Supporting information:

Correlation between microstructure, cation distribution and magnetism in $Ni_{1-x}Zn_xFe_2O_4$ nanocrystallites

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Powder diffraction data

Peak asymmetry

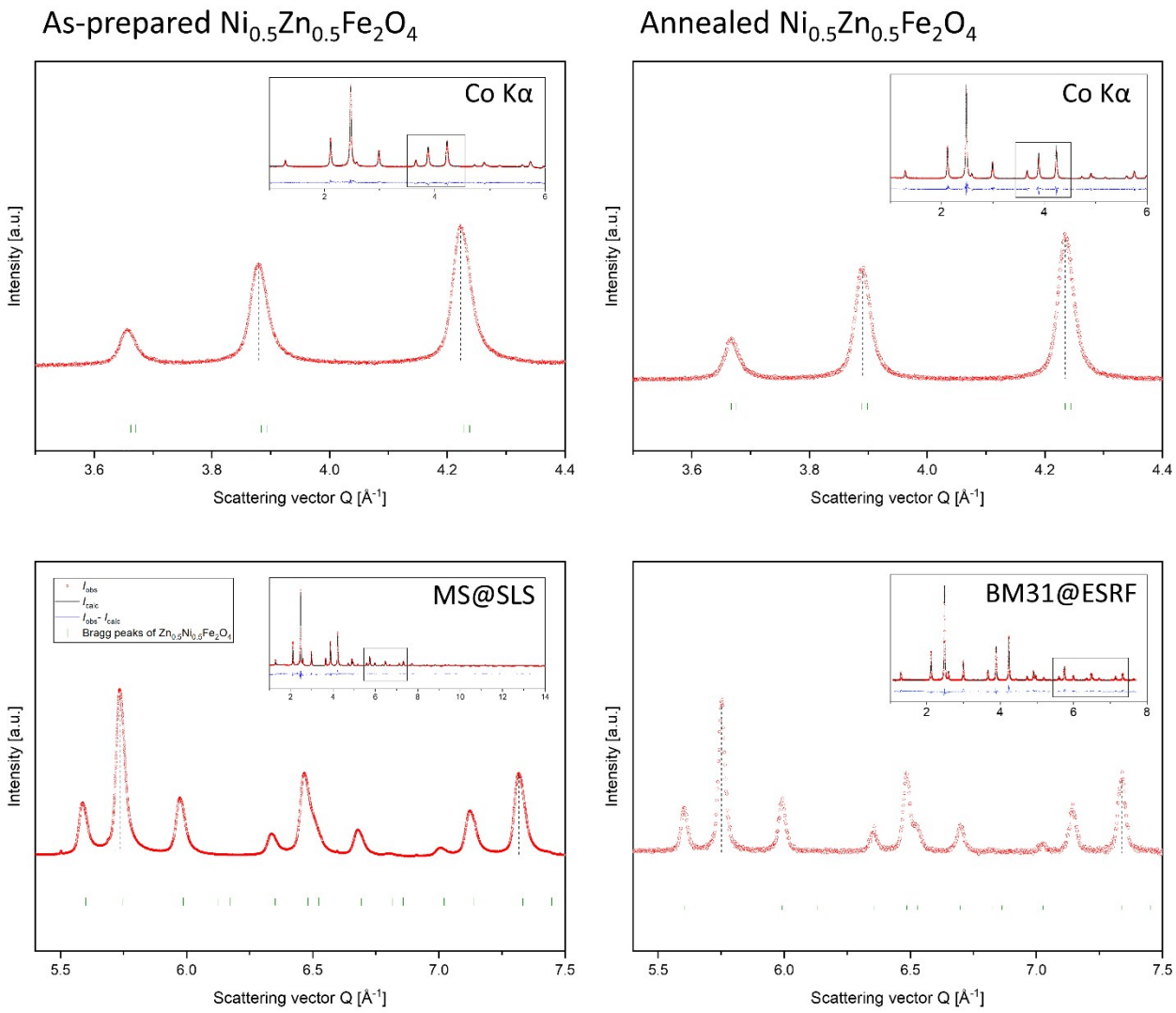

Figure S1: Comparison of peak asymmetry in PXRD datasets measured of as-prepared and annealed $Ni_{0.5}Zn_{0.5}Fe_2O_4$ measured with different in-house and synchrotron sources. The inserts show the entire *Q*-range that was measured with the region showed in more detail being indicated.

Diffraction data of $Ni_{1-x}Zn_xFe_2O_4$ (x=0.0-1.0)

Rietveld refinements (x=0.0-0.2)

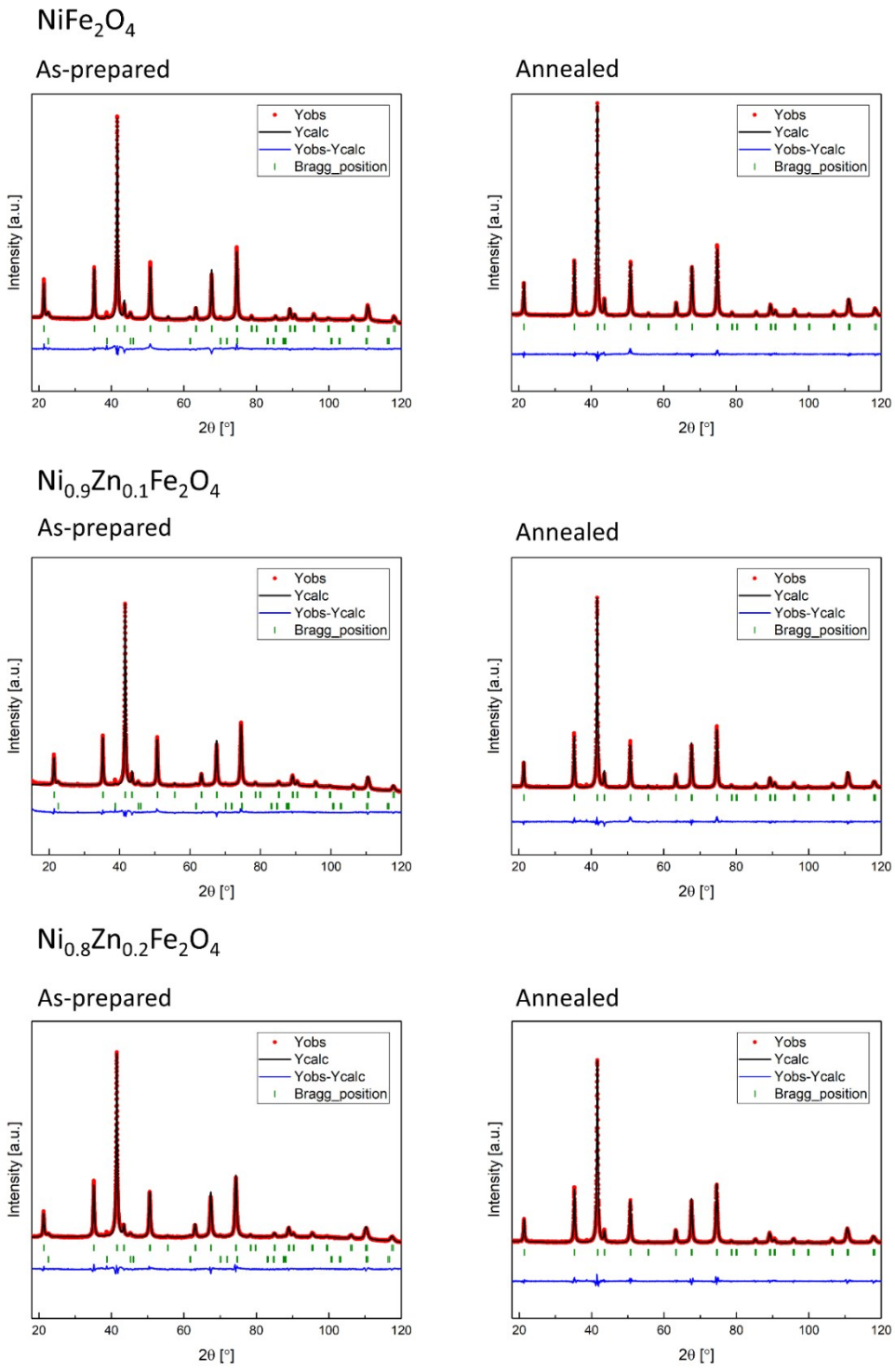

Figure S2: PXRD patterns of indicated samples measured with a Co Kα in-house source.

Rietveld refinements (*x*=0.3-0.5)

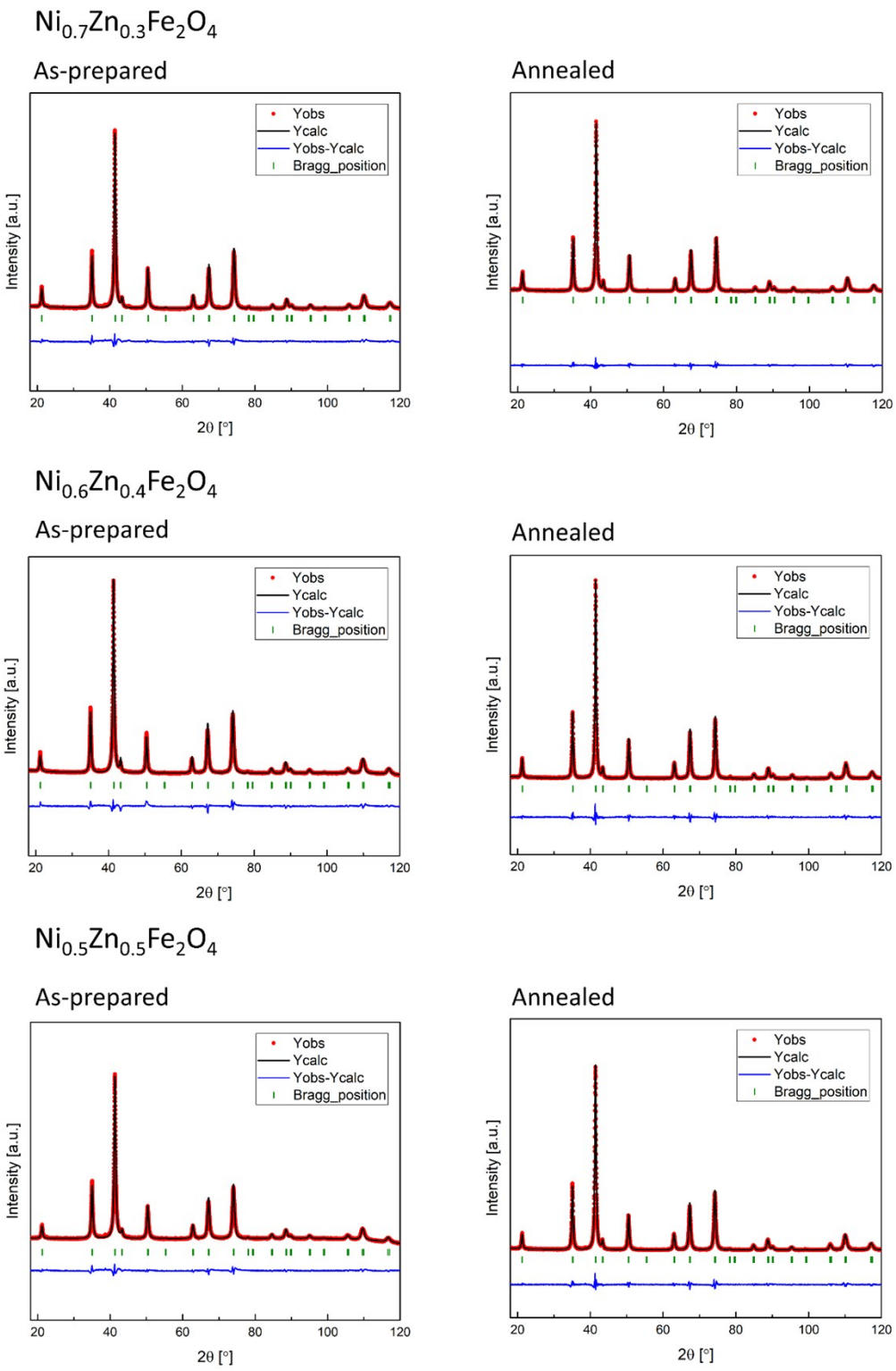

Figure S3: PXRD patterns of indicated samples measured with a Co Kα in-house source.

Rietveld refinements (*x*=0.6-1.0)

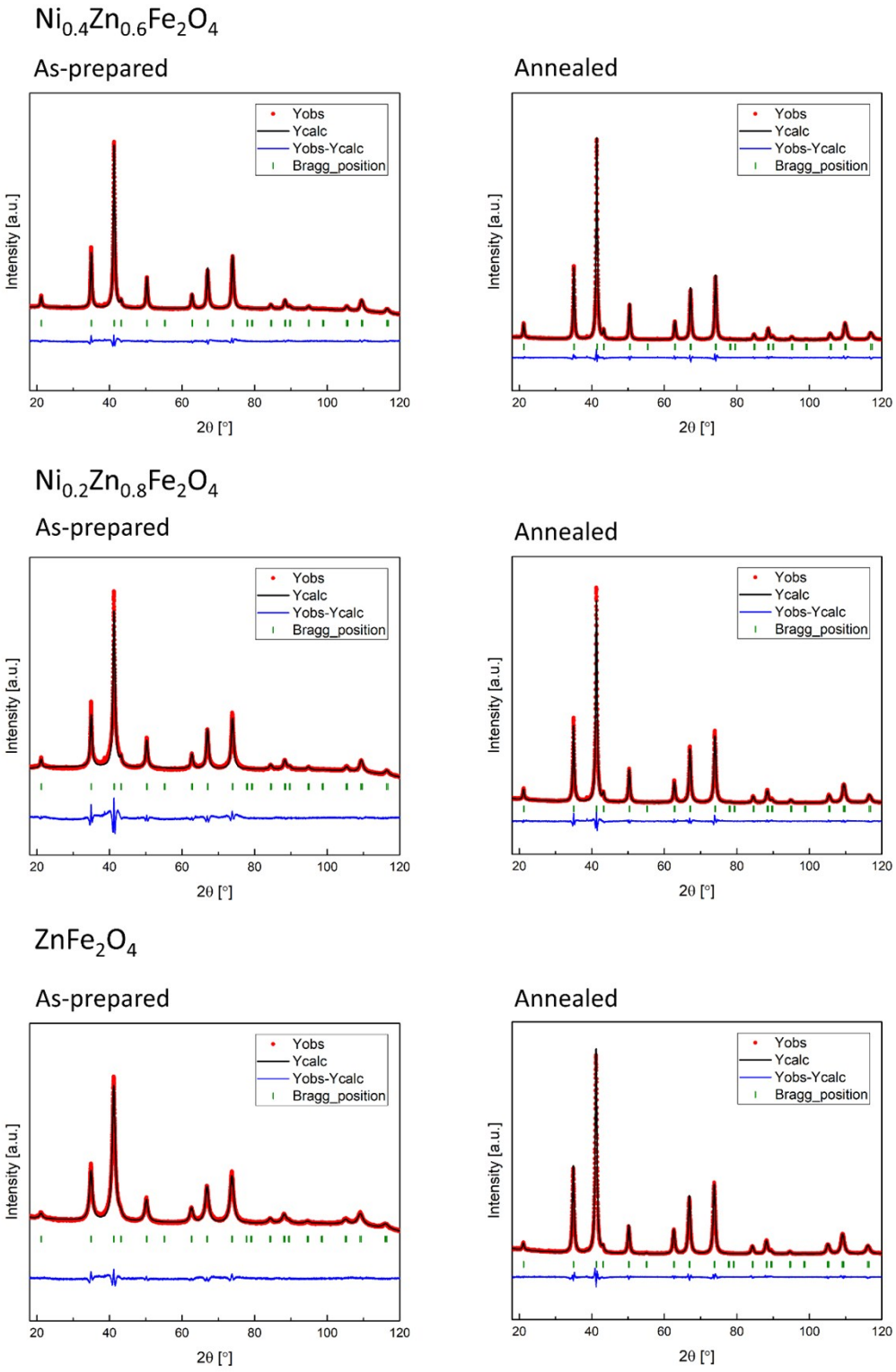

Figure S4: PXRD patterns of indicated samples measured with a Co Kα in-house source.

Diffraction data of $Ni_{1-x}Zn_xFe_2O_4$ (x=0.3-0.6)

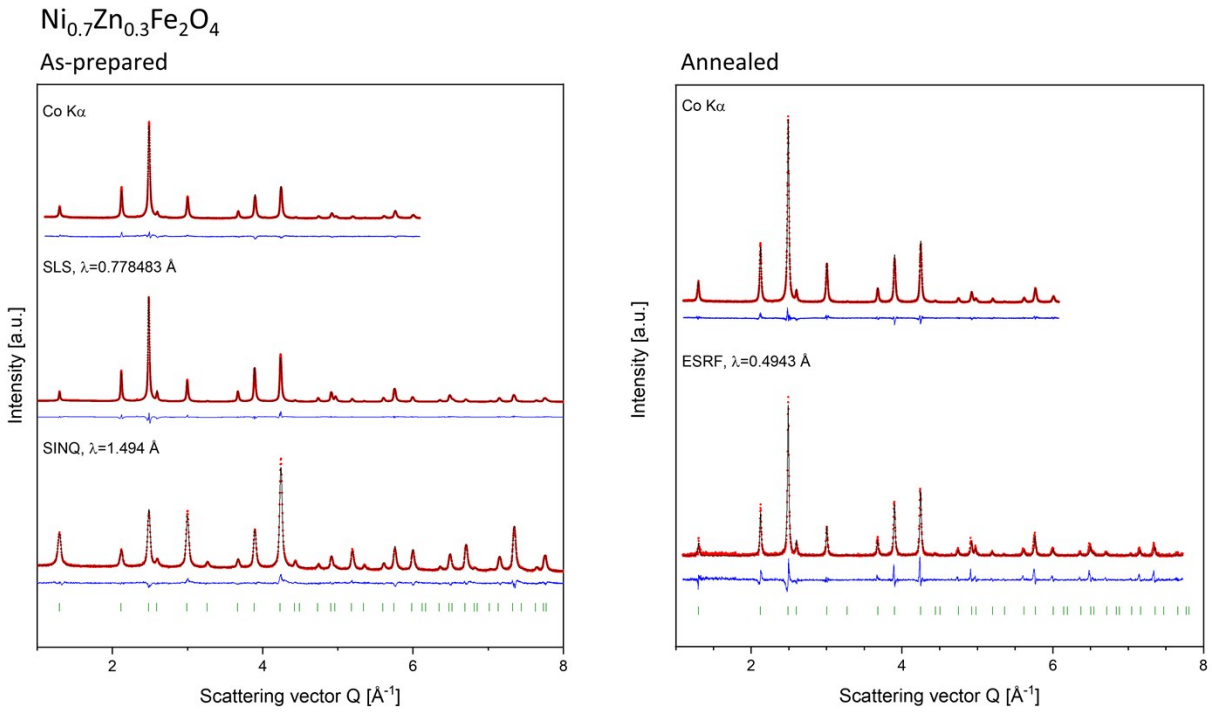

Figure S5: PXRD and NPD patterns of the indicated sample with x=3, measured at different sources.

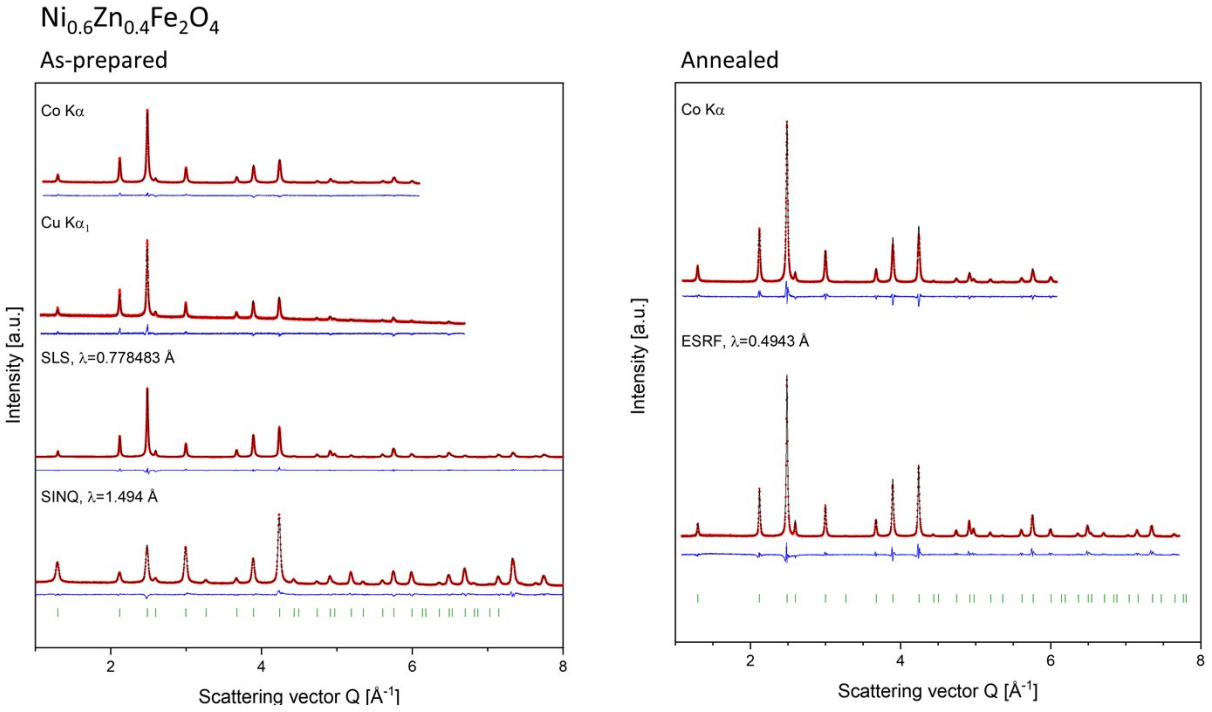

Figure S6: PXRD and NPD patterns of the indicated sample with x=0.4, measured at different sources.

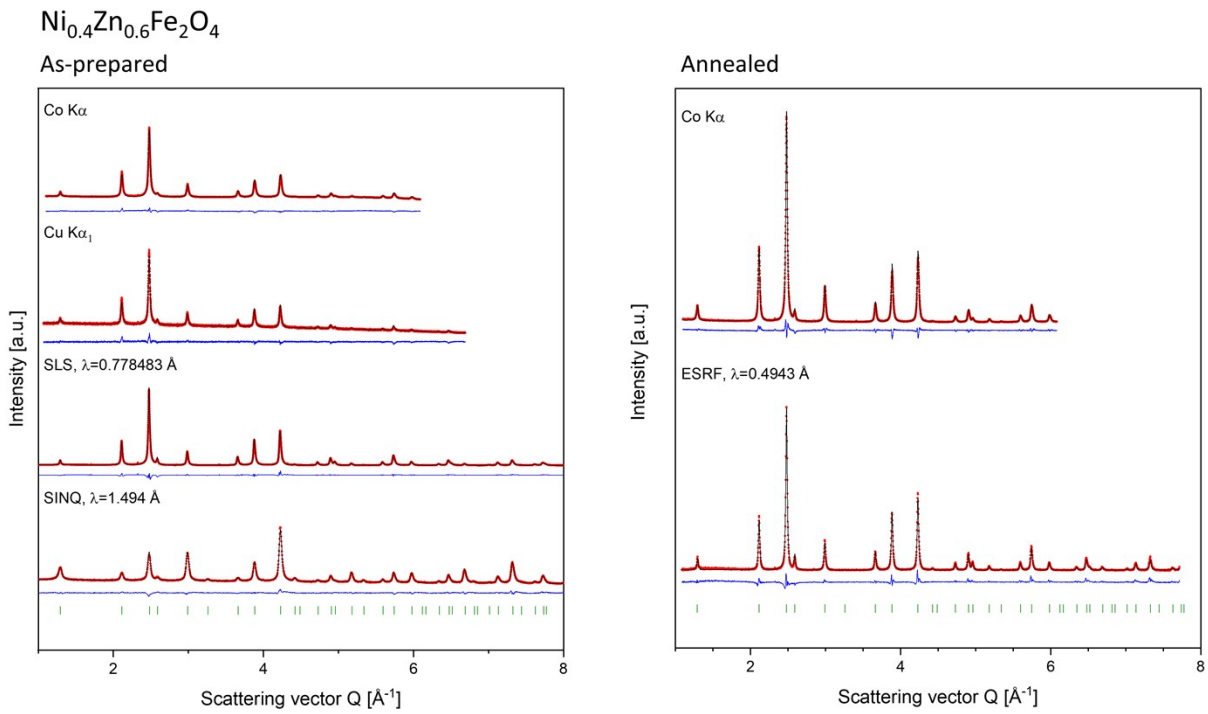

Figure S7: PXRD and NPD patterns of the indicated sample with *x*=0.5, measured at different sources.

Overview over refinements

Resonant scattering factors and neutron scattering lengths

Table S1: Resonant scattering factors used in the Rietveld refinements of the datasets from the individual sources and the neutron scattering lengths of the elements, as calculated with the web utility available online at Argonne National Laboratory.[1]

		Co Kα		Cu $Kα_1$		MS@SLS		BM31@ESRF		Neutron
	Z	f'	f''	f'	f''	f'	f''	f'	f''	fm
Zn	30	-1.086	0.885	-1.551	0.677	0.216	1.680	0.282	0.575	5.680
Ni	28	-1.569	0.666	-3.013	0.509	0.317	1.312	0.304	0.748	10.3
Fe	26	-3.352	0.490	-1.131	3.196	0.356	1.000	0.251	0.432	9.45
O	8	0.063	0.044	0.049	0.032	0.013	0.007	0.004	0.003	5.803

As-prepared samples

As-prepared samples with the Zn content *x*=0.3-0.6 were described with three different models, out of which the one that models the measured data the best was chosen. The three models are:

1) fixing Zn onto the tetrahedral and Ni onto the octahedral sites, while keeping the occupancies at the values expected for the nominal composition
2) fixing Zn and Ni to the tetrahedral and octahedral sites, respectively and fixing the total amount of Fe, but refining the cation occupancies freely, *i.e.* without considering nominal composition, while assuming fully occupied sites
3) allowing both, Zn and Ni to occupy both, tetrahedral and octahedral sites, and refining all occupancies with a linear restraint keeping the nominal composition constant. This yielded an overoccupation of Ni on octahedral sites, so that it was fixed to full occupancy on octahedral sites.

During the combined refinement, which constrains the samples' properties between patterns measured at different sources, the patterns were weighed in a specific ratio:

x=0.4-0.6: Cu Kα/Co Kα/MS@SLS/HRPT@SINQ = 0.2/0.2/0.3/0.3

x=0.3: Co Kα/MS@SLS/HRPT@SLS = 0.3/0.3/0.4

Values marked with *: Not refined, but fixed during the refinement according to the models described above and are here listed for easier comparison between the three models.

Values marked with ‡: Some refinements using Model 1 yielded unphysically high values for the magnetic moments (maximum for Fe^{3+}: 5 μ_B, according to five unpaired electrons). Fixing the moment to 5 μ_B instead of the refined value yielded magnetic R factors of 2.88 (*x*=0.5) and 4.53 (*x*=0.6) compared to 2.84 and 4.44, respectively.

1 R. B. von Dreele, M. R. Suchomel and B. H. Toby, *Advanced Photon Source - Compute X-ray Absorption.* Web utility based on the python software package "Absorb", available at: https://11bm.xray.aps.anl.gov/absorb/absorb.php.

Table S2: Overview of the refinement of the different models for *x*=0.3

		Model 1			Model 2			Model 3		
λ [Å]	Co Kα	1.78919/1.79321								
	SLS	0.778483								
	SINQ	1.494								
Phases		ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic
Cryst. size [nm]		27.4(2)	16.08(5)	14.1(9)	27.3(2)	16.05(5)	14.4(9)	27.3(2)	16.06(5)	14.4(9)
Cryst. structure										
Space group		Fd-3m			Fd-3m			Fd-3m		
Lattice par. [Å]		8.40264(7)	8.38081(9)	8.392(2)	8.40265(7)	8.38087(8)	8.391(2)	8.40265(7)	8.38087(9)	8.391(2)
Oxygen positions		0.2567(1)		-	0.2560(1)		-	0.25603(9)		--
$B_{iso, overall}$		0.637(7)			0.636(7)			0.638(7)		
Site occ. fractions										
Fe^{3+}, 16d		0.05416*			0.0500(1)			0.0506(1)		
Ni^{2+}, 16d		0.02917*			0.0334(1)			0.02917*		
Zn^{2+}, 16d		-			-			0.0035(1)		
Fe^{3+}, 8d		0.02917*			0.0334(1)			0.0327(1)		
Ni^{2+}, 8d		-			-			0*		
Zn^{2+}, 8d		0.01250*			0.0083(1)			0.0090(1)		
Inversion degree		-			-			0.28(1)		
Site magn. moments:										
μ_{tet} (μ_B)		4.2(2)			3.2(1)			3.7(1)		
μ_{oct} (μ_B)		3.0(1)			3.7(2)			3.3(1)		
Fit quality:										
R_{Bragg} [%]	Co Kα	5.46	5.83	-	3.98	4.07	-	4.07	4.20	-
	SLS	6.91	7.73		6.39	7.60		6.41	7.61	
	SINQ	3.74	4.12		4.53	4.80		4.34	4.60	
R_F [%]	Co Kα	3.34	3.40	-	2.97	2.70	-	3.00	2.77	-
	SLS	11.1	11.1		11.0	11.2		11.1	11.3	
	SINQ	2.55	2.53		3.12	2.98		3.06	2.92	
$R_{magnetic}$ [%]		-	-	3.36	-	-	4.15	-	-	4.17
χ^2 global		3.87			3.63			3.64		

Table S3: Overview of the refinement of the different models for *x*=0.4

		Model 1			**Model 2**			**Model 3**		
λ [Å]	Co Kα	1.78919/1.79321								
	Cu Kα	1.54059								
	SLS	0.778483								
	SINQ	1.494								
Phases		ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic
Cryst. size [nm]		17.44(6)	25.7(2)	15(1)	17.42(6)	25.6(2)	15(1)	17.43(6)	25.6(2)	15(1)
Cryst. structure										
Space group		Fd-3m			Fd-3m			Fd-3m		
Lattice par. [Å]		8.3872(9)	8.4120(7)	8.398(2)	8.38726(9)	8.41204(7)	8.398(2)	8.38725(9)	8.41204(7)	8.398(2)
Oxygen positions		0.25669(9)		-	0.25619(9)		-	0.25623(9)		-
$B_{iso,\ overall}$		0.768(7)			0.767(7)			0.770(7)		
Site occ. fractions										
Fe^{3+}, 16d		0.05833*			0.0546(2)			0.0553(1)		
Ni^{2+}, 16d		0.02500*			0.0287(2)			0.02500*		
Zn^{2+}, 16d		-			-			0.0031(1)		
Fe^{3+}, 8d		0,02500*			0.0288(1)			0.0281(1)		
Ni^{2+}, 8d		-			-			0*		
Zn^{2+}, 8d		0.01667*			0.0129(1)			0.0136(1)		
Inversion degree		-			-			0.18(1)		
Site magn. moments:										
μ_{tet} (μ_B)		4.4(2)			3.8(2)			3.7(2)		
μ_{oct} (μ_B)		2.7(1)			2.78(9)			2.72(9)		
Fit quality:										
R_{Bragg} [%]	Co Kα	7.29	6.35	-	6.24	5.94	-	6.32	5.98	-
	Cu Kα	7.03	7.97		6.98	7.79		7.17	7.91	
	SLS	7.69	6.63		7.29	6.15		7.34	6.19	
	SINQ	3.61	3.29		4.24	4.06		3.98	3.77	
R_F [%]	Co Kα	5.96	4.91	-	5.41	4.79	-	5.50	4.82	-
	Cu Kα	6.96	6.50		6.73	6.22		6.87	6.34	
	SLS	11.9	12.3		11.8	12.0		11.9	12.1	
	SINQ	2.29	2.11		2.60	2.64		2.49	2.53	
$R_{magnetic}$ [%]		-	-	2.66	-	-	2.64	-	-	1.82
$\chi^2_{\ global}$		3.15			3.01			3.01		

Table S4: Overview of the refinement of the different models for *x*=0.5

		Model 1			**Model 2**			**Model 3**		
λ [Å]	Co Kα	1.78919/1.79321								
	Cu Kα	1.54059								
	SLS	0.778483								
	SINQ	1.494								
Phases		ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic
Cryst. size [nm]		14.02(5)	24.5(2)	12(1)	14.01(5)	24.4(2)	13(1)	14.02(5)	24.4(2)	13(1)
Cryst. structure										
Space group		Fd-3m			Fd-3m			Fd-3m		
Lattice par. [Å]		8.3985(1)	8.4230(9)	8.407(3)	8.3985(1)	8.42302(9)	8.407(2)	8.3985(1)	8.4230(9)	8.407(2)
Oxygen positions		0.2564(1)		-	0.2559(1)		-	0.2560(1)		-
$B_{iso,\ overall}$		0.806(9)			0.807(9)			0.811(9)		
Site occ. fractions										
Fe^{3+}, 16d		0.06250*			0.0584(2)			0.0591(2)		
Ni^{2+}, 16d		0.02083*			0.0249(2)			0.0208(2)		
Zn^{2+}, 16d		-			-			0.00340(2)		
Fe^{3+}, 8d		0.02084*			0.0249(2)			0.0242(2)		
Ni^{2+}, 8d		-			-			0		
Zn^{2+}, 8d		0.02083*			0.0167(2)			0.0174(2)		
Inversion degree		-			-			0.163(1)		
Site magn. moments:										
μ_{tet} (μ_B)		5.1(2)‡			4.3(2)			4.4(2)		
μ_{oct} (μ_B)		2.4(1)			2.5(1)			2.6(1)8		
Fit quality:										
R_{Bragg} [%]	Co Kα	10.1	8.79	-	9.87	8.74	-	9.86	8.75	-
	Cu Kα	7.55	8.90		7.57	8.80		7.76	8.95	
	SLS	7.29	6.32		7.63	6.61		7.64	6.62	
	SINQ	3.44	3.18		4.05	3.79		3.81	3.57	
R_F [%]	Co Kα	9.22	7.66	-	9.07	7.51	-	9.08	7.55	-
	Cu Kα	6.33	6.58		6.14	6.41		6.25	6.50	
	SLS	12.7	12.4		12.9	12.3		12.9	12.5	
	SINQ	2.20	2.36		2.52	2.77		2.44	2.69	
$R_{magnetic}$ [%]		-	-	2.84	-	-	2.78	-	-	2.44
$\chi^2_{\ global}$		3.72			3.59			3.58		

Table S5: overview of the refinement of the different models for *x*=0.6

		Model 1			**Model 2**			**Model 3**		
λ [Å]	Co Kα	1.78919/1.79321								
	Cu Kα	1.54059								
	SLS	0.778483								
	SINQ	1.494								
Phases		ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic	ZNFO1	ZNFO2	ZNFO magnetic
Cryst. size [nm]		12.1(5)	24.2(2)	10(1)	12.1(5)	24.2(2)	10(1)	12.1(5)	24.2(2)	10(19
Cryst. structure										
Space group		Fd-3m			Fd-3m			Fd-3m		
Lattice par. [Å]		8.4069(1)	8.42834(9)	8.405(4)	8.4072(2)	8.42841(9)	8.407(3)	8.4072(2)	8.42841(9)	8.407(3)
Oxygen positions		0.2565(1)		-	0.2560(1)		-	0.2561(1)		-
$B_{iso,\ overall}$		0.942(9)			0.945(9)			0.951(9)		
Site occ. fractions										
Fe^{3+}, 16d		0.06666*			0.0617(2)			0.0626(2)		
Ni^{2+}, 16d		0.01667*			0.0216(2)			0.01666*		
Zn^{2+}, 16d		-			-			0.0041(2)		
Fe^{3+}, 8d		0.01667*			0.0217(2)			0.0208(2)		
Ni^{2+}, 8d		-			-			0*		
Zn^{2+}, 8d		0.02500*			0.0200(2)			0.0209(2)		
Inversion degree		-			-			0.16(1)		
Site magn. moments:										
μ_{tet} (μ_B)		5.9(5)‡			4.5(3)			4.7(4)		
μ_{oct} (μ_B)		2.0(2)			2.2(1)			2.2(1)		
Fit quality:										
R_{Bragg} [%]	Co Kα	10.2	8.20	-	9.06	8.04	-	9.04	8.09	-
	Cu Kα	8.79	9.77		8.89	9.68		9.12	9.90	
	SLS	8.83	6.97		8.85	6.50		8.88	6.53	
	SINQ	3.74	4.13		4.00	4.31		3.68	4.08	
R_F [%]	Co Kα	8.44	7.30	-	7.98	7.03	-	7.99	7.10	-
	Cu Kα	6.68	7.40		6.60	7.25		6.74	7.41	
	SLS	14.8	13.3		14.9	13.2		15.1	13.3	
	SINQ	2.52	2.61		2.55	2.75		2.42	2.70	
$R_{magnetic}$ [%]		-	-	4.44	-	-	3.76	-	-	3.39
χ^2 global		3.41			3.20			3.19		

Annealed samples

Annealed samples with *x*=0.3-0.6 were refined according to Model 3 (see previous section) to provide a comparison of the cation occupancies before and after annealing.

Values marked with "*" in the following were not refined, but fixed throughout the refinement and are given here to ease a comparison between the three models.

Table S6: Overview of the different samples modelled with Model 3

Zn content *x*		**0.3**	**0.4**	**0.5**	**0.6**
Wavelength [Å]	Co Kα	1.78919/1.79321			
	ESRF	0.4943			
Phases		ZNFO	ZNFO	ZNFO	ZNFO
Cryst. size [nm]		20.49(7)	23.02(6)	21.94(6)	20.15(5)
Cryst. structure					
Space group		Fd-3m			
Lattice par. [Å]		8.3698(1)	8.3801(1)	8.3849(1)	8.3996(1)
Oxygen positions		0.2571(2)	0.2584(2)	0.2577(3)	0.2587(2)
$B_{iso,\ overall}$		1.27(2)	0.88(2)	0.96(3)	1.01(2)
Site occ. fractions					
Fe^{3+}, 16d		0.0521(2)	0.0565(3)	0.0598(3)	0.0637(2)
Ni^{2+}, 16d		0.02916*	0.02500*	0.02083*	0.01667*
Zn^{2+}, 16d		0.0021(2)	0.0018(3)	0.0027(3)	0.0030(2)
Fe^{3+}, 8d		0.0313(2)	0.0268(3)	0.0235(3)	0.0197(2)
Ni^{2+}, 8d		0*	0*	0*	0*
Zn^{2+}, 8d		0.0104(2)	0.0149(3)	0.0181(3)	0.0220(2)
Inversion degree		0.16(1)	0.11(1)	0.13(1)	0.12(1)
Fit quality					
R_{Bragg} [%]	Co Kα	2.99	5.71	4.40	3.28
	ESRF	16.5	9.53	10.4	10.5
R_F [%]	Co Kα	2.42	2.97	2.55	2.08
	ESRF	12.3	7.34	8.41	8.13
$\chi^2_{\ global}$		1.77	4.13	4.74	4.02

Scanning transmission electron microscopy and energy-dispersive X-ray spectroscopy data

As-prepared $Ni_{0.5}Zn_{0.5}Fe_2O_4$

Table S2: Elemental atomic percentages from the quantitative analysis of the EDS spectra.

Element	Normalized content [wt. %]	Atomic content [at. %]	Error (3σ) [wt. %]
Zn	10.21	3.99	1.02
Ni	8.82	3.84	0.89
Fe	32.49	14.85	3.02
O	48.48	77.33	4.45
Total	100.00	100.00	

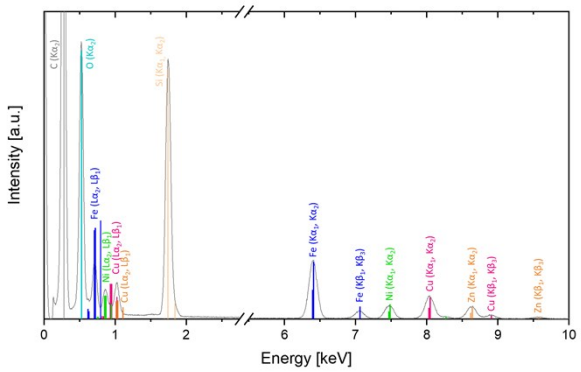

Figure S8: EDS spectrum of as-prepared $Ni_{0.5}Zn_{0.5}Fe_2O_4$.

Table S3: Elemental atomic percentages from the quantitative analysis of EDS spectra.

Element	Normalized content [wt. %]	Atomic content [at. %]	Error (3σ) [wt. %]
Zn	10.73	4.48	1.08
Ni	9.42	4.38	0.95
Fe	37.03	18.10	3.44
O	42.82	73.05	3.95
Total	100.00	100.00	

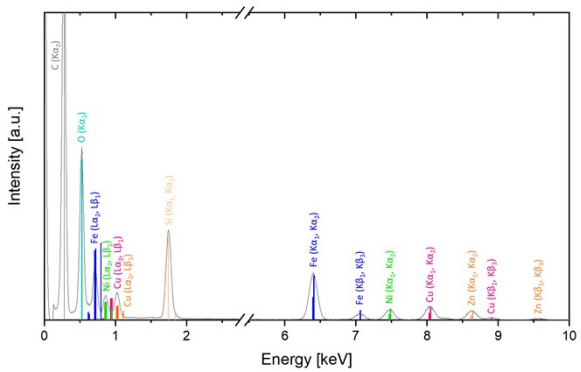

Figure S9: EDS spectrum of as-prepared $Ni_{0.5}Zn_{0.5}Fe_2O_4$.

Annealed $Ni_{0.5}Zn_{0.5}Fe_2O_4$

Table S4: Elemental atomic percentages from the quantitative analysis of EDS spectra.

Element	Normalized content [wt. %]	Atomic content [at. %]	Error (3σ) [wt. %]
Zn	12.88	6.08	3.10
Ni	11.49	6.05	1.26
Fe	42.20	23.34	1.13
O	33.43	64.53	3.89
Total	100.00	100.00	

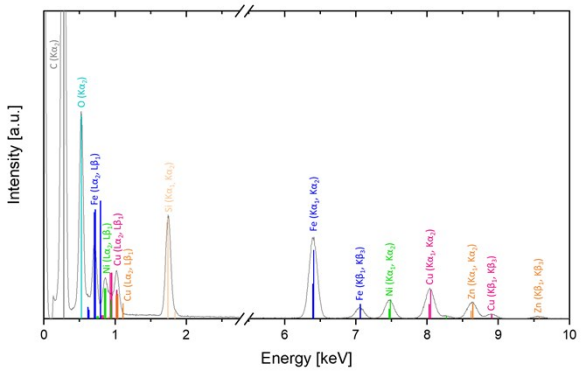

Figure S10: EDS spectrum of annealed $Ni_{0.5}Zn_{0.5}Fe_2O_4$.

Transmission electron microscopy images

TEM images of as-prepared $Ni_{0.5}Zn_{0.5}Fe_2O_4$

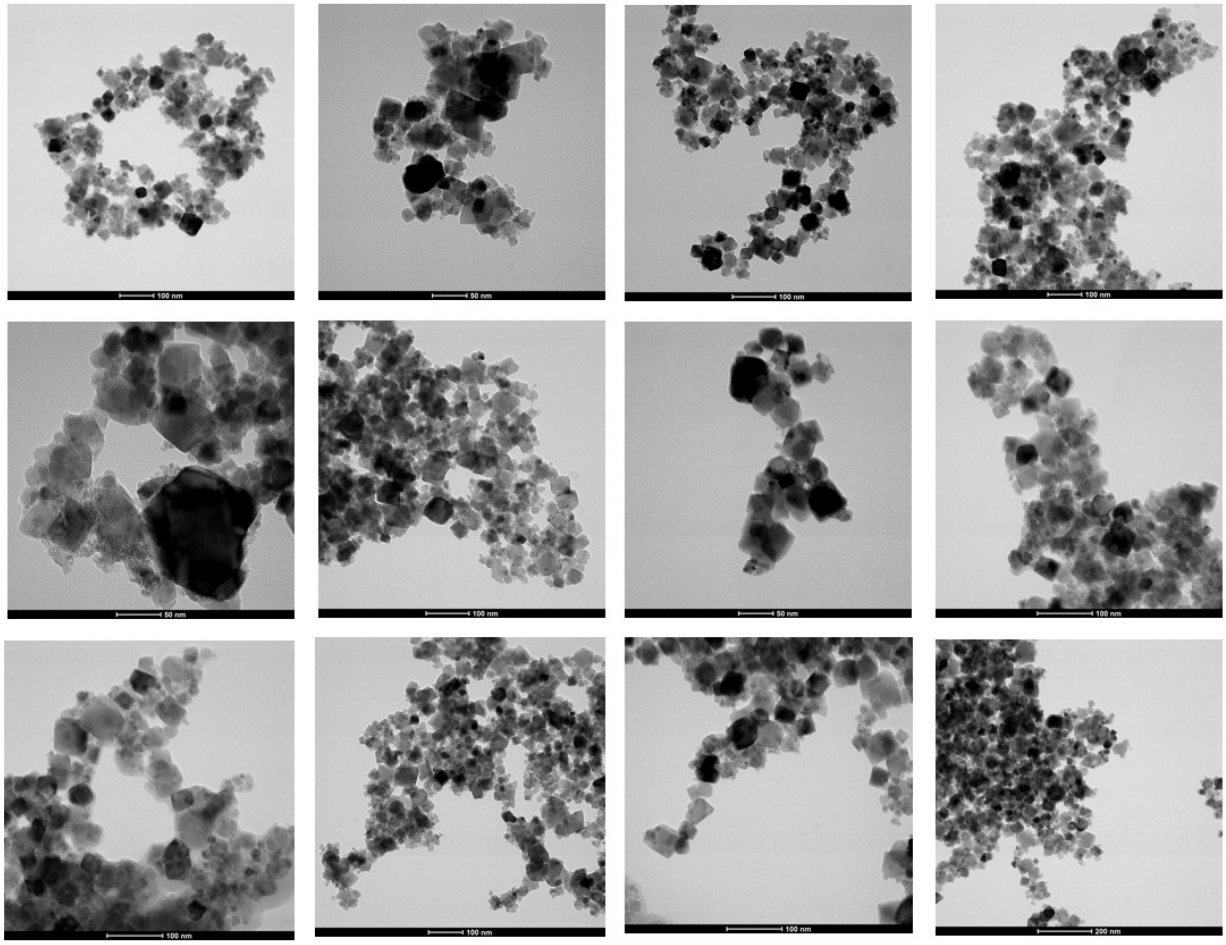

Figure S11: TEM images of as-prepared $Ni_{1-x}Zn_xFe_2O_4$.

TEM images of annealed $Ni_{0.5}Zn_{0.5}Fe_2O_4$

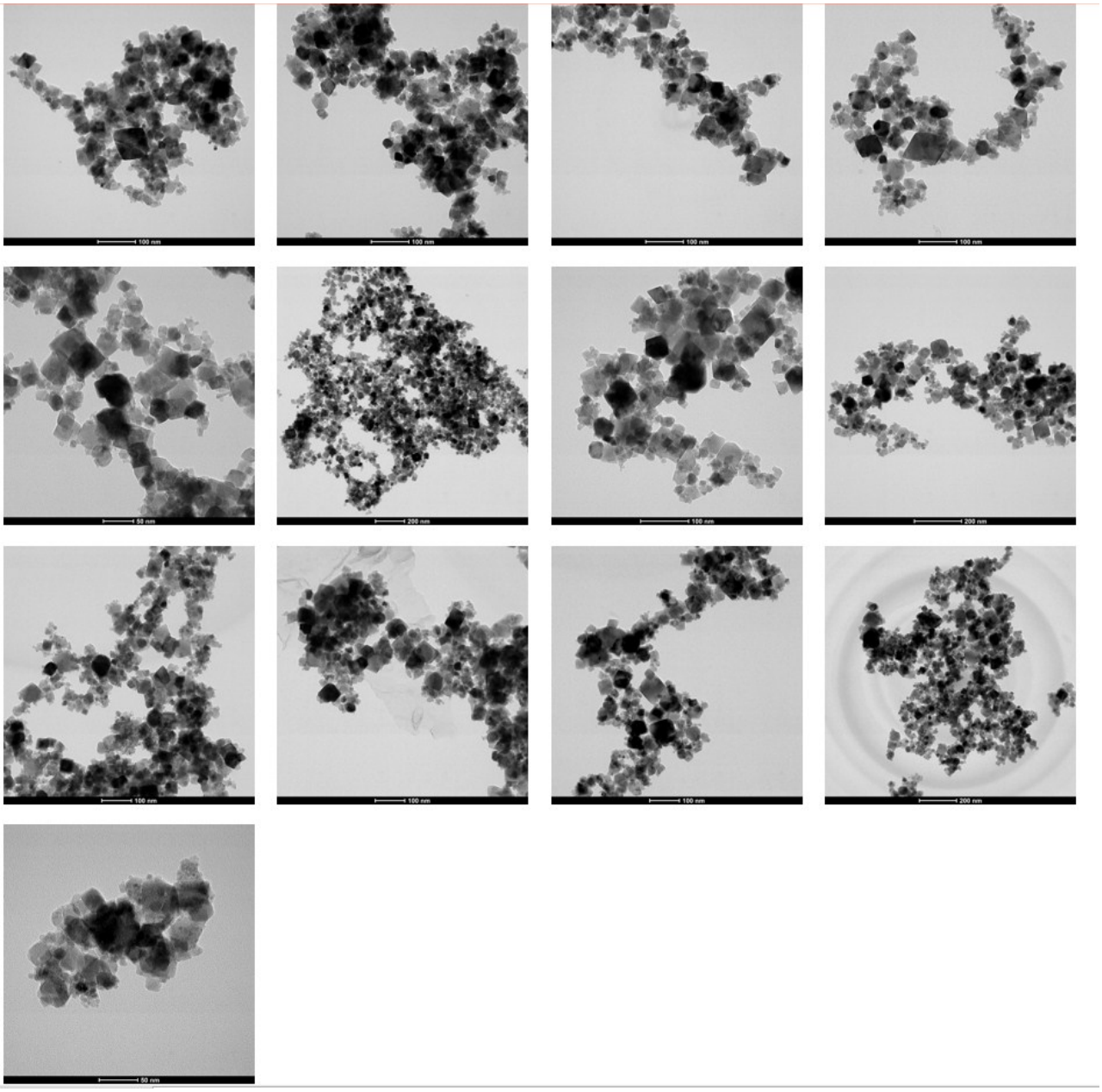

Figure S12: TEM images of annealed $Ni_{1-x}Zn_xFe_2O_4$.

Magnetic hysteresis curves

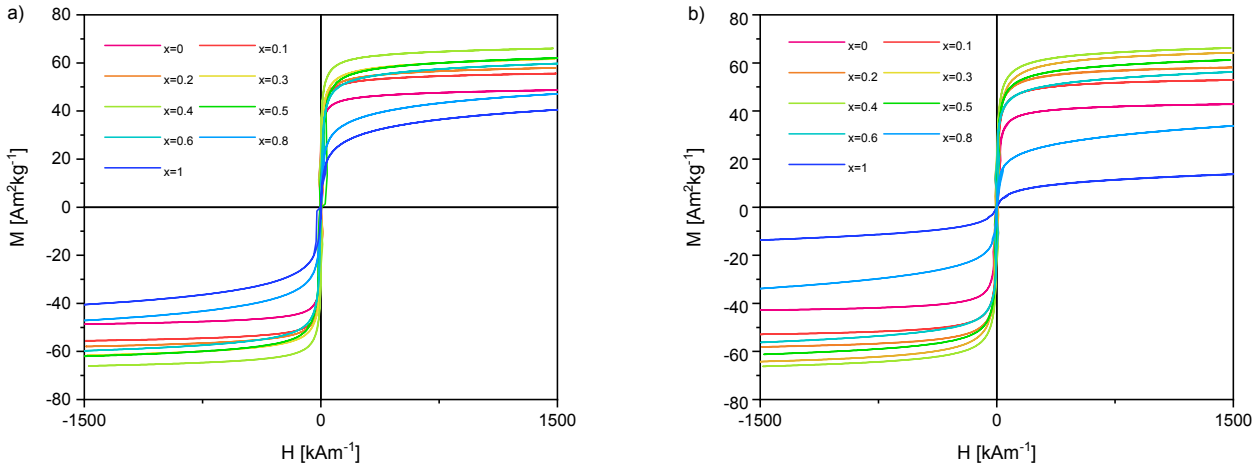

Figure S13. Magnetic hysteresis curves of the $Ni_{1-x}Zn_xFe_2O_4$ samples with different Zn contents. a) as-prepared, b) after annealing.