

Supporting information

Spinel structure

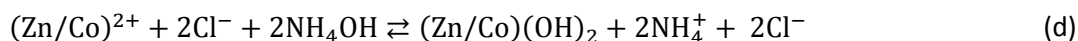
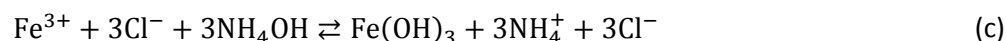
Spinel ferrites have the general chemical formula $(M)[Fe]_2O_4$, where the oxygen anions form a face-centered cubic (FCC) lattice and the divalent transition metal M occupies tetrahedral interstices '(...)', while twice as many trivalent iron occupies octahedral interstices '[...]'. The cation distribution in the spinel structure may vary between two extremes: *normal* and *inverse*, as defined by the *degree of inversion*. The formula for a spinel ferrite is given as



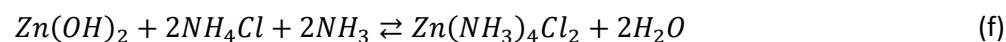
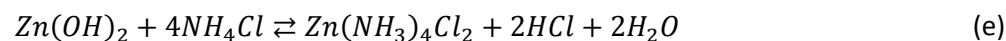
where γ is the degree of inversion varying between 0 and 1. The cation distribution is influenced by several parameters including coordination affinities,¹⁹ ionic sizes,^{20, 21} covalent bonding effects²¹ and crystal field stabilization energies.²¹

Additional information on sample preparation from chloride salts

The formation of the colloids is expected to happen according the reaction equations below.



The combination of ammonium and chloride in the precursor colloid may lead to the formation of ammonium salts that can coordinate to zinc- and cobalt hydroxide, thereby forming ammine complexes whose stability depend on the given element and the pH of the solution, as illustrated in reactions e) and f) for zinc hydroxide in an acidic and alkaline environment respectively^{9, 40}.



A possible way of achieving stoichiometric co-precipitation of all hydroxides is thus through the removal of chloride. Therefore iron(III) chloride was precipitated separately, until a pH of 8 was reached, and subsequently washed by means of centrifugation, followed by removal of the supernatant and re-suspension in deionized water. The washing procedure was repeated until a pH of approximately 7.5 was reached, after which the iron hydroxide precipitate was re-suspended to the initial volume. At lower pH the

supernatant assumed a yellow tint indicating the redissolution of iron hydroxide, and thus a pH of 7.5 was chosen as a compromise between retention of iron(III) hydroxide and removal of chloride. The suspension pH was monitored during addition of the precipitating agent using a pre-calibrated digital pH-meter (SevenMulti, Mettler Toledo).

The iron hydroxide colloid suspension was subsequently mixed in predetermined stoichiometric quantities with the aqueous solution of cobalt and zinc, followed by the addition of 25 weight% ammonia until a pH of 10 was reached. The colloidal precursor solution was then left to stir for 30 minutes, before further hydrothermal processing was initiated.

Preparation of diluted sample solutions for ICP OES

Approximately 5 mg of all samples were meticulously weighed on an analytical balance (Mettler-Toledo XP6), and transferred to 4mL glass sample containers with screw cap, where they were dissolved in a total of 4.00 ± 0.1 mL concentrated nitric acid with the help of ultrasonication in lukewarm water. The dissolved samples were subsequently diluted to a volume of 250.00 ± 0.15 mL with triple distilled water (Milli-Q water), attaining a concentration of 1.6% by volume concentrated HNO_3 . The samples were further diluted by transferring 2.5 mL dissolved sample solution into 15 mL plastic centrifuge tubes, and subsequently mixing it with 10 mL solution of 1% by volume concentrated HNO_3 in triple distilled water, using an adjustable-volume pipette (Thermo Scientific Finnpiptette F1, 0.5 to 5 mL, 2 to 0.5% accuracy). The resulting dissolved samples were thus diluted to a concentration of $(1.6\% \cdot 2.5 \text{ mL} + 1\% \cdot 10 \text{ mL}) / 12.5 \text{ mL} = 1.12\%$ concentrated nitric acid by volume.

Calculation of molar quantities from ICP-OES: The data, given as a mass fraction of a given element in mg per kg sample, was divided by the molar mass of the respective element, and multiplied by the total sample mass. The molar quantities n_x of each element per sample was hence determined as

$$n_x = \frac{C_x}{M_x} \cdot m_{\text{sample}} \quad (7)$$

where C_x is the concentration determined by ICP-OES measurement in grams per kg, M_x is the atomic mass in grams per mole of the given element and m_{sample} is the mass of the sample used to prepare the solution for ICP measurement given in kg. Since elements like oxygen and hydrogen cannot be detected by ICP-OES, assumptions were made regarding the relative content of oxygen.

Crystallite size determination from PXRD: For small crystallites with a cubic unit cell, size broadening can be described solely by the Lorentzian parameter Y in Fullprof, EdPCR, and from Scherrer's equation the following expression can be derived

$$\langle D \rangle_{vol}^{PXRD} = \frac{36 k \lambda}{\pi^2 Y} \quad (8)$$

where k is Scherrer's constant and λ is the wavelength³⁰. In this work Scherrer constant has been equated to 1. Using Equation 8 the volume weighted average sizes of crystalline grains, in units of nanometers, have been calculated.

Methodology of Rietveld refinement: The overall fit of the refined models is rather good, as can be seen from the difference plots and the included Bragg-R values and RF-factors. The diffractograms of all 9 as-prepared samples, are shown in Figure S1. It should be noted that for the three 45 minute samples, there was insufficient amounts of powder to fill the sample holders completely. This resulted in a reduction in the intensity for angles below a certain threshold 2θ angle, due to the probed sample area being smaller below said threshold. The over eliminated is corrected for in using the Fullprof software, however the low angle peaks cannot be accounted for exactly. Therefore the information from these samples must be regarded as being of a qualitative nature.

Preparation of sample pellets for VSM measurement

Using a table mounted manual press, with a hollow brass cylinder and steel piston, approximately 10mg of each sample was pressed into a pellet of 3mm diameter and approximately 1mm thickness. The pressed samples were carefully weighed on an analytical scale (Mettler AT20, Struers, $\sigma = 5\mu\text{g}$), and transferred to labelled containers. Between each sample, the cylinder and pistons were thoroughly cleaned with ethanol.

Pressed sample pellets were mounted in a hollow brass cylinder with a slit along its length with an internal diameter matching that of the pellets. The button shaped pellets were held in place within a specific range of the cylinder using two quartz spacers. The sample holder is threaded onto an extension rod, which is lowered into the internal volume of the PPMS where a superconducting electromagnet resides.

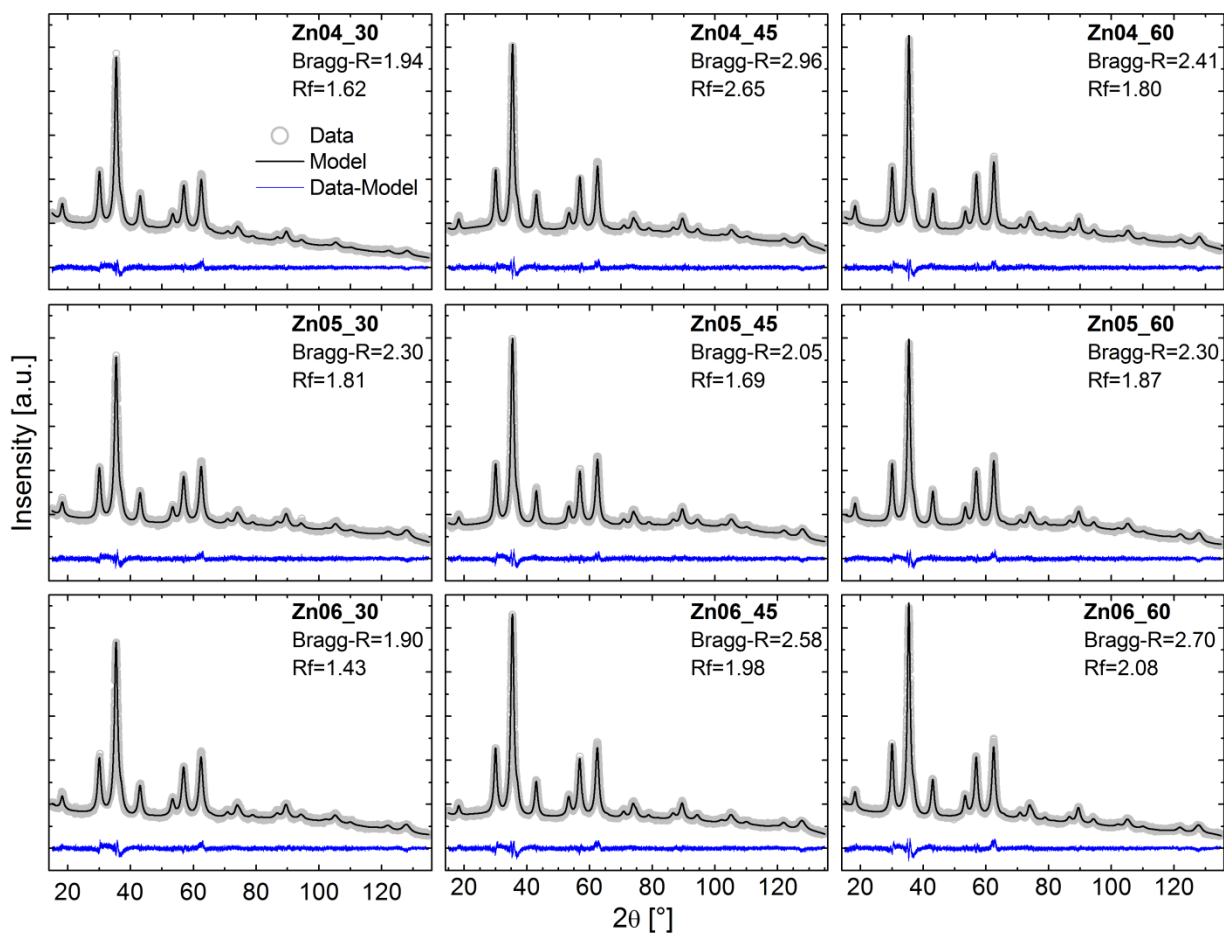


Figure S1. The observed PXRD patterns (grey circles), the calculated model (black line) and the difference plot (blue line) of batch E of the stoichiometry $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for $x = 0.4, 0.5$ and 0.6 is shown in the above figure, for reaction times 30, 45 and 60 minutes. Refinement of the diffraction data for the three 45 minute samples had to be corrected for over illumination. Occupancies were refined with some success for this batch. The Diffraction data was measured between 15 and 135 $^\circ 2\theta$ with Bragg-Brentano optics with incident slit size of $\frac{1}{2}$ degrees, and scan-speed of 1 degree per minute. Bragg-R factors and Rf-factors have been imbedded in the corresponding diffractogram windows

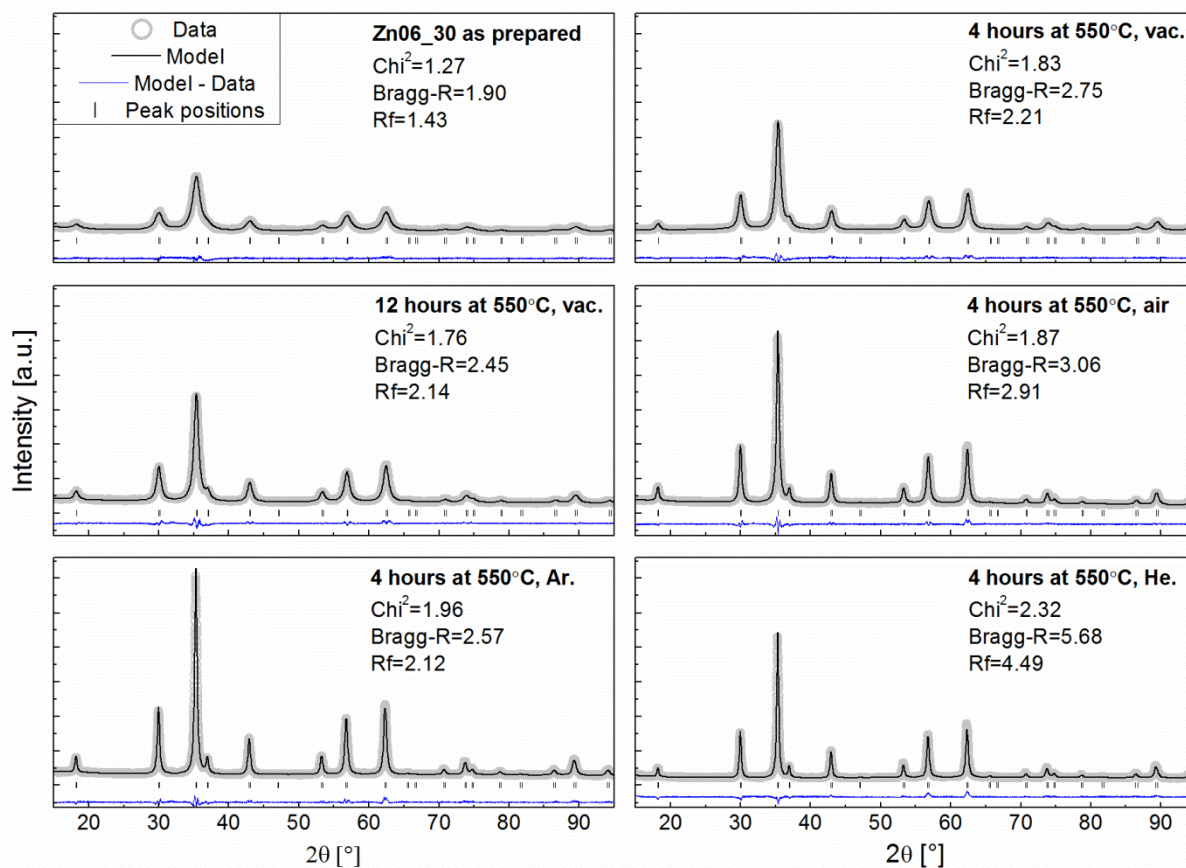


Figure S2. Refined powder diffraction patterns of differently annealed subsets of sample Zn06_30, including as a reference the sample as prepared. The data is displayed as grey circles, while the calculated model is displayed as a black solid line and the difference plot as a blue solid line. Bragg positions are marked with red bars. All windows are equally scaled. All diffraction patterns have been recorded with Bragg Brentano incident slit geometry using the diffracted beam monochromator.

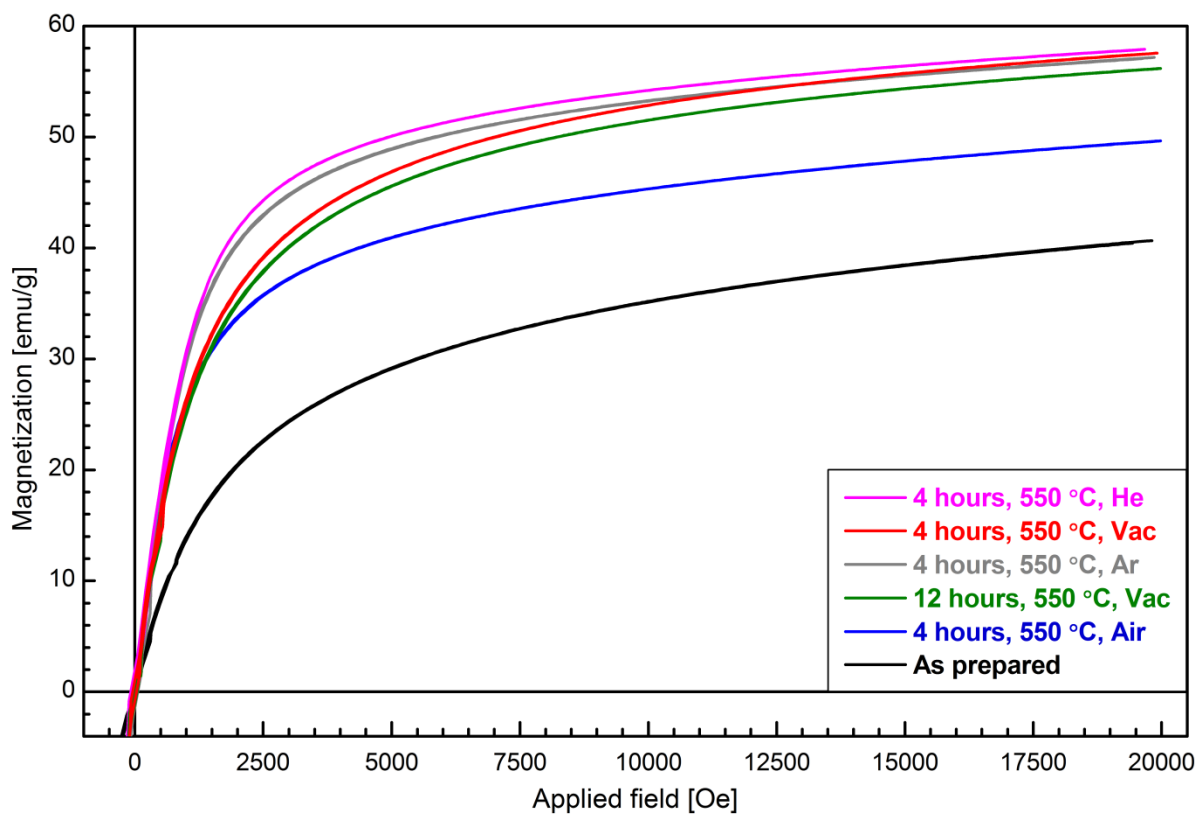


Figure S3. The first quadrant of the magnetization measurements of the differently annealed subsets of sample Zn06_30. The measurement was performed at 300K with an applied field between -2 T and 2 T.

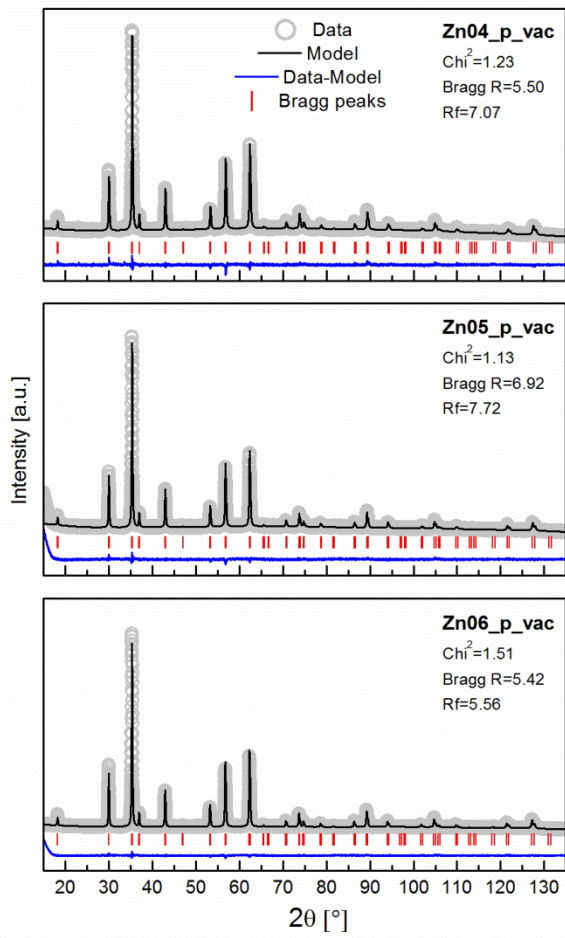


Figure S4. Refined high resolution PXRD data of the samples from the second annealing experiment that had first been pressed and then annealed. The data was acquired on ground samples after VSM measurements had been performed.