

Article

W-Type Hexaferrites Made in Seconds—An In Situ Powder Diffraction Study

Mathias Mørch, Amalie Povlsen Laursen, Jack Thomas-Hunt [†], Priyank Shyam  and Mogens Christensen ^{*,†}

Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, 8000 Aarhus, Denmark

* Correspondence: mogensc@mp.aau.dk

[†] Current address: Department of Materials and Production, Aalborg University, Fibigerstræde 16, 9220 Aalborg Ø, Denmark.

Abstract

The formation of W-type hexaferrite magnets was investigated using in situ synchrotron X-ray powder diffraction. Both the holding time and precursor composition were investigated to evaluate the effect on phase purity and crystallite size using Rietveld refinements. Based on the refinements, it was found that the formation of W-type hexaferrites initiates shortly after reaching 1200 °C and happens within a few seconds. M-type hexaferrite was formed at a lower temperature before being transformed into W-type hexaferrite. Despite the short holding times, at elevated temperatures, the crystallite sizes along the *a,b*-axis exceeded the detection limit of the powder diffraction data, as the peak widths associated with the *a,b*-planes became too narrow to resolve changes as function of time. Magnetization data recorded from the in situ prepared samples revealed a higher saturation magnetization in the W-type hexaferrites relative to conventional M-type hexaferrites. No appreciable coercivity was found, which can be attributed to different effects: (1) reduced anisotropy constant, (2) large crystallite growth resulting in multi-domain crystallites, or (3) exchange-coupling with soft spinel ferrite found in the sample. Based on this study, we conclude that W-type hexaferrites can be formed after a few seconds at 1200 °C and that crystallite growth happens subsequently after the formation of the W-type hexaferrite structure.

Keywords: permanent magnet; in situ diffraction; rapid sintering

1. Introduction

The properties of functional materials are defined by their composition and structure. Understanding the structure on the atomic scale and nanoscale is crucial for designing and optimizing new materials. Various external stimuli such as temperature, pressure, and atmosphere affect the material's structure and composition. The influence of the processing steps can have a marked influence on the resultant material's functionality. The structure and functionality are usually studied 'post-mortem', making property optimization a 'black-box', i.e., a trial-and-error process. Maintaining nanostructures at elevated temperatures is challenging, because crystal growth is happening on a short time scale at temperatures > 1000 °C. In situ ultrafast high-temperature sintering (UHS) allows for opening the 'black-box' by combining fast heating rates and high temperatures together with fast data acquisition, offering an 'operando' approach. This makes it possible to look into the chemical processes as they happen. Fast data acquisition is crucial for following the phase transformation and crystallite growth at high temperatures.



Academic Editor: Arcady Zhukov

Received: 22 June 2026

Revised: 10 July 2026

Accepted: 15 July 2026

Published: 3 August 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

To open the ‘black-box’, we have developed a novel setup—the Aarhus Rapid Ohmic Sintering (AROS) Furnace [1] inspired by Wang et al. [2]. This allows us to follow processes at high temperatures > 1200 °C on a < 0.1 s time scale using a highly penetrating, hard X-ray synchrotron beam. The in situ investigated sample can be easily retrieved for further investigations of its physical properties with complementary techniques like EBSD, VSM, etc. Here, we demonstrate the capabilities for an in situ diffraction study following the formation of permanent magnets, specifically the W-type hexaferrite $\text{SrZnNiFe}_{16}\text{O}_{27}$.

Permanent magnets are key materials for electrification of society and the two most widely used magnets, M-type hexaferrites ($\text{SrFe}_{12}\text{O}_{19}$) and neodymium magnets ($\text{Nd}_2\text{Fe}_{14}\text{B}$), make up 99% of the market. Hexaferrites are rare earth element-free magnets, and the cost per magnetic power ($(\text{kJ}/\text{m}^3)/\$$) is lower for hexaferrites [3], leading to their widespread use. In general, the energy product (BH_{max}) of a permanent magnet scales proportionally to the remanent magnetization (M_r) squared, if the material has sufficient coercivity. The best commercial ferrite magnets have $BH_{\text{max}} = 44(2) \text{ kJ}/\text{m}^3$, which is limited by their magnetization ($M_r \sim 74(2) \text{ Am}^2/\text{kg}$) as long as the coercivity (H_c) is high enough $H_c > \frac{1}{2}M_r$. In order to improve properties beyond the best commercial magnets it is thus necessary to achieve $M_r > 75 \text{ Am}^2/\text{kg}$ while retaining a high coercivity ($H_c > 191 \text{ kA}/\text{m}$).

Substitution of divalent metal ions in $\text{SrFe}_{12}\text{O}_{19}$ such as Co^{2+} or Zn^{2+} have shown great possibility for tuning both the magnetic anisotropy field (Co^{2+} ; $[\text{Ar}]3d^7$) [4] and the magnetic saturation (Zn^{2+} ; $[\text{Ar}]3d^{10}$) [5]. However, substituting Fe^{3+} by a divalent transition metal requires additional substitution elsewhere in the unit cell either; Fe^{3+} by a tetravalent ion (e.g., Ti^{4+}), or Sr^{2+} by a trivalent ion (e.g., La^{3+}). There are limits to the amount of divalent elements that can be substituted into $\text{SrFe}_{12}\text{O}_{19}$. The improvement by Zn^{2+} can be rationalized by the fact that $\text{SrFe}_{12}\text{O}_{19}$ is a ferrimagnet and has five distinct crystallographic sites for Fe^{3+} ; $\uparrow (2a, 4e, 12k)$ and $\downarrow (4f_1, 4f_2)$, where $2a$, $12k$ and $4f_2$ is octahedrally coordinated and $4f_1$ is tetrahedrally coordinated and $4e$ is half occupied with trigonal bipyramidal coordination. By inserting the Zn^{2+} ($[\text{Ar}]3d^{10}$) onto the $4f_1$ tetragonal site it is possible to enhance the magnetization by reducing the number of antiparallel atomic magnetic dipolar moments. A comparison of the crystal structures of MHF and WHF is shown in Figure S1 of the Supplementary Materials.

The W-type hexaferrites ($\text{SrFe}_{18}\text{O}_{27}$) are a potential candidate for an even better performance, because they already contain two Fe^{2+} that can be substituted with a non-magnetic $2+$ ion such as Mg^{2+} or Zn^{2+} . The W-type structure has seven distinct crystallographic sites for iron; $\uparrow (4f_1, 6g, 12k, 4f_2)$ and $\downarrow (4e, 4f_3, 4f_4)$, where $4f_1$, $6g$, $12k$ and $4f_3$ are octahedrally coordinated while $4e$, and $4f_4$ have tetrahedral coordination and $4f_2$ is half occupied on a trigonal bipyramidal site. This gives now two sites for Zn^{2+} to enter into the structure. Combined substitution of Co-Zn in W-type hexaferrite causes a change in the magnetic structure from uniaxial to planar [6].

In ideally aligned permanent magnets, the remanent magnetization is limited only by the saturation magnetization. Magnetic saturation in ferrites can be tuned with transition metal (TM) substitution as previously shown for spinel ferrites $\text{TM}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ [7,8], ($\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) [9], M-type hexaferrites ($\text{Sr}_{0.5}\text{La}_{0.5}\text{Zn}_{0.45}\text{Fe}_{11.55}\text{O}_{19}$) [5] and W-type hexaferrites ($\text{SrZnLi}_{0.5}\text{Fe}_{16.5}\text{O}_{27}$, $91 \text{ Am}^2/\text{kg}$) [10], ($\text{SrZnFe}_{17}\text{O}_{27}$, $88 \text{ Am}^2/\text{kg}$) [11,12], and ($\text{SrNiZnFe}_{16}\text{O}_{27}$, $80 \text{ Am}^2/\text{kg}$) [13].

To achieve a high coercivity it is a necessity to have a high magnetocrystalline anisotropy. According to experiments and theoretical calculations, W-type hexaferrites ($\text{SrFe}_{18}\text{O}_{27}$) have similar magnetocrystalline anisotropy energy to M-type hexaferrites ($\text{SrFe}_{12}\text{O}_{19}$) [14–16] which should make it possible to achieve similar coercivity. Nevertheless, there are no reports of small crystallite sizes and high coercivity in W-type hexaferrites.

Synthesizing W-type hexaferrites is challenging, because the phase only forms at high temperatures in a relative narrow temperature range from 1350 to 1440 °C according to the Sr-Fe-O phase diagram [17]. At elevated temperatures Fe^{3+} reduces to Fe^{2+} , due to oxygen leaving the sample. Unfortunately, M-type hexaferrite exhibits abnormal grain growth at an onset temperature of about 1260 °C [18,19]. The formation temperature of W-type hexaferrite and onset of abnormal grain growth makes it very difficult to prepare small crystallites of W-type hexaferrites. Exaggerated grain growth is detrimental to the magnetic properties, especially the coercivity [20].

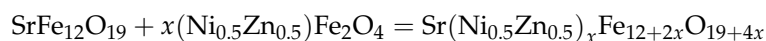
It is possible to lower the formation temperature from 1350 °C to 1200–1250 °C in $\text{SrFe}_{18}\text{O}_{27}$ by substituting Fe^{2+} with transition metal ions preferring the 2+ oxidation state. This was demonstrated for $\text{Co}^{2+}/\text{Ni}^{2+}/\text{Zn}^{2+}$ [13,21]. Here we have chosen to focus on $\text{Ni}^{2+}/\text{Zn}^{2+}$ as this is reported to have $M_s \sim 80 \text{ Am}^2/\text{kg}$ and relatively low synthesis temperature around 1250–1300 °C.

The rapid and ultra-high-temperature sintering furnace ARQS is ideal for following the phase formation and crystallite growth of W-type hexaferrites in situ. The in situ investigations are paramount for realizing whether it is possible to form the W-type hexaferrite before the abnormal grain growth initiates. This is to the best of our knowledge the first study of W-type hexaferrites' formation in situ.

2. Experimental

2.1. Synthesis

A sol-gel precursor was prepared for making $\text{SrNiZnFe}_{16}\text{O}_{27}$ hexaferrite. The metal nitrates ($\text{Sr}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in ~125 mL water. Citric acid was dissolved in ~75 mL water and added to the metal nitrate solution. Subsequently the pH was adjusted to ~7 with NH_4OH . The W-type hexaferrite can be thought of as a mixture of M-type hexaferrite and spinel ferrite.

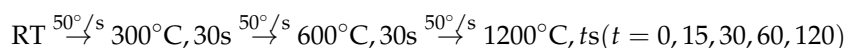


For the study varying the holding time t at the temperature 1200 °C, the stoichiometry was kept at $x = 1.9$ using slight surplus of Sr. Meanwhile, in the second series, the holding time t was fixed at 15 s and the stoichiometry was varied. Three different ratios were prepared and investigated: $x = 1.8, 1.9$, or 2.0 .

All gels were dried at ~100 °C for 24 h. The resulting powder was combusted in a convection oven at 350 °C for 30 min resulting in a loose powder which was subsequently crushed. The crushed powder was pressed into pellets of approximately 0.15 g with 6 mm diameter and 1 mm thickness. The compaction was done in a steel matrix at 1.0 GPa for 5 min and the pellets were later cut and placed into quartz capillaries with $\varnothing \sim 3\text{--}4 \text{ mm}$ and 0.01 mm wall thickness.

2.2. Powder Diffraction

The powder diffraction experiments were carried out at beamline P02.1 at DESY using a Varex XRD 4343CT detector (Varex Imaging, Salt Lake City, UT). Capillaries containing pellets were placed inside the felt in the ARQS furnace [1] (see the Supplementary Materials for more information about the ARQS furnace (Aarhus University, Aarhus, Denmark) where the following heating ramp was used for the experiments:



Individual experimental runs will be referred to by their dwell time, t , throughout the discussion. Powder diffraction data were collected continuously during heating and

cooling. The X-ray energy used for penetrating the sample was 60 keV ($\lambda = 0.2066 \text{ \AA}$) with a sample-to-detector distance of 1011.6 mm, full diffraction rings were collected up to $Q = 6.0 \text{ \AA}^{-1}$ and integrated using MatFRAIA v2022 using a 2θ step size of 0.005° [22]. To calibrate the sample to detector distance and describe the instrumental broadening, NIST Standard Reference Material 660b (LaB_6) powder in a similar pellet-like/sample geometry was also measured.

2.3. Vibrating Sample Magnetometry

The magnetic data was collected using a Quantum Design Physical Properties Measurement System with the Vibrating Sample Magnetometer option (PPMS-VSM, Quantum Design, San Diego, CA) with an applied magnetic field of $\pm 3 \text{ T}$ at 300 K. The saturation magnetization (M_s) was determined from the law of approach to saturation, while the coercivity (H_c) and remanent magnetization (M_r) were extracted by linear interpolation.

3. Results and Discussion

Collected data alongside with the temperature profile from $t = 120 \text{ s}$ experiments is shown in Figure 1. The heatmap reveals the different phase transitions occurring in the sample. The heatmaps for the various samples are more or less identical; only the holding time varies. Initially a precursor phase of spinel can be seen in the diffraction pattern; there is no evidence of any Sr-containing phases. The spinel peaks are very broad, suggesting small crystallite or a highly defective structure. In all experiments a clear transition is seen near the 1 m 15 s mark as exemplified in Figure 2. Here the temperature is raised from 600°C to 1200°C , initiating the formation of M-type hexaferrite, which is rapidly converted to W-type hexaferrite, once the temperature approaches 1200°C . This paper is concentrating on the formation and growth of W-type hexaferrite; therefore, the focus will be on the time stamp 1 m 15 s and onwards. The M-type hexaferrite formation will be used to estimate the sample temperature, because the temperature reproducibility of the furnace appears to be around $\pm 10\%$ of the set temperature; see Figures S2 and S3 and Table S1 of the Supplementary Materials for further details.

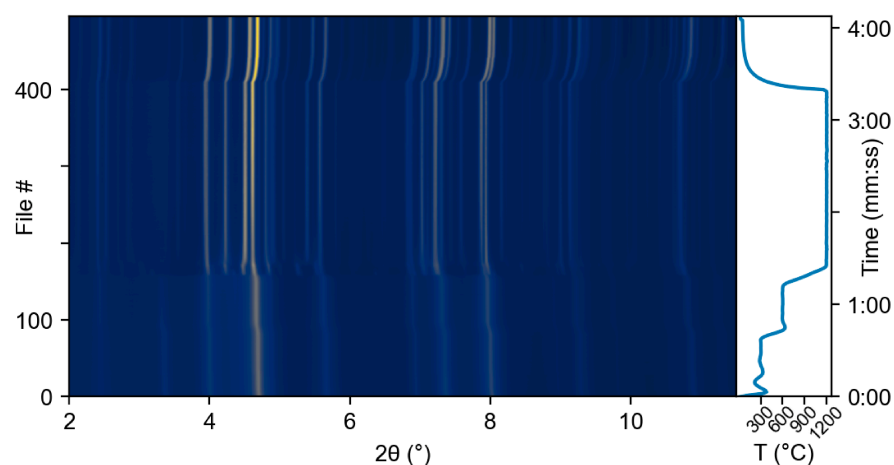


Figure 1. D heatmap of diffraction data (2θ , File #, where # is the number) left, and temperature profile ($^\circ\text{C}$, min:ss) right.

To obtain quantitative information describing the formation and growth during the in situ experiment, the integrated diffraction data was Rietveld-refined using TOPAS v7 [23]. The structural model is based on the structure reported by Mørch et al. [21] and is also found in the ICSD database as entry 38996. Figure 2 shows an example of a Rietveld refinement 3 min into the experiment, where the sample has been held at 1200°C for almost

2 min. At this point W-type hexaferrite is the dominant phase with a considerable phase fraction of spinel and slight amounts of M-type hexaferrite.

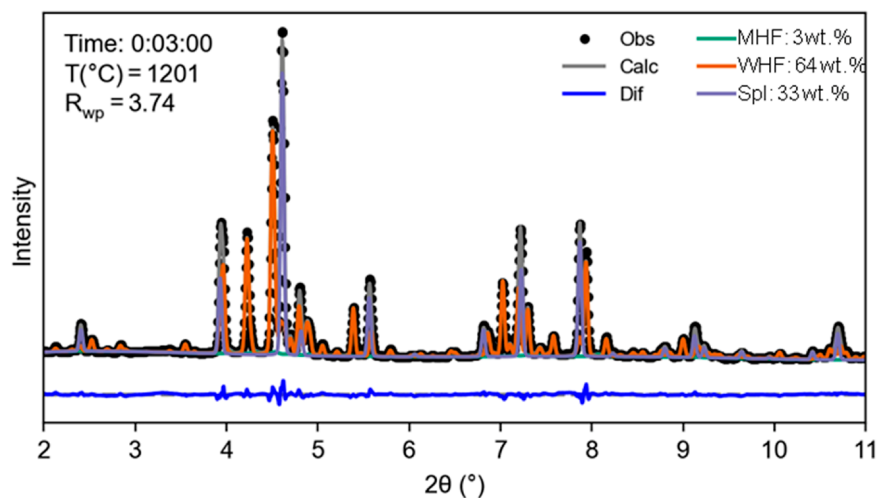


Figure 2. Three minutes into the 120 s experiment. Observed, calculated and difference plot along with the phase contributions from: MHF = $\text{SrFe}_{12}\text{O}_{19}$, WHF = $\text{SrNiZnFe}_{16}\text{O}_{27}$ and Spl = $(\text{NiZn})_{0.5}\text{Fe}_2\text{O}_4$.

Two studies were carried out: one investigating the effect of the holding time and a second looking at the effect of different ratios between M-type hexaferrite and spinel ferrite. The extracted information from the powder diffraction data is the phase fraction of the different observed crystalline phases and the crystallite size along the a,b -axis (width) and the c -axis (thickness). The size along the ab -axis very quickly grows out of the instrument resolution, which was determined from the NIST LaB_6 standard to be around 100 nm. Reliable information about the crystallite size along the a,b -axis cannot be extracted from the diffraction data and it is therefore not plotted or reported, but the size is expected to be $\gg 100$ nm. The reported crystallite size along the c -axis represents a theoretical minimum crystallite size as all peak broadening effects are attributed to size, this is done to minimize cross correlations. The absolute value of the size along the c -axis cannot be trusted, but the trends as function of time are reliable.

3.1. Holding Time

Five different holding times were investigated ($t = 0$ s, 15 s, 30 s, 60 s, and 120 s) to study the reproducibility of the temperature in the furnace and the reproducibility of the phase formation, alongside the effect of different holding times on the final growth of the phases. Figure 3 shows the extracted weight fraction of $\text{SrNiZnFe}_{16}\text{O}_{27}$ plotted alongside the crystallite thickness (size c [nm]) versus time as extracted from the TOPAS refinements.

The slow formation of $\text{SrNiZnFe}_{16}\text{O}_{27}$ in the 60 s experiment, and rapid increase in phase and size in the 30 s experiment hinted that the sample temperature could be different than the control temperature in the thermocouple. By comparing the refined lattice parameters of $\text{SrFe}_{12}\text{O}_{19}$ in the time interval 01 m 20 s–01 m 35 s to thermal expansion coefficients, it could be reasoned that the sample temperature was ~ 100 °C lower in the 60 s experiment and ~ 150 °C higher in the 30 s experiment. More details are given in Figures S4 and S5 and Table S1 of the Supplementary Materials.

In the experiments with sufficient temperature and time (15 s, 30 s, and 120 s) the formation of W-type hexaferrite occurs in ~ 15 s of reaching the W-hexaferrite formation temperature of 1200 °C (from 1 m 20 s to 1 m 35 s). In the two other experiments (0 s, and 60 s) the phase never fully forms, either due to too short time (0 s) or insufficient temperature (60 s). Textbooks often describes solid-state reaction to be “slow” with “prolonged periods”

of heating being necessary [24]. Here the reaction occurs very fast, due to the nanoscale dimensions of the precursor, causing shorter diffusion pathways and consequently faster reaction kinetics. Fast reactions are paramount if the nanostructure is to be maintained at these elevated temperatures.

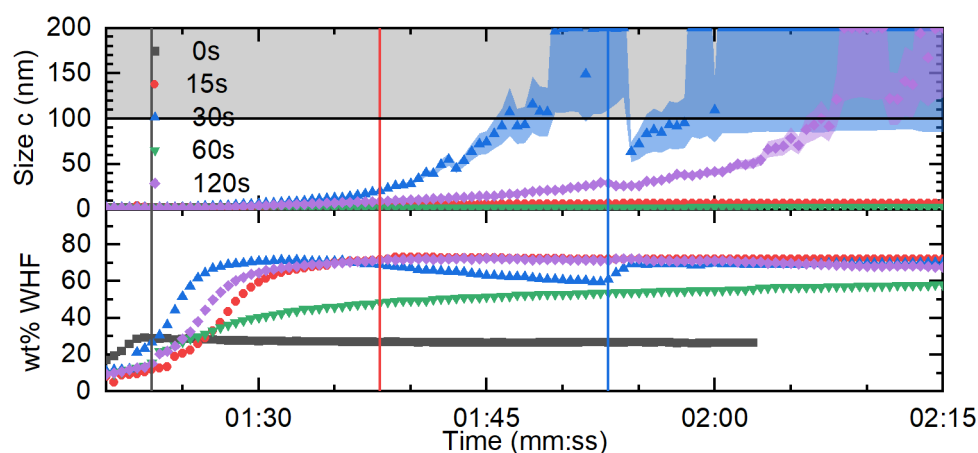


Figure 3. Weight% and crystallite thickness for $\text{SrNiZnFe}_{16}\text{O}_{27}$ vs. time. Horizontal line indicates the resolution limit. Colored vertical lines indicate when power is switched off. Colors denote the five different holding times, as given in the legend, and the grey shaded area marks the region above the instrument resolution limit (~ 100 nm), in which crystallite sizes cannot be reliably determined.

The rapid formation in the 30 s experiment is followed by a marked decrease in the observed phase fraction of W-type hexaferrite (~ 70 wt% $\rightarrow$ ~ 60 wt%); this is seen from 1 m 30 s to 1 m 52 s followed by a sharp increase from 1 m 52 s to 1 m 55 s. When looking at the growth in the refined crystallite thickness (size c [nm]) the higher temperature of the 30 s experiment markedly accelerates the growth. A sharp reduction in crystallite size is subsequent with an increase in W-type hexaferrite phase fraction that occurs around 1 m 52 s–1 m 55 s coinciding with the furnace being switched off. It is likely that at higher temperatures (1200 °C + ~ 150 °C), the phases begin to slowly melt and only recrystallize when the heating is turned off. This is corroborated by the scale factor tailing off and coming back up as the temperature is switched off; a figure of this is shown in Figure S7 of the Supplementary Materials. In the 120 s experiment the refined crystallite thickness grows much slower, but also increases outside of the resolution by the 2 m 10 s mark in the experiment. However, for the other experiments the apparent size along the c -axis remains below ~ 35 nm. The refined final phase fractions for the different experiments are given in Table 1 along with the magnetic properties for the different samples.

Table 1. Magnetic properties and refined weight fractions of the five samples of $\text{SrNiZnFe}_{16}\text{O}_{27}$ with different holding times and the three different M-type/spinel ratios.

Time (t)	0 s	15 s	30 s	60 s	120 s	15 s	15 s	15 s
Ratio (x)	1.9	1.9	1.9	1.9	1.9	1.8	1.9	2.0
WHF (wt%)	26.7(4)	72.0(6)	70.3(5)	57.8(6)	64.6(4)	81.6(4)	72.0(6)	74.2(5)
MHF (wt%)	45.0(6)	12.1(3)	0	17.4(4)	0.76(8)	1.1(1)	12.1(3)	3.12(2)
SPL (wt%)	28.3(8)	15.9(6)	29.7(5)	24.7(69)	34.6(4)	17.3(4)	15.9(6)	22.7(5)
M_s (Am ² /kg)	73.61(2)	75.78(1)	78.68(2)	76.59(1)	77.38(2)	78.52(1)	75.8(1)	76.29(1)
M_r (Am ² /kg)	26.36(1)	9.06(2)	2.74(2)	9.63(4)	3.48(3)	4.25(2)	9.06(2)	-
H_c (kA/m)	117.3(8)	30.3(4)	5.93(9)	18.8(6)	5.14(12)	10.9(2)	30.3(4)	-

Values in parentheses are the estimated standard uncertainties on the last digit of the preceding value.

The experiments with different holding times reveal that both time and temperature have a big effect on both the formation and growth of W-type hexaferrite where too high temperatures accelerate both growth and decomposition, but too low temperatures causes an incomplete transformation. As evidenced by the 120 s experiment, the bulk phase formation takes place in a matter of seconds, while growth continues over the next ~2 min. The temperature should be controlled better ± 50 °C, which at 1200 °C means within ~4% error margin and the time should be controlled better than ± 15 s at these temperatures.

3.2. Ratio Between M-Type and Spinel

Besides the study of holding time, three different precursor ratios were investigated to look at the effect of the final phase composition. The 2.0 ratio represents the ideal stoichiometry, while the excess Sr in the off-stoichiometry ratios 1.8 and 1.9 have previously been reported to improve the phase fraction of W-type hexaferrite produced [25,26]. The heating ramp was the same as the first experiments, and a holding time of $t = 15$ s was used. In Figure 4 the refined crystallite thickness (apparent size c [nm]) along with the weight fraction of $\text{SrNiZnFe}_{16}\text{O}_{27}$ are plotted for the three different precursor ratios.

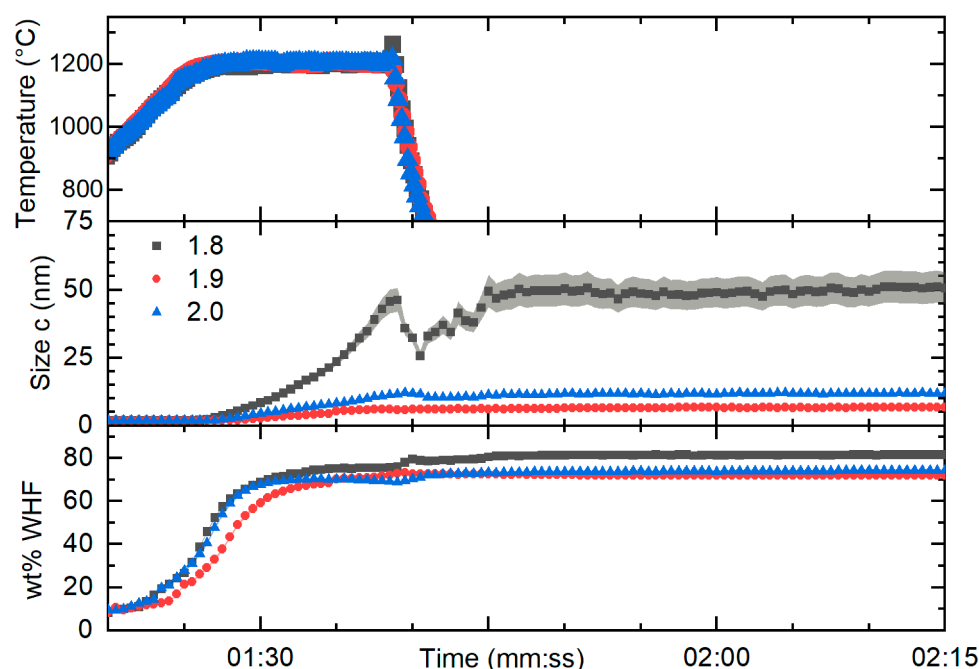


Figure 4. Temperature, weight fraction and crystallite thickness for the three different precursor compositions. The shaded region indicates estimated standard uncertainty.

In agreement with the experiments with different heating periods (15 s, 30 s, and 120 s), described in “Section 3.1, Holding Time”, the majority of the $\text{SrNiZnFe}_{16}\text{O}_{27}$ is formed within 15 s. The predominant growth in apparent crystallite size takes place after the phase formation. In other words, it appears that the formation of $\text{SrNiZnFe}_{16}\text{O}_{27}$ is decoupled from the crystal growth and that it should be possible to obtain small crystallites of the W-type hexaferrite. However, this window of opportunity is small as short time spans, high temperatures (~1200 °C) and the correct chemical composition is needed to produce phase pure samples. The highest refined weight% of W-hexaferrite is observed for the $x = 1.8$ ratio, along with the largest refined crystallite thickness. The refined weight fractions are tabulated in Table 1 together with the magnetic data. The ratio 1.8 achieves a phase purity of 81.6(4) wt% of W-type hexaferrite. From the refined lattice parameters of $\text{SrFe}_{12}\text{O}_{19}$ there is no indication of a considerable difference in temperature between the three experiments varying the ratio between M-type and spinel. The relative short

dimensions along the c -axis suggest that it is possible to form W-type hexaferrite with small crystallites potentially within the range necessary for having nonzero coercivity.

3.3. Magnetic Data

This paper focuses on the saturation magnetization (M_s) and coercivity (H_c). The saturation magnetization is a simple arithmetic sum of the mass phase fraction multiplied by the mass saturation magnetization of the individual phases: $M_{s,tot} = \sum m_{phase} \times M_{s,phase}$. The M-type hexaferrite $SrFe_{12}O_{19}$ has a saturation magnetization of $M_{s,MHF} = 74 \text{ Am}^2/\text{kg}$, while the spinel phase $Zn_{0.5}Ni_{0.5}Fe_2O_4$ has $M_{s,spl} = 62 \text{ Am}^2/\text{kg}$ [27] and $SrZnNiFe_{16}O_{27}$ has been reported to have $M_{s,WHF} = 80 \text{ Am}^2/\text{kg}$ [13]. For the 0 s and 15 s experiments, the expected $M_{s,tot}$ would be 72 and $76 \text{ Am}^2/\text{kg}$, respectively, which align well with the values obtained from the magnetization data and the law of approach (tabulated in Table 1).

Coercivity, however, is not a simple arithmetic sum. It depends on crystallite size, and, in multiphase systems, it is influenced by exchange-coupling between the individual phases. If the phases are uncoupled, the hysteresis loop exhibits discontinuous behavior, reflecting when an applied field is sufficient to rotate the magnetization in the individual phases. In exchange-coupled samples, the phases interact, resulting in smooth magnetization data in the second quadrant.

The M-type hexaferrite, when sufficiently small, has a coercivity in the range of 200–500 kA/m, while the spinel phase ($Zn_{0.5}Ni_{0.5}Fe_2O_4$) is soft ($H_c \sim 0 \text{ kA/m}$). The coercivity of $SrZnNiFe_{16}O_{27}$ is unknown; Knudsen et al. reported a value of 2 kA/m [13], but this was for a very large-grained sample.

Holding time: Following the in situ experiments, magnetization data were measured on the sintered samples. Figure 5 shows the 1st and 2nd quadrants illustrating the high saturation magnetization in all cases. All samples appear to have smooth hysteresis curves, suggesting that the three magnetic phases, W-type ($SrZnNiFe_{16}O_{27}$), M-type ($SrFe_{12}O_{19}$) and spinel ($Zn_{0.5}Ni_{0.5}Fe_2O_4$), are perfectly exchange-coupled. The samples have no appreciable coercivity, except the 0 s experiment. The 0 s, 15 s and 60 s holding times have comparable growth of the c -axis of the W-type phase, but with different phase fractions of $SrFe_{12}O_{19}$ 45, 12 and 17 wt%, respectively, and resulting coercivities of 117, 30 and 19 kA/m, which can be attributed to either $SrFe_{12}O_{19}$ or $SrZnNiFe_{16}O_{27}$, as spinel is a soft magnet. The 30 s and 120 s have <1% $SrFe_{12}O_{19}$, but around 30 wt% spinel. with coercivities dropping below 6 kA/m. This is either due to multi-domains in the $SrZnNiFe_{16}O_{27}$ and/or exchange-coupling with the soft spinel phase reducing the coercivity.

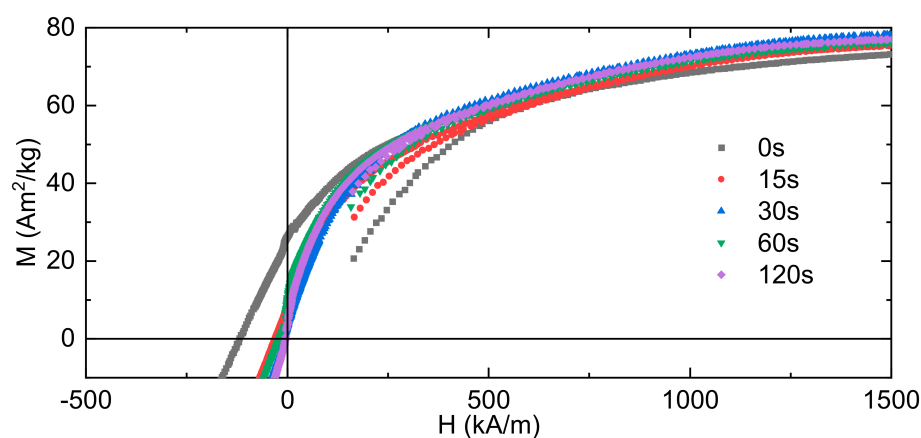


Figure 5. Hysteresis of the five samples of $SrNiZnFe_{16}O_{27}$ with different holding times.

In Table 1 the magnetic properties extracted from the magnetization data are presented. All samples except $t = 0 \text{ s}$ have a saturation magnetization exceeding $75 \text{ Am}^2/\text{kg}$, i.e., the

produced W-type hexaferrite phase has the potential to obtain a larger BH_{MAX} compared with conventional M-type hexaferrites such as the theoretical $BH_{MAX} = M_s^2/4\mu_0$, where μ_0 is the permeability of free space ($4\pi \times 10^{-7}$ H/m). However, the vanishing coercivity is inhibitive for making the W-type hexaferrites into permanent magnets; to be able to fulfill the theoretical BH_{MAX} the coercivity should be $H_c > M_s/2$.

Ratio between M-type and spinel: Magnetization data were also measured for samples made from the three different precursor compositions and the 1st and 2nd quadrant is shown in Figure 6. In all three cases the coercivity is vanishing, but a high saturation magnetization is observed. The extracted magnetic properties and the refined weight fractions from Rietveld refinements are collected in Table 1.

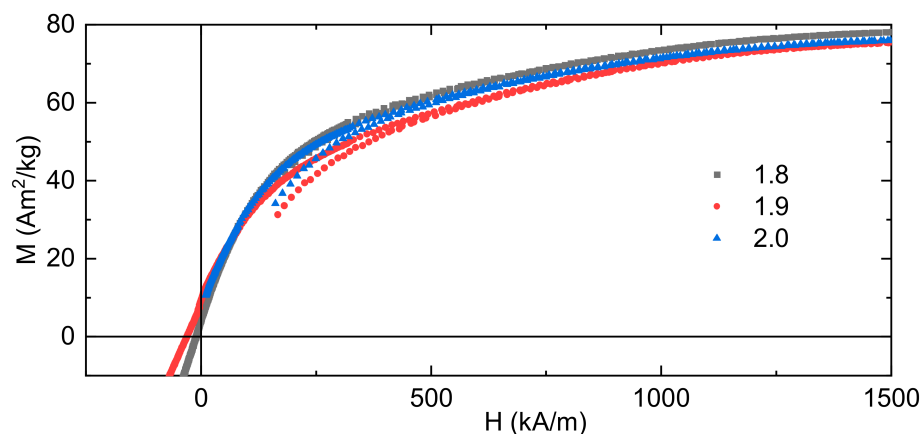


Figure 6. Hysteresis of the three different precursor compositions for $\text{SrNiZnFe}_{16}\text{O}_{27}$.

From the magnetic data it is evident that the sample from precursor ratio 1.8 has the highest phase fraction of $\text{SrNiZnFe}_{16}\text{O}_{27}$ and shows the highest saturation magnetization, which approaches the result by Knudsen et al., where a 90 wt% of W-type hexaferrite $\text{SrNiZnFe}_{16}\text{O}_{27}$ was obtained with a $M_s \sim 80 \text{ Am}^2/\text{kg}$ [13]. It is possible to calculate an expected value for the M_s of $\text{SrNiZnFe}_{16}\text{O}_{27}$ phase based on the weight fraction of WHF, MHF and SPL in Table 1 and the $M_{s,\text{MHF}} = 74 \text{ Am}^2/\text{kg}$ and $M_{s,\text{spl}} = 62 \text{ Am}^2/\text{kg}$ using all the extracted values in Table 1; the expected $M_{s,\text{WHF}}$ becomes $83(3) \text{ Am}^2/\text{kg}$, in good agreement with the values reported by Knudsen et al. [13].

3.4. Discussion

The smooth hysteresis curves of all the samples suggest that all three magnetic phases, M/W-type hexaferrite and spinel, are exchange-coupled, i.e., acting as a single phase. Due to the elevated temperature and the known abnormal grain growth of hexaferrites at around 1260°C , the vanishing coercivity is not an effect of superparamagnetism [28]. A study on M-type hexaferrite has also revealed that crystallites as small as 3.5 nm thick and 48 nm wide had a coercivity of 68 kA/m [29]. The vanishing coercivity can therefore most likely be attributed to three effects:

- (1) W-type hexaferrites have intrinsically vanishing coercivity, due to a low magnetocrystalline anisotropy constant. Based on the present experiments it is difficult to reach that conclusion, because the samples are not phase pure and size effects cannot be excluded. Theoretical calculations and experiments with single crystals suggest that the W-type hexaferrite ($\text{SrFe}_{18}\text{O}_{27}$) should have similar magnetocrystalline anisotropy to M-type hexaferrites ($\text{SrFe}_{12}\text{O}_{19}$) [14–16]. Therefore, it should be possible to obtain samples with coercivity. Furthermore, $\text{BaNi}_2\text{Fe}_{16}\text{O}_{27}$ and $\text{BaZnFe}_{17}\text{O}_{27}$ still had a lower although significant magnetocrystalline anisotropy constant [30].

- (2) The abnormal crystal growth has caused the crystalline grains of the M- and W-type to become very large and thereby effectively introducing multiple magnetic domains, which easily switch upon an applied external field. This is arguably the case for $t = 30$ s and 120 s, where excessive temperature and time causes the crystallites to grow out of resolution of the diffraction experiment. It should also be noted that $t = 30$ s and 120 s have vanishing content of M-type hexaferrite $< 1\%$, but relatively large content of the spinel phase around 30 wt%. In all cases, the peak width is outside the resolution of the diffraction experiment and the upper bound of stable single-domain crystallites is generally outside the resolution limit of diffraction experiments.
- (3) Based on the weight fraction and crystallite sizes extracted from the diffraction data $t = 15$ s and 60 s it is difficult to conclude whether the W-type structure $\text{SrZnNiFe}_{16}\text{O}_{27}$ has intrinsically vanishing coercivity or the low coercivity is an effect of exchange-coupling between the hard and the soft phases. It was recently experimentally and theoretically reported that exchange-spring magnets can be dominated by the behavior of the soft magnetic phase, i.e., the soft spinel phase dominates and short circuits the W-type hexaferrite, causing the vanishing coercivity [31,32].

More investigations are necessary, preferably with phase pure samples of W-type hexaferrite. Recent papers have reported that phase purity is highly dependent on the oxygen content in the sintering atmosphere [33–37]. Unfortunately, the graphite filament of the ARQS furnace cannot allow oxygen in the reaction chamber as this would cause the carbon filament to burn. Therefore, it is not possible with the present setup to make an in situ test with different oxygen atmospheres.

4. Conclusions

The formation of W-type hexaferrites was successfully studied in situ for the first time. The phase transformation took place over a time span of approximately 15 s at a temperature > 1200 °C. From the in situ diffraction data it is clear that the phase transformation and crystal growth are decoupled. The crystal growth takes place after the phase transformation has occurred which strongly suggests the possibility of obtaining nanocrystalline W-type hexaferrites. In conclusion it is possible to grow small sized W-type hexaferrite. The produced samples with >70 wt% W-type hexaferrite in the in situ experiment all showed saturation magnetization $> 75 \text{ Am}^2/\text{kg}$; however, all had vanishing coercivity $< 35 \text{ kA/m}$. Based on the results it was possible to extract a saturation magnetization value for W-type hexaferrite $\text{SrNiZnFe}_{16}\text{O}_{27}$ corresponding to $83(3) \text{ Am}^2/\text{kg}$. The lack of coercivity can be attributed to three different features: (1) low magnetocrystalline anisotropy constant for $\text{SrZnNiFe}_{16}\text{O}_{27}$ (W-type hexaferrite), (2) crystallite sizes producing multi-domain grains, (3) exchange-coupling with soft spinel phase. Based on theoretical calculations of the magnetocrystalline anisotropy and exchange-coupling between hard–soft magnetic phases, the most likely scenario for the low coercivity can be attributed to exchange-coupling between the W-type hexaferrite and the soft spinel phase. However, with the present data we cannot rule out crystallite size effects causing multi-domain magnetic structures.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst16080511/s1>, Figure S1: Crystal structures of M-Type (MHF) and W-Type (WHF) hexaferrites along with Wyckoff sites; Figure S2: Measured thermocouple temperature for the five different holding times; Figure S3: Power draw of the filament during the five different holding time experiments; Figure S4: Lattice parameter for the spinel phase (solid symbols) vs. time, and the set temperature (shown in black and white line, only 120 s experiment plotted for clarity) vs. time; Figure S5: Zoom on the refined lattice parameters for the five different holding

times at two different parts of the experiment; Figure S6: R_{wp} vs. time for the different holding times; Figure S7: Scale factor vs. time for the five different time experiments; Figure S8: R_{wp} vs. time for the three different precursor compositions; Table S1: Calculated offset temperature for the five different experiments, $a_{mm:ss}$ is the unit cell parameters and $\Delta T_{mm:ss}$ is the offset at the given temperature and time between the calculated temperature ($T_{Cal,mm:ss}$)—the measured temperature ($T_{M,mm:ss}$).

Author Contributions: Conceptualization, M.M., P.S. and M.C.; methodology, M.C.; formal analysis, M.M.; investigation, M.M., A.P.L., P.S. and M.C.; data curation, M.M., A.P.L., J.T.-H. and P.S.; writing—original draft, M.M. and M.C.; writing—review and editing, M.M., A.P.L., J.T.-H., P.S. and M.C.; visualization, M.M. and A.P.L.; supervision, M.C.; project administration, M.C.; funding acquisition, M.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Independent Research Fund Denmark—Green Transitions COMPASS (1127-00235B). We thank the Danish Agency for Science, Technology, and Innovation for funding the instrument center DanScatt (7129-00006B) supporting access to beamtime.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: Parts of this research were carried out at PETRA-III at DESY, a member of the Helmholtz Association (HGF). We would like to thank Henrik Jeppesen for assistance during the beamtime at beamline P02.1. Tommy Ole Kessler & Jeppe Dalgaard Mikkelsen are gratefully acknowledged for the design and engineering of the ARQS sample environment. Affiliation with the ESS lighthouses SMART and Q-MAT as well as the Center for Integrated Materials Research (iMAT) at Aarhus University is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Shyam, P.; Gjørup, F.H.; Mørch, M.I.; Laursen, A.P.; Eikeland, A.Z.; Kantor, I.; Jørgensen, M.R.V.; Christensen, M. Sintering in seconds, elucidated by millisecond in situ diffraction. *Appl. Mater. Today* **2023**, *35*, 101960. [CrossRef]
- Wang, C.; Ping, W.; Bai, Q.; Cui, H.; Hensleigh, R.; Wang, R.; Brozena, A.H.; Xu, Z.; Dai, J.; Pei, Y. A general method to synthesize and sinter bulk ceramics in seconds. *Science* **2020**, *368*, 521–526. [CrossRef] [PubMed]
- Luo, Y. Current Status and Future Development of the Magnetic Materials Industry in China. In *Handbook of Magnetism and Advanced Magnetic Materials*; John Wiley and Sons: Hoboken, NJ, USA, 2007. [CrossRef]
- Waki, T.S.; Okazaki, Y.; Tabata, M.; Kato, K.; Hirota, H.; Nakamura, H. Effect of oxygen potential on Co solubility limit in La–Co co-substituted magnetoplumbite-type strontium ferrite. *Mater. Res. Bull.* **2018**, *104*, 87–91. [CrossRef]
- Waki, T.; Nakai, S.; Tabata, Y.; Nakamura, H. Role of oxygen potential in dopant solubility in ferrite magnets: Enhanced Zn solubility and magnetization in La–Zn co-substituted magnetoplumbite-type strontium ferrite. *Mater. Res. Bull.* **2023**, *168*, 112470. [CrossRef]
- Morch, M.I.; Christensen, M. Controlling the magnetic structure in W-type hexaferrites. *J. Appl. Crystallogr.* **2023**, *56*, 597–602. [CrossRef] [PubMed]
- Gorter, E.W. Magnetization in ferrites; saturation magnetization of ferrites with spinal structure. *Nature* **1950**, *165*, 798. [CrossRef] [PubMed]
- Gorter, E.W. Saturation magnetization and crystal chemistry of ferrimagnetic oxides. *Philips Res. Rep.* **1954**, *9*, 295–320.
- Mukherjee, S.; Pradip, S.; Mishra, A.K.; Das, D. Zn substituted NiFe₂O₄ with very high saturation magnetization and negligible dielectric loss synthesized via a soft chemical route. *Appl. Phys. A* **2014**, *116*, 389–393.
- Ram, S.; Joubert, J.C. Synthesis and magnetic properties of SrZn₂-W type hexagonal ferrites using a partial 2Zn²⁺ → Li+Fe³⁺ substitution: A new series of permanent magnets materials. *J. Magn. Magn. Mater.* **1991**, *99*, 133–144. [CrossRef]
- You, J.-H.; Yoo, S.-I. Improved magnetic properties of Zn-substituted strontium W-type hexaferrites. *J. Alloys Compd.* **2018**, *763*, 459–465. [CrossRef]
- Toyota, S.J. Synthesis and Magnetic Properties of SrO 2FeO 8Fe₂O₃ W-type Hexagonal Ferrite. *Jpn. Soc. Powder Powder Metall.* **1997**, *44*, 17–21. [CrossRef]
- Knudsen, C.G.; Mørch, M.I.; Christensen, M. Texture formation in W-type hexaferrite by cold compaction of nonmagnetic interacting anisotropic shaped precursor crystallites. *Dalton Trans.* **2023**, *52*, 281–289. [CrossRef] [PubMed]
- Lotgering, F.; Locher, P.; Van Staplele, R.J. Anisotropy of hexagonal ferrites with M, W and Y structures containing Fe³⁺ and Fe²⁺ as magnetic ions. *Phys. Chem. Solids* **1980**, *41*, 481–487. [CrossRef]

15. Ueda, H.; Shakudo, H.; Santo, H.; Fujii, Y.; Michioka, C.; Yoshimura, K.J. Magnetocrystalline anisotropy of single crystals of M-, X-, and W-type strontium hexaferrites. *J. Phys. Soc. Jpn.* **2018**, *87*, 104706. [\[CrossRef\]](#)
16. Islam, R.; Madsen, S.P.; Christensen, M. Exploring the magnetic properties of W-type SrFe₁₈O₂₇ hexaferrite: Insights from a first-principles study. *Phys. Rev. B* **2024**, *109*, 024414.
17. Langhof, N.; Seifert, D.; Göbbels, M.; Töpfer, J.J. Reinvestigation of the Fe-rich part of the pseudo-binary system SrO–Fe₂O₃. *J. Solid State Chem.* **2009**, *182*, 2409–2416. [\[CrossRef\]](#)
18. Töpfer, J.; Schwarzer, S.; Senz, S.; Hesse, D.J. Influence of SiO₂ and CaO additions on the microstructure and magnetic properties of sintered Sr-hexaferrite. *J. Eur. Ceram. Soc.* **2005**, *25*, 1681–1688. [\[CrossRef\]](#)
19. Beseničar, S.; Drofenik, M.J. High coercivity Sr hexaferrites. *J. Magn. Magn. Mater.* **1991**, *101*, 307–309. [\[CrossRef\]](#)
20. Gjørup, F.H.; Saura-Múzquiz, M.; Ahlburg, J.V.; Andersen, H.L.; Christensen, M. Coercivity enhancement of strontium hexaferrite nano-crystallites through morphology controlled annealing. *Materialia* **2018**, *4*, 203–210. [\[CrossRef\]](#)
21. Mørch, M.I.; Ahlburg, J.V.; Saura-Múzquiz, M.; Eikeland, A.Z.; Christensen, M. Structure and magnetic properties of W-type hexaferrites. *IUCr* **2019**, *6*, 492–499. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Jensen, A.B.; Christensen, T.E.K.; Weninger, C.; Birkedal, H. Very large-scale diffraction investigations enabled by a matrix-multiplication facilitated radial and azimuthal integration algorithm: MatFRAIA. *J. Synchrotron Radiat.* **2022**, *29*, 1420–1428. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Coelho, A.A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++. *J. Appl. Crystallogr.* **2018**, *51*, 210–218. [\[CrossRef\]](#)
24. West, A.R. *Solid State Chemistry and Its Applications*; Wiley: Hoboken, NJ, USA, 2014.
25. Utsuno, S.; Sato, T.; Kaneko, Y.J. Synthesis of Anisotropic W-type Ferrite from M-type Ferrite and Spinel Ferrite Compounds. *Jpn. Soc. Powder Powder Metall.* **2015**, *62*, 575–579. [\[CrossRef\]](#)
26. Kaneko, Y.; Utsuno, S. Ferrite Particle and Production Methods Thereof. US20090246526, 11 August 2015.
27. Hölscher, J.; Andersen, H.L.; Saura-Múzquiz, M.; Garbus, P.G.; Christensen, M. Correlation between microstructure, cation distribution and magnetism in Ni_{1–x}Zn_xFe₂O₄ nanocrystallites. *CrystEngComm* **2020**, *22*, 515–524. [\[CrossRef\]](#)
28. Yoon, H.-H.; Kim, D.-Y. Effect of heating rate on the exaggerated grain growth during the sintering of Sr-hexaferrite. *Mater. Lett.* **1994**, *20*, 293–297. [\[CrossRef\]](#)
29. Saura-Múzquiz, M.; Granados-Miralles, C.; Andersen, H.L.; Stingaciu, M.; Avdeev, M.; Christensen, M. Nanoengineered high-performance hexaferrite magnets by morphology-induced alignment of tailored nanoplatelets. *ACS Appl. Nano Mater.* **2018**, *1*, 6938–6949. [\[CrossRef\]](#)
30. Chikazumi, S. *Physics of Ferromagnetism (The International Series of Monographs on Physics)*, 2nd ed.; Oxford University Press: New York, NY, USA, 2009.
31. Shyam, P.; Mørch, M.; Eikeland, A.Z.; Ahlburg, J.; Mamakhel, A.; Saura-Múzquiz, M.; Christensen, M. Combined characterization approaches to investigate magnetostructural effects in exchange-spring ferrite nanocomposite magnets. *Mater. Chem. Front.* **2022**, *6*, 2422–2437. [\[CrossRef\]](#)
32. Traistaru, O.; Shyam, P.; Christensen, M.; Madsen, S. Optimizing the energy product of exchange-coupled soft/hard Zn_{0.2}Fe_{2.8}O₄/SrFe₁₂O₁₉ magnets. *J. Appl. Phys.* **2022**, *132*, 163904. [\[CrossRef\]](#)
33. Obara, G.; Shiramizu, Y.; Tomita, H.; Yamazaki, Y. Influence of Oxygen Concentration during Semi-sintering on Crystalline Phase of Sr-Fe₂W-type Ferrites. *Funtai Oyobi Fummatsu Yakin/J. Jpn. Soc. Powder Powder Metall.* **2018**, *65*, 589–594. [\[CrossRef\]](#)
34. Yonaga, A.; Nakagawa, T.; Kobayashi, Y.; Ota, K.; Seino, S.; Yamamoto, T.A. Study on Formation Conditions and Magnetic Properties of the SrZn_xFe_{2–x}W-type Hexagonal Ferrites. *J. Jpn. Soc. Powder Powder Metall.* **2017**, *64*, 185–194. [\[CrossRef\]](#)
35. You, J.-H.; Kim, H.-J.; Lee, J.-W.; Yoo, S.-I. Phase stability of SrZn_xFe_(2–x)Fe₁₆O₂₇ (0.0 ≤ x ≤ 1.0) in low oxygen pressures. *Mater. Sci. Eng. B* **2022**, *277*, 115563. [\[CrossRef\]](#)
36. Nakai, S.; Waki, T.; Tabata, Y.; Kato, M.; Ohta, H.; Nakamura, H. Study on Factors Hindering the Single-Phase Formation of Divalent-Ion-Stabilized W-Type Ferrites. *Mater. Trans.* **2023**, *64*, 1072–1077. [\[CrossRef\]](#)
37. Nakai, S.; Waki, T.; Tabata, Y.; Nakamura, H. Low oxygen potential synthesis of W-type strontium ferrite SrFe₁₈O₂₇ in a closed atmosphere. *J. Ceram. Soc. Jpn.* **2025**, *133*, 235–241. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.