PbFePO4F2 with a 1/6th bond depleted Triangular Lattice

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We hydrothermally synthesized a layered PbFePO$_4$F$_2$ (P2$_1$/n). Fe$^{3+}$ cations ($S = 5/2$) within the layer are connected via F$^-$ and (PO$_4$)$^{3-}$ anions to give a novel (distorted) 1/6th bond depleted triangular lattice. The $\chi(T)$ suggests strong antiferromagnetic interactions with Weiss constant of $-125$ K, but geometrical frustration and low dimensionality appears to prohibit a long-range order down to 23 K.

Mixed-anion compounds have been a topic of extensive research owing to novel functional properties, including non-toxic pigments (e.g. LaTaO$_5$)$_2$, visible-light-responsive photocatalysts (e.g. Bi$_3$NbO$_8$Cl), nonlinear optical materials (e.g. Cs$_6$PO$_3$N$_2$NbOF$_4$), and electrodes (e.g. AgNa(VO$_2$F$_2$)$_2$). Inclusion of anion-groups (polyanion) such as (BO$_3$)$_3^-$, (CO$_3$)$_2^-$ and (PO$_4$)$_3^-$ further enriches chemical bonds and thus available functionalities. Fluorides combined with anion groups are particularly promising as nonlinear optical materials because of the ability of the fluorine ion to blue-shift the absorption edge, such as KBe$_2$BO$_3$F$_2$ and NH$_4$B$_4$O$_6$F$_7$ with (BO$_3$)$_3^-$ and (PO$_4$)$_3^-$ further enriches chemical bonds and thus available functionalities. Fluorides combined with anion groups are particularly promising as nonlinear optical materials because of the ability of the fluorine ion to blue-shift the absorption edge, such as KBe$_2$BO$_3$F$_2$ and NH$_4$B$_4$O$_6$F$_7$ with (BO$_3$)$_3^-$ and (PO$_4$)$_3^-$ further enriches chemical bonds and thus available functionalities.

Geometrically frustrated spin systems are known to exhibit exotic phenomena such as successive phase transitions, non-trivial spin textures and spin liquid state. The triangular lattice (Figure 1a) is an archetypal system that has been examined since the earliest days of research in frustrated magnetism. Later, the attention has shifted to kagomé lattice (Figure 1b), a 1/4th site depleted triangular lattice ($d = 1/4$) since the reduced coordination number of $z = 4$ (vs. 6) could enhance quantum fluctuations. The honeycomb lattice with a 1/3th site depletion ($d = 1/3$, $z = 3$), shown in Figure 1c, can be frustrated when the next-nearest-neighbour is added, and also represents the exactly solvable Kitaev model. Although much less investigated, other site depleted triangular lattice derivatives are reported, such as 1/4th and 1/6th site depleted triangular lattices (Figure 1d and e) in K$_3$Mn$_2$(VO$_4$)$_2$(OH)$_2$ and Mn$_5$(VO$_4$)$_2$(OH)$_6$ and a maple-leaf lattice (Figure 1f) in MgMn$_3$O$_3$3H$_2$O. Besides site depletion, bond depletion could also obtain triangular lattice derivatives, such as cube tile lattice with 1/3th bond depletion (Figure 1g) as found in CsFe$_2$(SeO$_3$)$_2$F$_6$.

When one alternately removes bonds along one direction, one obtains a lattice with $d = 0$ and $z = 6$, which we call hereafter a 1/6th bond depleted triangular lattice (Figure 1h). In this study, we have hydrothermally synthesized an iron phosphate fluoride containing (PO$_4$)$_3^-$ anions, PbFePO$_4$F$_2$. The consideration of exchange pathways suggests that PbFePO$_4$F$_2$ is an experimental realization of the distorted 1/6th bond depleted triangular lattice.

**Fig. 1** Evolutions of triangular lattice: (a) triangular lattice, (b) kagomé lattice, (c) honeycomb lattice, (d) 1/4th site depleted triangular lattice, (e) 1/6th site depleted triangular lattice, (f) maple-leaf lattice, (g) cube tile lattice, (h) 1/6th bond depleted triangular lattice (this work), where $d$ is the number of site depletion from triangular lattice and $z$ is the coordination number.

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depleted triangular lattice. Magnetic measurement indicates a sizable spin frustration and low dimensionality.

(a) 
(b) 

PbFePO$_4$F$_2$ was hydrothermally synthesized by using 0.2 g Pb$_2$O$_3$, 0.1 g FeO, 0.4 mL H$_3$PO$_4$, 0.8 mL 48% aqueous HF (caution!) Experimental details for synthesis and characterization are described in Supporting Information. Single crystal X-ray diffraction has revealed that this compound crystallizes in a layer structure with the space group $P2_1/n$. The PXRD is shown in Figure S1. The unit cell parameters are $a = 5.257(2)$ Å, $b = 12.404(5)$ Å, $c = 7.098(3)$ Å and $\beta = 102.8(1)^\circ$ ($Z = 4$). There are two Fe atoms, one Pb atoms, one P atom, two F atoms, four O atoms in its asymmetric unit. As shown in Figure 2, (FeF$_2$PO$_4$)$_{2-}$ layers, separated by 12-coordinated Pb$^{2+}$ cations, stack along [010] with a distance of 6.202(3) Å (half of the b axis). In the FeF$_2$PO$_4$ layer, two iron-centered heteroleptic octahedra, Fe(1)O$_6$F$_4$ and Fe(2)O$_6$F$_4$, are alternately connected through the F$^-$ and (PO$_4$)$^{3-}$ ligands to form the doubly-bridged Fe(1)–F(1)/PO$_4$–Fe(2) chains along [001] (Figure 2b). This provides the shortest Fe–Fe distance of 3.5490(15) Å. These chains are linked by the (PO$_4$)$^{3-}$ groups within the ab plane. The Fe(1)O$_6$F$_4$ octahedron has fluorine anions at the equatorial sites ($d_{Fe(1)-F(1)} = 1.941(5)$ Å $\times$ 2 and $d_{Fe(1)-F(2)} = 1.933(5)$ Å $\times$ 2) and oxide anions at the apical site ($d_{Fe(1)-O(3)} = 1.985(5)$ Å $\times$ 2). The Fe(2)O$_6$F$_4$ octahedron has equatorial O$^-$ anions ($d_{Fe(2)-O(2)} = 1.978(5)$ Å $\times$ 2, $d_{Fe(2)-O(4)} = 2.074(5)$ Å $\times$ 2) and apical F$^-$ anions ($d_{Fe(2)-O(1)} = 2.012(5)$ Å $\times$ 2). The P–O bond length in the PO$_4$ group ranges from 1.518 Å to 1.552 Å, which agree with those reported.39 Other bond lengths and angles are summarized in Table S2. The oxidation states of +3 in iron (calculated values: 3.03 for Fe(1) and 2.76 for Fe(2)), +5 in phosphorus (calculated value: 4.83) are confirmed by bond valence sum (BVS) calculations using values reported by Brese and O’Keefe (see Table S2).7 Upon heating, a powder sample starts to decompose around 200 °C (Figure S3) and the final product after TGA is identified as Pb$_3$O$_4$FeO$_2$ and hematite Fe$_2$O$_3$ (Figure S1). The weight loss of 6.2% is in good agreement with the calculated loss of 5.6%.

The temperature dependence of the magnetic susceptibility measured at 0.1 T is shown in Figure 3a. A Curie-Weiss fitting was conducted in a high temperature range between 150 K and 350 K, giving an effective magnetic moment of $\mu_{eff} = 5.96(1)$ $\mu_B$ and a Weiss constant $\theta = -125.6(6)$ K. The $\mu_{eff}$ value is fairly consistent with the theoretical value of 5.92 $\mu_B$ for $S = 5/2$. The value of $\theta$ indicates predominant antiferromagnetic interactions. As the temperature decreases, the magnetic susceptibility shows a kink around 23 K, suggesting the onset of an antiferromagnetic ordering. A slight upturn of $\chi(T)$ below 17 K is ascribed to a small amount of defects, referred as Curie tail,28, 29 a fitting yielded 0.63% of free $S = 5/2$ spins (Figure S4a). When measured at 0.1 T, the inset is magnified $\chi(T)$ around $T_N$. (b) Magnetization $M(H)$ for PbFePO$_4$F$_2$ at 300 K (blue) and 2 K (red).

Let us discuss the magnetic interactions in PbFePO$_4$F$_2$ from the viewpoint of the crystal structure. As mentioned earlier, Fe(1) and Fe(2) are connected via F$^-$ and (PO$_4$)$^{3-}$ anions along [001] (Figure 2b). Given the Fe(1)–F(1)–Fe(2) bridging angle of 127.7°, this pathway would provide, according to Goodenough-Kanamori rule,30, 31 strong antiferromagnetic superexchange interactions $J_1$ (see Figure 4 and S5a). These Fe chains are linked by (PO$_4$)$^{3-}$ groups within the ac plane, giving super-superexchange interactions. Here, Fe(2) cations in the neighboring chains ($d_{Fe(2)-Fe(2)} = 5.257(2)$ Å) are doubly-bridged by two PO$_4$ groups to give $J_2$, while Fe(1) is connected to Fe(2) ($d_{Fe(1)-Fe(2)} = 5.6557(18)$ Å) via a single PO$_4$ group to give $J_1'$ (Figure 4 and S5a). There is no magnetic exchange pathway between two Fe(1) cations despite a similar distance of $d_{Fe(3)-Fe(4)} = 5.257(2)$ Å. The interlayer interactions should be much smaller since the FeF$_2$PO$_4$ layers are separated by Pb cations.

As a result, the magnetism of PbFePO$_4$F$_2$ can be described by a ‘distorted’ 1/6th bond depleted triangular lattice with $J_1$, $J_2$ and $J_1'$, as shown in Figure 4. A degree of frustration is typically estimated using the frustration index $f$, which is defined by $f = |\theta|/T_N$. For PbFePO$_4$F$_2$, $f$ is calculated as $|\theta|/T_N = |-125.6|/23 = 5.5$, suggesting moderate frustration.13, 15, 32. In the absence of further magnetic measurements such as elastic/inelastic neutron scattering as well as DFT calculations, the sign and magnitude of $J_2$ and $J_1'$ remains unclear. However, the magnetic superexchange interaction mediated by PO$_4$ groups could be strong and significantly important, as manifested in VODPO$_4$·0.5D$_2$O$^{33}$ and (VO)$_2$P$_2$O$_7$ by inelastic neutron scattering, electron spin resonance (ESR) and nuclear magnetic
resonance (NMR) measurements. Thus, in PbFePO$_4$F$_2$ $J_2$ and $J_2'$ could be comparable in the magnitude with $J_1$. We believe that the present study will stimulate theoretical investigations of the 1/6th and other bond depleted triangular lattices.

**Conclusions**

An iron phosphate fluoride PbFePO$_4$F$_2$ has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. PbFePO$_4$F$_2$ is an experimental correspondence of a ‘distorted’ 1/6th bond depleted triangular lattice. Despite strong antiferromagnetic interactions with $\theta = -125.6(6)$ K, no long-range order occurred until 23 K possibly due to moderate frustration in this triangular-lattice derivative. Our work shows an illustration that the use of mixed anions or anion-groups is beneficial to explore and discover novel materials with promising lattices and possible exotic physical phenomena.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

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A 1/6th bond depleted triangular lattice has been experimentally realized in the novel compound PbFePO$_4$F$_2$ with moderately strong frustration.