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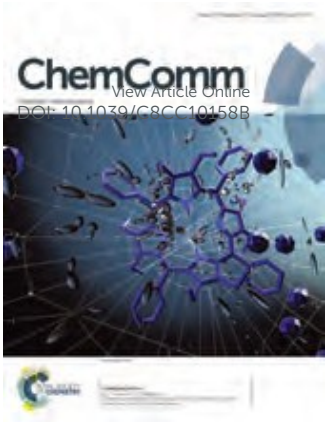

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COMMUNICATION

A Lithium Difluorophosphate $LiPO_2F_2$ with a Neutral Polytetrahedral Microporous Architecture

Guopeng Han,[a,b,†] Ying Wang,[a,†] Hao Li,[a,b] Zhihua Yang,[a] and Shilie Pan*[a]

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We present herein the first lithium difluorophosphate $LiPO_2F_2$ exhibiting a unique polytetrahedral microporous architecture. The unique fluorine coordination environments and interlaced $[LiO_2]^{3-}$ straight chains give rise to the neutral pore framework with 10-membered ring channel along the crystallographic *c* axis. A variety of measurements have been adopted to systemically characterize $LiPO_2F_2$. This work will contribute to the structural and functional diversity of phosphate chemistry by the exploration of the fascinating difluorophosphates.

The immensely widespread application of phosphates is dependent on the very large number of different phosphate phases and the diverse structures.[1] Among the variety of phosphates investigated in recent years, the fluorine-containing phosphates have aroused particular interest in inorganic chemistry not only because of the novelty in their structures, but also owing to their various and pretty useful properties, such as electrolyte for ion batteries, stabilizers for chloroethylene polymers, catalysts for reactive lubricants, antibacterial used in dentifrice formulations, and timber preservatives.[2] As a prominent presentative, Na_2PO_3F is a well-known fluorophosphate commonly used in toothpaste.[3]

Fluorophosphates, in which the fluorine atoms covalently connect with the phosphorus atoms, show additional compositional and structural diversity compared to orthophosphates. Very recently, it was proposed that the oxyfluoride $[BO_xF_{4-x}]$ and $[PO_xF_{4-x}]$ (1< x<4) species are superior material genomes to obtain excellent optical properties.[4] These oxyfluoride species with large polarizability anisotropies, wide HOMO−LUMO gaps, and high hyperpolarizabilities are beneficial for the deep-ultraviolet optical properties of borates or phosphates.

In particular, the difluorophosphate radical PO_2F_2 is preferred for deep-ultraviolet optical materials compared to other oxyfluoride tetrahedra. It is shown that difluorophosphates exhibit larger birefringence and band gaps than monofluorophosphates and orthophosphates.[4d] Besides, difluorophosphates were also studied as promising electrolyte salt or as electrolyte salt additive for Li/Na ion batteries.[5] Therefore, difluorophosphates are one of the most fascinating system for searching new functional materials. However, the crystal growth of difluorophosphates with high quality single crystal is difficult because of their rigorous growth conditions and relatively poor thermal stability. As yet, only four alkali / alkaline earth / ammonium difluorophosphates with single crystal diffraction data have been reported, *i.e.* KPO_2F_2,[6] $RbPO_2F_2$,[7] $CsPO_2F_2$,[8] and $NH_4PO_2F_2$.[9] In this contribution, we present the first lithium difluorophosphate $LiPO_2F_2$ exhibiting a unique microporous architecture and improved optical properties. The colourless block-shaped crystals with centimeter-size were obtained (Figure S1, ESI).

The $LiPO_2F_2$ crystals were prepared by hydrothermal method using LiF, P_2O_5, and HPF_6 as the raw materials. The crystal structure of $LiPO_2F_2$ was well-defined on the basis of single crystal diffraction data. The purity of the prepared sample was checked by powder X-ray diffraction (XRD) technique, which is consistent with the theoretical pattern from the single-crystal diffraction data (Figure S3, ESI). Details of the crystallographic data and structural refinements are provided in Table S1 in the ESI. The existence of fluorine and the P−F bonds was confirmed by elemental analysis (Figure S4, ESI), and IR spectroscopy, and the sites of F and O atoms were reasonably assigned by the bond valence sums (BVS) calculation.[10]

$LiPO_2F_2$ crystallizes in the monoclinic space group *C*2/*c*. There are twelve crystallographically different atoms in the asymmetric unit, including two Li atoms, two P atoms, four O atoms, and four F atoms (Figure S5, ESI). The Li and P atoms are all in tetrahedral coordination environments with O or F forming the LiO_4 and PO_2F_2 species, respectively. All O atoms are three-coordinated with two adjacent Li atoms and one adjacent P atom, and the F atoms are terminally bonded to one P atom. The PO_2F_2 tetrahedra are isolated from each

[a] G. Han, Dr. Y. Wang, H. Li, Prof. Z. Yang, Prof. S. Pan, CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China. Email: slpan@ms.xjb.ac.cn
[b] G. Han and H. Li. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
† These authors contributed equally to this work.

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other, while each LiO_4 tetrahedra are edge-shared with two adjacent LiO_4 tetrahedra forming infinite one-dimensional (1D) straight chains $[LiO_2]^{3-}$. The PO_2F_2 anion shows a distorted tetrahedral geometry with P-O bond lengths varying between 1.462(2) and 1.469(2) Å and P-F bond lengths ranging from 1.497(3) to 1.515(2) Å. The bond angle ranges of O-P-O, F–P–O, F–P–F in PO_2F_2 are 118.95(15)-121.67(18)°, 108.31(15)-109.67(15)°, and 99.2(3)-100.4(2)°, respectively. Since the PO_2F_2 units are isolated, the distortion of the bond angles from ideal tetrahedral value could be explained in terms of the valence-shell electron repulsion theory.[11] The LiO_4 units have these interatomic dimensions: Li–O bond lengths 1.910(5)-1.973(5) Å and O–Li–O bond angles 91.1(2)- 131.6(3)°. The significant deviations from the ideal tetrahedral angle are mainly caused by two bridging O atoms among the Li atoms.

It is interesting to note that $LiPO_2F_2$ exhibits infinite $[LiO_2]^{3-}$ straight chains in two different directions (Figures 1c, 1d), which is the first example in all fluorophosphates. The two types of $[LiO_2]^{3-}$ chains stack alternately along the crystallographic *c* axis, which are further polymerized with the PO_2F_2 tetrahedra by corner-sharing common O atoms forming a 3D microporous framework. The unique 3D framework affords a 10-membered ring channel along the [001] direction (Figure 1e). Topologically, the LiO_4 and PO_2F_2 tetrahedra could be regarded as 6-connected and 4-connected nodes, respectively. Thus, the $LiPO_2F_2$ architecture could therefore be reduced to a topological 4,4,4,6,6-c 5-nodal net with a point symbol of $\{3^2.4.5^2.6\}\{3^2.5.6^2.7\}\{3^4.4^2.5^2.6^3.7^3.8\}$ $\{3^4.4^3.5^4.6^4\}$ (Figure 2).

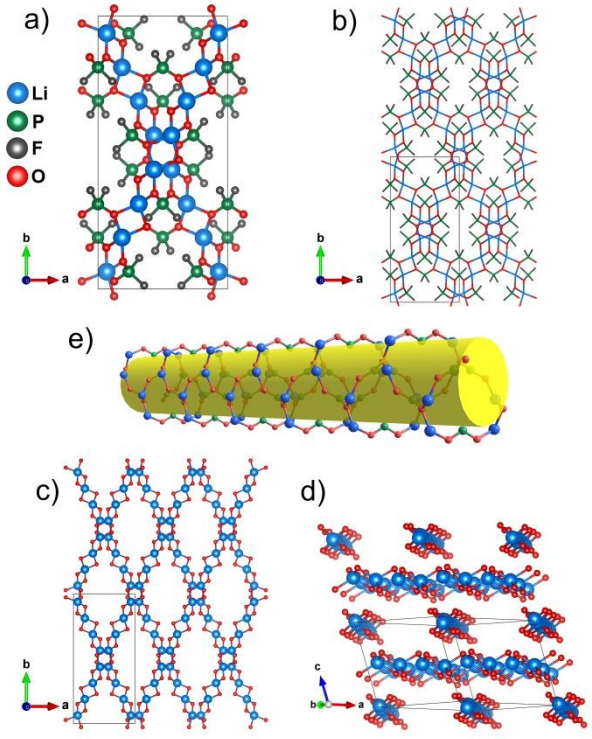

Figure 1. a) Projection of the $LiPO_2F_2$ structure and b) microporous architecture on the *ab* plane. Figures 1c and 1d present the interlaced $[LiO_2]^{3-}$ chains viewing along [001] and its perpendicular direction, respectively. e) The 10-membered ring channel along the [001] direction. The unit cells are indicated by the black boxes.

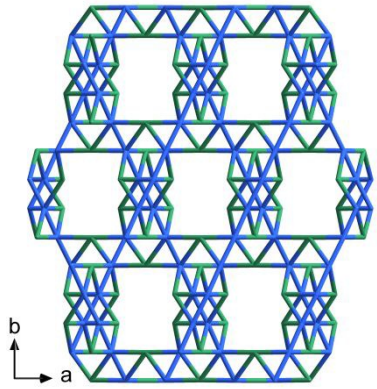

Figure 2. The topological structure of $LiPO_2F_2$.

There are two key factors affecting the formation of the unique microporous architectures. Firstly, fluorine plays an important role. Different from bridging O atoms, all F atoms in $LiPO_2F_2$ are terminally bonded to the P atom, which cut off the dense 3D -O-Li/P-O- framework and create a pore framework, and the F atoms are located at the inner surface of the channels. Secondly, the interlaced $[LiO_2]^{3-}$ chains are another important factor to support the basic microporous architecture of $LiPO_2F_2$ (Figures 1c and 1d). The ammonium, potassium, rubidium, and cesium difluorophosphates are isomorphous (Orthorhombic, *Pnma*) with the barium sulphate structure type, and they do not share any structural similarity with $LiPO_2F_2$. The cations certainly influence the backbone geometry of the structures mentioned above.[12] Besides, although the ClO_4 and SO_3F ions are isoelectronic with PO_2F_2, the structures of $LiClO_4$[13] and $LiSO_3F$[14] are also very different from that of $LiPO_2F_2$ (Figures S6, S7, ESI).

The microporous architecture of $LiPO_2F_2$ share similar features with zeolite aluminophosphates - one of the most widely known molecular sieves.[15] They are all neutral polytetrahedral frameworks, which usually exhibit less affinity for H_2O than the anionic zeolite frameworks caused by the absence of the dipole interaction between the electrostatic fields of the anionic framework and the extra-framework cations. Owing to the novel structure of $LiPO_2F_2$, some interesting properties, such as ionic conductivities, adsorptive and catalytic applications could be foreseen. For block $LiPO_2F_2$ crystal, a specific surface area of 38.6 m^2g^{-1} has been determined by N_2 adsorption/desorption experiments. Typical isotherms and pore size distribution are shown in Figure S8 in the ESI. It is worth mentioning that the Brunauer – Emmett – Teller (BET) surface area of $LiPO_2F_2$ is much larger than that of $K_3B_6O_{10}Br$ nanoparticles (0.05 m^2g^{-1}) and comparable to that of P25 TiO_2 (58 m^2g^{-1}).[16]

Owing to the characteristic vibration bands in terms of intensity and frequency, the coordination geometry of phosphorus can be detected by IR spectrum. Figure 3 represents the calculated and experimental bands of $LiPO_2F_2$, which are roughly consistent with each other. The strong vibration bands between 1400-800 cm^{-1} mainly originate from stretching modes of tetrahedrally surrounded phosphorus (PO_2F_2). More narrowly, the bands observed at 1273,

1163 cm^{-1} are designated as the asymmetric and symmetric stretching of P-O bonds, respectively. The bands at 934, 887 cm^{-1} are assigned to the asymmetric and symmetric stretching of P-F bonds, respectively. It is interesting to note that the title compound also shows the strong vibration bands in the lower frequency region (700-400 cm^{-1}), which are predominant due to the bending and rocking modes of PO_2F_2 groups and stretching vibrations modes of LiO_4 groups. In fact, the overall spectrum of $LiPO_2F_2$ agrees favourably with the spectra of other metal difluorophosphates.[17] Therefore, these results further confirm the rationality of X-ray single crystal structural analysis.

The thermal behaviour of $LiPO_2F_2$ was examined by thermal gravimetric (TG) and differential scanning calorimetry (DSC) technique. The result indicates that the stability of $LiPO_2F_2$ is below 350 °C. As shown in Figure 4a, a slow weight loss process could be observed on the TG curve between RT to 350 °C, which is probably caused by the hygroscopy of as-synthesized powder sample and release of H_2O thereof. From powder XRD patterns of $LiPO_2F_2$ at different temperature (Figure 4b), we may safely draw the conclusion that the peak observed around 381 °C on the DSC curve is an endothermic decomposition peak. The TG curve shows that the weight loss undergoes two steps in the range of 350−500 °C, resulting in a total weight loss of about 46%, which is attributed to the decomposition of $LiPO_2F_2$. The first step points to the loss POF_3(g) and the residual products are mainly lithium metaphosphate $LiPO_3$(s) and LiF(s). The second step points again to the loss POF_3(g) and the residual products are $Li_4P_2O_7$(s) and LiF(s). The XRD patterns at 500 and 600 °C consist of $Li_4P_2O_7$(s) and Li_3PO_4(s), respectively. Since the meta- and pyrophosphates show far higher thermal stabilities, the sequence of formation of $LiPO_3$, $Li_4P_2O_7$, and Li_3PO_4 with rising temperature is not just thermal release of P_4O_{10}(g) in this temperature range.[18] Thus, additional support for the very stable gaseous molecule POF_3 is provided. Thermal decompositions of $LiPO_2F_2$ are analysed in detail in the ESI.

Additionally, we investigated the electronic structures of $LiPO_2F_2$ based on the density functional theory (DFT) (Figures S11 and S12, ESI).[19] The title compound has an indirect band gap of 7.69 eV (HSE06) using the PWmat code,[20] which is one of the largest in alkali and alkaline earth metal fluorophosphates according to our previous work.[4d] The ultraviolet−visible-near-infrared transmittance spectrum shows a cut-off edge less than 180 nm (Figure S13, ESI), which further demonstrates that $LiPO_2F_2$ has a wide ultraviolet transmittance window comparable to recently reported oxyfluoride deep-ultraviolet optical crystals, such as LiB_6O_9F,[21] $Li_2B_6O_9F_2$,[4a, 22] $NH_4B_4O_6F$,[4c] γ-Be_2BO_3F,[23] $BaB_4O_6F_2$,[24] PbB_5O_8F,[25] $(NH_4)_2PO_3F$,[4d] and $K_4Si_3P_2O_7F_{12}$.[26] The projected densities of states reveal that the valence band (VB) maximum is dominated by O-2p orbital, while the conduction band (CB) is formed primarily by the hybridization orbitals of P, O, Li atoms. Namely, the states on both sides of the band gap are mainly composed of the orbitals from P/Li –O bonds in $LiPO_2F_2$. The F-2p orbital in $LiPO_2F_2$ exhibits quite large hybridization with the orbitals on the neighbour ions, which decreases the energy bandwidth of the VB and enlarges the band gap of $LiPO_2F_2$. Therefore, the absorption edge of fluorophosphates, especially for

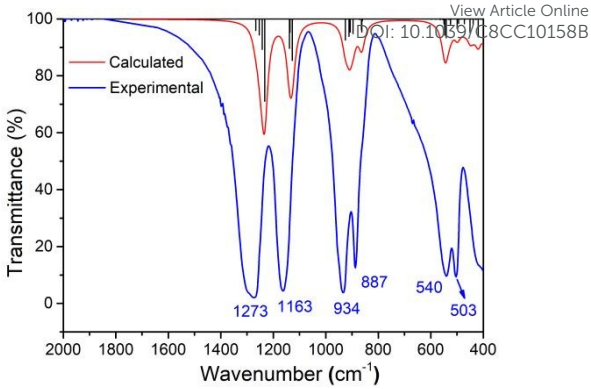

Figure 3. The spectra of as-synthesized $LiPO_2F_2$. The red curve and black bars denote band positions calculated by DFT.[19]

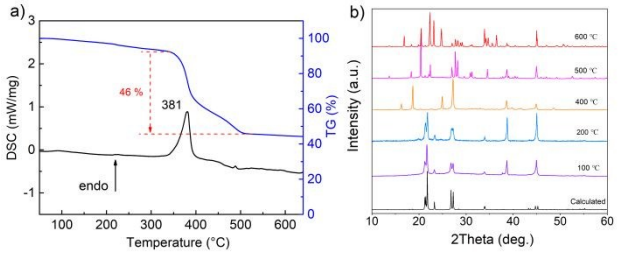

Figure 4. a) The TG-DSC curves of as-synthesized samples. The TG curve (blue solid line) shows two steps weight loss process in the temperature range of 350−500 °C. From the DSC curve (black solid line), a remarkable endothermic peak is observed at about 381 °C during the heating process. b) Powder XRD patterns of $LiPO_2F_2$: calculated one, annealed at 100, 200, 400, 500 and 600 °C for 10 h, respectively. $LiPO_2F_2$ decomposes at 381 C, and the residual products are mainly $LiPO_3$ (PDF# 26-1177) and LiF (PDF# 04-0857) at 400 °C, $Li_4P_2O_7$ (PDF# 13-0440) and LiF (PDF# 04-0857) at 500 °C, and Li_3PO_4 (PDF# 15-0760) and $Li_4P_2O_7$ (PDF# 13-0440) at 600 °C.

difluorophosphates, is blue-shifted compared with those of orthophosphates, which was also confirmed by the DFT calculations.[4d] In addition, all O atoms in $LiPO_2F_2$ bridge three neighbouring P/Li atoms, which is beneficial for large band gap of $LiPO_2F_2$. In addition, the calculated birefringence for $LiPO_2F_2$ is about 0.013 @1064 nm (Figure S14, ESI), which is smaller than those of other alkali metal difluorophosphates but larger than alkali or alkaline earth metal orthophosphates. From the insight of structure–property relationships, partial substitution of oxygen by fluorine in the PO_4 group results in the obvious anisotropy in both LUMO and HOMO. Therefore, the oxyfluoride PO_2F_2 groups have larger optical anisotropy than the PO_4 groups, as a result, difluorophosphates are more likely to produce larger birefringence than orthophosphates.

In summary, the first lithium difluorophosphate $LiPO_2F_2$ was synthesized under hydrothermal conditions and characterized by single-crystal XRD analysis, elemental analysis, IR spectra, and TG-DSC analysis. The structure is built up by isolated PO_2F_2 tetrahedra and interlaced 1D $[LiO_2]^{3-}$ straight chains forming a microporous 3D architecture. In addition, optical characterizations and theoretical analysis indicate that $LiPO_2F_2$ has a wide deep-ultraviolet transmittance window and large birefringence in comparison with orthophosphates owing to the unique oxyfluoride PO_2F_2 species. The BET(N_2) surface area of $LiPO_2F_2$ crystals are comparable to that of P25 TiO_2 nanoparticles, a commercial catalyst under ultraviolet light

irradiation. Considering the obvious advantages, we believe that difluorophosphates will provide an innovative avenue to get new materials with excellent functional properties in future.

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Conflicts of interest

There are no conflicts to declare.

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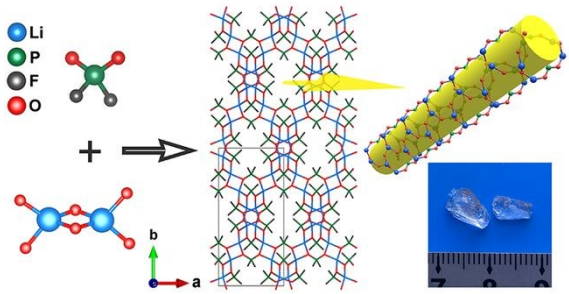

The first lithium difluorophosphate $LiPO_2F_2$ with a unique microporous architecture and improved optical properties was synthesized and characterized.