Supporting Information

$Li_3CaB_2O_5F$: A unique sandwich-like structure with Diverse and Wide Li-ions Di□usion Pathways

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Experimental Section

Reagents

LiF (Tianjin Fuchen Chemical Reagents Factory, 98.5%), Li_2CO_3 (Tianjin Fuchen Chemical Reagents Factory, 97.0%), CaF_2 (Tianjin Fuchen Chemical Reagents Factory, 98.5%), CaO (Tianjin Fuchen Chemical Reagents Factory, 98.0%), H_3BO_3 (Aladdin Chemical Industry Co., Ltd., 99.5%) and $NH_4H_2PO_4$ (Tianjin Fuchen Chemical Reagents Factory, 99%) are used as received.

Syntheses

Single crystals of $Li_3CaB_2O_5F$ were grown from high-temperature solution reaction with spontaneous crystallization technique. The mixtures were weighed as follows: LiF (0.0087 mol, 0.2266 g), CaF_2 (0.0002 mol, 0.0126), H_3BO_3 (0.0024 mol, 0.1496 g) and $NH_4H_2PO_4$ (0.0010 mol, 0.1113 g). The raw materials were pre-sintered at 400°C in a muffle furnace to decompose CO_2 and NH_3 fully. Then they were transferred to platinum crucibles. The sample was heated to 800 °C and held at this temperature for 1 h to ensure the mixture completely melted, and cooled to 570°C at a rate of 5°C/h, subsequently cooled to room temperature by switching off the furnace. Thus, colorless small crystals of $Li_3CaB_2O_5F$ were obtained.

Polycrystalline samples of $Li_3CaB_2O_5F$ were synthesized by conventional solid-state reaction method. Stoichiometric ratio of the reactants was ground thoroughly and the temperature was raised to 580 °C and then held at this temperature for 72 hours with several intermediate grindings. The purity was confirmed by powder X-ray diffraction (XRD) patterns.

Powder X-ray Diffraction

The polycrystalline samples of $Li_3CaB_2O_5F$ were measured by the SmartLab9KW X-ray diffractometer (Cu K_α radiation) at room temperature, and collecting the data under the same conditions that the angular range in the 2 θ of 10–70° with a step size of 0.01° and a step time of 2 s.

Single-Crystal X-ray Diffraction

The crystal data of $Li_3CaB_2O_5F$ was collected on a Bruker SMART APEX II 4K CCD diffractometer with Mo K_α radiation (λ = 0.71073 Å) at 293(2) K, and the data was integrated with a SAINT program[1]. We solved the structure using the SHELXTL system[2] and then refined the structure's atomic positions employing a full matrix least-squares technique. The crystal data and structural refinement are shown in Table S1 and the atomic coordination, atomic displacement parameters, selected bond lengths and angles are listed in Tables S2 and S3.

UV-vis-NIR Di□use Reflectance Spectroscopy

The UV-Vis-NIR di□use reflectance spectrum of $Li_3CaB_2O_5F$ was measured by using a Shimadzu SolidSpec-3700DUV spectrophotometer in the range of 190–2500 nm at 25 °C. The teflon was used as a reference material.

Infrared Spectroscopy

The infrared spectroscopy of $Li_3CaB_2O_5F$ was measured by using a Shimadzu IR A□nity spectrometer in the range of 500–4000 cm^{-1} at room temperature.

Thermal Stability Measurement

Di□erential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were measured on a NETZSCH STA 449C thermal analysis instrument. Powder samples (~10 mg) were respectively heated up to 800 °C at a rate of 5 °C/min under an atmosphere of flowing nitrogen.

Bond Valence Sum Maps (BVS-DMs)

The Bond-Str program of Fullprof software was used to calculate the bond valence sum difference maps (BVS-DMs)[3,4] of $Li_3CaB_2O_5F$. At each point on a 3D grid (120 × 120 × 150) within the unit cell, the absolute value of the difference (|ΔV|) between the calculated valence of Li and the ideal valence of 1 was plotted as an isosurface with the VESTA software[5]. The smallest migration path is calculated in proportion by the distance which is measured by two atoms.

Ionic Conductivity

The ionic conductivity of $Li_3CaB_2O_5F$ was used a instruments electrochemical workstation, CHI 660E. A pressed tablet of the powder sample for $Li_3CaB_2O_5F$ with a radius of 0.496 mm and a thickness of 1.96 mm were selected for their ionic conductivity test and then sintered at 550 °C for 48 h. Collecting the data under the conditions that the frequency range of 0.1 MHz to 1 Hz and the amplitude of 1 mV at room temperature.

The diffusion coefficient of Li ions (D) is calculated according to the following Eq.(1) and Eq. (2)

$$D=R^2T^2/2A^2n^4F^4C^2\sigma^2 \quad (1)$$

$$Z'=Rs+Rct+\sigma\omega^{-1/2} \quad (2)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode, n is the number of electrons per molecule during oxidization, F is the Faraday constant, C is the concentration of lithium-ion, σ is the Warburg factor which has a relationship with Z' as shown in Eq. (2), *R*s is the resistance between the electrolyte and electrode, *R*ct is the charge transfer resistance, and ω is angle frequency.

References

[1] SAINT: *Program for Area Detector Absorption Correction*, Ver, 4.05; Siemens Analytical X-ray Instruments: Madison, WI, 1995.

[2] Sheldrick, G. M. SHELXTL, *version 6.12*; Bruker Analytical Xray Instruments, Inc.: Madison, WI, 2001.

[3] B. Wen, J. Liu, N. A. Chernova, X. Wang, Y. Janssen, F. Omenya, P. G. Khalifah, M. S. Whittingham, *Chem. Mater.,* 2016, **28**, 2229.

[4] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B.,* 1998, **57**, 1505.

[5] K. Momma, F. Izumi, *J. Appl. Crystallogr*., 2008, **41**, 653.

Table S1. Crystal data and structure refinement for $Li_3CaB_2O_5F$.

Empirical formula	$Li_3CaB_2O_5F$
Formula weight	363.04
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	a = 25.685(2) Å
	b = 3.4697(3) Å
	c = 5.4404(4) Å
Z, Volume/Å^3	2, 484.84(7)
Density/ g·cm^{-3}	2.487
Absorption coefficient/mm^{-1}	1.257
Completeness to	99.60%
GOF on F^2	0.906
Final R indices [F_o^2>2s(F_o^2)][a]	R_1 = 0.0302,
	wR_2 = 0.1009
R indices (all data)	R_1 = 0.0362,
	wR_2 = 0.1104

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $Li_3CaB_2O_5F$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ca(1)	2108(1)	7500	8869(1)	9(1)	2.21
Li(1)	1159(2)	2500	436(10)	22(1)	0.72
Li(2)	316(2)	2500	4143(10)	23(1)	0.81
Li(3)	378(2)	7500	9324(10)	16(1)	1.06
B(1)	1766(2)	2500	4022(6)	31(1)	2.86
B(2)	977(2)	-1394(13)	6189(7)	10(1)	2.75
F(1)	396(1)	2500	729(3)	12(1)	1.10
O(1)	2076(1)	2500	5999(4)	9(1)	2.15
O(2)	1191(1)	-2500	8398(4)	15(1)	1.88
O(3)	1928(1)	2500	1675(4)	11(1)	2.08
O(4)	461(1)	-2500	5701(4)	19(1)	1.92
O(5)	1251(1)	436(9)	4222(5)	13(1)	1.74

Table S3. Bond lengths (Å) and angles (deg.) for $Li_3CaB_2O_5F$.

Ca(1)-O(1)#1	2.3354(14)	F(1)-Li(1)-O(2)#6	94.82(19)
Ca(1)-O(1)	2.3354(14)	F(1)-Li(1)-O(2)#7	94.83(19)
Ca(1)-O(3)#2	2.3568(13)	O(2)#6-Li(1)-O(2)#7	114.7(3)
Ca(1)-O(3)#3	2.3568(13)	F(1)-Li(1)-O(3)	156.5(3)
Ca(1)-O(2)#1	2.370(2)	O(2)#6-Li(1)-O(3)	97.78(19)
Ca(1)-O(1)#4	2.395(2)	O(2)#7-Li(1)-O(3)	97.78(19)
Ca(1)-O(3)#4	2.747(2)	F(1)-Li(1)-O(5)	91.8(2)
Li(1)-F(1)	1.965(6)	O(2)#6-Li(1)-O(5)	103.06(12)
Li(1)-O(2)#6	2.061(3)	O(2)#7-Li(1)-O(5)	140.9(2)
Li(1)-O(2)#7	2.061(3)	O(3)-Li(1)-O(5)	66.07(18)
Li(1)-O(3)	2.089(6)	F(1)-Li(1)-O(5)#5	91.8(2)
Li(1)-O(5)	2.194(6)	O(2)#6-Li(1)-O(5)#5	140.9(2)
Li(1)-O(5)#5	2.194(6)	O(2)#7-Li(1)-O(5)#5	103.06(12)
Li(2)-F(1)	1.869(6)	O(3)-Li(1)-O(5)#5	66.07(18)
Li(2)-O(4)#1	1.966(3)	O(5)-Li(1)-O(5)#5	38.1(2)
Li(2)-O(4)	1.966(3)	F(1)-Li(2)-O(4)#1	114.05(18)
Li(2)-O(4)#10	1.999(6)	F(1)-Li(2)-O(4)	114.05(18)
Li(2)-O(5)#5	2.506(6)	O(4)#1-Li(2)-O(4)	123.8(3)
Li(2)-O(5)	2.506(6)	F(1)-Li(2)-O(4)#10	98.7(3)
Li(3)-O(4)#1	1.983(6)	O(4)#1-Li(2)-O(4)#10	99.9(2)
Li(3)-F(1)#11	1.989(6)	O(4)-Li(2)-O(4)#10	99.9(2)
Li(3)-O(2)#1	2.148(6)	F(1)-Li(2)-O(5)#5	85.0(2)
B(1)-O(1)	1.338(4)	O(4)#1-Li(2)-O(5)#5	63.82(17)
B(1)-O(3)	1.343(4)	O(4)-Li(2)-O(5)#5	93.6(2)
B(1)-O(5)	1.508(4)	O(4)#10-Li(2)-O(5)#5	163.05(9)
B(1)-O(5)#5	1.509(4)	F(1)-Li(2)-O(5)	85.0(2)
B(2)-O(2)	1.376(4)	O(4)#1-Li(2)-O(5)	93.6(2)
B(2)-O(4)	1.403(5)	O(4)-Li(2)-O(5)	63.83(17)
B(2)-O(5)	1.430(5)	O(4)#10-Li(2)-O(5)	163.05(9)
B(2)-O(5)#14	1.900(5)	O(5)#5-Li(2)-O(5)	33.21(16)
O(5)-O(5)#5	1.432(7)	F(1)#2-Li(3)-F(1)#3	132.4(3)
O(1)#1-Ca(1)-O(1)	95.95(8)	F(1)#2-Li(3)-O(4)#1	113.46(16)
O(1)#1-Ca(1)-O(3)#2	83.06(5)	F(1)#3-Li(3)-O(4)#1	113.46(16)
O(1)-Ca(1)-O(3)#2	166.60(7)	F(1)#2-Li(3)-F(1)#11	91.73(19)
O(1)#1-Ca(1)-O(3)#3	166.59(7)	F(1)#3-Li(3)-F(1)#11	91.73(19)
O(1)-Ca(1)-O(3)#3	83.06(5)	O(4)#1-Li(3)-F(1)#11	95.4(3)
O(3)#2-Ca(1)-O(3)#3	94.80(7)	F(1)#2-Li(3)-O(2)#1	94.07(19)
O(1)#1-Ca(1)-O(2)#1	83.79(6)	F(1)#3-Li(3)-O(2)#1	94.07(19)
O(1)-Ca(1)-O(2)#1	83.79(6)	O(4)#1-Li(3)-O(2)#1	70.2(2)
O(3)#2-Ca(1)-O(2)#1	82.81(6)	F(1)#11-Li(3)-O(2)#1	165.6(3)
O(3)#3-Ca(1)-O(2)#1	82.81(6)	O(1)-B(1)-O(3)	125.5(3)
O(1)#1-Ca(1)-O(1)#4	110.80(4)	O(1)-B(1)-O(5)	117.6(3)
O(1)-Ca(1)-O(1)#4	110.80(4)	O(3)-B(1)-O(5)	109.9(3)

O(3)#2-Ca(1)-O(1)#4	81.85(6)	O(1)-B(1)-O(5)#5	117.6(3)
O(3)#3-Ca(1)-O(1)#4	81.85(6)	O(3)-B(1)-O(5)#5	109.9(3)
O(2)#1-Ca(1)-O(1)#4	157.27(7)	O(5)-B(1)-O(5)#5	56.7(3)
O(1)#1-Ca(1)-O(3)#4	75.05(5)	O(2)-B(2)-O(4)	117.8(3)
O(1)-Ca(1)-O(3)#4	75.05(5)	O(2)-B(2)-O(5)	125.4(3)
O(3)#2-Ca(1)-O(3)#4	117.28(4)	O(4)-B(2)-O(5)	116.4(3)
O(3)#3-Ca(1)-O(3)#4	117.28(4)	O(2)-B(2)-O(5)#14	97.9(3)
O(2)#1-Ca(1)-O(3)#4	148.03(7)	O(4)-B(2)-O(5)#14	92.4(2)
O(1)#4-Ca(1)-O(3)#4	54.70(6)	O(5)-B(2)-O(5)#14	73.9(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z #2 x,y+1,z+1 #3 x,y,z+1#4 -x+1/2,-y+1,z+1/2 #5 x,-y+1/2,z #6 x,y,z-1 #7 x,y+1,z-1 #8 x,-y+1/2,z-1 #9 x,y-1,z-1 #10 -x,-y,-z+1 #11 -x,-y+1,-z+1 #12 -x,-y+1,-z+2 #13 -x,-y+2,-z+2 #14 x,-y-1/2,z #15 -x+1/2,-y+1,z-1/2 #16 x,y-1,z #17 x,y-1,z+1

Table S4. Comparation of ionic conductivity on Li^+-based fluoroborates.

Compounds	Ionic conductivity ($S \cdot cm^{-1}$)
LiB_6O_9F	6.6×10^{-9} (673 K)
$Li_2B_6O_9F_2$	2.2×10^{-10} (473 K) 1.3×10^{-8} (573 K)
$Li_2B_3O_4F_3$	1.6×10^{-9} (473 K) 1.8×10^{-8} (523 K)
$Li_3CaB_2O_5F$	2.56×10^{-7} (298K)

Figure S1. The UV-Vis-NIR absorption spectrum of $Li_3CaB_2O_5F$.

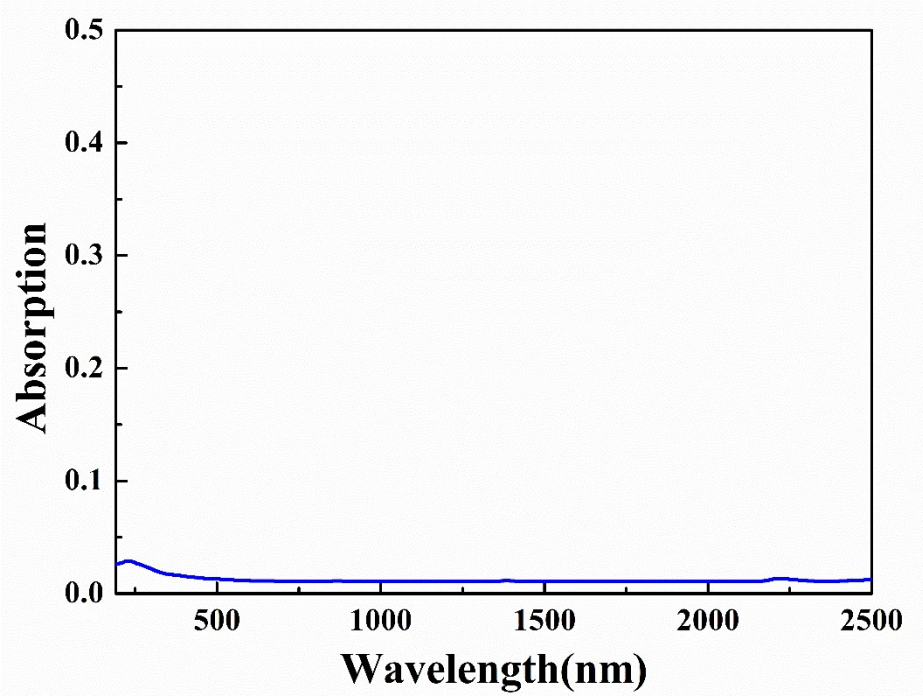

Figure S2. The Nernst curve of $Li_3CaB_2O_5F$.