Supporting Information

Li₃CaB₂O₅F: A unique sandwich-like structure with Diverse and Wide Li-ions Diffusion Pathways

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Experimental Section

Reagents
LiF (Tianjin Fuchen Chemical Reagents Factory, 98.5%), Li$_2$CO$_3$ (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$_3$BO$_3$ (Aladdin Chemical Industry Co., Ltd., 99.5%) and NH$_4$H$_2$PO$_4$ (Tianjin Fuchen Chemical Reagents Factory, 99%) are used as received.

Syntheses
Single crystals of Li$_3$CaB$_2$O$_5$F 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$_3$BO$_3$ (0.0024 mol, 0.1496 g) and NH$_4$H$_2$PO$_4$ (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$_3$CaB$_2$O$_5$F were obtained.

Polycrystalline samples of Li$_3$CaB$_2$O$_5$F 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$_3$CaB$_2$O$_5$F were measured by the SmartLab9KW X-ray diffractometer (Cu K$_\alpha$ radiation) at room temperature, and collecting the data under the same conditions that the angular range in the 2$\theta$ 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$_3$CaB$_2$O$_5$F was collected on a Bruker SMART APEX II 4K CCD diffractometer with Mo K$_\alpha$ radiation ($\lambda = 0.71073$ 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 Diffuse Reflectance Spectroscopy
The UV-Vis-NIR diffuse reflectance spectrum of Li$_3$CaB$_2$O$_5$F 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$_3$CaB$_2$O$_5$F was measured by using a Shimadzu IR Affinity spectrometer in the range of 500–4000 cm$^{-1}$ at room temperature.

Thermal Stability Measurement
Differential 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$_3$CaB$_2$O$_5$F. At each point on a 3D grid (120 × 120 × 150) within the unit cell, the absolute value of the difference ($|\Delta V|$) 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$_3$CaB$_2$O$_5$F was used an instruments electrochemical workstation, CHI 660E. A pressed tablet of the powder sample for Li$_3$CaB$_2$O$_5$F 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)
\[
D=R^2T^2/2A^2n^4F^4C^2\sigma^2 \quad (1)
\]
\[
Z'=R_s+R_{ct}+\sigma\omega^{1/2} \quad (2)
\]
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, \(\sigma\) 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 \(\omega\) is angle frequency.
References


Table S1. Crystal data and structure refinement for Li$_3$CaB$_2$O$_5$F.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<td>Empirical formula</td>
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<td>Crystal system</td>
<td>Orthorhombic</td>
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<td>Space group</td>
<td>Pnma</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td>$b$ = 3.4697(3) Å</td>
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</tr>
<tr>
<td>$c$ = 5.4404(4) Å</td>
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<tr>
<td>Z, Volume/Å$^3$</td>
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<td>Density/g·cm$^{-3}$</td>
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<td>Absorption coefficient/mm$^{-1}$</td>
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<tr>
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<td>GOF on $F^2$</td>
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<td>Final $R$ indices [$F_o^2 &gt; 2s(F_o^2)$][a]</td>
<td>$R_1 = 0.0302$, $wR_2 = 0.1009$</td>
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<tr>
<td>$R$ indices (all data)</td>
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</tbody>
</table>

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ 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 $\text{Li}_3\text{CaB}_2\text{O}_5\text{F}$. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
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<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
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<td>Symmetry transformations used to generate equivalent atoms:</td>
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<td>------------------------------------------------------------</td>
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</tr>
<tr>
<td>#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/z+2 #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</td>
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<tr>
<td>Compounds</td>
<td>Ionic conductivity (S·cm(^{-1}))</td>
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<tr>
<td>LiB(_6)O(_9)F</td>
<td>6.6 \times 10^{-9} (673 K)</td>
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<td>Li(_2)B(_6)O(_9)F(_2)</td>
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<td></td>
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<td></td>
<td>1.3 \times 10^{-8} (573 K)</td>
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<tr>
<td>Li(_2)B(_3)O(_4)F(_3)</td>
<td>1.6 \times 10^{-9} (473 K)</td>
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<td>1.8 \times 10^{-8} (523 K)</td>
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<tr>
<td>Li(_3)CaB(_2)O(_5)F</td>
<td>2.56 \times 10^{-7} (298K)</td>
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**Table S4.** Comparison of ionic conductivity on Li\(^+\)-based fluoroborates.
**Figure S1.** The UV-Vis-NIR absorption spectrum of Li$_3$CaB$_2$O$_5$F.
Figure S2. The Nernst curve of $\text{Li}_3\text{CaB}_2\text{O}_5\text{F}$. 