Sequence II; black, Sequence III [21]; red, glass and liquid [21]

FIGURE 9. Comparison of low-temperature heat capacities for various [C₄mim]PF₆ phases: blue, crI; green, crII; black, crIII; red, glass [21]

4. Discussion

4.1 Analysis of literature data
A summary of the temperatures and enthalpies of fusion available in the literature is given in Table 1. The original abbreviations for various polymorphs are presented in Table 2 for convenience.

Several studies combined [7], [16], [18], [19] spectroscopic and X-ray studies with calorimetric results. However, as demonstrated below, thermodynamic and structural data are often inconsistent and should be considered separately. We will discuss the assignment of phases in calorimetric results and then in the structural data. In some cases, interpretation of the experimental results differs from that provided in the original papers.

**TABLE 1**

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<td>275 ± 8</td>
<td>12.8 ± 0.6</td>
<td>AC</td>
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<tr>
<td>crII₄</td>
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<td>AC</td>
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<td>visual</td>
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<td>Endo and Nishikawa [19]</td>
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<td>Dománska and Marciniak [8]</td>
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<td>Jin et al. [11]</td>
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<td>284</td>
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<td>AC</td>
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<sup>a</sup> DSC, differential scanning calorimetry; AC, adiabatic calorimetry; visual, visual determination;  
<sup>b</sup> the reported uncertainties correspond to the 0.95 confidence interval for normal distribution ($k = 2$);  
<sup>c</sup> a sum of enthalpies of transition and fusion;  
<sup>d</sup> a peak maximum.

**TABLE 2**

Notation of crystal phases

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<tr>
<th>Reference</th>
<th>Literature notation</th>
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<td>crI</td>
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<tr>
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<td>crII</td>
<td>crI or crIII&lt;sup&gt;b&lt;/sup&gt;</td>
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\begin{tabular}{lll}
Endo et al. [20], [19], [22] & $\alpha$ & Sequence I \\
Saouane et al. [6] & $\beta$ & Sequence II \\
 & $\gamma$ & crIII \\
Endo et al. [18] & $\alpha$ & crI \\
 & $\beta$ & crII$_3$ \\
 & $\gamma$ & crII$_4$ or crIII$^c$
\end{tabular}

\textsuperscript{a} Sequence II from calorimetric measurements, crIII from X-ray data; \textsuperscript{b} crI was obtained after crystallization on heating starting from glass, the crystal obtained in another calorimetric experiment was crIII; \textsuperscript{c} crII$_3$ from DSC measurements and crIII from spectroscopic measurements.

4.2 Calorimetry

Melting of [C$_4$mim]PF$_6$ has been studied mainly by DSC (Table 1). Adiabatic calorimetry was used by Kabo et al. [21] and Triolo et al. [16].

Triolo et al. [16] described a number of polymorphs for the compound based on their measurements with adiabatic calorimetry. The crystalline phase they obtained by heating the glass underwent the only solid-phase transition with $\Delta_nH_m$(252 K) $\approx$ 1.4 kJ·mol$^{-1}$. This thermal behavior is similar to crI in our work. Heating of crI resulted in formation of another phase, which could also be obtained by crystallization of the liquid at $T = 260$ K. Two solid-phase transitions at $T_n = 177$ K ($\Delta_nH_m = 0.5$ kJ·mol$^{-1}$) and $T_n = 217.5$ K ($\Delta_nH_m = 0.3$ kJ·mol$^{-1}$) detected by Triolo et al. [16] for this phase can be assigned to the crII$_1$-to-crII$_2$ and crII$_2$-to-crII$_3$ transformations observed in the present work. Enthalpies of transition reported by Triolo et al. [16] are significantly lower than the values obtained in this work. The presence of crIII in their sample during measurements could account for the inconsistency, but this is speculation only. Triolo et al. [16] found that the crII$_3$ polymorph became unstable at $T = 246$ K and transformed into an unknown phase. We suggest
this phase to be crIII based on similar observations in our experiments. The observed phase transformations can be described as follows:

\[
glass \xrightarrow{194 \, K} \text{liq} \xrightarrow{220 \, K, \text{exo}} \text{crI} \xrightarrow{252 \, K, \text{endo}} \text{crII}\_4
\]

\[
\text{crII}_1 \xleftarrow{177 \, K, \text{endo}} \text{crII}_2 \xrightarrow{217.5 \, K, \text{endo}} \text{crII}_3 \xrightarrow{246 \, K, \text{exo}} \text{crIII}
\]

The temperature of fusion of \( T_{\text{fus}} = 284 \, K \) reported by Triolo et al. [16] for an independent run can be assigned to melting of either crII\_4 or crIII.

In a study using DSC, Endo et al. [18] reported \( T_{\text{fus}} = 285.3 \, K \) for [C\text{4mim}]PF\text{6}. While this value is close to that reported by Kabo et al. [21], it does not imply that both values should be assigned to the same polymorph. Kabo et al. [21] obtained the heat capacity curve from 5 \, K to \( T_{\text{fus}} \) and no trace of a solid-phase transition was found. Endo et al. [18] reported two solid-phase transitions at \( T = 250 \, K \) and \( T = 276 \, K \). The first transition corresponds to irreversible process, as reported in a subsequent paper from the same group [22]. Additionally, the enthalpy of fusion reported by Endo et al. [18] is 32% lower than the value obtained by adiabatic calorimetry [21].

It is probable that Endo et al. [18] observed melting of crII\_4 but not crIII. The crystal phase obtained below \( T = 250 \, K \) is then crI. A peak at \( T = 276 \, K \) was later observed by the authors in Sequences II and III [19]. The temperature-dependent Raman spectra had no changes that could be associated with this transformation [19]. This peak was found in the DSC curves obtained with different instruments in the same laboratory [18–20]. An anomaly with a maximum at \( T = 278 \, K \) was also observed by Troncoso et al. [9]. Therefore, the peak at \( T = 276 \, K \) is not a phase transition belonging to Sequence II. This peak may be caused by an unknown phase transition or fusion of crI. It is not possible to resolve this ambiguity without further research.

The reported transformations can be summarized as

\[
glass \xrightarrow{192 \, K} \text{liq} \xrightarrow{226.5 \, K, \text{exo}} \text{crI} \xrightarrow{250 \, K, \text{endo}} \text{crII}_4 \xleftarrow{285.3 \, K} \text{liq}
\]
Later, Endo and Nishikawa [19] noted that transformation of crII₃ into crIII occurs near \( T = 255 \) K and this process is accompanied by heat evolution. The temperatures and enthalpies of fusion for crII₃ and crIII were also reported (Table 1). The enthalpies of fusion agree within the experimental uncertainty with the results from adiabatic calorimetry. An important advantage of that work is that the instrument used allowed simultaneous spectroscopic and calorimetric measurements and provided structural information in addition to thermodynamic data. In summary, the following phase transformations were observed:

\[
\begin{align*}
\text{liq} & \xrightarrow{226.5 \text{ K, exo}} \text{crI} \xrightarrow{255 \text{ K, endo}} \text{crII} \xleftrightarrow{285.8 \pm 1.4 \text{ K}} \text{liq} \\
\text{crII₃} & \xrightarrow{255 \text{ K, exo}} \text{crIII} \xleftrightarrow{285.3 \pm 1.4 \text{ K}} \text{liq}
\end{align*}
\]

The same instrument was also used by Endo et al. [20], who reported somewhat different parameters of fusion for crII₄.

In a number of other works, complex phase behavior was also observed. A solid-phase transition at \( T_{tr} = 258.0 \) K with the enthalpy \( \Delta_H^{tr} = 10.67 \pm 0.11 \text{ kJ mol}^{-1} \) followed by fusion at \( T_{fus} = 276.4 \) K was observed by Domańska and Marciniak [8]. In the DSC curve obtained at a rate of 10 K min⁻¹, crystallization was immediately followed by the solid-phase transition, and the peak of fusion had a simpler shape than in later work by Choudhury et al. [7], who reported a DSC curve for [C₄mim]PF₆ from \( T = (103 \text{ to } 313) \) K. Crystallization of the supercooled liquid started at approximately \( T = 233 \) K. The authors found an irreversible solid-phase transition at \( T_{tr} \approx 263 \) K followed by a melting peak with complex shape. A complex melting curve was also noted by Troncoso et al. [9], who used a relatively low heating rate (0.075 K min⁻¹) and found that the melting curve included a maximum at \( T = 278 \) K. Based on the obtained DSC curve, Jin et al. [11] reported a transition at \( T \approx 272 \) K followed by melting of the compound. In all these works, mixtures of crystal phases were obtained, making the assignment to specific phases impossible.

4.3 Structural studies
An X-ray analysis of the crystal phase grown at $T = 243$ K by Choudhury et al. [7] showed that the crystal contains the $G'T$ conformer of the cation (Figure 10). A similar structure obtained by shock-induced crystallization was reported by Dibrov and Kochi [15]. Triolo et al. [16] noted that their X-ray powder diffraction data at $T = 190$ K agreed with the X-ray analysis by Choudhury et al. [7] and Dibrov and Kochi [15] recorded at $T = 180$ K and $T = 173$ K, respectively. Triolo et al. [16] concluded that this crystal belonged to Sequence II. If this conclusion was correct, then the diffraction patterns would be different since they corresponded to different phases crII$_1$ and crII$_2$. Based on the procedures used for crystallization [15], [16], the obtained diffractograms should be assigned to crIII. This conclusion agrees with the results by Saouane et al. [6], who reported the crystal structure of crIII at $T = 263$ K. A relatively small (8 %) admixture of $GT$ conformer observed by Saouane et al. [6] can be explained by pre-melting.

Saouane et al. [6] reported the following transformations:

$$\text{glass} \rightarrow \text{liq} \rightarrow \text{crI} \rightarrow \text{crII}_3 \rightarrow \text{crIII}$$

$$\text{liq} \rightarrow \text{crIII}$$

$$\text{glass} \rightarrow \text{liq} \rightarrow \text{crI} \rightarrow \text{crII}_3 \rightarrow \text{crIII}$$

Saouane et al. [6] are the only group to report the structure of crI and crII$_2$ at ambient pressure. They noted that crI contains 100 % of the $GT$ conformer of the cation at $T = 100$ K and 75 % $GT + 25 \% G'T$ conformer at $T = 193$ K. This disordering is likely associated with the hump near $T = 190$ K in the heat capacity curve of crI (Figure 1) observed in our measurements. A mixture of conformers with $TT$ being the predominant component was detected in crII$_2$.

X-ray studies discussed above [6], [7], [15], [16] demonstrated that at low temperatures crI and crIII are ordered. Thus, the entropy of these crystals is equal to zero at $T = 0$ K. While the X-ray data demonstrate that crII$_2$ is conformationally disordered, the calorimetric results from this work
demonstrate that crII is ordered, as evidenced by the equivalence of the entropies for the liquid calculated with all three phase sequences.

FIGURE 10. [C₄mim]⁺ conformers

Raman spectra of the crystal phases at ambient pressure are available at several temperatures (Table 3). They confirm the major conformers of the cation in each phase identified by the X-ray diffraction. Unambiguous identification of the phases is possible only when the spectra are accompanied by simultaneous calorimetric measurements or by a well-defined thermal history. Raman spectra have not been reported for many polymorphs of [C₄mim]PF₆, and the existing spectra for crI and crIII cannot be compared in detail, as they were recorded at different temperatures.

TABLE 3

Available Raman spectra for various polymorphs of [C₄mim]PF₆

<table>
<thead>
<tr>
<th>Phase</th>
<th>T / K</th>
<th>Reference</th>
</tr>
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<tbody>
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</table>
4.4 Elevated pressure

Gomes de Azevedo et al. [17] studied the pressure dependence of the melting temperature for [C₄mim]PF₆ from 0.1 MPa to 89 MPa from acoustic determinations. From these data, the slope $dP/dT_{\text{fus}} = (4.83 \pm 0.33) \text{ MPa K}^{-1}$ can be found. Russina et al. [23] reported $dP/dT_{\text{fus}} = 5.2 \pm 0.2 \text{ MPa K}^{-1}$ over the range (285 to 373) K based on their own high-pressure Raman measurements and data by Gomes de Azevedo et al. [17]. The Raman spectra reported by Russina et al. [23] demonstrated that crII₄ was formed. Later, this conclusion was confirmed by X-ray and Raman data [6].

If pressure is further increased at $T = 293$ K, one of phases belonging to Sequence I is formed [23], [6], [24]. At $P \geq 1.2$ GPa, a new sequence of two polymorphs was detected, and their crystallographic parameters and Raman spectra were reported [24]. Surprisingly, further increase of pressure resulted in amorphization of the structure and formation of either glass or liquid.
5. Conclusion

Adiabatic calorimetry was used to detect and to fully identify phase transformations for 1-butyl-3-methylimidazolium hexafluorophosphate at ambient pressure. Three sequences of crystal phases were found and the parameters of equilibrium phase transitions were reported. Crystal structures reported in literature were assigned to the phases obtained in this work. Many inconsistencies reported in the literature were identified based on the knowledge of the relative phase stabilities and transformation sequences reported in this work. Problems that previously prevented correct interpretation of the observed phase transformations include (i) incorrect thermodynamic interpretation of the observed phase transitions, and (ii) different polymorphs obtained from the same sample for separate calorimetric and structural studies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

References


