Supporting Information – Stoichiometry matters: Correlation between antisite defects, microstructure and magnetic behavior in the cathode material $Li_{1-z}Ni_{1+z}O_2$

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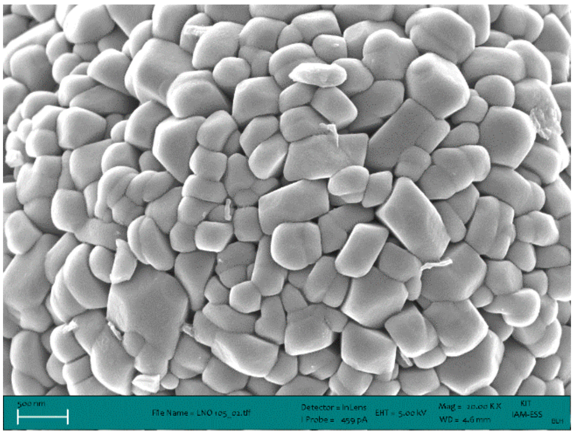
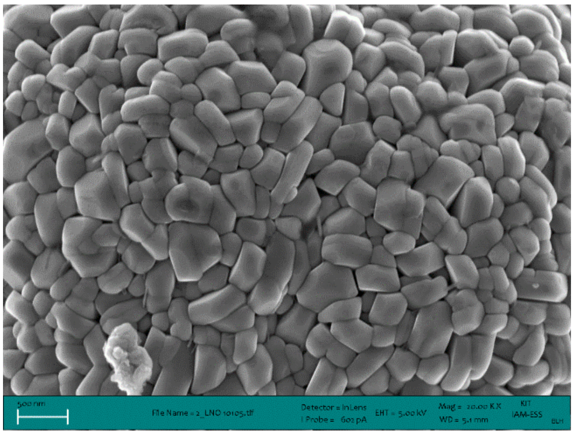
Exemplary SEM images for the determination of the particle size distribution

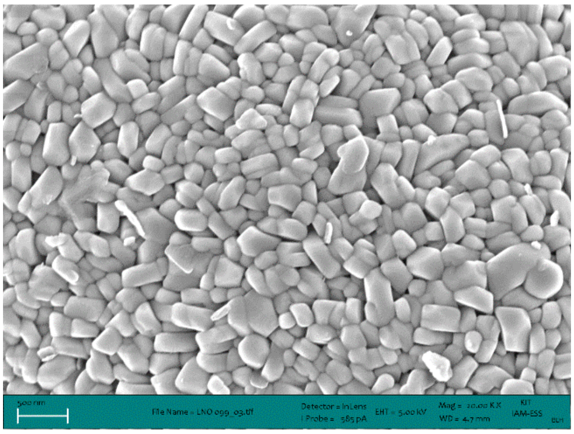
$z_{nominal}$ = -0.05



$z_{nominal}$ = -0.01



$z_{nominal}$ = 0.01



$z_{nominal}$ = 0.05

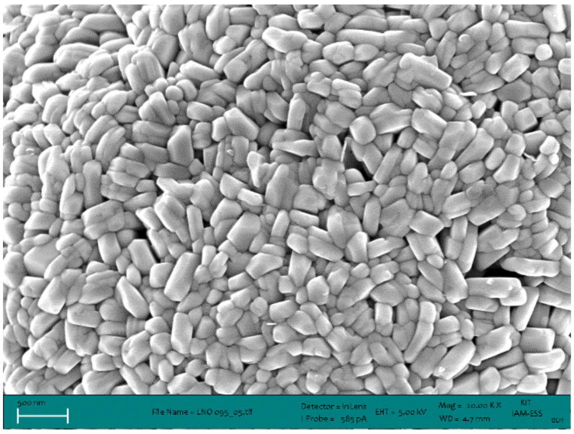
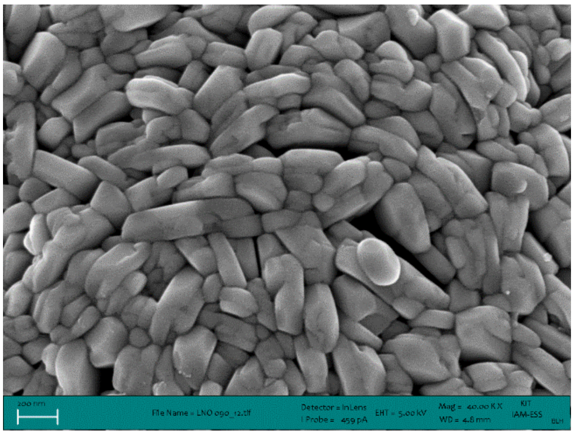
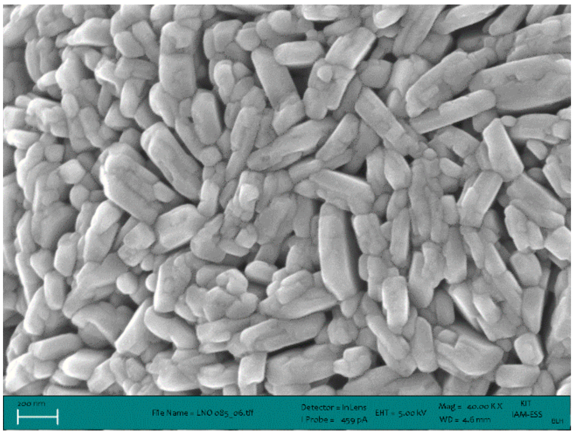


Figure S1: SEM images of $Li_{1-z}Ni_{1+z}O_2$ with $-0.05 \le z \le 0.05$, scale bar 500 nm.

$z_{nominal}$ = 0.10



$z_{nominal}$ = 0.15



$z_{nominal}$ = 0.20

$z_{nominal}$ = 0.25

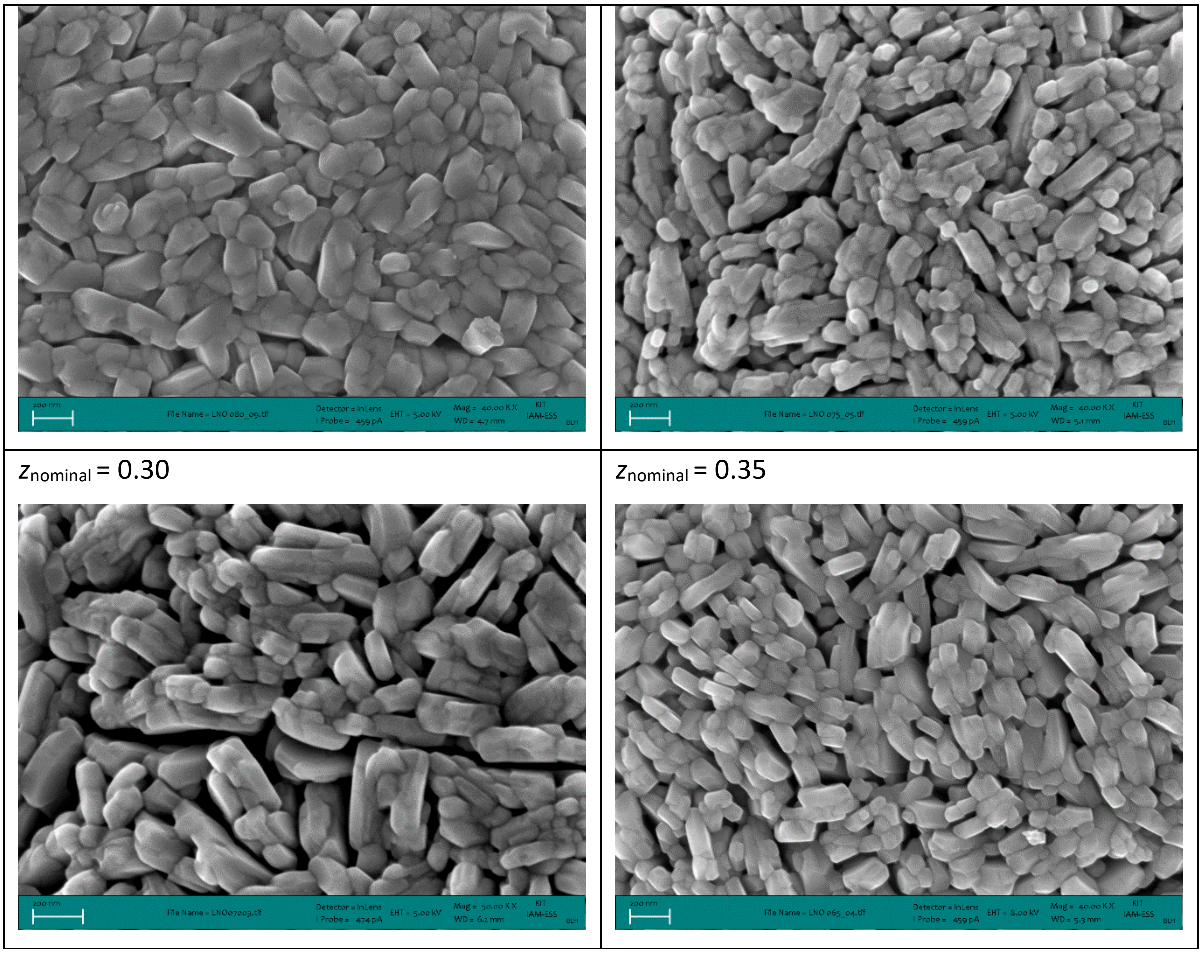


Figure S2: SEM images of $Li_{1-z}Ni_{1+z}O_2$ with $0.10 \leq z \leq 0.35$, scale bar 200 nm.

Elemental Analysis

Table S1: Summary of results from ICP-OES on metal content in $Li_{1-z}Ni_{1+z}O_2$.

$z_{nominal}$	**Eq. Li**	**Eq. Ni**
-0.05	1.03(4)	0.965(14)
-0.01	1.00(3)	0.999(14)
0.01	0.98(4)	1.017(14)
0.05	0.95(3)	1.051(15)
0.10	0.90(3)	1.099(15)
0.15	0.86(3)	1.142(16)
0.20	0.80(3)	1.195(17)
0.25	0.76(3)	1.239(17)
0.30	0.71(3)	1.289(18)
0.35	0.66(2)	1.337(19)

Diffraction patterns & crystallographic data

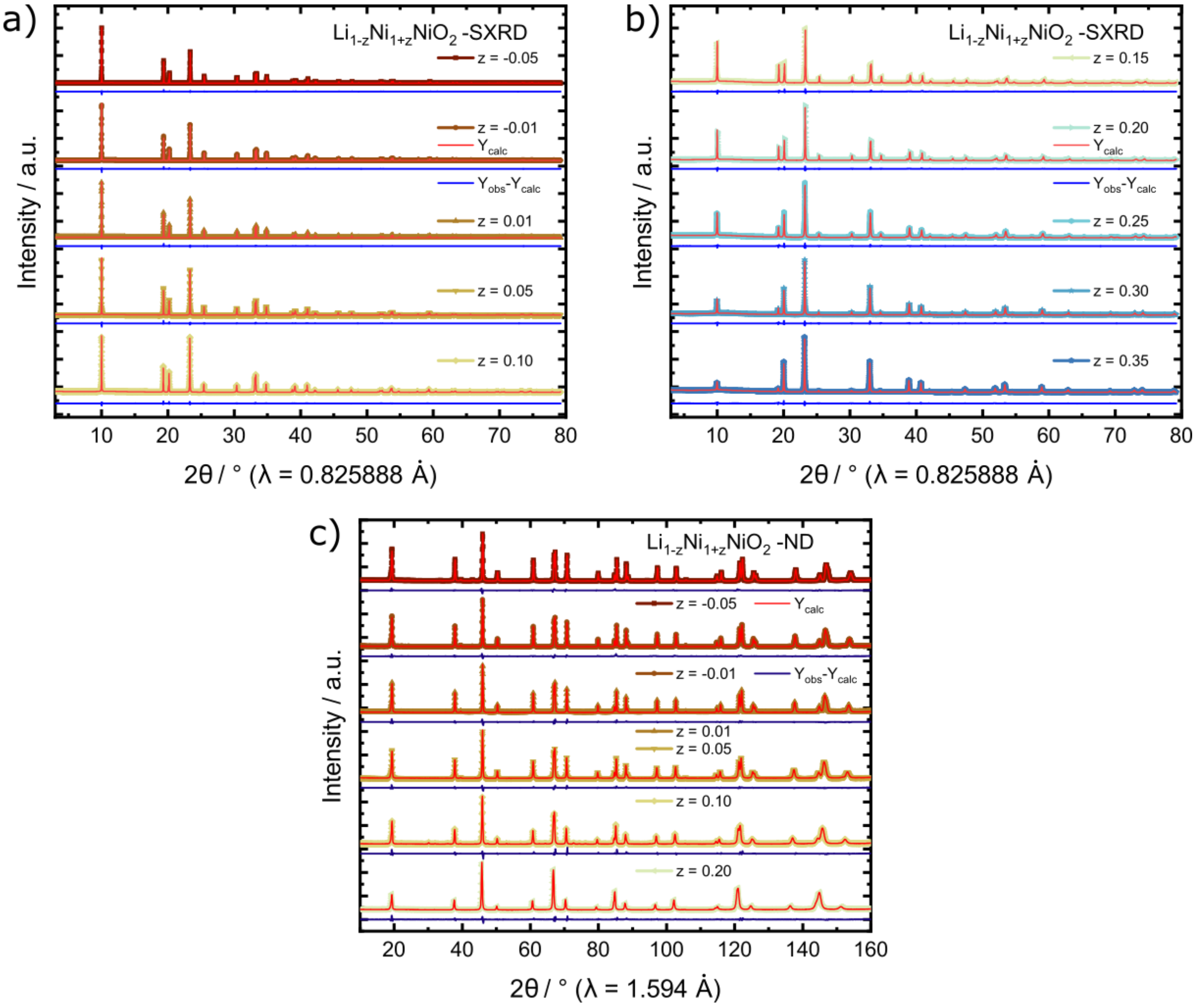


Figure 3: Patterns of $Li_{1-z}Ni_{1+z}O_2$ for a)+b) synchrotron X-ray diffraction for -0.05 ≤ z ≤ 0.35 and c) neutron diffraction for -0.05 ≤ z ≤ 0.1 and z = 0.20 with Y_{obs} in the color pattern used in the main manuscript as well as Y_{calc} in red and difference curve in blue.

Table S2: Atomic coordinates, site occupancy factors (SOF) and isotropic displacement parameteres B_{iso} for $Li_{1-z}Ni_{1+z}O_2$ at 303 K.

atom	**Wyckoff position & multiplicity**	**x**	**y**	**z**	**SOF**	B_{iso}
Li	3*b*	0	0	½	1-Ni_{Li}	B_{iso}(Li)
Ni	3*b*	0	0	½	Ni_{Li}	B_{iso}(Li)
Ni	3*a*	0	0	0	1-Li_{Ni}	B_{iso}(Ni)
Li	3*a*	0	0	0	Li_{Ni}	B_{iso}(Ni)
O	6*c*	0	0	z_O	1	B_{iso}(O)

X-ray absorption spectroscopy

For $Li_{1-z}Ni_{1+z}O_2$, the change in composition is associated with a change in the oxidation state of Ni. If we use the oxidation states of +1 and -2 for Li and O, respectively, then the oxidation state of Ni as a function of the Ni content present in the crystalline phase can be described as seen in Table S3. This was confirmed by X-ray absorption spectroscopy (XAS). The measurements clearly show a successive oxidation of Ni with decreasing z in $Li_{1-z}Ni_{1+z}O_2$ (Fig. S4). Assuming a Ni oxidation state of +3 for $LiNiO_2$ (z = 0), we clearly see a reduction toward 2+, and for the highest Li content (z = 0.35, $Li_{0.65}Ni_{1.35}O_2$) we see a reduction half way towards the state of NiO, i.e. we can conclude that the oxidation state is about 2.5, as suggested by Table S3.

Table S3: The calculated Ni oxidation state as a function of chemical composition.

$z_{nominal}$	total Ni from diffraction	z from diffraction	Chemical composition	Ni oxidation state
1	--	--	NiO	2.00
0.35	1.353	0.353	$Li_{0.647}Ni_{1.353}O_2$	2.48
0.3	1.298	0.298	$Li_{0.702}Ni_{1.298}O_2$	2.54
0.25	1.256	0.256	$Li_{0.744}Ni_{1.256}O_2$	2.59
0.2	1.211	0.211	$Li_{0.789}Ni_{1.211}O_2$	2.65
0.15	1.156	0.156	$Li_{0.844}Ni_{1.156}O_2$	2.73
0.1	1.122	0.122	$Li_{0.878}Ni_{1.122}O_2$	2.78
0.05	1.065	0.065	$Li_{0.935}Ni_{1.065}O_2$	2.88
0.01	1.041	0.041	$Li_{0.959}Ni_{1.041}O_2$	2.92
-0.01	1.023	0.023	$Li_{0.977}Ni_{1.023}O_2$	2.96
-0.05	1.008	0.008	$Li_{0.992}Ni_{1.008}O_2$	2.98

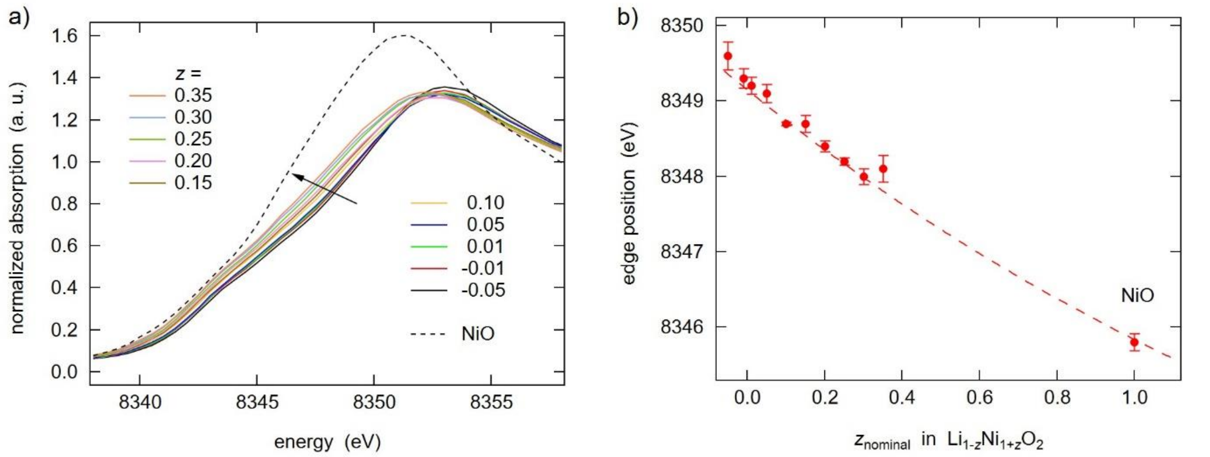


Figure S4: a) Ni K edge XAS spectra of $Li_{1-z}Ni_{1+z}O_2$ (-0.05 < z < 0.35) and b) edge position as a function of nominal z, where NiO has z = 1.

Magnetometry

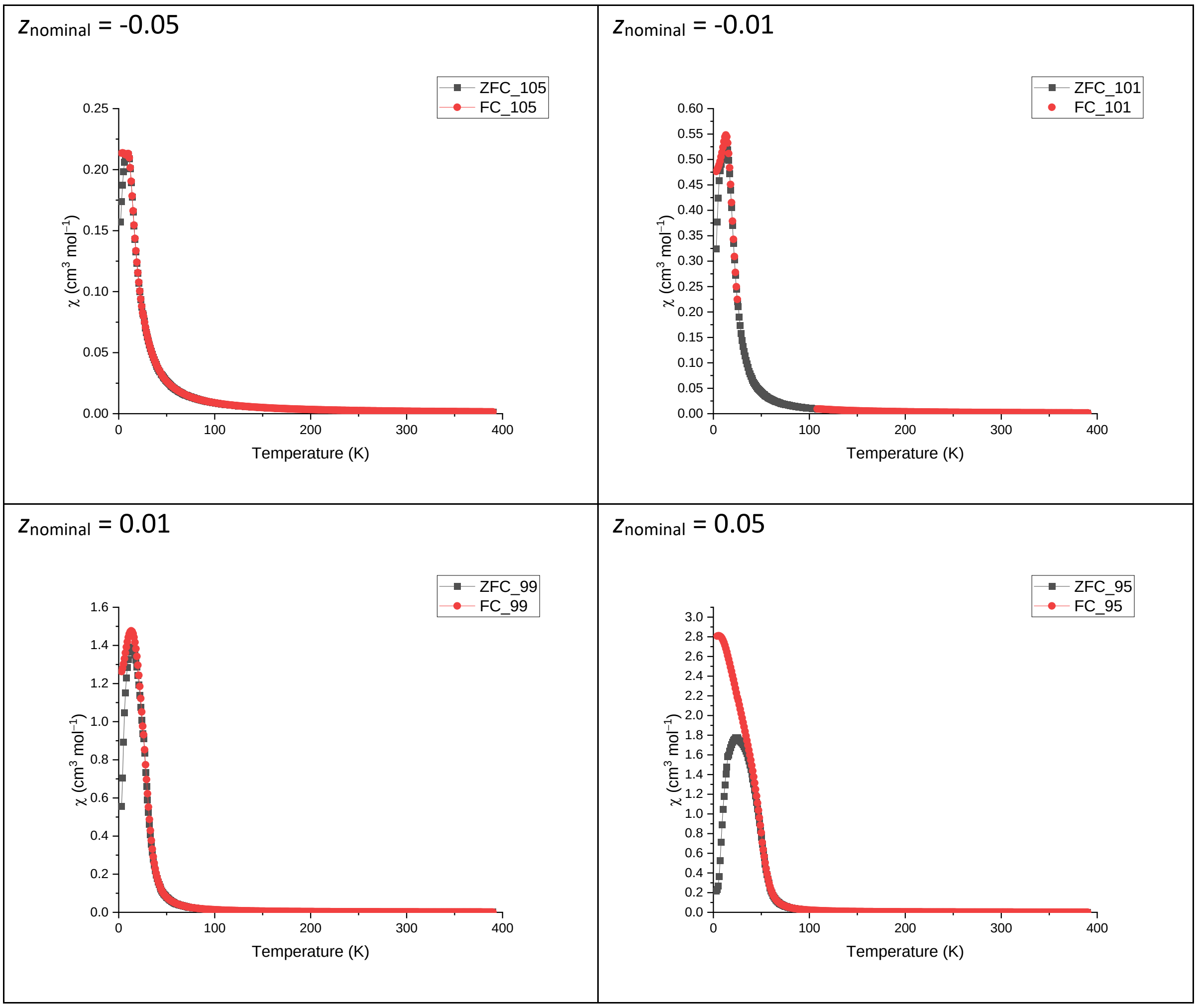


Figure S5: Molar magnetic susceptibility vs. temperature curves for $Li_{1-z}Ni_{1+z}O_2$ for -0.05 ≤ z ≤ 0.05 range.

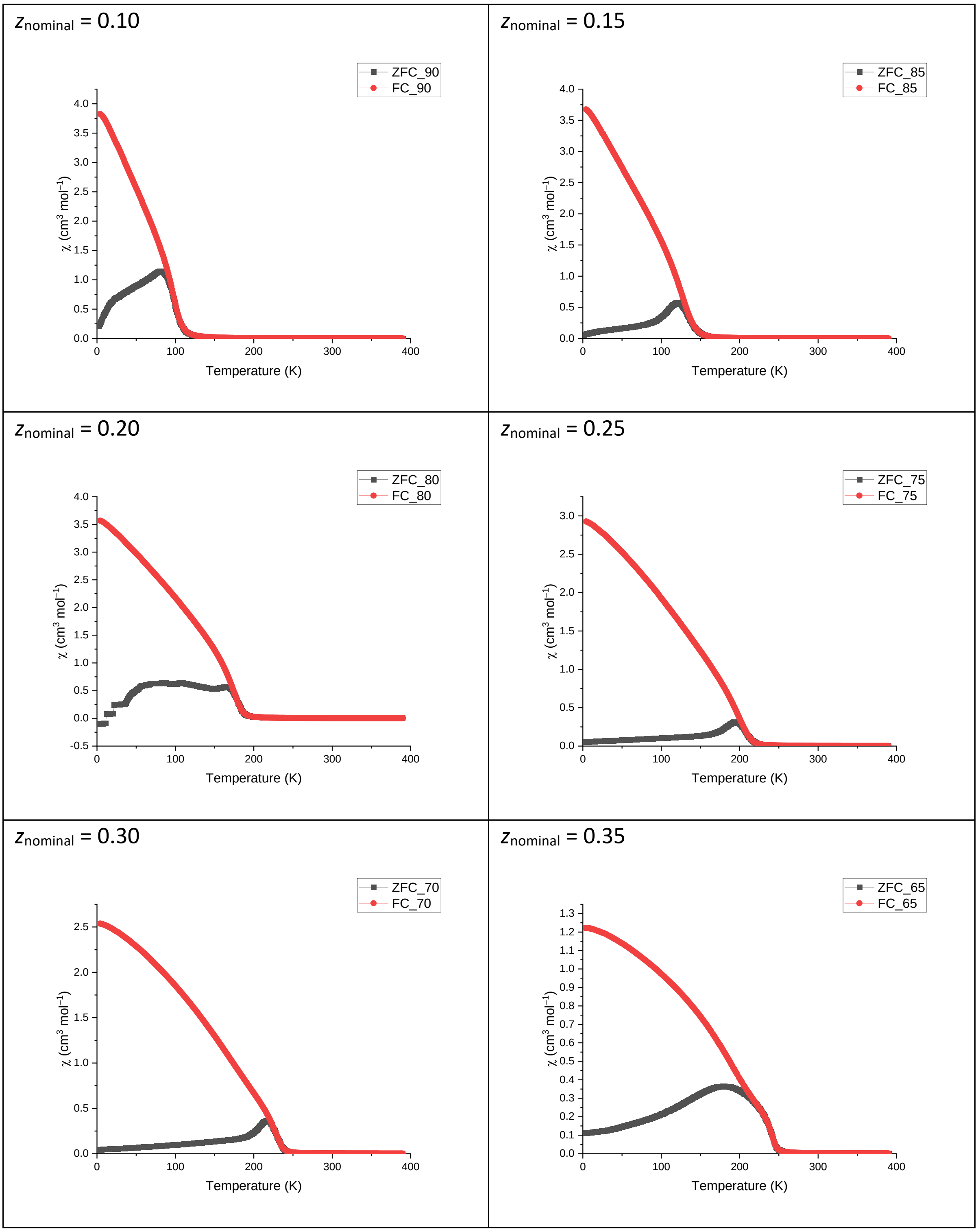


Figure S6: Molar magnetic susceptibility vs. temperature curves for $Li_{1-z}Ni_{1+z}O_2$ for 0.10 ≤ z ≤ 0.35 range.

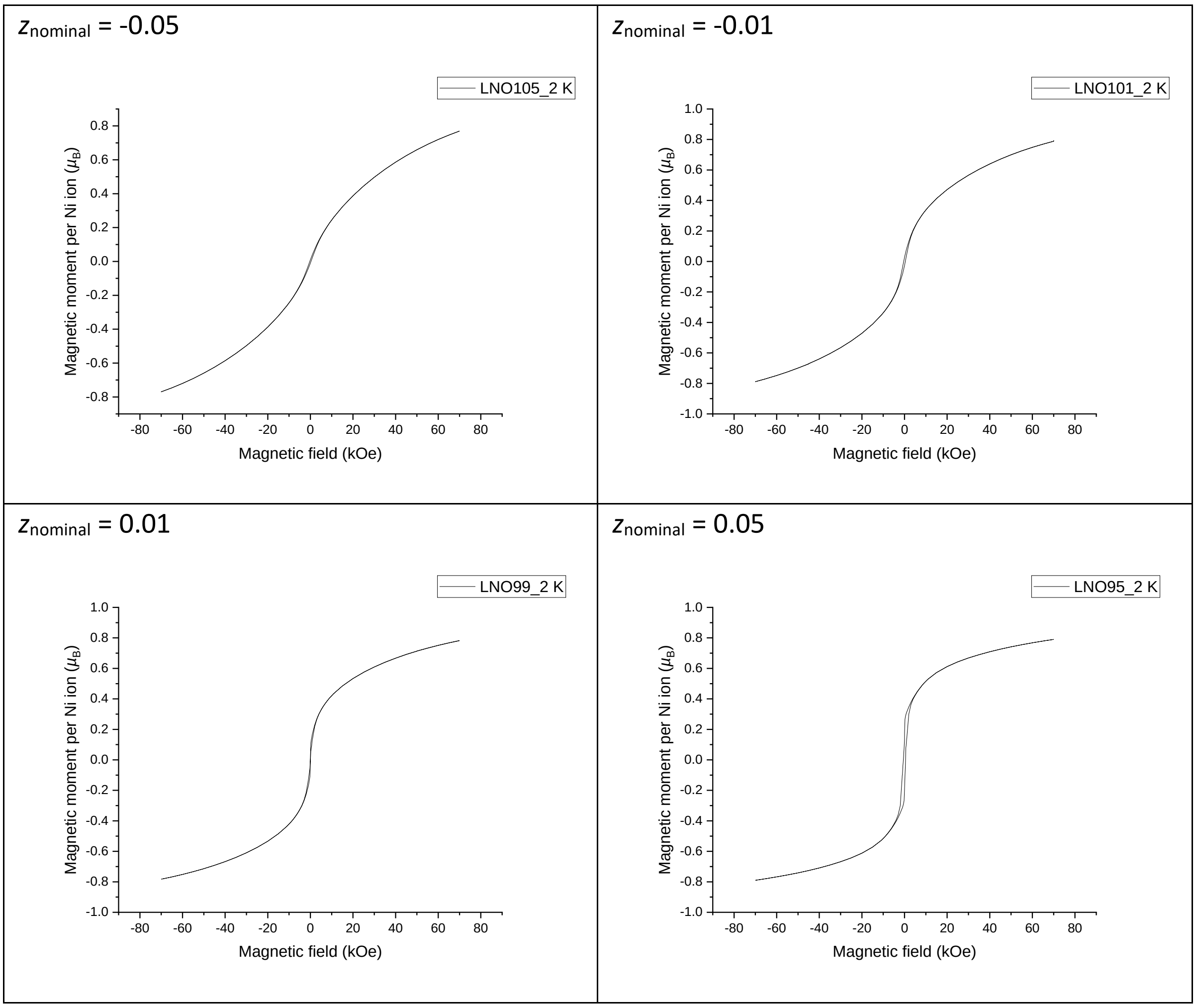


Figure S7: Magnetic moment vs. magnetic field curves measured at 2 K for $Li_{1-z}Ni_{1+z}O_2$ for $-0.05 \leq z \leq 0.05$ range.

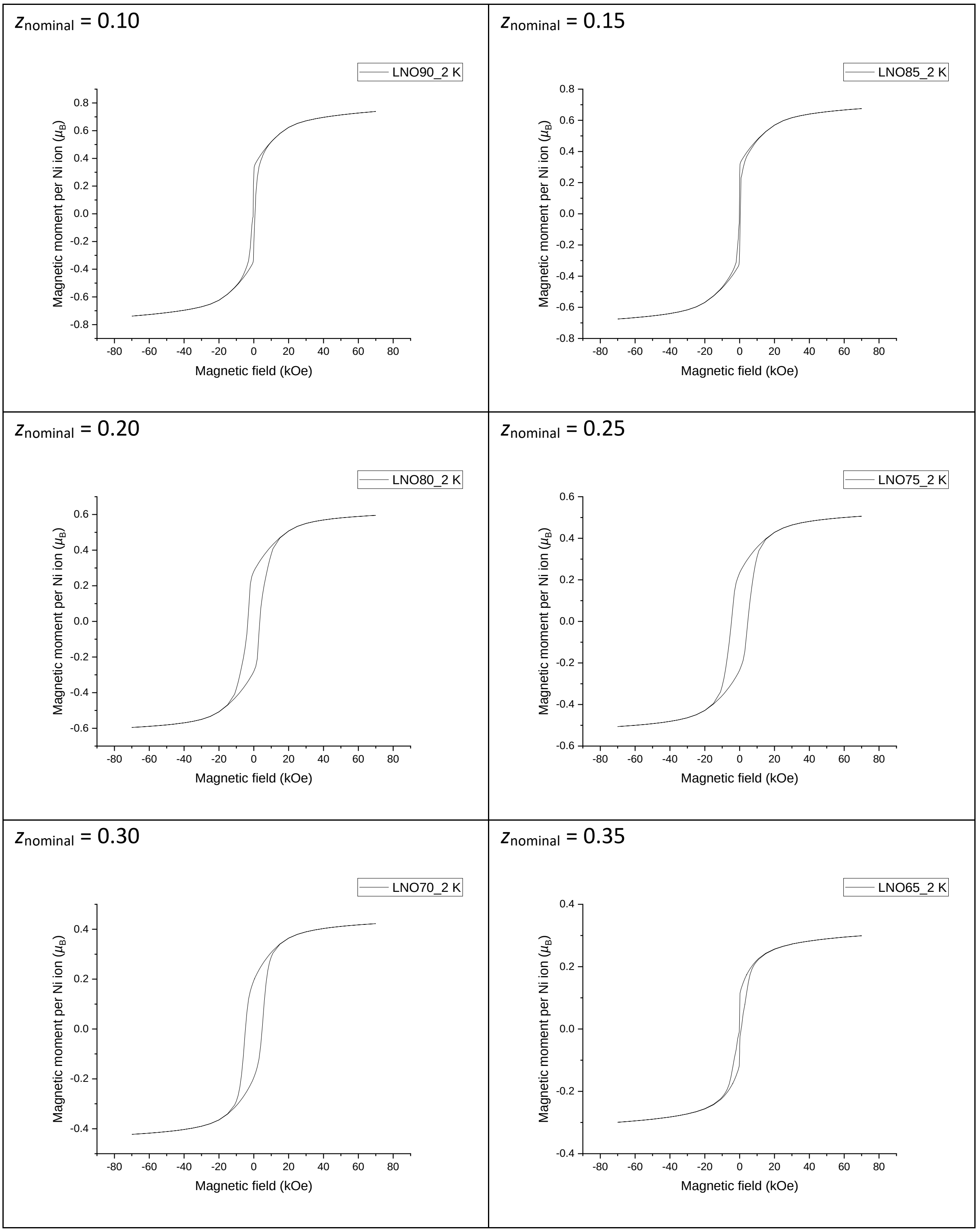


Figure S8: Magnetic moment vs. magnetic field curves measured at 2 K for $Li_{1-z}Ni_{1+z}O_2$ for 0.10 ≤ z ≤ 0.35 range.