Judging phase purity of hematite ($\alpha$-Fe$_2$O$_3$) nanoparticles through structural and magnetic studies

J Sharmila Justus*, S Dawn Dharma Roy*, K Saravanakumar† and A Moses Ezhil Raj♣

1 Department of Physics & Research Centre, Women’s Christian College, Nagercoil–629 001, Tamil Nadu, India
2 Department of Physics & Research Centre, Nesamony Memorial Christian College, Marthandam–629 165, Tamil Nadu, India
3 Department of Physics, Kongunadu Arts and Science College, Coimbatore–641 029, Tamil Nadu, India
4 Department of Physics & Research Centre, Scott Christian College (Autonomous), Nagercoil–629 003, Tamil Nadu, India

E-mail: sharmi.fiziks@gmail.com

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tables and figures

Abstract

The effect of post-growth annealing on the phase transformation leading to phase pure hematite ($\alpha$-Fe$_2$O$_3$) nanoparticles is reported in this work. Co-precipitation technique was used to synthesise iron oxide nanoparticles by adjusting the pH of the solution. The xerogel was dried at 80°C and the obtained powder was calcined in the temperature range 400–800°C for 3 h. in air. Annealing temperature was prefixed on the basis of the thermal degradation pattern of the starting precursor. X-ray diffraction (XRD) study endorsed the presence of mixed phases FeO, FeO$_2$ and $\alpha$-Fe$_2$O$_3$ in the as-prepared sample. On annealing, the minor phases transform gradually to $\alpha$-Fe$_2$O$_3$, as confirmed through thermal studies. Performed Rietveld analysis confirms the presence of impurity phases in samples annealed at low temperature. Phase pure sample crystallizes in the rhombohedral corundum structure (space group, $R-3c$) with $a = 5.04044$ Å, $c = 13.7628$ Å and $c/a = 2.73048$. FT-Raman spectral investigations allowed for a clear assignment of the $\alpha$-Fe$_2$O$_3$ phase. Chemical analysis advocated the only presence of Fe$^{3+}$ ions that octahedrally coordinated with hexagonally close packed O$^{2-}$ ions that constitute corundum structure. Electron microscopy (TEM) images proved the non-spherical particle distribution in the range 80–100 nm with mean particle size of 93 nm. Structural phase transition with annealing temperature was further confirmed through the fluctuations in the magnetic structure. In analogues to XRD, magnetic study also served as a judging tool to identify purity and the presence of mixed phases in hematite.

1. Introduction

Iron oxide has various polymorphs and so their phases exist in various forms, including goethite ($\gamma$-FeOOH), wüstite (FeO), iron oxide (Fe$_2$O$_3$), hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_3$O$_4$) and magnetite (Fe$_3$O$_4$), with each phase structure giving rise to specific magnetic properties [1]. As interaction of the spin magnetic moment with the crystal lattice varies, the atomic-level structure of the material can be understood. Considerable efforts have been taken already to speed-up structure solution of any phase pure/impure materials by developing theoretical and experimental crystal structure prediction techniques [2–5]. However during structural estimations, phase composition, structural defects, morphology of the study materials has to be taken critically as it amend the magnetic properties much [6–8]. Since extensive research and development was devoted in the sol-gel processing and fabrication of nanomaterials, extensive care should be urged for ensuing phase pure products. In such processing methods, the role of annealing temperature is inevitable in determining the morphology, stoichiometry and phase of the metal oxide nanostructures that still remains elusive [9, 10].

Among metal oxides, $\alpha$-Fe$_2$O$_3$ is the versatile and stable phase of iron oxide exhibiting antiferromagnetic character in the bulk form [11]. Hematite has the corundum crystallographic structure, where the anions have a hexagonal closed packed structure and the cations occupy 2/3 of the octahedral sites [12]. Crystal structure of $\alpha$-Fe$_2$O$_3$ is temperature sensitive; its magnetization depends strongly on distances between atoms that vary with
processing temperature. Hence annealing is an attractive post-growth processing option to understand the gradual transformation of phase composition [13]. Such phase transition and composition can be analysed readily with X-ray diffraction technique [14]. Present study is the initial stride in reporting the phase purity of the annealed iron oxide nanoparticles. Phase composition obtained through XRD studies were then confirmed once again through the magnetic studies. Observed changes in the magnetic behavior of the annealed samples are analogues to the results obtained through XRD analysis. Magnetic studies can thus serve as an additional tool to judge the phase purity of any materials.

2. Experimental procedure

2.1. Synthesis

Analytical grade iron (III) chloride tetrahydrate (99.9%), sodium hydroxide (98%) and ethylene glycol (99.8%) were purchased from Sigma-Aldrich and used as received. In a typical synthesis, Iron (III) chloride was dissolved in a mixture of deionized water and ethylene glycol (to reduce the acidic nature of the ferric salt solution) at room temperature for a concentration of 0.1 M. NaOH solution (0.1 M) was then slowly added to the above solution on continuous stirring. The hydroxide ions (OH\(^-\)) in the solution react with the Fe\(^{3+}\) ions in the acidic ferric salt solution to form iron (III) hydroxide.

\[
\text{FeCl}_3 + 3\text{NaOH} \rightarrow \text{Fe(OH)}_3 + 3\text{NaCl}
\]

As pH value of the precursor solution decides the phase of the prepared material, its value was maintained at the predefined value (pH = 3) using ammonia solution. When ammonia was added, the hydroxide ions remove the hydrogen ions attached to the iron ions and from water ligands. When enough hydrogen ions have been removed, a neutral complex precipitate FeOOH (hydrated iron (III) oxide) was formed.

\[
\text{Fe(OH)}_3 \rightarrow \text{FeOOH} + H_2O
\]

\[
2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + H_2O
\]

Hydrated iron (III) oxide was reduced to hematite on stirring continuously for 1 h at 100 °C. On removal of hydrogen ions from the reaction product, Fe\(^{3+}\) ions are reduced to Fe\(^{2+}\) ions and form α-Fe\(_2\)O\(_3\). This reduction is conceivable only at lower pH values. A small fraction of Fe\(^{2+}\) ions still there for the formation of impurity phases FeO, and FeO\(_2\), as reduction is partial, not complete. Obtained precipitate was then repeatedly washed with ethanol and distilled water and dried in air at 80 °C. To make the product more crystalline, the as-prepared sample was then annealed at 400, 600 and 800 °C for 3 h. Entire preparation steps are displayed in the form of a flow chart in figure 1.

2.2. Characterization

Well-defined and established characterization methods are essential for identifying structural transformations in the study material. Thermal stability and mass degradation with phase transitions in the precursor and iron oxide samples were analyzed initially using the Perkin Elmer, Diamond TG/DTA instrumentation. X-ray powder diffraction (XRD) patterns of as-prepared and calcined powder samples were recorded using a diffractometer (PANalytical-X pert Pro) with Cu K\(_\alpha\) radiation at room temperature (λ = 1.5406 Å). GSAS with EXPGUI interface was used to refine and extract crystallographic parameters. The metal-oxide phase formation of the prepared hematite nanoparticles was examined by FT Raman spectroscopy (BRUKER RFS 27) in the wave number range 50–4000 cm\(^{-1}\). The X-ray Photoelectron Spectrum (XPS) of the sample was recorded in ESCA spectrometer (PHI 5600ci) using Al-K\(_\alpha\) X-rays. Morphology and particle size distributions were examined by Transmission Electron Microscopy (TEM) (Philips, CM 200). The magnetic hysteresis measurements at room temperature were acquired on a Vibrating Sample Magnetometer (Lakeshore VSM-7410).

3. Results and discussion

3.1. Thermal studies

As iron oxide is a polymorphic material, its gradual transformation and the thermal stability of each phase are analysed using TGA studies. Figure 2 shows the decomposition behavior of the starting precursor (Ferric chloride), as-prepared and annealed samples Fe\(_2\)O\(_3\)-400 and Fe\(_2\)O\(_3\)-800.

In figure 2(a), dehydration and decomposition of the precursor proceed simultaneously at temperatures above 100 °C. After dehydration, a stable Fe(OH)\(_2\)Cl is formed representing the first plateau region in the temperature range 250–300 °C. Above 350 °C, observed second plateau corresponds to the formation of Fe\(_2\)O\(_3\) [15]. The TG curve of the as-prepared sample (figure 2(b)) is in analogous to that of the starting precursor. Initial process of dehydration is extended up to 120 °C, and then the gradual removal of chlorine from the sample leads
to the weight loss that extends up to 300 °C. Since iron has more number of oxidation states, finally formed product may contain FeO, FeO₂, etc. However on heating above 600 °C, observed weight loss indicates transformation of the co-ordinated FeO and FeO₂ phases to α-Fe₂O₃. TG study thus confirms the need of annealing at high temperatures for the formation of α-Fe₂O₃. Hence, the as-prepared samples were calcined at two different temperatures, viz., 400 °C and 800 °C and their decomposition patterns recorded are shown in figures 2(c) and (d) respectively. Sample calcined at 400 °C shows gradual removal of mass on heating up to 800 °C. This indicates the transformation of phases FeO and FeO₂ to Fe₂O₃. However the calcined sample at 800 °C is stable without weight loss confirms α-Fe₂O₃ formation without any impurity phases.
The XRD patterns of the as-prepared and calcined iron oxide nanoparticles are shown below in figure 3. Structural analysis phases. In calcined sample Fe₂O₃-800, absence of exothermic peaks evidenced the formation of the expected product α-Fe₂O₃. Thermogravimetry study thus revealed the need of calcination at 800 °C for the formation of Fe₂O₃ phase without any impurity phases. DTG plots (not shown) also indicated similar variations in which the observed three exothermic peaks in the as-prepared sample represent the dehydration and the formation of FeO and FeO₂ phases. In calcined sample Fe₂O₃-800, absence of exothermic peaks evidenced the formation of the expected product α-Fe₂O₃.

3.2. Structural analysis

The XRD patterns of the as-prepared and calcined iron oxide nanoparticles are shown below in figure 3. The prominent peak located at 2θ = 32.6899° of the as-prepared sample corresponds to the reflection from the (1 0 4) plane of rhombohedral lattice of α-Fe₂O₃. Other observed diffraction peaks at 2θ = 20.232°, 31.7144°, 45.5101° and 47.0092° not matches to α-Fe₂O₃ phase. Among the impurity peaks, the peak at 31.7144° could be assigned to the FeO₂ phase of iron oxide and the other three peaks to the FeO phase. Observed results suggest the formation of the metastable phase FeO₂ along with stable phases Fe₂O₃ and FeO on removal of hydrogen from the peroxide FeOOH. Because of the fragile tendency of O−O bonds in FeOOH, the peroxides [O₂]²⁻ and superoxides [O₂]⁻ species are often present in metastable states [16]. One such metastable phase FeO₂ is regarded as mixed-valence oxide, falling into the stoichiometry range between FeO and Fe₂O₃, considered as the homologous series of nFeO·mFeO₂ [17]. So the as-prepared sample is FeO₂ with impurity phases FeO and Fe₂O₃ phases. Also the observed diffraction peaks of the as-prepared sample are diffuse, suggesting the need of calcination to improve its crystalline character. Hence the as-prepared sample was then calcined at three different temperatures 400, 600 and 800 °C to study the phase transformations with annealing temperatures.

Figure 3(b) is the XRD pattern of the annealed sample at 400 °C. Observed prominent peak at 2θ = 31.6306° (h k l = 0 1 0) is a strong evidence for the presence of Fe₂O₃ phase (COD Card No.: 96-900-9105, hexagonal, SG = P-3m1). So on increasing the annealing temperature to 400 °C, the fragile bond stiffens that alter the ionic radius and give rise to thermally stable oxygen rich Fe₂O₃ [18]. Growth of FeO phase weakens, however all the peaks corresponding to Fe₂O₃ phase begins to rise at respective 2θ positions. While reductions of a metal oxide, formation of lower oxides occur as oxygen escapes from the lattice. This process resulted crystallographic structural transformation from FeO to Fe₂O₃ and α-Fe₂O₃ phases [19].

On increasing isochronal annealing of as-prepared samples at 600 °C, the intensity of the FeO₂ peak tends to decrease with the increase in intensities of the peaks correspond to α-Fe₂O₃ (figure 3(c)). This observed finding is in agreement with the similar reported for iron oxide nanoparticles [20]. However, peak corresponding to Fe₂O₃ persists, suggesting the need of further annealing at an elevated temperature. Figure 3(d) shows the XRD pattern of the sample annealed at 800 °C. All the peaks of the sample located at the specified 2θ positions are consistent with the standard value of single phase α-Fe₂O₃ (ICDD No. 01-079-0007) [21–23]. The most intense peak observed at 2θ = 33.2374° corresponds to the reflections from the (1 0 4) plane. The unit cell of α-Fe₂O₃ is hexagonal [24, 25] and contains only octahedrally coordinated Fe³⁺ ions (corundum structure). Thus for the formation of the hematite α-Fe₂O₃ phase without impurity phases, high temperature annealing is essential [26].
Table 1. Lattice parameters of the prepared iron oxide nanoparticles.

| Sample Details  | Lattice Parameter (Å) | Volume of unit cell (Å³) | Density (g cm⁻³) | Crystallite Size nm | Dislocation density × 10¹⁵ (lines m⁻²) | Microstrain |
|-----------------|-----------------------|--------------------------|------------------|---------------------|----------------------------------------|-------------|
| As-prepared     | a = 5.4780 c = 13.4216 | 348.7920                 | 4.5601           | 35                  | 0.8034                                 | 0.0035      |
| Calcined at 400 °C | a = 5.0252 c = 13.8027 | 301.856                  | 5.2691           | 18                  | 2.9259                                 | 0.0062      |
| Calcined at 600 °C | a = 5.0260 c = 13.7496 | 300.792                  | 5.2877           | 41                  | 0.5853                                 | 0.0029      |
| Calcined at 800 °C | a = 5.0305 c = 13.7423 | 301.175                  | 5.2810           | 60                  | 0.2752                                 | 0.0020      |
| Standard value  | a = 5.0265 c = 13.7360 | 300.790                  | 5.29             | —                   | —                                      | —           |
Based on the (h k l) values of reflection planes corresponding to the α-Fe₂O₃ phase, the lattice parameters were calculated and are listed in table 1.

Obtained lattice parameters for the as-prepared sample $a = b = 5.4780 \, \text{Å}, c = 13.4216 \, \text{Å}$ are not in match with the standard values of α-Fe₂O₃ phase. This may be due to the presence of additional FeO and FeO₂ phases. Since the sample has both FeO and FeO₂ phases, slight displacements in peak positions lead to more deviations in its lattice parameters. However, the lattice parameters of the annealed sample match well with the standard values. Annealed sample at 800 °C has the ‘a’ and ‘c’ values that perfectly matches with the standard values. Corresponding unit cell volume and density values are also in support of the formation of pure α-Fe₂O₃ phase. For the annealed samples at 600 °C and 800 °C, the cell edge elongates along the a-axis and contracts along the c-axis, hence the cell volume increases and the density decreases.

On careful inspection of the width of reflection peaks, it broadens non-uniformly at low temperature processing up to 400 °C. This non-uniform broadening can be explained due to strains and faults broadening [27, 28]. On increasing the temperature to 400 °C, structural reorientation occurs and therefore the peak broadens that reduces the crystallite size of the Fe₂O₃ phase. Further heating treatment systematically increase

section planes corresponding to the 002, 004, 111, 105, 200, and 201 reflection peaks, it broadens non-uniformly at low temperature

3.3. Rietveld analysis

Distribution of cations alters all physical properties of nanomaterials, the exact location of cations and anions are essential. Rietveld structure refinement is a versatile method to judge the exact locations of atoms in a crystal structure. Since α-Fe₂O₃ crystallizes in the rhombohedral corundum structure (space group, R-3c), magnetic unit cell contains two formula units (Fe₆O₈). A stable α-Fe₂O₃ structure is in AFM configuration below the Néel temperature (955 K) [32]. For the unit cell with the AFM spin ordering, the symmetry is reduced to the subgroup R-3 in which each Fe atom is octahedrally coordinated with six O atoms. In this AFM state, spin configuration may vary depending upon the arrangement of spin up and spin down ions in the c-axis [33]. Variations in the c/a ratio values and also the separation between two types of Fe-Fe bonding lengths decide the ferromagnetic (FM) and antiferromagnetic (AFM) ordering in α-Fe₂O₃ [34]. In order to extract all these structural parameters to correlate the magnetic behavior, Rietveld refinement-based quantitative phase analysis is more accurate and precise. In the present study, Rietveld refinement using GSAS [35] with EXPFGUI [36] interface was used to extract crystallographic parameters for the assigned space group and Wyckoff position of Fe and O atoms. Diffraction profiles were modeled by using a multitemporal Simpson’s rule integration of the pseudo–Voigt function. The fitting quality of the experimental data were checked by using the goodness of fit, $\chi^2$; that must tend to 1 and two reliability factors, $R_p$ and $R_{wp}$. Since impurity phase is present in Fe₂O₃-600 sample, the goodness of fit is 1.118. However for the phase pure Fe₂O₃-800 sample, the structure is converged further and therefore $\chi^2 = 0.885$. Other refined crystallographic parameters for the α-Fe₂O₃ samples are listed in table 2.

As evidenced from the refined pattern of the annealed sample at 600 °C, the impurity phase is visible along with α-Fe₂O₃ phase. For the sample annealed at 800 °C, observed and the calculated peaks are in perfect match and therefore the peak level difference is not traceable. Hence that sample is pure and more crystalline. The fitting quality of the experimental data was checked by using the parameters: $\chi^2$, $R_p$, and $R_{wp}$. Since impurity phase is present in Fe₂O₃-600 sample, the goodness of fit is 1.118. However for the phase pure Fe₂O₃-800 sample, the structure is converged further and therefore $\chi^2 = 0.885$. Other refined crystallographic parameters for the α-Fe₂O₃ samples are listed in table 2.

The structure of hematite was solved by considering rhombohedral symmetry constraints and the lattice parameter obtained are restrained to hexagonal unit cell. Table 2 provides all the structural parameters such as lattice parameters and bonding factors. The axis ratio c/a of hematite is usually shortened along the c-axis and therefore the obtained value of 2.73 is comparable with its ideal value of 2.83 [38]. Iron atom in the structure is octahedrally coordinated with oxygen and these oxygen atoms are marginally rotated against each other. Obtained structure predicts the presence of two Fe atom pairs with unequal Fe—Fe distance, noted as Type A and Type B along the hexagonal c-axis. Among the six O atoms surrounding each Fe atom, three are located at

5.4780 Å, $c = 13.4216 \, \text{Å}$. The defect parameter such as dislocation density and microstrain values found to decreases with annealing temperatures that reveals gradual removal of impurity phases from α-Fe₂O₃. Impurity traces are thus gradually removed on annealing and finally the pure α-Fe₂O₃ phase is retained. XRD is therefore considered as a suitable tool for monitoring the gradual evolution of α-Fe₂O₃ phase with annealing temperatures.

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the corners of an equilateral triangle above the central Fe atom, with a F–O length of 2.11 Å. The other three oxygen atom form similar equilateral triangle below the central Fe atom, whose F-O length is 1.946 Å. Since the percentage of impurity phase in Fe$_2$O$_3$-600 sample is only 4.87%, obtained crystallographic data of the two samples are almost identical.

### 3.4. Purity confirmation of α-Fe$_2$O$_3$ Phase

Structural transformation from impure to single hematite phase was confirmed the XRD studies. Before elaborating the magnetic studies, phase purity, chemical composition and morphology of α-Fe$_2$O$_3$ sample was an again analysed using FT-Raman, XPS and HR-TEM studies.

#### 3.4.1. Metal-oxide phase analysis

Raman spectroscopy allows characterization of molecular or chemical composition of most of organic and inorganic samples in complement to X-ray diffraction [39–41]. The corundum crystal structure of hematite with
two molecular Fe₂O₃ groups in a unit cell was already predicted through Raman spectroscopy [42]. Cations (C₃ site symmetry) are octahedrally coordinated with two layers of anions (C₂ site symmetry) with severe distortion [43]. For this distorted structure, the irreducible representation for the optical modes of hematite at the Brillouin zone is represented by [44]:

\[ \Gamma_0 = 2A_{1g} + 2A_{1u} + 3A_{2g} + 2A_{2u} + 5E_g + 4E_u \]

Among these modes, the symmetrical (g) and the asymmetrical (u) modes are respectively Raman and infrared active [45]. The irreducible representations for the acoustical modes are:

\[ \Gamma_a = 1A_{2u} + 1E_u \]

Unit cell of corundum has centre of symmetry and therefore vibrations that are Raman allowed are forbidden in IR. So in optical mode, A₁g and E₉ vibrations are Raman active and infrared inactive; while A₂u and E₈ vibrations are infrared active and Raman inactive. The A₁u and A₂g vibrations are inactive in both infrared and Raman experiments. Hence seven Raman modes (2A₁g + 5E₉) are allowed in corundum and this was experimentally proved through light scattering studies by Beatie and Gilson [46]. So the rhombohedral structure of α-Fe₂O₃ can also be proved through Raman spectral investigations. Figure 5 is the recorded Raman spectrum of pure α-Fe₂O₃ sample.

As reported, observed Raman active optical phonon modes fall below the frequency range 620 cm⁻¹ in which the Raman shift of the modes A₁g (1) and E₉ (1) are in the low frequency region around 200 cm⁻¹ [47]. The peak centered at 291 cm⁻¹ is a doublet assigned to E₉ (2) + E₉ (3) and the peak centered at 413 cm⁻¹ is belongs to the symmetrical E₉ (4) vibrations. The shoulder peak at 502 cm⁻¹ is due to A₁g (2) vibrations. It was already predicted theoretically that the phonon frequencies denoted A₁g (1), E₉ (3) and A₁g (2) give rise to less intense bands [48]. Observed results of the present investigations are similar to the theoretically predicted and also experimentally proved for the hematite phase of iron oxide. The band located at 625 cm⁻¹ assigned to E₉ mode of vibration also suggests the formation of pure hematite without any impurities [48]. Presence of a band at 1287 cm⁻¹ can be assigned to the interaction of two magnons created on antiparallel close spin sites [49, 50]. It is the second order overtone associated with the longitudinal phonon mode near 660 cm⁻¹. Raman spectral investigation is thus analogous to the XRD studies that prove the crystalline purity of the α-Fe₂O₃ phase.

3.4.2. Chemical environment analysis

The chemical state of Fe ions in an iron compound can exist as Fe²⁺ or Fe³⁺ or combination of these two. With the purpose of identifying the oxidation of Fe ions, X-ray photoelectron spectroscopic investigation has been carried out on pure hematite nanoparticles. Figure 6 shows the survey spectrum, which is quantified in terms of peak intensities and peak positions of the pure hematite nanoparticles.

XPS survey spectrum informs the chemical composition and quantifies each element from the peak position and its intensity respectively. Presence of Fe and O peaks in their respective binding energy sites without any impurity elements is a clear evidence for the purity of the sample. However, presence of carbon may be the adsorbed species on heating the sample in air, which is usually taken as a calibrating element. In addition to survey spectrum, peak positions Fe 2p peak and the satellite peaks of Fe 2p⁰₁/₂ and Fe 2p⁰₃/₂ give information
related to the ionic states of Fe $^{51, 52}$. The Fe 2p peak is therefore deconvoluted to identify the existence Fe$^{2+}$ and/or Fe$^{3+}$ ions. The deconvoluted XPS Fe 2p peak is shown in figure 7.

The Fe 2p has two entities: Fe 2p$^{1/2}$ (724.18 eV, not shown in figure) and Fe 2p$^{3/2}$ (709.88 eV), due to spin–orbit interaction of the state. The envelope of Fe 2p$^{3/2}$ peak is more intense and asymmetric in the high binding energy. Width of the peak is sufficient (FWHM = 4.34 eV) because of the inclusion of electrostatic interactions, spin–orbit coupling between the 2p core hole and unpaired 3d electrons of the photo-ionized Fe cation and crystal field interactions $^{53}$. The peak position of Fe 2p$^{3/2}$ is exactly at 709.88 eV and its satellite peak is 7.76 eV away from the high binding energy side $^{54, 55}$. The 2p$^{3/2}$ peaks from low-spin Fe$^{2+}$ compounds display no multiplet interactions because all the six 3d electrons are spin paired. However, the Fe$^{3+}$ high spin 2p$^{3/2}$ peak can exhibit an asymmetric tail to higher binding energy $^{56}$. Expected multiplet splitting in Fe 2p$^{3/2}$ is due to unpaired electrons in its outer valence shells. Splitting may also arise due to the ejected electrons from the core–shell and these unfilled core shells couple with the open valence shell to form several multiplet of different energy with separation given by Van Vleck’s theorem $^{57}$. Accordingly, the Fe 2p$^{3/2}$ peak has a doublet in the steep leading edge and this doublet is fitted with two narrow peaks (FWHM = 1.46 eV) of similar width and intensity within a separation of 1.10 eV. In addition to these two peaks, the remainder portion of the Fe 2p$^{3/2}$ peak can be fitted with a series of similar peaks of decreasing intensity. This multiplet structure was already reported by Gupta and Sen $^{53}$ for the highly ionic Fe$^{3+}$ free ions. Present study also predicts the same multiplet splitting due to the presence of highly ionic Fe$^{3+}$ ions that octahedrally coordinated with hexagonally close

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**Figure 6.** XPS survey spectrum of the hematite nanoparticles.

**Figure 7.** Deconvoluted XPS Fe 2p$^{3/2}$ spectrum of α-Fe$_2$O$_3$ nanoparticles.
packed O\(^{2-}\) ions and form the corundum structure \([54, 55]\). Presence of satellite peak due to charge transfer screening is an additional confirmation for the existence of Fe\(^{3+}\) ions in \(\alpha\)-Fe\(_2\)O\(_3\) \([58–60]\).

The surface valence states of O ions of the representative \(\alpha\)-Fe\(_2\)O\(_3\) sample were identified and the results are shown in figure 8.

The deconvoluted peak of the O 1s spectrum is resolved into two components, included lattice oxygen (Fe-O, 529.19 eV) and surface hydroxyl (–OH, 530.92 eV) species \([21]\). The result demonstrates the existence of hydroxyl species on the surface of the Fe\(_2\)O\(_3\) particles. Such hydroxides can form on some metal and oxide surfaces because of reaction with moisture on exposing the sample in air. Besides, heating the sample at 800 °C, coordinated OH indicates the surface reactiveness of the particles.

In overall observation of the attributes of Fe 2p and O 1s core levels, the valence states of Fe and O are +3 and -2 respectively. The average atomic ratio between Fe and O was found by calculating the area under the peaks of Fe and O. Obtained Fe : O ratio 1 : 2.17 against the ideal ratio 1 : 1.5 confirms the presence of more oxygen in Fe\(_2\)O\(_3\) lattice. Departure from the ideal stoichiometry may also be due to the presence of OH groups on the surface as reported previously by Bharathi et al \([61]\).

### 3.4.3. Surface and electron diffraction studies

Transmission Electron Microscope (TEM) is the only microscopy in which simultaneous identification of surface morphology and phase indexing using SAED are possible. Figure 9 illustrates TEM micro image of hematite nanoparticles and its particle size distribution.

The image show single primary particles in some regions of the focused zone and in other regions typical agglomeration of particles are observed in the hematite sample. Agglomerate includes several primary particles and is therefore termed as secondary particles. Primary particles are held together by weak surface forces (van der Waals, capillary, etc) or by strong chemical bonds. On inspecting the agglomerates, the edges of every particle are clearly seen suggesting the presence of soft agglomerates than hard agglomerates \([62]\). Fe\(_2\)O\(_3\) sample comprise irregularly shaped nanoparticles, mostly rectangular and their edges are polygon shaped. For measuring particle size and their distributions, automated software package (DM3-Image J) \([63]\) was used. Mean particle size obtained is 93 nm and the aspect ratio is 1.32. Based on the particle size data, particle size distribution was plotted as a histogram stating the frequency of occurrence versus the size range \([64]\). Inset of figure 9 shows the particle size distribution histogram of the prepared hematite nanoparticles. The particle size distribution is in the range from 40 to 140 nm and most of the particles are in the range 80–90 nm. Obtained mean particle size 93 nm is almost equal to the histogram value.

In addition to extract the size and shape of hematite nanoparticles, TEM can also be used to determine the crystal structure from the selected area electron diffraction pattern. This is usually done by comparing the experimental intensity versus the scattering vector length diagram of the 2D SAED pattern with the diffraction lines of known phases. As the hematite phase of the prepared sample was already confirmed through PXRD, determining the crystal phase through SAED pattern is an easy task and serves as a confirmatory trail again. Figure 10 shows the bright field selected area electron diffraction (SAED) pattern of \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles annealed at 800 °C.
SAED pattern reveals more concentric rings because of the polycrystalline nature of the $\alpha$-Fe$_2$O$_3$ samples annealed at 800 °C. From the radius of a diffraction rings and with the knowledge of the standard diffraction data, each diffraction ring could be indexed. The distance, $r_{hkl}$ on the pattern between the spot (hkl) and the spot (000) is related to the interplanar spacing between the (hkl) planes of atoms, $d_{hkl}$, by the following equation [65, 66]:

$$ r_{hkl} = \frac{\lambda L}{d_{hkl}} $$

where, ‘L’ is the distance between the sample and the film/screen. Therefore the diffraction pattern is a projection of the reciprocal lattice with projection factor $\lambda L$, because reciprocal lattice vectors have length $1/d_{hkl}$.

The inter-planar d-spacing obtained from the SAED pattern and the indexed (h k l) values are listed in table 3. The ICDD standard and the experimentally obtained d-values through XRD studies are also given for comparison.
The magnetic property of a material usually depends on the crystal structure, especially on the oxidation state of Fe ion is not 2+, even in low-spin have a magnetic moment of 2μB. The spin-polarized calculation reveals paramagnetic behaviour, without saturation magnetization and coercivity. This paramagnetic state of wüstite is because of its nonstoichiometric rock salt structure, with a closed-packed fcc O2− lattice in which Fe2+ ions occupy the octahedral interstitial sites [67]. Usually FeO is paramagnetic at room temperature and this kind of result was already reported for high energy ball milled and collooidly synthesized FeO nanoparticles [68, 69]. Magnetic behavior of the iron oxide sample annealed at 400 °C is shown in figure 11(b). Prepared sample at this annealed temperature is dominantly in Fe2O3 phase along with traces of FeO and Fe3O4. Basically in Fe2O3, the oxidation state of Fe ion is not 2+, but close to 3+. On having 3d electronic configuration in FeO2, Fe3+ ions even in low-spin have a magnetic moment of 2μB. In addition to cations, the anion σ− states are half-filled in FeO2, and thus they can also contribute to the total magnetic moment [70, 71]. The spin-polarized calculation shows that magnetic state lowers the total energy of the system leading to ferromagnetic setting and the O–O bond connecting adjacent octahedra becomes 2.232 Å [18]. So the hysteresis loop of the sample calcined at 400 °C shows a weak ferromagnetic behavior with a remanent magnetization of 0.2063 emu g−1 and magnetic coercivity of about 30 G.

The sample annealed at 800 °C is purely hematite and has no other phases. Since the crystal structure of the material has influence over magnetic transitions, the arrangement of atoms and its spin states are to be considered to decide its magnetic properties. The unit cell of α-Fe2O3 is hexagonal and the primitive cell is rhombohedral. The unit cell consists of two pairs of bilayered Fe atoms along the (1 1 1) axis. Type A pair has shorter Fe–Fe distance than the type B Fe pair. These four Fe atoms (A, B, C, and D) can antiferromagnetically arrange in three ways with specific spin orientations. In model (a), A and D may orient upwards, C and D may orient downwards. In model (b), A and B align upwards, C and D align downwards, and in model (c), A and C upwards, B and D downwards [72]. In all these models, this specific structure persuade antiferromagnetically (AF) ordered spins along the c-axis below the Morin transition temperature (TM = 263 K). Above TM, the basal plane has spins that exhibits antiferromagnetism along with ferromagnetism component due to spin–flip transition [72, 73]. The fourth model also possible, in which all the Fe atoms are aligned upwards resulting ferromagnetism.

Table 3. d-spacing values measured from SAED pattern, ICCD and XRD.

| d-spacing values (Å) | ICCD standard | XRD | SAED | Miller Index | Ratio of ring radius R_{n+1}/R_n | Ratio of d-spacing d_n/d_{n+1} |
|----------------------|---------------|-----|------|--------------|---------------------------------|-------------------------------|
| 3.677                | 3.67816       | 3.67397 | (0 1 2) | 1.3625       | 1.3625                          |
| 2.69649              | 2.69584       | 2.69649 | (1 0 4) | 1.0806       | 1.0806                          |
| 2.51425              | 2.51460       | 2.49350 | (1 1 0) | 1.1343       | 1.1343                          |
| 2.20384              | 2.20386       | 2.19887 | (1 1 3) | 1.1973       | 1.1973                          |
| 1.83890              | 1.83960       | 1.83732 | (0 2 4) | 1.1007       | 1.1007                          |
| 1.69275              | 1.69375       | 1.66921 | (3 1 6) | 1.0532       | 1.0532                          |
| 1.59733              | 1.59930       | 1.58484 | (0 1 8) | 1.0964       | 1.0964                          |
| 1.45160              | 1.45367       | 1.44586 | (3 0 0) | 1.0187       | 1.0187                          |
| 1.41194              | —             | 1.41898 | (1 2 5) | —            | —                               |

Obtained Miller indices and d-spacing values from the SAED pattern are comparable to the ICCD standard and the valued obtained from XRD diffraction studies. The ratio of ring radius, R_{n+1}/R_n of (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (0 1 8), (3 0 0), and (1 2 5) planes of Fe2O3 are respectively 1.3625, 1.0806, 1.1343, 1.1973, 1.1007, 1.0532, 1.0964, 1.0187 and 1.2913. Obtained R_{n+1}/R_n values are equal to the ratio of the reciprocal of interplanar spacing, d_n/d_{n+1} that meet the characteristic of Fe2O3 corundum structure without any addition phases.

3.5. Effect of structural purity and magnetic behavior

Likewise in XRD, structural evolution of α-Fe2O3 on annealing can also be assessed through magnetic study. Variation of magnetization against magnetic field at room temperature was measured for the as-prepared and annealed samples at 400 and 800 °C. Obtained magnetic hysteresis loop by cycling the magnetic field between −15000 to 15000 G are shown in figure 11.

On visualization, the shape of the curve itself is self explanatory regarding the nature of the sample and its phase purity. The magnetic property of a material usually depends on the crystal structure, especially on arrangement anions with cation [67]. Figure 11(a) shows the magnetization curve of the as-prepared iron oxide nanoparticles. XRD studies revealed that the as-prepared sample is crystalline and is in mixed phase consisting of FeO (wüstite), FeO2, and Fe2O3 phases, in which the wüstite is dominant. Shape of the magnetization curve reveals paramagnetic behaviour, without saturation magnetization and coercivity. This paramagnetic state of wüstite is because of its nonstoichiometric rock salt structure, with a closed-packed fcc O2− lattice in which Fe2+ ions occupy the octahedral interstitial sites [67]. Usually FeO is paramagnetic at room temperature and this kind of result was already reported for high energy ball milled and colloidal synthesized FeO nanoparticles [68, 69]. Magnetic behavior of the iron oxide sample annealed at 400 °C is shown in figure 11(b). Prepared sample at this annealed temperature is dominantly in Fe2O3 phase along with traces of FeO and Fe3O4. Basically in Fe2O3, the oxidation state of Fe ion is not 2+, but close to 3+. On having 3d electronic configuration in FeO2, Fe3+ ions even in low-spin have a magnetic moment of 2μB. In addition to cations, the anion σ− states are half-filled in FeO2, and thus they can also contribute to the total magnetic moment [70, 71]. The spin-polarized calculation shows that magnetic state lowers the total energy of the system leading to ferromagnetic setting and the O–O bond connecting adjacent octahedra becomes 2.232 Å [18]. So the hysteresis loop of the sample calcined at 400 °C shows a weak ferromagnetic behavior with a remanent magnetization of 0.2063 emu g−1 and magnetic coercivity of about 30 G.

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orientation of the Fe atoms along the c-axis. Accordingly, for antiferromagnetic ordering, obtained c/a value, Fe-Fe (A pair) and Fe-Fe (B pair) distances are respectively in the range 2.67–2.77, 2.803–2.859 Å and 3.958–4.033 Å. Similarly for the ferromagnetic ordering, reported values are 2.85, 2.689 Å and 4.380 Å. In the present study, obtained structural parameter on refining the structural data of the Fe₂O₃-800 sample are c/a = 2.73048, Fe-Fe (A) = 2.8984 Å and Fe-Fe (B) = 4.0935. On comparing the values with the AFM and FM values, a conclusion may be attained in favor of the presence AFM behavior in Fe₂O₃-800 sample. However, the magnetic curve of the sample exhibits larger magnetic coercivity of about 1778 G (figure 11(c)). Usually, enhanced shape anisotropy induces larger magnetic coercivity. Since the particles in Fe₂O₃-800 sample are non-spherical with aspect ratio 1.7, observed enhanced coercivity can be considered due to shape anisotropy [32]. Thus magnetization judges the purity of the prepared iron oxide sample by revealing AFM character if the phase is hematite and is ferromagnetic or paramagnetic if additional phases FeO₂ and FeO are dominant.

4. Conclusions

Iron oxide has been synthesized by the simple and cost effective co-precipitation method by controlling the pH of the precursor. Structural analysis revealed the presence of impurity phases FeO and FeO₂ along with the major α-Fe₂O₃ in as-prepared sample. As thermogravimetry analysis exposed the need of annealing, as-prepared samples were annealed for structural transformations. The impurity phases were gradually removed on annealing at 800 °C and the sample was completely transformed to α-Fe₂O₃ phase. Rietveld structural refinement also confirmed the attainment of phase pure α-Fe₂O₃ and its hexagonal unit cell consists of two pairs of bilayered Fe atoms along (1 1 1). Hematite phase was further confirmed through FT-Raman, XPS and TEM analysis. On annealing, gradual structural transformation from the mixed phase to pure α-Fe₂O₃ phase was further confirmed through magnetic studies. Phase refinement from mixed to pure α-Fe₂O₃ exhibited magnetic structure variation through paramagnetic, ferromagnetic and antiferromagnetic with large coercivity. From the observed findings, present study recommended either XRD or magnetic study is adequate to identify the purity of hematite phase present in the iron oxide sample prepared through co-precipitation technique.

Figure 11. Room temperature magnetization curves of iron oxide nanoparticles.
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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

ORCID iDs

J Sharmila Justus © https://orcid.org/0000-0001-6570-8446
K Saravanakumar © https://orcid.org/0000-0002-0304-133X
A Moses Ezhil Raj © https://orcid.org/0000-0002-4261-8904

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