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Electronic Supplementary Information (ESI)

for

$[NH_2NH_3][M(HCOO)_3]$ ($M = Mn^{2+}$, Zn^{2+}, Co^{2+} and Mg^{2+}): structural phase transitions, prominent dielectric anomalies and negative thermal expansion, and magnetic ordering

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Table S1a. Detailed crystallographic data for **1Mn**, at 110, 200, 290 and 400 K

1Mn, formula = $C_3H_8MnN_2O_6$, fw = 223.05				
T, K	110	200	290	400
crystal system	Orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*P na*2_1	*P na*2_1	*P na*2_1	*P nma*
a, Å	8.9319(3)	8.9503(3)	8.9448(3)	8.8505(3)
b, Å	7.8190(2)	7.8214(2)	7.8403(3)	11.8785(4)
c, Å	11.6928(5)	11.7189(5)	11.7669(5)	7.9240(3)
α, °	90	90	90	90
β, °	90	90	90	90
γ, °	90	90	90	90
V, Å^3	816.61(5)	820.37(5)	825.21(5)	833.06(5)
Z	4	4	4	4
D_c, gcm^{-3}	1.814	1.806	1.795	1.778
μ (Mo K_α), mm^{-1}	1.613	1.606	1.597	1.581
F (000)	452	452	452	452
Crystal size, mm^3	0.38×0.32×0.22	0.38×0.32×0.22	0.38×0.32×0.22	0.39×0.34×0.18
T_{min}, T_{max}	0.657, 0.705	0.642, 0.709	0.621, 0.710	0.606, 1.000
θ_{min}, θ_{max}, °	3.40, 28.70	3.46, 28.68	3.46, 28.71	3.43, 28.26
no. total reflns.	15236	15362	15111	12844
no. uniq. reflns (R_{int})	2093 (0.0666)	2101 (0.0700)	2113 (0.0725)	1077 (0.0406)
no. obs. [I≥2σ(I)]	1540	1439	1378	873
no. params	118	118	118	79
Flack parameters	0.24(2)	0.27(2)	0.22(2)	
[a]$R1$, [b]$wR2$ [I≥2σ(I)]	0.0248, 0.0435	0.0243, 0.0408	0.0259, 0.0426	0.0297, 0.0779
[a]$R1$, [b]$wR2$ (all data)	0.0465, 0.0461	0.0530, 0.0438	0.0659, 0.0474	0.0374, 0.0830
GOF	0.912	0.885	0.885	1.226
[c]Δρ, e/Å^3	0.276, −0.289	0.333, −0.324	0.249, −0.323	0.227, −0.331
[d]Max. and mean Δ/σ	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.000, 0.000

a. $R1 = \sum||F_o|-|F_c||/\sum|F_o|$; *b*. $wR2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; *c*. Maximum and minimum residual electron density; *d*. Maximum and mean sigma/shift.

Table S1b. Detailed crystallographic data for **2Zn**, at 110, 200, 290 and 375 K

2Zn, formula = $C_3H_8ZnN_2O_6$, fw = 233.48				
T, K	110	200	290	375
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P\,na2_1$	$P\,na2_1$	$P\,na2_1$	$P\,nma$
a, Å	8.6640(3)	8.6806(3)	8.6748(3)	8.5958(3)
b, Å	7.7157(2)	7.7235(3)	7.7488(3)	11.6442(5)
c, Å	11.4824(4)	11.5056(3)	11.5478(4)	7.8468(3)
α, °	90	90	90	90
β, °	90	90	90	90
γ, °	90	90	90	90
V, Å^3	767.58(4)	771.39(4)	776.23(5)	785.40(5)
Z	4	4	4	4
D_c, gcm^{-3}	2.020	2.010	1.998	1.975
μ (Mo K_α), mm^{-1}	3.196	3.181	3.161	3.124
F (000)	472	472	472	472
Crystal size, mm^3	0.29×0.25×0.24	0.29×0.25×0.24	0.29×0.25×0.24	0.29×0.24×0.22
T_{min}, T_{max}	0.382, 0.483	0.382, 0.483	0.382, 0.483	0.721, 1.000
θ_{min}, θ_{max}, °	3.395, 28.700	3.395, 28.700	3.395, 28.700	2.940, 30.183
no. total reflns.	14003	14258	14396	11343
no. uniq. reflns (R_{int})	1944(0.0659)	1965(0.0665)	1988(0.0739)	1024(0.072)
no. obs. [I≥2σ(I)]	1427	1369	1329	756
no. params	118	118	118	79
Flack parameters	0.32(1)	0.32(1)	0.30(1)	
[a]$R1$, [b]$wR2$ [I≥2σ(I)]	0.0230, 0.0426	0.0227, 0.0402	0.0233, 0.0395	0.0294, 0.0727
[a]$R1$, [b]$wR2$ (all data)	0.0452, 0.0457	0.0481, 0.0429	0.0553, 0.0435	0.0422, 0.0795
GOF	0.931	0.942	0.892	1.154
[c]Δρ, e/Å^3	0.499, −0.399	0.479, −0.494	0.362, −0.445	0.370, −0.320
[d]Max. and mean Δ/σ	0.000, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000

a. $R1 = \sum||F_o|-|F_c||/\sum|F_o|$; *b*. $wR2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; *c*. Maximum and minimum residual electron density; *d*. Maximum and mean sigma/shift.

Table S1c. Detailed crystallographic data for **3Co**, at 110, 200, 290 and 405 K

3Co, formula = $C_3H_8CoN_2O_6$, fw = 227.04				
T, K	110	200	290	405
crystal system	orthorhombic	orthorhombic	orthorhombic	hexagonal
space group	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,6_3$
a, Å	7.9435(2)	7.9415(2)	7.9341(3)	7.9157(3)
b, Å	13.8339(4)	13.8460(5)	13.8697(7)	7.9157(3)
c, Å	7.3016(2)	7.3103(2)	7.3361(3)	7.4836(3)
α, °	90	90	90	90
β, °	90	90	90	90
γ, °	90	90	90	120.00
V, Å^3	802.37(4)	803.83(4)	807.29(6)	406.09(3)
Z	4	4	4	2
D_c, gcm^{-3}	1.880	1.876	1.868	1.857
μ (Mo K_α), mm^{-1}	2.136	2.132	2.123	2.110
F (000)	460	460	460	230
Crystal size, mm^3	0.50×0.40×0.26	0.50×0.40×0.26	0.50×0.40×0.26	0.24×0.24×0.14
T_{min}, T_{max}	0.483, 0.583	0.483, 0.583	0.483, 0.583	0.707, 1.000
θ_{min}, θ_{max}, °	3.79, 28.70	3.79, 28.70	3.78, 28.77	2.965, 30.180
no. total reflns.	16158	16313	14202	6226
no. uniq. reflns (R_{int})	2071(0.0656)	2074(0.0723)	2077(0.0794)	672(0.0281)
no. obs. [I≥2σ(I)]	1771	1711	1607	648
no. params	117	117	117	65
Flack parameters	−0.01(1)	−0.01(2)	0.02(2)	−0.01(3)
[a]$R1$, [b]$wR2$ [I≥2σ(I)]	0.0244, 0.0458	0.0263, 0.0490	0.0279, 0.0497	0.0157, 0.0422
[a]$R1$, [b]$wR2$ (all data)	0.0361, 0.0474	0.0405, 0.0509	0.0497, 0.0525	0.0167, 0.0432
GOF	0.988	0.965	0.955	1.118
[c]Δρ, e/Å^3	0.399, −0.405	0.393, −0.365	0.371, −0.463	0.229, −0.173
[d]Max. and mean Δ/σ	0.001, 0.000	0.000, 0.000	0.001, 0.000	0.000, 0.000
The supposed primitive, nearly hexagonal cell for LT phases by adding a *C*-center in the *oP* unit cell				HT *C*-centred unit cell
a, Å	7.9435	7.9415	7.9341	7.9157
b, Å	7.9762	7.9809	7.9893	13.7104
c, Å	7.3016	7.3103	7.3361	7.4836
α, °	90	90	90	90
β, °	90	90	90	90
γ, °	119.87	119.84	119.77	90
V, Å^3	401.19	401.92	403.65	812.18

a. $R1 = \sum||F_o|-|F_c||/\sum|F_o|$; *b*. $wR2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; *c*. Maximum and minimum residual electron density; *d*. Maximum and mean sigma/shift.

Table S1d. Detailed crystallographic data for **4Mg**, at 110, 200, 292 and 400 K

4Mg, formula = $C_3H_8MgN_2O_6$, fw = 192.42				
T, K	110	200	292	400
crystal system	orthorhombic	orthorhombic	orthorhombic	hexagonal
space group	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,6_3$
a, Å	7.8999(2)	7.8928(2)	7.8888(2)	7.8798(3)
b, Å	13.7505(4)	13.7693(4)	13.7799(4)	7.8798(3)
c, Å	7.3829(2)	7.4007(2)	7.4295(2)	7.5682(4)
α, °	90	90	90	90
β, °	90	90	90	90
γ, °	90	90	90	120.00
V, Å^3	801.99(4)	804.30(4)	807.64(4)	406.96(3)
Z	4	4	4	2
D_c, gcm^{-3}	1.594	1.589	1.583	1.570
μ (Mo K_a), mm^{-1}	0.219	0.218	0.217	0.216
F (000)	400	400	400	200
Crystal size, mm^3	0.40×0.40×0.23	0.40×0.40×0.23	0.40×0.40×0.23	0.40×0.40×0.23
T_{min}, T_{max}	0.877, 0.953	0.877, 0.953	0.877, 0.953	0.758, 1.000
θ_{min}, θ_{max}, °	3.78, 28.29	3.78, 28.29	3.77, 28.27	4.02, 28.19
no. total reflns.	14126	14119	14178	6712
no. uniq. reflns (R_{int})	1993(0.0329)	1993(0.0333)	1996(0.0339)	678(0.0256)
no. obs. [I≥2σ(I)]	1864	1827	1756	654
no. params	117	117	117	65
Flack parameters	−0.1(2)	−0.2(2)	−0.2(3)	0.0(4)
[a]$R1$, [b]$wR2$ [I≥2σ(I)]	0.0249, 0.0652	0.0283, 0.0747	0.0307, 0.0808	0.0260, 0.0698
[a]$R1$, [b]$wR2$ (all data)	0.0285, 0.0644	0.0330, 0.0761	0.0387, 0.0835	0.0272, 0.0705
GOF	1.141	1.099	1.052	1.117
[c]Δρ, e/Å^3	0.177, −0.219	0.275, −0.220	0.245, −0.267	0.189, −0.201
[d]Max. and mean Δ/σ	0.000, 0.000	0.000, 0.000	0.000, 0.000	0.005, 0.001
The supposed primitive, nearly hexagonal cell for LT phases by adding a *C*-center in the *oP* unit cell				HT *C*-centred unit cell
a, Å	7.8999	7.8928	7.8888	7.8798
b, Å	7.9291	7.9355	7.9391	13.6482
c, Å	7.3829	7.4007	7.4295	7.5682
α, °	90	90	90	90
β, °	90	90	90	90
γ, °	119.88	119.82	119.79	90
V, Å^3	401.00	402.15	403.82	813.92

a. $R1 = \sum||F_o|-|F_c||/\sum|F_o|$; *b*. $wR2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; *c*. Maximum and minimum residual electron density; *d*. Maximum and mean sigma/shift.

Table S2. Selected bond distances (Å) and bond angles (°) and geometries of the N−H···O hydrogen bonds (N···O distances, Å, and N−H···O angles, °) of **1Mn** and **2Zn**.

1Mn (0.97)				
T, K	110	200	290	400
Mn−O	2.175(2) − 2.196(2)	2.178(2) − 2.194(2)	2.178(2) − 2.196(2)	2.184(2) − 2.191(2)
C−O	1.245(2) − 1.265(2)	1.241(3) − 1.261(3)	1.229(3) − 1.255(3)	1.229(2) − 1.237(2)
N−N	1.448(2)	1.446(2)	1.431(3)	1.396(6)
cis- O−Mn−O	85.87(6) − 95.11(6)	86.14(6) − 94.91(7)	86.37(7) − 94.26(7)	87.82(5) − 92.18(5)
trans- O−Mn−O	175.05(6) − 178.71(7)	175.36(6) − 178.76(7)	176.10(8) − 179.08(8)	180.00
Mn−O−C	116.5(1) − 123.1(2)	117.1(1) − 123.3(2)	118.3(2) − 123.4(2)	121.8(1) − 125.8(3)
O−C−O	124.3(2) − 125.0(2)	124.2(2) − 125.8(2)	125.4(3) − 126.6(2)	125.8(3) − 126.5(2)
N(1)−H···O_{HCOO}	2.840(2) − 2.901(3)	2.852(3) − 2.915(3)	2.876(3) − 2.926(4)	2.947(3) − 3.013(3)
strong	164.6 − 171.1	164.9 − 170.8	164.9 − 173.4	160 − 169
N(1)−H···O_{HCOO}	2.996(3) − 3.101(3)	3.004(3) − 3.108(3)	2.990(4) − 3.110(3)	2.947(3) − 3.013(3)
weak	112.3 − 117.2	113.7 − 118.5	114.5 − 121.7	117 − 138
N(2)−H···O_{HCOO}	3.007(3) − 3.075(3)	3.019(3) − 3.094(3)	3.035(4) − 3.125(4)	3.099(6), 108
	136.8 − 139.8	137.4 − 140.7	135.7 − 139.8	
Mn···Mn	5.880 − 5.943	5.890 − 5.949	5.908 − 5.951	5.939 − 5.940

2Zn (0.88)				
T, K	110	200	290	375
Zn−O	2.100(2) − 2.107(2)	2.100(2) − 2.111(2)	2.099(2) − 2.115(2)	2.106(2) − 2.116(2)
C−O	1.238(4) − 1.280(4)	1.237(4) − 1.274(4)	1.233(5) − 1.265(5)	1.234(3) − 1.244(3)
N−N	1.444(3)	1.436(3)	1.424(4)	1.399(7)
cis- O−Zn−O	86.26(7) − 94.98(8)	86.37(8) − 94.75(8)	86.52(9) − 94.42(9)	87.69(7) − 92.31(7)
trans- O−Zn−O	176.07(8) − 178.72(8)	176.41(9) − 178.84(9)	176.63(10) − 178.98(9)	180.0
Zn−O−C	117.2(2) − 122.0(2)	117.4(2) − 122.5(2)	118.2(2) − 123.1(2)	121.6(2) − 121.9(2)
O−C−O	123.5(2) − 124.6(2)	123.9(3) − 125.1(2)	124.4(2) − 125.5(3)	124.9(3) − 125.8(2)
N(1)−H···O_{HCOO}	2.849(3) − 2.903(3)	2.856(3) − 2.920(4)	2.878(4) − 2.944(4)	2.928(3) − 3.107(3)
strong	165.0 − 169.0	165.1 − 171.3	165.3 − 171.0	161 − 169
N(1)−H···O_{HCOO}	2.966(4) − 3.075(3)	2.974(4) − 3.082(4)	2.970(4) − 3.088(4)	2.928(3) − 3.107(3)
weak	113.8 − 117.2	113.3 − 118.5	117.4 − 122.5	117 − 139
N(2)−H···O_{HCOO}	3.003(3) − 3.059(3)	3.016(3) − 3.078(4)	3.034(4) − 3.125(4)	3.111(6), 106
	135.5 − 138.7	134.3 − 138.3	133.0 − 137.9	
Zn···Zn	5.764 − 5.802	5.775 − 5.811	5.791 − 5.817	5.819 − 5.822

Table S3. Selected bond distances (Å) and bond angles (°) and geometries of the N−H···O hydrogen bonds (N···O distances, Å and N−H···O angles, °) of **3Co** and **4Mg**.

3Co (0.89)				
T, K	110	200	290	405
Co−O	2.059(1) − 2.125(1)	2.062(2) − 2.124(1)	2.063(2) − 2.122(2)	2.092(2) − 2.093(1)
C−O	1.249(2) − 1.262(2)	1.243(3) − 1.255(2)	1.238(3) − 1.249(3)	1.233(3) − 1.238(3)
N−N	1.458(2)	1.448(3)	1.436(3)	1.396(6)
cis- O−Co−O	80.17(5) − 96.64(5)	80.40(6) − 96.36(6)	80.62(7) − 96.01(7)	82.75(5) − 92.73(7)
trans- O−Co−O	170.45(6) − 175.11(6)	170.81(6) − 175.08(6)	171.35(7) − 175.14(7)	173.44(5)
Co−O−C	119.9(1) − 129.7(1)	120.7(1) − 130.1(2)	121.4(2) − 130.7(2)	125.3(1) − 125.4(1)
O−C−O	124.1(2) − 124.7(2)	124.4(2) − 125.5(2)	125.5(2) − 126.2(2)	126.4(2)
N(1)−H···O_{HCOO}	2.813(2) − 2.891(2)	2.816(2) − 2.905(2)	2.824(2) − 2.933(2)	2.88(1) − 3.05(1)
strong	154.0 − 169.9	154.7 − 168.7	155.8 − 165.8	155 − 161
N(1)−H···O_{HCOO}	2.878(2)	2.879(2)	2.881(2)	3.05(1)
weak	114.5	115.4	118.6	125
N(2)−H···O_{HCOO}	2.948(2) − 3.263(2)	2.956(2) − 3.267(2)	2.962(2) − 3.264(2)	3.14(1)
	109 − 152	109 − 148	106 − 146	170
N−H···N	3.065(2)	3.061(3)	3.058(3)	2.93(1) − 3.11(1)
	176.7	176.9	176.4	143 − 165
Co···Co	5.807 − 5.978	5.809 − 5.979	5.820 − 5.982	5.907

4Mg (0.86)				
T, K	110	200	292	400
Mg–O	2.047(1) − 2.097(1)	2.050(1) − 2.096(1)	2.054(1) − 2.096(1)	2.078(1) − 2.079(1)
C−O	1.239(2) − 1.261(2)	1.236(2) − 1.257(2)	1.228(2) − 1.245(2)	1.226(2) − 1.228(2)
N−N	1.449(2)	1.441(2)	1.422(3)	1.29(1)
cis- O–Mg–O	82.05(4) − 95.44(5)	82.22(5) − 95.42(5)	82.52(5) − 94.94(5)	84.48(4) − 92.02(6)
trans- O–Mg–O	172.40(5) − 175.95(5)	172.82(5) − 176.02(5)	174.06(6) − 176.14(5)	175.09(4)
Mg−O−C	121.1(1) − 131.3(1)	121.7(1) − 131.7(1)	123.0(1) − 131.9(1)	127.4(1)
O−C−O	125.4(2) − 126.0(1)	126.1(2) − 126.7(2)	126.7(2) − 127.8(2)	128.6(1)
N(1)−H···O_{HCOO}	2.821(2) − 2.897(2)	2.825(2) − 2.910(2)	2.841(2) − 2.945(2)	2.87(1) − 3.14(1)
strong	154.1 − 169.8	154.3 − 167.2	155.6 − 163.7	163 − 168
N(1)−H···O_{HCOO}	2.904(2)	2.905(2)	2.898(2)	3.05(1)
weak	114.5	116.5	120.1	117
N(2)−H···O_{HCOO}	2.940(2) − 3.320(2)	2.956(2) − 3.267(2)	2.946(2) − 3.379(2)	3.06(1) − 3.15(2)
	106 − 156	109 − 148	101 − 138	130 − 156
N−H···N	3.096(2)	3.090(3)	3.084(3)	2.949(7) − 3.120(7)
	175.8	174.2	172.9	125 − 146
Mg···Mg	5.800 − 5.986	5.810 − 5.988	5.828 − 5.988	5.917

Table S4. IR absorption bands (cm^{-1}) and their assignments for **1Mn** to **4Mg** (s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, br: broad)

Assignment	**1Mn**	**2Zn**	**3Co**	**4Mg**
N−H, stretching	3328 m	3330 m	3336 m	3341 s
	3205 m	3280 sh	3276 m	3272 s
	3091 m	3088 m	3056 m	3058 m
$2\nu_4$	2937 vw br	3016 vw	2966 vw br	2971 vw
	2875 w		2883 w	
C−H stretching	2845 m	2889 w	2842 m	2867 w
$2\nu_5$	2749 vw	2747 vw	2725 vw	2727 vw
	2663 vw	2631 vw	2612 vw	2673 vw
N−H bending	1641 s	1641 s	1637 sh	1645 sh
COO, stretching, antisym., ν_4	1585 s	1585 s	1601 sh	1604 s
	1526 sh	1524 sh	1582 s	1524 sh
COO deformation, antisym., ν_5	1387 s	1380 s	1383 sh	1380 s
COO stretching, sym., ν_2	1357 s	1359 s	1367 s	1367 sh
N−N	1111 w	1111 w	1107 w	1113 w
C−H, out of plane deformation, ν_6	958 vw	1067 w	1027 vw	962 m
	941 vw		961 s	
COO deformation, sym., ν_3	798 m	941 m	816 m	812 m
		808 m	810 m	
$\rho_r(NH_2)$	771 w	699 vw		

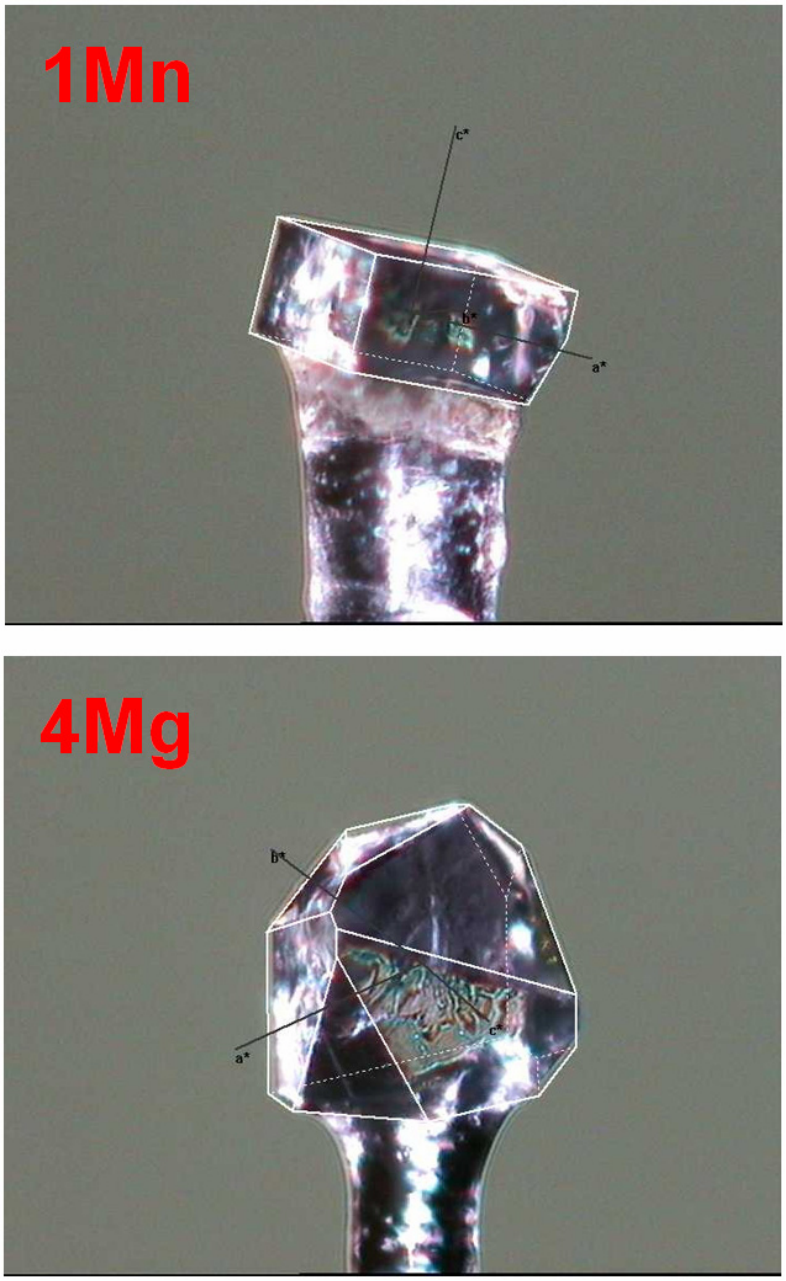

Fig. S1. The crystal images of **1Mn** and **4Mg** under the optical microscope of CCD-2, showing the shapes and indexed faces. **2Zn** is similar to **1Mn**, and **3Co** similar to **4Mg**.

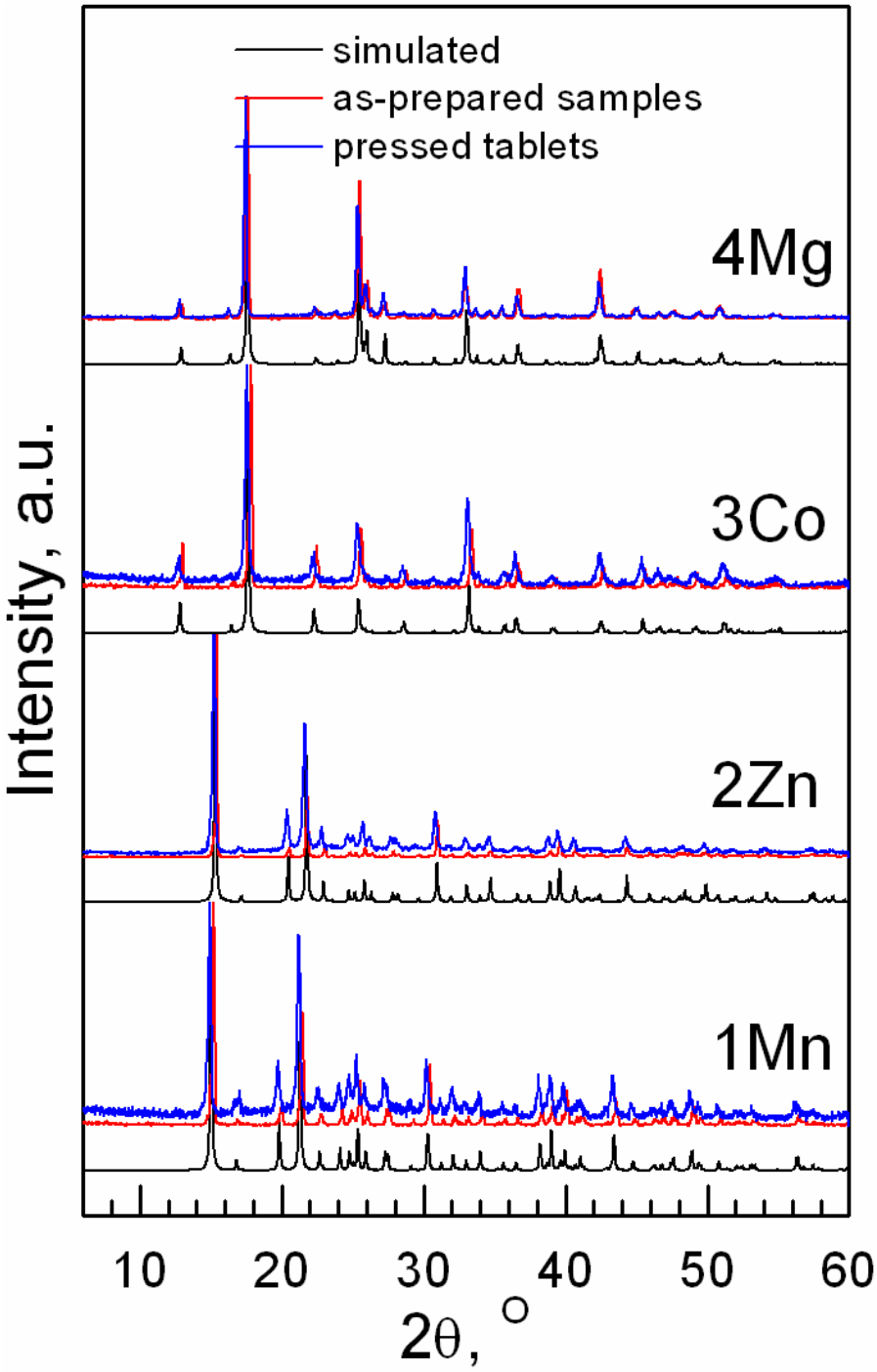

Fig. S2. PXRD patterns for as-prepared and pressed samples of the four compounds and the simulated one based on their single crystal structures at room temperature.

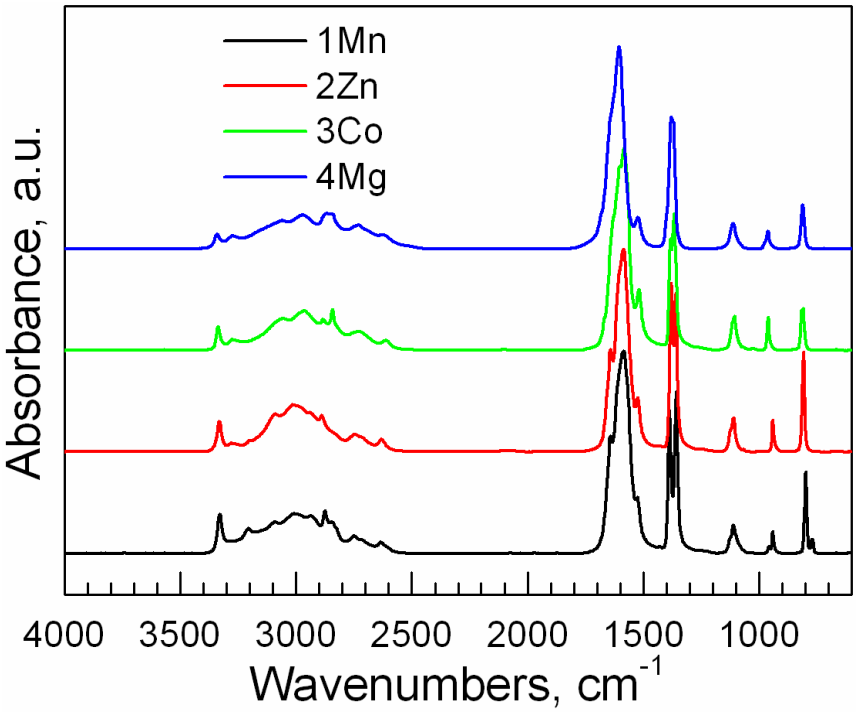

Fig. S3. IR spectra of the four compounds between 4000 and 600 cm^{-1}.

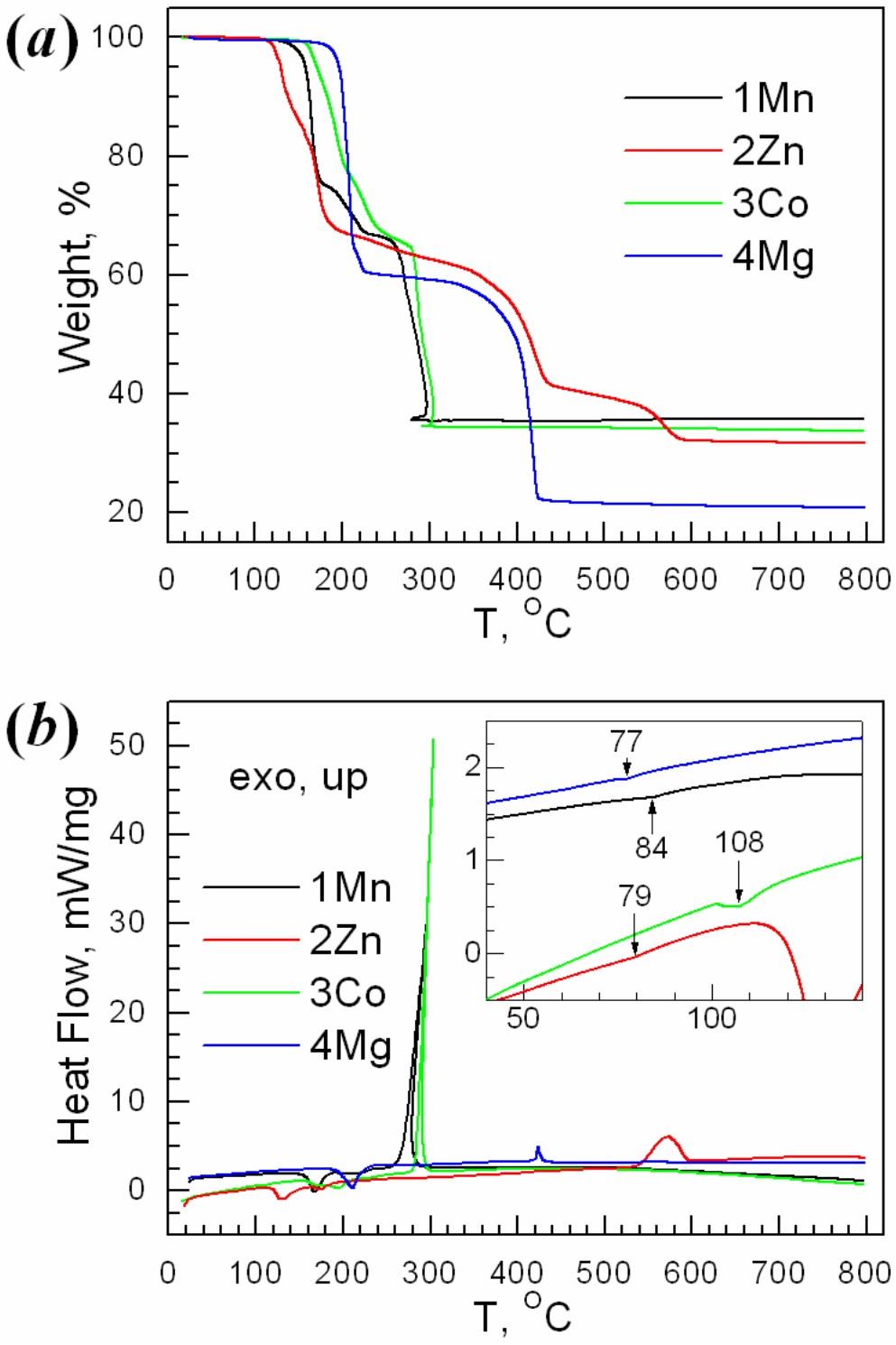

Fig. S4. Combined TGA (a) and DSC (b) runs for the four compounds at a rate of 5 °Cmin^{-1} under air atmosphere. Inset, the details from 40 to 140 °C show the small endothermic peaks.

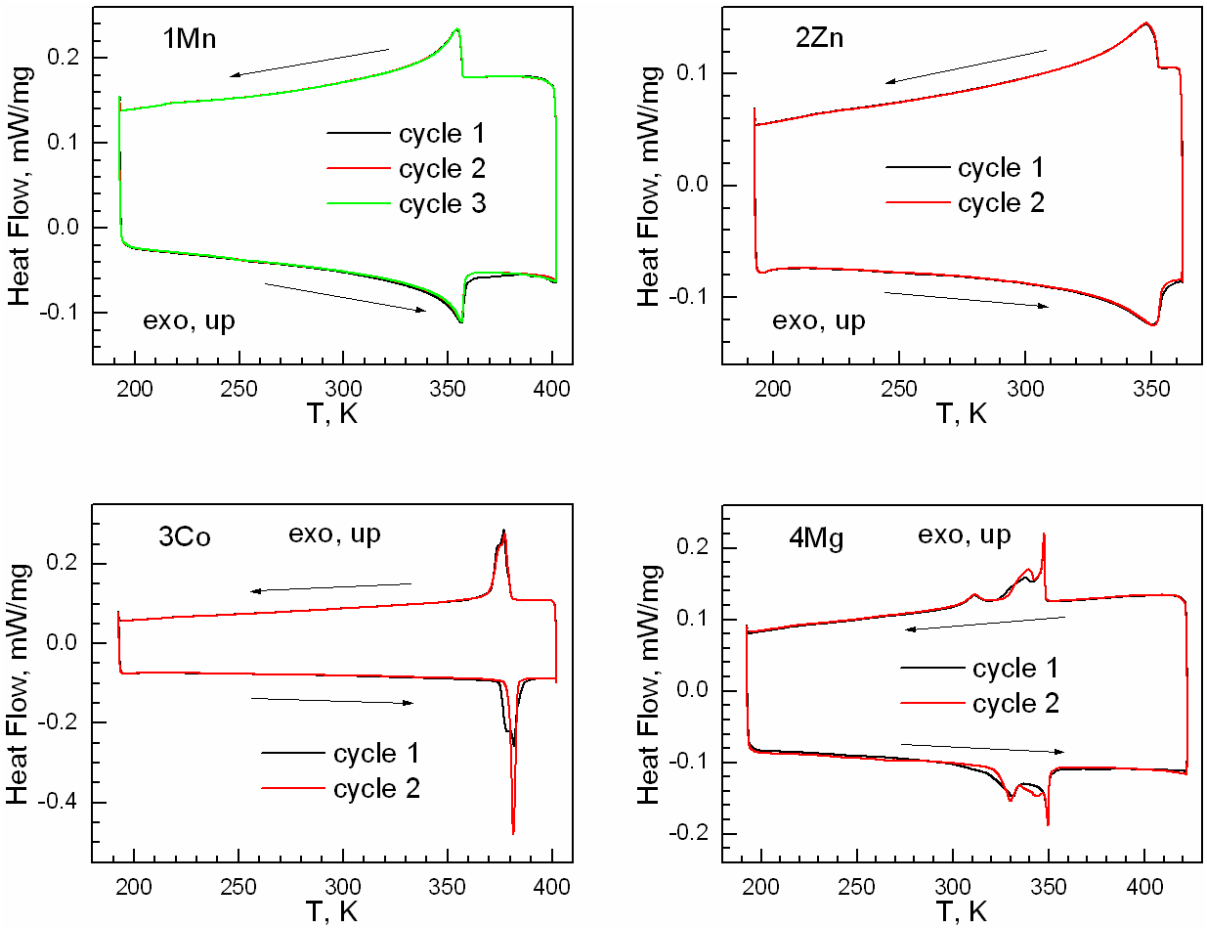

Fig. S5. DSC cycles for **1Mn**, **2Zn**, **3Co** to **4Mg**.

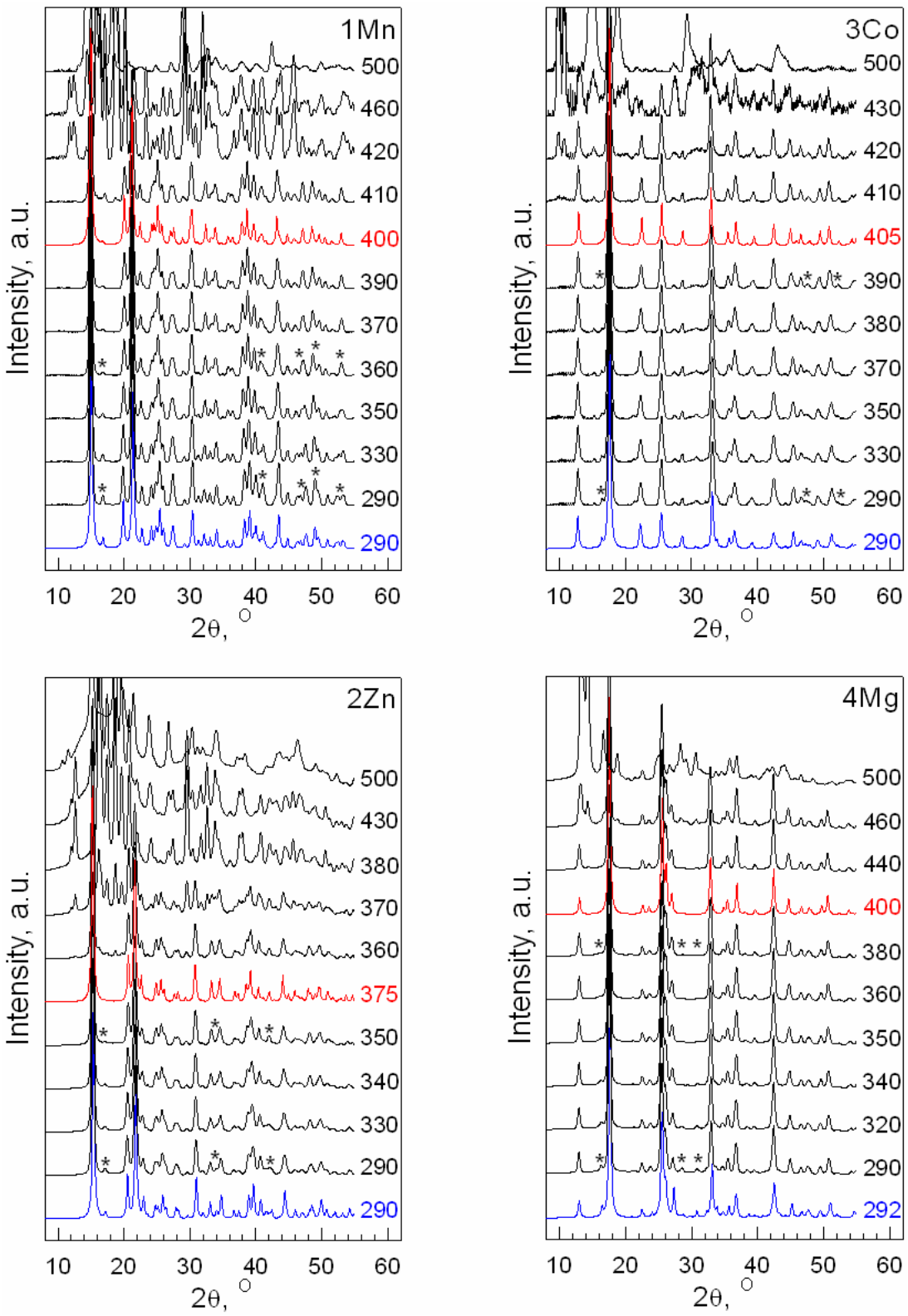

Fig. S6. VT PXRD patterns for tablet samples of the four materials on heating. Blue and red patterns are simulated ones based on the crystal structures determined at the temperatures, and the changes indicating phase transitions in the patterns are highlighted by stars.

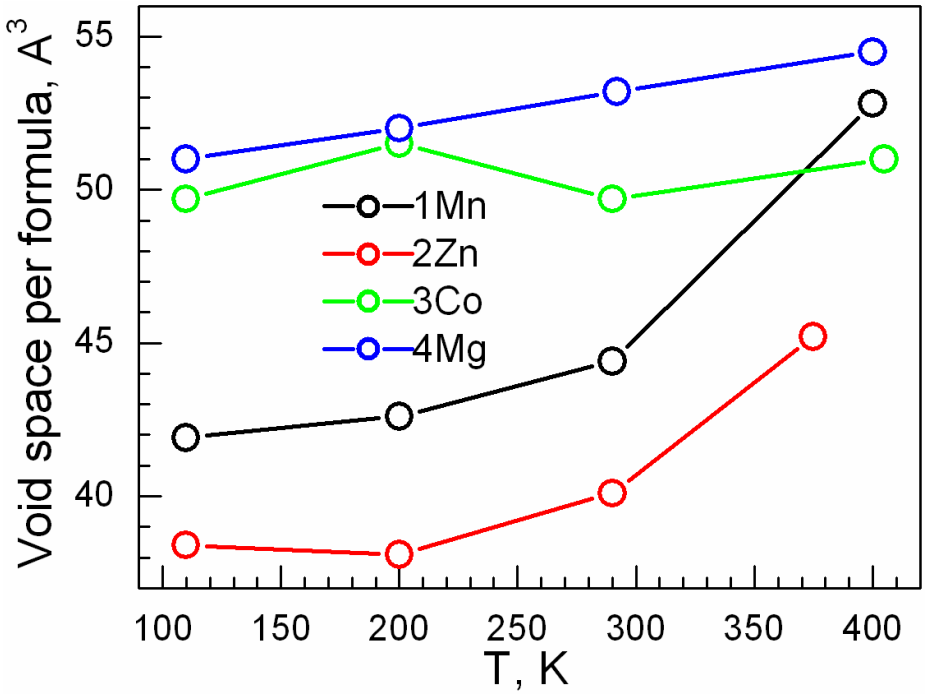

Fig. S7. The temperature-dependent void space per formula for **1Mn**, **2Zn**, **3Co** to **4Mg**.

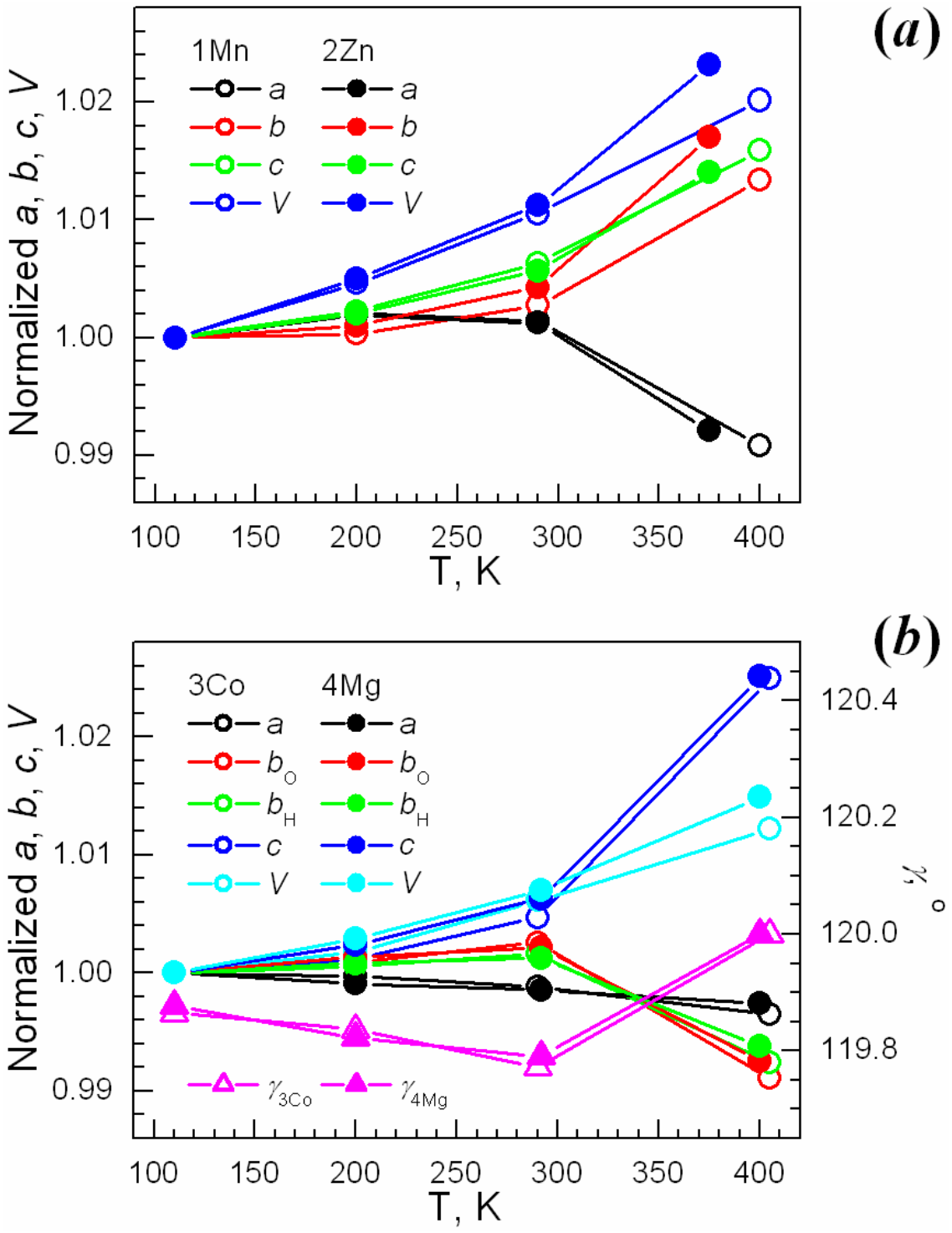

Fig. S8. The temperature evolution of the cell dimensions normalized on the data at 110 K. (a) **1Mn** and **2Zn**. For HT phases the axes were chosen the same as LT phases. (b) **3Co** and **4Mg**. b_O and b_H are the *b* axes for the orthorhombic cells and the hexagonal ones, respectively, see text and Table S1c and S1d.

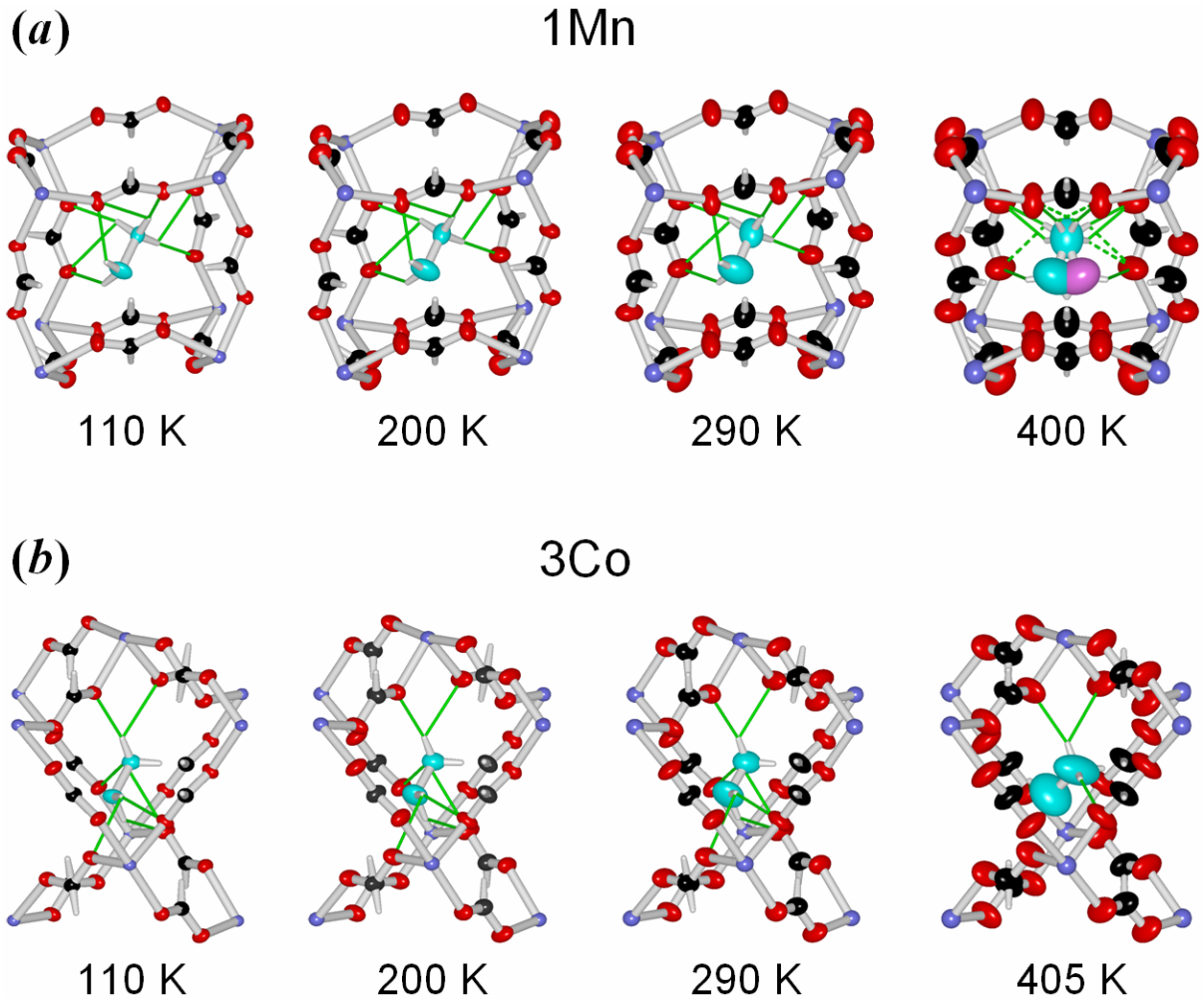

Fig. S9. The temperature evolution of the thermal ellipsoids (at 80% probability) of non-H atoms (same color schemes and orientations as those in Fig. 2 and Fig. 3) in the structures at the four temperatures, (a) **1Mn** and (b) **3Co**.

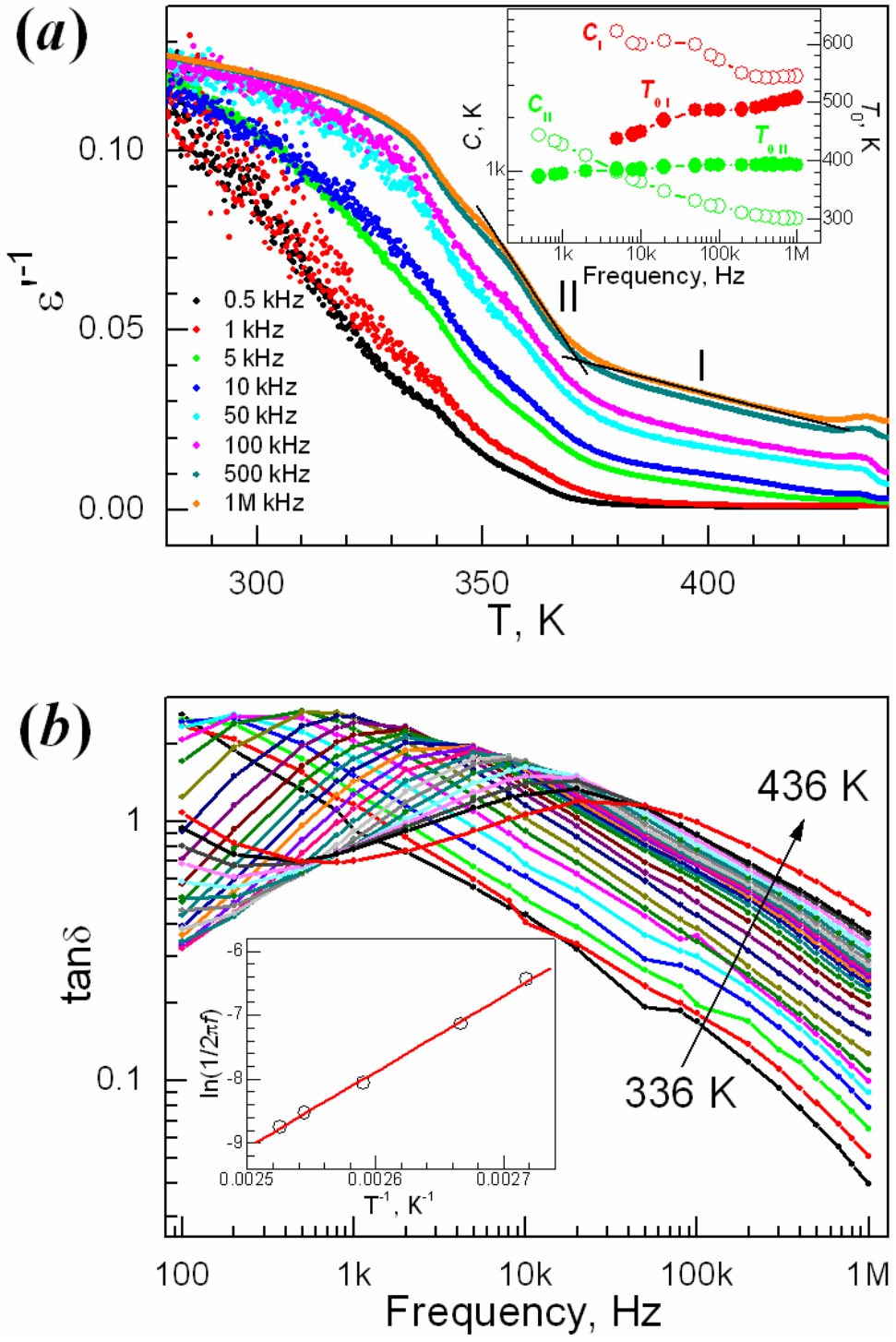

Fig. S10. Additional dielectric data for **4Mg**. (a) The $1/\varepsilon'$ *vs* T plots at several frequencies, inset the plots of C_I, T_{0I}, C_{II} and T_{0II} *vs* frequency. (b) The isothermal *tanδ vs f* plots from 336 to 436 K, in log-log scale, inset, the Arrhenius plot for the dielectric relaxation observed around 360 K at low frequencies.

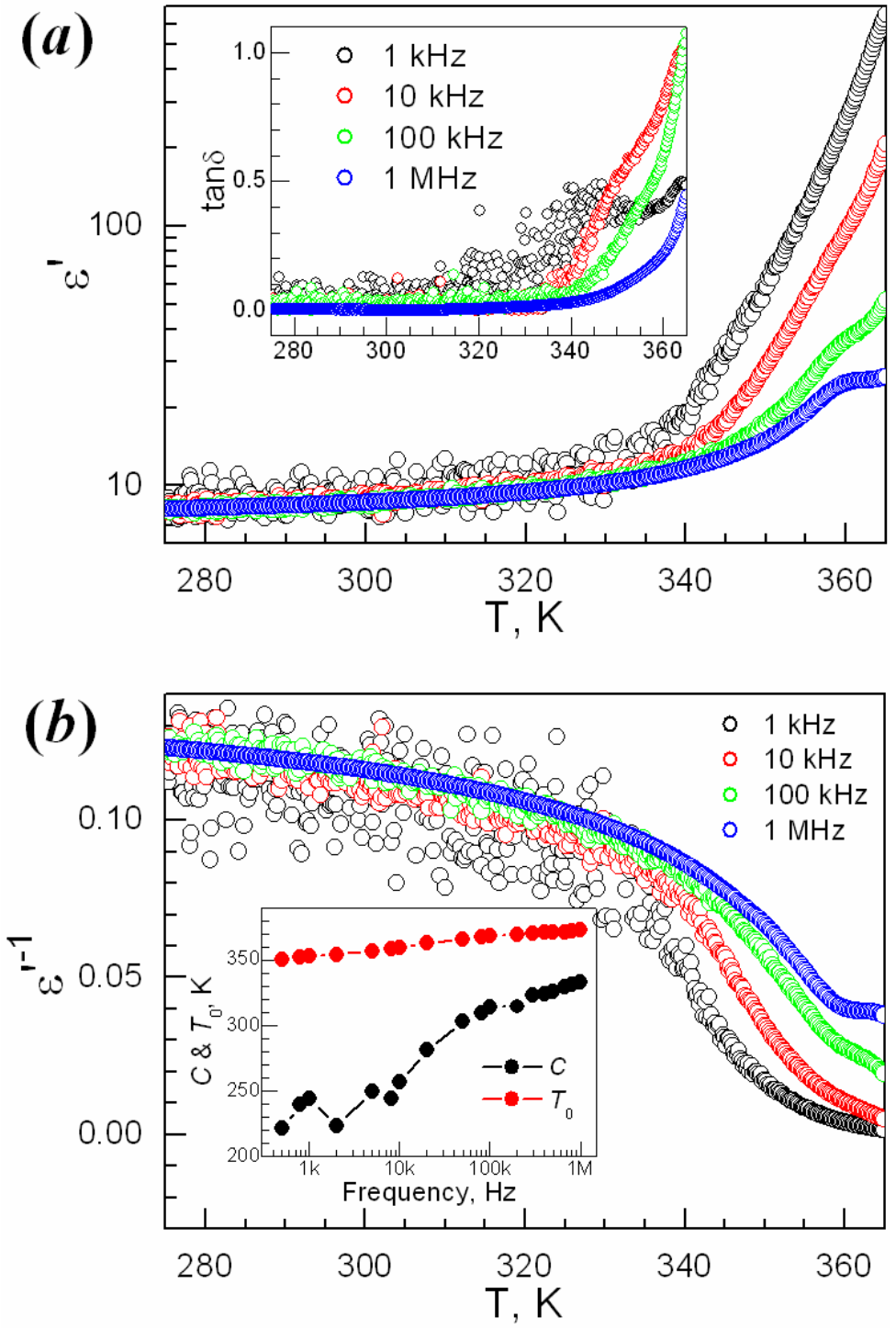

Fig. S11. Temperature-dependent traces of the dielectric permittivities on heating for **2Zn**: (a) *ε' vs T*, and inset *tanδ vs T*, at 1 kHz, 10 kHz , 100 kHz and 1 MHz, (b) the relevant 1/*ε' vs T* plots, and inset the plots of *C* and T_0 *vs* frequency derived from data below T_C.

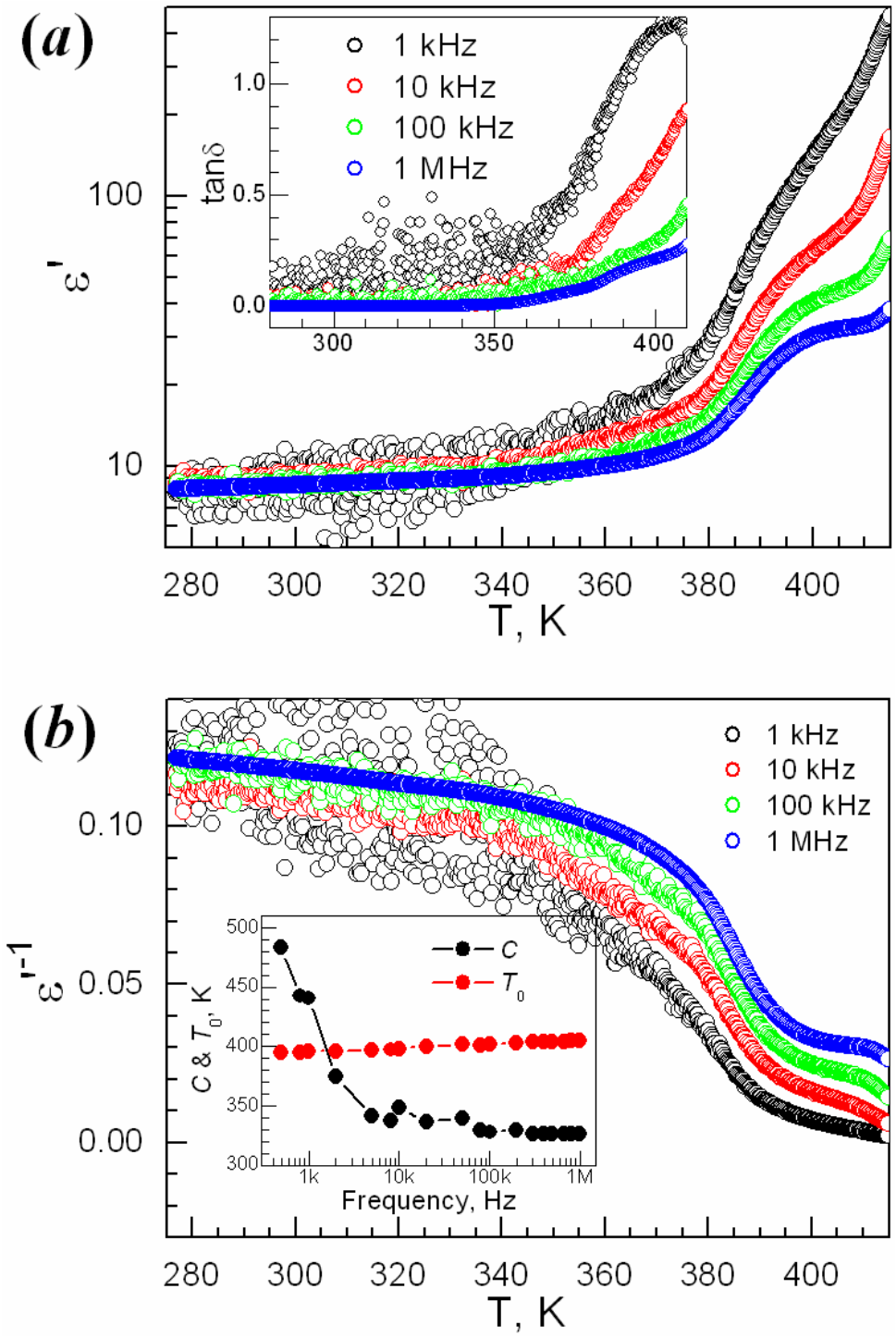

Fig. S12. Temperature-dependent traces of the dielectric permittivities on heating for **3Co**: (a) *ε' vs T*, and inset *tanδ vs T*, at 1 kHz, 10 kHz , 100 kHz and 1 MHz, (b) the relevant 1/*ε' vs T* plots, and inset the plots of *C* and T_0 *vs* frequency derived from data below T_C.

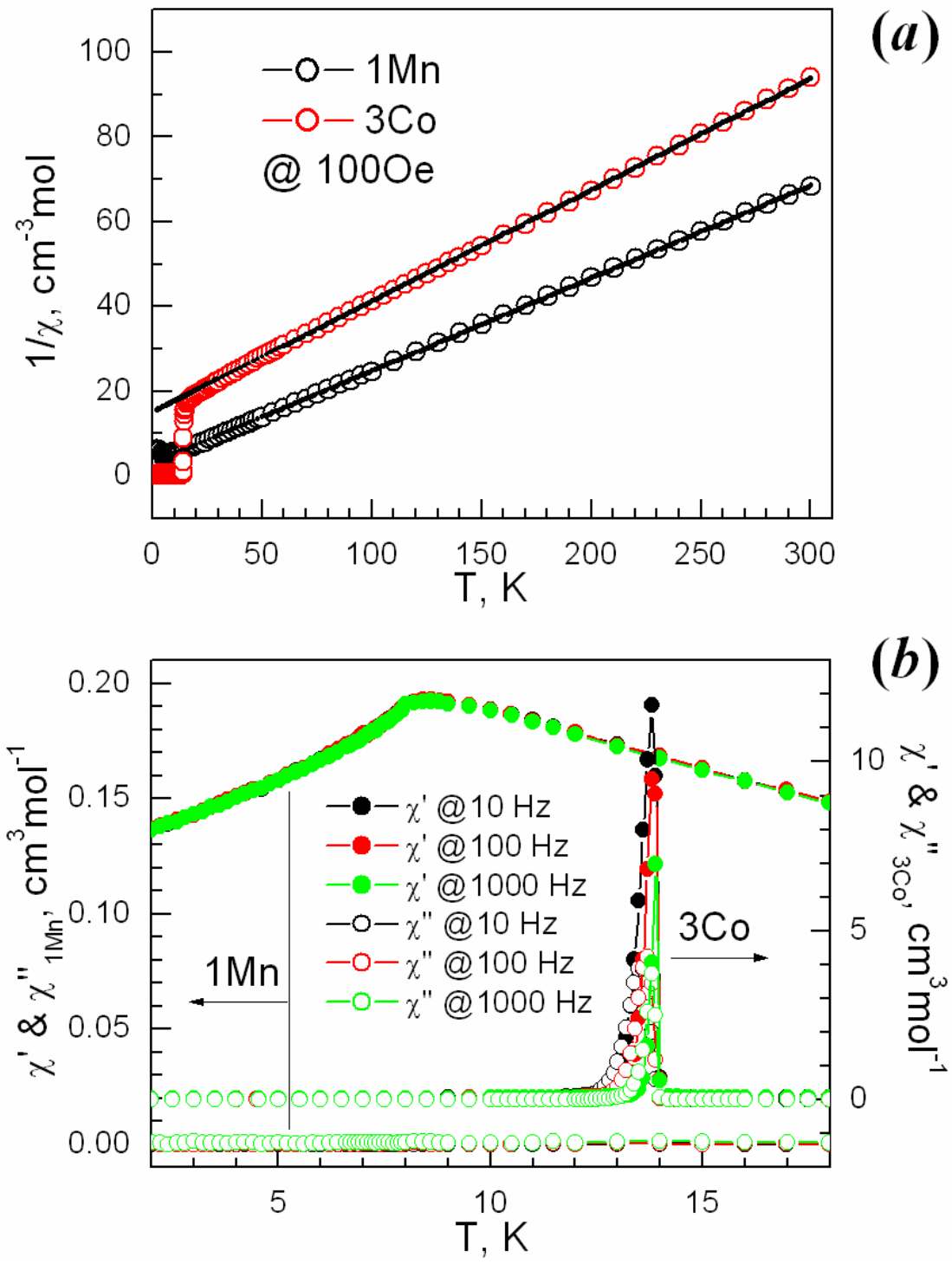

Fig. S13. Additional magnetic data for **1Mn** and **2Co**. (a) The 1/χ *vs T* plots, with the Curie-Weiss fittings in black lines. (b) The temperature-dependent traces of ac susceptibilities.