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Supporting Information

Weakly Coordinating Borophosphates – $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$ (M = Mg, Mn, Co, Zn, Cd)

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Table of Contents

Powder X-ray Diffraction Pattern

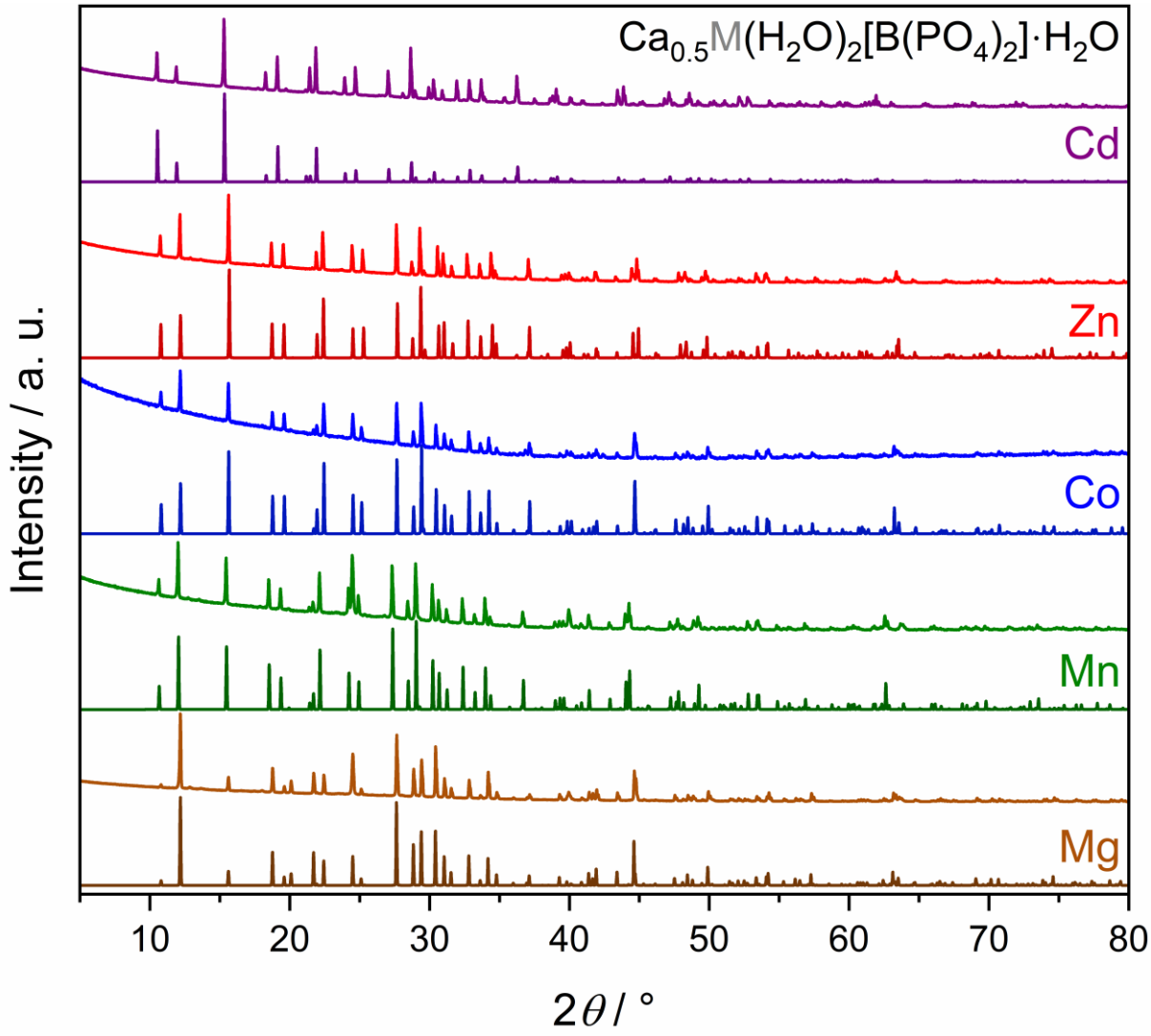

Figure S1. Powder X-ray diffraction patterns of $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$ (M = Mg, Mn, Co, Zn, Cd) compared to the calculated out of single-crystal data.

Rietveld Refinement

Table S1. Crystal data and structure refinement of $Ca_{0.5}Zn(H_2O)_2[B(PO_4)_2]\cdot H_2O$ determined from powered XRD data via Rietveld refinement. Respective standard deviations are given in parentheses

molar weight / g·mol^{-1}	340.21
Temperature / K	300(2)
space group	$P3_121$ (no. 152)
a / Å	9.4806(6)
c / Å	15.6269(3)
V / Å^3	1216.41(2)
Z	6
ρ / g·cm^{-3}	2.858(11)
radiation; wavelength λ / Å	Cu-K_α; 1.54184
diffractometer	Bruker D8 Advance
θ range / °	2.5-40
R_{Bragg}	0.019
R_p	0.020
R_{wp}	0.032
GooF	3.30
S.O.F Ca1A	0.249
S.O.F Ca1B	0.251

Crystal Data and Structure Refinements

Table S2. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $Ca_{0.5}Mg(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Mg1	6c		0.89782(13)	0.44890(16)	0.58336(7)	0.0126(3)
Ca1A	6c	0.2563(17)	0.8891(4)	0.2498(4)	0.74382(17)	0.0202(4)
Ca1B	6c	0.2437(17)	0.7514(4)	0.1108(5)	0.75595(18)	0.0202(4)
P1	6c		0.82964(11)	0.6130(1)	0.74707(5)	0.0085(2)
P2	6c		0.78303(11)	0.61304(10)	1.08612(5)	0.0086(2)
O1	6c		0.7073(3)	0.1955(3)	0.61647(16)	0.0205(6)
H11	6c		0.601(3)	0.190(5)	0.6117(19)	0.0250
H12	6c		0.714(4)	0.166(5)	0.6758(11)	0.0250
O2	6c		0.7072(3)	0.5119(3)	0.54972(15)	0.0199(6)
H21	6c		0.616(3)	0.409(3)	0.5283(19)	0.0240
H22	6c		0.668(4)	0.527(4)	0.6059(13)	0.0240
O11	6c		0.8193(3)	0.5833(3)	0.84547(13)	0.0105(5)
O12	6c		0.8588(3)	0.4848(3)	0.70781(14)	0.0162(6)
O13	6c		0.6817(3)	0.6169(3)	0.71478(13)	0.0149(5)
O14	6c		0.9782(3)	0.7878(3)	0.73164(14)	0.0112(5)
O21	6c		0.7644(3)	0.5839(3)	0.98784(12)	0.0106(5)
O22	6c		0.7873(3)	0.8086(3)	0.89901(13)	0.0103(5)
O23	6c		0.6260(3)	0.4848(3)	1.12533(14)	0.0160(6)
O24	6c		0.9357(3)	0.6178(3)	1.11842(14)	0.0142(5)
B1	6c		0.8494(5)	0.6977(4)	0.9169(2)	0.0090(7)
O3	3a		0.8513(6)	1	2/3	0.0661(18)
H31	6c	0.5	0.766(9)	0.992(11)	0.707(5)	0.0790
H32	6c	0.5	0.838(13)	0.888(6)	0.669(6)	0.0790
O4	3b		0.8510(6)	0.8510(6)	1/2	0.0703(18)
H41	6c	0.5	0.898(12)	0.969(4)	0.487(7)	0.0840
H42	6c	0.5	0.945(8)	0.832(11)	0.492(8)	0.0840

Table S3. Anisotropic displacement parameters U_{ij} / Å^2 in $Ca_{0.5}Mg(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Mg1	0.0099(5)	0.0134(7)	0.0139(5)	0.0054(6)	0.0001(4)	-0.0055(4)
Ca1A	0.0248(12)	0.0264(12)	0.0130(8)	0.0155(9)	0.0001(8)	-0.0001(8)
Ca1B	0.0248(12)	0.0264(12)	0.0130(8)	0.0155(9)	0.0001(8)	-0.0001(8)
P1	0.0086(5)	0.0086(4)	0.0069(3)	0.0031(4)	0.0004(3)	-0.0011(3)
P2	0.0113(5)	0.0082(4)	0.0066(3)	0.0050(4)	0.0018(3)	0.0008(3)
O1	0.0150(15)	0.0237(15)	0.0221(13)	0.0092(13)	-0.0005(11)	-0.0058(11)
O2	0.0160(15)	0.0187(15)	0.0216(13)	0.0062(13)	-0.0007(11)	-0.0083(11)
O11	0.0131(13)	0.0087(12)	0.0075(9)	0.0037(10)	0.0020(9)	0.0004(8)
O12	0.0215(15)	0.0154(14)	0.0124(11)	0.0097(12)	0.0021(10)	-0.0028(10)
O13	0.0101(12)	0.0208(14)	0.0113(10)	0.0058(11)	-0.0018(9)	-0.0025(10)
O14	0.0088(12)	0.0117(13)	0.0113(10)	0.0038(11)	-0.0008(9)	0.0027(9)

O21	0.0153(13)	0.0085(12)	0.0042(9)	0.0032(11)	0.0029(8)	-0.0003(8)
O22	0.0100(13)	0.0116(13)	0.0109(10)	0.0067(11)	0.0012(9)	0.0013(9)
O23	0.0162(13)	0.0119(14)	0.0139(11)	0.0025(11)	0.0056(10)	0.0013(9)
O24	0.0172(14)	0.0193(14)	0.0127(11)	0.0141(12)	-0.0017(10)	0.0006(10)
B1	0.0098(19)	0.0114(17)	0.0068(13)	0.0060(17)	0.0013(13)	-0.0013(14)
O3	0.039(3)	0.030(3)	0.127(6)	0.0151(16)	0.0075(18)	0.015(4)
O4	0.040(3)	0.040(3)	0.140(6)	0.027(3)	-0.0072(19)	0.0072(19)

Table S4. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Mn1	6c		0.09695(6)	0.54843(7)	0.41664(3)	0.01846(14)
Ca1A	6c	0.2531(19)	0.1057(4)	0.7483(4)	0.25694(16)	0.0226(4)
Ca1B	6c	0.2469(19)	0.2514(4)	0.8943(4)	0.24332(16)	0.0226(4)
P1	6c		0.1660(1)	0.3853(1)	0.25193(4)	0.01136(18)
P2	6c		0.21936(11)	0.38528(10)	-0.08518(4)	0.01129(18)
O1	6c		0.2964(3)	0.8118(4)	0.38021(16)	0.0248(6)
H11	6c		0.408(2)	0.834(6)	0.376(2)	0.0300
H12	6c		0.264(4)	0.818(6)	0.3221(12)	0.0300
O2	6c		0.2970(3)	0.4845(3)	0.45313(16)	0.0251(6)
H21	6c		0.396(3)	0.584(3)	0.470(2)	0.0300
H22	6c		0.325(4)	0.458(5)	0.3974(15)	0.0300
O11	6c		0.1822(3)	0.4152(3)	0.15436(12)	0.0143(5)
O12	6c		0.1373(3)	0.5139(3)	0.28823(14)	0.0204(5)
O13	6c		0.3095(3)	0.3813(3)	0.28759(14)	0.0187(5)
O14	6c		0.0191(3)	0.2140(3)	0.26672(13)	0.0133(4)
O21	6c		0.2328(3)	0.4152(3)	0.01235(12)	0.0142(5)
O22	6c		0.2141(3)	0.1950(3)	0.09955(13)	0.0132(4)
O23	6c		0.3769(3)	0.5137(3)	-0.12153(14)	0.0210(5)
O24	6c		0.0716(3)	0.3811(3)	-0.12085(14)	0.0186(5)
B1	6c		0.1515(5)	0.3036(4)	0.08317(18)	0.0113(6)
O3	3a		0.1450(8)	0	1/3	0.076(2)
H31	6c	0.5	0.234(11)	0.047(13)	0.291(7)	0.0910
H32	6c	0.5	0.152(16)	0.095(9)	0.362(8)	0.0910
O4	3b		0.1449(8)	0.1449(8)	1/2	0.077(2)
H41	6c	0.5	0.126(17)	0.096(17)	0.442(4)	0.0930
H42	6c	0.5	0.071(14)	0.190(16)	0.501(9)	0.0930

Table S5. Anisotropic displacement parameters U_{ij} / Å^2 in $Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Mn1	0.0146(2)	0.0198(3)	0.0192(2)	0.0074(2)	0.00001(19)	-0.00973(19)
Ca1A	0.0270(12)	0.0268(12)	0.0149(7)	0.0141(9)	0.0011(7)	0.0009(7)
Ca1B	0.0270(12)	0.0268(12)	0.0149(7)	0.0141(9)	0.0011(7)	0.0009(7)
P1	0.0129(4)	0.0118(4)	0.0071(3)	0.0044(3)	0.0010(2)	-0.0011(2)
P2	0.0155(4)	0.0111(4)	0.0073(3)	0.0067(3)	0.0021(3)	0.0012(2)
O1	0.0218(14)	0.0296(15)	0.0233(11)	0.0130(12)	0.0003(10)	-0.0069(11)

O2	0.0214(13)	0.0249(15)	0.0250(11)	0.0086(12)	-0.0016(10)	-0.0087(11)
O11	0.0194(12)	0.0120(11)	0.0083(8)	0.0054(10)	0.0016(8)	0.0004(7)
O12	0.0298(15)	0.0177(13)	0.0140(9)	0.0121(12)	0.0042(10)	-0.0023(9)
O13	0.0125(11)	0.0234(13)	0.0142(9)	0.0046(10)	-0.0033(8)	-0.0015(9)
O14	0.0120(11)	0.0136(11)	0.0126(9)	0.0051(9)	-0.0010(8)	0.0023(8)
O21	0.0202(13)	0.0117(10)	0.0075(8)	0.0056(10)	0.0017(8)	0.0004(7)
O22	0.0134(11)	0.0150(12)	0.0136(9)	0.0089(10)	0.0030(8)	0.0030(8)
O23	0.0228(13)	0.0167(13)	0.0155(10)	0.0038(11)	0.0073(9)	0.0025(9)
O24	0.0247(14)	0.0237(13)	0.0153(10)	0.0180(11)	-0.0008(9)	0.0020(9)
B1	0.0138(17)	0.0123(14)	0.0078(11)	0.0066(14)	0.0013(11)	0.0002(11)
O3	0.044(3)	0.042(3)	0.141(7)	0.0208(17)	0.006(2)	0.012(4)
O4	0.047(3)	0.047(3)	0.144(7)	0.028(3)	-0.003(2)	0.003(2)

Table S6. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $Ca_{0.5}Co(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Co1	6c		0.10143(5)	0.55074(6)	0.41671(3)	0.01193(12)
Ca1A	6c	0.2506(19)	0.1127(5)	0.7533(5)	0.2563(2)	0.0231(5)
Ca1B	6c	0.2494(19)	0.2463(5)	0.8867(5)	0.2436(2)	0.0231(5)
P1	6c		0.16936(11)	0.38870(11)	0.25301(5)	0.0084(2)
P2	6c		0.21926(12)	0.38871(11)	-0.08630(5)	0.0084(2)
O1	6c		0.2906(3)	0.8087(4)	0.38209(17)	0.0219(6)
H11	6c		0.407(2)	0.837(5)	0.379(2)	0.0260
H12	6c		0.264(4)	0.821(5)	0.3219(12)	0.0260
O2	6c		0.2911(3)	0.4825(4)	0.45159(17)	0.0217(6)
H21	6c		0.391(3)	0.573(3)	0.4774(19)	0.0260
H22	6c		0.327(4)	0.457(5)	0.3983(15)	0.0260
O11	6c		0.1829(3)	0.4201(3)	0.15501(13)	0.0096(5)
O12	6c		0.1413(3)	0.5191(3)	0.29116(14)	0.0159(6)
O13	6c		0.3152(3)	0.3829(3)	0.28719(15)	0.0136(5)
O14	6c		0.0198(3)	0.2155(3)	0.26771(15)	0.0096(5)
O21	6c		0.2366(3)	0.4194(3)	0.01190(13)	0.0103(5)
O22	6c		0.2158(3)	0.1962(3)	0.10063(15)	0.0098(5)
O23	6c		0.3779(3)	0.5188(3)	-0.12476(14)	0.0156(6)
O24	6c		0.0678(3)	0.3829(3)	-0.12045(15)	0.0137(6)
B1	6c		0.1534(5)	0.3059(4)	0.0834(2)	0.0093(7)
O3	3a		0.1427(7)	0	1/3	0.078(2)
H31	6c	0.5	0.225(12)	0.052(11)	0.287(5)	0.0930
H32	6c	0.5	0.157(14)	0.095(8)	0.368(6)	0.0930
O4	3b		0.1424(7)	0.1424(7)	1/2	0.082(2)
H41	6c	0.5	0.121(16)	0.086(14)	0.444(4)	0.0980
H42	6c	0.5	0.095(13)	0.215(11)	0.492(8)	0.0980

Table S7. Anisotropic displacement parameters U_{ij} / Å^2 in $Ca_{0.5}Co(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23

Co1	0.0109(2)	0.0125(3)	0.0118(2)	0.0054(2)	0.0000(2)	-0.00409(19)
Ca1A	0.0285(14)	0.0295(14)	0.0131(10)	0.0158(10)	-0.001(1)	-0.0006(10)
Ca1B	0.0285(14)	0.0295(14)	0.0131(10)	0.0158(10)	-0.001(1)	-0.0006(10)
P1	0.0079(4)	0.0085(4)	0.0067(4)	0.0026(4)	0.0014(3)	-0.0011(3)
P2	0.0107(5)	0.0086(4)	0.0066(4)	0.0055(4)	0.0025(3)	0.0013(3)
O1	0.0154(14)	0.0252(15)	0.0235(15)	0.0089(13)	-0.0005(12)	-0.0070(13)
O2	0.0171(14)	0.0236(16)	0.0219(15)	0.0082(12)	-0.0012(12)	-0.0096(13)
O11	0.0121(13)	0.0085(11)	0.006(1)	0.0036(10)	0.0021(9)	0.0007(9)
O12	0.0219(15)	0.0148(13)	0.0118(13)	0.0098(12)	0.0038(11)	-0.0025(11)
O13	0.0087(12)	0.0182(14)	0.0114(13)	0.0048(11)	-0.0012(10)	-0.0011(11)
O14	0.0066(11)	0.0106(13)	0.0105(12)	0.0035(10)	-0.0011(9)	0.0027(9)
O21	0.0143(13)	0.0082(11)	0.0066(10)	0.0043(10)	0.0017(9)	-0.0007(9)
O22	0.0101(13)	0.0106(13)	0.0109(12)	0.0069(11)	0.0015(10)	0.0028(10)
O23	0.0166(13)	0.0120(13)	0.0123(13)	0.0029(11)	0.0067(10)	0.0025(11)
O24	0.0184(14)	0.0211(14)	0.0095(13)	0.0158(12)	0.001(1)	0.0020(11)
B1	0.012(2)	0.0101(16)	0.0063(17)	0.0055(18)	0.0011(16)	-0.0005(14)
O3	0.044(3)	0.044(4)	0.144(7)	0.0221(19)	0.006(2)	0.011(4)
O4	0.043(3)	0.043(3)	0.164(7)	0.026(3)	-0.001(2)	0.001(2)

Table S8. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $Ca_{0.5}Zn(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Zn1	6c		0.09034(5)	0.54517(6)	0.41667(3)	0.01535(11)
Ca1A	6c	0.249(2)	0.1140(5)	0.7555(5)	0.2549(2)	0.0282(4)
Ca1B	6c	0.251(2)	0.2443(5)	0.8855(5)	0.2449(2)	0.0282(4)
P1	6c		0.16742(10)	0.3886(1)	0.25377(5)	0.00975(16)
P2	6c		0.22105(11)	0.38859(10)	-0.08713(5)	0.00987(16)
O1	6c		0.2897(4)	0.8089(4)	0.3807(2)	0.0286(7)
H11	6c		0.398(4)	0.820(7)	0.373(3)	0.0340
H12	6c		0.281(6)	0.827(8)	0.4422(13)	0.0340
O2	6c		0.2900(4)	0.4814(4)	0.4527(2)	0.0290(7)
H21	6c		0.389(4)	0.564(6)	0.483(3)	0.0350
H22	6c		0.330(6)	0.448(7)	0.403(2)	0.0350
O11	6c		0.1821(3)	0.4203(3)	0.15508(14)	0.0116(4)
O12	6c		0.1392(4)	0.5182(3)	0.29265(17)	0.0190(5)
O13	6c		0.3131(3)	0.3825(3)	0.28785(16)	0.0170(5)
O14	6c		0.0182(3)	0.2161(3)	0.26833(16)	0.0121(4)
O21	6c		0.2383(3)	0.4203(3)	0.01157(14)	0.0116(4)
O22	6c		0.2160(3)	0.1979(3)	0.10174(16)	0.0120(4)
O23	6c		0.3789(3)	0.5184(3)	-0.12614(17)	0.0195(5)
O24	6c		0.0695(3)	0.3825(3)	-0.12128(16)	0.0171(5)
B1	6c		0.1542(5)	0.3082(4)	0.0834(2)	0.0099(6)
O3	3a		0.1371(11)	0	1/3	0.116(5)
H31	6c	0.5	0.244(14)	0.07(2)	0.305(13)	0.1390
H32	6c	0.5	0.14(3)	0.07(2)	0.383(12)	0.1390
O4	3b		0.1366(11)	0.1366(11)	1/2	0.105(4)
H41	6c	0.5	0.14(3)	0.070(19)	0.453(10)	0.1260

H42	6c	0.5	0.18(3)	0.245(10)	0.474(11)	0.1260

Table S9. Anisotropic displacement parameters U_{ij} / Å^2 in $Ca_{0.5}Zn(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Zn1	0.01366(18)	0.0177(2)	0.01330(17)	0.00682(17)	0.00007(14)	-0.00626(14)
Ca1A	0.0346(13)	0.0360(14)	0.0151(8)	0.0183(10)	-0.0015(9)	-0.0018(9)
Ca1B	0.0346(13)	0.0360(14)	0.0151(8)	0.0183(10)	-0.0015(9)	-0.0018(9)
P1	0.0090(3)	0.0088(3)	0.0092(3)	0.0028(3)	0.0023(2)	-0.0016(3)
P2	0.0125(4)	0.0089(3)	0.0093(3)	0.0062(3)	0.0038(3)	0.0016(3)
O1	0.0223(15)	0.0339(17)	0.0279(15)	0.0128(13)	0.0001(12)	-0.0126(13)
O2	0.0232(15)	0.0306(17)	0.0288(15)	0.0102(13)	0.0000(12)	-0.0123(13)
O11	0.0146(11)	0.0105(10)	0.0083(9)	0.0052(9)	0.0030(8)	-0.0002(8)
O12	0.0283(15)	0.0126(11)	0.0164(11)	0.0104(11)	0.0086(10)	-0.0015(9)
O13	0.0102(11)	0.0236(13)	0.013(1)	0.0055(10)	-0.0005(8)	-0.0014(10)
O14	0.0084(10)	0.0107(11)	0.015(1)	0.0033(9)	-0.0010(8)	0.0026(8)
O21	0.0145(11)	0.0104(10)	0.0089(9)	0.0054(9)	0.0029(8)	0.0001(8)
O22	0.0110(11)	0.0123(11)	0.0146(10)	0.0072(9)	0.0026(8)	0.0031(9)
O23	0.0199(12)	0.0136(12)	0.0171(12)	0.0024(10)	0.0105(9)	0.0018(9)
O24	0.0222(13)	0.0233(13)	0.0143(11)	0.0178(11)	0.0009(10)	0.0016(10)
B1	0.0104(15)	0.0096(12)	0.0092(13)	0.0046(13)	0.0022(11)	-0.0002(11)
O3	0.049(4)	0.049(5)	0.249(17)	0.025(2)	0.015(4)	0.031(7)
O4	0.049(3)	0.049(3)	0.214(13)	0.023(4)	-0.014(3)	0.014(3)

Table S10. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $Ca_{0.5}Cd(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Cd1	6c		0.09587(4)	0.54798(5)	0.41657(3)	0.02635(14)
Ca1A	6c	0.249(2)	0.1000(6)	0.7448(6)	0.2583(3)	0.0206(7)
Ca1B	6c	0.251(2)	0.2550(6)	0.8999(6)	0.2426(3)	0.0206(7)
P1	6c		0.16238(17)	0.38393(16)	0.25088(8)	0.0127(3)
P2	6c		0.22099(18)	0.38400(16)	-0.08398(8)	0.0133(3)
O1	6c		0.2999(4)	0.8164(5)	0.3770(2)	0.0257(9)
H11	6c		0.240(4)	0.784(6)	0.3242(17)	0.0310
H12	6c		0.405(3)	0.831(6)	0.363(3)	0.0310
O2	6c		0.2993(4)	0.4832(5)	0.4561(2)	0.0265(10)
H21	6c		0.399(3)	0.579(4)	0.473(2)	0.0320
H22	6c		0.316(5)	0.470(6)	0.3959(12)	0.0320
O11	6c		0.1855(4)	0.4141(4)	0.15431(19)	0.0162(8)
O12	6c		0.1310(5)	0.5109(4)	0.2841(2)	0.0239(9)
O13	6c		0.3005(4)	0.3812(4)	0.2913(2)	0.0214(9)
O14	6c		0.0173(4)	0.2139(4)	0.2647(2)	0.0137(8)
O21	6c		0.2280(4)	0.4139(4)	0.01212(19)	0.0168(8)
O22	6c		0.2147(4)	0.1973(4)	0.0972(2)	0.0126(8)
O23	6c		0.3798(4)	0.5109(4)	-0.1163(2)	0.0250(9)
O24	6c		0.0800(4)	0.3809(4)	-0.1233(2)	0.0226(9)
B1	6c		0.1518(8)	0.3040(6)	0.0824(3)	0.0126(12)

O3	3a		0.1448(7)	0	1/3	0.076(3)
H31	6c	0.5	0.251(6)	0.074(13)	0.309(9)	0.0910
H32	6c	0.5	0.078(10)	0.046(14)	0.317(10)	0.0910
O4	3b		0.1457(9)	0.1457(9)	1/2	0.085(3)
H41	6c	0.5	0.067(14)	0.14(2)	0.459(8)	0.1020
H42	6c	0.5	0.097(16)	0.14(2)	0.556(5)	0.1020

Table S11. Anisotropic displacement parameters U_{ij} / Å^2 in $Ca_{0.5}Cd(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Cd1	0.0209(2)	0.0298(3)	0.0254(2)	0.0105(2)	0.0002(2)	-0.0169(2)
Ca1A	0.027(2)	0.024(2)	0.0120(17)	0.0131(14)	0.0027(15)	0.0009(15)
Ca1B	0.027(2)	0.024(2)	0.0120(17)	0.0131(14)	0.0027(15)	0.0009(15)
P1	0.0186(8)	0.0107(7)	0.0069(7)	0.0059(6)	0.0012(6)	-0.0017(5)
P2	0.0197(9)	0.0096(7)	0.0074(7)	0.0050(6)	0.0024(6)	0.0013(5)
O1	0.021(2)	0.030(2)	0.026(2)	0.013(2)	0.0004(18)	-0.007(2)
O2	0.023(2)	0.024(2)	0.025(2)	0.0060(19)	-0.0023(18)	-0.005(2)
O11	0.027(2)	0.0089(17)	0.0076(17)	0.0055(17)	0.0009(16)	0.0009(14)
O12	0.040(2)	0.018(2)	0.014(2)	0.0143(19)	0.002(2)	-0.0051(19)
O13	0.017(2)	0.029(2)	0.011(2)	0.0057(17)	-0.0060(17)	0.0002(18)
O14	0.017(2)	0.0126(19)	0.011(2)	0.0070(16)	-0.0024(15)	0.0003(16)
O21	0.029(2)	0.0111(17)	0.0061(17)	0.0066(16)	0.0034(16)	0.0007(15)
O22	0.0104(19)	0.0101(19)	0.014(2)	0.0031(17)	-0.0012(16)	0.0018(15)
O23	0.028(2)	0.015(2)	0.018(2)	0.0000(18)	0.0088(17)	0.0033(19)
O24	0.033(2)	0.027(2)	0.017(2)	0.0223(19)	-0.0015(18)	-0.0006(18)
B1	0.021(4)	0.012(3)	0.003(3)	0.008(3)	0.001(3)	0.000(2)
O3	0.044(3)	0.054(5)	0.134(9)	0.027(3)	0.011(3)	0.023(5)
O4	0.053(4)	0.053(4)	0.157(9)	0.031(4)	-0.011(3)	0.011(3)

Crystal Images

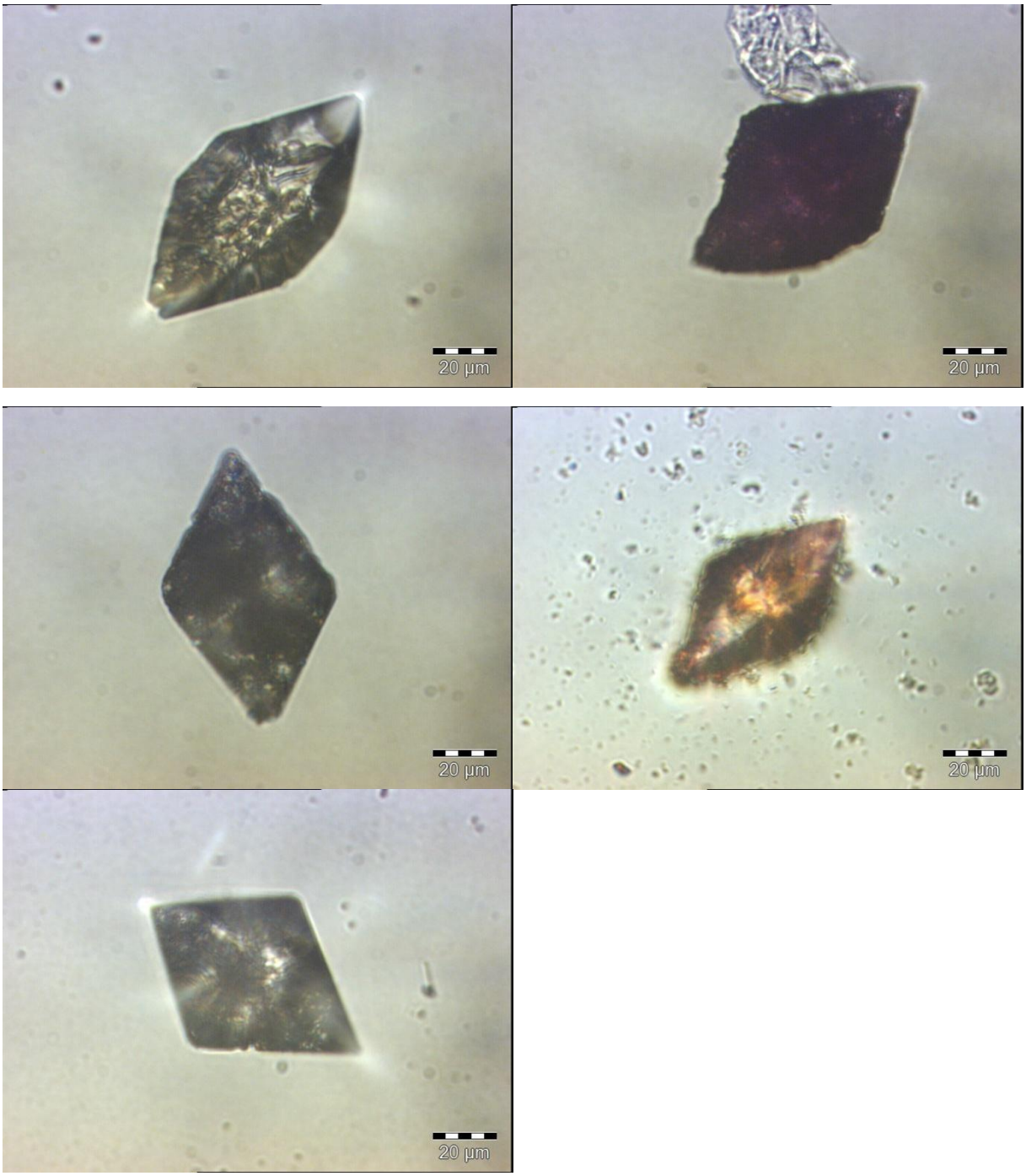

Figure S2. Microscope pictures of respective crystals of $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$. Order in reading direction M = Cd, Co, Zn, Mn, Mg.

UV-Vis Spectra and Tanabe-Sugano Analysis

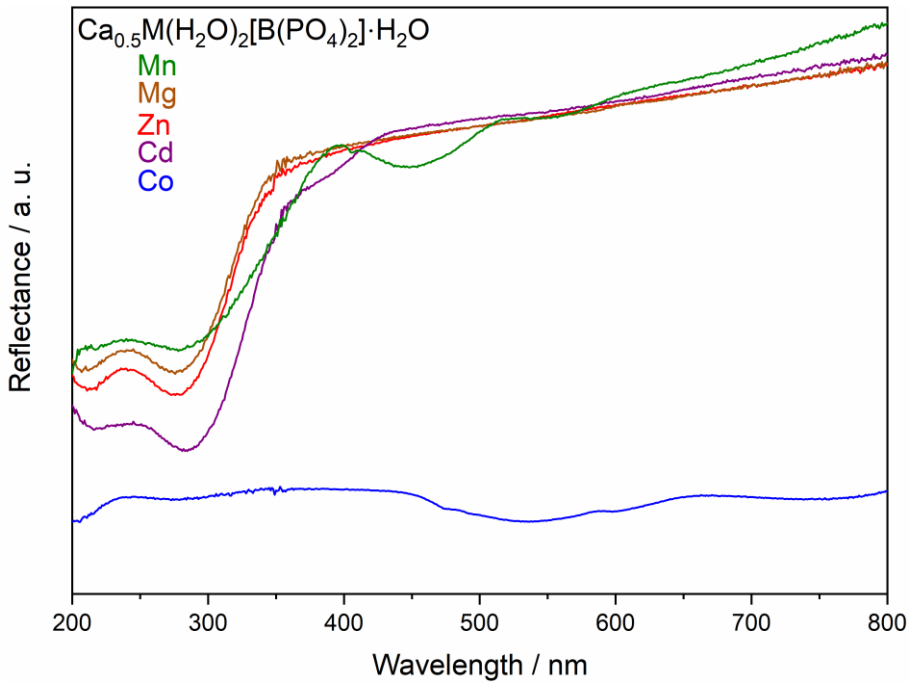

Figure S3. UV-vis spectra of $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$ (M = Mg, Mn, Co, Zn, Cd).

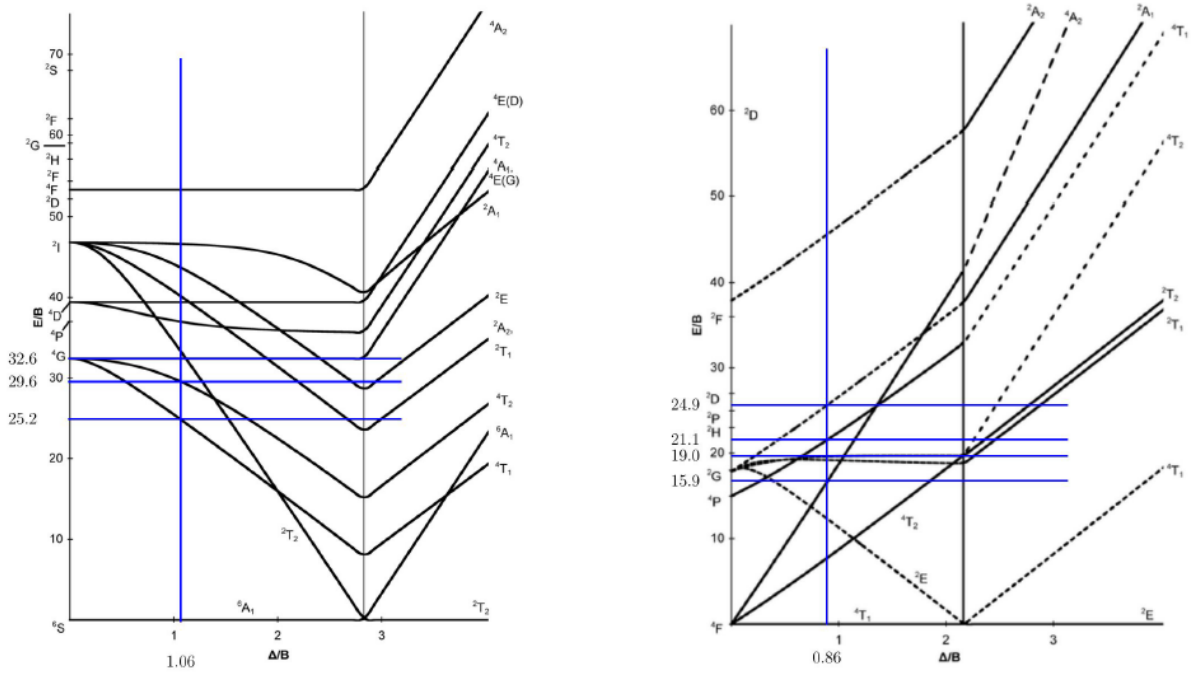

Figure S4. Tanabe-Sugano diagrams for Mn^{2+} (electronic configuration d^5) and Co^{2+} (electronic configuration d^7). Diagrams were taken and edited after [1,2].

Table S12. The assignment of the excited states to the respective wavelengths, the estimated energies *E*, the Racah parameter *B*, and the ligand field splitting *Δ* and for M = Mn. Standard deviations of *λ* were estimated from the fit data within the program OriginLab[3], following deviations were estimated by the partial derivatives

Mn^{2+} (d^5)	*λ* / nm	*E* / cm^{-1}	*E*/*B*	*B* / cm^{-1}

$^4A_1(G)$, $^4E(G)$	407.9(7)	24515(42)	32.6(1)	752(4)
$^4T_2(G)$	451.4(4)	22153(20)	29.6(1)	748(4)
$^4T_1(G)$	536.2(9)	18469(47)	25.2(1)	733(6)
				$\overline{B}$ = 744(5) cm^{-1}
				Δ = 789(13) cm^{-1}

Table S13. The assignment of the excited states to the respective wavelengths, the estimated energies E, the Racah parameter B, and the ligand field splitting Δ and for M = Co. Standard deviations of λ were estimated from the fit data within the program OriginLab[3], following deviations were estimated by the partial derivatives

Co^{2+} (d^7)	λ / nm	E / cm^{-1}	E/B	B / cm^{-1}
$^2A_1(G)$	474.8(5)	20958(22)	24.9(1)	842(4)
$^4T_1(P)$	533.3(2)	18752(7)	21.1(1)	889(5)
$^2T_2(G)$	612.3(9)	16332(24)	19.0(1)	858(6)
$^4A_2(F)$	734.1(9)	13622(17)	15.9(1)	856(6)
				$\overline{B}$ = 861(5) cm^{-1}
				Δ = 712(13) cm^{-1}

Thermal Analysis

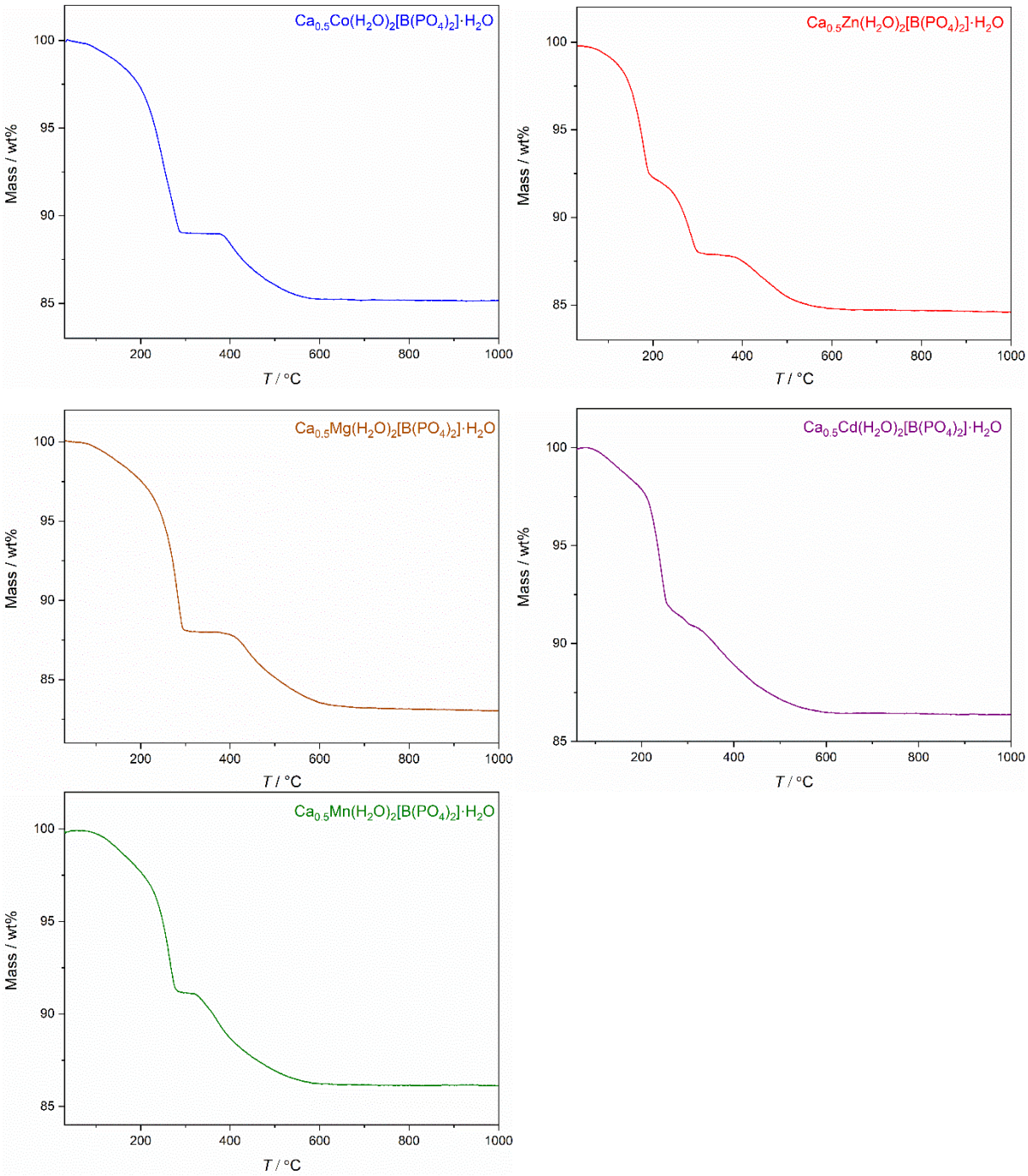

Figure S5. Thermogravimetric analysis of $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$ (M = Co, Zn, Mg, Cd, Mn).

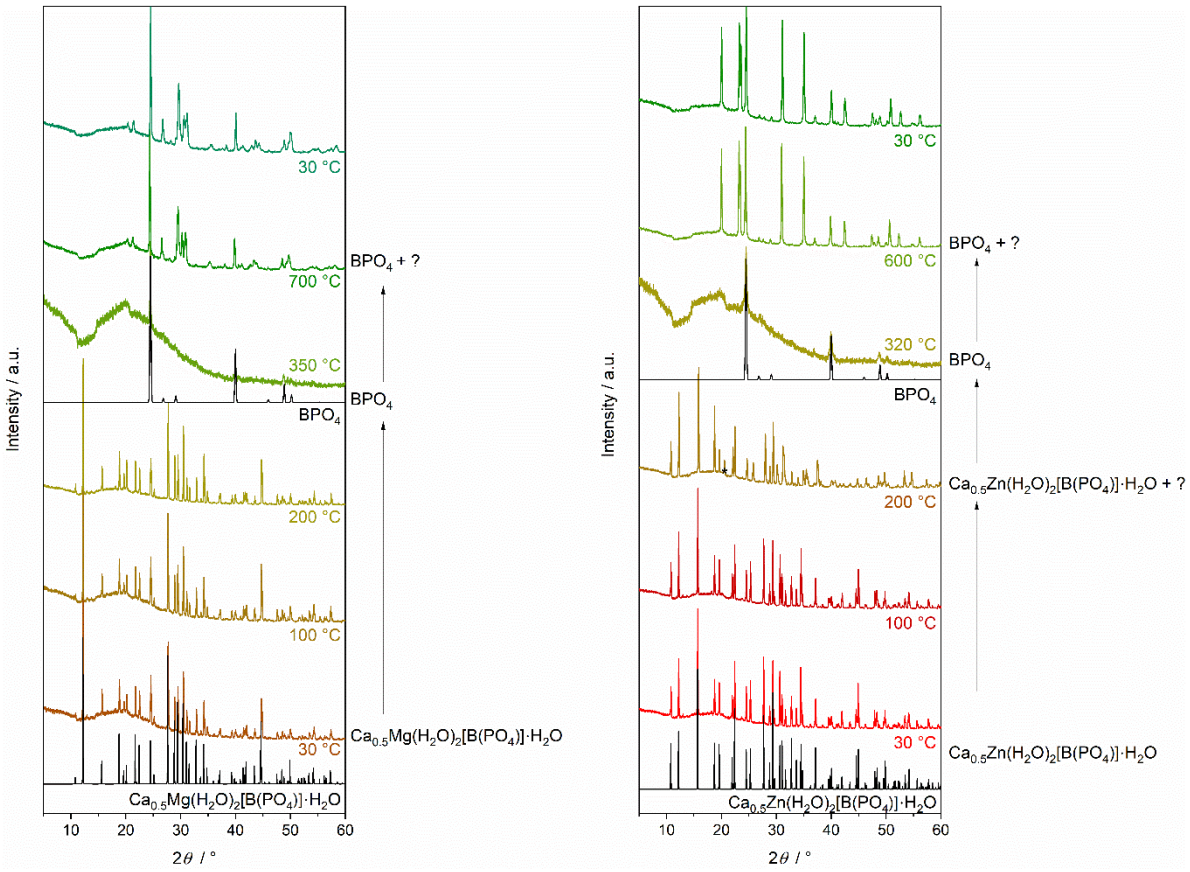

Figure S6. Varied Temperature Powder X-ray Diffraction (VT-PXRD) of $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$ (M = Zn, Mg).

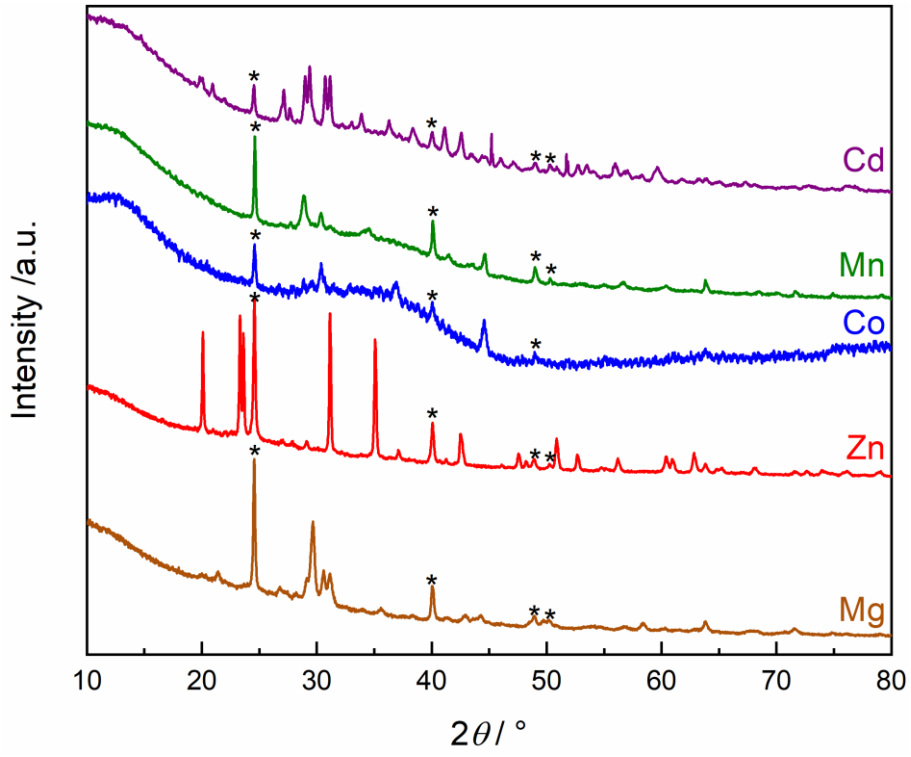

Figure S7. Powder X-ray diffraction patterns after thermogravimetric analysis of $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$ for M = Mg (700°C), M = Zn (600°C), M = Co, Mn, Cd (620°C). Asterisks mark the BPO_4 phase.

Energy Dispersive X-ray Spectroscopy

$Ca_{0.5}Mg(H_2O)_2[B(PO_4)_2]\cdot H_2O$

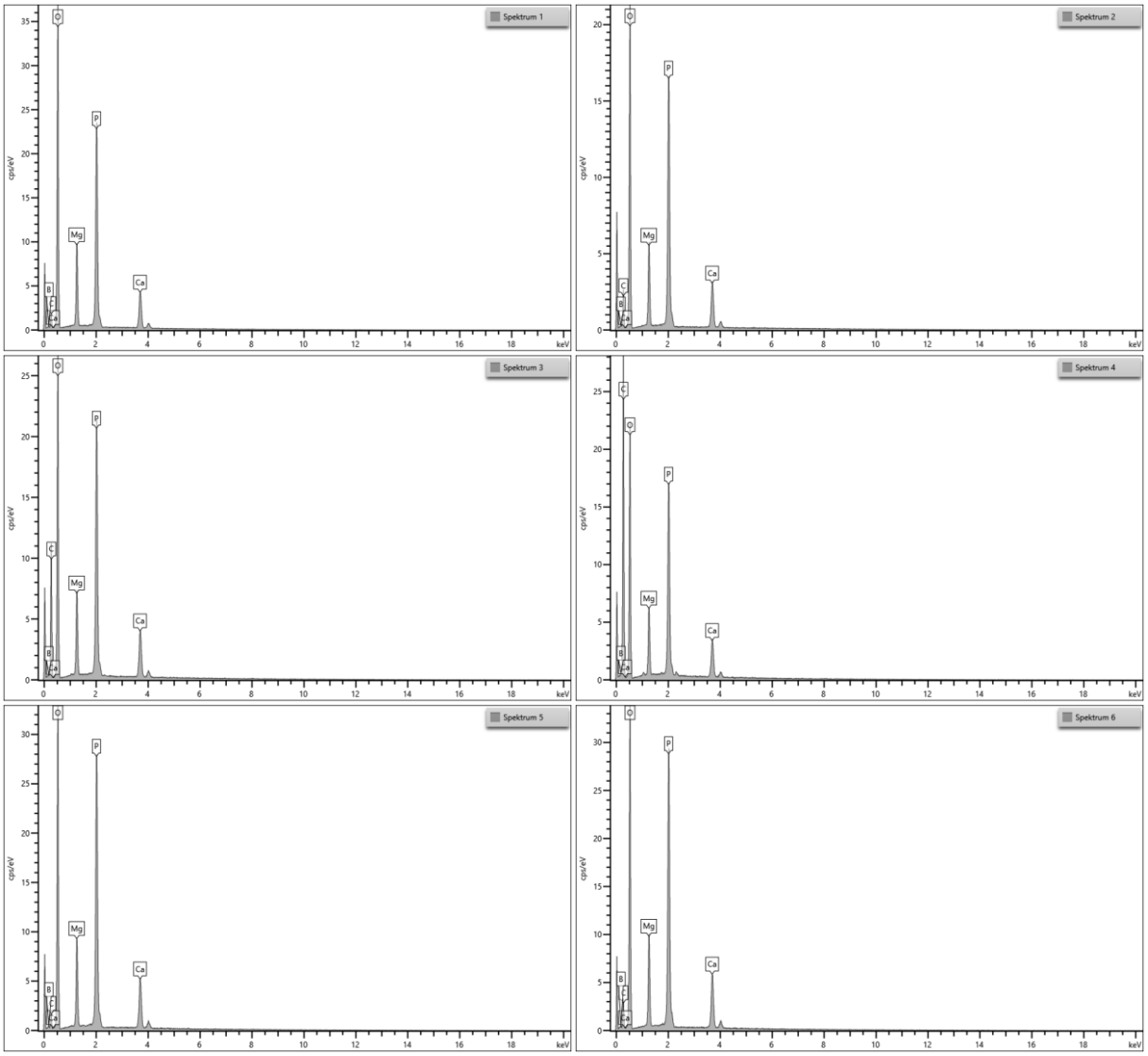

Figure S8. Energy dispersive X-ray spectra of $Ca_{0.5}Mg(H_2O)_2[B(PO_4)_2]\cdot H_2O$.

Table S14. Summary of energy dispersive X-ray spectroscopy of $Ca_{0.5}Mg(H_2O)_2[B(PO_4)_2]\cdot H_2O$ of the relevant ions compared to the expected values out of the sum formular from single-crystal X-ray diffraction. The elements B and O are neglected due to limit of accuracy of EDS measurements for light elements

$Ca_{0.5}Mg(H_2O)_2[B(PO_4)_2]\cdot H_2O$	Ø (Mass %)	Normalised to Ca	Expected according to sum formula
Ca	2.71	1	1
Mg	5.40	2	2
P	11.19	4	4

$Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$

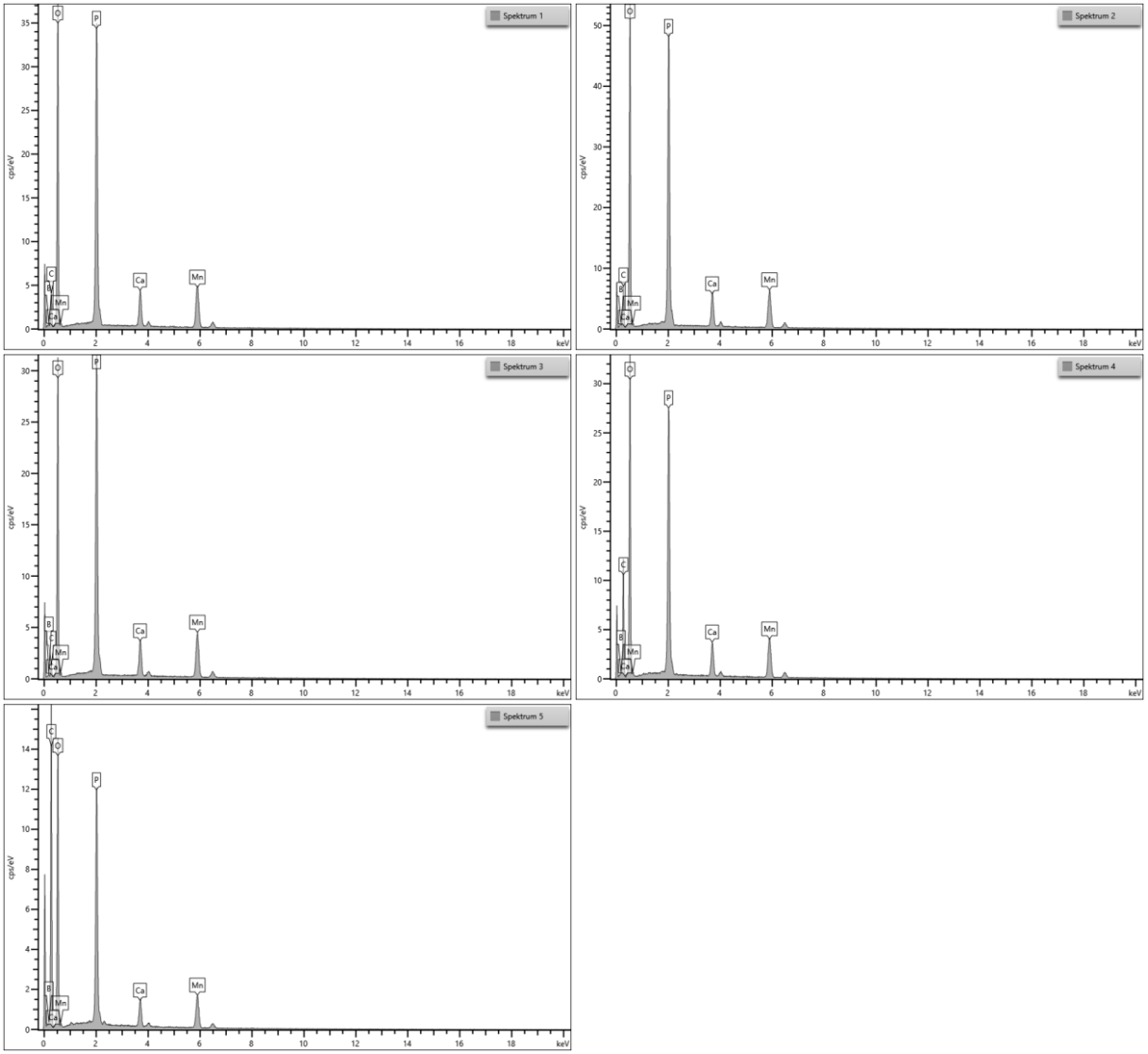

Figure S9. Energy dispersive X-ray spectra of $Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$.

Table S15. Summary of energy dispersive X-ray spectroscopy of $Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$ of the relevant ions compared to the expected values out of the sum formular from single-crystal X-ray diffraction. The elements B and O are neglected due to limit of accuracy of EDS measurements for light elements

$Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$	Ø (Mass %)	Normalised to Ca	Expected according to sum formula
Ca	1.87	1	1
Mn	3.89	2	2
P	12.06	6	4

$Ca_{0.5}Co(H_2O)_2[B(PO_4)_2]\cdot H_2O$

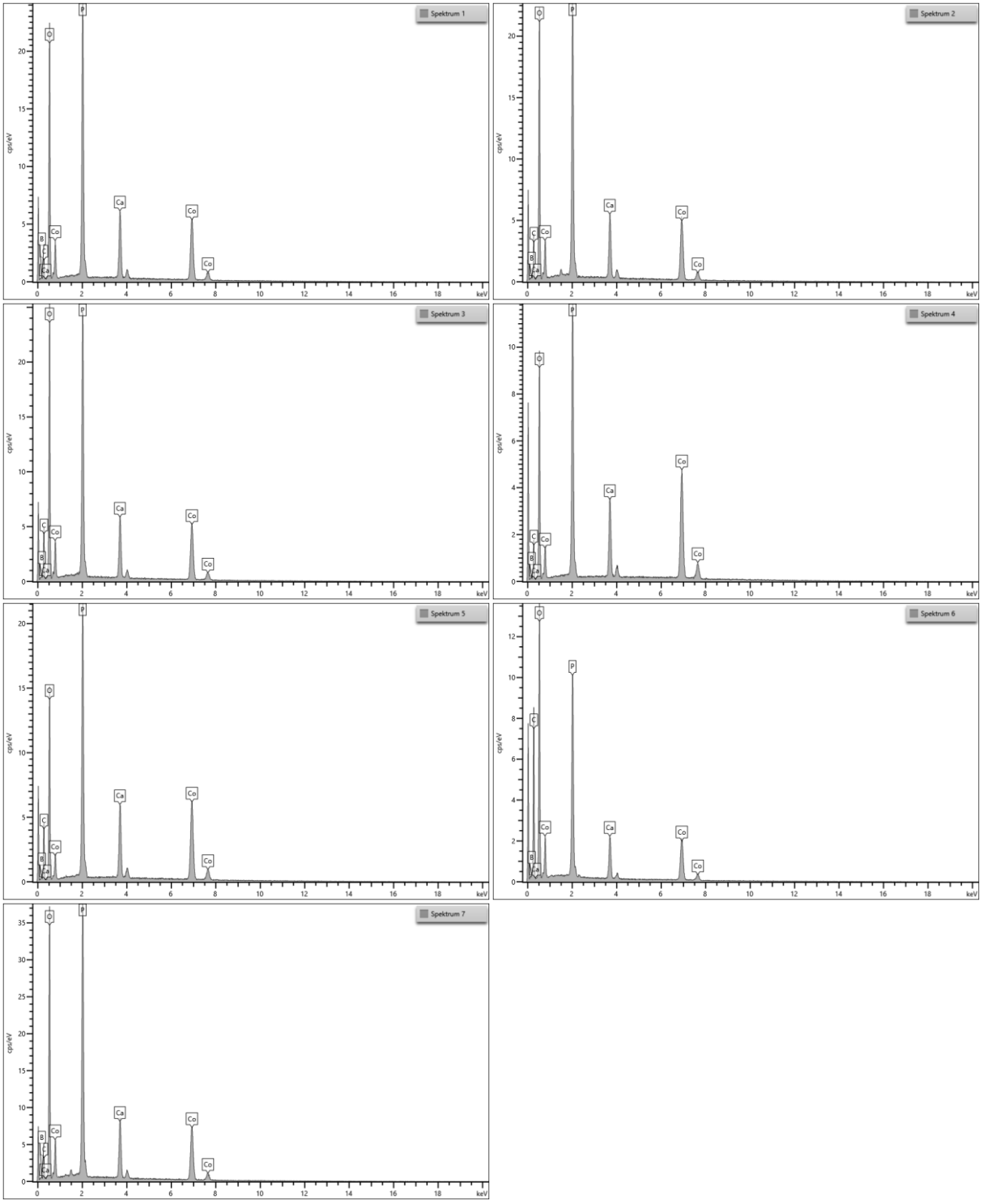

Figure S10. Energy dispersive X-ray spectra of $Ca_{0.5}Co(H_2O)_2[B(PO_4)_2]\cdot H_2O$.

Table S16. Summary of energy dispersive X-ray spectroscopy of $Ca_{0.5}Co(H_2O)_2[B(PO_4)_2]\cdot H_2O$ of the relevant ions compared to the expected values out of the sum formular from single-crystal X-ray diffraction. The elements B and O are neglected due to limit of accuracy of EDS measurements for light elements

$Ca_{0.5}Co(H_2O)_2[B(PO_4)_2]\cdot H_2O$	Ø (Mass %)	Normalised to Ca	Expected according to sum formula

Ca	3.83	1	1
Co	9.17	2	2
P	13.07	3	4

$Ca_{0.5}Zn(H_2O)_2[B(PO_4)_2]\cdot H_2O$

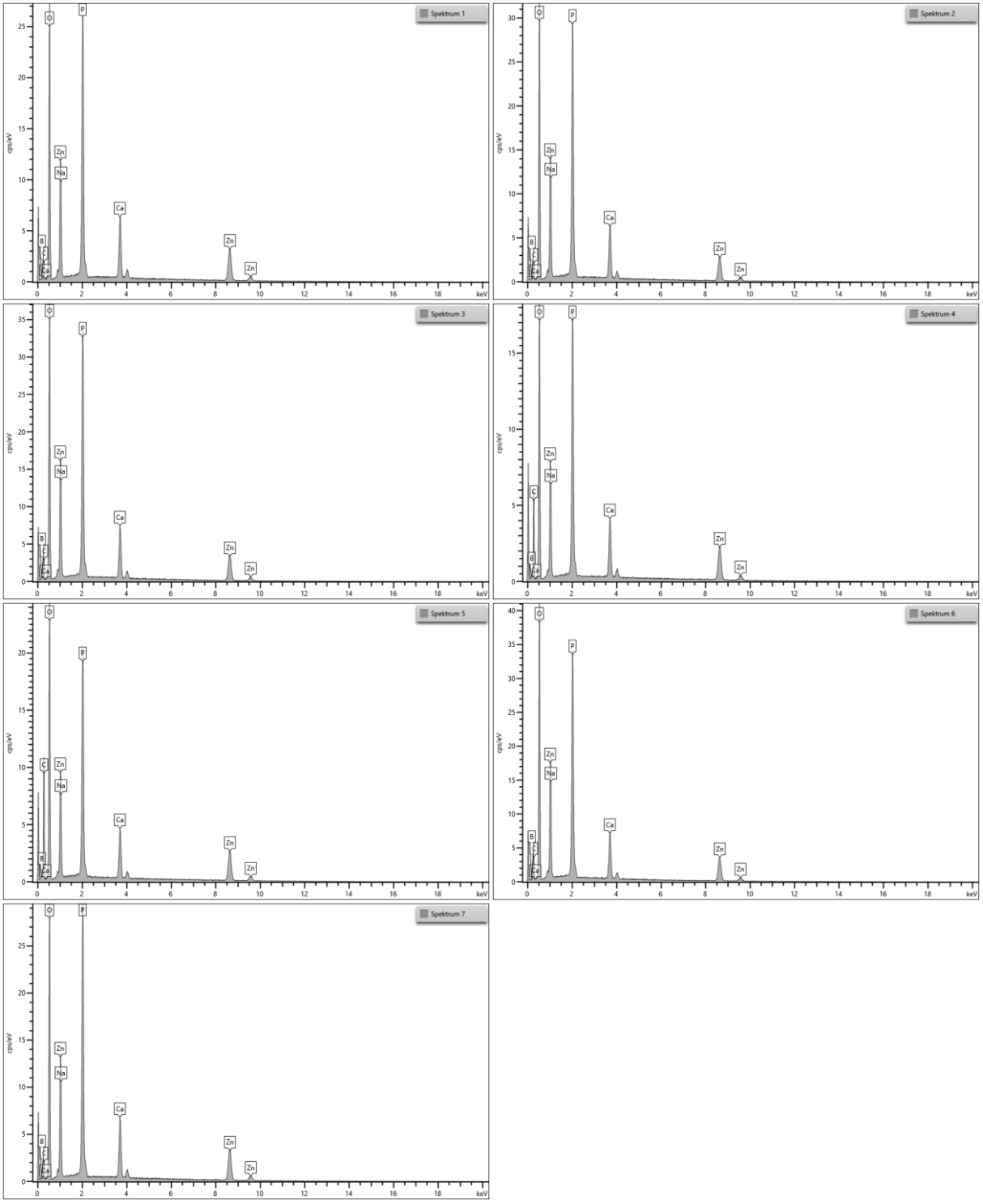

Figure S11. Energy dispersive X-ray spectra of $Ca_{0.5}Zn(H_2O)_2[B(PO_4)_2]\cdot H_2O$.

Table S17. Summary of energy dispersive X-ray spectroscopy of $Ca_{0.5}Zn(H_2O)_2[BO_6(PO_4)_2]\cdot H_2O$ of the relevant ions compared to the expected values out of the sum formular from single-crystal X-ray diffraction. The elements B and O are neglected due to limit of accuracy of EDS measurements for light elements

$Ca_{0.5}Zn(H_2O)_2[B(PO_4)_2]\cdot H_2O$	Ø (Mass %)	Normalised to Ca	Expected according to sum formula

Ca	3.12	1	1
Zn	6.23	2	2
P	12.17	4	4

$Ca_{0.5}Zn(H_2O)_2[B(PO_4)_2]\cdot H_2O$

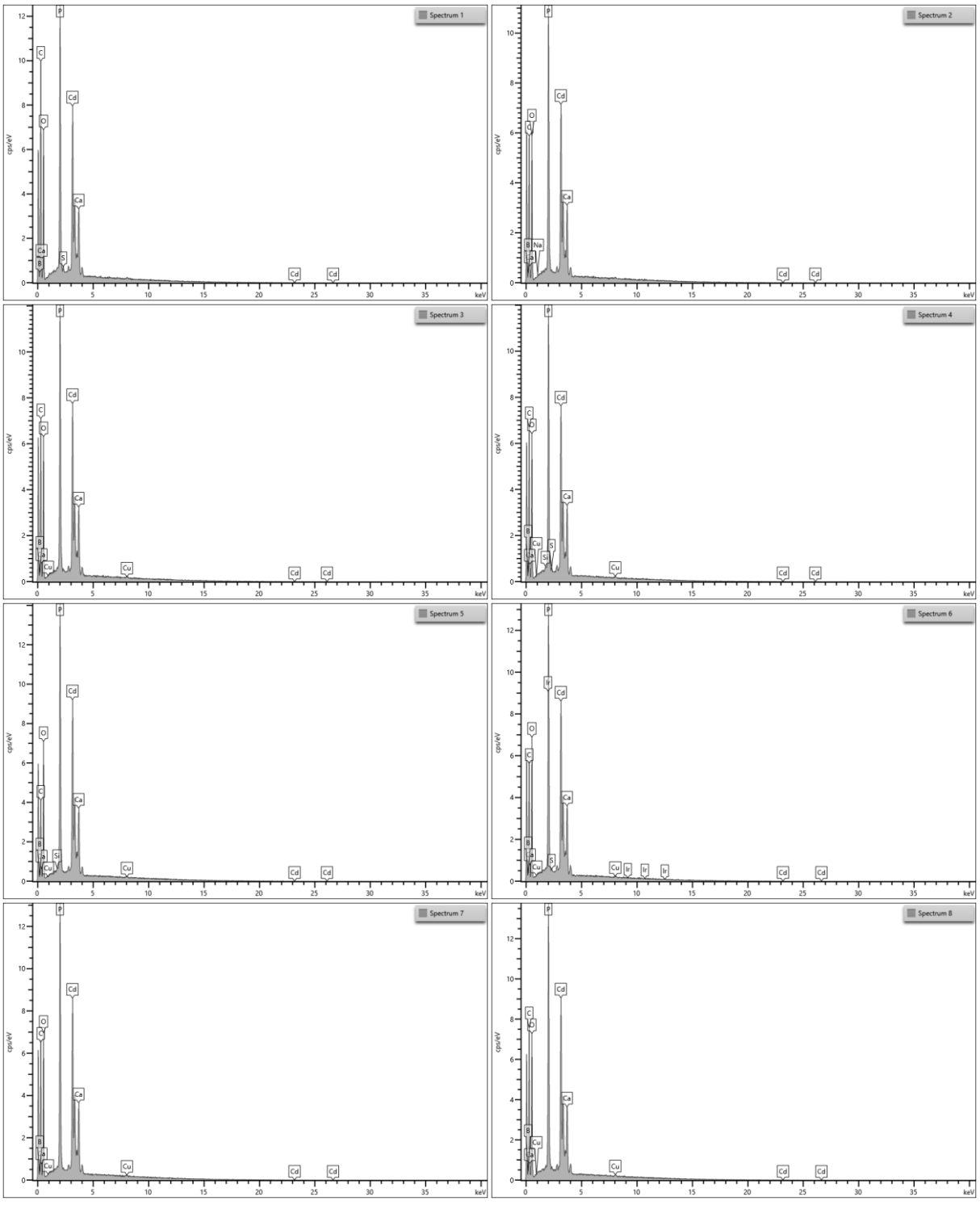

Figure S12. Energy dispersive X-ray spectra of $Ca_{0.5}Cd(H_2O)_2[B(PO_4)_2]\cdot H_2O$.

Table S18. Summary of energy dispersive X-ray spectroscopy of $Ca_{0.5}Zn(H_2O)_2[BO_6(PO_4)_2]\cdot H_2O$ of the relevant ions compared to the expected values out of the sum formular from single-crystal X-ray diffraction. The elements B and O are neglected due to limit of accuracy of EDS measurements for light elements

$Ca_{0.5}Cd(H_2O)_2[B(PO_4)_2]\cdot H_2O$	Ø (Mass %)	Normalised to Ca	Expected according to sum formula

Ca	0.75	1	1
Cd	1.54	2	2
P	2.99	4	4

Selected Ionic Radii after Shannon

Table S19. Ionic radii / pm after Shannon[4] with respect to their coordination number

Ion	Charge	Coordination	Ionic radius / pm
Mg	2	VI	72
Mn	2	VI	83 (high spin)
Co	2	VI	75 (high spin)
Zn	2	VI	74
Cd	2	VI	95
Ca	2	VI	100
Ca	2	VII	106
B	3	IV	11
P	5	IV	17
O	-2	II	135
O	-2	III	136
O	-2	IV	138

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MAPLE Calculations

Table S20. Calculated MAPLE values of the binary and tertiary compounds

Compound	MAPLE Value in kJ mol^{-1}
P_2O_5[5]	42887
B_2O_3[6]	21924
CaO[7]	4048
H_2O[8]	5017
MgO[9]	4605
MnO[9]	4368
CoO[9]	4555
ZnO[10]	4612
CdO[11]	4105

Symmetry Reduction and Systematically Absent Reflections

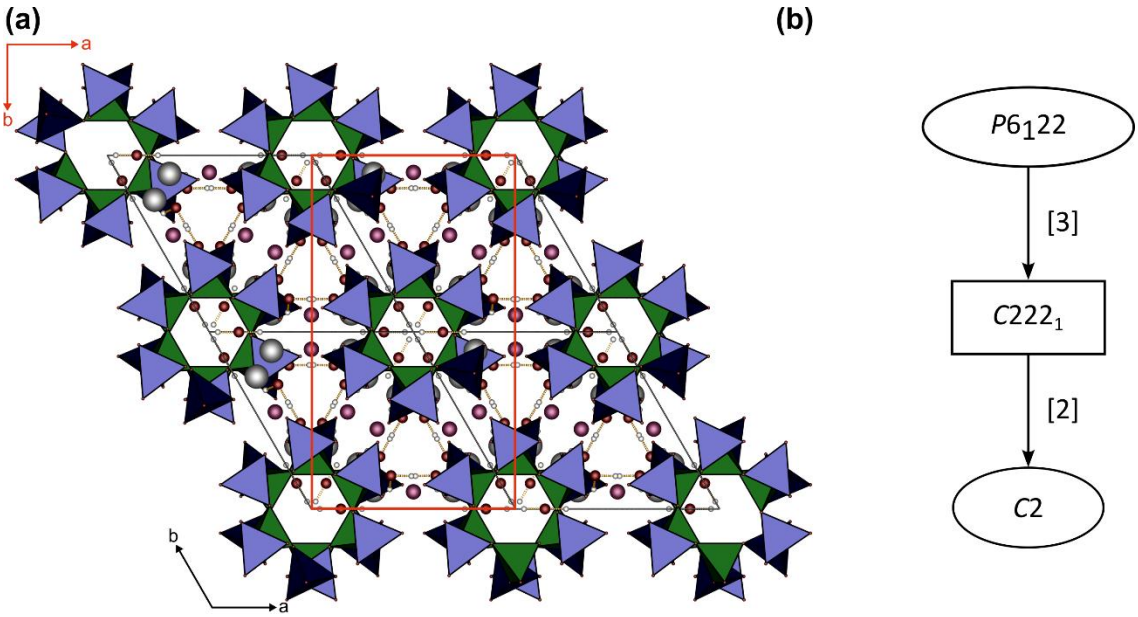


Figure S13. Relationship of the axis between the hexagonal (black) and monoclinic (red) crystal system (a) and schematic group-subgroup graph with index 6 (b).

Table S21. Comparison of refinement parameters during the symmetry reduction from the hexagonal to the monoclinic system

		$P6_522$/ $P6_122$	$C222_1$	$C211$	$P3_121$ $P3_221$
Mg	R_{int}	0.1797	0.1585	0.1534	0.1628
	R_1	0.0460	0.0580	0.0655	0.0357
	wR_2	0.1199	0.0675	0.0683	0.0697
	WGHT	0.0489	0.0294	0.0233	0.0347
		0.1209	0	0	0
Mn	R_{int}	0.1110	0.1099	0.1080	0.1104
	R_1	0.0263	0.0317	0.0378	0.0300
	wR_2	0.0640	0.0648	0.0704	0.0649
	WGHT	0.0353	0.0366	0.0376	0.0354
		0.8437	0.8802	0	0.5247
Co	R_{int}	0.0613	0.0422	0.1388	0.1447
	R_1	0.0308	0.0242	0.0520	0.0296
	wR_2	0.0958	0.0649	0.0587	0.0533
	WGHT	0.0421	0.0400	0.0183	0.0251
		0.05486	1.7501	0	0
Zn	R_{int}	0.0467	0.0279	0.0266	0.0284
	R_1	0.0370	0.0215	0.0223	0.0244
	wR_2	0.1170	0.0568	0.0564	0.0649
	WGHT	0.0421	0.0219	0.0164	0.0306
		0.5886	5.7433	4.8408	1.8764
Cd	R_{int}	0.2309	-	0.1968	0.2097
	R_1	0.0455	-	0.0914	0.0687
	wR_2	0.0556	-	0.0299	0.0467
	WGHT	0.0228	-	0	0.0119
		0	-	0	0

Table S22. First 21 systematically absent reflections rejected in $Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$, refined in the hexagonal space group $P6_122$. 190 systematically absent reflections rejected were observed in total

h	k	l	Fo^2	Sigma	Why rejected
0	0	3	1.16	0.25	systematically absent but >3sig(I)
0	0	3	1.73	0.25	systematically absent but >3sig(I)
0	0	3	1.29	0.25	systematically absent but >3sig(I)
0	0	3	1.16	0.24	systematically absent but >3sig(I)
0	0	3	1.41	0.28	systematically absent but >3sig(I)
0	0	3	1.29	0.24	systematically absent but >3sig(I)
0	0	3	1.41	0.25	systematically absent but >3sig(I)
0	0	3	1.44	0.28	systematically absent but >3sig(I)
0	0	3	1.63	0.25	systematically absent but >3sig(I)
0	0	3	1.22	0.24	systematically absent but >3sig(I)
0	0	3	1.70	0.29	systematically absent but >3sig(I)
0	0	3	1.35	0.11	systematically absent but >3sig(I)
0	0	3	1.59	0.24	systematically absent but >3sig(I)
0	0	3	1.78	0.24	systematically absent but >3sig(I)
0	0	3	1.87	0.32	systematically absent but >3sig(I)
0	0	3	0.68	0.12	systematically absent but >3sig(I)
0	0	9	0.66	0.16	systematically absent but >3sig(I)
0	0	9	0.69	0.18	systematically absent but >3sig(I)
0	0	9	0.86	0.14	systematically absent but >3sig(I)
0	0	15	0.81	0.26	systematically absent but >3sig(I)
0	0	17	0.99	0.33	systematically absent but >3sig(I)

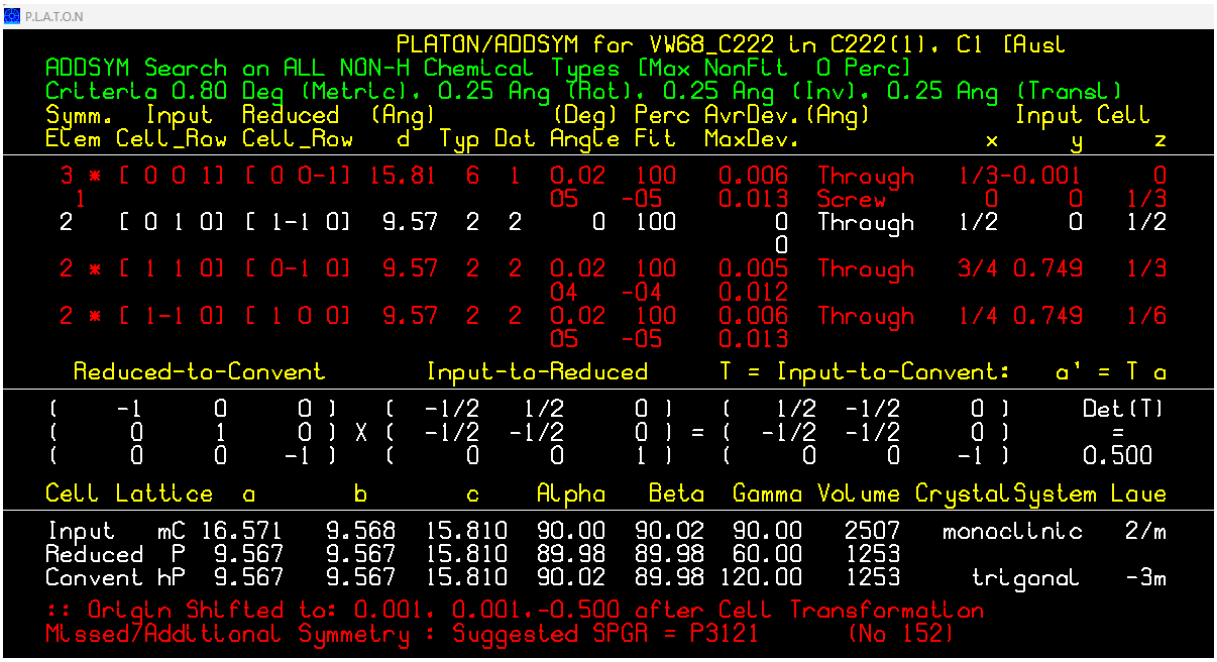
Table S23. Systematically absent violations in $Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$, refined in the orthorhombic space group $C222_1$. 18 systematically absent violations were observed in total

h	k	l	Fo^2	Sigma	Why rejected
0	0	3	1.16	0.25	observed but should be systematically absent
0	0	3	1.73	0.25	observed but should be systematically absent
0	0	3	1.29	0.25	observed but should be systematically absent
0	0	3	1.16	0.24	observed but should be systematically absent
0	0	3	1.41	0.28	observed but should be systematically absent
0	0	3	1.29	0.24	observed but should be systematically absent
0	0	3	1.41	0.25	observed but should be systematically absent
0	0	3	1.44	0.28	observed but should be systematically absent
0	0	3	1.63	0.25	observed but should be systematically absent
0	0	3	1.22	0.24	observed but should be systematically absent
0	0	3	1.70	0.29	observed but should be systematically absent
0	0	3	1.35	0.11	observed but should be systematically absent
0	0	3	1.59	0.24	observed but should be systematically absent
0	0	3	1.78	0.24	observed but should be systematically absent
0	0	3	1.87	0.32	observed but should be systematically absent
0	0	9	0.68	0.12	observed but should be systematically absent
0	0	9	0.66	0.16	observed but should be systematically absent
0	0	9	0.69	0.14	observed but should be systematically absent

Table S24. Chain stretching factors f_s[1] and pitch-to-radius ratios ξ[2] of the titled compounds $Ca_{0.5}M(H_2O)_2[B(PO_4)_2]\cdot H_2O$ ordered according to their relative ionic radii

M	*L*	*m*	*r*	f_s	ξ
Mg	15.73	3.61	2.47	0.727	6.36
Zn	15.59	3.62	2.53	0.717	6.17
Co	15.71	3.62	2.50	0.723	6.27
Mn	15.81	3.64	2.52	0.723	6.29
Cd	15.93	3.66	2.55	0.725	6.25

[1] f_s = *L* / (*m P*) with pitch length *L* repetition unit length *m*, and periodicity *P* (here *P*=6)
[2] ξ = L / *r*



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P.L.A.T.O.N

                PLATON/ADDSYM for VW68_C222 in C222(1). C1 [Ausl
ADDSYM Search on ALL NON-H Chemical Types [Max NonFit  0 Perc]
Criteria 0.80 Deg (Metric), 0.25 Ang (Rot), 0.25 Ang (Inv), 0.25 Ang (Transl)
Symm.  Input  Reduced  (Ang)        (Deg) Perc AvrDev.(Ang)          Input Cell
Elem Cell_Raw Cell_Raw   d  Typ Dot Angle Fit  MaxDev.                x      y      z
 3 * [ 0 0 1] [ 0 0-1] 15.81  6   1  0.02  100  0.006  Through  1/3-0.001      0
  1                              05   -05   0.013  Screw        0      0    1/3
 2   [ 0 1 0] [ 1-1 0]  9.57  2   2     0  100     0  Through  1/2      0    1/2
                                                   0
 2 * [ 1 1 0] [ 0-1 0]  9.57  2   2  0.02  100  0.005  Through  3/4  0.749    1/3
                                04   -04   0.012
 2 * [ 1-1 0] [ 1 0 0]  9.57  2   2  0.02  100  0.006  Through  1/4  0.749    1/6
                                05   -05   0.013

  Reduced-to-Convent       Input-to-Reduced     T = Input-to-Convent:   a' = T a

(    -1     0     0 )   (  -1/2   1/2     0 )   (   1/2  -1/2     0 )     Det(T)
(     0     1     0 ) X (  -1/2  -1/2     0 ) = (  -1/2  -1/2     0 )       =
(     0     0    -1 )   (     0     0     1 )   (     0     0    -1 )   0.500

Cell Lattice  a        b        c       Alpha   Beta   Gamma  Volume CrystalSystem Laue
Input    mC 16.571   9.568   15.810   90.00   90.02  90.00    2507   monoclinic   2/m
Reduced  P   9.567   9.567   15.810   89.98   89.98  60.00    1253
Convent hP   9.567   9.567   15.810   90.02   89.98 120.00    1253     trigonal   -3m
:: Origin Shifted to: 0.001, 0.001,-0.500 after Cell Transformation
Missed/Additional Symmetry : Suggested SPGR = P3121      (No 152)
```

Figure S14. Platon ADDSYM report of $Ca_{0.5}Mn(H_2O)_2[B(PO_4)_2]\cdot H_2O$ in *C*211 (no. 5). Due to the pseudosymmetry, the hexagonal space group $P6_122$ (no. 178) is suggested.

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