

Supplementary Material

Experimental

Pure MnPS_3 phase was synthesized using the ceramic method as described in the literature.^{S1} The potassium precursor was synthesized by stirring for 24 h at room temperature a suspension of the solid phase MnPS_3 with an aqueous 2 M KCl solution.^{S2} The obtained light green potassium precursor was characterized by SEM-EDX giving the $\text{K}_{0.4}\text{Mn}_{0.8}\text{PS}_3 \cdot \text{H}_2\text{O}$ stoichiometry.

The potassium precursor, $\text{K}_{0.4}\text{Mn}_{0.8}\text{PS}_3 \cdot \text{H}_2\text{O}$ (300 mg) was suspended in 15 mL of a methanolic solution of 0.32 mmol of the corresponding nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 95 mg; $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 78 mg; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 93 mg; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 94 mg], in a 50 mL reactor. The suspension was irradiated with microwave radiation (800 W) for six minutes, using a LAVIS-1000 Multi-Quant microwave equipment with a frequency of 2459 MHz. The solid was filtered, washed with ethanol and water several times before its characterization. Both reactions at four and twelve minutes were done in order to obtain the optimum time for the exchange of the potassium ions by the transition metal ions. While four minutes was not enough to produce the complete exchange and some remnant potassium ions were detected by SEM-EDX, an irradiation time of twelve minutes gave a solid with the same stoichiometry as that obtained for six minutes.

The new layered phases $\text{M}'_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$ were characterized by FTIR, SEM-EDX, atomic absorption and X-ray powder diffraction. Nickel, cobalt, copper, zinc and manganese analyses were carried out on an AAnalyst 700 Perkin Elmer equipment, using an acetylene/air flame. FT-IR spectra were registered, using KBr pellets, on a Bruker Vector 22 equipment. Powder diffraction data were recorded with a Bruker D8 Advance diffractometer, using monochromatic $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), selected with an incident beam curved-crystal germanium monochromator, and a

LynxEye detector. The diffraction patterns were collected over the angular range 5-120° (2 θ) with a counting time of 215 s per step and a step length of 0.008° (2 θ). Whole powder pattern fittings were made by means of the program FULLPROF^{S3} (pattern-matching with Le Bail fit) in the WinPLOTR interface.^{S4} Scanning electron microscopy (SEM) was done using a Jeol Scanning Microscope (JSM-5410), with an Oxford Link Isis energy dispersive X-ray detector (EDXS). Diffuse reflectance spectra of solid samples at room temperature were recorded on a Perkin-Elmer equipment (Lambda 1050 UV/Vis/NIR Spectrometer). Band gaps for the different phases were obtained by Tauc's method and determined from the linear regression of the data.^{S5} The magnetization measurements were obtained in the temperature range of 6 - 285 K at 100 Oe using a Quantum Design SQUID magnetometer MPMS-XL5.

Table S1: Atomic absorption for bimetallic phases.

Exp (calc.)	Mn	M'
MnPS ₃	29.35 (30.16)	-
Co _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	23.33 (23.45)	6.53 (6.29)
Ni _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	22.47 (23.46)	6.76 (6.26)
Cu _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	23.24 (23.34)	7.02 (6.75)
Zn _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	22.54 (23.45)	6.51 (6.98)

Table S2: Unit cell parameters and agreement factors obtained from the pattern matching of the diffractograms.

	MnPS ₃ [^{S5}]	Co _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O [CoPS ₃ ^{S6}]	Ni _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O [NiPS ₃ ^{S6}]
<i>a</i>	6.07734(5) [6.07]	6.0471(7) [5.90]	5.9893(6) [5.81]
<i>b</i>	10.57620(9) [10.52]	10.855(1) [10.22]	10.575(2) [10.07]
<i>c</i>	6.79879(7) [6.79]	6.8065(6) [6.66]	6.7882(9) [6.63]
β	107.3752(8) [107.35]	107.579(9) [107.16]	107.57(1) [106.98]
Chi ²	9.48	1.30	1.82
R _p	9.58	4.23	7.34
R _{wp}	16.6	5.44	9.32

	Cu _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O	Zn _{0.2} Mn _{0.8} PS ₃ ·0.25H ₂ O [ZnPS ₃ ^{S7}]
<i>a</i>	6.0526(7)	6.0491(8) [5.97]
<i>b</i>	10.607(1)	10.553(2) [10.34]
<i>c</i>	6.8328(4)	6.818(1) [6.76]
β	107.69(1)	107.84(1) [107.14]
Chi ²	2.66	1.73
R _p	6.82	8.18
R _{wp}	9.22	10.5

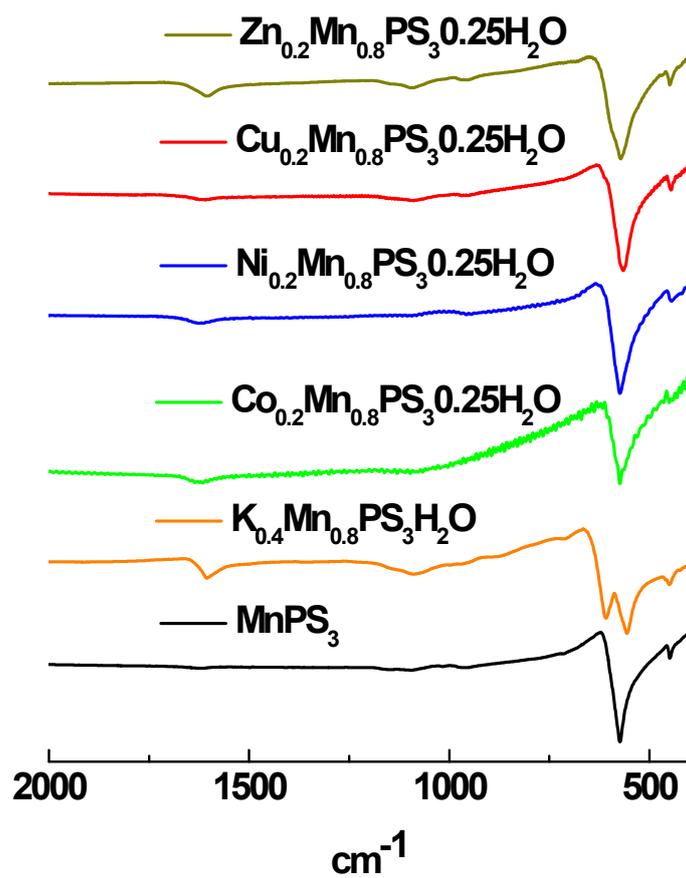


Fig. S1. FTIR spectra of pristine phase, MnPS_3 ; $\text{K}_{0.4}\text{Mn}_{0.8}\text{PS}_3 \cdot \text{H}_2\text{O}$ and bimetallic phases.

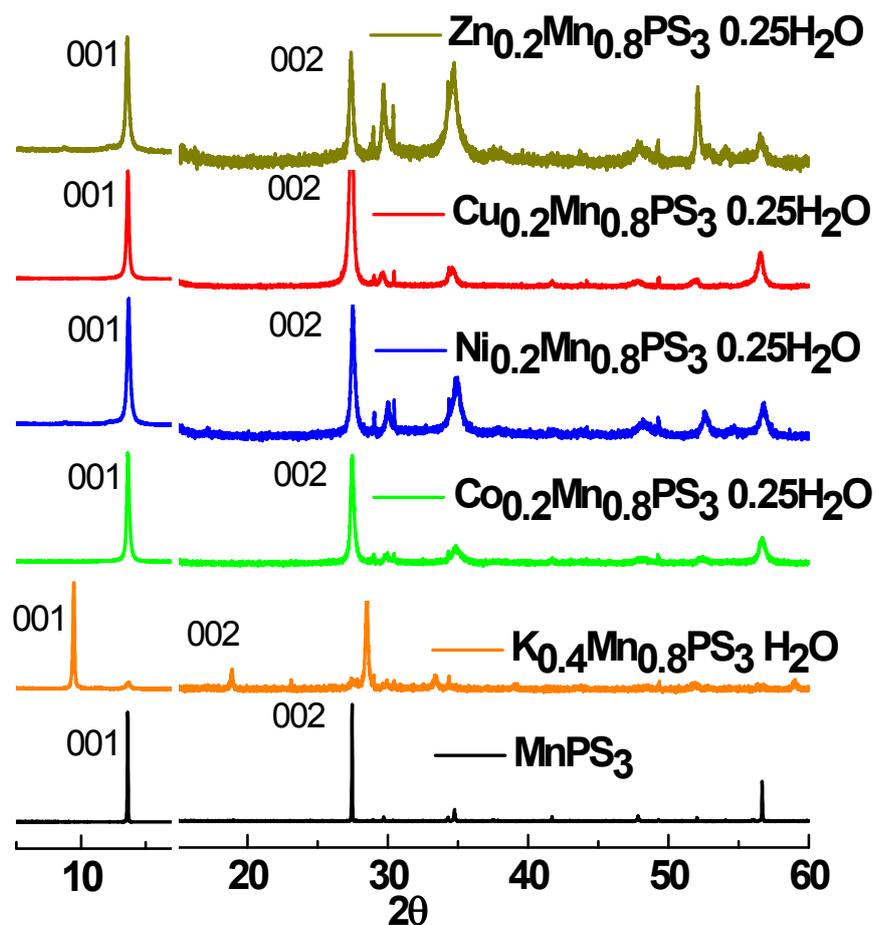


Fig. S2. Powder X- Ray diffractograms of pristine phase, $\text{K}_{0.4}\text{Mn}_{0.8}\text{PS}_3 \cdot \text{H}_2\text{O}$ and bimetallic phases. Due to the low intensity of lines from 15 to 60° this part of the diffractograms is zoomed x5. Peaks located between 25 to 35° in 2θ correspond to different preferred orientations, as reported by Villanueva et al.^{S8}

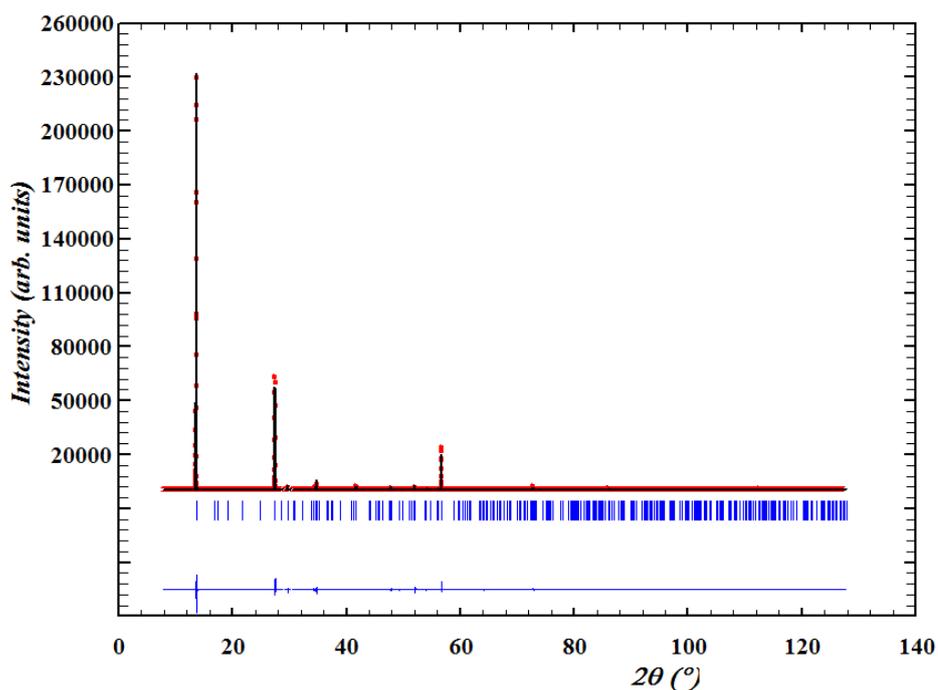


Fig S3a: Pattern matching for MnPS₃: experimental pattern (red dots), calculated pattern (black line), difference between experimental and calculated patterns (blue line), and blue bars are calculated Bragg positions.

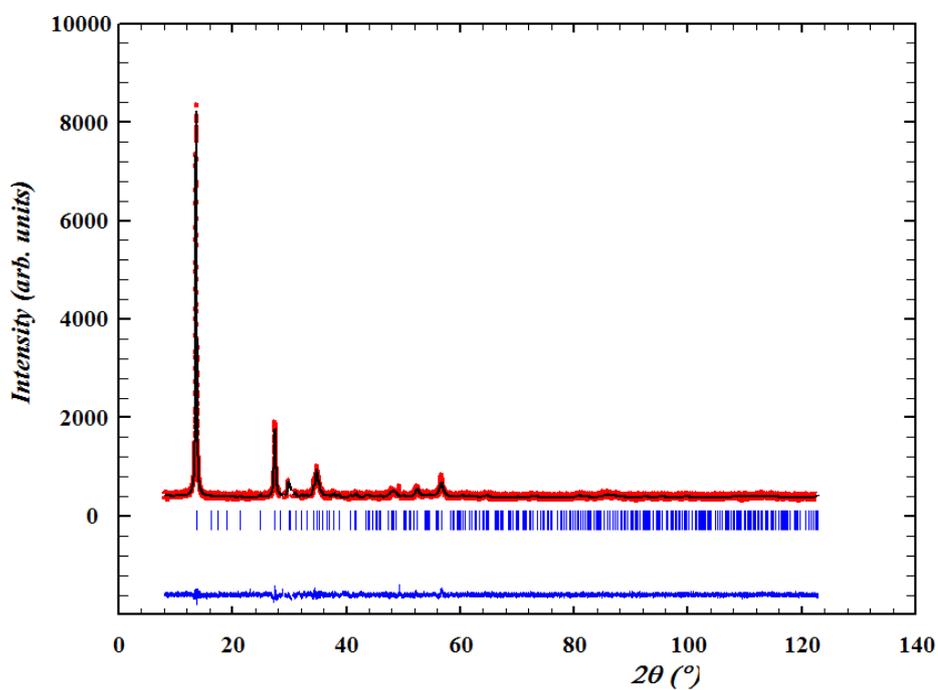


Fig. S3b: Pattern matching for Co_{0.2}Mn_{0.8}PS₃·0.25H₂O: experimental pattern (red dots), calculated pattern (black line), difference between experimental and calculated patterns (blue line), and blue bars are calculated Bragg positions.

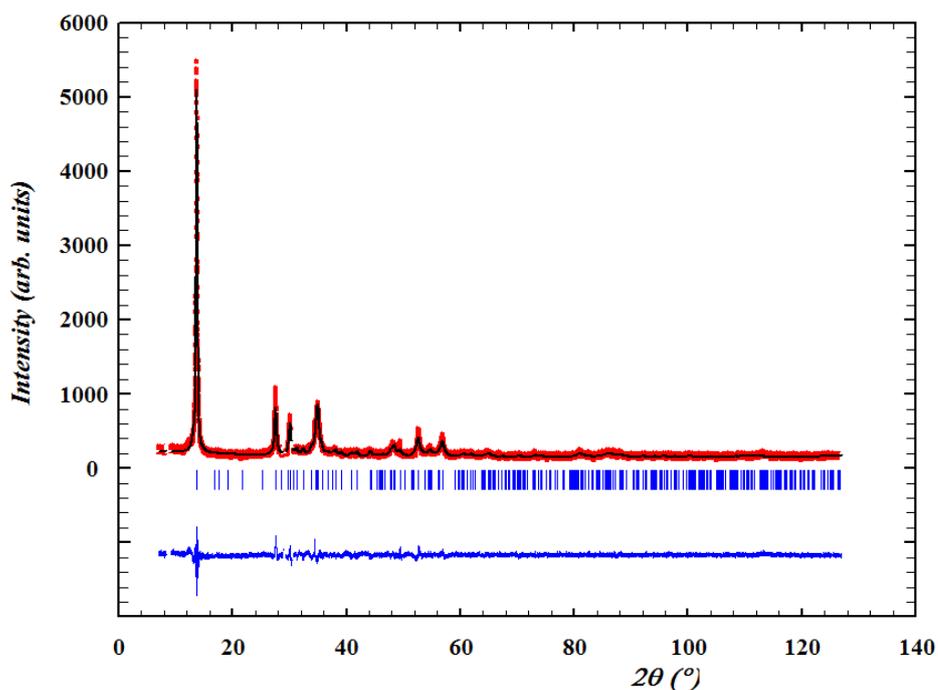


Fig. S3c: Pattern matching for $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$: experimental pattern (red dots), calculated pattern (black line), difference between experimental and calculated patterns (blue line), and blue bars are calculated Bragg positions.

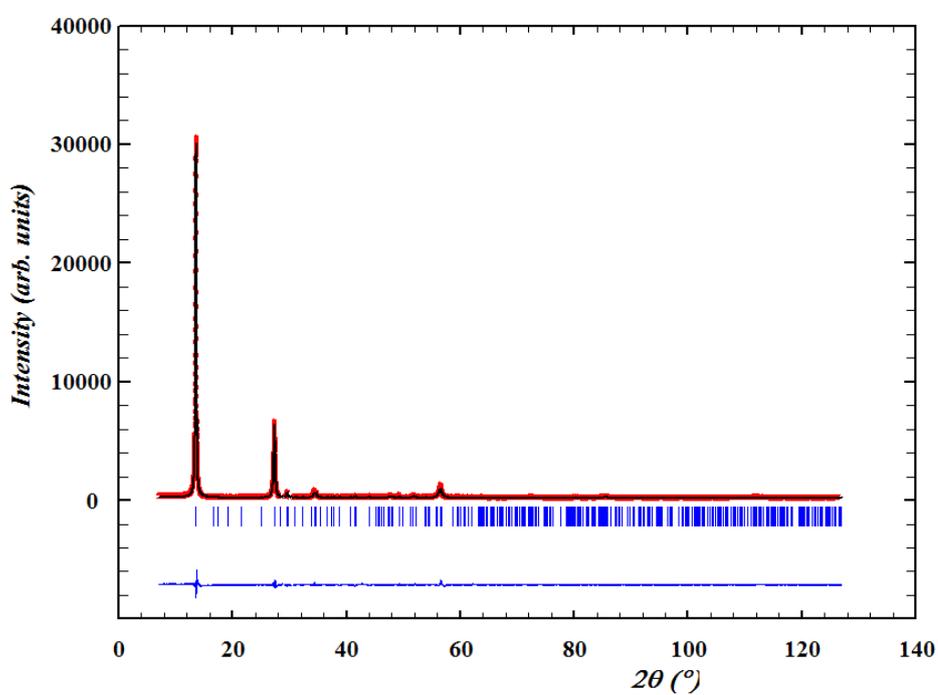


Fig. S3d: Pattern matching for $\text{Cu}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$: experimental pattern (red dots), calculated pattern (black line), difference between experimental and calculated patterns (blue line), and blue bars are calculated Bragg positions.

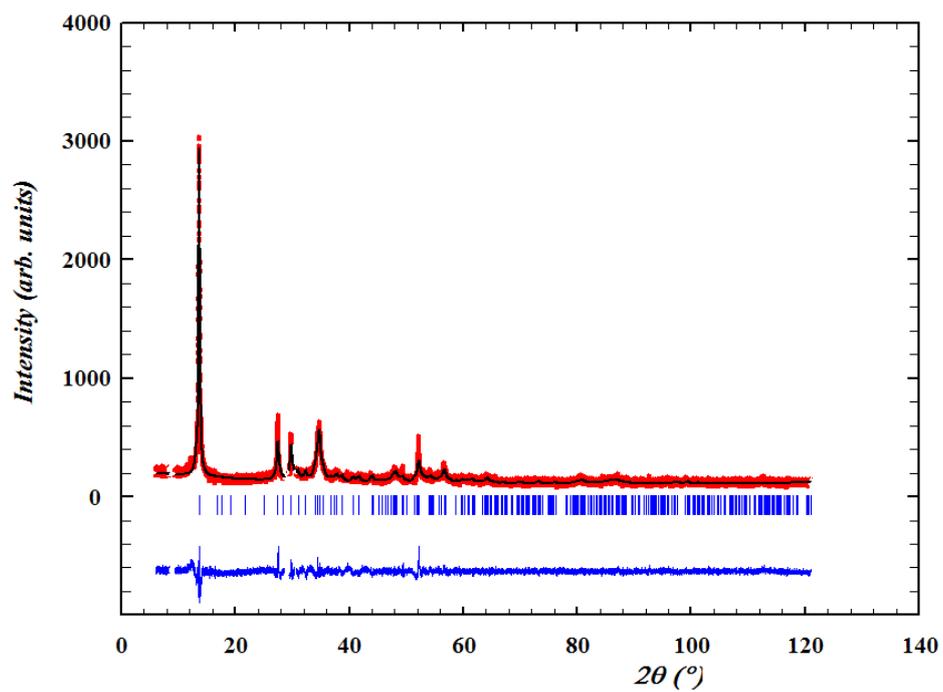


Fig. S3e: Pattern matching for $\text{Zn}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$: experimental pattern (red dots), calculated pattern (black line), difference between experimental and calculated patterns (blue line), and blue bars are calculated Bragg positions.

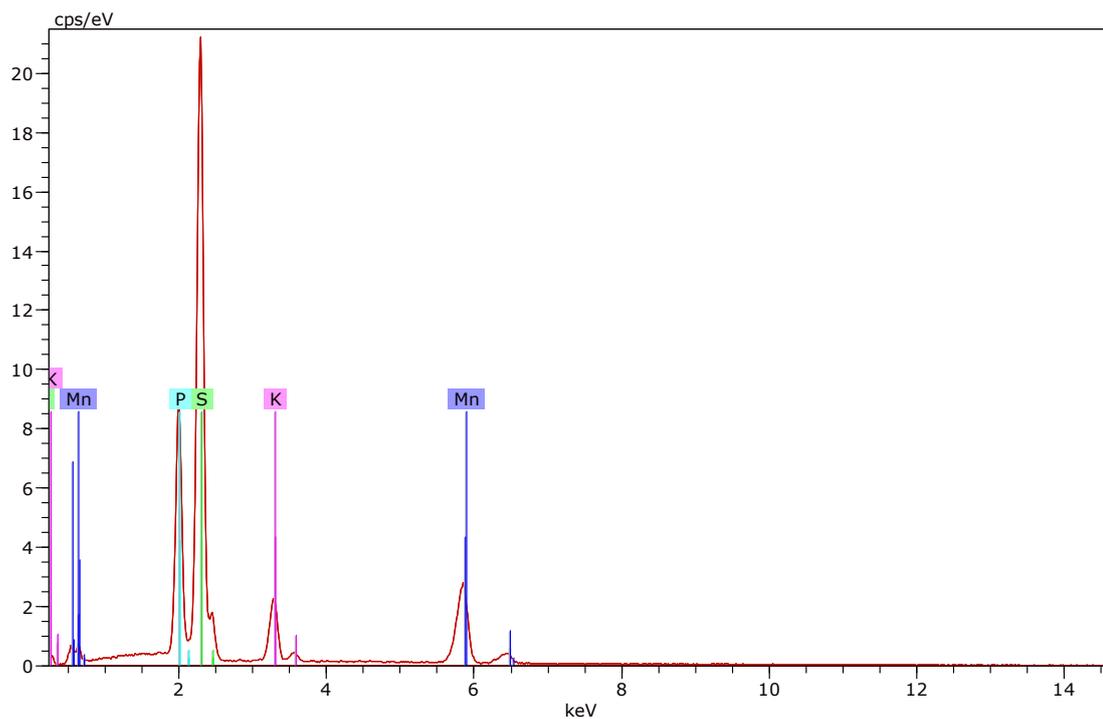


Fig. S4a: EDXS analysis of $K_{0.4}Mn_{0.8}PS_3 \cdot H_2O$

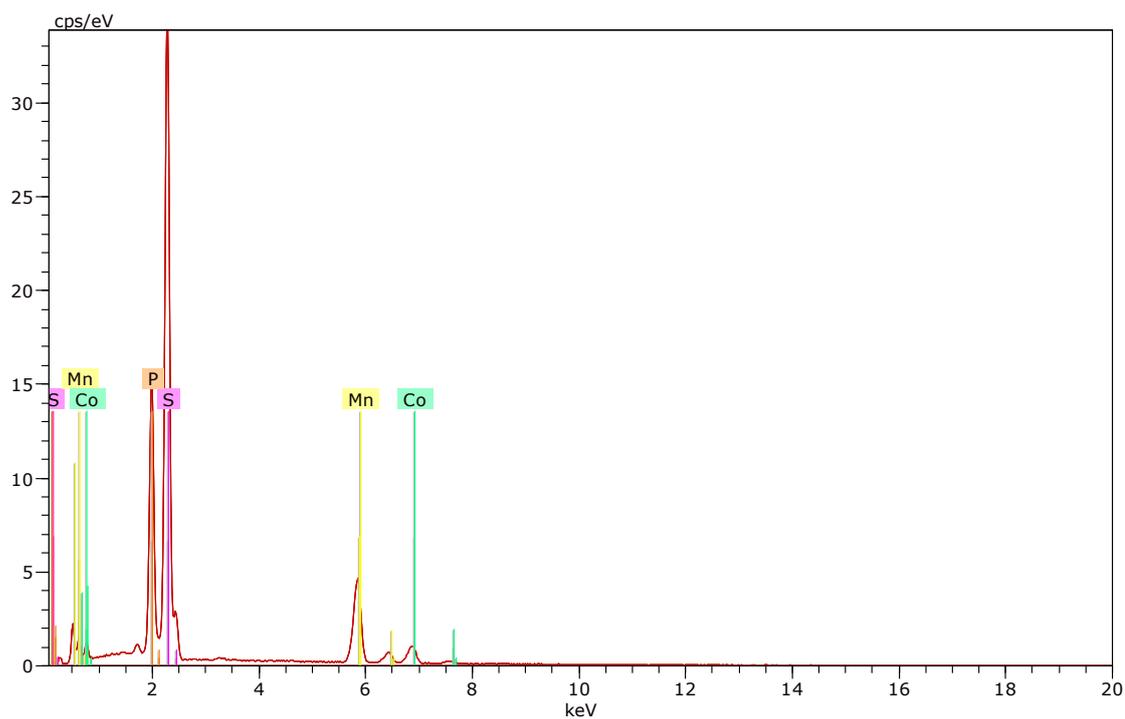


Fig. S4b: EDXS analysis of $Co_{0.2}Mn_{0.8}PS_3 \cdot 0.25H_2O$

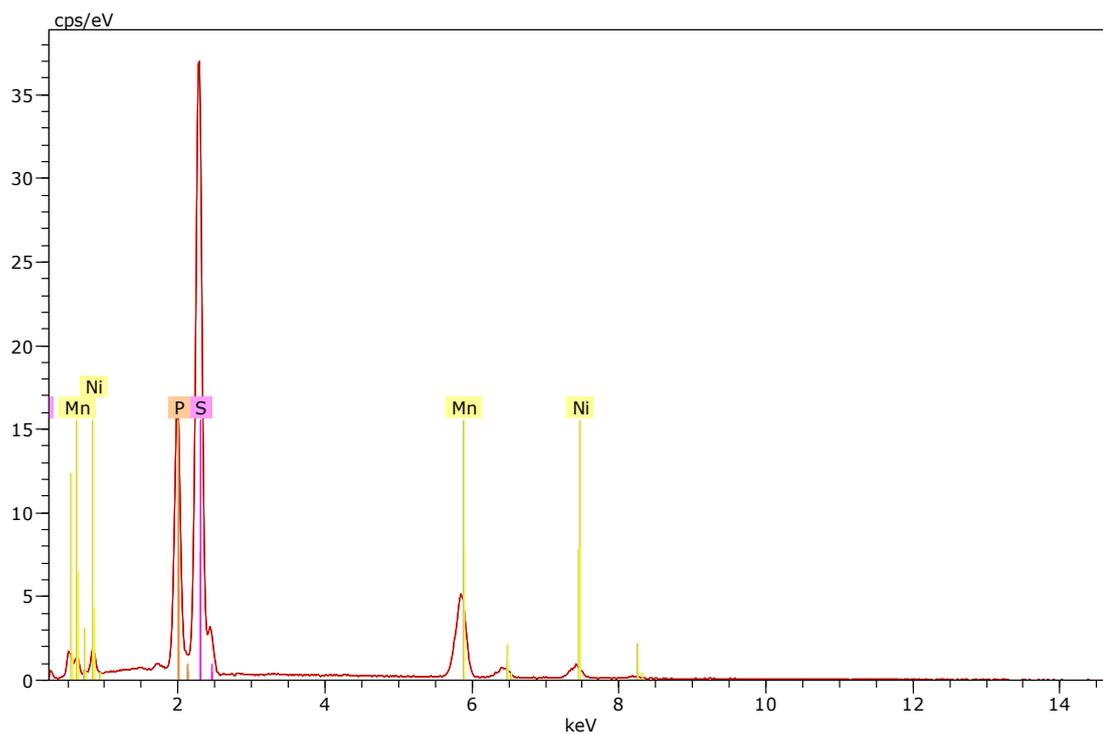


Fig. S4c: EDXS analysis of $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$

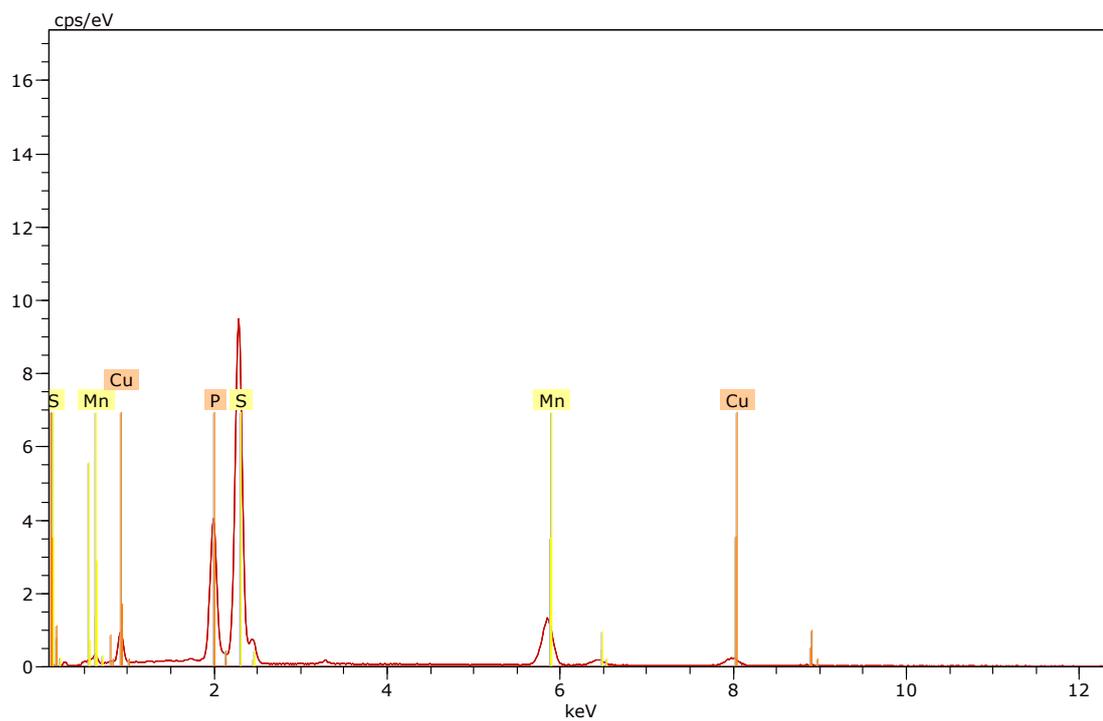


Fig. S4d: EDXS analysis of $\text{Cu}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$.

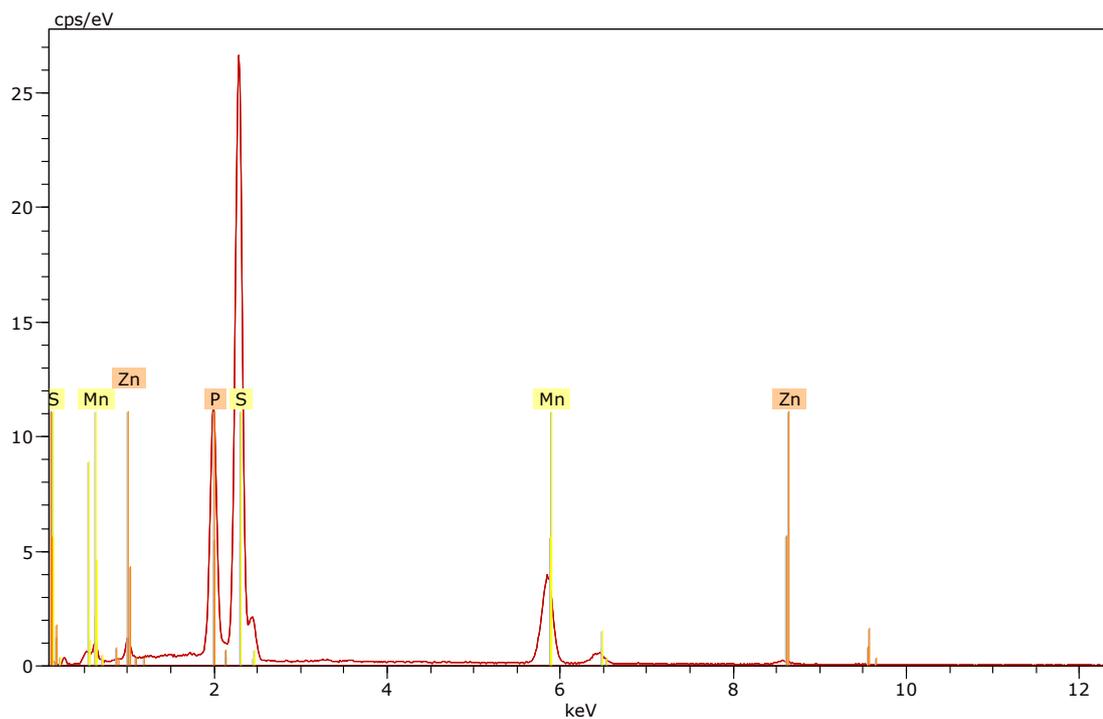


Fig. S4e: EDXS analysis of $\text{Zn}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$.

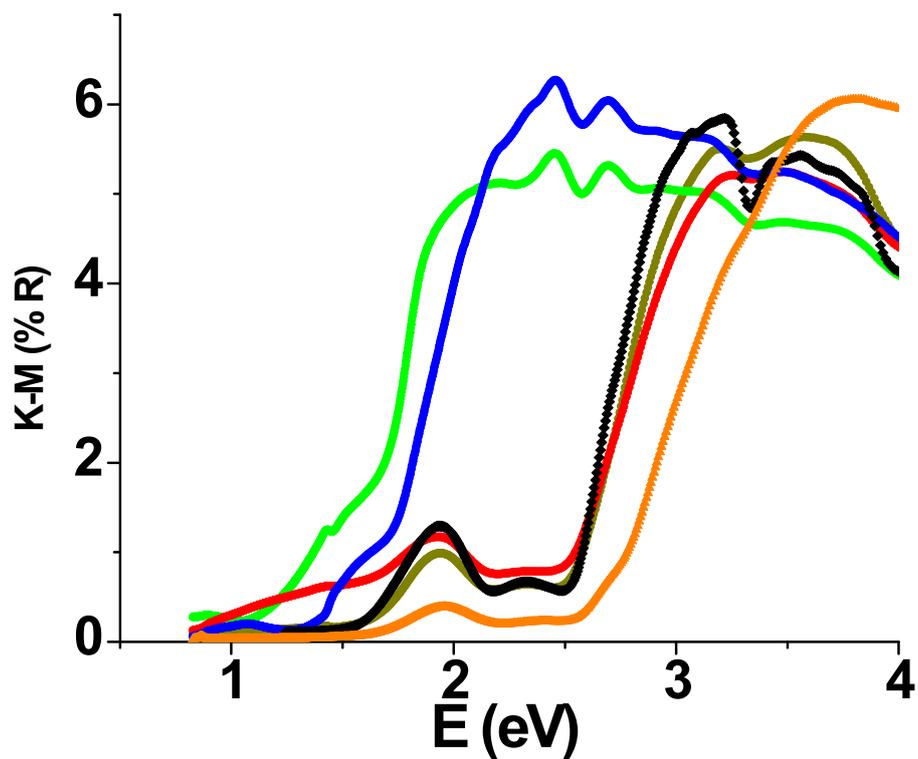


Fig. 5. Solid State UV-visible spectra of MnPS_3 (\blacklozenge), $\text{K}_{0.4}\text{Mn}_{0.8}\text{PS}_3 \cdot \text{H}_2\text{O}$ (\blacktriangle), $\text{Co}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$ (\bullet), $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$ (\bullet), $\text{Cu}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$ (\bullet) and $\text{Zn}_{0.2}\text{Mn}_{0.8}\text{PS}_3 \cdot 0.25\text{H}_2\text{O}$ (\bullet).

References.

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