Anomalously large formula unit volume and its effect on the thermal behavior of LiBF₄

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Abstract. Crystal structure of $LiBF_4$ has been determined by single-crystal X-ray diffraction. $LiBF_4$ crystallizes as a merohedral twin in the trigonal space group $P3_121$ with $a = 4.892(5)$ Å, $c = 11.002(12)$ Å, $V = 228.0(4)$ Å^3, $Z = 3$ at 200 K. The twin is generated by a twofold rotation about $[1\ \bar{1}\ 0]$ direction. Lithium cation is coordinated by four fluorine atoms in a distorted tetrahedral manner, where two Li-F distances of 1.862(5) and 1.846(5) Å are observed. The formula unit volume ($FUV = V / Z$) of 77.9 Å^3 for $LiBF_4$ at 298 K is considerably larger than 72.7 Å^3 for $NaBF_4$ and 72.5 Å^3 for $AgBF_4$ in spite of the smaller size of Li^+, indicating a loose ionic packing of $LiBF_4$. Thermodynamic evaluation of the decomposition temperature for $LiBF_4$ is performed by using the empirical relationship between the standard entropy and FUV obtained. The result indicates that the large FUV of $LiBF_4$ contributes to its higher decomposition temperature than that of $LiPF_6$.

Introduction

Lithium salts are now widely used for supporting electrolytes of primary and secondary lithium batteries.[1] Crystal structures of lithium salts give some hints to understand their physical properties including the coordination environment around the lithium cation in the solution.[2] Description of the structures of some lithium hexafluorocomplex (LiAF$_6$) salts have been seen in the literatures since 1956 and they have been compared with a series of other alkali metal and silver hexafluorocomplex salts. All the LiAF$_6$-type (A = P, V, As, Nb, Mo, Ru, Rh, Sb, Ta, W, Re, Os, Ir, Pt and Au) salts exhibit rhombohedral symmetry and are isostructural with each other.[3-7] The structure of LiClO$_4$ which crystallizes into an orthorhombic space group was determined in a recent report.[8] Lithium salts of bulky anions such as CF$_3$SO$_3^-$ and N(SO$_2$CF$_3$)$_2^-$ are also structurally characterized from their powder diffraction data.[9,10]

Although LiBF$_4$ is known as one of the common electrolytes for lithium batteries and the large number of reports are available on the structures of other MBF$_4$-type (M = univalent cation) salts,[11-15] all the attempts to determine the crystal structure of LiBF$_4$ have been unsuccessful.[15-17]

In this study, we report the first successful results of the crystal structure determination of LiBF$_4$. Thermal behavior of lithium salts has been investigated in relation to the drying process of the salts at elevated temperatures. According to previous reports, LiBF$_4$ is thermally more stable than LiPF$_6$.[18-22] The effect of structural characteristics of LiBF$_4$ on its thermal decomposition temperature will be described using thermodynamic calculations to explain the higher thermal stability of LiBF$_4$ than LiPF$_6$.

Experimental Section

Apparatus and Reagents. Volatile materials (BF$_3$, aHF) were handled in an all PTFE vacuum line equipped with PTFE valves. Manipulation of the non-volatile materials was performed in a dry box (M. Braun). The residual water in the atmosphere within the dry-box never exceeded 1 ppm. The reactions were carried out in FEP (tetrafluoroethylene-hexafluoropropylene) reaction vessels (height 250–300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with PTFE valves and PTFE coated stirring bars. Prior to their use all reaction vessels were treated with elemental fluorine. Anhydrous HF (Fluka, Purum) was treated with K$_2$NiF$_6$ (Ozark Mahoning) for

several hours prior to use. LiF (Merck, 99.99 %) and BF_3 (Union Carbide Austria GmbH, 99.5%) were used as supplied. $LiBF_4$ was prepared by reaction of LiF with BF_3 in HF.

Preparation of Single Crystals of $LiBF_4$. $LiBF_4$ (approximately 150 mg) was placed into the wider tube of the T-shaped reaction vessel and dissolved in anhydrous HF. This solution was decanted into the narrower arm of the reaction vessel. The crystals were grown with a small temperature gradient of 10 K (running tap water-ambient temperature). Crystals were isolated from the mother liquid, immersed in perfluorinated oil (ABCR, FO5960) in the dry-box, selected under microscope, and transferred into the cold nitrogen stream of the diffractometer.

Crystal Structure Determination. Single-crystal data from $LiBF_4$ were collected on a Mercury CCD area detector coupled with a Rigaku AFC7S diffractometer using monochromatized MoKα-radiation. Crystals of $LiBF_4$ exhibit a strong affinity to twinning resulting in non-reproducible unit cell parameters for each crystal. After several quick tests, an appropriate single crystal with the minor amounts of extra-domains was selected. Obtained data were corrected for Lorentz, polarization and absorption effects, and processed using Rigaku CrystalClear software suite program package.[23] Using the SIR-92[24] program implemented in program package TeXsan[25] an appropriate model was found. Because of rather high R-value (~0.15) for complete model, the TwinRotMax utility from program package PLATON[26] was used for twinning detecting. The twinning matrix of [0-1 0 -1 0 0 0 0 -1], corresponding to a two-fold rotation around [1 $\bar{1}$ 0] direction, and estimated domains ratio of 0.63 : 0.37 were determined. Britton and Yeates tests, being performed using TWIN3.0 softvare,[27] have detected the same twinning law with approximate 0.6 : 0.4 domains ratio. Finally structure was refined by the SHELXL-97[28] program applying the twinning matrix. Refined ratio between two domains appears to be equal to 0.61 : 0.39.

Results and Discussion

The unit cell parameters and refinement statistics for $LiBF_4$ are given in Table 1. Selected bond distances and angles are listed in Table 2.

Structural Characteristics of LiBF$_4$. The structure of LiBF$_4$ was solved using the data at 200 K. LiBF$_4$ crystallizes in the trigonal space group *P*3$_1$21. ORTEP diagram of the unit cell is shown in Fig. 1. The asymmetric unit contains one Li, one B and two F atoms. Li cations are located at positions on *z* = 0, 1/3 and 2/3 planes which are related to each other by the 3$_1$ screw symmetry. B atoms in BF$_4^-$ occupy positions on *z* = 1/6, 1/2 and 5/6 planes which are also related to each other by the 3$_1$ screw symmetry. BF$_4^-$ exhibits an ideal tetrahedral shape (B-F = 1.387(3) and 1.391(3) Å; F-B-F = 109.2(3) − 109.74(14)°) without any disordering. Figure 2 shows the coordination environment around Li$^+$ in LiBF$_4$. Li$^+$ is coordinated by four fluorine atoms belonging to four different BF$_4$ anions, where two bond distances of 1.846(5) and 1.862(5) are observed. The shortest F$\cdots$F distance, corresponding to fluorine atoms belonging to two different BF$_4^-$ anions, is 2.939 Å. Table 3 gives the structural parameters of a series of MBF$_4$ salts (M = Na, Ag, K, Rb and Cs) which were reported in previous studies.[29-32] AgBF$_4$, KBF$_4$, RbBF$_4$ and CsBF$_4$ are isostructural and show orthorhombic symmetry (BaSO$_4$-type structure), whereas NaBF$_4$ exhibits a different orthorhombic structure (CaSO$_4$-type structure). The structure of LiBF$_4$ determined in the present study belongs to a trigonal system which has never been found in known MBF$_4$ salts. The coordination number around M$^+$ in MBF$_4$ decreases with decrease in size of M$^+$ in the order of ten for AgBF$_4$, KBF$_4$, RbBF$_4$ and CsBF$_4$, eight for NaBF$_4$ and four for LiBF$_4$. It should be noted that lithium ion is coordinated by six ClO$_4$ anions even in the case of LiClO$_4$ where ClO$_4^-$ is a little larger tetrahedral ion.[8] The unusually small coordination number of four around Li$^+$ in LiBF$_4$ enables the formation of wide space surrounded by the frame forming an infinite network structure in the lattice (Figure 3).

Thermal Stability of LiBF$_4$. As mentioned in the introduction part, it is known that the decomposition temperature of LiBF$_4$ is higher than that of LiPF$_6$.[18-22] Thermal decompositions of MBF$_4$ and MPF$_6$ proceed according to the following reactions (1) and (2), respectively:

$$MBF_4 \text{ (s)} \rightarrow MF \text{(s)} + BF_3 \text{ (g)} \tag{1}$$

$$MPF_6 \text{ (s)} \rightarrow MF \text{(s)} + PF_5 \text{ (g)} \tag{2}$$

Table 4 shows some thermodynamic parameters at 298 K related to the decomposition of $LiBF_4$ and $LiPF_6$. The standard entropy values, $S°$, of LiF, BF_3 and PF_5 are literarily available.[33] The decomposition enthalpy, $\Delta_{dec}H°$, (reactions (1) and (2)) are also reported previously.[34,35] The standard entropy values of $LiBF_4$ and $LiPF_6$ in Table 4 were calculated by using the following method. An empirical relationship between $S°$ and FUV (formula unit volume = V / Z) for solid crystalline compounds was first proposed by Mallouk and Bartlett.[36,37] Jenkins and Glasser added a theoretical meaning to this correlation and extended it to a wide variety of compounds.[38] For inorganic salts, the regression line takes the form of the equation (3):[36,37]

$$S° \text{ (J mol}^{-1} \text{ K}^{-1}) = 1.757 \text{ x } FUV(\text{Å}^3) \tag{3}$$

The decomposition entropy, $\Delta_{dec}S°$, of MBF_4 and MPF_6 is introduced by the following equations (4) and (5):

$$\Delta_{dec}S° = S°(MF) + S°(BF_3) - S°(MBF_4) \tag{4}$$

$$\Delta_{dec}S° = S°(MF) + S°(PF_5) - S°(MPF_6) \tag{5}$$

Finally, the decomposition temperature, T_{dec_calc}, is estimated from the room temperature reaction entropy and enthalpy change by the equations (6), (7) and (8):[38]

$$\Delta_{dec}G°_{298} = \Delta_{dec}H°_{298} - T_{dec\_calc}\Delta_{dec}S°_{298} \tag{6}$$

$$\Delta_{dec}G°_{T\_dec} = \Delta_{dec}H°_{T\_dec} - T_{dec\_calc}\Delta_{dec}S°_{T\_dec} = 0 \tag{7}$$

$$T_{dec\_calc} = \Delta_{dec}H°_{T\_dec}/ \Delta_{dec}S°_{T\_dec} \approx \Delta_{dec}H°_{298} / \Delta_{dec}S°_{298} \tag{8}$$

The approximation used in the equation (8) is introduced by the fact that ΔH and ΔS are temperature-dependent quantities, but in general they do not change very much with temperature unless a phase transition is involved.

It should be noted that either $LiBF_4$ or $LiPF_6$ does not exhibit any phase transition up to the decomposition temperatures.[14,15,35] The T_{dec_calc} of $LiBF_4$ in Table 4 is certainly higher than that of

$LiPF_6$, which agrees with the experimental data.[18-22,35] Since the difference between $\Delta_{dec}H°_{298}$ values of the two compounds is not large compared with the difference between $\Delta_{dec}S°_{298}$ values, the contribution of the latter is expected to be dominant. When one compares thermal stabilities of MBF_4 and MPF_6, where M is common, MBF_4 seems to have an advantage of being thermally more stable than MPF_6 from the equations (4) and (5) because $S°(BF_3)$ is smaller than $S°(PF_5)$ and $S°(MF)$ is common in both the cases. However, the difference in their lattice volumes, which influences the third terms of the right sides in the equations (4) and (5) through the equation (3), could be large enough to make the PF_6 salt more thermally stable. For the purpose of using this calculation, the unit cell parameters for $LiBF_4$ were also determined at 298 K (Table 1). $LiBF_4$ has the same structure at 298 K as that at 200 K with a little lattice expansion. The FUV of $LiBF_4$ calculated from the crystallographic data is 77.9 $Å^3$ at 298 K which is unexpectedly much larger than those of $NaBF_4$ (72.7 $Å^3$) and $AgBF_4$ (72.5 $Å^3$) in spite of the smaller size of Li^+ than those of Na^+ and Ag^+ (see Table 3 and 5).[30,32,40] The unit cell parameters of $LiPF_6$ are shown in Table 3. The FUV for $LiPF_6$ (88.2 $Å^3$) is 79.9 % of that for $NaPF_6$ (110.4 $Å^3$), whereas the FUV for $LiBF_4$ is 104.5 % of that for $NaBF_4$. It may be easy to understand this point by comparing the FUV of $LiBF_4$ (77.9 $Å^3$) with that of $LiClO_4$ (71.4 $Å^3$) which is composed of Li^+ and a slightly larger tetrahedral ClO_4^- anion (average Cl-O bond length: 1.44 Å).[8] Because Li-F bond distances observed in $LiBF_4$ are not longer than expected from their ionic radii (Table 2 and 5), one can say that the $LiBF_4$ lattice contains more empty space than those of the other tetrafluoroborates (see Fig. 3). The loose $LiBF_4$ structure, i.e. large FUV value, results in the small $\Delta_{dec}S°$ through the equations (3) and (4), leading the higher decomposition temperature of $LiBF_4$ than that of $LiPF_6$.

Conclusion

Crystal structure of $LiBF_4$ determined by single-crystal X-ray diffraction has been reported. $LiBF_4$ crystallizes in the trigonal unit cell, where lithium cation is coordinated by four fluorine atoms in a distorted tetrahedral manner. Formula unit volume (FUV = V / Z) of $LiBF_4$ at 298 K (77.9 $Å^3$) is considerably larger than those for $NaBF_4$ (72.7 $Å^3$) and $AgBF_4$ (72.5 $Å^3$) in spite of the smaller ionic radius of Li^+. It has been elucidated using an empirical relationship between the standard entropy

and FUV that the loose ionic packing of the $LiBF_4$ structure contributes to the large standard entropy of $LiBF_4$ and the higher decomposition temperature of $LiBF_4$ than that of $LiPF_6$.

Supporting Information Available: Crystallographic data (CIF) is available free of charge via the Internet at http://pubs.acs.org.

Table 1. Crystal data and refinement results for $LiBF_4$

	$LiBF_4$	
Empirical formula	$Li_1B_1F_4$	$Li_1B_1F_4$[c]
Formula weight	93.75	93.75
Crystal system	Trigonal	Trigonal
Space group	$P3_121$	$P3_121$
a / Å	4.892(5)	4.9458(8)
c / Å	11.002(12)	11.035(2)
V / Å^3	228.0(4)	233.76(12)
Z	3	3
T / K	200	298
d_c / g cm^{-3}	2.048	1.998
μ / mm^{-1}	0.283	-
R_1 ($I>2\sigma(I)$)[a]	0.0384	-
wR_2 ($I>2\sigma(I)$)[b]	0.0882	-

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2 =[\Sigma w[|F_o|^2-|F_c|^2]^2/\Sigma w|F_o|^2]^{1/2}$

[c] Only the unit cell parameters were determined.

Table 2. Selected bond distances (Å) and angles (degree) for LiBF$_4$

B1–F1	1.387(3)
B1-F2	1.391(3)
Li1-F1	1.862(5)
Li1-F2	1.846(5)
F1-B1-F1	109.7(4)
F1-B1-F2	109.21(12)
F1-B1-F2	109.74(14)
F2-B1- F2	109.2(3)
F2-Li1-F2	117.1(5)
F2-Li1-F1	107.67(10)
F2-Li1-F1	104.87(11)
F1-Li1-F1	115.1(4)

Table 3. Structural parameters for MBF$_4$ (M = Na, Ag, K, Rb and Cs) and LiPF$_6$

	NaBF$_4$[b]	AgBF$_4$[c]	KBF$_4$[d]	RbBF$_4$[e]	CsBF$_4$[e]	LiPF$_6$[f]
Space group	*Cmcm*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*R3*
a / Å	6.2619	5.312	5.4800	5.63	5.88	5.077
b / Å	6.7916	6.752	7.0299	7.29	7.64	-
c / Å	6.8368	8.089	8.6588	9.10	9.67	-
α / °	-	-	-	-	-	57.98
V / Å^3	290.8	290.1	333.6	373.5	434.4	88.2
Z	4	4	4	4	4	1
FUV / Å^3 [a]	72.7	72.5	83.4	93.4	108.6	88.2
T / °	r.t.	-73	r.t.	r.t.	r.t.	r.t.

[a] *FUV = V / Z.* [b] Ref. 30. [c] Ref. 32. [d] Ref. 31. [e] Ref. 29. [f]Ref. 3.

Table 4. Some thermodynamic parameters related to the decompositions of $LiBF_4$ and $LiPF_6$

$S°_{298}$			$\Delta_{dec}S°_{298}$ [a]	$\Delta_{dec}H°_{298}$ [a]	T_{dec_calc} [a, b]	T_{dec_obs} [a]
/ J mol^{-1} K^{-1}			/ J mol^{-1} K^{-1}	/ kJ mol^{-1}	/K	/K
$LiBF_4$(c)	LiF(c)	BF_3(g)				
136.9 [c]	35.7 [d]	254.4 [d]	153.2	89.5 [e]	584	>573 [g, h], 583[i]
$LiPF_6$(c)	LiF(c)	PF_5(g)				
155.0 [c]	35.7 [d]	300.8 [d]	181.5	84.3 [f]	464	467 [f], 500 [i]

[a] $\Delta_{dec}S°_{298}$ and $\Delta_{dec}H°_{298}$: Entropy and enthalpy values for decomposition at 298 K. T_{dec_calc} and T_{dec_obs}: Calculated and observed thermal decomposition temperatures. Thermal decompositions of $LiBF_4$ and $LiPF_6$ occur according to the equations:

$LiBF_4$(c) → LiF(c) + BF_3(g), $LiPF_6$(c) → LiF(c) + PF_5(g)
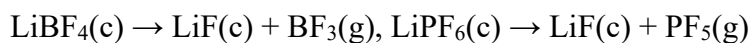
[b] $T_{dec\_calc} = \Delta_{dec}H°_{298}/ \Delta_{dec}S°_{298}$

[c] These values are obtained according to the reported numerical relationship:[36,37]

$S°_{298}$ (J mol^{-1} K^{-1}) = 1.757 x FUV(Å^3)

The FUV of $LiBF_4$ at 298 K is 77.92 Å^3 (See Table 1.)

[d] Ref. 33. [e] Ref. 34. [f] Ref. 35. [g] Ref. 18. [h] Ref. 19. [i] Ref. 20.

Table 5. Ionic radii of M^+ ions[40]

M^+	r_+ (C.N. = 4) [a]	r_+ (C.N. = 6) [a]
Li^+	0.59	0.76
Na^+	0.99	1.02
Ag^+	1.00	1.15
K^+	1.37	1.38
Rb^+	-	1.52
Cs^+	-	1.67

[a] C.N. means coordination number.

Figure captions

Fig. 1 ORTEP diagram of the LiBF$_4$ unit cell: (a) the view from the z-axis and (b) the view perpendicular to the z-axis. Displacement ellipsoids are shown at 50 % probability level.

Fig. 2 Coordination environment around Li$^+$ in the LiBF$_4$ structure.

Fig. 3 The network structure in the LiBF$_4$ lattice containing wide space. The large and small open spheres denote B and F atom, respectively. The octant-shaded sphere denotes Li atom.

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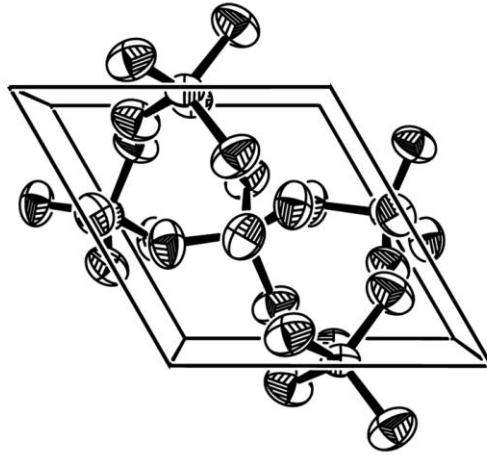
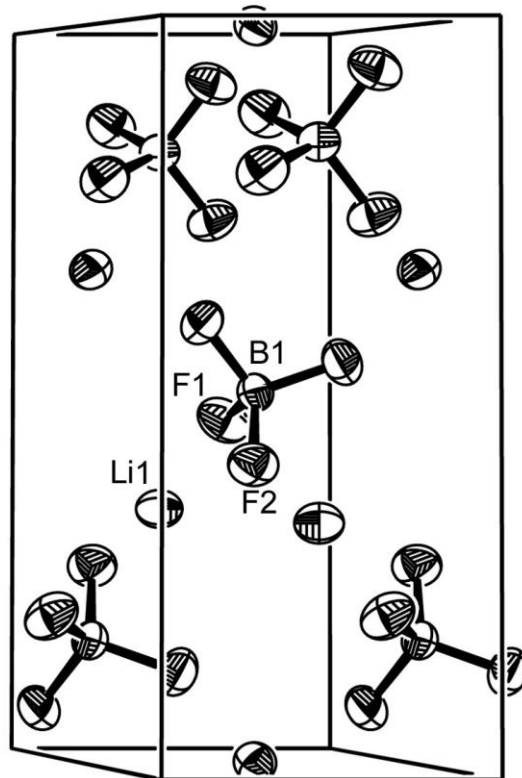Fig. 1 ORTEP diagram of the LiBF$_4$ unit cell: (a) the view from the z-axis and (b) the view perpendicular to the z-axis. Displacement ellipsoids are shown at 50 % probability level.
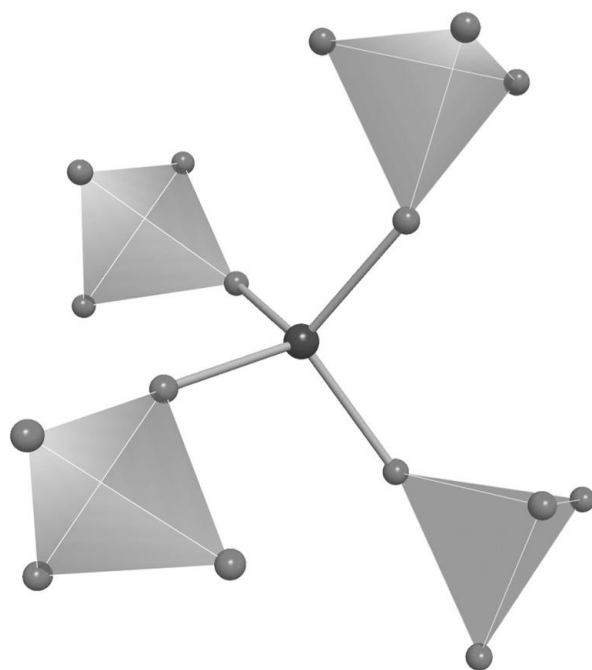
Fig. 2 Coordination environment around Li$^+$ in the LiBF$_4$ structure.
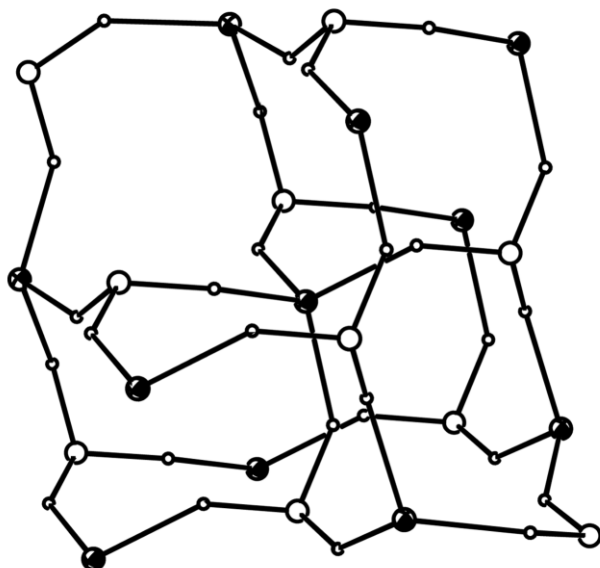
Fig. 3 The network structure in the LiBF$_4$ lattice. The large and small open spheres denote B and F atom, respectively. The octant-shaded sphere denotes Li atom.