

Temperature-driven structural thermodynamic analysis of cubic spinel iron oxide nanoparticles synthesis via ascorbic acid-assisted co-precipitation

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Received 10 May 2026, Revised 25 May 2026, Accepted 5 June 2026

ABSTRACT

Iron oxide nanoparticles possess remarkable properties including high surface area, strong magnetic response and good biocompatibility. The co-precipitation method is widely used because of its simplicity, mild operating conditions and high scalability. Using ascorbic acid as reducing agent helps maintain the $\text{Fe}^{2+}/\text{Fe}^{3+}$ balance, which improves dispersion stability and supports the formation of magnetite. In this study, iron oxide nanoparticles were synthesized at reaction temperatures from 30 °C to 90 °C. X-ray diffraction (XRD) patterns, field emission scanning electron microscope (FESEM) images and vibrating sample magnetometer (VSM) curves were evaluated to determine the phase evolution, crystallite size, full width at half maximum (FWHM), particle morphology, and magnetic properties. Standard thermodynamic parameters were calculated to link with the experimentally observed structural quality magnetic transformations. The results show that 70 °C is the minimum temperature required to form a stable cubic spinel iron oxide phase. The lower investigated temperature at 50 °C forms only hematite ($\alpha\text{-Fe}_2\text{O}_3$) due to accelerated oxidation and insufficient thermal energy. The reaction temperature at 80 °C produced a uniform agglomerated particulates due to their highly magnetic behaviour as evaluated by VSM. The best structural quality, with the largest crystallite size of 7.42 nm and the narrowest FWHM of 0.0205 rad was recorded at 80 °C. Reaction temperatures from 70 °C to 90 °C show exothermic and spontaneous formation of the spinel phase. However, pushing the reaction to 90 °C limits structural and magnetic optimization. At this temperature, the saturation magnetisation (M_s) decreases from 30.6170 emu/g (at 80°C) to 22.6610 emu/g. This behaviour indicates that excessive thermal energy promotes aggressive nucleation, which reduces crystal order and magnetic behaviour. Reaction temperatures from 70 °C to 90 °C also confirm the exothermic, spontaneity and randomness of the reaction. This investigation serves as a crucial preliminary screening and feasibility phase to establish the baseline temperature level required for subsequent Design of Experiment (DOE).

Keywords: Iron oxide nanoparticles, Co-precipitation, Ascorbic acid, Thermodynamics, X-ray diffraction, Phase evolution

1. INTRODUCTION

Iron oxide nanoparticles typically have a cubic spinel structure, typically ranging from 1 to 100 nm in diameter. Their high surface area [1] and unique superparamagnetic properties allow them to be manipulated by external magnetic fields, enabling applications in targeted drug delivery [2], wastewater treatment [3] and heterogenous catalysis. Applying magnetite as a coating material or nanofiller greatly improves the separation and purification efficiency [4].

The co-precipitation method is the most common technique for synthesizing iron oxide nanoparticles compared to hydrothermal or solvothermal [5], sol-gel [6], thermal decomposition [7] and green biosynthesis [8]. It is simple, operates under mild conditions, and is easily scalable, producing nanoscale magnetite (5-20 nm) with high purity and crystallinity [9].

In general, the formation of iron oxide nanoparticles through co-precipitation begins with the dissolution of Fe^{2+} and Fe^{3+} salts in water, followed by the addition of a high concentration alkali that precipitates tiny solids. The detailed chemical pathway consists of three main stages [10]:

- (i) Initial precipitation of intermediate hydroxides.
- (ii) Solid-state transformation, where thermal dehydration and co-condensation into the cubic inverse spinel structure occurs.
- (iii) Oswald ripening, where smaller dissolved particles redeposit onto larger ones to promote crystal growth.

A major challenge during co-precipitation is maintaining a sufficient amount of Fe^{2+} ions. Under ambient conditions, rapid oxidation of Fe^{2+} to Fe^{3+} is expected, leading to the formation of non-magnetic hematite phase [11]. Bubbling nitrogen or argon is commonly practiced suppressing this transformation [12]. Another approach is the use of ascorbic acid to maintain the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio at 1:2 [13]. In this case, ascorbic acid is introduced during the reaction as a reducing agent that partly contributes to control core nucleation and growth, rather than applied after particle formation for surface coating and to ensure colloidal stability, enhancing dispersion, biocompatibility and MRI contrast properties [14].

Temperature generally plays an important role in providing the activation energy dehydration and in controlling the rate of ion diffusion during the crystal-growth phase. As a result, the crystallite size and overall structural quality of the iron oxide are affected [15], [16]. Temperature also influences the thermodynamic behaviour during phase formation. This includes determining the standard changes in enthalpy, entropy and Gibbs free energy at different reaction temperatures. From these values, the spontaneity and driving force of the reaction can be assessed, and the size- and shape – dependent stability can be understood and predicted. Ultimately, the dynamics of these parameters can be linked to the growth of kinetics and phase evolution. However, most current studies focus on the thermodynamics of pollutant adsorption of iron oxides [17], [18] rather than the thermodynamics of nanoparticle formation itself. This study aims to fill that gap by acting as preliminary screening stage to identify temperature factors and to establish baseline boundaries. This screening stage is crucial for defining the temperature ranges for subsequent optimization using Design of Experiments (DOE). It correlates phase evolution and crystal quality with the calculated thermodynamic properties and identifies the minimum reaction temperature for iron oxide nanoparticles formation in ascorbic acid-assisted co-precipitation.

2. EXPERIMENTAL DETAILS

2.1. Materials

Ferrous chloride tetrahydrate, ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 97%), Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%) and ammonium hydroxide (NH_4OH) solution at 29% concentration were purchased from Sigma Aldrich. Ascorbic acid with purity of 99.8% acted as the reducing and capping agent, was obtained from HmbG Reagent Chemicals. All chemicals were used as received without further purification.

2.2. Samples Preparation

Iron oxide nanoparticles were produced from co-precipitation method. 0.30 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.81 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 150 mL deionised water in molar ratio of 1:2 and then stirred at a constant speed of 350 rpm using magnetic stirrer on a heating plate at room temperature. Subsequently, 0.05 g of ascorbic acid was added to the solution to maintain the Fe^{2+} ions. Then, 5 ml

of NH_4OH was added dropwise until the solution reached a pH of 10. At this point, characteristic brownish-black precipitate started to form. The resulting suspension was then heated at the target temperatures of 50 °C, 70 °C, 80 °C, or 90 °C in a water bath for 120 minutes. The precipitates were separated from the solution using a strong neodymium magnet and repeatedly washed with deionised water until the pH of supernatant turned neutral. The isolated powders were dried at 60 °C for 24 hours prior to characterisations.

2.3. Samples Characterisations

The phases of the precipitates formed were qualitatively analysed using X-ray diffraction (XRD) on a Bruker D8 Advance with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) by recording the patterns over a 2θ range of 20 to 80° with a step size of 0.02° and a scanning rate of 0.5°/min. The average crystallite size (D) was calculated from the intense reflection of the spinel structure using the Scherrer equation [19] as shown in Equation (1),

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is the non-spherical shape factor (0.9), β is the FWHM of the diffraction peak in radians and θ is the Bragg angle.

Because the nanoparticles are extremely small (below 10 nm), their diffraction peaks are naturally very broad, causing the observed FWHM values above 0.02 rad. In comparison, the instrumental broadening of the diffractometer is only about 0.0012 rad, which is much smaller than the broadening caused by the sample itself. When the instrumental value is subtracted using the standard correction formula, the change in peak width is less than 0.2%. The difference is too small to affect the Scherrer calculation, so the instrumental broadening can be considered negligible for this analysis [20].

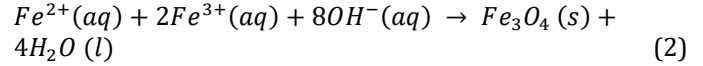
Morphology of nanoparticles was observed using field emission scanning electron microscope (FESEM) (NOVA NanoSEM, FEI, Hillsboro, Oregon, US) operating at acceleration voltages between 10.00 kV and 15.00 kV under high vacuum mode. Images were captured at 35,000x and 100,000x magnifications. A qualitative separation test was performed using an external neodymium magnet to evaluate the macroscopic magnetic properties. Room temperature magnetic properties including saturation magnetisation (M_s), remanent magnetisation (M_r) and coercivity (H_c) were quantified using a Vibration Sample Magnetometer (VSM, Lakeshore 7404 Series) across an applied magnetic field range of -13,000 to +13,000.

This screening stage focuses on confirming the baseline transitions during the reaction. Since this work serves as a feasibility study to identify the active thermal boundaries before moving into full DOE optimisation, replications with error bars or standard deviations were not conducted at this point. Instead, the reliability of the observed trends is supported by the consistency of the results obtained from

independent characterization methods. This is considered sufficient for establishment of the baseline temperature range for further systematic studies.

2.4. Thermodynamic Analysis

Thermodynamic behaviour of iron oxide nanoparticles formation was analysed by determining the standard enthalpy change (ΔH°_{rxn}), standard entropy change (ΔS°_{rxn}) and standard free Gibbs energy (ΔG°_{rxn}) of each species involved in co-precipitation reaction at target reaction temperatures. The thermodynamic analyse the main precipitation reaction producing magnetite (Fe_3O_4) to emphasize the initial nucleated phase prior to any secondary phase such as maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The reaction is represented by Equation (2) [21],



The standard enthalpy ($\Delta H^\circ_{f,i}$), and entropy (ΔS°_i) of species i at each temperature T were calculated using standard thermodynamic equations as shown in Equations (3) and (4) [22],

$$\Delta H^\circ_{f,i}(T) = \Delta H^\circ_{f,i}(298.15) + C^\circ_{p,i}(T - 298.15) \quad (3)$$

$$\Delta S^\circ_i(T) = S^\circ_i(298.15) + C^\circ_{p,i} \ln\left(\frac{T}{298.15}\right) \quad (4)$$

The standard thermodynamic properties required for the calculation are listed in Table 1.

Table 1. Standard thermodynamic properties of reactants and products at 298 K.

Species	ΔH°_f (kJ/mol)	Ref.	S° (kJ/mol.K)	Ref.	C°_p (kJ/mol.K)	Ref.
$\text{Fe}_3\text{O}_4(\text{s})$	-1118.400	[22]	0.145890	[23]	0.143400	[24]
$\text{H}_2\text{O}(\text{l})$	-285.830	[22]	0.069950	[23]	0.075351	[23]
$\text{Fe}^{2+}(\text{aq})$	-90.295	[23]	-0.102171	[23]	0.023.000	[23]
$\text{Fe}^{3+}(\text{aq})$	-50.056	[23]	-0.282404	[23]	-0.108000	[23]
$\text{OH}^-(\text{aq})$	-230.015	[23]	-0.010900	[23]	-0.148532	[25]

The ΔH°_{rxn} and ΔS°_{rxn} were calculated using Equation (5) and (6), by incorporating the stoichiometric coefficients for reactants n_i and products, n_j :

$$\Delta H^\circ_{rxn}(T) = \sum \nu_i \Delta H^\circ_{f,i}(\text{products}) - \sum \nu_i \Delta H^\circ_{f,i}(\text{reactants}) \quad (5)$$

$$\Delta S^\circ_{rxn}(T) = \sum \nu_i S^\circ_i(\text{products}) - \sum \nu_j S^\circ_j(\text{reactants}) \quad (6)$$

Finally, ΔG°_{rxn} was calculated from Equation (7) using the values of total ΔH°_{rxn} and ΔS°_{rxn} obtained using the fundamental equation [22],

$$\Delta G^\circ_{rxn}(T) = \Delta H^\circ_{rxn}(T) - T\Delta S^\circ_{rxn}(T) \quad (7)$$

This thermodynamic model assumes ideal, macro-scale equilibrium conditions, infinitely dilute ions, and bulk crystal properties. On the other hand, it is understood that nano-scale systems deviate from these ideal values due to high surface energies, localised pH and chemical variations, and rapid intermediate reaction steps [26],[27]. Nevertheless, these classical calculations provide a useful foundation for comparing theoretical thermodynamic trends with the actual experimental crystal growth.

3. RESULTS AND DISCUSSION

3.1. Phase Evolution Analysis

The XRD patterns as shown in Figure 1 clearly show the phase evolution of the precipitates formed at co-precipitation temperatures of 30 °C, 50 °C, 70 °C, 80 °C and

90 °C. All major diffraction peaks are indexed to their corresponding Miller indices.

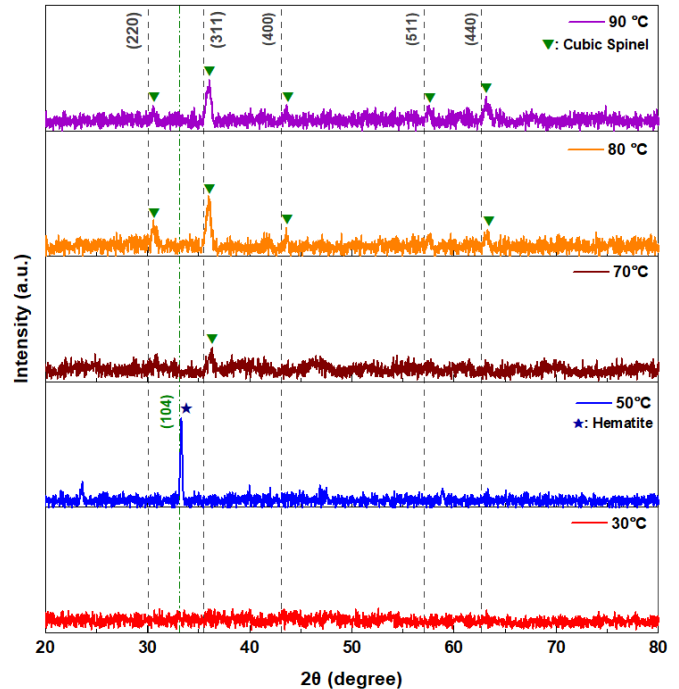
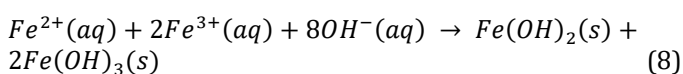


Figure 1. XRD patterns of precipitates formed at reaction temperatures of 30 °C, 50 °C, 70 °C, 80 °C and 90 °C.

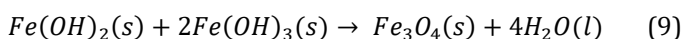
Characteristic reflections of a cubic inverse spinel iron oxide emerge within the reaction temperature range of 70 °C to 90 °C. However, the diffraction peaks exhibit a slight shift from the standard magnetite pattern according to JCPDS 01-075-0449 due to lattice strain and nanoscale surface

effects [28], [29]. The cubic inverse spinel structure is confirmed based on the characteristic reflections appearing at (220), (311), (400), (511) and (440). However, it is important to note that standard XRD analysis has limited capacity to distinguish between magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which is known as its fully oxidized derivative sharing the identical cubic inverse spinel structure with very close lattice constants ($a = 8.896 \text{ \AA}$ for magnetite versus $a = 8.346 \text{ \AA}$ for maghemite) [30]. These configurations merge entirely due to their small nanoparticle dimensions that causes the line broadening in XRD patterns.

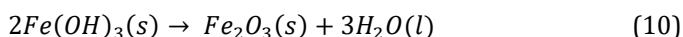
These temperatures provide sufficient thermal energy to initiate the formation of intermediate hydroxides from FeCl_2 , FeCl_3 and NH_4OH based on the following reaction as shown in Equation (8) [21],



The two intermediate hydroxides then undergo dehydration and transform into the cubic inverse spinel framework, which remains suspended in water as shown in Equation (9) [21],



At temperature of 50 °C, the thermal energy is insufficient for these reactions to proceed effectively. As a result, only the diffraction peak of hematite ($\alpha\text{-Fe}_2\text{O}_3$) was detected (JCPDS 01-089-8104), corresponding to the (104) plane. At this temperature, Fe^{2+} is not adequately stabilized by ascorbic acid, causing $\text{Fe}(\text{OH})_2$ to oxidize into $\text{Fe}(\text{OH})_3$, which subsequently forms hematite as the stable phase as shown in Equation (10),



Meanwhile, no spinel-related peaks were observed at the lowest temperature of 30 °C. Weak and broad features of the XRD pattern at this temperature indicate that precipitation is incomplete; hence, there is an absence of crystalline iron oxide phases.

At reaction temperatures of 70 °C to 90 °C with a reaction time of 120 minutes, ascorbic acid effectively reduces Fe^{3+} to Fe^{2+} and maintains the nominal stoichiometric ratio of 1:2. This prevents over-oxidation and ensures that phase evolution proceeds toward the cubic spinel phase.

Overall, this behaviour differs from other reports on iron oxide synthesis without a reducing agent, where spinel phase can form at lower temperatures of 25 °C to 40 °C [31] [32] [33]. In contrast, the presence of ascorbic acid makes the process more dependent on reaction temperature. Temperatures above 50 °C accelerate the formation of intermediate hydroxides, while dehydration and transformation into the cubic inverse spinel structure occur only when the reaction temperature reaches 70 °C and above. Therefore, 70 °C marks as the minimum tested

temperature required to nucleate a stable cubic spinel iron oxide phase under the investigated conditions.

3.2. Analysis of Crystallite Size and Structural Quality

Figure 2 shows the crystallite size and structural quality (FWHM) of precipitates synthesized at 70 °C, 80 °C and 90 °C of reaction temperatures, where the cubic spinel iron oxide phase is successfully nucleated.

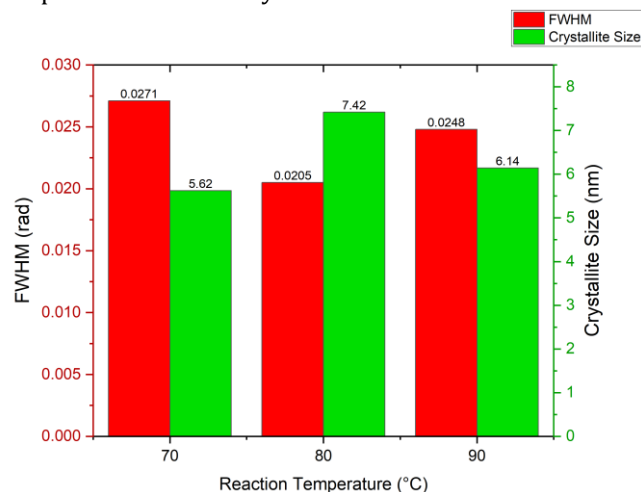


Figure 2. Crystallite size and structural quality of cubic spinel iron oxide phase synthesized at reaction temperatures from 70 °C to 90 °C.

At temperature of 70 °C, the diffusion of ions and molecular species is slow, and therefore the growth of the crystallites is limited, eventually weakening the Ostwald ripening process [31], [34]. This creates the smallest crystallite size of 5.62 nm. The thermal energy is also not sufficient for structural ordering, as shown by the broadest FWHM to 0.0271 rad.

However, as the reaction temperature increases to 80 °C, diffusion becomes faster and enhances the Ostwald ripening, allowing the crystallites to grow to 7.42 nm. The narrowest FWHM (0.0205 rad) confirms that this temperature provides an ideal thermal environment to transform intermediate hydroxides into a more structurally ordered of spinel iron oxide matrix [31], [34].

Supplying more heat by increasing the reaction temperature to 90 °C leads to the dissolution of less crystalline or less stable precursors such as ferrihydrite, lepidocrocite, goethite, and occasionally hematite [35]. This triggers aggressive nucleation and rapid growth of the more stable phases but results in smaller crystallites of 6.14 nm. The rapid growth also hinders structural optimisation, as indicated by the increase in FWHM to 0.0248 rad.

Across all investigated temperatures, the crystallite sizes remained below 20 nm. This range consistently associated with near-superparamagnetic properties in iron oxides, with the reaction temperature of 80 °C exhibiting a marked improvement in structural order [36].

3.3. Morphological and Magnetic Performance Analysis

The surface morphology and aggregation characteristics of the iron oxide nanoparticles synthesized at 80 °C are displayed in Figure 3.

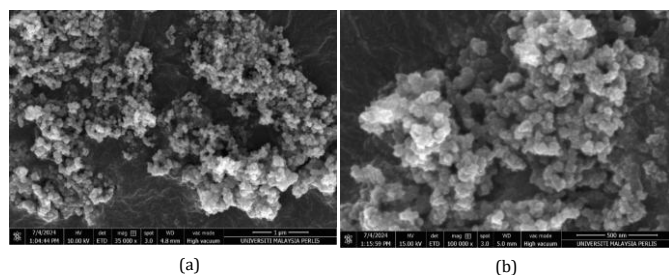


Figure 3. FESEM micrograph of the iron oxide nanoparticles synthesized at 80 °C at magnifications of (a) 35,000x and (b) 100,000x.

Figure 3(a) reveals a highly nanostructured, continuous network composed of interconnected nanoparticle clusters, whereas Figure 3(b) which zooms in to reveal that these clustered networks are composed of extremely small, near-spherical primary nanoparticles. The widespread physical agglomeration is a typical observation for magnetic nanoparticles in the sub-10 nm range due to evaporative capillary forces, high thermodynamic surface energy and magnetic dipole-dipole interactions [37]. Due to this heavy agglomeration, the determination of individual particle boundaries to construct a size distribution histogram is not possible. Therefore, this study relies primarily on the Scherrer method to measure the core crystallite size (7.42 nm). This XRD-calculated crystallite size confirms that the

FESEM clusters consists of single-crystallite domains that physically aggregate into larger cluster networks.

As shown in Figure 4(a), the dry, black powder synthesized at 80 °C responds rapidly to the external magnetic field, aligning cleanly against the vial wall and demonstrating a strong magnetic response. This is due to the quantified magnetic properties and superparamagnetic behaviour of the iron oxide nanoparticles as presented in Figure 4(b). The extracted magnetic parameters as summarized in Table 2.

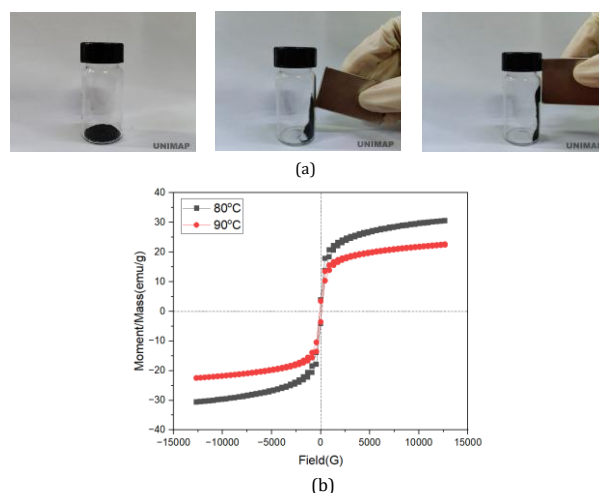


Figure 4. Magnetic characteristics of the synthesized iron oxide nanoparticles. (a) Macroscopic magnetic attraction of the synthesized sample at 80 °C toward an external neodymium magnet, and (b) Room temperature VSM hysteresis loops of the iron oxide nanoparticles synthesized at 80 °C and 90 °C.

Table 2. Magnetic parameters extracted from room temperature VSM measurement for iron oxide nanoparticles synthesized at 80 °C and 90 °C.

Reaction Temperature (°C)	Saturation Magnetisation M_s (emu/g)	Coercivity, H_c (Oe)	Remanent Magnetisation, M_r (emu/g)	Squareness Ratio, M_r/M_s
80	30.6170	99.1720	4.0627	0.1327
90	22.6610	110.7400	3.5216	0.1561

VSM measurements were focused on the 80 °C and 90 °C samples to obtain a high-resolution and comparative physical understanding of the structure-magnetisation correlation in developed cubic spinel systems. Both samples display narrow hysteresis loops with extremely low squareness ratio (M_r/M_s) of 0.1327 for 80 °C sample and 0.1561 for the 90 °C sample. The small, non-zero coercivity ($H_c = 99.1720$ Oe at 80 °C and 110.74 Oe at 90 °C) and remanent magnetization ($M_r = 4.0627$ emu/g and 3.5216 emu/g, respectively) represent a near-superparamagnetic transition state. This behaviour is highly typical of capped nanoparticles. It is driven by weak dipole – dipole interactions within the clusters [38].

The saturation magnetisation (M_s) of the 80 °C sample (30.6170 emu/g) is significantly higher than that of 90 °C sample (22.6610 emu/g) which correlates perfectly with the crystallite size calculated from XRD analysis (7.42 nm at

80 °C vs 6.14 nm at 90 °C). As crystallite size decreases, the surface -to- volume ratio increases, promoting to a larger volume fraction of magnetically disordered surface layer and a higher relative mass contribution from the non-magnetic capping shell. Because of that, the net saturation magnetisation of 90 °C sample is reduced. This confirms that the structural and magnetic qualities of the synthesised cubic spinel iron oxide nanoparticles can be controlled by modifying the reaction temperature.

3.4. Thermodynamic Analysis on Cubic Spinel Iron Oxide Nanoparticles Formation

The standard thermodynamic parameters of ΔH_{rxn}° , ΔS_{rxn}° and ΔG_{rxn}° were calculated across the successful spinel phase zone (70 °C to 90 °C) and summarized in Table 3.

Table 3. Calculated standard thermodynamic parameters for the formation of cubic spinel iron oxide nanoparticles.

Temperature (°C)	ΔH_{rxn}° (kJ/mol)	ΔS_{rxn}° (kJ/mol.K)	ΔG_{rxn}° (kJ/mol)
70	-146.95	1.443	-642.13
80	-128.23	1.497	-656.83
90	-109.51	1.549	-672.06

The calculated ΔH_{rxn}° confirms that the co-precipitation process is exothermic ($\Delta H_{rxn}^{\circ} < 0$), indicating that heat is released at all reaction temperatures of 70 °C to 90 °C. The amount of heat released becomes lower as the temperature increases, mainly because more energy is required for hydration of precursor ions (specifically Fe^{2+} and Fe^{3+}), nucleation and the continuous growth of high purity cubic spinel phases. Higher energy is also needed to form better crystal quality as supported by the FWHM results in Figure 2.

The ΔS_{rxn}° values are positive and show an increasing trend with temperature. This is expected because heating up to 90 °C promotes the release of water from iron complexes, which enhances the randomness of nanoparticle movement in the solution. This also play a role in increasing the disorder of the system. At the same time, surface water gains enough energy to free themselves, leaving a more concentrated solution. This condition promotes rapid nucleation, which explains the smaller magnetite crystallite as 6.14 nm.

The negative ΔG_{rxn}° values indicate that the reaction is spontaneous and becomes more thermodynamically favourable at higher reaction temperatures. The most negative value at 90 °C aligns with the higher disorder and the rapid nucleation behaviour that drives the transformation of the outer magnetite layers into maghemite ($\gamma-Fe_2O_3$). While this transformation remains undetected in XRD profiles due to peak overlap, it is clearly identified by the significant drop in M_s to 22.5 emu/g. Therefore, although 90 °C maximises theoretical spontaneity, an intermediate processing temperature of 80 °C is required to balance thermodynamics and crystallization kinetics to optimise both the structural order and magnetic properties of iron oxide nanoparticles.

CONCLUSION

This study evaluated the structural, morphological, and thermodynamic properties of cubic spinel iron oxide nanoparticles synthesised from ascorbic acid-assisted co-precipitation. The main conclusions are listed as follows:

1. This work serves as a preliminary screening and feasibility stage to establish baseline temperature ranges. 70 °C shows the minimum tested reaction temperature required to initiate nucleation of a stable, single-phase cubic inverse spinel structure. Reaction temperatures below 50 °C produce only hematite ($\alpha-Fe_2O_3$) due to insufficient thermal energy for dehydration.

2. Reaction temperature of 80 °C serves as ideal thermal environment to balance thermodynamics and crystallization kinetics with highest structural order with the largest crystallite size of 7.42 nm and the narrowest FWHM of 0.02025 rad. This result establishes the critical input boundary for future temperature factor in Design of Experiments (DOE) optimisation. This temperature also shows near-superparamagnetic behaviour, with saturation magnetisation (M_s) of 30.6170 emu/g and a low squareness ratio ($M_r/M_s = 0.1327$).

3. Bulk thermodynamic calculations show that the formation reaction is exothermic and spontaneous. Further heating to 90 °C increases the thermodynamic driving force but results in a significant drop in saturation magnetisation to 22.6610 emu/g. This is due to aggressive nucleation and topotactic surface oxidation of magnetite to maghemite ($\gamma-Fe_2O_3$), which can be successfully controlled by maintaining the reaction temperature at 80 °C as verified by this screening.

ACKNOWLEDGEMENTS

The authors express gratitude for the financial assistance provided by the Ministry of Higher Education (MoHE) Malaysia through the Fundamental Research Grant Scheme (FRGS) [Grant No. FRGS/1/2022/TK08/UNIMAP/02/76].

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