Morphological and magnetic features of Ru(III) doped magnetite ultrafine nanoparticles

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Abstract
Magnetite nanoparticles constitute a class of nanoparticles which is easily manipulated using a magnetic field. Magnetite nanoparticles doped with ruthenium (Ru) ions [Ru_xFe_{3-x}O_4] were synthesized via co-precipitation method where 0.0 \leq x \leq 0.5 with step 0.1. The obtained nanopowder was investigated via x-ray diffraction, FTIR, FESEM. It was shown that Ru ions were incorporated successfully into a magnetite structure with a slight influence on the value of the lattice parameter which increased from 8.354 Å at x = 0.0 to 8.403 Å at x = 0.3, while crystallite size deteriorated from 20.1 nm at x = 0.0 to be around 3 nm at x = 0.3. In addition, the surface roughness average was influenced by the dopant content, where it decreased from 35.6 nm at the pure magnetite to be 25.87 nm at x = 0.3. The ICP examination indicated that the measured contents of Ru ions through competitions were around 41 ppm and increased to 190 ppm comparing with 43 and 199 ppm as a theoretical value both x = 0.1 and 0.5. Regarding magnetic properties, the coercivity raised from 40.11 Oe and raised 44.66 Oe for x = 0.0 and 0.5, respectively. This manipulated behavior of magnetite due to dopant suggests that desired properties could be achieved via the dopant strategy to be used for several applications.

1. Introduction

Nanostructure spinel oxide with the general formula (AB_2O_4) that have been crystallized in spinel structure has a thorough interest over decades due to their numerous applications such as catalysts, pigments, and biomedical engineering applications [1, 2]. One of the most common ferrites is magnetite (ideal formula: Fe^{3+} (Fe^{2+}Fe^{3+})_2O_4) which is found in a wide range of extraterrestrial materials, as well as in terrestrial igneous, metamorphic, and sedimentary environments [3]. In the recent few decades, Magnetic nanoparticles, especially magnetite (Fe_3O_4), have grown extensive attention [4, 5]. They display unique properties such as low toxicity against human cells and convenience biocompatibility under physiological conditions [6, 7]. In addition, by reducing their particle size, they may transform to be superparamagnetic materials [8, 9]. Currently, magnetite nanoparticles are approved by the US food and drug administration (FDA) to be used in humans for therapy and as MRI contrast agents [10, 11]; in addition to many biomedical applications under investigations such as magnetic targeting, cell separation, drug delivery and for hyperthermia treatment of cancer [12]. Therefore, more efforts have been devoted to the synthesis of magnetite nanoparticles. Many preparation routes were reported, including coprecipitation, sonochemistry, colloidal method, combustion synthesis, solvothermal synthesis, hydrothermal method, microemulsion method, and thermal decomposition [13]. Magnetic nanoparticles are the subject of intense international research owing to the potential applications, and according to a Scopus statistical analysis of the search results, it was found that the magnetite researches is increasing with time. It is found that in 2019 there are over 3500 research articles reporting the ‘magnetite’ as it was illustrated in figure 1.
Consequently, the development of an innovative synthetic methodology is crucial to enrich the convenient properties of these compounds [14]. As a spinel-group mineral, magnetite crystallized in a space group of Fd–3 m, and due to its nature as an inverted spinel group, Fe$^{2+}$ ions occupy the octahedral sites, whilst Fe$^{3+}$ ions are distributed on both tetrahedral and octahedral sites [15]. However, the structure resilience of magnetite allows being substituted with a numerous number of cations which lead to the formation of many compositional variations [16, 17]. In such a way, divalent cations including Mn$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, Co$^{2+}$, and Zn$^{2+}$ can replace Fe$^{2+}$ sites, while trivalent cations such as Mn$^{3+}$, Cr$^{3+}$, and Al$^{3+}$ may substitute Fe$^{3+}$ sites [18, 19]. Therefore, a chemical composition may be classified as an intermediate between normal and inverse spinel structures. Generally, in spinel ferrite, superparamagnetism could be obvious if the particles were less than 30 nm. However, larger particles may display ferro- or ferromagnetic properties. In addition to that, this highly dependent magnetic behavior on both size and morphology demands more attention to tailor these properties to display desired behavior [17].

Suhong Zhang et al synthesized magnetite nanoparticles via co-precipitation method at a weakly basic solution at a low temperature. They found that the magnetization measurement confirmed the magnetite possesses a quasi-superparamagnetic property [20]. Whilst Junya Zhang et al have investigated the influence of magnetite nanoparticles on the performance of antibiotic resistance genes through the anaerobic digestion of swine manure. They showed that the magnetite could enhance methane production by 6.0% [21].

On the other hand, Mahmoud F Zawrah et al have investigated magnetite with particle size less than 10 nm for heavy metal removal. The results displayed that the adsorbents retained about 90% for Pb$^{2+}$, 40% for Cu$^{2+}$, and 30% for Zn$^{2+}$ of their initial adsorption efficiency after 3 cycles, which may suggest them to be used several times [22]. Regarding dopant magnetite, Zargar et al synthesized polyethylene glycol coated on the surface of Zn$_{0.3}$Fe$_{2.7}$O$_4$ magnetic nanoparticles, and the cell culture studies showed that under-investigated samples are non-toxic, which may suggest them to be used for biomedical applications [23]. In addition, Vojoudi et al designed a homemade column contain magnetite mesoporous coated with silica to be used for organic pollutants removal from aqueous solutions. The results showed that the maximum absorption capacity was 162 mg ml$^{-1}$ in the case of everzol blue, which may indicate this strategy to be used for the removal of anionic dyes in aqueous solutions [24].

A transition metal nanoparticle (NPs) such as Ru was extensively used as catalysts. Many metals have been tested in hydrolysis. The Ru NPs demonstrated very high activity in ex:Ru$^0$/Fe$_3$O$_4$ and Ru$^0$/SiO$_2$Fe$_3$O$_4$. They were found to be highly active and reusable catalysts in hydrolytic dehydrogenation [25]. Ruthenium (II) complexes prove to be suitable dye-encapsulated silica due to its good stability [26]. Also, ruthenium (II) complexes with silica nanoparticles can be applied in bio-detection and bioanalysis [27]. A new synthesized kind of biocompatible nanostructure contains magnetite core and ruthenium (II) complexes encapsulated silica shell [28]. On the other hand, ruthenium complexes have been investigated through a plethora of compounds to inhibit the proliferation of tumor cells [29–34]. For instance, poly-pyridine Ru(III) complexes had been investigated for their antitumor activity. Xuanhao Zhao et al displayed that the utilization of a phenylethynyl group in Ru(II) complexes may strongly improve antitumor activity, which may introduce a significant guide to...
optimize antitumor drugs [29]. Nevertheless, the combination of Ru ions and magnetite is not common to be investigated thoroughly.

Having the ideas mentioned above; due to the hyperthermia behavior of magnetite under alternative magnetic fields associating with those anti-tumor activities that are own to Ru$^{3+}$, one can combine these properties together by introducing the Ru$^{3+}$ ions into the magnetite structure on account of Fe$^{3+}$.

Therefore, the aim of this piece of work is to investigate the influence of Ru$^{3+}$ ions incorporation on the physicochemical characteristics of the magnetite spinel matrix.

2. Materials and methods

2.1. Materials
All chemicals used were of analytical reagent grade, and of the highest purity available. The chemicals list included; tetrahydrate ferrous chloride FeCl$_2$.4H$_2$O (>99.9%) (LOBA, India), hexahydrate ferric chloride FeCl$_3$.6H$_2$O (>97.9%) were purchased from LOBA, India, ammonium hydroxide 30%, ruthenium (III) chloride trihydrate (RuCl$_3$.3H$_2$O), and hydrochloric acid (HCl) with concentration about 30%–34%. Nitrogen gas has been used with a purity of 99.5%. 1, 10 Phenanthroline (M.wt = 180.21 g mol$^{-1}$). Sodium salicylate (M.wt = 160.11 g mol$^{-1}$). The distilled water used in all preparations usually collected from glass equipment.

2.2. Synthesis of magnetite nanoparticles (MNPs)
Ultrafine magnetite nanoparticles (MNPs) were synthesized using the co-precipitation technique. 0.02 M of FeCl$_3$.6H$_2$O and 0.01 M of FeCl$_2$.4H$_2$O were prepared in deionized water for each one while nitrogen gas flows through the mixture continuously. Then ammonium hydroxide was added drop wisely to the mixture during the stirring process until the suspension becomes homogeneous. The complete precipitation of Fe$_3$O$_4$ occurs at pH above 9, while the continuous bubbling of nitrogen gas is maintained to prevent the formation of the hematite as a secondary phase. The black precipitate was washed several times with distilled water several times, to make sure of removing all the excess ions from the solution. Then it is dried in a dryer at 50–60 °C to obtain the black powder of the magnetite. The doped samples were carried out via reducing the content of FeCl$_3$.6H$_2$O upon the following equation:

\[
(2 - x)\text{FeCl}_3.6\text{H}_2\text{O} + \text{FeCl}_2.4\text{H}_2\text{O} + x\text{RuCl}_3.3\text{H}_2\text{O} \rightarrow \text{Fe}^{2+}\text{Ru}_x\text{Fe}_{2-x}^{3+}\text{O}_4
\]

Where 0.0 ≤ x ≤ 0.5 with step 0.1; the synthesis procedure is illustrated in figure 2.

2.3. Crystal structure
The phase identification and structural analysis were carried out using X-ray diffractometer model (Analytical-x’ Pertpro carried out using Cu k$_{α1}$ radiation, λ = 1.5404 Å, 45 kV, 40 mA, Netherlands) at room temperature for...
all samples. The data were collected over the range of 2θ between 10 and 70° with step 0.02 and step time 0.5 s. The average size of the crystallites was estimated from the diffraction patterns using Scherrer’s equation \( L = \frac{0.9 \lambda}{\beta \cos \theta} \) [35–37]. Where \( \lambda \) is the target wavelength, \( \beta \) is the corrected full width at half maximum (FWHM) and \( \theta \) is the incident angle (2θ is the diffraction angle).

2.4. FT-IR measurements

The spectra of Fourier transformer infrared (FT-IR) were carried out by FT-IR spectrometer (Perkin-Elmer system 2000) on a range of 4000 to 400 cm\(^{-1}\); at Cairo University Microanalytical center.

2.5. Surface morphology

The surface morphology of the specimens was investigated via field emission scanning electron microscope (FESEM) under an operating voltage of 20–30 kV with model QUANTA-FEG250 (Netherlands).

2.6. Roughness measurements

After the investigation of MNPs surface morphology under FESEM, the output graphs were inserted into Gwyddion 2.45 software to be examined [38–40]. The micrographs were utilized with tiff extensions. Then, they were cut from the edges using the same software to avoid their boundaries. Lastly, the 3D micrograph was processed for each specimen while the resolution of micrographs was fixed at 1400 × 900 pixels to simplify the comparison process among them. Finally, some of the roughness parameters were calculated via the same software.

In order to confirm the proposed general formula [Ru\(_2\)Fe\(_{3-x}\)O\(_4\)] of the prepared nano-material; its elemental constituents were measured using spectroscopic techniques:

2.7. Inductively coupled plasma (ICP) measurements

For the analysis of elemental components, an Optima 7300 DV ICP spectrometer (PerkinElmer, USA) with axial plasma observation was utilized.
2.8. Spectrophotometric measurements
The spectrophotometric microdetermination of elemental constituents of the prepared nanomaterials in solutions was carried out using Optizen recording Spectrophotometer, UV–vis range from 150–1100 nm model 5u470/pop 127022-00 and quartz cell of 1 cm optical length was used.

2.9. Magnetic properties
The investigation of the magnetic properties of the as-synthesized Ru-MNPs with their different ratios was carried out using a vibrating sample magnetometer (VSM) at room temperature in the magnetic field range −20 K Oe to 20 K Oe.

3. Results and discussion

3.1. X-ray diffraction (XRD)
The XRD of MNPs doped with different content of Ru upon the formula [Fe²⁺RuₓFe⁴⁺₃−ₓO₄]; 0.0 ≤ x ≤ 0.5 with step 0.1 is shown in figure 3. The patterns show that the investigated Ru-MNP was crystallized in a single phase with a spinel cubic structure without additional peaks for other phases. All XRD planes of Ru-MNP were indexed according to ICDD card no. 01-088-0315.

| x  | L (nm) | a (Å)  | V (Å³) | ÷ × 10⁻³ | Dc (g cm⁻³) |
|----|--------|--------|--------|----------|-------------|
| 0.0| 20     | 8.354  | 583.01 | 3.07     | 5.27        |
| 0.1| 12     | 8.366  | 585.66 | 11.49    | 5.53        |
| 0.2| 10     | 8.341  | 580.51 | 11.87    | 5.55        |
| 0.3| 3      | 8.403  | 593.42 | 13.28    | 5.48        |
| 0.4| 3      | 8.386  | 589.93 | 13.32    | 5.62        |
| 0.5| 8      | 8.356  | 583.52 | 9.24     | 5.78        |

At x = 0.0; the observed diffraction peaks (220), (222), (400), (442), (511), and (440), at 2θ = 30, 35.5, 43, 53.5, 57 and 62.2° respectively were corresponded to those of pure magnetite. It is noticed that the XRD peaks broadened at the higher content of Ru(III) ions, which may refer to two reasons; lattice distortion and low crystallinity. Therefore, it is expected that the crystallinity plunges with increasing x which may refer to the successful incorporation of Ru(III) ions into magnetite crystals. In addition, there is no peak shift detected which attributed to the resemblance of ionic radii between the host and the doped ions. In addition to that, with increasing of x, crystallite size plummets from 20.1 nm at x = 0.0 to reach around 8 nm at x = 0.5, while the lowest value of crystallite size was achieved at x = 0.4 and it was 3 nm as it is reported in table 1.

From table 1, it is reported that the value of the lattice parameter (a) raises around 0.14% following the increasing of Ru content from x = 0.1 to x = 0.0. This hypothesis could be explained by supposing that Ru³⁺ at (6-folds) have partially replaced Fe³⁺ (6-folds), where their ionic radii were 0.68 and 0.645 Å, respectively. Simultaneously, whilst lattice strain does not exceed 3.07 × 10⁻³ at x = 0.0, it jumped to 11.49 × 10⁻³ at x = 0.1; which may indicate the great influence of ionic substitution into magnetite structure, despite the obvious similarity in ionic radii of both Ru³⁺ and Fe³⁺. Moreover, the crystallite size behaves against lattice distortion, therefore crystallite size dropped from 20.1 to 12.5 nm at x = 0.0 and x = 0.1 respectively. This dip matches well with the speculation that ionic substitution induces distortion positions in a lattice, which may inhibit the crystal growth in the grains.

By increasing Ru content, crystallite size keeps deterioration down to the lowest value at x = 0.3 and 0.4, which is around 3 nm for both contents. While the lattice parameter (a) achieved its highest value (8.403 Å) which refers to 0.85% of lattice expansion compared with x = 0.0, this behavior was significant in the unit cell volume. Thus it jumped with around 1.75% than x = 0.0, whilst lattice distortion reached its summit with a value of about 13.32 × 10⁻³ at x = 0.4.

It is clear that theoretical density increases significantly with Ru content rising. This could be attributed to the fractions of higher atomic weight that have been contributed to the magnetite structure. Moreover, theoretical density has peaked at x = 0.5 with 8.2% more than the pure one.
3.2. FT-IR analyses

Figure 4 shows the FT-IR spectra of Ru-MNPs at different Ru concentrations. The FT-IR is utilized to identify the main functional groups of the demanding material. Therefore, it is obvious that the recognized bands of Figure 4.

Table 2. Characteristic bands of Ru-MNPs at different content of Ru.

| x  | 0.0  | 0.1  | 0.2  | 0.3  | 0.4  | 0.5  | Assignment       | Reference |
|----|------|------|------|------|------|------|------------------|----------|
|    |      |      |      |      |      | 438.7 | Fe-O (41, 45)    |          |
|    |      |      |      |      |      | 455.1 |                  |          |
| 569.9 | 568.9 |      |      |      |      |       |                  |          |
| 585.3 | 588.3 | 577.6 | 574.7 |      |      |       |                  |          |
| 1390.4 | 1386.6 | 1386.5 |         |      |      |       |                  | [42]     |
| 1630.5 | 1634.4 | 1630.5 | 1628.6 | 1630.5 | 1628.5 | H–O–H bending (43) |          |
| 3424 | 3419.2 | 3423.9 | 3437.5 |      |      |       |                  | [43]     |
| 3438.5 | 3444.2 |      |      |      |      |       |                  |          |

Figure 5. TEM micrographs of magnetite doped with different contents of Ru ions; (a) x = 0.0, (b) x = 0.4.

3.2. FT-IR analyses

Figure 4 shows the FT-IR spectra of Ru-MNPs at different Ru concentrations. The FT-IR is utilized to identify the main functional groups of the demanding material. Therefore, it is obvious that the recognized bands of
magnetite appear for all the ratios confirming the formation of the pure magnetite phase. The characteristic bands below 700 cm\(^{-1}\) come from the vibrational mode of Fe–O bonds belonging to iron oxide \([41]\).

The absorption band of 1386.5 cm\(^{-1}\) that has been displayed at \(x = 1.0\) could be assigned to the Fe–O bond \([42]\). The broad bands that appear around 3419.2–3444.2 cm\(^{-1}\) may be attributed to the stretching mode of water that is absorbed through the porous structure. The bands between 1628.5–1634.4 cm\(^{-1}\) could belong to the bending mode of H–O–H, which may refer to the high content of hydroxyl groups on the Ru-MNPs surface \([43, 44]\). The characteristic bands of Ru-MNPs are reported in table 2.

### 3.3. Particles size and distribution

TEM micrographs exhibit that pure MNPs were formed in agglomerated spherical shapes with diameters around 40–65 nm as obvious in figures 5(a), (b). While the doped one was at \(x = 0.4\) possesses particle size in the range of 28–54 nm. It might be noticed that additional Ru ions content induced low crystallinity for the as-synthesized particles. This shrinkage is referred to as the high content of crystallographic defects accompanied by the redistribution of cation among nonequivalent lattice sites. Therefore, additional Ru ions may manipulate both particle size and distribution of MNPs.

### 3.4. Morphological feature

The FESEM was utilized to visualize very small topographic details on the surface of the as-prepared samples. Figures 6(a), (b) shows the surface morphology of Ru-MNPs at \(x = 0.0\) and 0.3 respectively. It is obvious that the pure MNPs appear as agglomerated spheres with an average diameter of around 100 nm with an observed intergranular porosity. While \(x = 0.3\) represents more agglomerated grains. This tendency of agglomeration at the higher content of Ru ions may be attributed to the higher anisotropy of structure due to the intrinsic lattice defects that raised with Ru substitutions \([39]\).

On the other hand, the surface roughness parameters are reported in table 3. It is shown that the roughness average \((R_s)\) decreases massively from 35.60 nm at the pure magnetite to reach 25.87 nm for the Ru ratio \(x = 0.3\); which may refer to the higher energy of the pure MNPs surface compared with the doped one. Also, the Root means square roughness \((R_q)\) follows the same behavior literally; which \(x = 0.3\) is higher than the pure magnetite and matches well with the results from FESEM micrographs. The importance of roughness behavior
comes from its ability to control the interaction behavior of the MNPs with their environment. In addition to that, enhancement of surface roughness improves the biocompatibility of the implant material because the rough surface offers numerous sites of defects able to interacting with the host environment to reduce its energy \cite{37, 39}. Therefore, manipulating surface morphology may lead to controlling the release of surface ions into the host material; which may introduce a great benefit for biological applications \cite{46, 47}.

### 3.5. Elemental analysis (EDX)

Figure 7 demonstrates the EDX spectrum; which is carried out for the sample of x = 0.3. The spectrum shows two major peaks which were assigned to Fe, O, and these major peaks are around 246, 82 and 369 keV which corresponds to the binding energies of Fe \cite{25}. It also confirms that no other impurities have been identified. Also, the EDX shows that Ru is the only element detected; which confirms the successful preparation for the magnetite doped Ru. It refers that the measured elemental ratios in the composition is \([Ru_{0.14}Fe_{2.14}O_4]\) which is close to the nominals formula.

In order to confirm the proposed general formula \([Ru_xFe_{3-x}O_4]\) of the prepared nano-material; its elemental constituents were measured using spectroscopic techniques.

### 3.6. Inductively coupled plasma (ICP)

International standards recommend more modern instrumental methods of atomic emission or x-ray fluorescence analysis \cite{48}, including inductively coupled plasma atomic emission spectrometry (ICP-AES) with spectrometer calibration by standard aqueous solutions corresponding to the composition of the analyzed samples. This method has been used to analyze and determine the Ru contribution through MNPs comparing with the theoretical calculation as presented in table 4.

It could be observed that the theoretical calculations of Ru ions through magnetite started from 43 ppm and grew to reach 199 ppm, while the measured one was slightly diverged to start with 41 ppm reaching to its maximum one of 190 ppm for x = 0.1 and 0.5, respectively.

### 3.7. Spectrophotometric measurements

In the present work; the properties of the prepared magnetic nanomaterials with chemical formula \([Ru_xFe_{3-x}O_4]\), where x = \((0.0, 0.1, 0.2, 0.3, 0.4, 0.5)\) were investigated. The characteristics of the nanomaterials depend upon their crystal sizes, shapes, and structures, which were characterized by advanced and sophisticated...
methods of analyses using different spectroscopic techniques to determine iron and ruthenium as the main constituent as follows:

3.7.1. Spectrophotometric microdetermination of standard ferric chloride without an indicator and with sodium salicylate as an indicator

Standard ferric chloride solution is measured spectrophotometrically without an indicator and with sodium salicylate as an indicator at $\lambda_{\text{max}} = 300$ nm, with molar absorptivity $\varepsilon = 0.9819 \times 10^3$ mol$^{-1}$ cm$^{-1}$; while ferric chloride using sodium salicylate as indicator reaction product attains maximum absorption at $\lambda_{\text{max}} = 530$ nm with molar absorptivity $\varepsilon = 1.3549 \times 10^3$ mol$^{-1}$ cm$^{-1}$ respectively. From these curves, $\lambda_{\text{max}} = 530$ nm is selected to determine Fe$^{3+}$ in the prepared nanomaterials.

Figure 8. (a), (b) the absorption spectra of standard ferric chloride at $\lambda_{\text{max}} = 300$ nm without indicator. And at $\lambda_{\text{max}} = 330$ with sodium salicylate as an indicator respectively.

Figure 9. The absorption spectra of standard Ruthenium chloride, (a) without indicator, (b) with 1,10-phenanthroline indicator.

Table 4. Shows the ICP comparing the difference between the theoretical and the practical of the ruthenium content in the nanomaterials.

| x  | Theoretical Ru content (ppm) | Practical Ru content (ppm) |
|----|------------------------------|---------------------------|
| 0  | 0.0                          | 0.0                       |
| 0.1| 43                           | 41                        |
| 0.2| 84                           | 47                        |
| 0.3| 124                          | 100                       |
| 0.4| 162                          | 155                       |
| 0.5| 199                          | 190                       |
3.7.2. Spectrophotometric of standard ruthenium chloride with/without indicator

Standard ruthenium chloride solution is scanned spectrophotometrically without an indicator and with 1, 10-phenanthroline as an indicator at figures 9(a), (b), respectively. The obtained absorption spectra indicated that ruthenium chloride reached the \( \lambda_{\text{max}} \) at 310 nm, with molar absorptivity \( \varepsilon = 0.06 \times 10^2 \text{ lm mol}^{-1} \text{ cm}^{-1} \) whereas the \( \lambda_{\text{max}} \) of the ruthenium chloride 1, 10-phenanthroline reaction product was 450 nm with \( \varepsilon = 0.01349 \times 10^3 \text{ lm mol}^{-1} \text{ cm}^{-1} \).

Among of many spectrophotometric methods for ruthenium determination, the method based on the complexation of Ru(III) by 1,10-phenanthroline is remarkably pragmatic, cheap, and simple for varied laboratory usage. 1,10-phenanthroline is a bidentate \( N,N \)-donor ligand which binds to ruthenium forming inert, stable and colored chelate tris(phenanthroline) Ru(III), which therefore is an exceptional candidate for spectrophotometric measurements. Ruthenium was also tested spectrophotometric without and with 1,10-phenanthroline and the results obtained are given in figure 9.

It shows two main peaks at \( \lambda_{\text{max}} = 310 \text{ nm} \) without an indicator and with an indicator at \( \lambda_{\text{max}} = 450 \text{ nm} \) respectively. From these curves \( \lambda_{\text{max}} = 310 \text{ nm} \) is selected to determine ruthenium without an indicator and \( \lambda_{\text{max}} = 450 \text{ nm} \) using 1,10-phenanthroline as an indicator in the prepared nanomaterials.

Therefore it appreciates determining both Fe\(^{3+}\) and Ru\(^{3+}\) in their nanomaterials mixture using sodium salicylate as a selective indicator for ferric and 1,10-phenanthroline as a selective indicator for ruthenium without noticed interference, aiming to confirm ICP-EAS for ruthenium and to confirm the general formula of the prepared nanomaterials \([\text{Ru}_x \text{Fe}_{(3-x)} \text{O}_4] \), where \( x = (0.0, 0.1, 0.2, 0.3, 0.4, 0.5) \).

3.7.3. Chemical analyses of the constituents of magnetite doped with ruthenium ions \([\text{Ru}_x \text{Fe}_{(3-x)} \text{O}_4] \)

The measured spectra of the prepared nanomaterials solutions of different ratios without an indicator (figure 10(a)) with 1,10-phenanthroline indicator (figure 10(b)), and with salicylate indicator (figure 10(c)) are given.

![Figure 10](image-url)
From these curves (figure 10(a)) the absorbance is linearly increased as the concentration of ruthenium increases with increasing the x ratio, which only a slight deviation from linearity is observed, the only explanation for this increase is the presence of the ruthenium in the structure as both of their absorbance have merged at $\lambda = 335$ nm which proofs the investigated chemical structure. Since the linear range is wide, this method is suitable for the determination of ruthenium in milligram amounts of its complex nanocomposites.

The obtained data of microdetermined Ru ($\mu$ gm l$^{-1}$) in nanocomposite without an indicator is given in table 5.

At figure 10(b) obtained by using 1,10-phenanthroline indicator, the absorbance is linearly increased as the concentration of ruthenium increases with increasing the x ratio; which can be indicated due to the presence of the ruthenium ions and obtained data of Ru measured by the indicator is given in table 6. Thus, spectrophotometric measurements match well with the ICP-AES results, whereas Ru ions have been incorporated successfully into magnetite structure with adequate concentrations. Whilst at figure 10(c), the microdetermination analysis for Fe$^{3+}$ in the Fe$^{2+}$Ru$_x$Fe$_{2-x}$O$_4$ using sodium salicylate as an indicator the absorbance is linearly decreased as the concentration of ruthenium increases with increasing the x ratio as shown by the data represented in table 7. It can be explained as the Ru ions replaced the Fe$^{3+}$ in the chemical structure of nano-materials during increasing its ratio for $x = 0.1 \pm 0.5$. This analysis revealed the successful spectrophotometric measurements of Fe$^{3+}$ and Ru$^{3+}$ ions with and without indicators [49]. On the other hand, it is noticed that the concentration of Fe$^{3+}$ determined spectrophotometrically using sodium salicylate indicator decreasing with the increase of Ru$^{3+}$ in the entity of the prepared nanomaterials varied ratio.

| Table 5. Microdetermination of the ruthenium ions in the prepared nanomaterials Ru$_x$Fe$_{3-x}$O$_4$ with different X ratios; where X = (0.0, 0.1, 0.2, 0.3, 0.4, 0.5) without indicator at $\lambda = 310$ nm. |
|---|---|---|---|---|---|
| x wt. Taken ($\mu$ gm ml$^{-1}$) | x wt. found ($\mu$ gm ml$^{-1}$) | Recovery % | SD | RSD% |
| 0.1 | 10.107 | 9.31 | 92.07 | 0.0989 | 1.0638 |
| 0.2 | 20.214 | 14.40 | 71.25 | 0.0778 | 0.5400 |
| 0.3 | 30.321 | 31.17 | 102.82 | 0.1061 | 0.3402 |
| 0.4 | 40.428 | 39.49 | 97.68 | 0.7071 | 1.7905 |
| 0.5 | 50.535 | 49.27 | 97.30 | 0.7071 | 1.4352 |

| Table 6. Microdetermination of the ruthenium ions in the prepared nanomaterials Ru$_x$Fe$_{3-x}$O$_4$ with different x ratios; where x = (0.0, 0.1, 0.2, 0.3, 0.4, 0.5) with 10 phenanthroline as indicator at $\lambda = 450$. |
|---|---|---|---|---|---|
| x wt. Taken ($\mu$ gm ml$^{-1}$) | x wt. found ($\mu$ gm ml$^{-1}$) | Recovery % | SD | RSD% |
| 0.0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 10.11 | 11.49 | 113.67 | 0.6364 | 5.5394 |
| 0.2 | 20.21 | 23.67 | 117.10 | 0.4596 | 1.9417 |
| 0.3 | 30.32 | 31.76 | 104.74 | 0.4738 | 1.4918 |
| 0.4 | 40.43 | 40.43 | 100.02 | 0.7778 | 1.9236 |
| 0.5 | 50.54 | 51.30 | 101.52 | 0.9192 | 1.7918 |

| Table 7. Microdetermination of the Fe$^{3+}$ ions in the prepared nanomaterials Ru$_x$Fe$_{3-x}$O$_4$ with different X ratios; where x = (0.0, 0.1, 0.2, 0.3, 0.4, 0.5) with sodium salicylate as indicator $\lambda = 530$ nm. |
|---|---|---|---|---|---|
| x wt. Taken ($\mu$ gm ml$^{-1}$) | x wt. found ($\mu$ gm ml$^{-1}$) | Recovery % | SD | RSD% |
| 0.0 | 167.52 | 167.84 | 100.19 | 0.7071 | 0.4213 |
| 0.1 | 161.94 | 162.70 | 100.47 | 0.4242 | 0.2607 |
| 0.2 | 156.35 | 158.61 | 101.45 | 0.7071 | 0.4458 |
| 0.3 | 150.77 | 151.74 | 100.65 | 1.0201 | 0.7922 |
| 0.4 | 145.18 | 144.17 | 99.30 | 1.1371 | 0.7847 |
| 0.5 | 139.60 | 139.05 | 99.61 | 0.9192 | 0.6611 |
may be attributed to the insertion of Ru$^{3+}$ on the expenses of Fe$^{3+}$ during the variation of the ruthenium ratio from $x = 0.1$ to 0.5. This conclusion is confirmed by the plot of found $\mu$g ml$^{-1}$ Ru and Fe against ratio $x$ in figure 11.

Figure 11. The curve of wt. found ($\mu$g ml$^{-1}$) (a) of Ru$^{3+}$ ions and X ratio in the prepared nanomaterials at 310 nm without an indicator, (b) of Ru$^{3+}$ ions and X ratio in the prepared nanomaterials at 450 nm using 1,10 phenanthroline as an indicator, and (c) curve of Fe$^{3+}$ versus X ratio at 530 nm using sodium salicylate as an indicator.

Figure 12. Magnetic hysteresis loops of the Ru-MNPs as a function of Ru ions.
| x   | Ms emu/g | Mr emu/g | M_r+emu/g | M_r-emu/g | M_r/M_s ×10⁻³ | H_c (Oe) | H_c+ (Oe) | H_c- (Oe) | H_erb (Oe) | Area erg/g |
|-----|----------|----------|-----------|-----------|--------------|----------|----------|----------|-----------|------------|
| 0   | 103.09   | -103.09  | 2.48      | 3.73      | 3.1          | 40.11    | 48.15    | -32.05   | -8.05     | 8637       |
| 0.1 | 91.19    | -91.19   | 2.42      | 4.09      | 3.25         | 44.96    | 56.1     | -33.82   | -11.14    | 7987       |
| 0.2 | 27.03    | -27.072  | 1.01      | 1.5       | 1.25         | 46.34    | 56.81    | -45.96   | -10.85    | 2248       |
| 0.3 | 11.106   | -11.094  | 0.269     | 0.14      | 0.2          | 28.79    | 20.88    | -36.71   | 7.915     | 7872       |
| 0.4 | 15.715   | -15.73   | 0.43      | -0.8      | 0.59         | 37.74    | 49.07    | -35.86   | -13.21    | 1308       |
| 0.5 | 26.912   | -26.914  | 0.81      | -1.1      | 0.95         | 35.37    | 44.66    | -37.59   | -7.065    | 2360       |
3.8. Magnetic properties

The behavior of hysteresis Loops \( M-H \) for the composition of Ru-MNPs is illustrated in figure 12. In addition to that, table 8 shows a deterioration of saturation magnetization \( M_s \) from 103.09 emu g\(^{-1}\) at \( x = 0.0 \) to be 26.912 emu g\(^{-1}\) at \( x = 0.5 \); which may be attributed to the insertion of Ru\(^{3+}\) on the expenses of Fe\(^{3+}\) during the variation of ruthenium ratio from \( x = 0.1 \) to 0.5 and consequently decrease of ferric contribution of magnetic properties of the prepared nanomaterials due to lowering of its concentration.

The degeneration of the magnetization of B site, which is partially replaced by Ru ions. This is because the total magnetization of \( \text{Ru}_x\text{Fe}_{3-x}\text{O}_4 \) is computed by \( M = M_A - M_B \) where \( M_A \) and \( M_B \) are the magnetizations of A and B sites in the general formula of \( \text{AB}_2\text{O}_4 \). The remanence magnetization \( M_r \) values decrease with growing the content of Ru ions into the magnetite structure from 3.1038 emu g\(^{-1}\) at \( x = 0.0 \) up till 0.95184 emu g\(^{-1}\) at \( x = 0.5 \). On the other hand, this slight enhancement of coercivity may be attributed to two sources; particle shape elongation and magnetocrystalline anisotropy. It grows from 40.11 Oe at \( x = 0.0 \) until 56.81 Oe at \( x = 0.2 \); then it degenerates incredibly to be 44.655 Oe at \( x = 0.5 \) as it is shown in figures 13(a)–(d).

Ruthenium is the single element to possess unique distinguished magnetic properties [50]. This discovery was related to quantified tetragons in the films with up to 12 nm thickness. The magnetization decreased with Ru\(^{3+}\) replacing some Fe\(^{3+}\) ions on the octahedral site from 103.09 emu g\(^{-1}\) at \( x = 0.0 \) down to 11 at \( x = 0.3 \). This decrease is certainly due to the difference between the magnetic moments of both Fe\(^{3+}\) ions \((5.85 \text{ B.M})\) and that of Ru\(^{3+}\) \((2.09 \text{ B.M.})\).

Herein, we must mention that the moment of iron ions originated from 3d\(^3\) electrons in high spin configuration. In our case for Fe\(^{3+}\) the 3d orbital splitted into \( t_{2g}^3 e_{g}^2 \) at a high spin configuration which is common for ferrites. On the other hand, by doping Ru\(^{3+}\) on the expense of Fe\(^{3+}\), the magnetic moment of the octahedral site decreased resulting in lowering the net saturation magnetization. When increasing Ru\(^{3+}\), at \( x > 0.3 \); a probable cation redistribution among tetrahedral and octahedral sites takes place. In this case, one expected that some Ru\(^{3+}\) resides on A sites instead of the corresponding Fe\(^{3+}\) cations where the inverse spinel is kept unchanged. Consequently, the magnetic moment associated with A sites decreases which in turns magnified the net moment. In other words, the magnetic dilution of A site with Ru\(^{3+}\) increased the magnetization while that on B site results in an opposite trend. One can accordingly argue that at \( x > 0.3 \), Ru\(^{3+}\) reside in the tetrahedral crystal field causing the increase of the magnetization. All samples possess very small values of squareness ratio indicating the soft character of the nano magnetite under investigation. The values at the coercive field are very small but didn’t vanish at any concentration at this ultrafine size of particles.

Accordingly, the investigated samples could be regarded as single domain nanoclusters. From a closer look to the M–H loop, one could observe the shift of loop away from the origin. All samples exhibit a clear right shift except \( x = 0.3 \) that possesses a left shift. This well-known phenomenon is reported in our earlier work as room...
temperature exchange bias. The latter is commonly observed for small-sized particles as in our case. Herein, we reported the positive exchange bias for Ru$^{3+}$ doped magnetite nanoclusters.

The clear reason is that surface spins are predominantly frozen as compared with a small number of ordered bulk spins as the surface/volume ratio is considered enormous in these reduced dimensions. The samples will look like two different magnetic ordered configurations in close proximity with each other. The exchange bias field ($H_{EB}$) could be computed as [51]:

$$H_{EB} = -\frac{(H_- + H_+)}{2}$$

Where $H_-$ and $H_+$ represent the magnetization intercept with the $-$ve and $+$ve on the field axis. It could be noticed from the values reported in table 8, $H_{EB}$ reached its lowest value at $x = 0.3$ and it was $-13.21$ Oe, while the highest one was $-7.065$ Oe at $x = 0.5$. These values could be explained by supposing that a weak ferromagnetic component close to the crystal surface interact with antiferromagnetic spins in the core [51, 52]. It is also matched with the model of core/shell which may suggest these compositions for many applications including memory elements [53].

4. Conclusion

Different stoichiometric amounts of Ru ions were incorporated into the magnetite structure using the co-precipitation method. A thorough investigation via XRD displayed that unit cell volume has enlarged from 583.01 Å$^3$ at $x = 0.0$ to be 593.42 Å$^3$ at $x = 0.3$. In addition, lattice distortion has incredibly grown from 3.07 at $x = 0.0$ to achieve 13.28 at $x = 0.3$. FESEM micrographs illustrated that pure magnetite was formed in agglomerated spherical grains with diameters around 100 nm. The ICP examination indicated that the measured contents of Ru ions through competitions were around 41 ppm and increased to 190 ppm comparing with 43 and

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