Electronic Supporting Information

Magnetic and spectroscopic properties of Ni-Zn-Al ferrite spinel: from the nanoscale to microscale

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Structural properties:

X-ray density ($\rho_{X\text{-}ray}$) of the samples wascalculated by considering that a basic unite cell of the cubic spinel structure containseight ions, using the following equation:[1]

$$\rho_{X-ray} = \frac{8.M}{N_A.a^3} \quad S1$$

where M is the molecular weight of each compound, N_A is Avogadro's number, a is the as-calculated lattice parameter converted in cm units and 8 represents the number of molecules in a unit cell ofspinel lattice.

Thebulk density ρ_{th}estimated using the following relation:[1]

$$\rho_{th} = \frac{m}{\pi.r^2.h} \quad S2$$

where h is the thickness of the pellet, r is the radius, and m is the mass of pellet .

The apparent porosity, P, in each sample was calculated using the following equation:[1]

$$P(\%) = \frac{\rho_{X-ray} - \rho_{th}}{\rho_{X-ray}} \times 100 \quad S3$$

Assuming all the particles to be spherical, the specific surface area was calculated from the relation:[2]

$$S = \frac{6000}{D_{SC}.\rho_{X-ray}} \quad S4$$

wherethe constant 6000 is called form factor for spherical particles, D_{SC} is the diameter of the particle and "$\rho_{X\text{-}ray}$"is the X-ray density.

The theoretical lattice parameter (a_{th}) can be calculated using the following equation:[3]

$$a_{th} = \frac{8\left[(r_A + r_o) + \sqrt{3}(r_B + r_o)\right]}{3\sqrt{3}} \quad S5$$

Where, $r_A = \sum_i C_i r_i$, $r_B = \frac{1}{2}\sum_i C_i r_i$ are the average ionic radii per molecule for the respective A and B-sites; here, C_i is the concentration of the element i with ionic radius r_i on a particular site.

The oxygen positional parameter (u) can be determined using the relations:[3]

$$u = \left[(r_A + r_o)\frac{1}{a\sqrt{3}} + 0.25\right] \quad S6$$

The tetrahedral and octahedral bond lengths (d_{AE}) and (d_{BE}), tetrahedral edge (d_{AL}), shared and unshared octahedral edge (d_{BL}) and (d_{BEu}), the distance between magnetic ions (i.e. hopping lengths) of A-site (L_A) and of B-site (L_B) can be evaluated by:[4]

$$d_{AE} = a\sqrt{2}\left(2u - \frac{1}{2}\right) \quad S7$$

$$d_{AL} = a\sqrt{3}\left(u - \frac{1}{4}\right) \quad S8$$

$$d_{BL} = a\sqrt{3(u\ )^2 - \frac{11}{4}u + \frac{43}{64}} \quad S9$$

$$d_{BEu} = a\sqrt{4(u)^2 - 3u\ + \frac{11}{16}} \quad S10$$

$$d_{BE} = a\sqrt{2}(1-2u) \quad S11$$

$$L_A = \frac{a\sqrt{3}}{4} \; S12$$

$$L_B = \frac{a\sqrt{2}}{4} \; S13$$

where a is the lattice parameter experimental.

Fig. S2 shows the interionic distances and bond angles between ions of spinel ferrites. The bond lengths and bond angles between the cations are calculated by the following relations:[5]

Me-O distances

$$p = a\left(\frac{5}{8} - u\right) \quad S14 \quad , \quad q = a\sqrt{3}(u - 0.25) \; S15 \quad , \quad r = a\sqrt{11}(u - 0.25) \; S16 \quad , \quad s = a\sqrt{3}\left(\frac{1}{3}u + \frac{1}{8}\right) S17$$

Me-Me distances

$$b = \frac{a\sqrt{2}}{4} \; S18 \quad , \quad c = \frac{a\sqrt{11}}{8} \; S19 \quad , \quad d = \frac{a\sqrt{3}}{4} \; S20 \quad , \quad e = \frac{3a\sqrt{3}}{8} \; S21 \quad , \quad f = \frac{a\sqrt{6}}{4} \; S22$$

Bond angles

$$\cos(\theta_1) = \frac{p^2 + q^2 - c^2}{2pq} \; S23 \quad , \quad \cos(\theta_2) = \frac{p^2 + r^2 - e^2}{2pr} \; S24 \quad , \quad \cos(\theta_3) = \frac{p^2 - b^2}{2p^2} \; S25$$

$$\cos(\theta_4) = \frac{p^2 + s^2 - f^2}{2ps} \; S26 \qquad \cos(\theta_5) = \frac{r^2 + q^2 - d^2}{2rq} \; S27$$

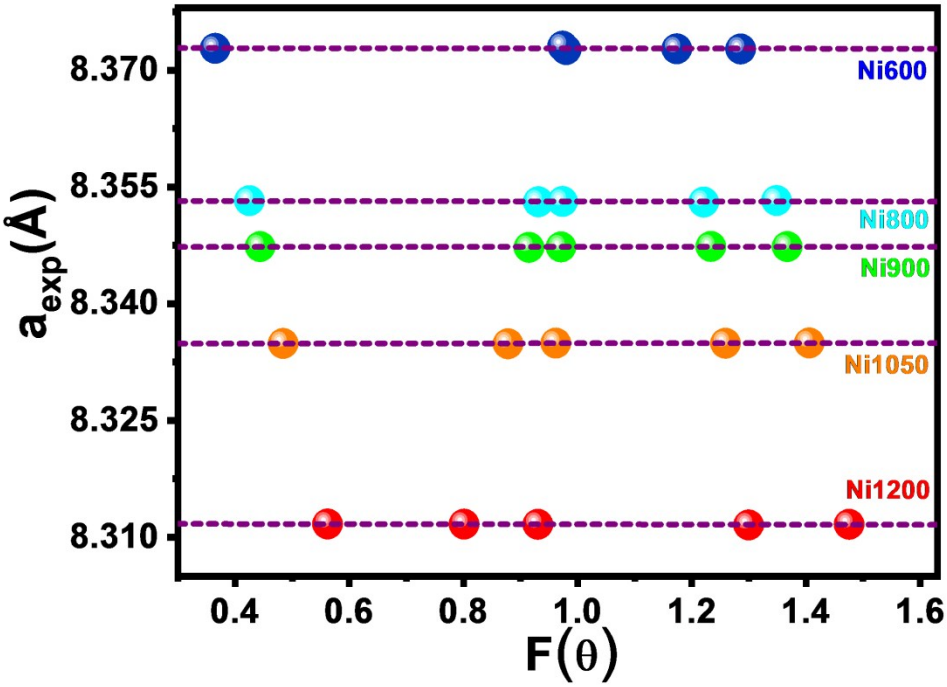

Fig. S1 Lattice constants as function of the Nelson-Riley function F(θ) for all samples

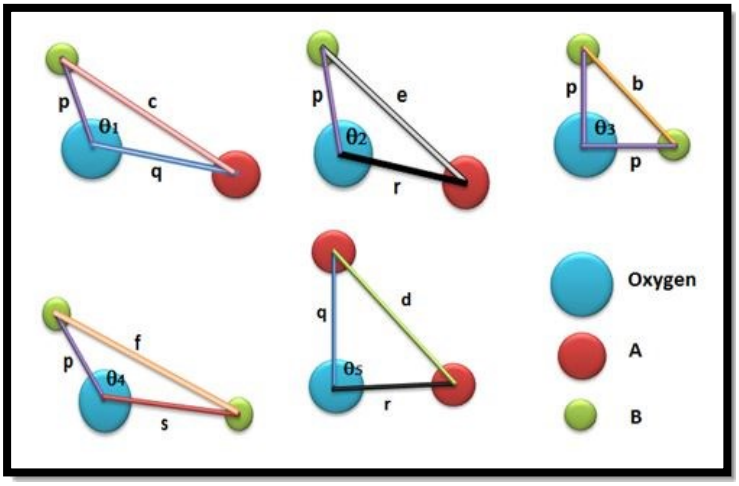

Fig. S2 The interionic distances and bond angles between ions of spinel ferrites

Table S1 Lattice constants (a_{exp}, a_0, a_R and a_{th}), unit cell volume (V), Rietveld refinement parameters, specific surface area (S), X-ray density ($\rho_{X\text{-}ray}$), apparent density (ρ_{exp}), porosity (P), hopping length (L_A and L_B), mean ionic radii (r_A and r_B), oxygen positional parameter (*u*) tetrahedral bond length (d_{AE}), octahedral bond length (d_{BE}), tetrahedral edge (d_{AL}), sharedoctahedral edge (d_{BL}) and unshared octahedral edge (d_{BEu}) of NZFAO samples.

Parameter	Ni600	Ni800	Ni900	Ni1050	Ni1200
a_{exp}(Å)	8.368	8.338	8.325	8.307	8.278
a_0(Å)	8.372	8.353	8.347	8.334	8.311
a_R(Å)	8.372	8.347	8.334	8.334	8.311
a_{th}(Å)	8.354	8.352	8.350	8.348	8.341
V (Å^3)	586.063	579.782	577.1315	573.294	567.385
χ^2	2.49	2.10	1.29	2.07	3.00
R_P (%)	20.9	14.7	24.9	22.0	51.8
R_{wp} (%)	13.1	8.45	11.1	10.4	21.8
R_e (%)	8.26	5.82	9.71	7.23	12.6
S (m^2/g)	69.81	48.14	39.56	26.72	22.29
$\rho_{x\text{-}ray}$ (g.cm^{-3})	5.046	5.100	5.124	5.158	5.212
ρ_{exp} (g.cm^{-3})	3.234	3.284	3.334	3.358	3.408
P (%)	35.904	35.615	34.938	34.889	34.605
r_A (Å)	0.6668	0.6569	0.6492	0.6404	0.6360
r_B (Å)	0.6341	0.6390	0.6429	0.6473	0.6495
U	0.3884	0.3882	0.3879	0.3876	0.3874
L_A(Å)	3.625	3.617	3.614	3.609	3.594
L_B (Å)	2.960	2.953	2.951	2.946	2.934
d_{AE}(Å)	3.275	3.259	3.247	3.233	3.225
d_{BE}(Å)	2.641	2.636	2.639	2.640	2.643
d_{AL}(Å)	2.006	1.995	1.998	1.979	1.975
d_{BL}(Å)	1.986	1.980	1.979	1.997	1.977
d_{BEu}(Å)	2.967	2.956	2.951	2.944	2.941

Table S2 Interatomic distance, bond angles, crystallite size observed from XRD (D_{SC}) and particle size determined from SEM (D_{SEM}), cation distribution of NZFAO samples

Parameter	Ni600	Ni800	Ni900	Ni1050	Ni1200
p (Å)	1.9798	1.9744	1.9738	1.9721	1.9720
q (Å)	2.0060	1.9958	1.9884	1.9798	1.9752
r (Å)	3.8410	3.8217	3.8075	3.7910	3.7823
s (Å)	3.6881	3.6740	3.6668	3.6574	3.6534
b (Å)	2.9585	2.9479	2.9433	2.9369	2.9344
c (Å)	3.4691	3.4567	3.4513	3,4439	3.4409
d (Å)	3.6234	3.6104	3.6048	3.5970	3.5940
e (Å)	5.4351	5.4156	5.4072	5.3955	5.3910
f (Å)	5.1243	5.1059	5.0980	5.0869	5.0826
θ_1 (°)	121.00	121.07	121.16	121.25	121.32
θ_2 (°)	135.61	135.83	136.18	136.52	136.76
θ_3 (°)	128.06	127.92	127.72	127.5	127.38
θ_4 (°)	126.74	126.71	126.68	126.64	126.62
θ_5 (°)	68.49	68.65	68.87	69.1	69.26
D_{SC}(nm)	17	24.5	29.8	43.9	52.2
D_{SEM} (nm)	13.6	22.28	37.62	180	4620
Cation distribution	$(Zn_{0.4}Al_{0.12}Fe_{0.48})$ $[Ni_{0.6}Al_{0.38}Fe_{1.02}]$	$(Zn_{0.4}Al_{0.21}Fe_{0.39})$ $[Ni_{0.6}Al_{0.29}Fe_{1.11}]$	$(Zn_{0.4}Al_{0.28}Fe_{0.32})$ $[Ni_{0.6}Al_{0.22}Fe_{1.18}]$	$(Zn_{0.4}Al_{0.36}Fe_{0.24})$ $[Ni_{0.6}Al_{0.14}Fe_{1.26}]$	$(Zn_{0.4}Al_{04.}Fe_{0.2})$ $[Ni_{0.6}Al_{0.1}Fe_{1.3}]$

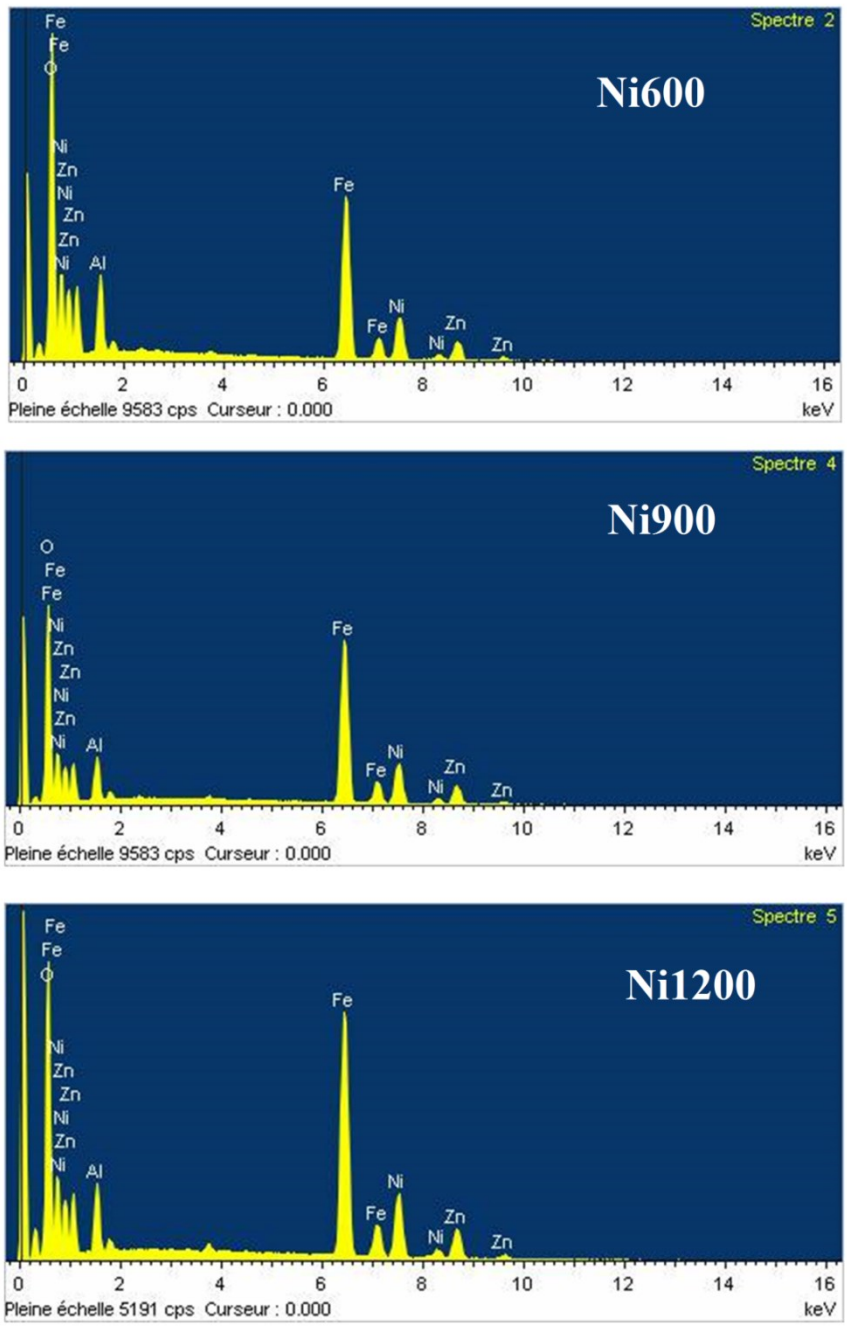

Fig. S3 EDS analysis of Ni600, Ni900 and Ni1200 samples

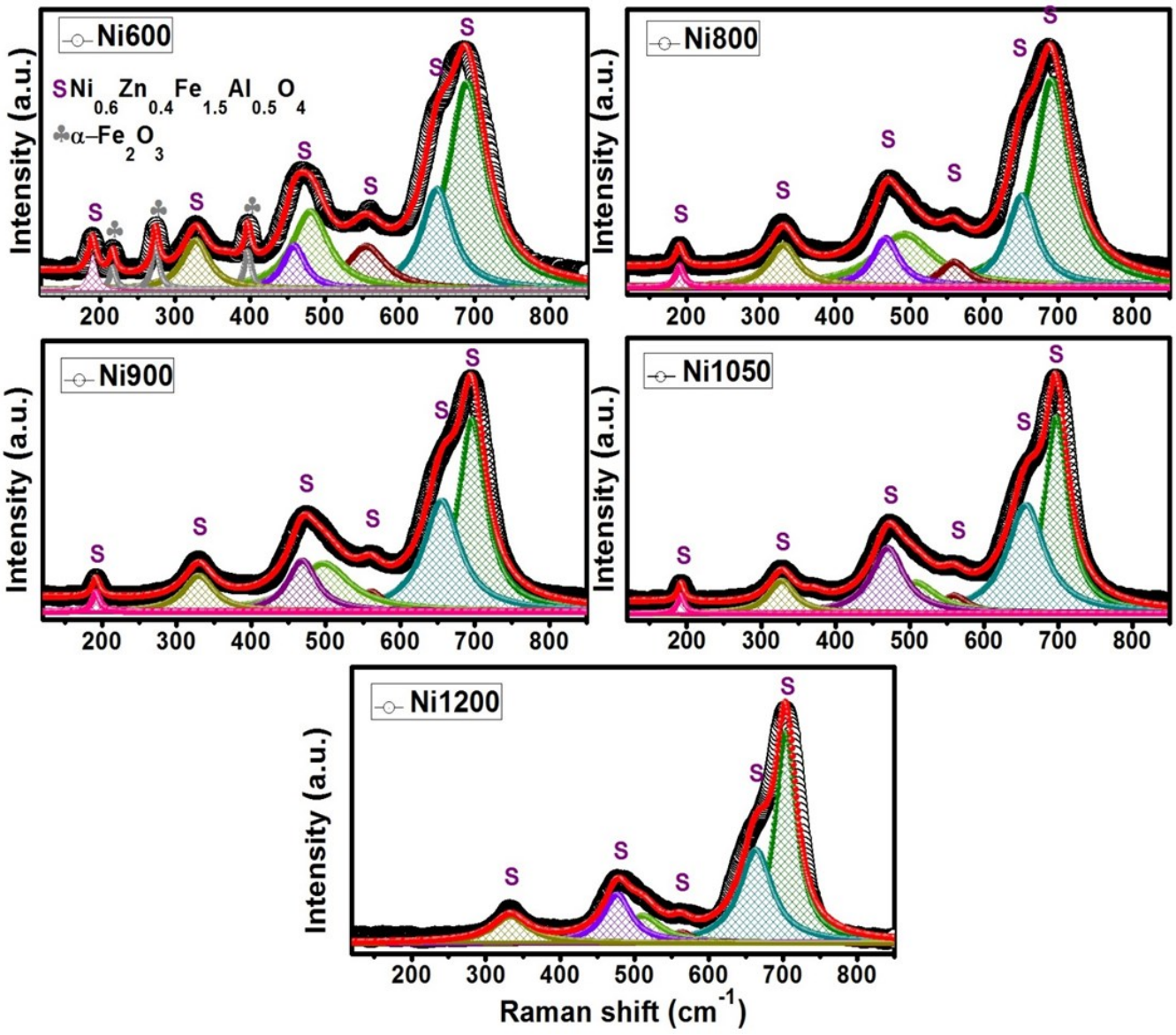

Fig. S4 Deconvoluted Raman spectra at 300 K of NZFAO samples annealed at different temperature fitted with the Lorentzian function.

Table S3 Raman band position and force constants of the tetrahedral and octahedral sites of different samples

Sample	Raman band position (cm^{-1})						Force constants (N/m)	
	$A1g^{(1)}$	$A1g^{(2)}$	$F2g^{(3)}$	$F2g^{(2)}$	Eg	$F2g^{(1)}$	F_T	F_O
Ni600	690.22	650.15	555.69	481.04	327.94	189.76	203.95	116.94
Ni800	691.54	651.36	493.52	468.38	330.83	191.33	195.29	122.03
Ni900	696.80	656.13	469.11	469.11	330.46	192.34	190.81	124.09
Ni1050	697.893	657.04	560.49	471.39	328.33	192.96	182.86	125.14
Ni1200	703.90	663.86	563.63	477.27	333.57	---	181.67	130.52

Table S4 Band position (υ), threshold energy (E_{th}), force constant (K), elastic parameters and Debye temperature (θ) of the annealed NZAFO samples determined from FTIR spectra recorded at 300 K.

Parameter	Ni600	Ni800	Ni900	Ni1050	Ni1200
ν_A (cm^{-1})	557.8	565.1	571.7	576.2	581.4
ν_B (cm^{-1})	403.6	406.7	407.5	407.5	409.8
ν_{av} (cm^{-1})	480.7	485.9	489.6	491.8	495.6
ν_{th} (cm^{-1})	670.1	712.6	718.4	719	724.7
$E_{th} \times 10^{-2}$ (eV)	8.28	8.80	8.87	8.88	8.95
K_T (N/m)	133.2	130.0	128.4	124.6	123.9
K_O (N/m)	177.1	184.4	188.7	192.8	197.0
K_{av} (N/m)	155.1	157.2	158.5	158.7	160.4
C_{11}(GPa))	185.3	188.5	190.4	191.0	193.7
B (GPa)	185.3	188.5	190.4	191.0	193.7
ν_l(m/s)	6059.8	6079.5	6095.7	6085.2	6096.2
ν_s(m/s)	3498.6	3510.0	3519.3	3513.3	3519.6
ν_m(m/s)	3884.1	3896.7	3907.0	3900.4	3907.4
G (GPa)	61.7	62.8	63.4	63.7	64.5
σ	0.35	0.35	0.35	0.35	0.35
E (GPa)	166.6	169.6	171.2	172.0	174.1
θ_D(K)	691.2	698.7	704	707.2	712.7
θ_E (K)	529.0	532.6	534.9	535.1	538

Table S5 Elastic data corrected to zero porosity for the annealed NZFAO samples.

Model	Parameter	Ni600	Ni800	Ni900	Ni1050	Ni1200
Elastic theory	σ_0	0.478	0.477	0.474	0.474	0.472
	G_0 (GPa)	153.6	154.5	151.8	152.2	152.4
	E_0 (GPa)	526.4	526.2	509.7	510.6	508.2
	v_{s0} (m/s)	3947.2	3982.8	3983.2	3975.6	3978.5
	v_{l0} (m/s)	11023.9	10995.1	10875.8	10846.5	10804.6
	v_{m0} (m/s)	4484.4	4523.6	4522.9	4514.2	4516.9
	C_l	1.2542	1.2553	1.2580	1.2582	1.2593
	Ce	1.9038	1.9029	1.9009	1.9008	1.8999
	C_σ	0.75	0.75	0.75	0.75	0.75
Ledbetter and Datta model	A_1	1.7092	1.7169	1.7349	1.7362	1.7438
	A_2	169.695	174.299	180.486	180.960	185.75
	A_3	-46613.7	-48161.5	-48866,5	-49234,6	-50451,23
	E_0 (GPa)	357.1	354.0	352.2	353.4	355.6
	G_0 (GPa)	125.6	124.2	123.7	124.16	124.97
	B_0 (GPa)	760.4	790.2	769.9	768.4	769.7
	B_0/ G_0	6.05	6.36	6.22	6.18	6.37

Table S6 Thermodynamic parameters (lattice energy (U_L),shortest wave(σ_{max}), high frequency cutoff (f_{max}), approximate mean elastic wave (ν_{max}), molar heat capacity at constant volume (Cv), Debyetemperature(θ_I),and minimum lattice thermal conductivity (Π_{min}))of the annealed NZAFO samples.

Parameter	Ni600	Ni800	Ni900	Ni1050	Ni1200
U_L (eV)	-139.1	-141.5	-141.5	-141.0	-141.1
$\sigma_{max}\times 10^7$ (m^{-1})	2.473	2.482	2.486	2.491	2.500
$f_{max}\times 10^{11}$ (s^{-1})	1.580	1.598	1.610	1.619	1.633
ν_{max} (cm^{-1})	528.7	534.6	538.6	541.7	546.4
θ_I (K)	760.2	768.8	774.5	779.0	785.7
C_V ($J.mol^{-1}.K^{-1}$)	104.9	103.7	102.9	102.4	101.5
Π_{min} ($W.cm^{-1}.s^{-1}$)	1.041	1.050	1.054	1.057	1.061

Table S7 Energy band gap (Eg), Urbach energy (E_u), refractive index (n_o), and high-frequency dielectric constant (ε_α) of Ni-Zn-Al ferrite samples.

Sample	Eg	E_u	n_o	ε_α
Ni600	4.5	0.7	2.19	4.80
Ni800	3.75	0.25	2.29	5.26
Ni900	3.67	0.22	2.30	5.32
Ni1050	3.56	0.18	2.32	5.40
Ni1200	3.1	0.11	2.39	5.73

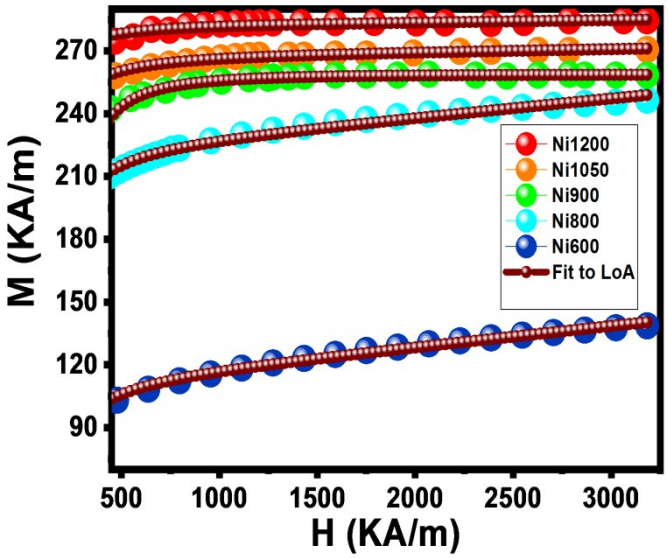

Fig. S5 Room temperature hysteresis loops of NZAFO ferrites annealed at 600,800, 900, 1050 and 1200 °C.

Table S8 ESR parameters of the annealed NZAFO samples at 300 K

Parameter	Ni600	Ni800	Ni900	Ni1050	Ni1200
Δ_{Hpp} (Oe)	813.52	767.72	671.95	547.84	457.6
H_r (Oe)	2405.02	2670.09	2757.15	2852.04	2993.43
G	2.762	2.488	2.409	2.329	2.219
$T_2 .10^{-11}$ (s)	2.919	3.434	4.052	5.141	6.459
$T_1 .10^{-12}$ (s)	2.510	2.133	1.808	1.425	1.134
$R_1 .10^{11}$ (s^{-1})	3.983	4.686	5.528	7.014	8.814
$R_2 .10^{10}$ (s^{-1})	3.425	2.911	2.467	1.945	1.548
R_2/R_1	0.085	0.062	0.044	0.027	0.017

Table S9 Molar volume (V_{mat}), saturation magnetization (Ms) in (A/m) at 300 K, average particle size (D_{SEM}) obtained from SEM images, andtransverse relaxivity (r_2) of the NZAFO annealed at 600, 800, and 900 °C samples

Sample	Parameter			
	$V_{mat}.10^{-5}(m^3/mol)$	M_s(A/m)	$D_{SEM} .10^{-8}$ (m)	r_2 (L/s.mmol)
Ni600	4.4116	109200	1.36	1.37977
Ni800	4.36442	220400	2.228	14.92308
Ni900	4.34446	259140	3.762	58.54921

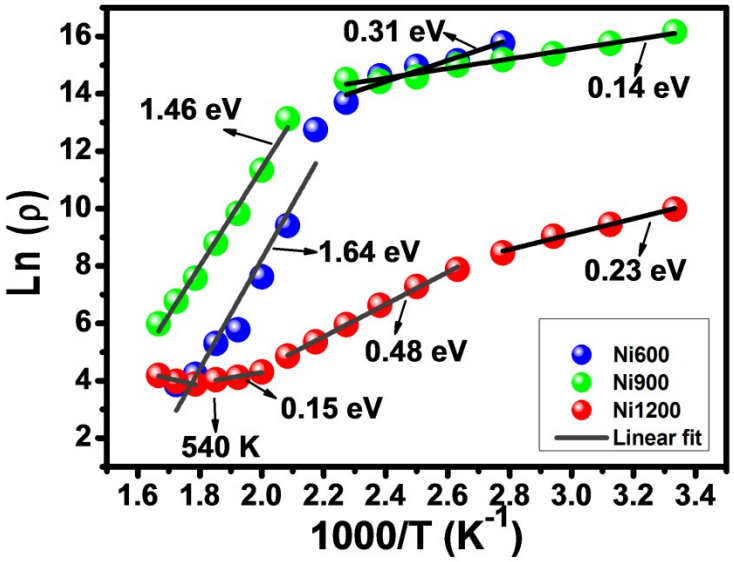

Fig. S6 Ln(ρ) vs1000/T for NZAFO ferrites annealed at 600, 900 and 1200 °C.

Reference

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