

Supporting Information for

Perovskite-derived structure modulation in the iron sulfate family

Yuanqi Lan^{a,b†}, Qi Yan^{a,c†}, Xinyuan Zhang^d, Wenjiao Yao^{a}, Chenchen Wang^e, Chun-sing Lee^e, Philip Lightfoot^{f*}, Yongbing Tang^{a,b*}*

^a Advanced Energy Storage Technology Research Center, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, 518055, China

^b School of Chemical Science, University of Chinese Academy of Sciences, Beijing 100049, China

^c Nano Science and Technology Institute, University of Science and Technology of China, Suzhou, 215123, China

^d Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystals, Tianjin University of Technology, Tianjin, 300384, China

^e Center of Super - Diamond and Advanced Films and Department of Chemistry, City University of Hong Kong, Hong Kong SAR, 999077, P. R. China

^f School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK

[†]Y.Q. Lan and Q. Yan equally contributed to this work.

* Corresponding authors: wj.yao@siat.ac.cn; pl@st-andrews.ac.cn; tangyb@siat.ac.cn

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Table of Content

1. Experimental Procedures
2. Figure S1. Structural illustration of *I*.
3. Figure S2. Structural illustration of *II*.
4. Table S1. Crystallographic information of crystal *I*, *II* and *III*.
5. Table S2. Atomic parameters of crystal *I*.
6. Table S3. Atomic parameters of crystal *II*.
7. Table S4. Atomic parameters of crystal *III*.
8. Figure S3. Photos of crystallites of *I*, *II* and *III*.
9. Figure S4. Basic characterisation of crystal *I*.
10. Figure S5. Basic characterisation of crystal *I*.
11. Figure S6. Basic characterisation of crystal *I*.
12. Figure S7. Fe environment in *I*, *II*, and *III*.

Experimental Procedures

Materials

Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99.0%, AR), iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99.0%, AR), oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 99.5%, AR), sodium carbonate anhydrate (Na_2CO_3 , 99.8%, GR), sodium perchlorate (NaClO_4 , 99.99%, metal basis), sodium sulfate anhydrate (Na_2SO_4 , AR, 99.0%), sodium metal, and hydrofluoric acid (HF, AR, 40%) were purchased from Shanghai Aladdin Bio-Chem technology Co., Ltd. Sulfuric acid (H_2SO_4 , AR, 98%) was purchased from Dongjiang Reagent. Glass microfiber filter used as separator (Whatman, GF/A, 125 mm), battery-grade propylene carbonate (PC) and 4-fluoro-1,3-dioxolan-2-one fluoroethylene carbonate (FEC) were purchased from Suzhou Dodochem Technology Co., Ltd. Super-P used for conductive reagent and N-methyl-2-pyrrolidone (NMP) were purchased from Guangdong Canrd New Energy Technology Co., Ltd. Aluminium (Al) foil (thickness of 20 μm) and polyvinylidene fluoride (PVDF) binder was purchased from Shenzhen Kejing Star technology company. All reagents were used directly without further treatment.

Synthesis

Single crystals of $\text{Na}_3\text{Fe}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ (*I*) were synthesised by a hydrothermal method. Reactants with ratio of $\text{Na}_2\text{SO}_4:\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 1:1$ (1 for 1 mmol) were dissolved in the mixture of 0.5 mL deionized water and 70 μL H_2SO_4 (~1.3 mmol). The mixture of reactants was transferred into a 25 mL Teflon-lined stainless-steel autoclave, heated to 190 °C and maintained for three days in an oven. The yellow cubic single

crystals were picked out, washed by deionised water and dried at 65 °C for 1 hour. The obtained crystals were stored in a sealed container with dry silica gel.

Single crystals of $\text{Na}_6\text{Fe}(\text{SO}_4)_4$ (**II**) were synthesised by a hydrothermal method. Reactants with ratio of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}:\text{Na}_2\text{SO}_4:\text{FeCl}_2 \cdot 4\text{H}_2\text{O} = 5:4:2$ (1 for 1 mmol) were dissolved in 0.5 mL deionised water. The mixture of reactants was then transferred into a 20 mL Teflon-lined stainless-steel autoclave, heated to 200 °C and maintained for 3 days in an oven. The light yellow rhombic single crystals were picked out, washed by deionised water and dried at 65 °C for 1 hour. The obtained crystals are stable in air.

Single crystals of $\text{Na}_{12}\text{Fe}_3(\text{SO}_4)_6\text{F}_8$ (**III**) were synthesised by a hydrothermal method. 2 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was firstly added into 200 μL HF (~4 mmol) in a fume cupboard. 54 μL H_2SO_4 (~1 mmol) was diluted gently into 0.5 mL deionised water. The two solutions were then mixed and transferred into a 25 mL Teflon-lined stainless-steel autoclave. Finally, 2.4 mmol Na_2CO_3 was added into the obtained mixture, and the release of gas was immediately observed. When no further gas generation was seen, the autoclave was sealed, heated to 170 °C and maintained for 3 days in an oven. The light red granular crystals were picked out, washed by deionised water and dried in 65 °C for 1 hour. The obtained crystals are stable in air for around one week.

Characterization

Structures of the three compounds were solved by single crystal X-ray diffraction (XRD). Diffraction data were collected at room temperature on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda =$

0.71073 Å). The structures were then solved by direct methods and refined using SHELX-2014 incorporated in the WinGX program. Powder XRD patterns of hand-milled crystallites were recorded in a SmartLab Rigaku diffractometer, which was operated at 40 kV and 50 mA with Cu K α radiation ($\lambda = 1.54056$ Å) in the 2θ range of 10°-90°. The Fourier transform infrared (FTIR) spectrum was recorded at room temperature by a Bruker INVENIO S FTIR spectrometer. The Raman spectrum was collected by a Horiba XploRA plus Raman microscope.

Electrochemical measurement

The Na₃Fe(SO₄)₃·H₂O composite cathodes were made of active material, Super-P, and PVDF at the weight ratio of 6:3:1. Na₃Fe(SO₄)₃·H₂O from hydrothermal reactions was firstly ground by hand. The obtained powder was mixed with Super-P by ball milling for four hours, and then hand-ground with PVDF for 30 minutes. The whole mixture was ground with some NMP as dispersant to form a uniform slurry and coated on Al foil with a mass loading of approximately 1.5 mg cm⁻² active material and dried at 80 °C in vacuum overnight. The dried foil was cut into disk electrodes with a diameter of 10 mm. 1 M NaClO₄ in solution of PC and FEC (V_(PC):V_(FEC)=7:3) sodium foil with a diameter of 12 mm, and glass microfiber filter with a diameter of 16 mm was applied as electrolyte, counter electrode, and separator, respectively. CR2032 coin cells used for electrochemical test were assembled in an Ar-filled glovebox (MIKROUNA universal 2440-750) with water and oxygen contents ≤ 0.1 ppm. Cyclic voltammetry was performed on an AUTOLAB M204 electrochemical workstation. Galvanostatic

charge-discharge tests were conducted on a battery test system (NEWARE CT-4008).

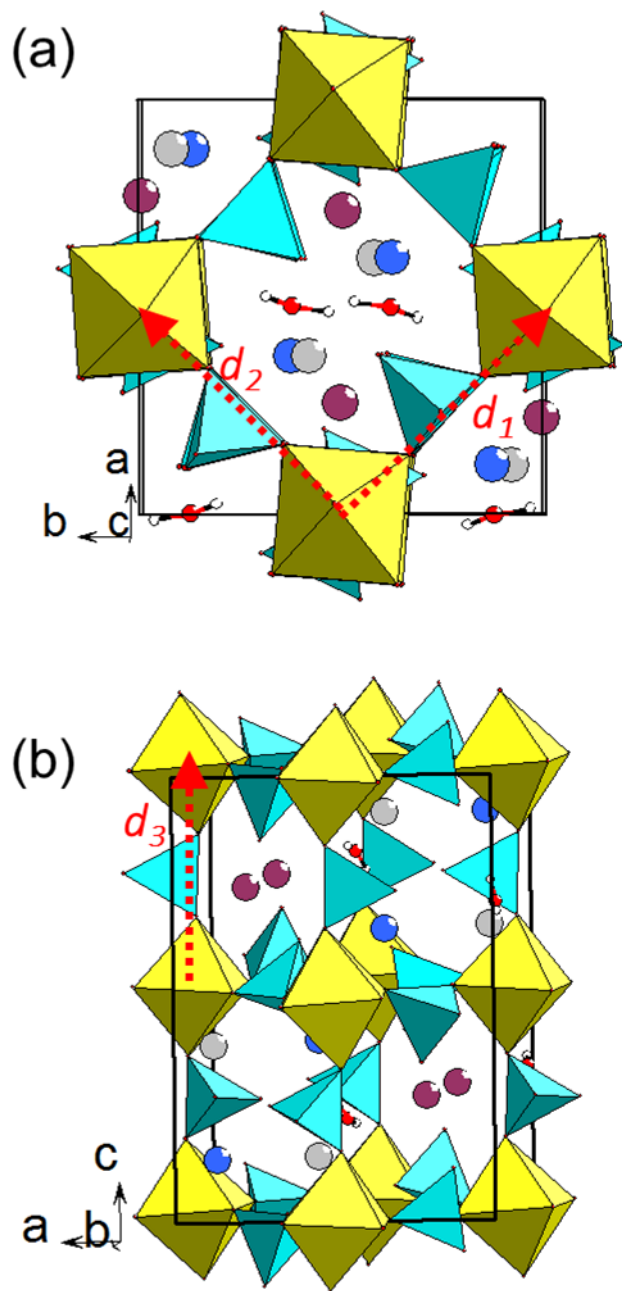


Figure S1. Structure of *I*. Unit cell projected (a) along the *c*-axis. (b) along the *b*-axis. FeO₆ octahedra yellow, SO₄ tetrahedra light blue. The three distinct extra framework Na⁺ sites are shown in different colours. The directions of *d*₁, *d*₂ and *d*₃ are indicated by red dotted arrows.

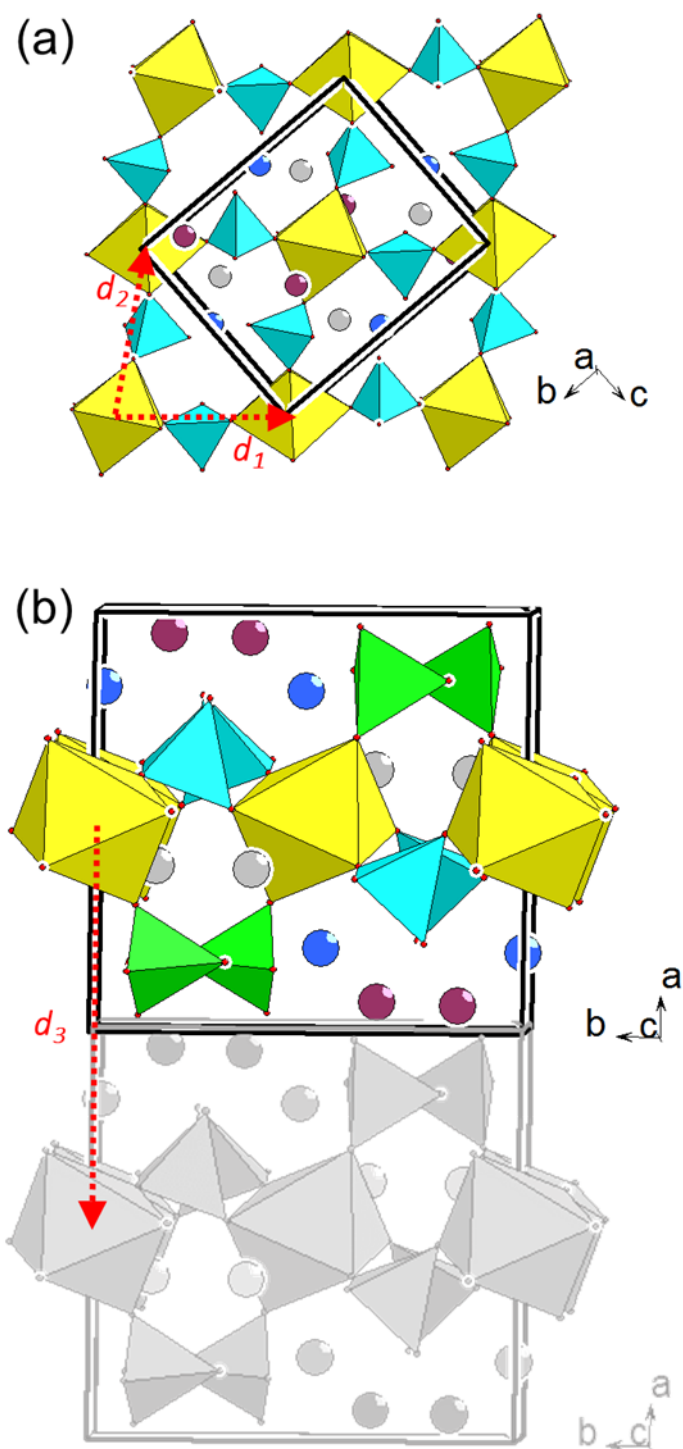


Figure S2. Structure of *II*. Single perovskite like layer showing (a) view perpendicular to the layer (b) view parallel to a single layer. FeO_6 octahedra yellow, in-layer SO_4 tetrahedra light blue, apical SO_4 tetrahedra green; the three distinct Na^+ sites are shown in different colours. Note that the apical SO_4 groups have been omitted in (a) to show more clearly the topology of the perovskite-like layer. The gray unit cell in (b) indicates an adjacent layer. The red dotted arrows show the directions of d_1 , d_2 and d_3 .

Table S1. Crystallographic information of crystal *I*, *II* and *III*

	<i>I</i>	<i>II</i>	<i>III</i>
Formula	Na ₃ Fe(SO ₄) ₃ · H ₂ O	Na ₆ Fe(SO ₄) ₄	Na ₁₂ Fe ₃ (SO ₄) ₆ F ₈
ICSD No.	2031475	2050477	2099156
Mr (g/mol)	431.02	578.03	1171.79
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	9.1253(7)	9.684(3)	9.4765(8)
<i>b</i> (Å)	8.8443(7)	9.259(3)	9.5081(9)
<i>c</i> (Å)	12.6798(11)	8.244(2)	9.6072(8)
α (degree)	90	90	113.231(3)
β (degree)	90.442(3)	113.359(8)	105.646(2)
γ (degree)	90	90	108.917(2)
<i>V</i> (Å ³)	511.66(1)	678.6(3)	669.18(1)
<i>Z</i>	2	2	1
<i>F</i> (000)	852	568	570
<i>d</i> _{calc} (g/cm ³)	2.798	2.829	2.908
θ range (degree)	2.740-27.851	2.291-27.134	2.555-27.099
No. of reflections	6381	5950	14846
No. of refined parameters	192	126	244
R (all data)	0.1147/0.1358	0.0548/0.0877	0.0356/0.0669
Final R [<i>I</i> > 2 σ (<i>I</i>)]	0.0613/0.1091	0.0381/0.0781	0.0275/0.0622
Goodness-of-fit on F ²	1.093	1.033	1.017

Table S2. Atomic parameters of crystal *I*.

Atom	Ox.	Wyck.	Site	x/a	y/b	z/c
Fe1	+3	2c	-1	1/2	0	1/2
Fe2	+3	2d	-1	1.00000	1/2	1/2
S1	+6	4e	1	0.30898(18)	0.30924(18)	0.49362(13)
S2	+6	4e	1	0.92856(18)	0.54380(19)	0.25124(13)
S3	+6	4e	1	0.77910(18)	0.21675(18)	0.55177(14)
Na1	+1	4e	1	0.3813(3)	0.6245(3)	0.6315(2)
Na2	+1	4e	1	1.1179(3)	0.0782(3)	0.6093(2)
Na3	+1	4e	1	0.2686(3)	0.5064(3)	0.2509(2)
O1	-2	4e	1	1.0246(5)	0.5120(5)	0.1583(3)
O2	-2	4e	1	0.8322(5)	0.3517(5)	0.4925(3)
O3	-2	4e	1	0.1461(5)	0.3281(5)	0.5058(3)
O4	-2	4e	1	0.3297(5)	0.1412(5)	0.5077(4)
O5	-2	4e	1	1.0179(5)	0.4872(5)	0.3433(3)
O6	-2	4e	1	0.9064(6)	0.7049(5)	0.2622(4)
O7	-2	4e	1	0.6424(5)	0.1727(5)	0.4914(4)
O8	-2	4e	1	0.3545(6)	0.3560(5)	0.3895(4)
O9	-2	4e	1	0.3873(6)	0.3860(5)	0.5765(4)
O10	-2	4e	1	0.7953(5)	0.4581(6)	0.2433(4)
O11	-2	4e	1	0.8840(5)	0.0954(5)	0.5438(4)
O12	-2	4e	1	0.7458(6)	0.2535(6)	0.6598(4)
O13	-2	4e	1	1.0024(6)	-0.1253(6)	0.7072(4)
H1	+1	4e	1	1.026(9)	-0.190(6)	0.753(4)
H2	+1	4e	1	0.988(9)	-0.035(3)	0.691(5)

Table S3. Atomic parameters of crystal *II*.

Atom	Ox.	Wyck.	Site	x/a	y/b	z/c
Fe	+2	2b	-1	1/2	1/2	1/2
S1	+6	4e	1	0.35725(10)	0.19721(10)	0.28096(12)
S2	+6	4e	1	0.84141(10)	0.3489(1)	0.65996(12)
Na1	+1	4e	1	1.18710(17)	0.48801(16)	1.0325(2)
Na2	+1	4e	1	0.61478(19)	0.36561(18)	0.1883(2)
Na3	+1	4e	1	0.9354(2)	0.65184(17)	0.5827(2)
O1	-2	4e	1	0.7001(3)	0.3995(3)	0.6749(3)
O2	-2	4e	1	0.8358(3)	0.1908(3)	0.6464(3)
O3	-2	4e	1	0.4733(3)	0.3126(3)	0.3463(4)
O4	-2	4e	1	0.3651(3)	0.1060(3)	0.4298(3)
O5	-2	4e	1	0.8570(3)	0.4128(3)	0.5064(4)
O6	-2	4e	1	0.3918(3)	0.1081(3)	0.1546(4)
O7	-2	4e	1	0.2084(3)	0.2636(3)	0.1955(4)
O8	-2	4e	1	0.9658(3)	0.3932(3)	0.8241(4)

Table S4. Atomic parameters of crystal *III*.

Atom	Ox.	Wyck.	Site	x/a	y/b	z/c
Fe1	+3	1c	-1	0	1/2	0
Fe2	+3	1b	-1	0	0	1/2
Fe3	+2	1h	-1	1/2	1/2	1/2
S1	+6	2i	1	0.53414(8)	0.83001(8)	0.81171(8)
S2	+6	2i	1	0.08964(8)	0.25700(9)	0.35619(8)
S3	+6	2i	1	0.38928(8)	0.62735(9)	0.22698(8)
Na1	+1	2i	1	0.89171(14)	0.81975(15)	1.01930(15)
Na2	+1	2i	1	0.32338(15)	-0.00120(15)	0.36537(15)
Na3	+1	2i	1	0.33675(14)	1.07265(15)	0.78516(15)
Na4	+1	2i	1	0.22203(14)	0.78207(15)	0.92245(15)
Na5	+1	2i	1	-0.15704(16)	0.35107(17)	-0.44250(16)
Na6	+1	2i	1	0.29936(15)	0.44557(15)	0.79397(16)
F1	-1	2i	1	0.10815(19)	0.7501(2)	0.0998(2)
F2	-1	2i	1	0.14063(19)	0.1599(2)	0.74130(19)
F3	-1	2i	1	0.16847(19)	-0.0732(2)	0.4972(2)
F4	-1	2i	1	0.06674(19)	0.4836(2)	-0.1765(2)
O1	-2	2i	1	0.5670(2)	0.7498(2)	0.6649(2)
O2	-2	2i	1	0.5287(3)	0.9855(3)	0.8187(3)
O3	-2	2i	1	0.3759(2)	0.7073(3)	0.7868(3)
O4	-2	2i	1	0.6742(3)	0.8870(3)	0.9687(3)
O5	-2	2i	1	0.2350(2)	0.4258(2)	0.4254(2)
O6	-2	2i	1	0.1330(2)	0.1933(3)	0.4732(3)
O7	-2	2i	1	0.0512(3)	0.1290(3)	0.1859(3)
O8	-2	2i	1	-0.0550(3)	0.2824(3)	0.3545(3)
O9	-2	2i	1	0.2052(2)	0.4982(3)	0.1338(3)
O10	-2	2i	1	0.4787(2)	0.5510(2)	0.2953(2)
O11	-2	2i	1	0.4170(3)	0.7894(3)	0.3640(3)
O12	-2	2i	1	0.4421(3)	0.6533(3)	0.1052(3)

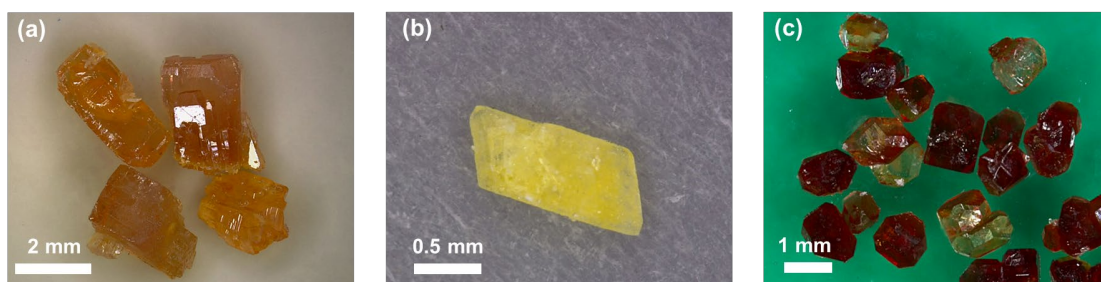


Figure S3. Photo of crystallites of (a) *I*, (b) *II*, (c) *III*.

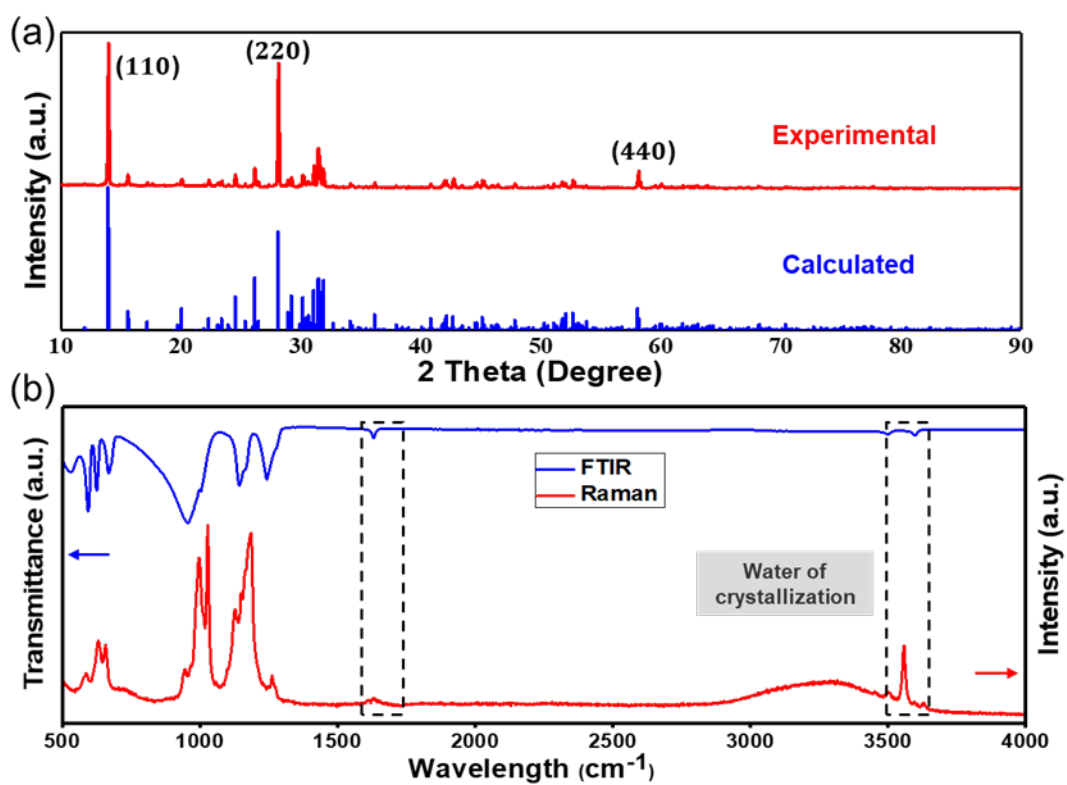


Figure S4. Basic characterisation of crystal *I*. Powder XRD pattern (a), Raman and FTIR spectra (b).

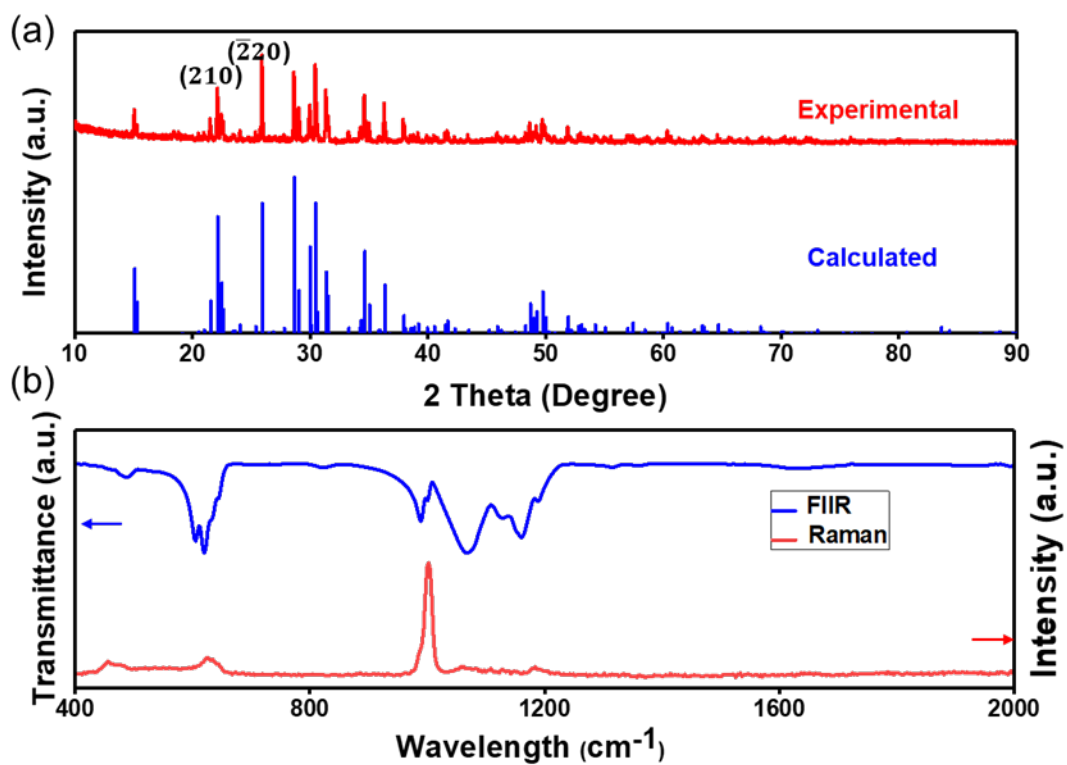


Figure S5. Basic characterisation of crystal *II*. Powder XRD pattern(a), Raman and FTIR spectra (b).

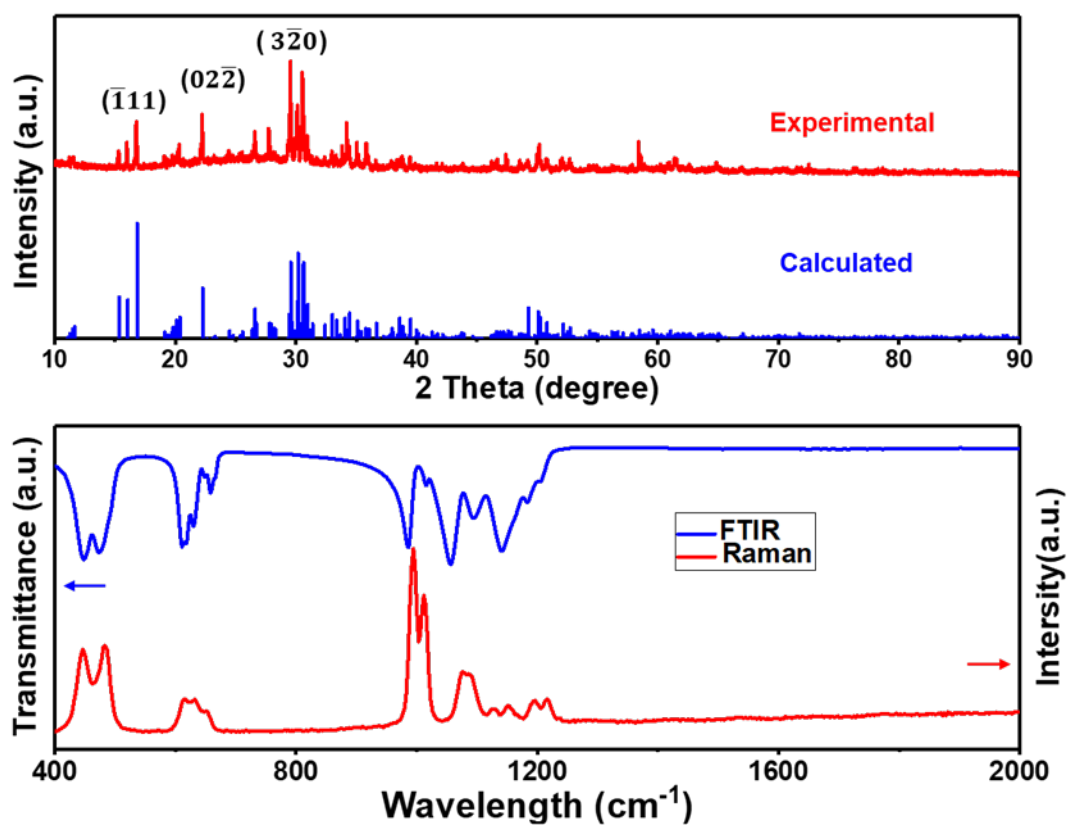


Figure S6. Basic characterisation of crystal *III*. Powder XRD pattern (a), Raman and FTIR spectra (b).

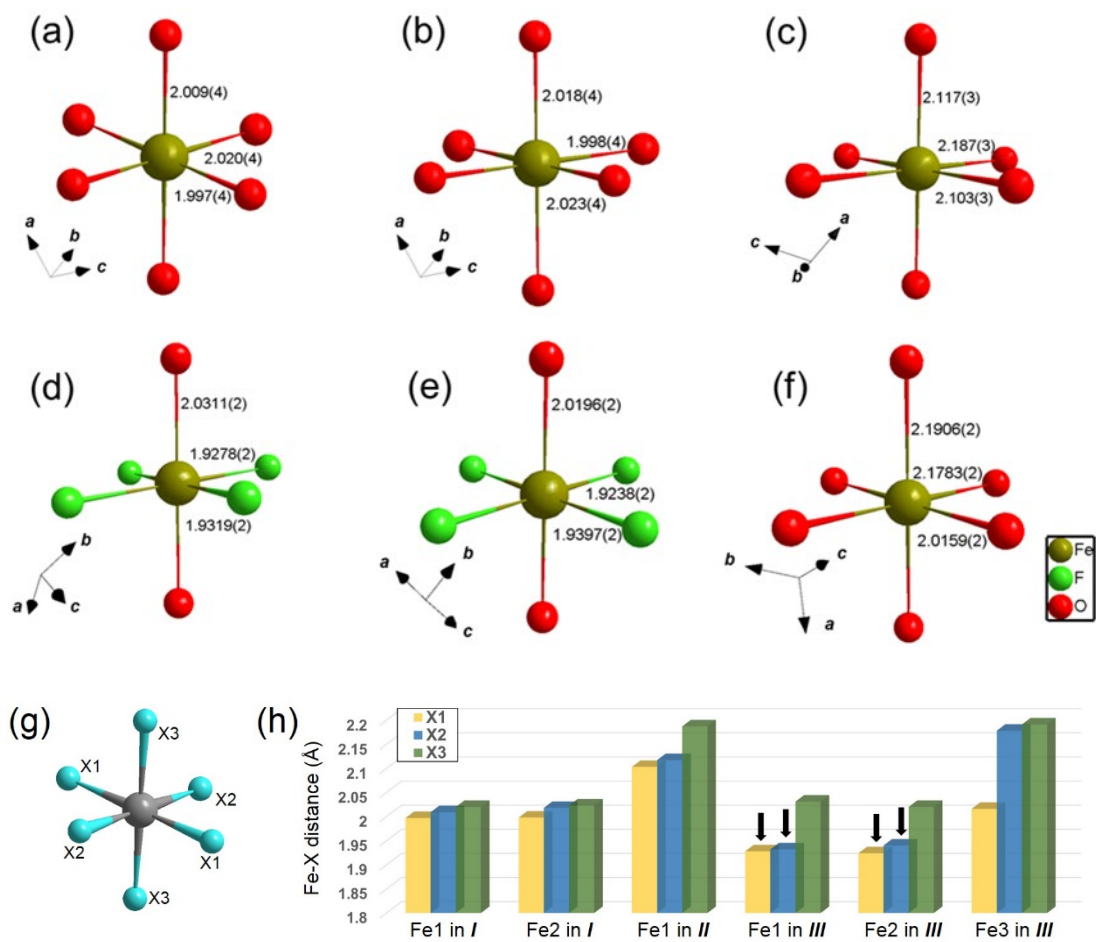


Figure S7. Fe environment in *I* (a-b), *II* (c), and *III* (d-f), (g) generalized FeX₆ environment and (h) corresponding Fe-X bond length.

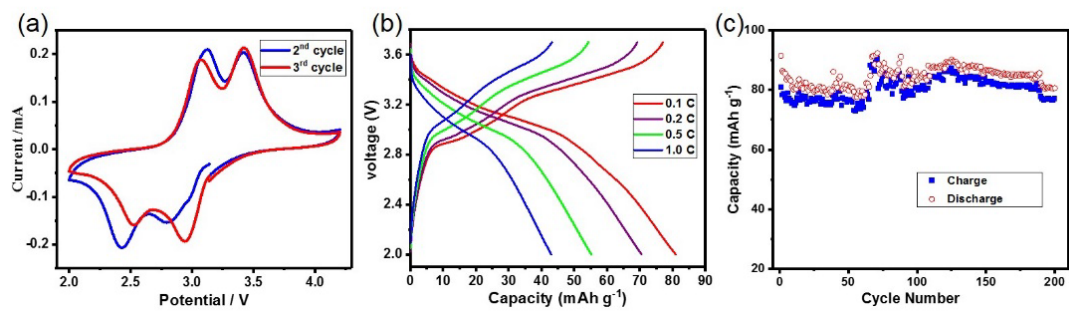


Figure S8. Electrochemical properties of *I*. (a) Typical CV curve, (b) Charge-discharge curves, (c) Cycling performance at 0.2 C.