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# In Situ and Ex Situ X-ray Diffraction and Small-Angle X-ray Scattering Investigations of the Sol–Gel Synthesis of Fe<sub>3</sub>N and Fe<sub>3</sub>C

Matthew S. Chambers,\* Robert D. Hunter, Martin J. Hollamby, Brian R. Pauw, Andrew J. Smith, Tim Snow, Ashleigh E. Danks, and Zoe Schnepf\*



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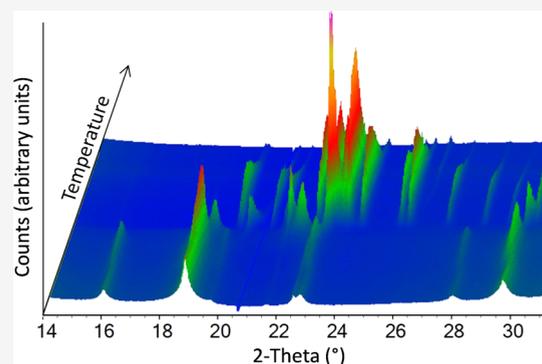


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Supporting Information

**ABSTRACT:** Iron nitride (Fe<sub>3</sub>N) and iron carbide (Fe<sub>3</sub>C) nanoparticles can be prepared via sol–gel synthesis. While sol–gel methods are simple, it can be difficult to control the crystalline composition, *i.e.*, to achieve a Rietveld-pure product. In a previous *in situ* synchrotron study of the sol–gel synthesis of Fe<sub>3</sub>N/Fe<sub>3</sub>C, we showed that the reaction proceeds as follows: Fe<sub>3</sub>O<sub>4</sub> → FeO<sub>x</sub> → Fe<sub>3</sub>N → Fe<sub>3</sub>C. There was considerable overlap between the different phases, but we were unable to ascertain whether this was due to the experimental setup (side-on heating of a quartz capillary which could lead to thermal gradients) or whether individual particle reactions proceed at different rates. In this paper, we use *in situ* wide- and small-angle X-ray scattering (wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS)) to demonstrate that the overlapping phases are indeed due to variable reaction rates. While the initial oxide nanoparticles have a small range of diameters, the size range expands considerably and very rapidly during the oxide–nitride transition. This has implications for the isolation of Rietveld-pure Fe<sub>3</sub>N, and in an extensive laboratory study, we were indeed unable to isolate phase-pure Fe<sub>3</sub>N. However, we made the surprising discovery that Rietveld-pure Fe<sub>3</sub>C nanoparticles can be produced at 500 °C with a sufficient furnace dwell time. This is considerably lower than the previous reports of the sol–gel synthesis of Fe<sub>3</sub>C nanoparticles.



## 1. INTRODUCTION

Interstitial iron compounds  $\theta$ -Fe<sub>3</sub>C and  $\epsilon$ -Fe<sub>3</sub>N (Figure 1a,b) have recently gained attention due to their potential applications as nanoparticle catalysts in the oxygen reduction reaction,<sup>1</sup> the Fischer–Tropsch process,<sup>2,3</sup> and ammonia decomposition.<sup>4</sup> They are particularly appealing due to their potential to replace precious metals such as Pt in these processes.<sup>5,6</sup> Furthermore, Fe<sub>3</sub>C and Fe<sub>3</sub>N nanoparticles possess interesting magnetic properties and could be used in biomedical applications.<sup>7–9</sup> There are various synthetic routes to produce Fe<sub>3</sub>N and Fe<sub>3</sub>C nanoparticles, including laser ablation,<sup>10</sup> ammonolysis,<sup>11</sup> solvothermal synthesis,<sup>8,12</sup> nanocasting,<sup>13</sup> and sol–gel synthesis.<sup>14–16</sup> Sol–gel chemistry is particularly promising due to its simplicity both in reactants and technical implementation. Sol–gel synthesis uses gel or gel-like mixtures of metal and organic species as precursors for ceramic materials.<sup>17</sup> Heating the gel leads to nucleation and growth of ceramic material (*e.g.*, metal oxides, nitrides, and carbides). For example, Fe<sub>3</sub>C can be produced by heating a mixture of Fe(NO<sub>3</sub>)<sub>3</sub> and gelatin to 700 °C in nitrogen.

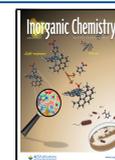
To understand how Fe<sub>3</sub>C is formed in sol–gel synthesis, we previously reported an *in situ* synchrotron X-ray powder diffraction study.<sup>16</sup> The data showed that thermal decomposition of Fe(NO<sub>3</sub>)<sub>3</sub>/gelatin proceeds through several intermediates, including Fe<sub>3</sub>O<sub>4</sub> and FeO<sub>x</sub> (Figure 1c,d). The

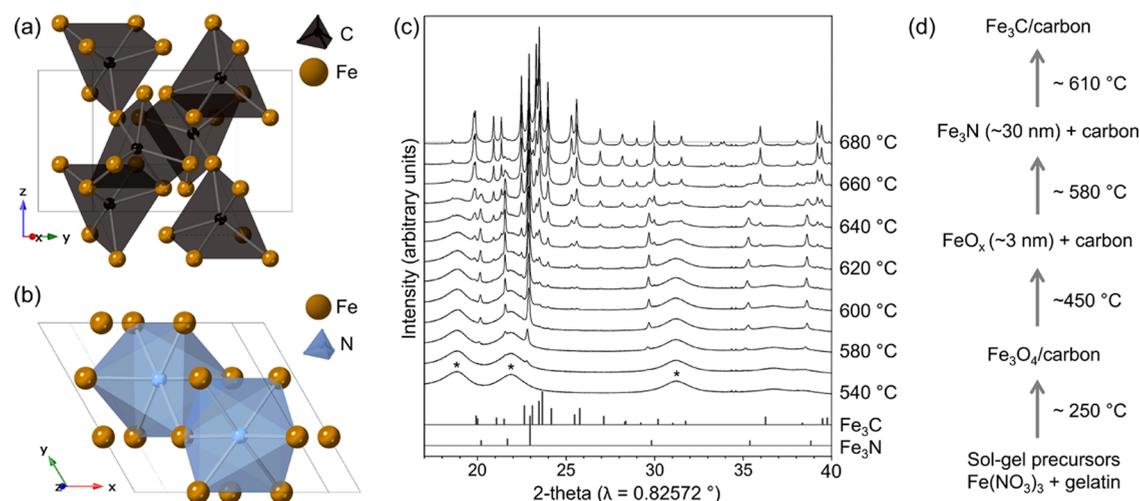
iron oxide peaks were very broad, indicating small crystallite sizes (mean diameter estimated as 3 nm by Scherrer equation). The broad iron oxide peaks were gradually replaced with sharp Fe<sub>3</sub>N peaks from 560 °C and Fe<sub>3</sub>C peaks from 610 °C. This indicated that the nitride and carbide phases comprised much larger crystalline domains (estimated 30 and 60 nm diameters, respectively). Peak shifts suggested that the Fe<sub>3</sub>N to Fe<sub>3</sub>C phase transition was caused by carbon diffusion via a carbonitride intermediate.

Recently, we reported a further *in situ* synchrotron investigation of the Fe(NO<sub>3</sub>)<sub>3</sub> system using total scattering.<sup>18</sup> This revealed that there is a dramatic increase in order within the iron oxide nanoparticles between 300 and 350 °C. This was indicated by a transition from no correlations in the pair distribution function (PDF) at  $r > 6$  Å at the lower temperature to correlations up to 40 Å at 350 °C. This could result either from sintering of very small crystallites or a fast crystallization of amorphous FeO<sub>x</sub> clusters. Additionally,

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**Figure 1.** Crystal structures of (a)  $\theta$ - $\text{Fe}_3\text{C}$  and (b)  $\varepsilon$ - $\text{Fe}_3\text{N}$ .<sup>18</sup> (c) *In situ* synchrotron X-ray diffraction data showing part of the mechanism of formation of  $\text{Fe}_3\text{C}$  from a gelatin/iron nitrate precursor<sup>16</sup> and (d) schematic showing the approximate onset of each phase transition. Peaks marked with \* correspond to  $\text{FeO}_x$  (Wüstite). Images modified with permission.

small-box PDF refinements revealed the presence of locally distorted  $\text{NFe}_6$  octahedra within  $\text{Fe}_3\text{N}$ , with a twist angle<sup>19,20</sup> of  $\varphi = 49.51(1)^\circ$ ; more trigonal prismatic in nature than the high-symmetry, long-range twist angle of  $\varphi = 57.96^\circ$ . As  $\text{Fe}_3\text{C}$  contains  $\text{CFe}_6$  trigonal prisms, this is potentially further evidence that carbon is doped into the  $\text{Fe}_3\text{N}$  lattice, replacing N atoms.

The previous experiments offered many insights into the sol–gel synthesis of  $\text{Fe}_3\text{C}$ , but several questions remain. The first is how the particle size evolves over the whole reaction. Analysis of powder diffraction data using the Scherrer equation was used to give an estimate of the mean particle size for each phase but could give no information on particle size distribution. Furthermore, the *in situ* diffraction data showed significant overlap between the different phases, with  $\text{FeO}_x$ ,  $\text{Fe}_3\text{N}$ , and  $\text{Fe}_3\text{C}$  all coexisting between 610 and 660 °C. It is unclear whether this is a factor inherent to the system (*i.e.*, some crystallites are reduced more readily than others) or whether it is a feature of the *in situ* synchrotron experimental setup where a hot air blower was used to heat the sample within a quartz capillary, potentially resulting in a thermal gradient across the sample. Therefore, we have performed an *in situ* synchrotron study using a quartz capillary inside a modified tube furnace to provide a more consistent heating rate. We recorded small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) simultaneously so that particle size distribution could be coupled to the evolution of the different crystalline phases. We then report a detailed *ex situ* experimental study of this system to probe the effect of heating conditions on the stability of the various phases. These papers together give a complete and rigorous picture of the  $\text{Fe}(\text{NO}_3)_3/\text{gelatin}$  sol–gel system across multiple length scales.

## 2. EXPERIMENTAL PROCEDURE

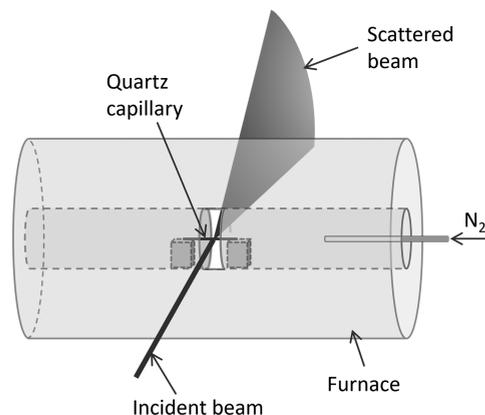
**2.1. Synthesis.** For all samples, the gelatin precursor was prepared as discussed in previous literature.<sup>16</sup> Briefly, a hot aqueous gelatin solution (10% w/w, 10 g; Sigma-Aldrich, G2500) was mixed with aqueous iron nitrate (10% w/v, 20.2 mL,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Sigma-Aldrich), forming a viscous orange gel. The gel was dried in air at 70 °C to form a brittle orange-brown foam. For the samples studied with powder diffraction *ex situ*, the brittle foam samples were ground with a mortar and pestle and were heated under  $\text{N}_2$  atmosphere with a

heating rate of 5, 7.5, or 10 °C<sup>-1</sup> to various final temperatures and with various dwell times, which are discussed below. For SAXS–WAXS experiments, the orange foam was preheated at 250 °C under nitrogen in a muffle furnace to remove water and avoid expansion of the sample within the capillary during the experiment.

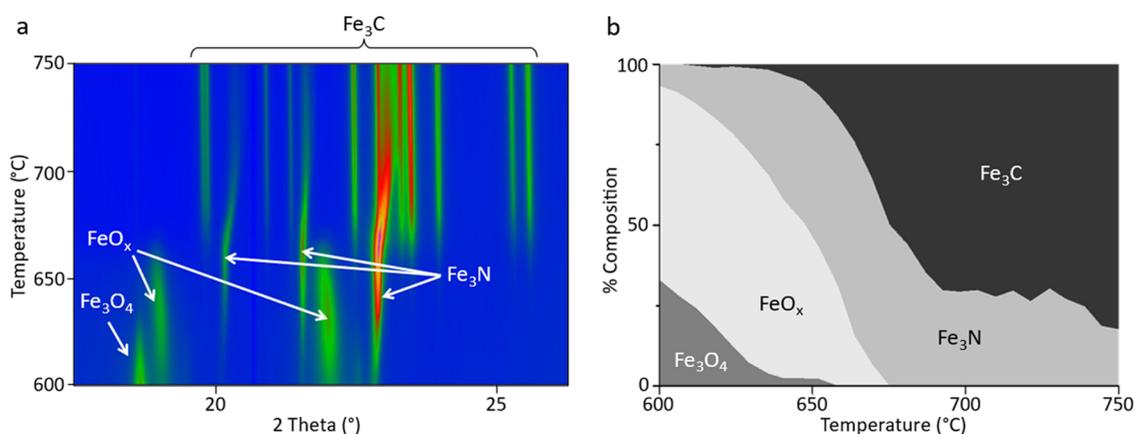
**2.2. Ex Situ Powder Diffraction.** *Ex situ* powder diffraction was performed on a Bruker D2 PHASER using an approximate 2:1 mixture of  $\text{Co K}\alpha_1$  ( $\lambda = 1.7899$  Å) and  $\text{K}\alpha_2$  ( $\lambda = 1.7929$  Å) radiation, Ni filter, and LYNXEYE detector. Samples were mounted on Si zero-background slides and scanned over a range of  $10^\circ \leq 2\theta \leq 80^\circ$ .

**2.3. SAXS–WAXS.** For SAXS/WAXS experiments, a preheated gelatin/ $\text{Fe}(\text{NO}_3)_3$  sample was ground to powder and loaded into a quartz capillary (0.7 mm diameter, 0.02 mm wall thickness) and packed on either side with quartz wool to prevent the movement of the powder during heating. Measurements were performed on the I22 beamline at Diamond Light Source, using a beam energy of 15 keV (wavelength = 0.8266 Å), a sample to detector distance of 2.730 m, and a beam size of  $200 \mu\text{m} \times 180 \mu\text{m}$ . The scattered X-rays were detected using a Pilatus P3-2M unit from Dectris, which has a pixel size of  $172 \mu\text{m} \times 172 \mu\text{m}$ . The capillary was heated inside a modified tube furnace (Figure 2) with small slits cut in both sides for the incident and scattered beam, and nitrogen gas was flowed around the capillary during heating. Full details on the data correction and analysis procedures can be found in the Supporting Information.

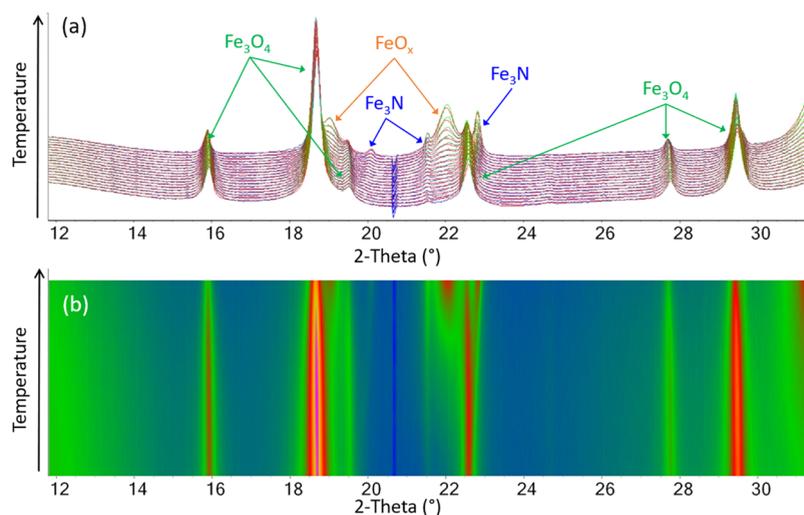
**2.4. Rietveld Refinement.** Rietveld refinements were performed using TOPAS v6.<sup>21,22</sup> Starting models for four phases were derived from the following sources:  $\text{Fe}_3\text{C}$  from Wood et al.,<sup>23</sup>  $\text{Fe}_3\text{N}$  from



**Figure 2.** Schematic of the experimental setup (not to scale).



**Figure 3.** (a) Surface plot of *in situ* synchrotron WAXS data, where the colors represent an increase in peak intensity from blue to green to pink and (b) graph of % phase composition (from Rietveld refinement) during heating of the sample.



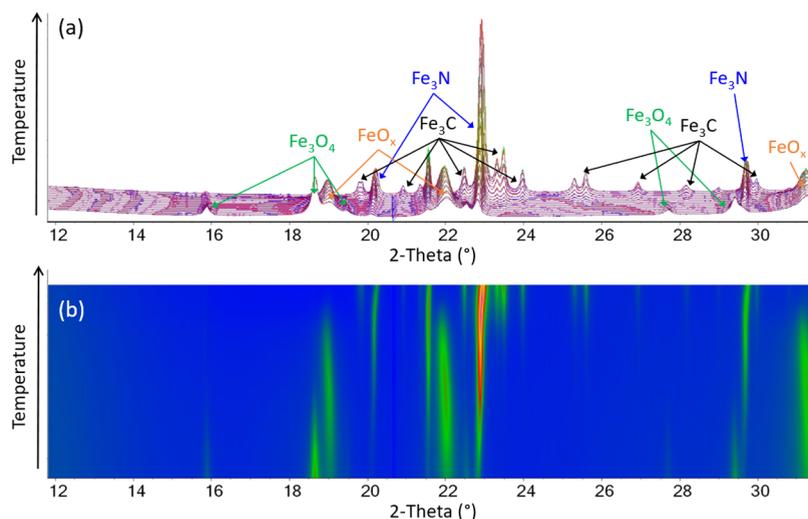
**Figure 4.** (a) Rietveld plots obtained from the WAXS data for temperatures 500–600 °C, vertically stacked along the *y*-axis, where the colors represent an increase in peak intensity from blue to green to pink and the orange line is the calculated pattern. The difference between the calculated and observed pattern is shown in Figure S1. (b) Surface plot of the same data, where the colors represent the same peak intensity increase.

Jacobs et al.,<sup>24</sup> FeO<sub>x</sub> (refined with a fixed stoichiometry of FeO) from Fjellvåg et al.,<sup>25</sup> and Fe<sub>3</sub>O<sub>4</sub> from Fleet<sup>26</sup> (refined as fixed stoichiometry Fe<sub>3</sub>O<sub>4</sub>). Backgrounds were refined as twelfth-order Chebyshev polynomials. Peak shapes were described using a Thompson-Cox-Hastings pseudo-Voigt function. Additionally, a zero-point error was refined. In the *ex situ* refinements, a strain-size line-broadening function<sup>27</sup> was included for Fe<sub>3</sub>O<sub>4</sub> at low temperatures, refining both the size and strain components, while for the WAXS refinements, two independent functions were included for FeO<sub>x</sub> and Fe<sub>3</sub>N. WAXS data were converted from *Q* to *2θ* using an in-house Python script, given that  $Q = \frac{4\pi \sin \theta}{\lambda}$ . This was done as the Thompson-Hastings-Cox peak shape is defined in units of *2θ*. To determine which phases were present in the WAXS refinements, preliminary refinements were performed with all four phases; phases found to not be present were then eliminated from certain temperature ranges and scan numbers. To study the thermal evolution of the Fe<sub>3</sub>N and Fe<sub>3</sub>C cell parameters, parametric refinements<sup>28</sup> were performed against the data in the temperature range of 675–800 °C (first scan at this temperature), where Fe<sub>3</sub>N and Fe<sub>3</sub>C are the only crystalline phases present.

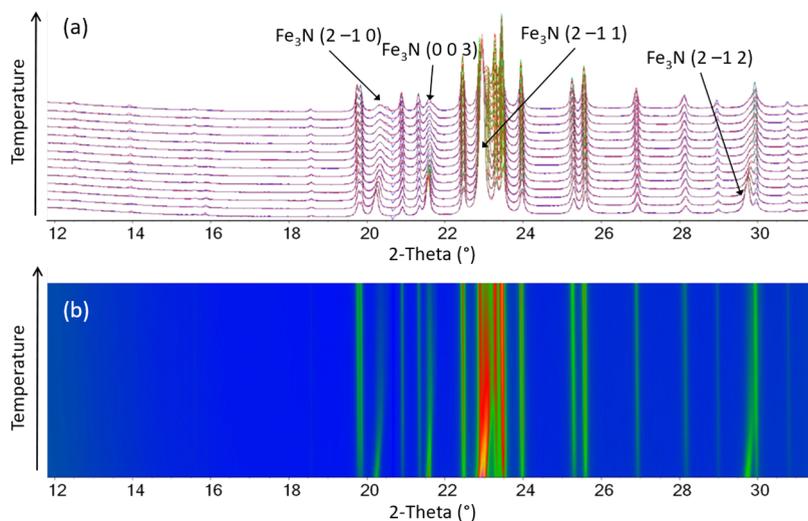
### 3. RESULTS AND DISCUSSION

**3.1. *In Situ* SAXS–WAXS Experiment.** A sample of Fe(NO<sub>3</sub>)<sub>3</sub>/gelatin was preheated to 250 °C in nitrogen and then loaded to a quartz capillary and heated under a nitrogen atmosphere in a modified tube furnace. Synchrotron WAXS and SAXS data were collected throughout, and then Rietveld refinements were performed against 200 scans (78 of which are at 800 °C), starting from the same initial models for each phase. Figure 3a shows a surface plot of the WAXS data within the 600–750 °C region, where most of the phase transformations occur and the data clearly illustrate the Fe<sub>3</sub>O<sub>4</sub>–FeO<sub>x</sub>–Fe<sub>3</sub>N–Fe<sub>3</sub>C sequence. Phase compositions (from Rietveld refinement) are shown in Figure 3b and indicate the gradual transformation of the oxide phases to nitride and then carbide. To learn more from this data, it is useful to examine different regions of the heating process in turn.

Figure 4 shows the Rietveld plots obtained for the temperatures 500–600 °C. In this range, Fe<sub>3</sub>O<sub>4</sub> is gradually reduced to FeO<sub>x</sub>. The peaks from FeO<sub>x</sub> are very broad, which could be caused by the small size of the particles and/or the highly disordered nature of FeO<sub>x</sub>.<sup>25</sup> Fe<sub>3</sub>N begins to make a minor but noticeable contribution to the patterns at ~530 °C,



**Figure 5.** (a) Rietveld plots obtained from the WAXS data for temperatures 600–675 °C, vertically stacked along the y-axis, where the colors represent an increase in peak intensity from blue to green to pink and the orange line is the calculated pattern. The difference between the calculated and observed pattern is shown in Figure S1. (b) Surface plot of the same data, where the colors represent the same peak intensity increase.



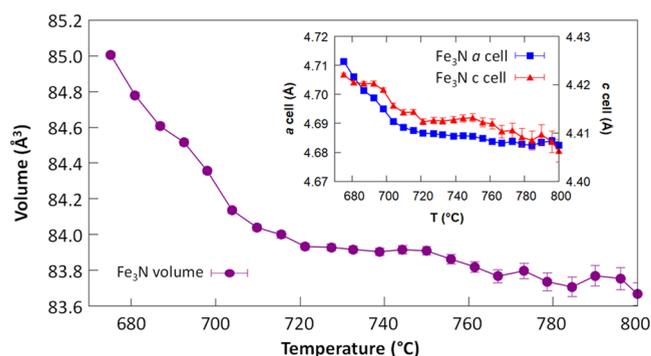
**Figure 6.** (a) Rietveld plots obtained from the WAXS data for temperatures 675–750 °C, vertically stacked along the y-axis, where the colors represent an increase in peak intensity from blue to green to pink and the orange line is the calculated pattern. The difference between the calculated and observed pattern is shown in Figure S1. (b) Surface plot of the same data, where the colors represent the same peak intensity increase.

where the (2 $\bar{1}0$ ) and (002) peaks are visible at  $2\theta \approx 19.9$  and  $21.5^\circ$ , respectively. Due to the peak broadening function used in these refinements,<sup>27</sup> it is difficult to obtain precise compositions, but throughout this entire temperature range, the iron oxides dominate the composition. The gap in the diffraction data between 20 and  $21^\circ$  is related to the detector.

Figure 5 shows the Rietveld plots obtained for the temperatures 600–675 °C. In this range, the Fe<sub>3</sub>O<sub>4</sub> is completely consumed, alongside an increase in the intensity of the FeO<sub>x</sub> peaks. Fe<sub>3</sub>N emerges alongside FeO<sub>x</sub>, and Fe<sub>3</sub>C forms toward the end of this temperature region, alongside the disappearance of the FeO<sub>x</sub> phase. By 675 °C, the only two (crystalline) phases present are Fe<sub>3</sub>N and Fe<sub>3</sub>C. The Rietveld plots for the 675–750 °C range are given in Figure 6. In a similar manner to the FeO<sub>x</sub> peaks, the Fe<sub>3</sub>N peaks first increase in intensity and sharpen with increasing temperature, indicating the growth of the particles and/or an increase in

crystallinity. However, as Fe<sub>3</sub>C emerges, the Fe<sub>3</sub>N peaks broaden significantly and then disappear. A shift to higher  $2\theta$  can be observed from 675 °C in the Fe<sub>3</sub>N peaks, which is particularly noticeable in the (2 $\bar{1}0$ ), (003), (2 $\bar{1}1$ ), and (2 $\bar{1}2$ ) peaks. This is most apparent in the surface plot shown in Figure 6b. This indicates a decrease in the cell parameters rather than the expected increase from thermal expansion. For a more quantitative analysis, parametric variable-temperature refinements were performed in the temperature range of 675–800 °C. Parametric refinements were performed as the same two phases (Fe<sub>3</sub>N and Fe<sub>3</sub>C) are present in this temperature range, and this allows more accurate cell parameters to be obtained. The results for Fe<sub>3</sub>N cell parameters are shown in Figure 7.

It is difficult to obtain accurate cell parameters in this system due to the broadening of the peaks, the overlap of Fe<sub>3</sub>C and Fe<sub>3</sub>N peaks, and the interference of the detector issue at  $2\theta =$



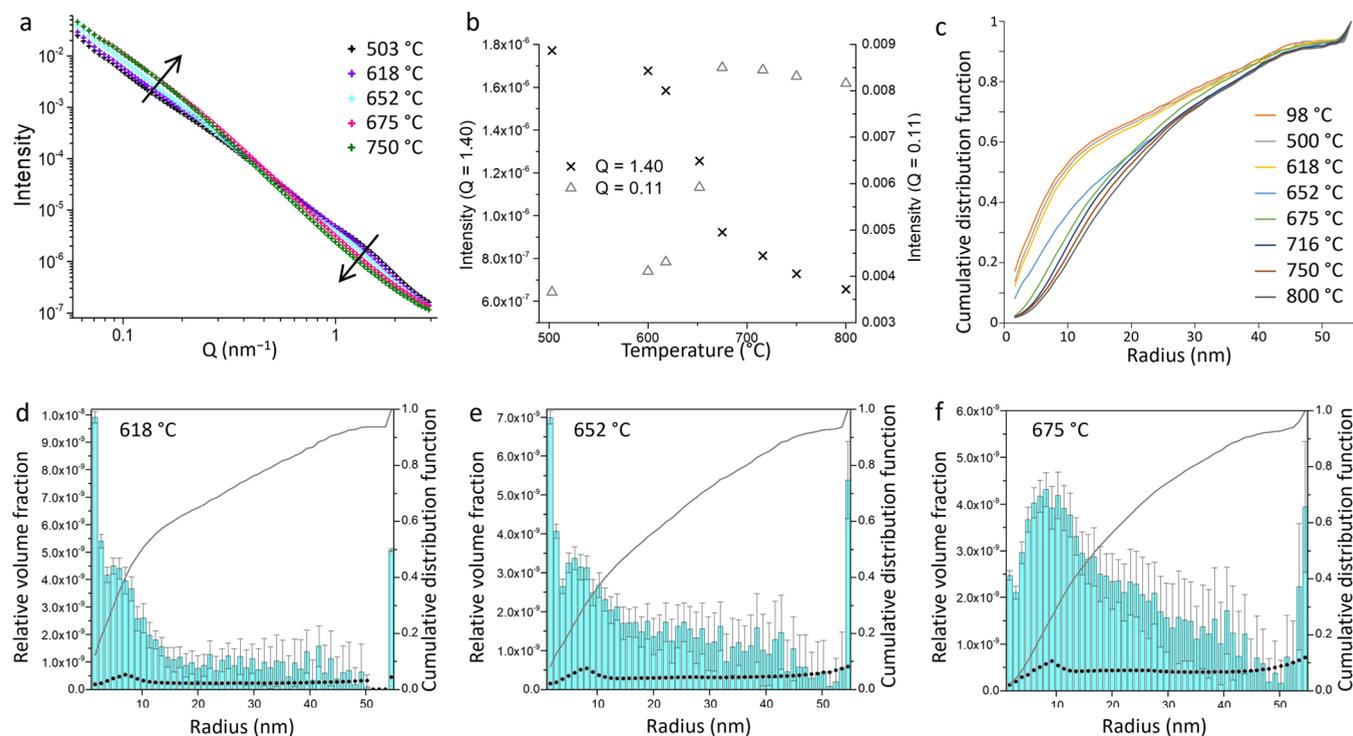
**Figure 7.** Thermal evolution of the cell parameters of  $\text{Fe}_3\text{N}$  in the temperature range of 675–800 °C.

20.7° (which affects the  $(2\bar{1}0)$  peak at the higher temperatures). However, there is a clear trend between 675 and 710 °C of the peaks shifting to a higher  $2\theta$ , which indicates a contraction of the lattice. Lattice contractions in  $\text{Fe}_3\text{N}$  can be ascribed to loss of nitrogen,<sup>29</sup> as iron nitride can be nonstoichiometric ( $\text{Fe}_x\text{N}$ ). Alternatively, the substitution of nitrogen atoms with carbon atoms in the formation of a ternary carbonitride phase has also been shown to result in a lattice contraction.<sup>30</sup> Given the excess of carbon that is present in our system, it seems more likely that this data shows the existence of an iron carbonitride intermediate. This would also fit with our previous observations of local distortions of the  $\text{Fe}_6\text{N}$  octahedra to a more trigonal pyramidal character during the  $\text{Fe}_3\text{N}$  to  $\text{Fe}_3\text{C}$  transition.<sup>18</sup>

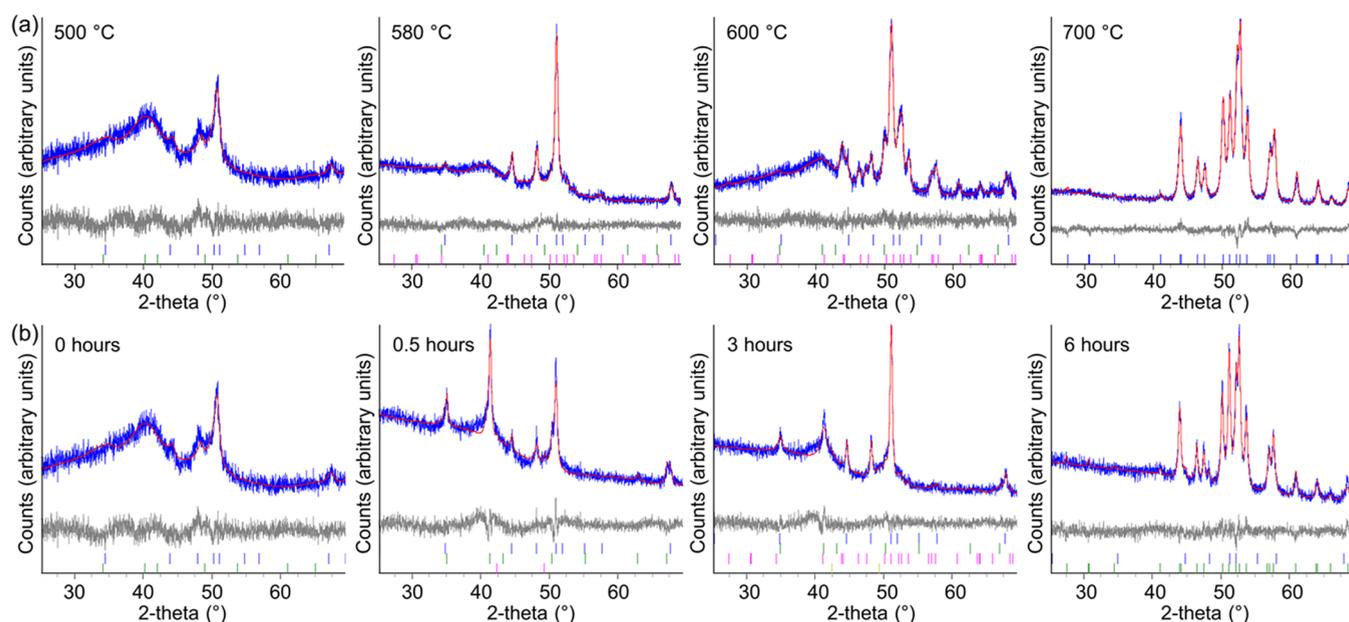
SAXS data were collected at the same time as the WAXS data to examine the evolution of the particle sizes. The SAXS

data at a selection of temperatures (chosen to cover the regions of the phase transformations) are shown in Figure 8a, and there is clearly a gradual decrease in intensity at high  $Q$  alongside an increase in intensity at low  $Q$ . The change is not large but indicates an increase in the number of larger scattering features within the sample, as the temperature increases. The shift in intensity is not uniform. This is clearly shown in plots of intensity vs temperature at  $Q = 1.40$  and  $0.11$  (Figure 8b). These plots show that the change in scattering intensity occurs over a short temperature range between ~618 and 675 °C. This is concurrent with the oxide-to-nitride transformation and is consistent with the observation of sharper Bragg diffraction peaks for the nitride phase.

The SAXS data were analyzed using the Monte Carlo method<sup>31</sup> to extract form-free size distributions. The data and corresponding fit lines for a selection of temperatures are shown in the Supporting Information (Figures S2–S10). We chose not to perform fits across all of the data sets, as this was unlikely to add any insight into the system. Radius histograms for the selected samples, scaled by relative volume fraction, are shown in Figures 8 and S11. From 98–600 °C, there is very little change in the particle size distribution, with approximately 50% of the particles having a radius <10 nm. In our previous investigation of this system using total scattering, we observed a dramatic increase in correlations >10 Å between 300 and 350 °C.<sup>18</sup> The suggested conclusion from that study was that poorly crystalline regions of iron oxide were undergoing a rapid crystallization step rather than sintering of smaller crystals. The consistency in the particle size distributions from SAXS across this temperature range adds further weight to that argument. This is because SAXS would distinguish between small and large crystallites, whereas no



**Figure 8.** Graphs of (a) SAXS data at a selection of temperatures, (b) plots of intensity vs temperature at  $Q = 1.40$  and  $Q = 0.11$ , and (c) cumulative distribution functions of particle radius for a range of temperatures. Particle size histograms derived from the SAXS data at (d) 618 °C, (e) 652 °C, and (f) 675 °C, with blue bars showing relative volume fraction, black dots showing minimum visibility limit, and gray lines showing the cumulative distribution function.



**Figure 9.** XRD data (Co  $K\alpha$ ) and Rietveld plots obtained *ex situ* from the sol–gel synthesis of  $\text{Fe}(\text{NO}_3)_3/\text{gelatin}$  system with a heat rate of  $5\text{ }^\circ\text{C min}^{-1}$  and (a) 0 h dwell time at various temperatures and (b) different dwell times at a maximum temperature of  $500\text{ }^\circ\text{C}$ . The blue curves represent the observed data; the red curves, the calculated pattern; and the gray curves, the difference between the two patterns. The tick marks represent different reference peaks, including  $\text{Fe}_3\text{O}_4$  (green),  $\text{FeO}_x$  (orange),  $\text{Fe}_3\text{N}$  (blue), and  $\text{Fe}_3\text{C}$  (pink).

change in scattering intensity would be shown for a transition between a disordered iron oxide cluster and a crystal of the same size. The particle size distributions from SAXS data show a shift to larger particles between  $618$  and  $675\text{ }^\circ\text{C}$ , which correlates with the emergence of  $\text{Fe}_3\text{N}$  peaks in the WAXS data. This is consistent with much sharper diffraction peaks for the iron nitride phase and further supports the conclusion that the iron nitride particles are larger than the iron oxide precursor particles. What is surprising is the rate at which the particle size increases. This can be seen more clearly in a plot of the cumulative distribution functions (Figure 8c), where there is a sudden jump to higher particle radii between  $618$  and  $652\text{ }^\circ\text{C}$ . This strongly indicates that the iron oxide-to-nitride transition involves mass transport of iron through the carbon matrix rather than direct nitridation of individual oxide particles, a mechanism that was proposed but not proven in our previous work.<sup>16</sup> Overall, the particle size distribution during the  $\text{Fe}_3\text{N}$  and  $\text{Fe}_3\text{C}$  evolution is much broader than is observed when the system contains only  $\text{FeO}_x$ . Given that the distributions will contain contributions from the iron oxide, nitride, and carbide phases, it is perhaps not surprising that they are broad. Smaller nanoparticles are likely to react faster, and  $\text{Fe}_3\text{C}$  nanoparticles that form early in the synthesis will have more time to sinter and grow. However, sol–gel chemistry is well known for producing particles that are relatively similar in size due to the homogeneous nature of the starting material. In this system, the rapid growth during the oxide-to-nitride transition indicates that the iron species are highly mobile, resulting in polydispersity despite a relatively narrow particle size distribution in the oxide precursor.

**3.2. Ex Situ Experimental Study.** *In situ* SAXS/WAXS data showed progressive transitions from oxide–nitride–carbide with considerable overlap between the three phases. However, since the system was heated continuously, it did not allow for the stabilization of the system at the nitride stage. To investigate whether it is possible to produce phase-pure iron

nitride in a laboratory furnace by this sol–gel method, we conducted an extensive *ex situ* experimental study. Figure 9a shows diffraction patterns of  $\text{Fe}(\text{NO}_3)_3/\text{gelatin}$  samples heated at  $5\text{ }^\circ\text{C min}^{-1}$  to various temperatures with no dwell time at the maximum temperature. Composition data from Rietveld refinement can be found in Table 1. The poor crystallinity of

**Table 1.** Weight Percentage Compositions for Samples Heated at  $5\text{ }^\circ\text{C min}^{-1}$  to Various Temperatures with 0 h Dwell Time. Errors are Shown in Brackets

	$\text{Fe}_3\text{O}_4$	$\text{Fe}_3\text{N}$	$\text{Fe}_3\text{C}$
$500\text{ }^\circ\text{C}$	60(18)	40(18)	
$560\text{ }^\circ\text{C}$	41(12)	59(12)	
$580\text{ }^\circ\text{C}$	23(7)	70(7)	7(2)
$600\text{ }^\circ\text{C}$	25(8)	16(2)	58(6)
$650\text{ }^\circ\text{C}$			100
$700\text{ }^\circ\text{C}$			100

the samples and low signal-to-noise ratio means that the composition values have large errors, but some useful trends can still be identified. At  $500\text{ }^\circ\text{C}$ , the XRD pattern is noisy and shows broad peaks for  $\text{Fe}_3\text{N}$  (40%) and  $\text{Fe}_3\text{O}_4$  (60%). Heating up to  $560\text{ }^\circ\text{C}$  results in a similar composition (41%  $\text{Fe}_3\text{N}$ , 59%  $\text{Fe}_3\text{O}_4$ ), though with slightly sharper peaks, as might be expected from increased crystallization at the higher temperature (Figure S12). At  $580\text{ }^\circ\text{C}$ , most of the sample is  $\text{Fe}_3\text{N}$  (70%), but  $\text{Fe}_3\text{C}$  appears in small quantities (7%), and the sample still contains  $\text{Fe}_3\text{O}_4$  (23%). At  $600\text{ }^\circ\text{C}$ ,  $\text{Fe}_3\text{C}$  is the dominant phase (58%), yet  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{N}$  remain in the sample. By  $700\text{ }^\circ\text{C}$ , the sample is 100%  $\text{Fe}_3\text{C}$ , with relatively sharp peaks, indicating higher crystallinity. These data show that it is not possible to isolate a pure iron nitride phase with a fast reaction time, which reflects the results from the *in situ* study.

To try and isolate the intermediate iron nitride phase, we heated samples of the iron nitrate/gelatin precursor to various

temperatures with a dwell time of 0.5 or 1 h. The composition data for both series show the same general trend (Tables S1 and S2), where iron oxide is gradually converted to iron nitride and then carbide. The samples held at 500 °C for 0.5 and 1 h show sharper diffraction peaks for iron oxide than the sample with no dwell time, which is consistent with crystallinity increasing with the longer sintering time. However, the sharp iron oxide peaks at 500 °C give way to broader iron oxide peaks at 520 °C (Figure S13), suggesting that the iron oxide crystallites become smaller and more disordered as they are consumed during carbothermal reduction. Another observation from these data is that complete formation of Fe<sub>3</sub>C happens at lower temperatures (e.g., 575 °C at 1 h hold compared to 650 °C with no dwell time). To probe this further, we investigated the effect of different dwell times at 500 °C. The data (Figure 9b) show that it is in fact possible to achieve an almost Rietveld-pure sample of Fe<sub>3</sub>C at 500 °C (Table 2), which is substantially lower than has previously

**Table 2. Weight Percentage Compositions for Samples Heated at 5 °C min<sup>-1</sup> to 500 °C with Various Dwell Times. Errors are Shown in Brackets**

	Fe <sub>3</sub> O <sub>4</sub>	FeO	Fe <sub>3</sub> N	Fe <sub>3</sub> C
0 h	60(18)		40(18)	
0.5 h	60(3)	8(3)	31(2)	
1 h	60(2)		40(2)	
2 h	44(5)		41(5)	15(3)
3 h	27(5)	31(10)	37(6)	4.1(18)
6 h			4.4(7)	95.6(7)

been found in sol–gel synthesis. As in the previous cases, the Fe<sub>3</sub>C phase begins to form while FeO<sub>x</sub> is still present, demonstrating the stability of the Fe<sub>3</sub>C phase and the challenge in isolating Rietveld-pure Fe<sub>3</sub>N. While apparently phase-pure samples of Fe<sub>3</sub>N have been prepared previously from sol–gel synthesis, Rietveld refinements were not performed, and so it is likely that there were minor iron oxide and carbide contributions that were not accounted for.<sup>15</sup>

#### 4. CONCLUSIONS

*In situ* WAXS and SAXS studies have been used to probe the evolution of FeO<sub>x</sub>, Fe<sub>3</sub>N, and Fe<sub>3</sub>C nanoparticles from a Fe(NO<sub>3</sub>)<sub>3</sub>/gelatin sol–gel precursor. We have demonstrated that the oxide–nitride–carbide transformation happens over a range of timescales, meaning some particles transform quickly to carbide while others remain in an oxide phase until much higher temperatures. It is proposed that this is due to the nanoparticles of the oxide intermediate being of varying size, which affects the rate of carbothermal reduction and nitridation. While the oxide particle size distribution is fairly small, this broadens rapidly during the oxide–nitride phase transition, indicating that the nitride particle form by mass transport of iron from several adjacent iron oxide particles. The *in situ* WAXS data show convincing evidence for the presence of an iron carbonitride intermediate. This suggests that the iron nitride-to-carbide transformation occurs by diffusion of carbon atoms into the nitride particles. Finally, we demonstrate that while it is very difficult to isolate a phase-pure sample of Fe<sub>3</sub>N via this sol–gel method, Rietveld-pure Fe<sub>3</sub>C can be produced at the remarkably low temperature of 500 °C with a long furnace dwell time. While we have only studied the Fe–N–C system, many other transitions metals can also form

nitrides and carbides so these observations may also provide helpful insight into those systems.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03442>.

Additional experimental information, SAXS data with fits, additional particle size histograms, *ex situ* XRD data, and crystalline compositions based on Rietveld refinement (PDF)

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##### Notes

The authors declare no competing financial interest.

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