The High-Temperature Polymorph of $LiBF_4$

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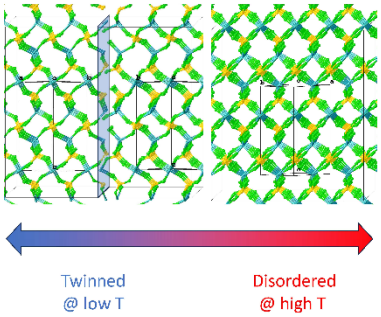

ABSTRACT: The single-crystal-to-single-crystal phase transition is determined using X-ray crystallography on $LiBF_4$, resolving a longstanding ambiguity in the existence of a high-temperature polymorph of $LiBF_4$. $LiBF_4$ possesses an endothermic phase change at 28.2 °C with ΔH = 1180 J mol^{-1} and ΔS = 3.92 J $mol^{-1}K^{-1}$ based on DSC. Single-crystal X-ray diffraction shows that the low temperature phase collected at 200K is a twinned trigonal P system with a twin law indicating reflection through the 110 plane. The same crystal collected above the phase transition temperature at 313 K is a C-centered orthorhombic system describable as the superposition of the two low-temperature twin geometries undergoing interconversion. The geometries of the high- and low-temperature phases are consistent with the calorimetry experiments, and with previous NMR findings indicating BF_4 geometric reorientations above 300 K.

Among the most ubiquitous polyatomic, weakly coordinating anions is tetrafluoroborate, BF_4^-. As a common spectator anion in organic and inorganic syntheses, numerous salts of this important anion are available as inexpensive commercial chemicals. Structures of many alkali and alkaline earth metal salts of BF_4^- have been determined using single-crystal X-ray diffraction, SC-XRD, beginning in the 1930's by Finbak and Hassel, and including more recent examples as well.[1] Early structures included salts of Na, K, Rb, Cs, and NH_4^+.[2] One of the interesting properties of this category of tetrafluoroborate salts is that each of these has been shown to undergo a solid-to-solid phase transformation to an alternative polymorph, characterized by via SC-XRD, in each case transforming from an orthorhombic phase at low temperature to a cubic phase at higher temperature.[3] Conspicuously absent from the alkali metal series is $LiBF_4$, though a phase transition for this salt has been proposed, but has been controversial. There has been significant debate on the existence of the phase transition of $LiBF_4$, or lack thereof, for this species spanning decades, as summarized below.

In 1969, Cantor and coworkers reported no observation of a solid transition for $LiBF_4$ using a metal dilatometer to determine density and expansivity of the molten salt.[4] However, in March 1970, Shuster and Marano determined and reported the transitional phase of $LiBF_4$ to occur between 108-110 °C using differential thermal analysis.[5] Later findings from Dworkin in 1972 did not seem to corroborate this result; these authors reported no evidence of this phase transition using copper block drop calorimetry.[6]

In 1984, Reynhardt and Lourens discovered a change in magnetic moment of the fluorine nucleus by ^{19}F NMR of $LiBF_4$ at 300.1 K.[7] They hypothesized that this apparent change in magnetic moment was triggered by a change in local symmetry around the fluorine atom resulting from a structural change in the $LiBF_4$ lattice. In 1993, Gorbunov et al. reported a phase transition in $LiBF_4$ using adiabatic calorimetry at 300.7 K,[8] a temperature similar to that observed by Lourens for the magnetic phase transition of the ^{19}F nucleus. In 1997, Plakhotnik and coworkers reported a similar result using differential scanning calorimetry (DSC) at 300.7 K, [9] and this result was corroborated again by Henderson in 2011.[10] In 2006 the first single crystal of anhydrous $LiBF_4$ was reported at 200 K by Žemva and coworkers,[11] but up to the present, no crystallographic evidence of a phase transition for $LiBF_4$ has been reported. We report here a redetermination of the low-temperature SC-XRD structure of $LiBF_4$ and the structure of the high-temperature polymorph. The corresponding structural changes are described in context of previous literature.

To reassess the existence of thermodynamic evidence of a phase change, differential scanning calorimetry (DSC) data was collected for the pure $LiBF_4$ salt, shown in Figure 1**.** It contains a sharp melting endotherm at 28.2 °C (301.4 K), consistent with the findings of Gorbunov, Lourens, Plakhotnik, and

Henderson.[7-10] The enthalpy and entropy for the formation of the high-temperature phase were calculated from the heating trace, giving $\Delta H = 1180$ J mol^{-1} and $\Delta S = 3.92$ J mol^{-1}K^{-1}. These values differ from the thermodynamic values of the phase transition reported by Gorbunov et al., of $\Delta H = 3010$ J/mol and $\Delta S = 12.0$ +/- 0.3 Jmol^{-1}K^{-1}. This might be due to contamination of Gorbunov's sample by the trihydrate, which also melts at approximately room temperature,[8] and would increase the observed exotherm since heats of fusion are rather larger than heats of polymorphic transitions.

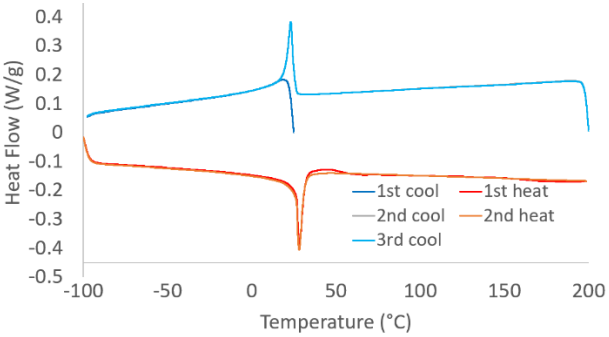

Figure 1. DSC thermogram of $LiBF_4$ with melt peaks at 28.2 °C.

Based on our DSC measurement, anhydrous $LiBF_4$ melts at 309.2 °C (see Supporting Information), a value consistent with that reported by Dworkin of 310 °C using copper block drop calorimetry.[6] ΔH_{fus} and ΔH_{fus} computed from the integral of the DSC are 11.5 kJ/mol and 19.7 J/mol·K respectively, about 20% lower than those reported by Dworkin.[6]

To examine the structural difference attributed to the thermal signals in the DSC, SC-XRD utilized. A single crystal of $LiBF_4$ was taken directly from commercially available bulk $LiBF_4$ powder without recrystallization. The crystal was then heated to 313 K under temperature-controlled nitrogen gas, and SC-XRD data was collected at that temperature. The same crystal was then cooled to 200 K at a rate of 6 K per minute, and recollected at that temperature to capture the single-crystal-to-single-crystal phase transition. The asymmetric unit structures are shown in Figure 2.

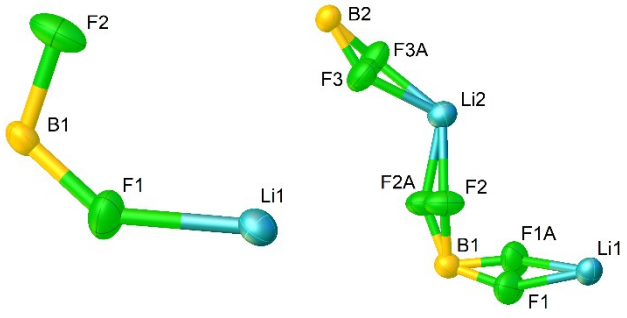

Figure 2. Thermal ellipsoid plost of the asymmetric unit of $LiBF_4$. Left: Structure at 200K in the $P3_221$ space group. Ellipsoids set at 50% probability level. Right: Structure at 313 K in the $C222$ space group. Ellipsoids set at 30% probability level.

The space group for the 200 K structure collected in this work is assigned as $P3_221$, identical to the reflection of previously reported $P3_121$ space group reported by Žemva.[11] The structure nevertheless exists as a twinned structure described by a reflection through the 110 crystallographic plane as evidenced by twin refinement, which improves R_1 from 22.9% to 3.66%, with the minor (reflected) twin component representing 44.2(4)% of the crystal based on twin refinement. Figure 3 (left) shows an overlay of the major structure and the twin component, showing that the twin component can be described by a rotation of the BF_4 anion with respect to its lithium neighbors. The slight canting of the BF_4 ions as viewed down the [110] direction in Figure 3 (left) illustrates the lack of two-fold or reflection symmetry about *c*. This twinning behavior can be attributed to the twin components representing degenerate, opposite-handed chiral space groups, each of which is obtained due to random chance during crystal nucleation.

In Figure 3-right, the 313 K structure is shown, viewed down the same axis (the [110] direction is equivalent in the trigonal P and orthorhombic C settings). One can see from this diagram that the arrangement of atoms is quite similar, except that the imposed permanent cant of the BF_4^- anion is disrupted at higher temperature, and the anion takes on a two-component disorder. In Figure 3-right, we can see that the high temperature phase effectively represents a rapid interconversion of the geometries of the two twin components of the low-temperature phase.

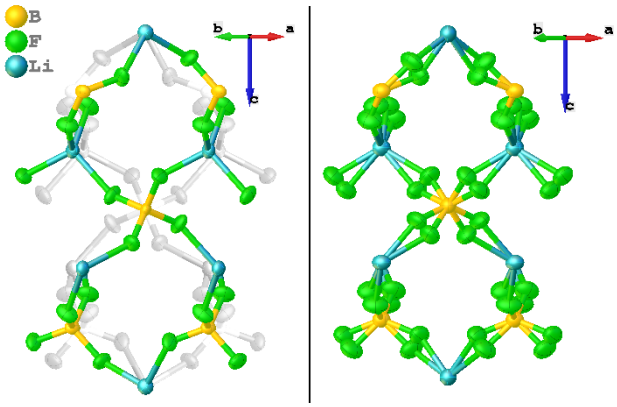

Figure 3. Thermal ellipsoid plots showing equivalent selection of packed atoms for each polymorph viewed along the [110] direction (equivalent view for both space groups). Left: atoms from the $P3_221/P3_121$ polymorph. The reflection twin component is shown overlaid in gray. $T = 200$ K. Ellipsoids set at 50% probability level. Right: atoms from the $C222$ space group. $T = 313$ K. Ellipsoids set at 30% probability level.

The appearance of both orientations together at 313 K imparts new two-fold symmetry about the *c* axis not present in the trigonal structure (Figure 3). The disorder however disrupts the right-handed helices of the vertical [Li-F-B-F-]$_\infty$ chains shown in Figure 3-left such that the 3_2 screw axis symmetry is lost at high temperature. The appearance of crystallographic disorder at high temperature, as well as the reduction in crystallographic symmetry from the trigonal to the orthorhombic settings are consistent with the increase in entropy observed from DSC, Figure 1. Further, the disruption of permanent short F-Li contacts at higher temperature is consistent with the endothermic conversion to the high-temperature phase due to the requirement for bond disruption. The geometric descriptions from the single-crystal X-ray data are consistent with the findings of Reynhardt et al., who observed a decrease in the magnetic second moment of the ^{19}F nucleus above the phase transition temperature, which they attributed to molecular reorientations of the molecular components[7] (i.e., the BF_4 anion), entirely consistent with the picture shown in Figure 3.

In conclusion, DSC confirms the existence of a phase transition for $LiBF_4$, and single crystal x-ray diffraction has been used to visualize the single-crystal-to-single-crystal phase transition from a trigonal to orthorhombic lattice. The geometric arrangements of the atoms in the low- and high-temperature polymorphs show that a two-component reflection twin overcomes local strong F-Li contacts at about 300K, and that the geometries of the two twin components begin interconverting in the high-temperature phase, changing the overall symmetry. The observed geometries are consistent with the positive ΔH and ΔS values from DSC, and with previous findings from ^{19}F NMR indicating orientational averaging above 300 K.[7] The findings put to rest a decades-long debate on the elusive second polymorph for $LiBF_4$, and completing the periodic series polymorphic alkali tetrafluoroborate salts.

ASSOCIATED CONTENT

Crystallographic information files (CIF), also available from CCDC under deposition # 2299467-2299468), experimental protocols, powder X-ray diffraction patterns and crystallographic tables. This material is available free of charge via the Internet at http://pubs.acs.org. Additional references are cited in the supporting information.

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Author Contributions

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ABBREVIATIONS

SC-XRD, single-crystal X-ray diffraction; DSC, differential scanning calorimetry; NMR, nuclear magnetic resonance.

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