

A General Synthetic Method for MPO_4 (M=Co, Fe, Mn) Frameworks Using Deep-Eutectic Solvents

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Experimental Section

Described below are the typical synthesis conditions used to prepare metal phosphate materials. These synthesis conditions are sensitive to extra water being added through the highly hygroscopic choline chloride. To limit extra water the choline chloride was kept under vacuum when not in use. All chemicals were purchased from Sigma-Aldrich and used without further purification.

Synthesis of DEL-1: 0.12 g of CoCO_3 , 0.12 g of H_3PO_4 (85%), 0.7 g choline chloride, and 0.88 g N,N'-dimethylurea were added to a Teflon lined autoclave. The autoclave was sealed and heated for 18hrs at 180°C before being removed from the oven and allowed to cool for ~1hr. The product was suction washed with ethanol only. These crystals will dissolve if washed with DI water. After the suction filtration thin sheets of blue crystals can be seen under an optical microscope. Collecting a pure phase for this material is rather difficult because once the crystals have formed they begin to phase transform to the DEL-2 crystal. 18hrs skirts the time range where no crystals to completely layered DEL-1 crystals are recovered.

Synthesis of DEL-2: 0.12 g of CoCO_3 or 0.25 g of $\text{CoAcetate}\cdot 4\text{H}_2\text{O}$, 0.12 g of H_3PO_4 (85%), 0.7 g choline chloride, and 0.88 g N,N'-dimethylurea were added to a Teflon lined autoclave. The autoclave was sealed and heated for 4 days at 180°C before being removed from the oven and allowed to cool for 1-2 hrs. The product was suction washed with ethanol first, and then DI water. Ethanol is used first in case Co ions have yet to react and are still in solution, which with water may precipitate to form a pink $\text{NH}_4\text{CoPO}_4\cdot\text{H}_2\text{O}$ crystal. The final products are blue rectangular prism crystals. Originally we used $\text{CoAcetate}\cdot 4\text{H}_2\text{O}$ in the synthesis, but changed to CoCO_3 because the lower water content slows the decomposition, making it easier to reproduce consistent results.

Synthesis of DEL-3: 0.12 g of CoCO_3 , 0.12 g of H_3PO_4 (85%), 0.7 g choline chloride, and 0.88 g N,N'-dimethylurea were added to a Teflon lined autoclave. The autoclave was heated for 1 day at 220°C before being removed from the oven and cooled for 1 hour. The product was suction washed with ethanol and DI water. This reaction resulted in a mixed phase of layered and cubic crystals. A cubic crystal was solved to determine the structure of DEL-3.

Synthesis of NH_4CoPO_4 -ABW: 0.12 g of CoCO_3 , 0.12 g of H_3PO_4 (85%), 0.7 g choline chloride, and 0.88 g N,N'-dimethylurea were added to a Teflon lined autoclave. The autoclave was sealed and heated for 10-14 days at 180°C before being removed from the oven and allowed to cool for 1-2 hrs. The product was suction washed with ethanol, and then DI water. Blue crystals with rough looking walls were recovered.

Synthesis of NH_4CoPO_4 -HEX: 0.25 g of $\text{CoAcetate}\cdot 4\text{H}_2\text{O}$, 0.12 g of H_3PO_4 (85%), 0.7 g choline chloride, and 0.88 g N,N'-dimethylurea were added to a Teflon lined autoclave. The autoclave was sealed and heated for >6 days at 200°C before being removed from the oven and allowed to cool for 1-2 hrs. The product was suction washed with ethanol, and then DI water. Blue hexagonal crystals with rough looking walls were recovered.

Synthesis of CoPO₄-DFT: 0.12 g of CoCO₃, 0.12 g of H₃PO₄ (85%), 0.7 g choline chloride, and 0.86 g 2-imidizolidone were added to a Teflon lined autoclave. The autoclave was sealed and heated for 3-7 days at 200⁰C before being removed from the oven and allowed to cool for 1 hr. The product was suction filtered with DI water. Blue crystals were recovered.

Synthesis of FePO₄-DFT: 0.20 g FeCl₂*4H₂O, 0.12 g of H₃PO₄ (85%), 0.7 g choline chloride, and 0.86 g 2-imidizolidone were added to a Teflon lined autoclave. The autoclave was sealed and heated for 4 days at 200⁰C before being removed from the oven and allowed to cool for 1 hr. The product was suction filtered with DI water. Reddish-brown crystals were recovered.

Synthesis of MnPO₄-DFT: 0.20 g MnCl₂*4H₂O, 0.12 g of H₃PO₄ (85%), 0.7 g choline chloride, and 0.86 g 2-imidizolidone were added to a Teflon lined autoclave. The autoclave was sealed and heated for 3 days at 200⁰C before being removed from the oven and allowed to cool for 2 hours. The cooling time may be important for this sample. If cooled less than 1 hour little to no crystals were found. The product is suction filtered with DI water. After suction filtration lime colored crystals and a white powder impurity will be present. To remove the white impurity the contents were put into a scintillation vial. The vial was filled with DIH₂O, capped, and then shook for 15-30 seconds. The crystals are dense enough to fall by gravity to the bottom of the vial, but some of the white impurity makes the DIH₂O have a cloudy white appearance. This cloudy water solution was pipetted out of the vial. This process was repeated a couple times until the water looked nearly clear. At this point the clear lime crystals and white impurity too heavy/large to be removed as a supernatant sits at the bottom of the vial. The vial was again filled with DIH₂O and sonicated for 5 minutes. Immediately after sonication the vial contents were separated via suction filtration by washing with ethanol and DIwater. By performing these purification steps we got nearly pure >99% lime green crystals that we could then analyze. The crystals, though large enough, were highly polycrystalline and therefore unsuitable for single crystal x-ray diffraction.

Single Crystal XRD: Diffraction data was recorded on a Rigaku R-AXIS SPIDER Image Plate diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) for DEL-1 at 150 K. DEL-2 and DEL-3 were collected on a APEX Bruker-AXS CCD x-ray diffractometer equipped with a monicap collimator with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 200 K. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques using the SHELXTL program. The hydrogen atoms on the organic motifs were added on calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms.

Powder XRD scans: All scans were collected on a PanAnalytical X'Pert diffractometer with a CuK α radiation in Bragg-Bentaro geometry. Scans were collected in continuous mode from 5-70 2theta at a scan speed of 0.02 deg/sec.

Table S1: Crystallographic data for DEL-1–3

	DEL-1	DEL-2	DEL-3
empirical formula	C ₅ H ₃₂ N ₅ O ₂₀ P ₅ Co ₄	C ₄ H ₂₈ N ₅ O ₂₀ P ₅ Co ₅	C ₉ H ₄₄ N ₁₀ O ₄₀ P ₁₀ Co ₁₀
<i>M</i>	872.93	915.81	1831.54
temp / K	153(2)	200(2)	200(2)
crystal system	Orthorhombic	Orthorhombic	Tetragonal
space group	Cmcm	Pnn2	P-42(1)c
<i>a</i> /Å	26.631(5)	13.361(7)	9.880(2)
<i>b</i> /Å	7.6331(15)	13.789(7)	9.880(2)
<i>c</i> /Å	6.8120(14)	14.017(7)	13.333(3)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	90
<i>V</i> /Å ³	1384.7(5)	2582(2)	1301.6(5)
<i>Z</i>	2	4	1
ρ_{calcd} /g cm ⁻³	2.094	2.236	2.337
μ /mm ⁻¹	2.732	3.549	3.521
F(000)	880	1828	908
reflns collected	3054	18493	14337
unique reflns	741	5023	1270
<i>R</i> _{int}	0.0474	0.1037	0.0220
<i>S</i>	1.085	1.053	1.090
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0402	0.0693	0.0376
<i>wR</i> ₂ ^b (all data)	0.1159	0.1748	0.1070

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

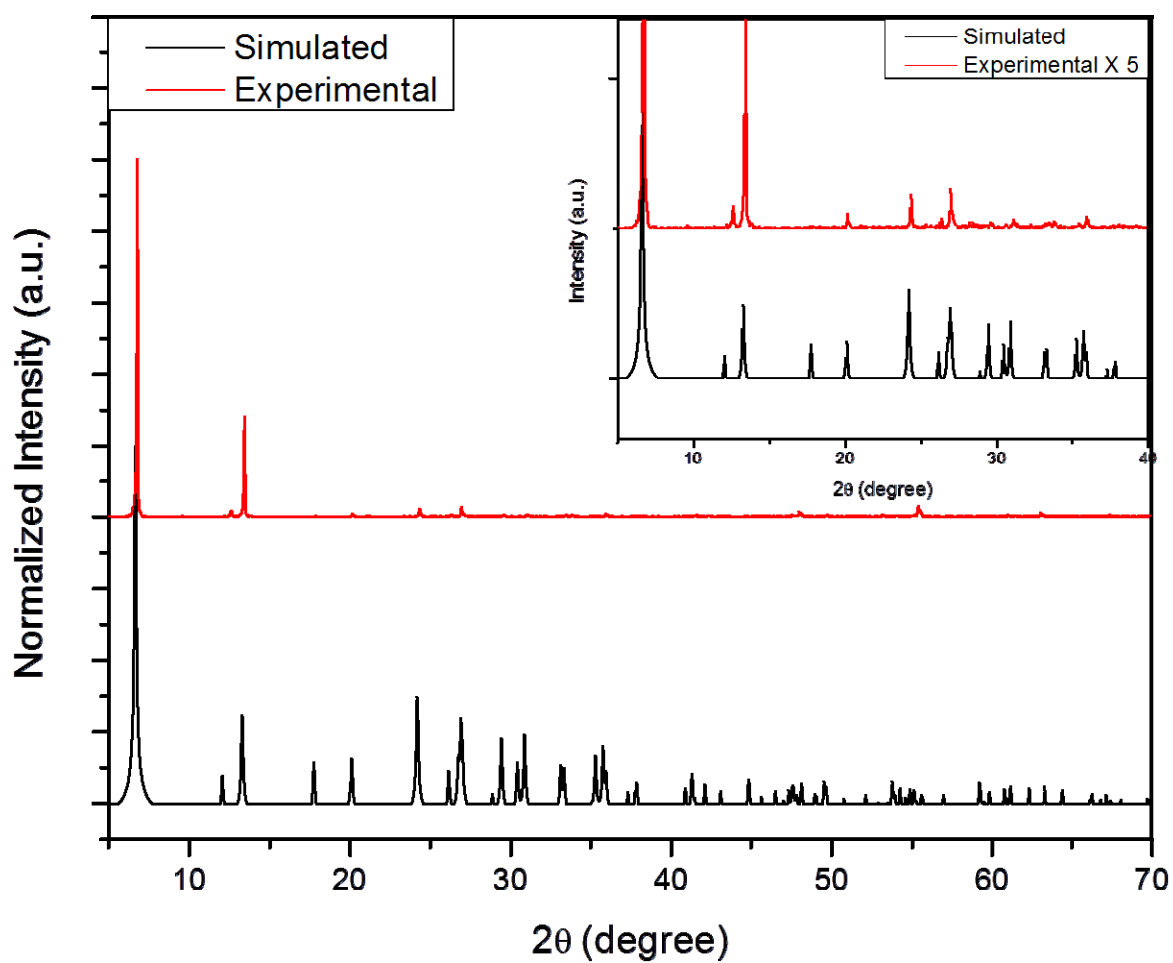


Figure S1: Simulated and experimental PXRD for DEL-1. Since the crystals are thin, plate crystals strong preferred orientation is present in this pattern. The inset shows a comparison of the simulated pattern against the experimental pattern with its intensity multiplied by 5.

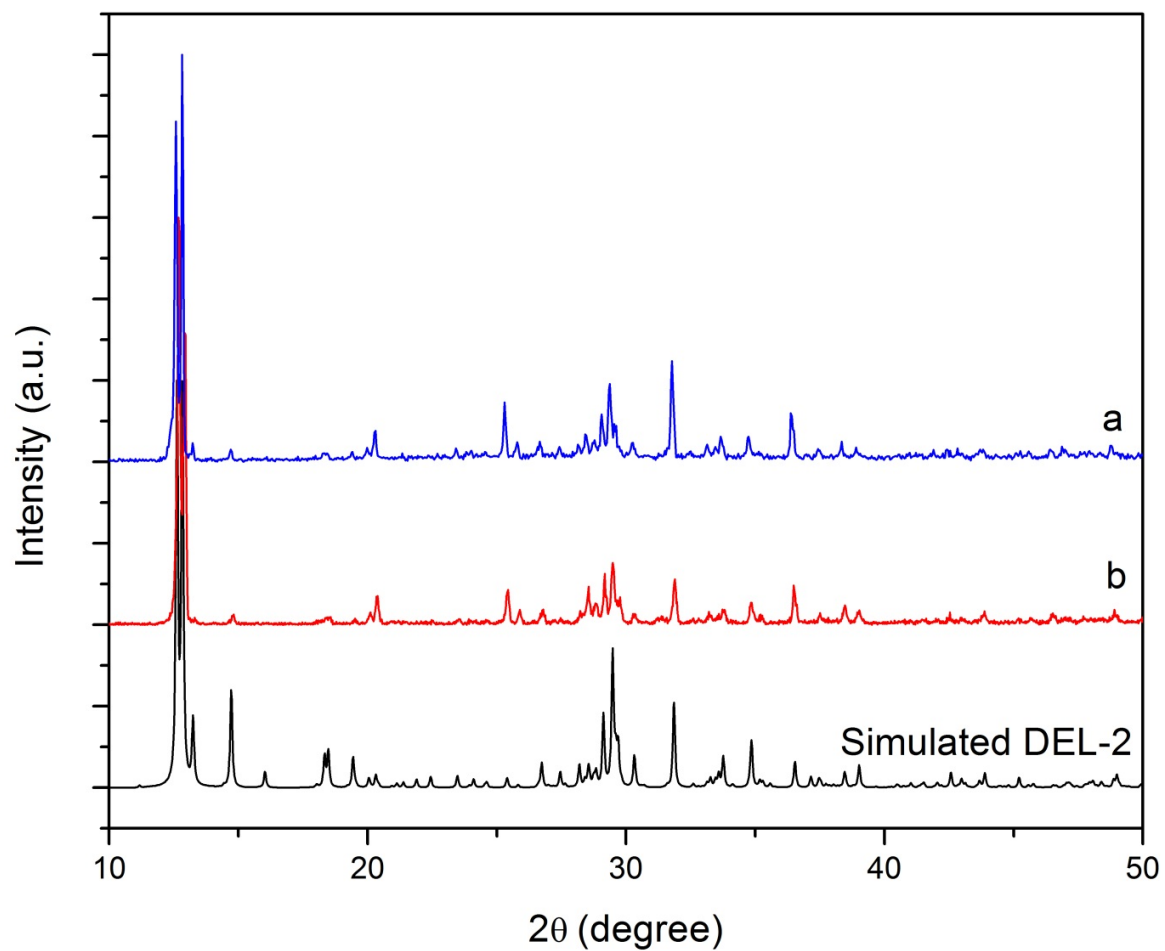


Figure S2: Comparison of simulated and experimental Powder XRD for DEL-2 synthesis from a) $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ precursor and b) $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ precursor.

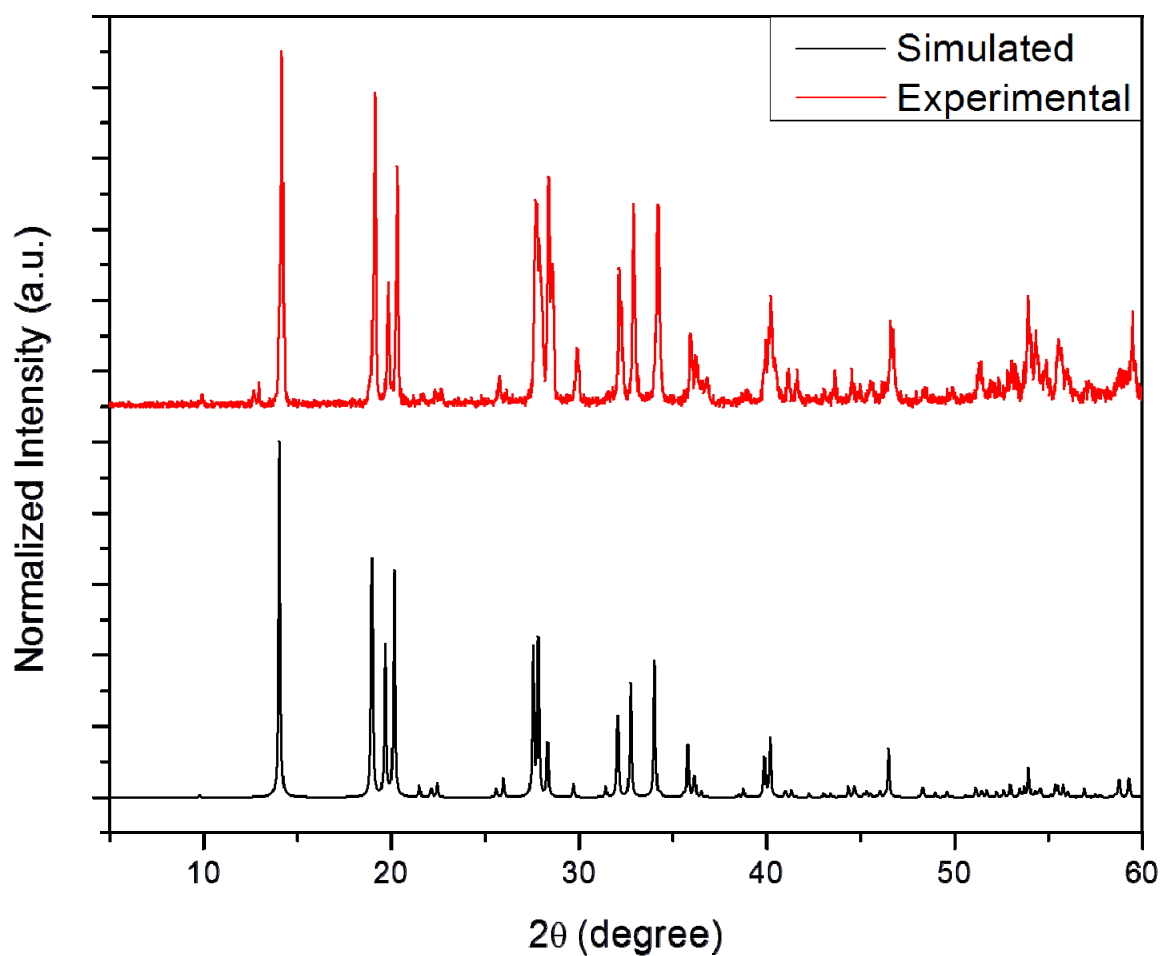


Figure S3: Simulated and experimental PXRD for $\text{NH}_4\text{CoPO}_4\text{-ABW}$. The simulated pattern is from a 50/50 twinned Reitveld refinement reported by Feng, P. et al. [ref. 1]

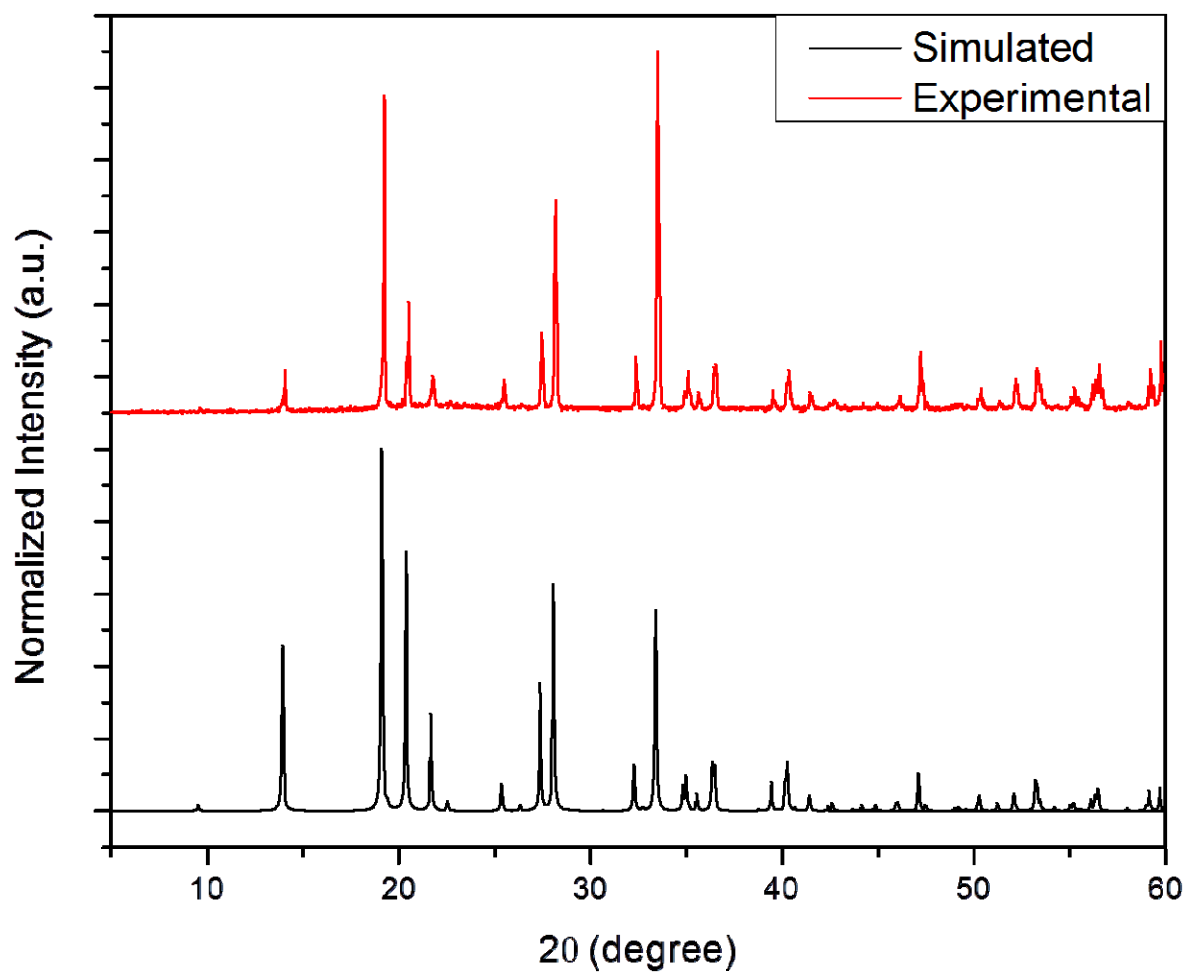


Figure S4: Simulated and experimental PXRD for NH₄CoPO₄-HEX. The simulated pattern comes from the solved structure by Feng, P et al. [ref. 1]

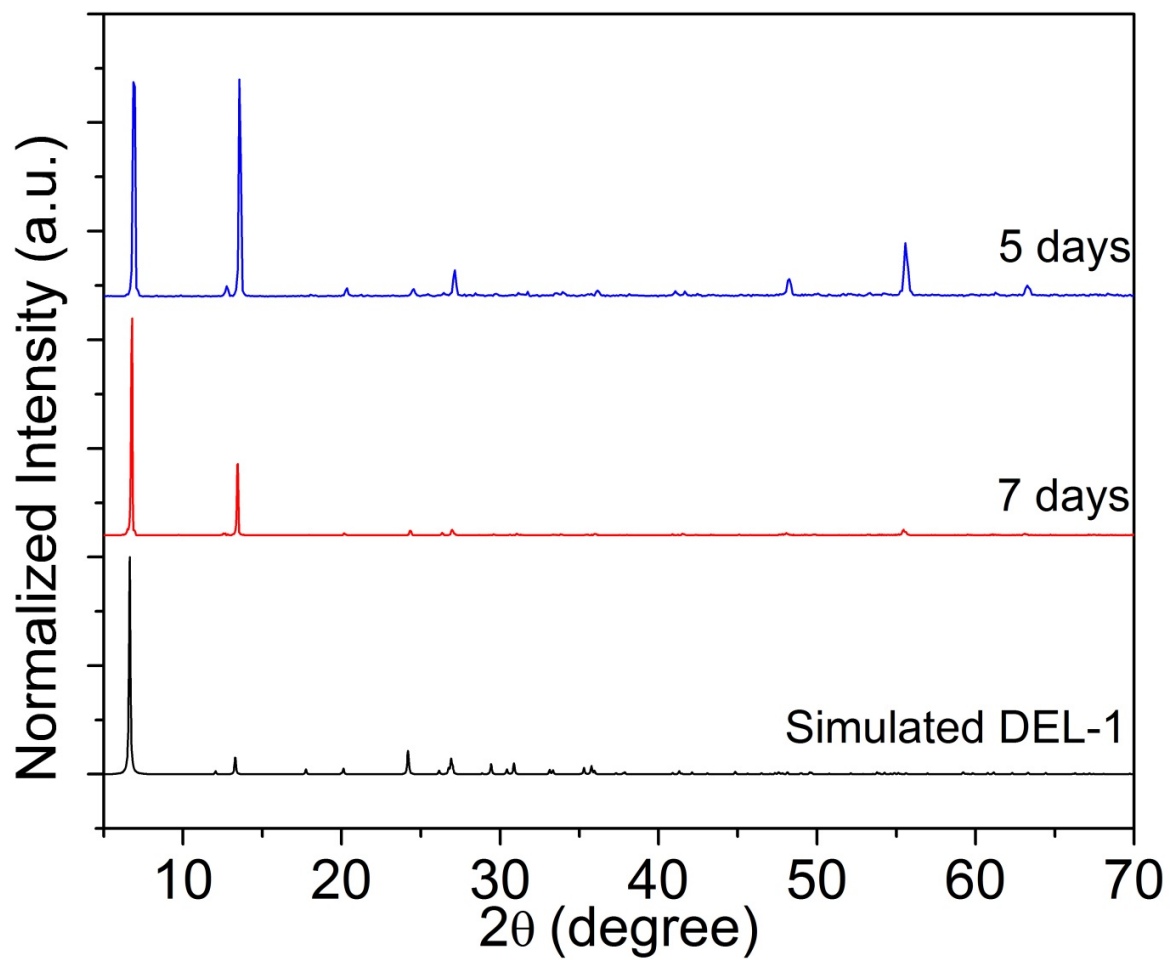


Figure S5: Synthesis product when heated at 130°C. After 7 days no phase change to the 3-D DEL-2 framework is observed.

Thermogravimetric Analysis Experiments: Scans were collected on Perkin Elmer Pyris Diamond TG/DTA 6300 from 40⁰C to 900⁰C in air. The scan speed was 10 degC/min.

CHN Experiments: Analysis was performed by Micro-Analysis, Inc. (2038 Telegraph Road/Wilmington, DE 19808)

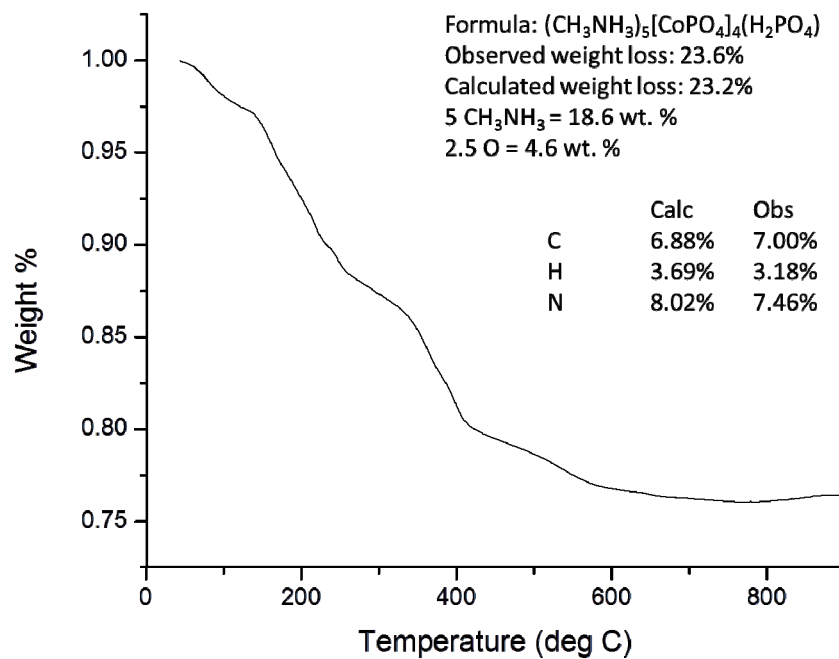


Figure S6: TGA and CHN data for DEL-1. At 900⁰C crystal phase is $\text{Co}_2\text{P}_2\text{O}_7$ according to PXRD analysis.

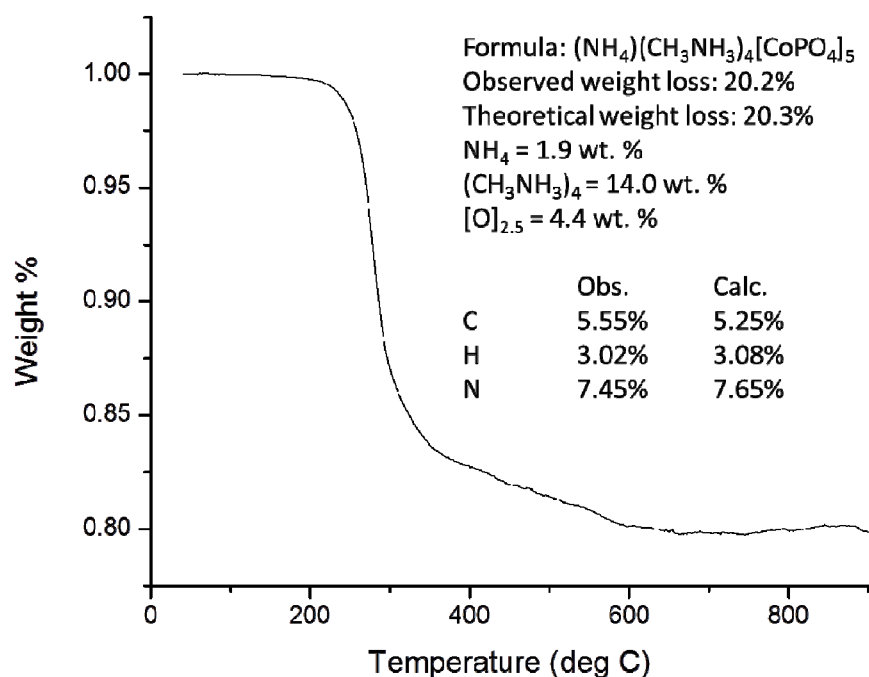


Figure S7: TGA and CHN data for DEL-2. At 900°C crystal phase is $\text{Co}_2\text{P}_2\text{O}_7$ according to PXRD analysis.

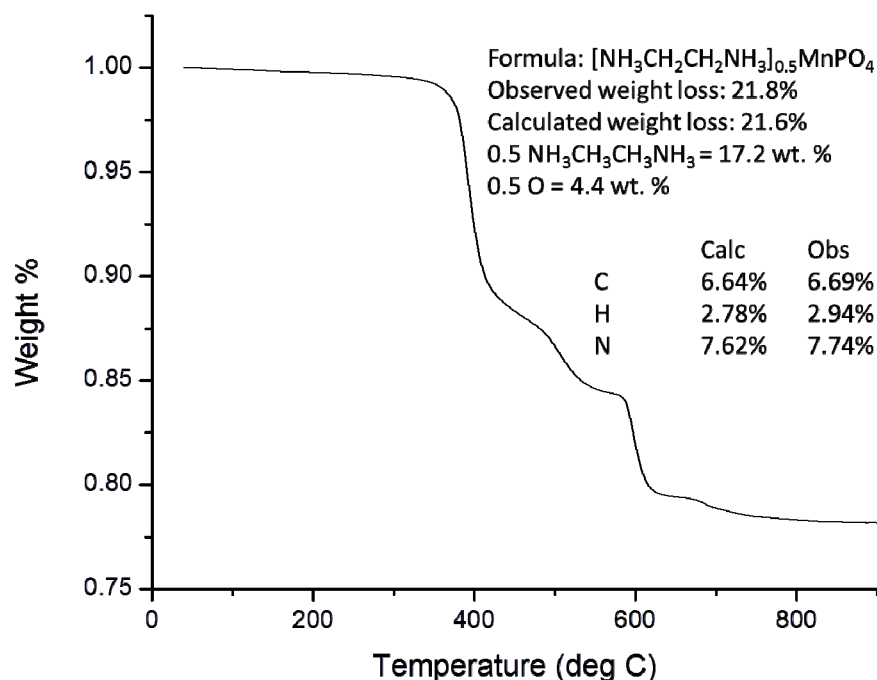


Figure S8: TGA and CHN data for $\text{MnPO}_4\text{-DFT}$. At 900°C crystal phase is $\text{Mn}_2\text{P}_2\text{O}_7$ according to PXRD analysis.

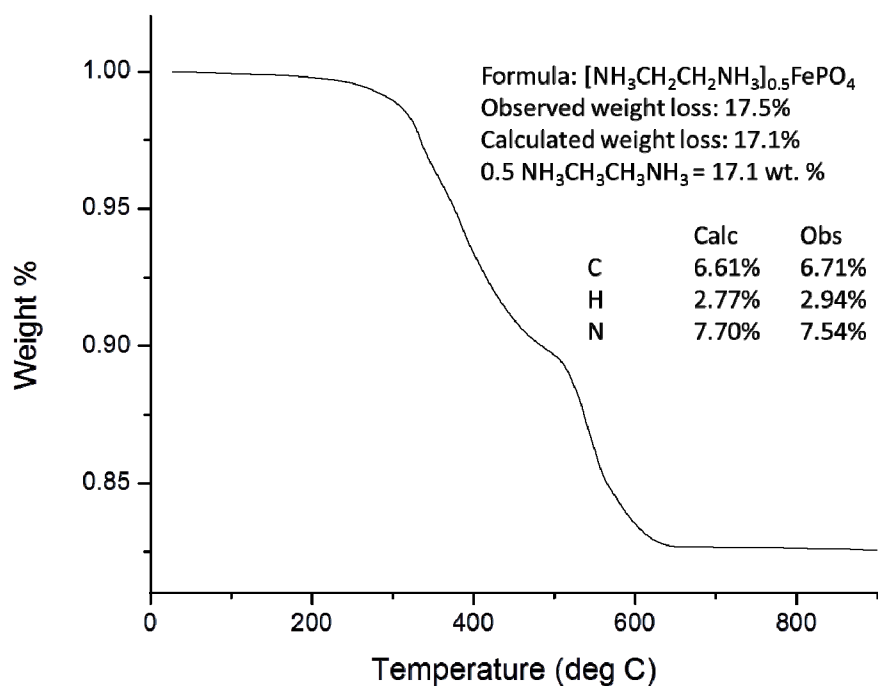


Figure S9: TGA and CHN data for FePO_4 -DFT. At 900°C crystal phase is FePO_4 according to PXRD analysis.

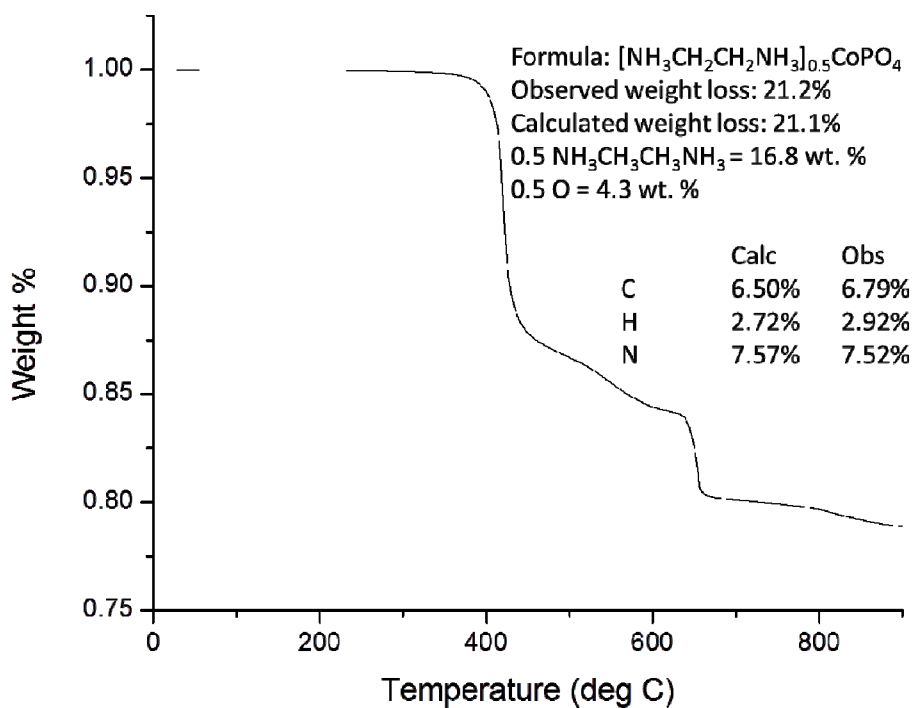


Figure S10: TGA and CHN data for CoPO_4 -DFT. At 900°C crystal phase is $\text{Co}_2\text{P}_2\text{O}_7$ according to PXRD analysis.

Inductively Coupled Plasma-Optical Emission Spectroscopy: ICP-OES data was collected by the University of Delaware Soil Lab on a Thermo Elemental Intrepid II XSP Duo View. The samples were microwave digested in nitric acid before analysis.

Table S2: ICP-OES Results

Structure	Atom	Calc wt%	Exp wt%	Atom	Calc wt%	Exp wt%
DEL-1	Co	27.0	28.1	P	17.7	16.3
DEL-2	Co	32.7	30.5	P	17.2	15.3
CoPO₄-DFT	Co	31.9	30.3	P	16.8	16.3
FePO₄-DFT	Fe	30.7	27.1	P	17.0	15.5
MnPO₄-DFT	Mn	30.4	32.3	P	17.1	16.2

Works Cited:

1. Feng, P. Y.; Bu, X. H.; Tolbert, S. H.; Stucky, G. D. *Journal of the American Chemical Society* **1997**, *119*, 2497.