Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Synthesis of (MgCoNiCuZn)O entropy-stabilized oxides using solution-based routes: influence of composition on phase stability and functional properties

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List of tables.

Table S1. Coherence length values in the multiphasic powders calcined at 450°C

sample	CuO tenorite L_c^T (nm)[a]	ZnO wurtzite L_c^W (nm)[b]	Co spinel oxide L_c^S (nm)[c]	rock-salt L_c^R (nm)[d]
HEO-Mg	22	18	18	*multiple peaks*
HEO-Co	20	13	-	*multiple peaks*
HEO-Ni	26	12	*not detected*	*multiple peaks*
HEO-Cu	-	15	*poorly resolved*	14
HEO-Zn	25	-	*not detected*	*multiple peaks*
HEO	29	28	*poorly resolved*	26

[a] calculated from (002) lines using Scherrer formula. [b] from the (100) Bragg reflections. [c] from the (220) lines. [d] from the (200) lines.

Table S2. Summary of the EDS characterizations

sample	Mg[a]	Co[a]	Ni[a]	Cu[a]	Zn[a]
HEO-Mg	-	0.26(4)	0.24(2)	0.26(2)	0.23(1)
HEO-Co	0.22(4)	-	0.25(2)	0.28(2)	0.25(1)
HEO-Ni	0.25(3)	0.24(1)	-	0.26(1)	0.244(7)
HEO-Cu	0.25(1)	0.263(5)	0.245(4)	-	0.239(4)
HEO-Zn	0.23(3)	0.258(9)	0.25(1)	0.261(8)	-
HEO	0.22(2)	0.199(6)	0.189(5)	0.207(7)	0.182(4)

[a] from EDS data and analyses of magnesium, cobalt, nickel, copper and zinc K lines. Scans were performed over 4 to 5 different areas to derive mean values and standard deviations. Measurements were carried out on the sintered bars after grinding.

Table S3. Values of the fitted parameters (R, T, and n) for the high-frequency contribution for all compounds at selected temperatures

temp /K	HEO **R**	HEO **t**	HEO **n**
295	3.37E+07	2.24E-04	9.50E-01
345	3.81E+06	2.93E-05	9.60E-01
395	7.77E+05	5.66E-06	9.30E-01
445	2.28E+05	1.49E-06	8.70E-01

temp /K	HEO-Co **R**	HEO-Co **t**	HEO-Co **n**
295	3.36E+06	2.26E-05	9.10E-01
345	4.27E+05	2.78E-06	9.30E-01
395	8.40E+04	5.90E-07	7.50E-01
445	2.20E+04	1.35E-07	6.20E-01

temp /K	HEO-Cu **R**	HEO-Cu **t**	HEO-Cu **n**
295	1.19E+08	1.20E-03	9.90E-01
345	1.40E+07	1.64E-04	9.40E-01
395	6.20E+06	1.77E-05	9.60E-01
445	1.50E+06	2.18E-05	7.00E-01

temp /K	HEO-Mg **R**	HEO-Mg **t**	HEO-Mg **n**
295	7.50E+06	6.50E-05	9.70E-01
345	1.09E+06	9.30E-06	9.00E-01
395	1.60E+05	1.33E-06	8.40E-01
445	1.02E+05	2.50E-07	9.20E-01

temp /K	HEO-Ni **R**	HEO-Ni **t**	HEO-Ni **n**
295		7.23E-04	9.70E-01
345	4.60E+07	3.30E-04	9.60E-01
395	4.70E+06	3.20E-05	9.50E-01
445	5.97E+05	4.10E-06	9.60E-01

temp /K	HEO-Zn **R**	HEO-Zn **t**	HEO-Zn **n**
295	4.80E+07	7.20E-04	9.60E-01
345	6.90E+06	7.97E-05	8.00E-01
395	1.87E+06	1.54E-05	9.20E-01
445	2.63E+05	2.27E-06	9.20E-01

Table S4. Sample dimensions used for the impedance measurements

sample	Surface (mm^2)	Thickness (mm)
HEO	13.5	1.8
HEO-Cu	13.3	2
HEO-Mg	21.3	1.1
HEO-Co	16.8	2
HEO-Ni	16.1	2.2
HEO-Zn	18.9	1.6

List of figures.

Figure S1: (a) TGA curves of the dried gels recorded at 10°C/min heating rate under N_2/O_2 gas flow. (b) DTA signals under identical conditions.

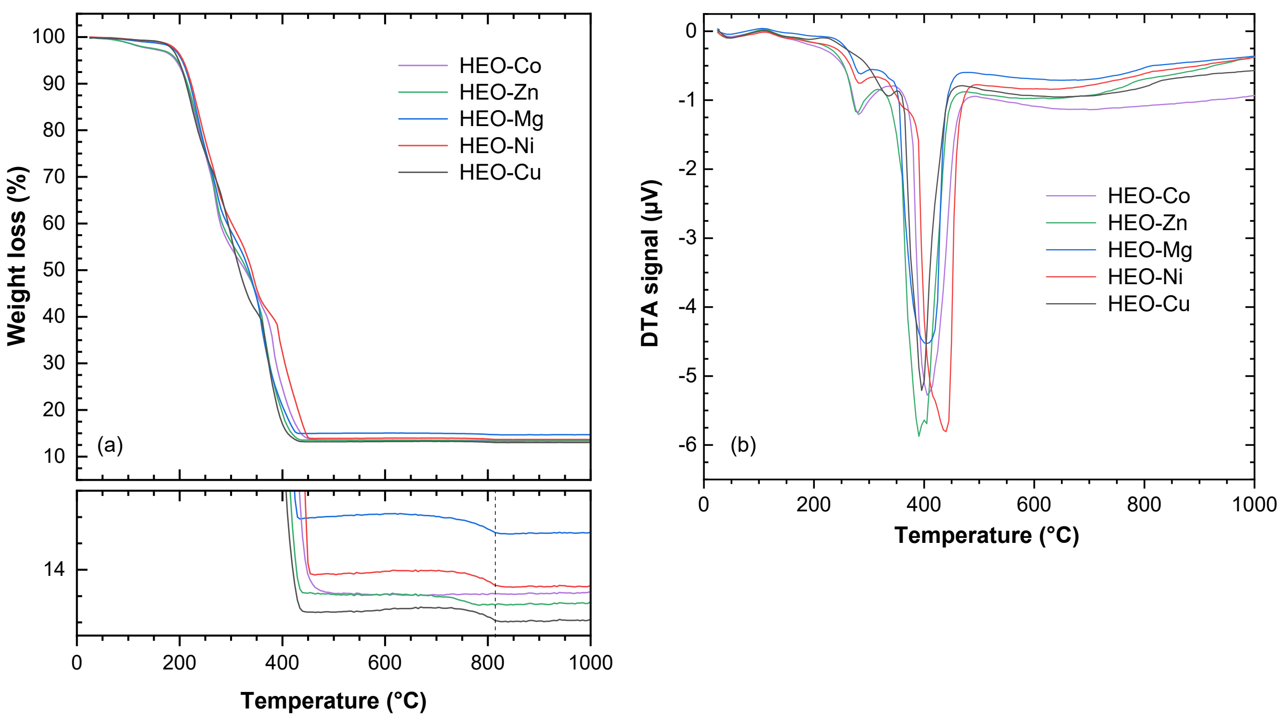


Figure S2: SEM images of the calcined gels showing the grain morphology before sintering at 1000°C.

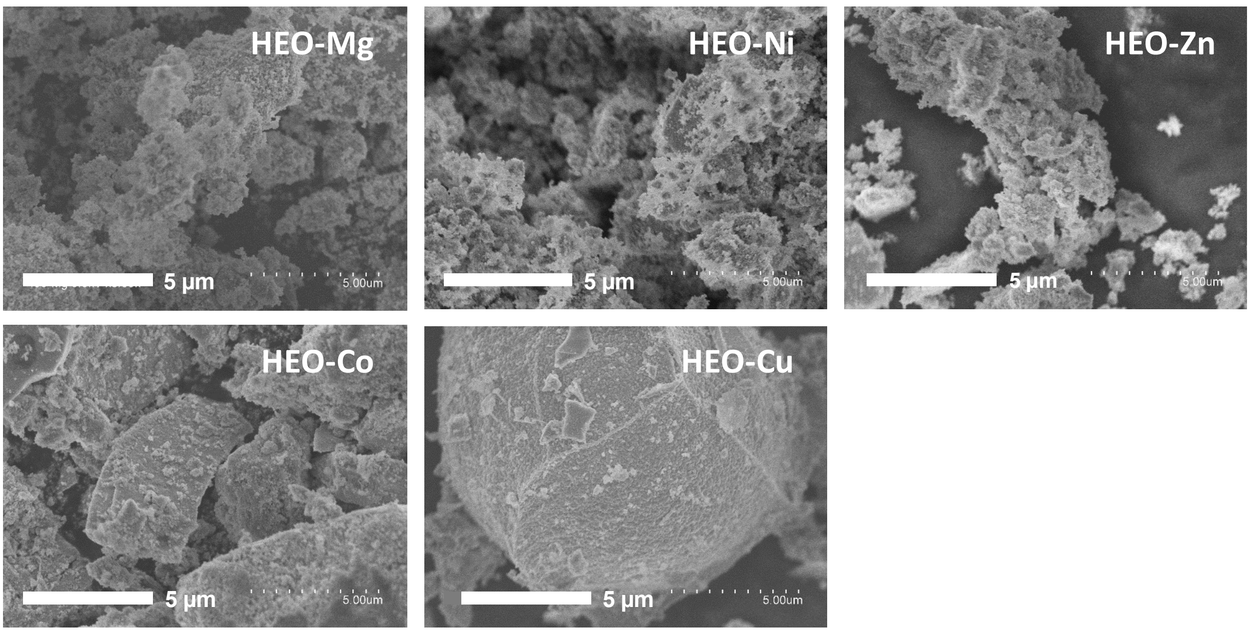


Figure S3: (a) X-ray diffraction pattern of the sample combining the Mg, Co, Ni, Cu and Zn elements after calcination of the Pechini resin at 450°C in air for 4 h. (b) *In situ* XRD patterns measured during the warming run. Profiles were displaced along the vertical axis to facilitate comparisons. Arrows mark the peaks of the tenorite (CuO) residual phase, which disappears with the emergence of the rock-salt multi-element oxide. Note that the asymmetry of the (200) peaks on the bottom right panel accounts for the K1, K2 splitting.

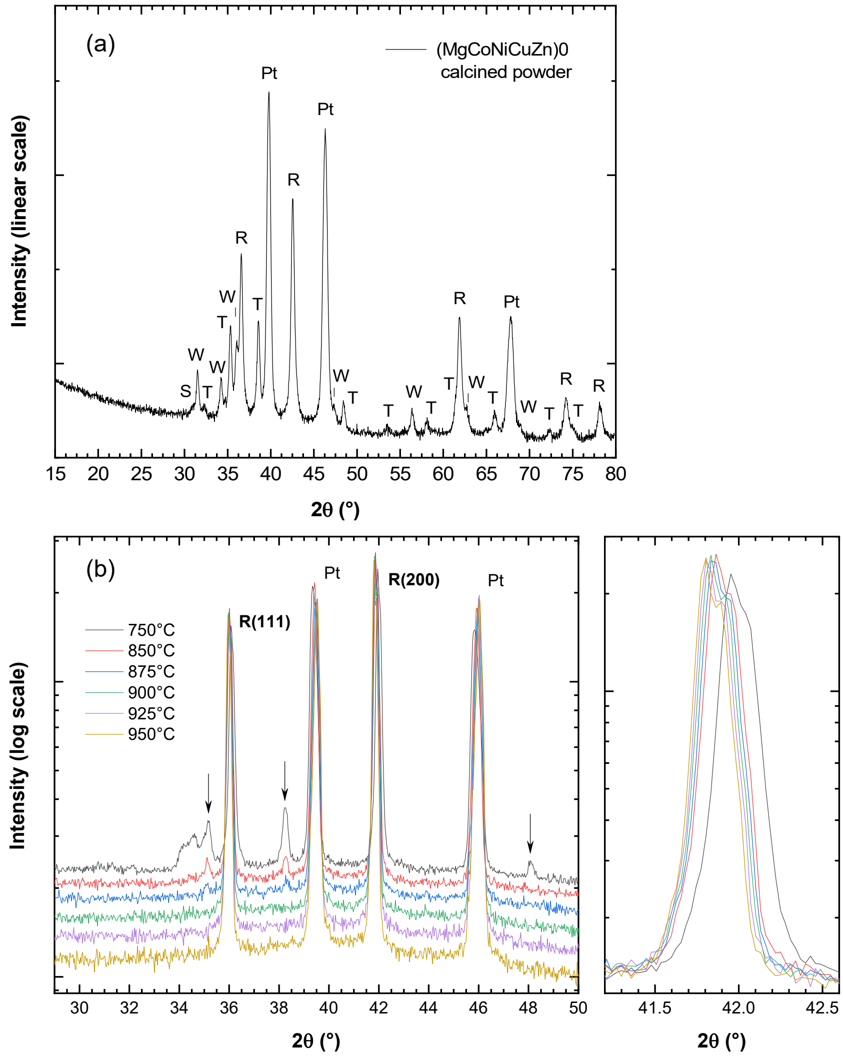
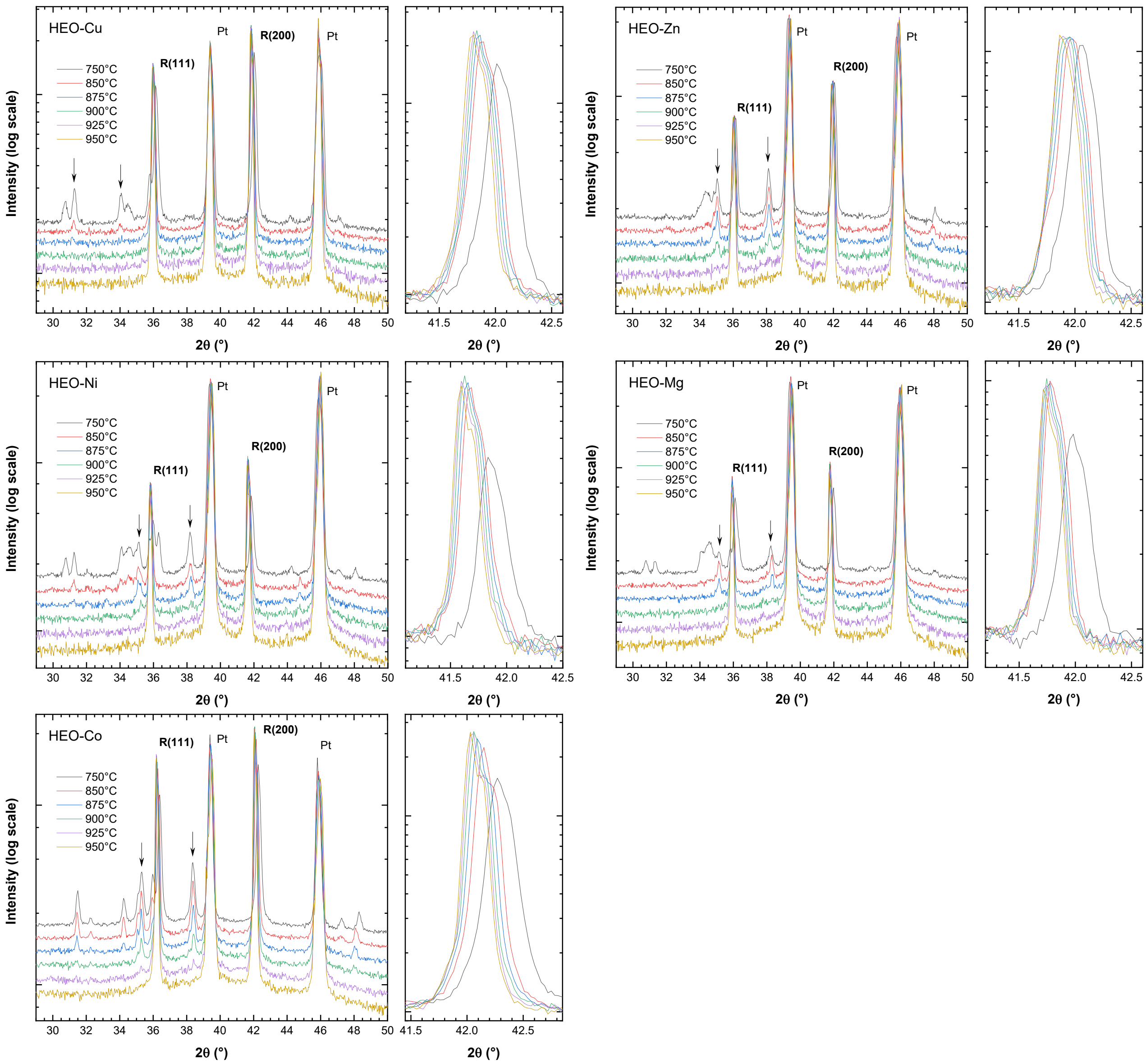


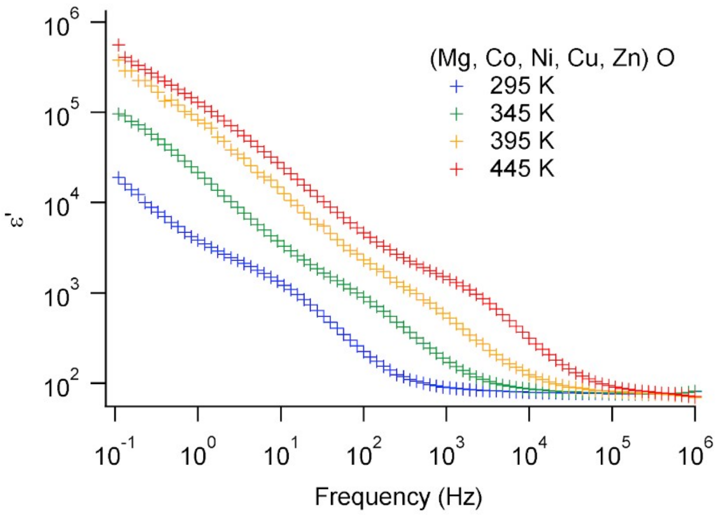
Figure S4: *In situ* XRD patterns measured during the warming run for the pre-calcined powders deposited onto the Pt strip. Arrows systematically mark the ZnO or CuO residual phases. The T_{onset} values, defined from the disappearance of all secondary phases, correspond to patterns in which the baseline change below the main side phases (tenorite or wurtzite) is comparable or smaller than the noise level. The data at 875°C can serve as comparison with *ex situ* measurements of similar 4-cation formulations prepared by standard solid-state reaction routes.1 It is important to note that Tonset cannot be directly identified to Ttrans solvus as defined in ref 1 where specimens were first equilibrated for 12 h at the target temperature. Note that the asymmetry of the (200) peaks at 950°C (right panels) systematically accounts for the K⍰1, K⍰2 splitting.

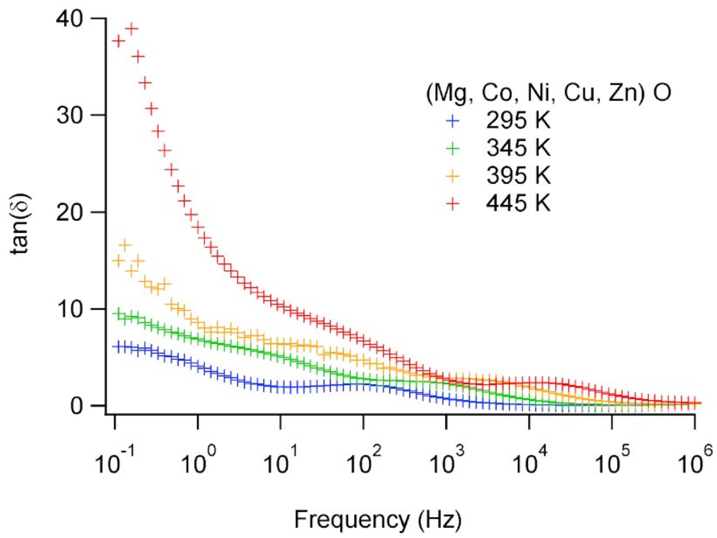


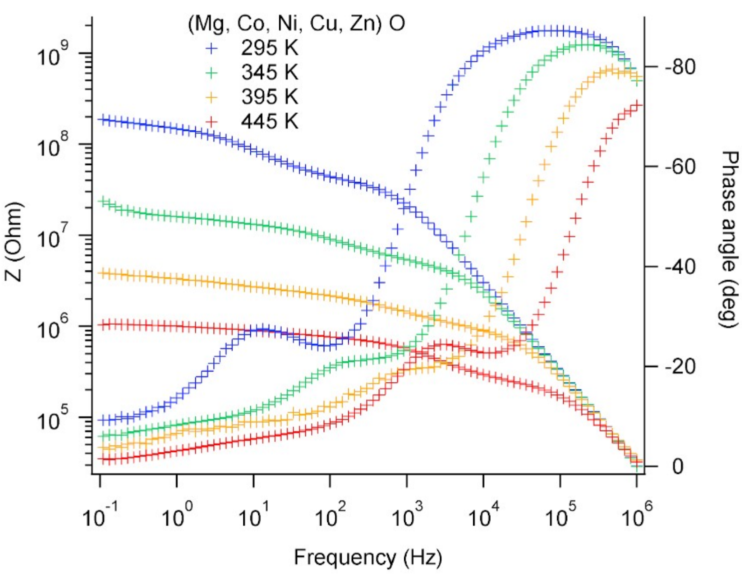
[1] C.M. Rost, E. Sachet, T. Borman, A. Moballegh, E.C. Dickey, D. Hou, J.L. Jones, S. Curtarolo and J.-P. Maria, *Nat. Commun.*, 2015, **6**, 8485.

Figure S5: Impedance data, real and imaginary parts of the dielectric constant as a function of frequency for all the samples, at different temperatures.

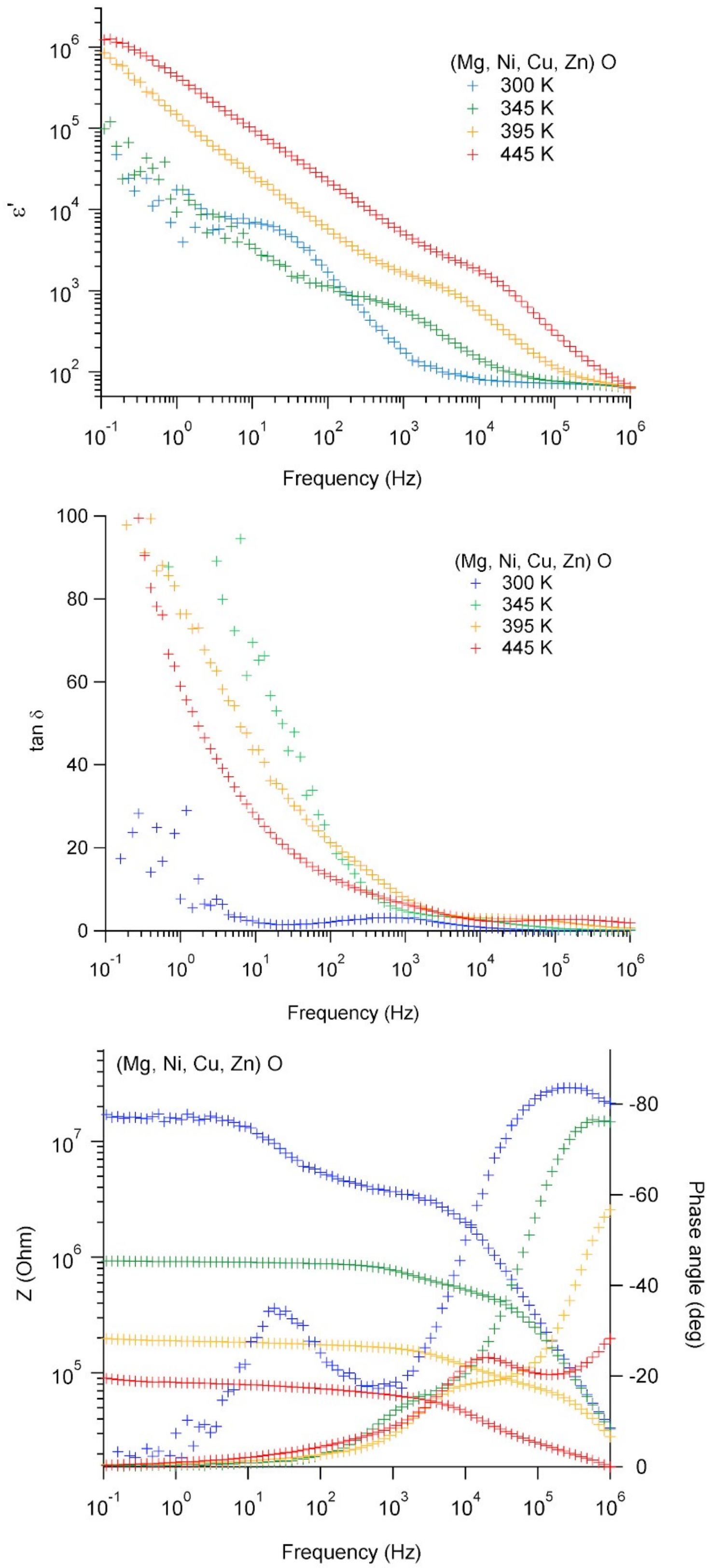
a) HEO





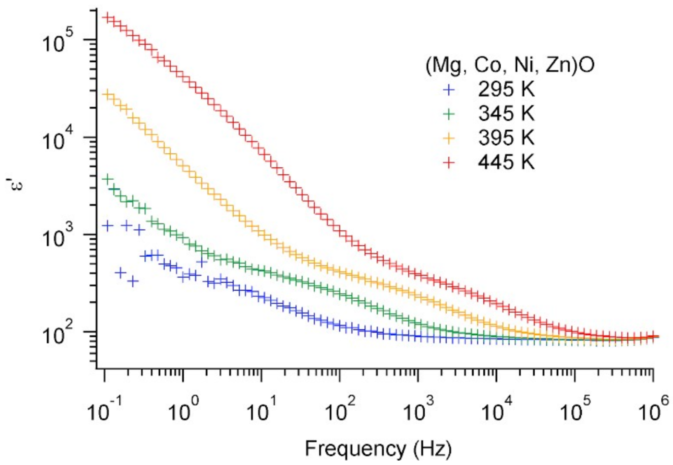


b) HEO-Co

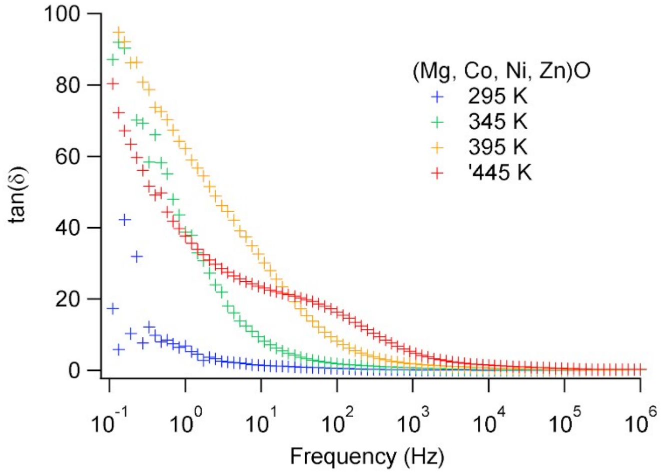


(Mg, Ni, Cu, Zn) O
300 K
345 K
395 K
445 K
ε'
Frequency (Hz)
(Mg, Ni, Cu, Zn) O
300 K
345 K
395 K
445 K
tan δ
Frequency (Hz)
(Mg, Ni, Cu, Zn) O
Z (Ohm)
Phase angle (deg)
Frequency (Hz)

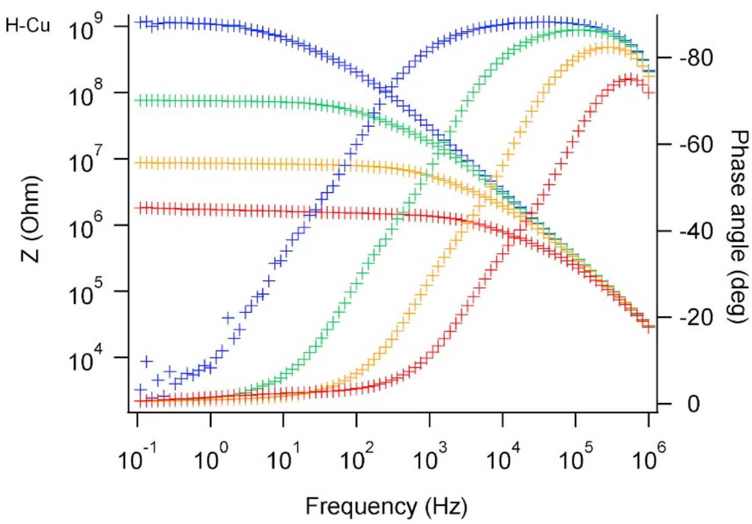
c) HEO-Cu



(Mg, Co, Ni, Zn)O
295 K
345 K
395 K
445 K
ε'
Frequency (Hz)

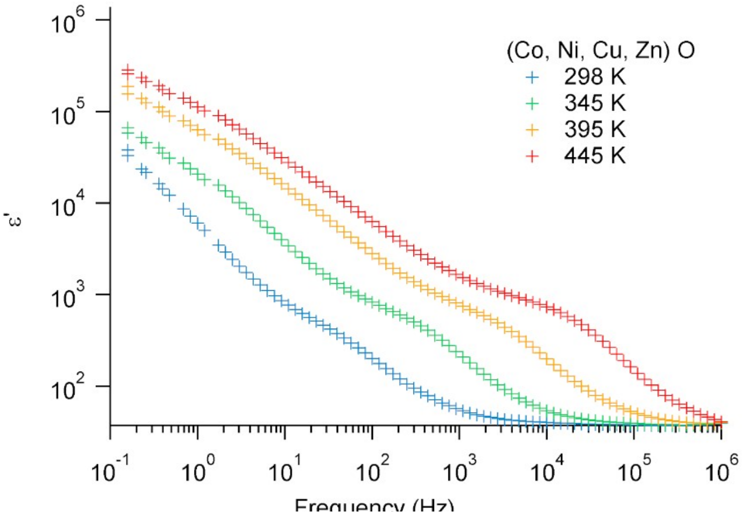


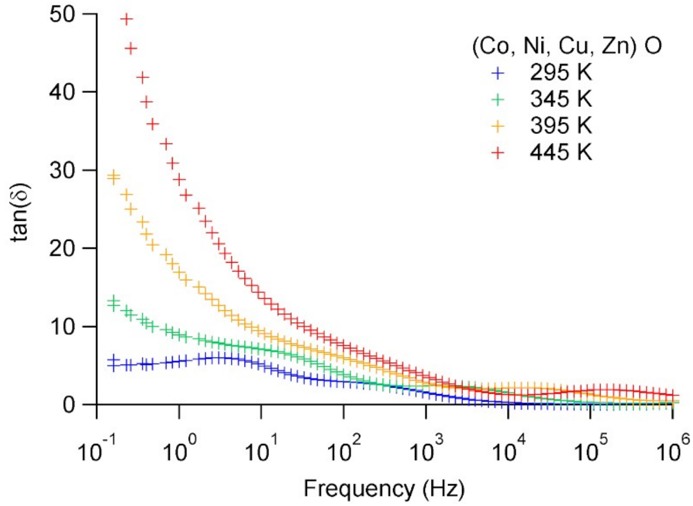
(Mg, Co, Ni, Zn)O
295 K
345 K
395 K
'445 K
tan(δ)
Frequency (Hz)

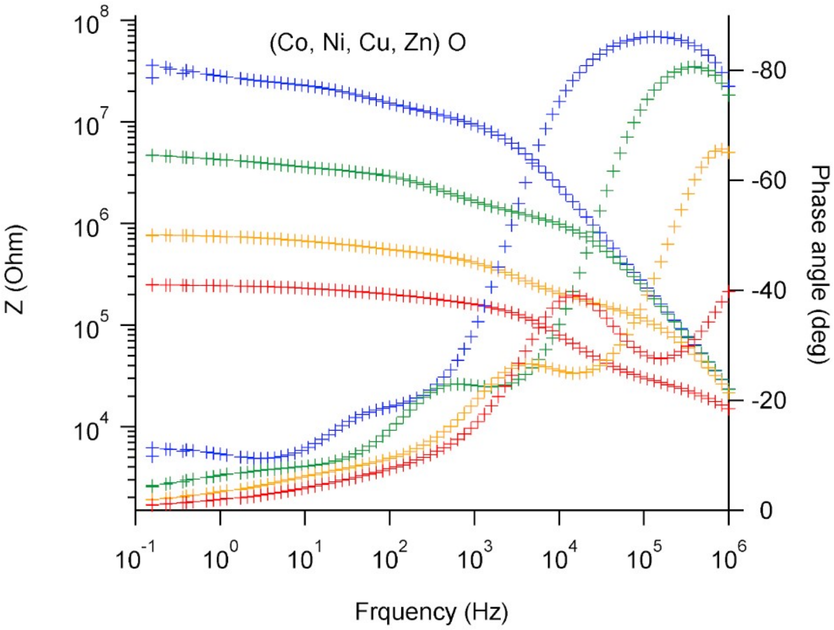


H-Cu
Z (Ohm)
Phase angle (deg)
Frequency (Hz)

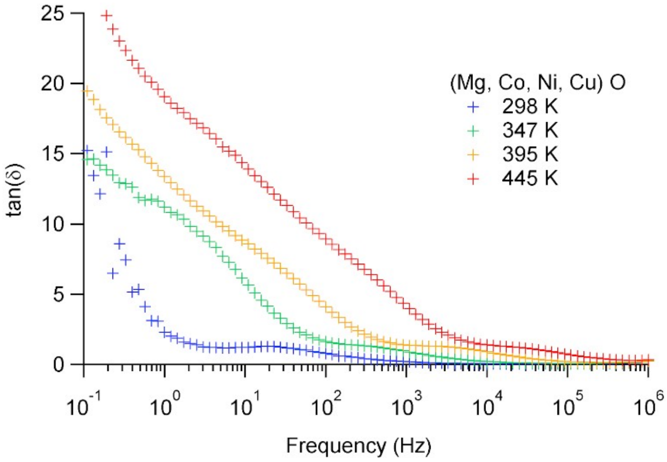
d) HEO-Mg

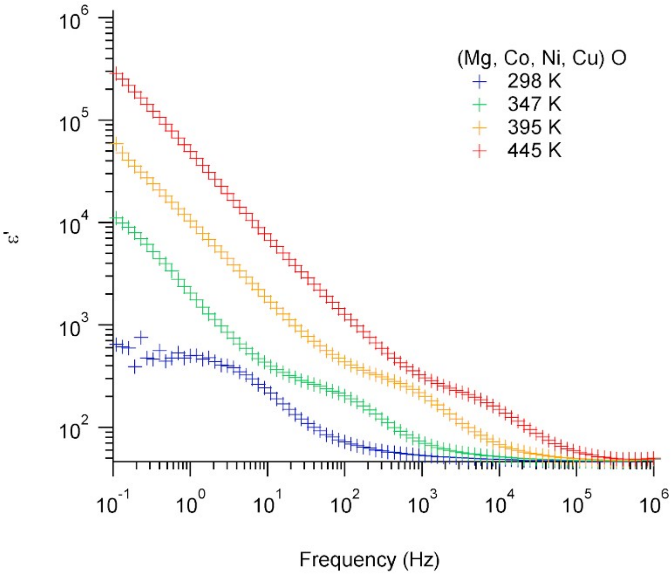

(Co, Ni, Cu, Zn) O
298 K
345 K
395 K
445 K
ε'
Frequency (Hz)


(Co, Ni, Cu, Zn) O
295 K
345 K
395 K
445 K
tan(δ)
Frequency (Hz)


(Co, Ni, Cu, Zn) O
Z (Ohm)
Phase angle (deg)
Frquency (Hz)

e)HEO-Zn


(Mg, Co, Ni, Cu) O
298 K
347 K
395 K
445 K
tan(δ)
Frequency (Hz)


(Mg, Co, Ni, Cu) O
298 K
347 K
395 K
445 K
ε'
Frequency (Hz)

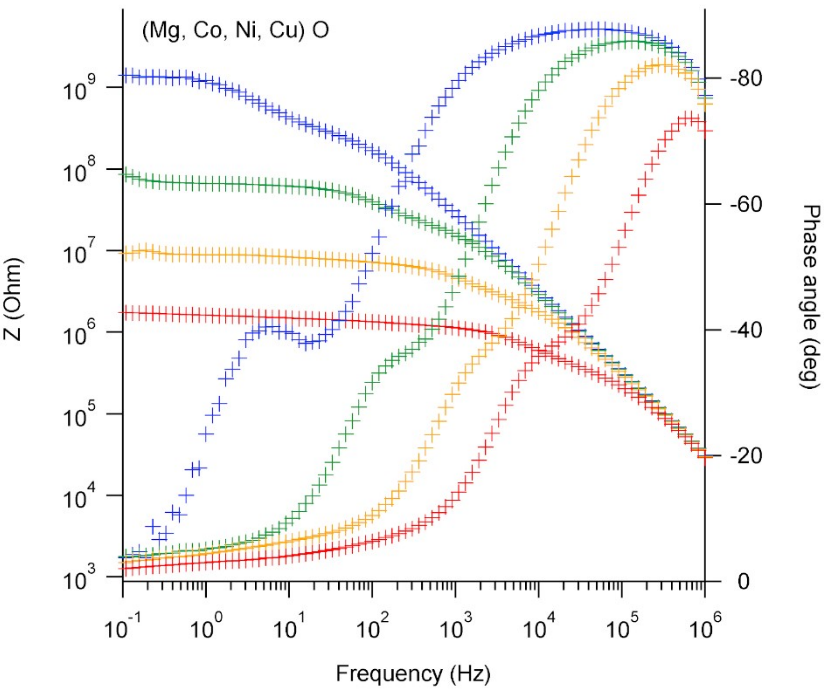

(Mg, Co, Ni, Cu) O
Z (Ohm)
Phase angle (deg)
Frequency (Hz)

Figure S6: Distribution of relaxation times (DRT) for HEO-Ni at 395 K, the same measurement as in Figure 7 of the manuscript, obtained with Gaussian discretization method and a regularization parameter equal to 0.01; calculated with pyDRTtools (see http://dx.doi.org/10.1016/j.electacta.2015.09.097).

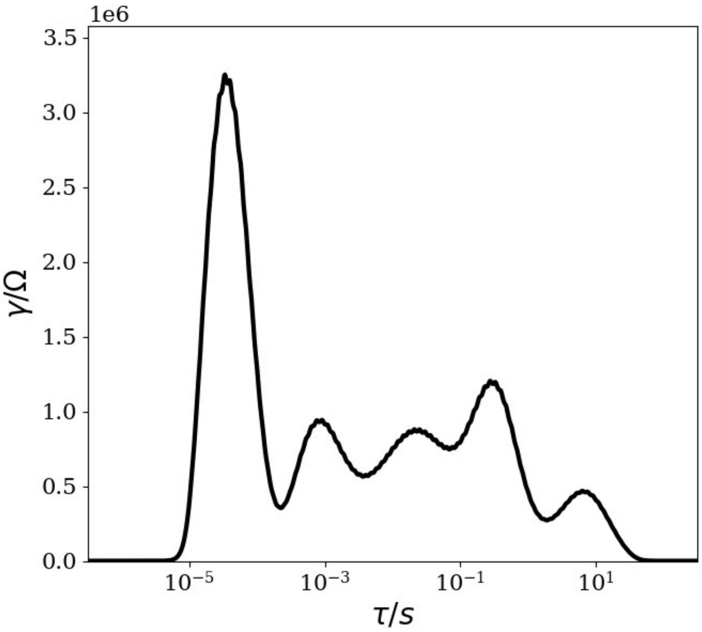
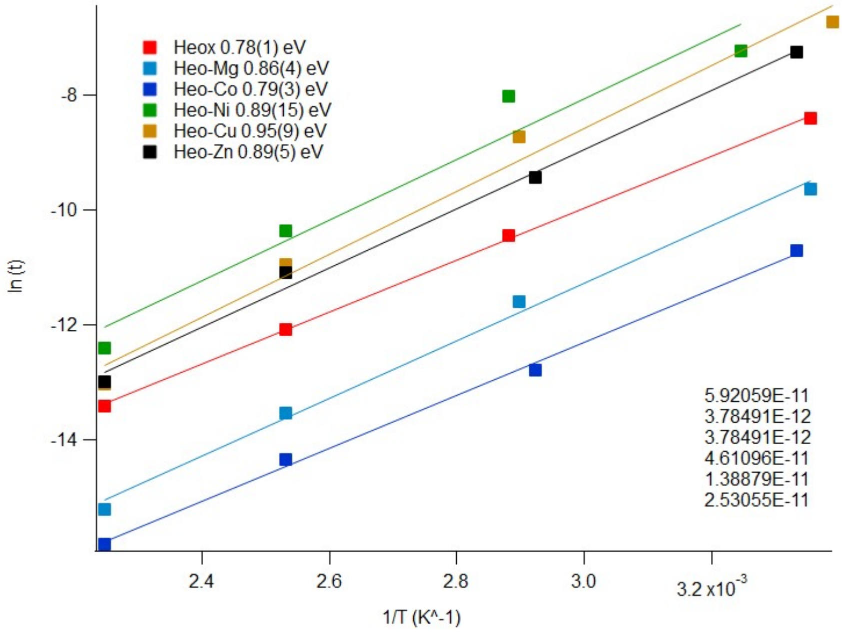


Figure S7: Temperature dependence of the relaxation times for the studied compounds with calculated energy gaps and infinite time relaxation values.



sample	inf relaxation time	Gap (eV)
HEO	5.92E-11	0.78(1) eV
HEO-Mg	3.78E-12	0.86(4) eV
HEO-Co	3.78E-12	0.79(3) eV
HEO-Ni	4.61E-11	0.89(15) eV
HEO-Cu	1.39E-11	0.95(9) eV
HEO-Zn	2.53E-11	0.89(5) eV

Figure S8: Real part of AC conductivity for the 5-cation HEO synthesized through the Pechini route at 295, 345, 395 and 445 K.

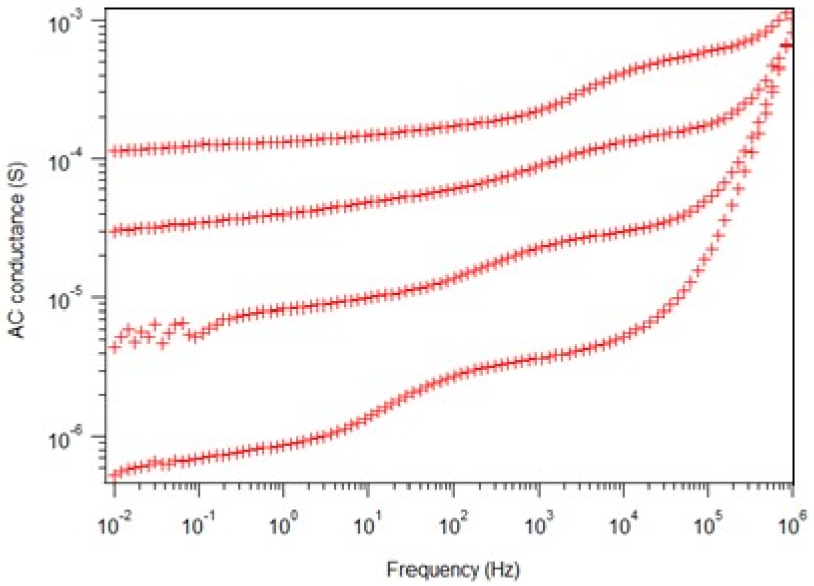
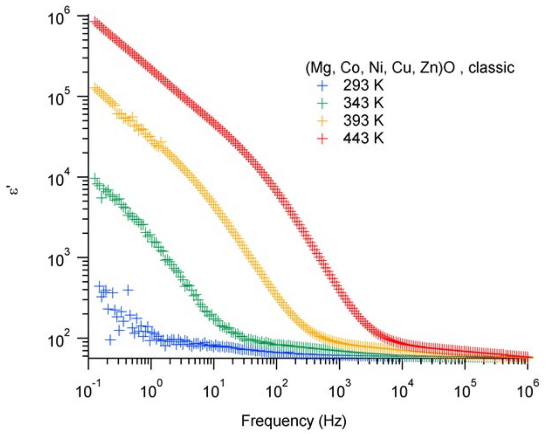
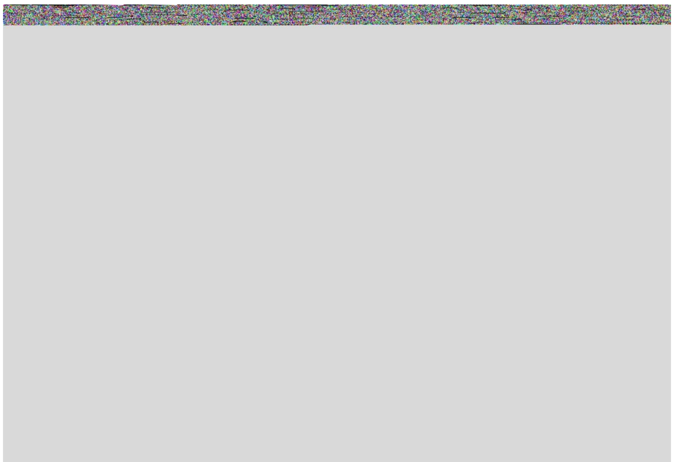
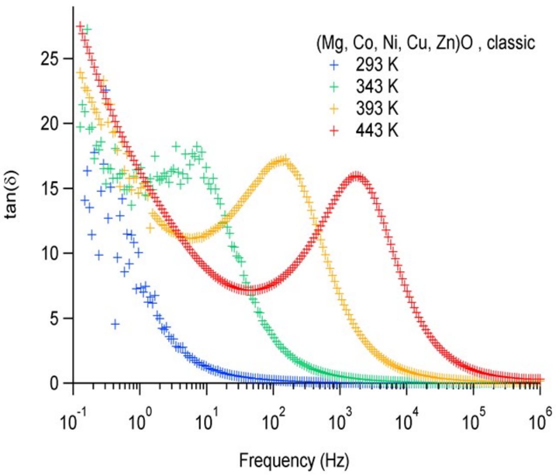
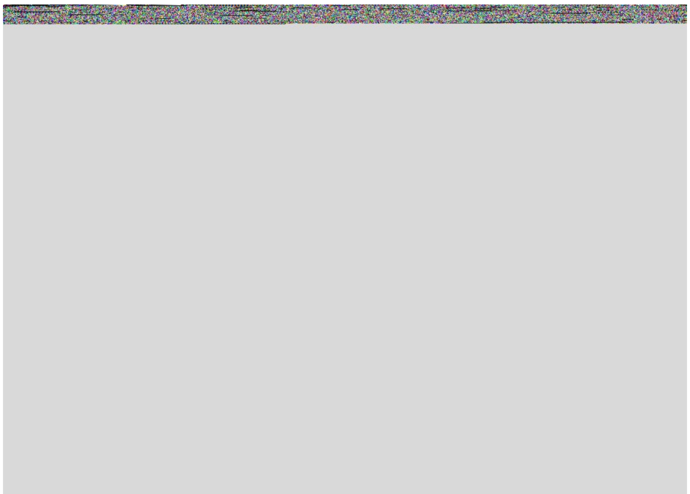


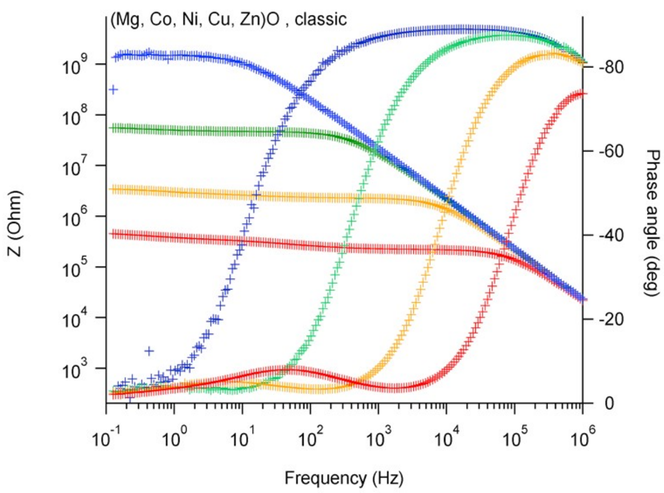
Figure S9: Impedance spectra for a 5-cation HEO sample obtained by a classical solid synthesis route (on the right side we reproduce the spectra for the samples obtained by Pechini method).











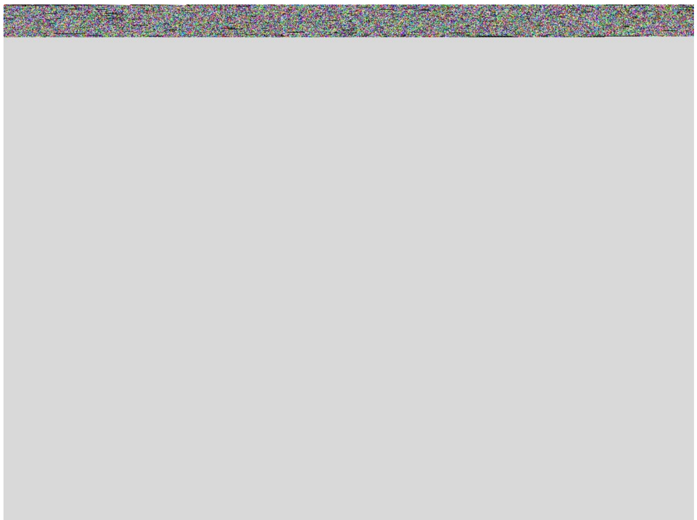


Figure S10: Magnetization curves at 10 K of the 4 and 5-cation powders sintered at 1000°C. Straight dashed lines are guide for the eyes.