crystals

MDPI

Supplementary Materials: Mixed Metal Phosphonates: Structure and Proton Conduction Manipulation through Various Alkaline Earth Metal Ions

Song-Song Bao *, Nan-Zhu Li, Yu-Xuan Wu and Yang Shen

1. Single crystal details

Table S1. Crystallographic data for **CoMg·4H$_2$O**, **CoSr·2H$_2$O,** and **CoBa**.

	CoMg·4H$_2$O	**CoSr·2H$_2$O**	**CoBa**
Formula	$C_9H_{32}N_3O_{19}P_3ClCoMg$	$C_{18}H_{54}N_6O_{33}P_6Cl_2Co_2Sr_2$	$C_{18}H_{43}N_6O_{29}P_6Cl_2Co_2Ba_2$
M	697.97	1432.50	1456.84
Crystal size [mm]	0.30 × 0.10 × 0.05	0.40 × 0.10 × 0.10	0.30 × 0.30 × 0.05
crystal system	Monoclinic	Triclinic	Trigonal
space group	$P2_1/n$	P-1	R-3c
a [Å]	14.7564(13)	8.867(3)	8.5991(15)
b [Å]	9.9760(9)	16.131(6)	8.5991(15)
c [Å]	18.0294(16)	17.132(6)	97.615(18)
α [Å]	90	90.702(6)	90
β [Å]	109.893(2)	96.716(6)	90
γ [Å]	90	96.613(6)	120
V [Å^3]	2495.7(4)	2416.6(15)	6251(3)
Z	4	2	6
D_c [g cm^{-3}]	1.858	1.969	2.322
μ [mm^{-1}]	1.103	3.283	3.113
F(000)	1440	1444	4290
R_{int}	0.075	0.054	0.049
GoF on F^2	1.01	1.02	1.12
R_1,wR_2[a] [$I>2\sigma(I)$]	0.0570, 0.1354	0.0664, 0.1514	0.0940, 0.2339
(all data)	0.1068, 0.1589	0.1290, 0.1832	0.0993, 0.2374
$(\Delta\rho)_{max}$,$(\Delta\rho)_{min}$/eÅ^{-3}	1.08, -0.86	1.99, -1.77	1.86, -3.09
CCDC number	2214708	2214709	2214710

Table S2. Selected bond lengths (Å) and angles (°) for **CoMg·4H$_2$O**

Co(1)-N(1)	1.937(5)	Mg(1)-O(2A)	2.040(4)
Co(1)-N(2)	1.944(6)	Mg(1)-O(7B)	2.070(5)
Co(1)-N(3)	1.941(5)	Mg(1)-O(8C)	2.078(5)
Co(1)-O(1)	1.930(4)	Mg(1)-O(5)	2.031(5)
Co(1)-O(4)	1.952(4)	Mg(1)-O(1W)	2.263(4)
Co(1)-O(9)	1.925(4)	Mg(1)-O(2W)	2.182(5)
P(1)-O(1)	1.524(4)	P(2)-O(6)	1.554(5)
P(1)-O(2)	1.495(4)	P(3)-O(7)	1.517(4)
P(1)-O(3)	1.575(5)	P(3)-O(8)	1.510(4)
P(2)-O(4)	1.535(4)	P(3)-O(9)	1.548(4)
P(2)-O(5)	1.480(5)		
N(1)-Co(1)-N(2)	88.9(2)	O(5)-Mg(1)-O(1W)	85.7(2)
N(1)-Co(1)-N(3)	88.7(2)	O(5)-Mg(1)-O(2W)	89.9(2)
N(1)-Co(1)-O(1)	88.6(2)	O(5)-Mg(1)-O(2A)	92.6(2)
N(1)-Co(1)-O(4)	178.3(2)	O(5)-Mg(1)-O(7B)	91.7(2)
N(1)-Co(1)-O(9)	92.1(2)	O(5)-Mg(1)-O(8C)	175.9(2)
N(2)-Co(1)-N(3)	88.2(2)	O(1W)-Mg(1)-O(2W)	79.7(2)
N(2)-Co(1)-O(1)	90.8(2)	O(1W)-Mg(1)-O(2A)	172.5(2)
N(2)-Co(1)-O(4)	89.8(2)	O(1W)-Mg(1)-O(7B)	87.5(2)
N(2)-Co(1)-O(9)	177.9(2)	O(1W)-Mg(1)-O(8C)	90.8(2)
N(3)-Co(1)-O(1)	177.2(2)	O(2W)-Mg(1)-O(2A)	93.1(2)
N(3)-Co(1)-O(4)	92.3(2)	O(2W)-Mg(1)-O(7B)	166.9(2)
N(3)-Co(1)-O(9)	90.0(2)	O(2W)-Mg(1)-O(8C)	87.5(2)
O(1)-Co(1)-O(4)	90.4(2)	O(2A)-Mg(1)-O(7B)	99.9(2)
O(1)-Co(1)-O(9)	91.1(2)	O(2A)-Mg(1)-O(8C)	90.7(2)
O(4)-Co(1)-O(9)	89.3(2)	O(7B)-Mg(1)-O(8C)	90.1(2)

Symmetrical codes: A: 1/2-x,-1/2+y, 1/2-z; B:x,-1+y, z; C:-x,-y,-z

Table S3. Selected bond lengths (Å) and angles (°) for **CoSr·2H$_2$O**

Sr(1)-O(1W)	2.659(5)	Co(2)-O(16)	1.952(5)
Sr(1)-O(2)	2.641(5)	Co(2)-N(4)	1.932(7)
Sr(1)–O(2W)	2.603(6)	Co(2)-N(5)	1.960(7)
Sr(1)-O(4)	2.595(5)	Co(2)-N(6)	1.939(7)
Sr(1)-O(10)	2.453(5)	P(1)-O(1)	1.489(5)
Sr(1)-O(8B)	2.478(5)	P(1)-O(2)	1.541(5)
Sr(1)-O(4A)	2.592(5)	P(1)-O(3)	1.552(5)
Sr(2)–O(1)	2.472(5)	P(2)-O(4)	1.495(5)
Sr(2)-O(3W)	2.693(5)	P(2)-O(5)	1.533(5)
Sr(2)-O(4W)	2.603(5)	P(2)-O(6)	1.547(5)
Sr(2)-O(5W)	2.521(7)	P(3)-O(7)	1.543(5)
Sr(2)-O(11)	2.657(5)	P(3)-O(8)	1.475(6)
Sr(2)-O(14)	2.601(5)	P(3)-O(9)	1.566(6)
Sr(2)-O(14C)	2.589(5)	P(4)-O(10)	1.496(5)
Co(1)-O(2)	1.928(5)	P(4)-O(11)	1.553(5)
Co(1)-O(5)	1.937(5)	P(4)-O(12)	1.538(5)
Co(1)-O(7)	1.936(5)	P(5)-O(13)	1.547(5)
Co(1)-N(1)	1.933(7)	P(5)-O(14)	1.508(6)
Co(1)-N(2)	1.942(7)	P(5)-O(15)	1.519(5)
Co(1)-N(3)	1.956(7)	P(6)-O(16)	1.532(5)

Co(2)-O(11)	1.948(5)	P(6)-O(17)	1.571(5)
Co(2)-O(13)	1.929(5)	P(6)-O(18)	1.499(6)
O(1W)-Sr(1)-O(2)	74.62(15)	O(5W)-Sr(2)-O(14)	85.63(19)
O(1W)-Sr(1)-O(2W)	136.73(15)	O(5W)-Sr(2)-O(14C)	81.70(19)
O(1W)-Sr(1)-O(4)	93.03(15)	O(11)-Sr(2)-O(14)	87.55(15)
O(1W)-Sr(1)-O(10)	91.49(16)	O(11)-Sr(2)-O(14C)	127.21(17)
O(1W)-Sr(1)-O(8B)	147.93(17)	O(14)-Sr(2)-O(14C)	66.78(16)
O(1W)-Sr(1)-O(4A)	66.57(15)	O(2)-Co(1)-O(5)	88.2(2)
O(2)-Sr(1)-O(2W)	80.77(15)	O(2)-Co(1)-O(7)	91.2(2)
O(2)-Sr(1)-O(4)	76.26(15)	O(2)-Co(1)-N(1)	89.4(2)
O(2)-Sr(1)-O(10)	129.06(16)	O(2)-Co(1)-N(2)	92.3(2)
O(2)-Sr(1)-O(8B)	125.19(16)	O(2)-Co(1)-N(3)	178.3(2)
O(2)-Sr(1)-O(4A)	127.14(15)	O(5)-Co(1)-O(7)	89.4(2)
O(2W)-Sr(1)-O(4)	115.10(15)	O(5)-Co(1)-N(1)	177.6(2)
O(2W)-Sr(1)-O(10)	77.07(17)	O(5)-Co(1)-N(2)	90.9(2)
O(2W)-Sr(1)-O(8B)	74.95(16)	O(5)-Co(1)-N(3)	93.4(2)
O(2W)-Sr(1)-O(4A)	151.26(16)	O(7)-Co(1)-N(1)	91.0(2)
O(4)-Sr(1)-O(10)	154.46(16)	O(7)-Co(1)-N(2)	176.5(2)
O(4)-Sr(1)-O(8B)	71.23(16)	O(7)-Co(1)-N(3)	88.4(2)
O(4)-Sr(1)-O(4A)	71.59(15)	N(1)-Co(1)-N(2)	88.8(3)
O(8A)-Sr(1)-O(10)	92.10(17)	N(1)-Co(1)-N(3)	89.0(3)
O(4B)-Sr(1)-O(10)	87.31(17)	N(2)-Co(1)-N(3)	88.1(3)
O(4B)-Sr(1)-O(8B)	81.78(16)	O(11)-Co(2)-O(13)	87.9(2)
O(1)-Sr(2)-O(3W)	78.30(16)	O(11)-Co(2)-O(16)	91.3(2)
O(1)-Sr(2)-O(4W)	72.67(17)	O(11)-Co(2)-N(4)	89.2(2)
O(1)-Sr(2)-O(5W)	85.89(19)	O(11)-Co(2)-N(5)	93.3(2)
O(1)-Sr(2)-O(11)	113.41(16)	O(11)-Co(2)-N(6)	177.6(2)
O(1)-Sr(2)-O(14C)	87.24(16)	O(13)-Co(2)-O(16)	89.9(2)
O(3W)-Sr(2)-O(4W)	125.05(15)	O(13)-Co(2)-N(4)	177.0(3)
O(3W)-Sr(2)-O(5W)	143.43(19)	O(13)-Co(2)-N(5)	90.4(3)
O(3W)-Sr(2)-O(11)	72.36(16)	O(13)-Co(2)-N(6)	94.4(3)
O(3W)-Sr(2)-O(14)	94.06(16)	O(16)-Co(2)-N(4)	91.0(2)
O(3W)-Sr(2)-O(14C)	64.95(16)	O(16)-Co(2)-N(5)	175.4(2)
O(4W)-Sr(2)-O(5W)	79.61(18)	O(16)-Co(2)-N(6)	88.0(2)
O(4W)-Sr(2)-O(11)	77.93(16)	N(4)-Co(2)-N(5)	89.0(3)
O(4W)-Sr(2)-O(14)	129.93(16)	N(4)-Co(2)-N(6)	88.6(3)
O(4W)-Sr(2)-O(14C)	153.35(16)	N(5)-Co(2)-N(6)	87.4(3)
O(5W)-Sr(2)-O(11)	143.94(19)		

Symmetry codes: A: 1-x, -y, 1-z; B: -x, -y, 1-z; C: 1-x, 1-y, 1-z.

Table S4. Selected bond lengths (Å) and angles (°) for **CoBa**

Ba(1)-O(1)	2.886(9)	Co(1)-O(1)	1.935(10)
Ba(1)-O(1W)	2.948(8)	Co(1)-N(1)	1.946(10)
Ba(1)-O(1A)	2.886(10)	Co(1)-O(1A)	1.935(11)
Ba(1)-O(1WA)	2.948(8)	Co(1)-N(1A)	1.946(13)
Ba(1)-O(1B)	2.886(10)	Co(1)-O(1B)	1.935(13)
Ba(1)-O(1WB)	2.948(14)	Co(1)-N(1B)	1.946(15)
Ba(1) -O(2C)	2.726(10)	P(1)-O(1)	1.517(10)
Ba(1) -O(2D)	2.724(13)	P(1)-O(2)	1.481(10)
Ba(1) -O(2E)	2.727(12)	P(1)-O(3)	1.520(16)
O(1)-Ba(1)-O(1W)	91.3(2)	O1(B)-Ba(1)-O(2C)	148.8(3)
O(1)-Ba(1)-O(1A)	55.8(3)	O1(B)-Ba(1)-O(2D)	97.7(4)
O(1)-Ba(1)-O(1WA)	66.1(2)	O(1A)-Ba(1)-O(2E)	148.8(4)
O(1)-Ba(1)-O(1B)	55.8(4)	O(1WB)-Ba(1)-(O2C)	60.5(3)
O(1)-Ba(1)-O(1WB)	121.9(2)	O(1WB)-Ba(1)-O(2D)	69.3(4)
O(1)-Ba(1)-O(2C)	126.1(3)	O(1B)-Ba(1)-O(1WA)	121.9(3)
O(1)-Ba(1)-O(2D)	148.8(3)	O(2C)-Ba(1)-O(2D)	85.1(4)
O(1)-Ba(1)-O(2E)	97.6(3)	O(1)-Co(1)-N(1)	89.5(4)
O(1A)-Ba(1)-O(1W)	121.9(3)	O(1)-Co(1)-O(1A)	88.5(4)
O(1W)-Ba(1)-O(1WA)	119.7(4)	O(1)-Co(1)-N(1A)	94.0(5)
O(1W)-Ba(1)-O(2C)	137.7(2)	O(1A)-Co(1)-N(1)	176.8(6)
O(1W)-Ba(1)-O(2E)	69.3(4)	N(1)-Co(1)-N(1A)	88.2(5)
O(1A)-Ba(1)-O(1WA)	91.3(3)	O(1B)-Co(1)-N(1)	94.0(5)
O(1A)-Ba(1)-O(1WB)	66.1(3)	O(1A)-Co(1)-N(1B)	94.0(5)
O(1A)-Ba(1)-O(2C)	97.7(3)	O(1A)-Ba(1)-O(2D)	126.1(4)

Symmetry codes: A: -y, x-y, z; B: -x+y, -x, z; C: -2/3+y, -1/3+x, 1/6-z; D: 1/3-x, -1/3-x+y, 1/6-z; E: 1/3+x-y, 2/3-y, 1/6-z.

2. Powder X-ray diffraction and Infrared Spectra

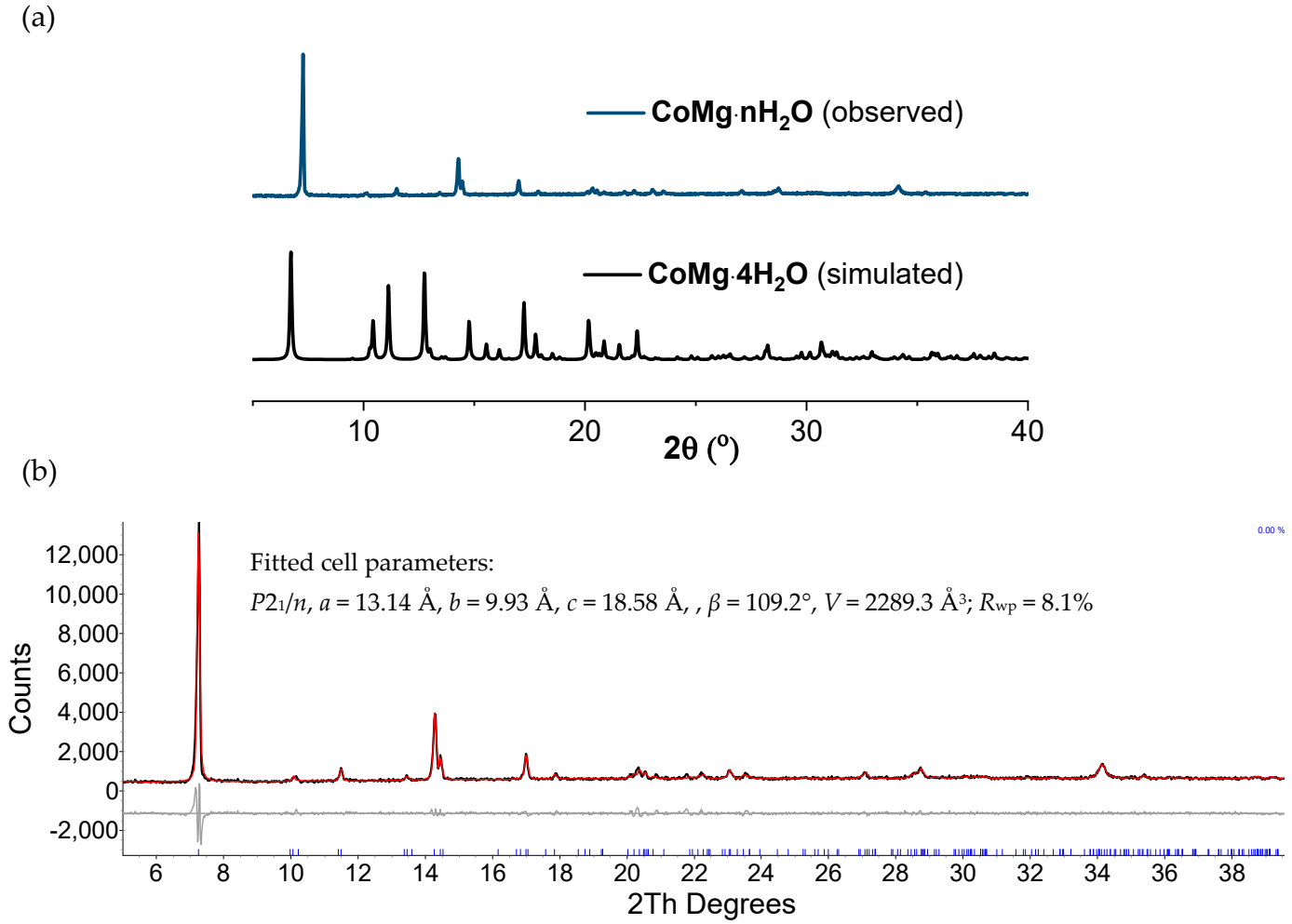
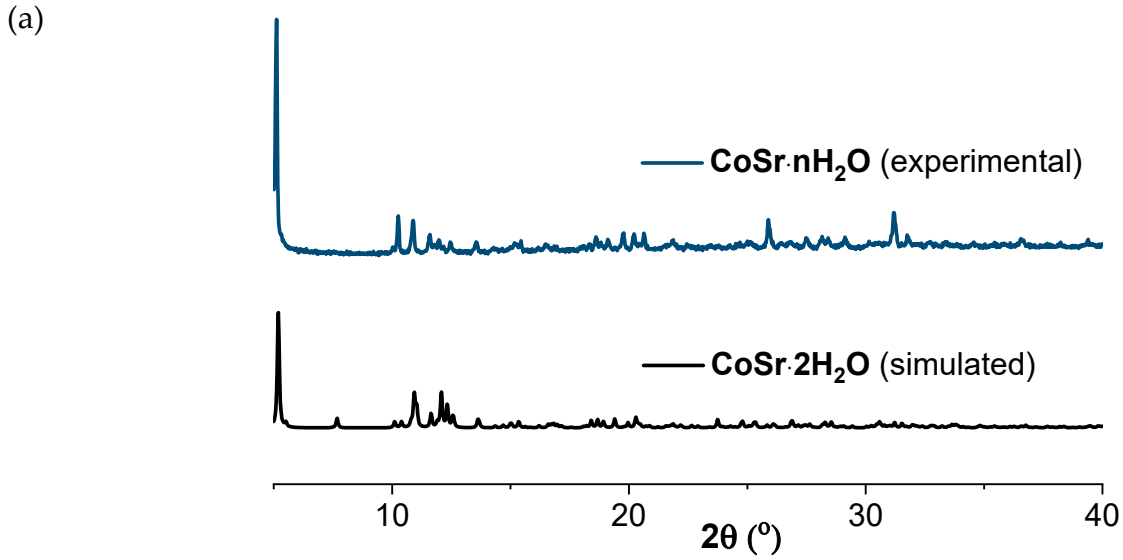


Figure S1. (**a**) Comparison of the observed and simulated powder X-ray diffraction patterns of **CoMg·nH₂O**. (**b**) The observed pattern is fitted by the Pawley method using Topas 5.0 program. The fitting result is identical to the cell parameters of the reported compound **CoCa·2H₂O**, indicating that the collected product lost two lattice water molecules per formula unit in the air and formed the dihydrate phase **CoMg·2H₂O**.



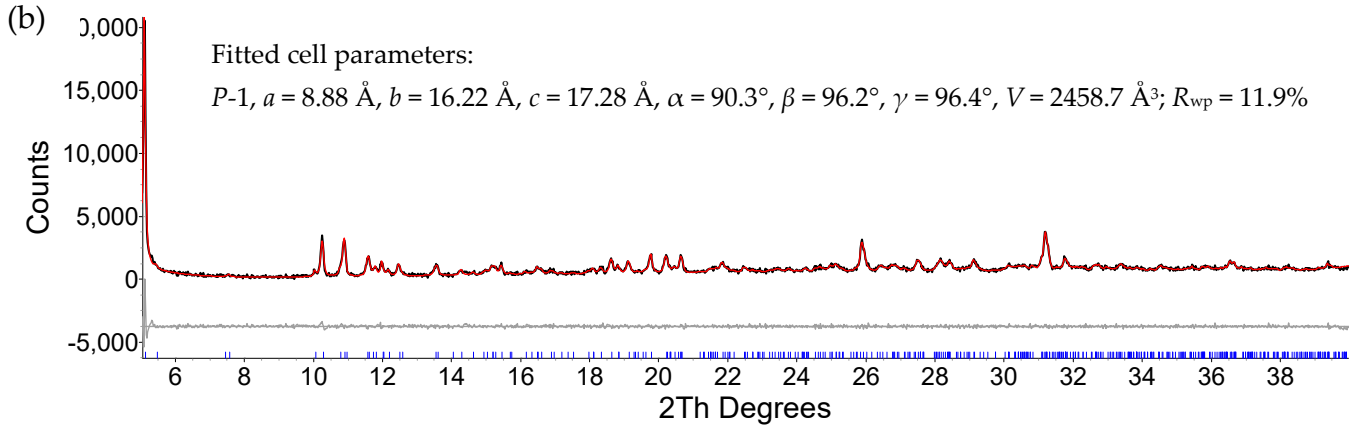


Figure S2. (**a**) Comparison of the observed and simulated powder X-ray diffraction patterns of **CoSr·nH2O**. (**b**) The observed pattern is fitted by the Pawley method using Topas 5.0 program. The fitting result indicates that the collected product maintained the layered structure in the air, and the slight difference between the observed and simulated patterns arose from the removal of partial lattice water.

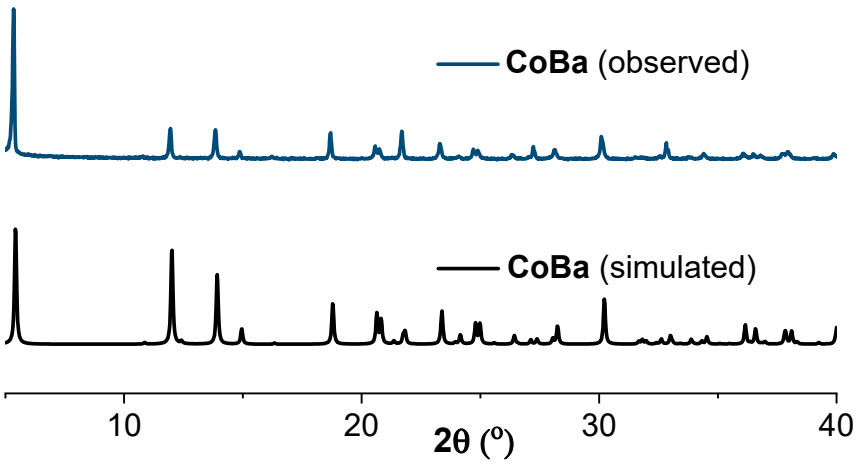


Figure S3. Comparison of the observed and simulated powder X-ray diffraction patterns of **CoBa**.

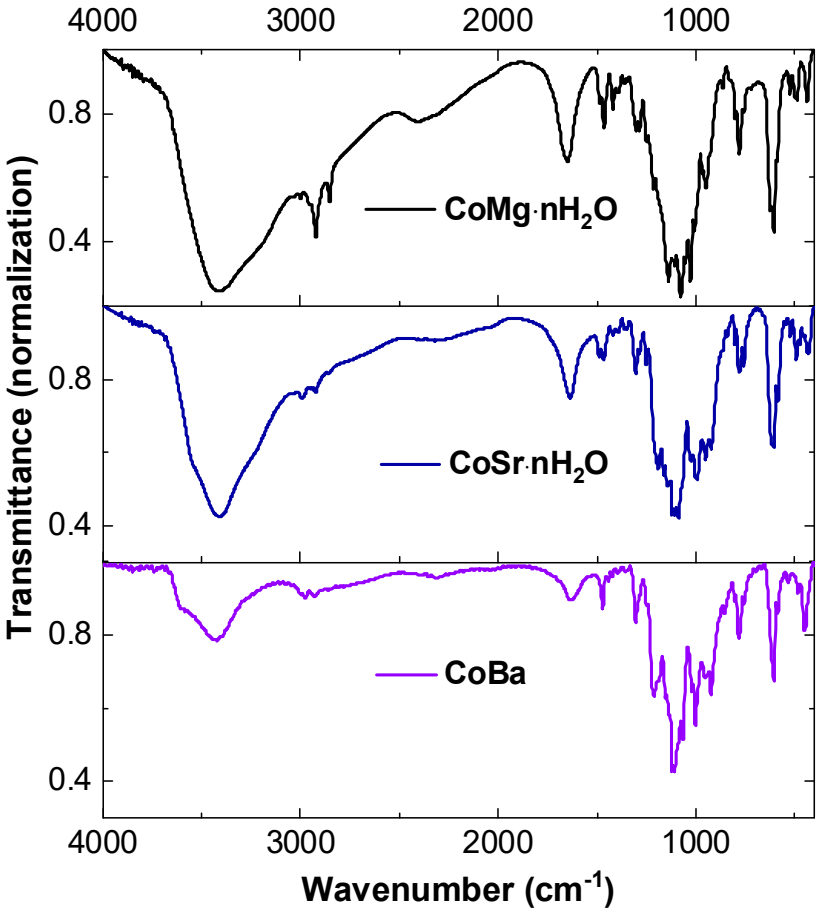


Figure S4. IR spectra of **CoMg·nH2O**, **CoSr·nH2O,** and **CoBa**.

3. Impedance analyses

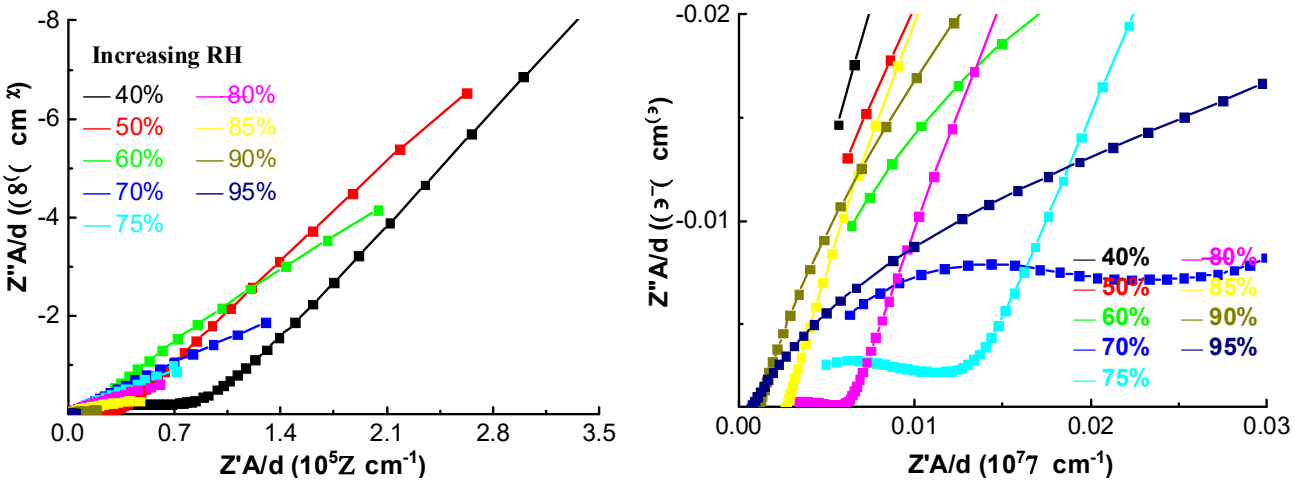


Figure S5. Nyquist plots for the pellet of **CoMg·nH₂O** at 25 °C and various RH. Left: RH increases from 40 to 95%; Right: the enlarged graph view.

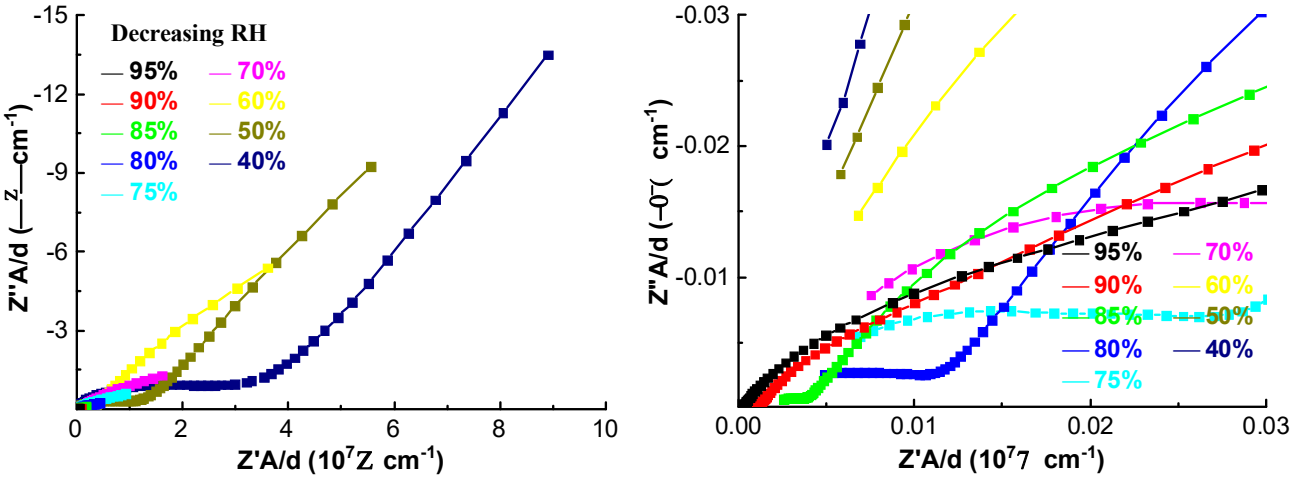


Figure S6. Nyquist plots for the pellet of **CoMg·nH₂O** at 25 °C and various RH. Left: RH decreases from 95 to 40%; Right: the enlarged graph view.

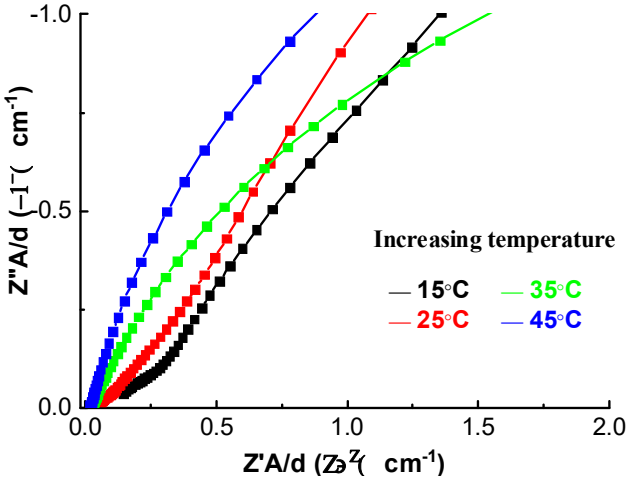


Figure S7. Nyquist plots for the pellet of **CoMg·nH₂O** at 95% RH and various temperatures.

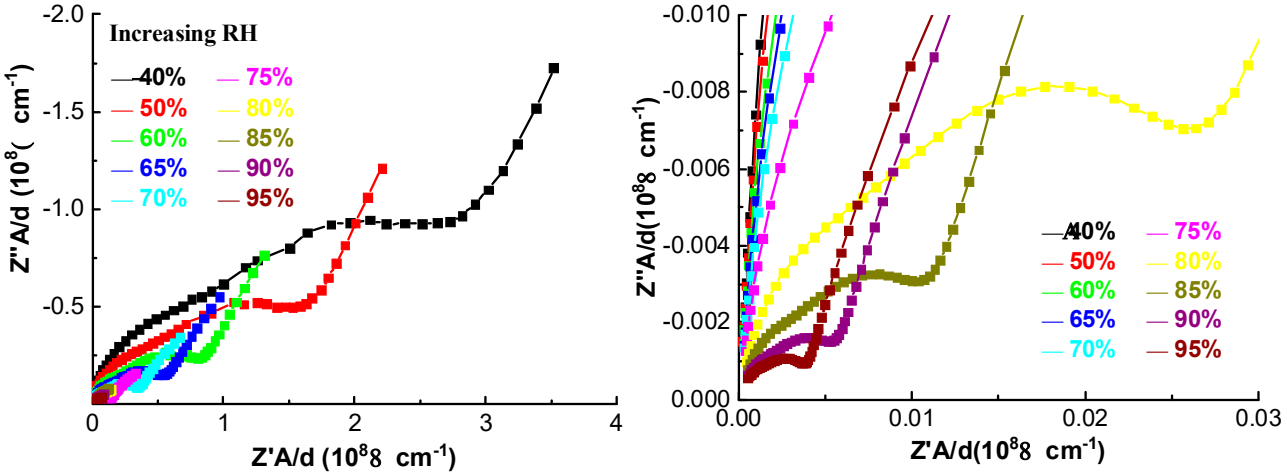


Figure S8. Nyquist plots for the pellet of **CoSr·nH₂O** at 25 °C and various RH. Left: RH increases from 40 to 95%; Right: the enlarged graph view.

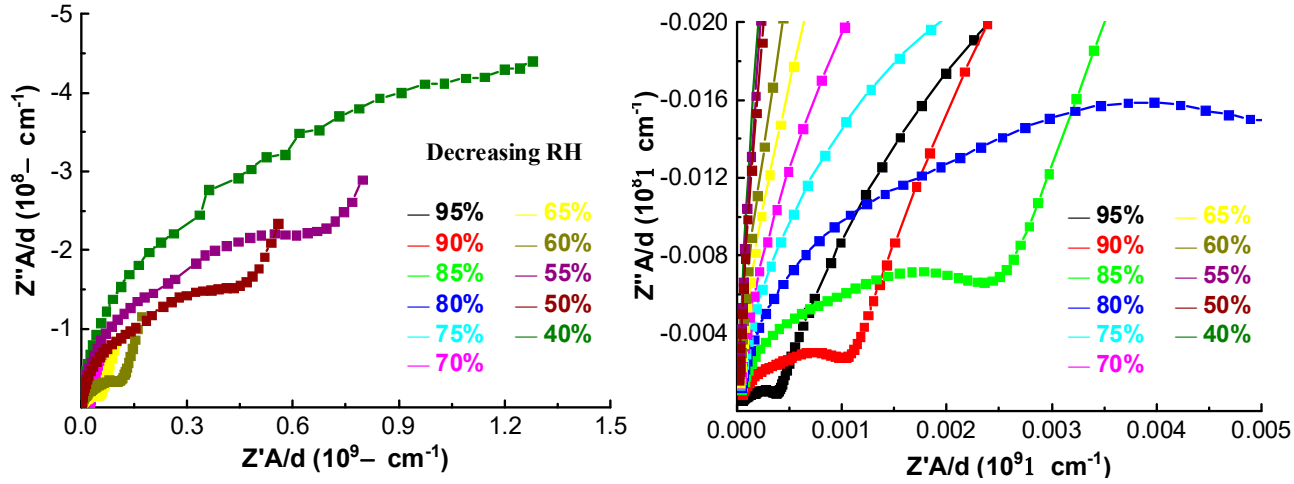


Figure S9. Nyquist plots for the pellet of **CoSr·nH₂O** at 25 °C and various RH. Left: RH decreases from 95 to 40%; Right: the enlarged graph view.

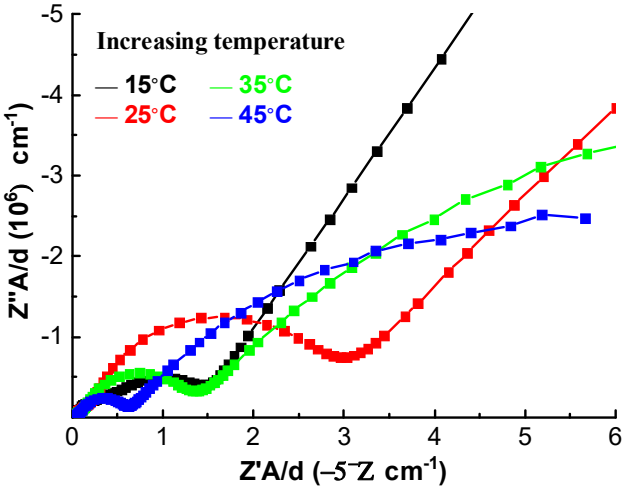


Figure S10. Nyquist plots for the pellet of **CoSr·nH₂O** at 95% RH and various temperatures.

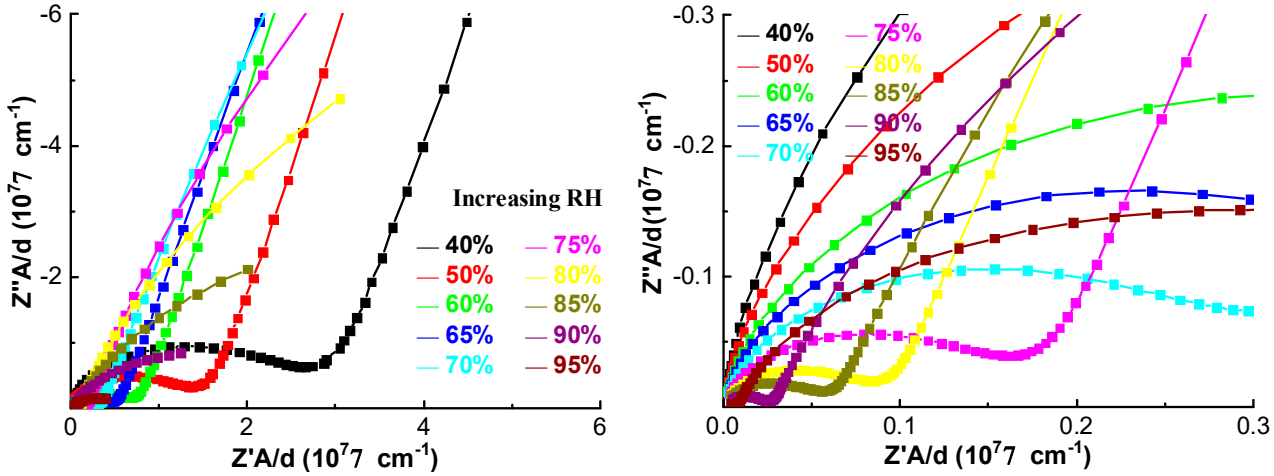


Figure S11. Nyquist plots for the pellet of **CoBa** at 25 °C and various RH. Left: RH increases from 40 to 95%; Right: the enlarged graph view.

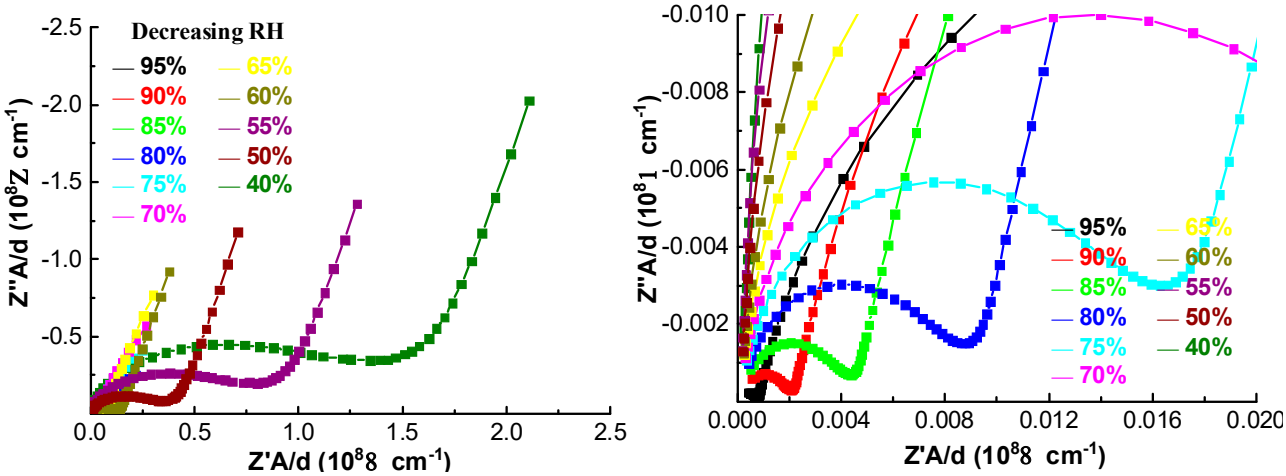


Figure S12. Nyquist plots for the pellet of **CoBa** at 25 °C and various RH. Left: RH decreases from 95 to 40%; Right: the enlarged graph view.

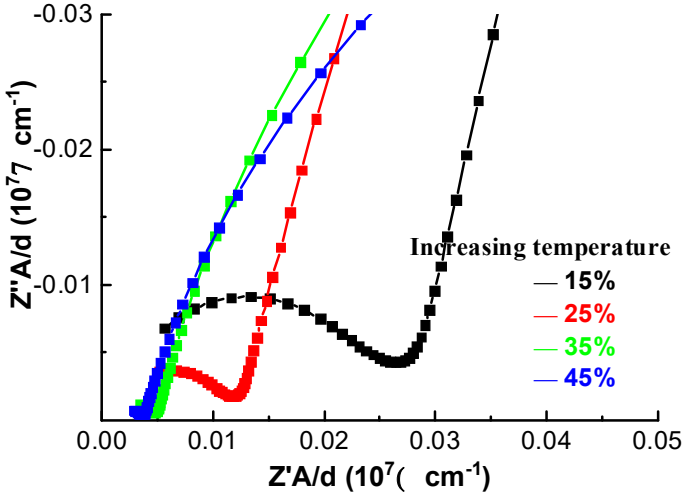


Figure S13. Nyquist plots for the pellet of **CoBa** at 95% RH and various temperatures.