Structural, Magnetic Properties and Electron Paramagnetic Resonance for BaFe$_{12-x}$Hg$_x$O$_{19}$ Hexaferrite Nanoparticles Prepared by Co-Precipitation Method

M.M.E. Barakat $^{a,b}$, D. El-Said Bakeer $^{c,d}$ and Abdel-Hamed Sakr $^d$

$^a$ Physics Department, Faculty of Science, Taibah University, Yanbu, Saudi Arabia; $^b$ Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt; $^c$ Physics Department, Faculty of Science and Arts, Taibah University, Al-Ula, Saudi Arabia; $^d$ Physics Department, Faculty of Science, Damanhour University, Damanhour, Egypt

ABSTRACT
Barium hexaferrite nanoparticles are synthesized through co-precipitation technique at different annealing temperature. Series of BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles, $0.00 \leq x \leq 0.30$, are prepared under the best verified conditions (annealed at 1000°C) to investigate the effect of partial substitution of Hg$^{2+}$ ions on the physical properties of BaFe$_{12}$O$_{19}$ nanoparticles. The hysteresis loops at room temperature show the behavior of hard ferromagnetic. The estimated values of saturation magnetization $M_s$, remnant magnetization $M_r$ and magnetic moment $m_B$ rise as Hg$^{2+}$ ions content increases till $x = 0.10$, beyond which they reduce. A reverse trend is obtained for intrinsic coercivity $H_i$ and coercivity $H_c$ versus Hg$^{2+}$ ions content. BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles are investigated through the measurements of electron paramagnetic resonance (EPR). The calculated EPR parameters show an enhancement for BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles up to $x = 0.10$. The obtained results reveal that samples under investigation can be suitable candidate for different industrial applications.

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1. Introduction
One type of magneto-plumbite group of oxides is M-type hexagonal ferrites with formula $\text{MFe}_{12}\text{O}_{19}$ ($\text{M} = \text{Ba}, \text{Sr}$). Specific attention for barium hexaferrite BaFe$_{12}$O$_{19}$ is always increasing as a result of its large saturation magnetization, strong uniaxial magnetic anisotropy, high Curie temperature, better coercivity, good chemical stability and perfect corrosion resistivity, as well as its low price for production [1]. Therefore, it plays an important role in the magnetic media as the production of permanent magnetic materials, microwave devices and magnetic recording media [2–5].

The structural and magnetic properties for BaFe$_{12}$O$_{19}$ can be achieved either by the substitution with different ions or by using different preparation techniques. The magnetic properties of barium hexaferrite can be enhanced by the partially ions substitution, especially at Fe$^{3+}$ site either with di-, tri- or tetravalent ions [6,7]. The partial ions substitution at Fe$^{3+}$ site leads to change the net magnetic moment per unit and tailor magnetic properties of BaFe$_{12}$O$_{19}$. The enhancement of the net magnetization for this magnetic material can be occurred when the substituted ions occupy spin down sites [8]. Many researchers [9–12] have been investigated the impact of using the suitable transition ions substation ratio at Fe site on coercivity, anisotropy and saturation magnetization for barium hexaferrite. A significant change in both magnetic and structural properties was obtained as a result of the influence of transition ions on the grains growth. On the other hand, the structural and lattice parameters, crystallite and grain sizes, as well as the dislocation density of hexaferrite samples were strongly affected by the composition and preparation conditions. Several techniques can be used for synthesizing hexaferrites such as micro-emulsion [13], sol–gel [14,15], combustion [16], co-precipitation [17], hydro-thermal [18], etc. The most efficient technique for preparing hexaferrites is co-precipitation technique due to its low cost, energy-efficient, easy method and short reaction time [19].

The aim of the present study is not only to obtain the optimum calcination temperature of the preparation of barium hexaferrite nanoparticles by the chemical co-precipitation method but also to study the effect of...
Hg$^{2+}$ ions substitution on the structural and magnetic properties of it. In order to improve its properties to be a suitable candidate in for different industrial application.

2. Experimental techniques

2.1. Samples preparation

Barium hexaferrite nanoparticles, BaFe$_{12}$O$_{19}$ were synthesized by an efficient co-precipitation technique at different annealing temperature (700, 800, 900 and 1000°C) to obtain the optimum annealing temperature necessary for achieving pure phase of barium hexaferrite. The starting materials for this synthesis are barium chloride, (BaCl$_2$.2H$_2$O), ferric chloride (FeCl$_3$) and sodium hydroxide (NaOH). Stoichiometric amounts ratios of these chlorides were dissolved in distilled water, then mixed through magnetic stirrer at 60°C. An alkaline solution (NaOH) was put into the salt solution till pH reached to 12.0. The resulting solution was heated at 90°C with continuous stirring for two hours. The precipitate was collected by magnet and washed with distilled water many times until the pH of the filtrate reached to 7.0 in order to remove unwanted impurities. Then, the precipitate was dried at 80°C. Finally, the dried powders were put into a ceramic crucible of 400–4000cm$^{-1}$ using FTIR 8400S Shimadzu spectrophotometer. The magnetic properties of the prepared samples are studied by vibrating sample magnetometer VSM, Lakeshore 7410, at room temperature. EPR spectra are measured by EPR spectrometer, Bruker Elexys 500, at room temperature.

In order to investigate the effect of partial substitution of Hg$^{2+}$ ions on BaFe$_{12}$O$_{19}$ nanoparticles, a series of BaFe$_{12−x}$Hg$_x$O$_{19}$ nanoparticle, x = 0.00, 0.05, 0.10, 0.20 and 0.30, were synthesized through the indicated co-precipitation technique under the best verified conditions (annealed at 1000°C).

2.2. Measurements

Phase identification of barium hexaferrite is carried out by X-ray powder diffractometer (Bruker D8 advance) with Cu-K$_{α}$ radiation ($λ = 1.54056$ Å) in $2θ$ range 10–80°.

The lattice parameters $a$ and $c$ are determined using the following formula [20]:

$$d_{hkl} = \left( \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{2}{c^2} \right)^{−1/2} \tag{1}$$

where $d_{hkl}$ is the crystal face distance and $(hkl)$ are the Miller indices.

The unit cell volume for barium hexaferrite can be estimated using the lattice parameters $a$ and $c$ from the following relation:

$$V = \frac{\sqrt{3}}{2}a^2c \tag{2}$$

The theoretical (X-ray) density ($ρ_x$) and bulk density ($ρ_b$) of the prepared powders are determined by applying Eqs.3,4, respectively.

$$ρ_x = \frac{ZM_{wt}}{N_AV} \tag{3}$$

$$ρ_b = \frac{m}{πr^2h} \tag{4}$$

where $Z = 2$ indicating 2 formula units, $M_{wt}$ is material molecular weight, $m$ is the pellet mass, $r$ is the pellet radius and $h$ is the pellet thickness.

The percentage porosity ($P\%$) of the samples is estimated in terms of both the theoretical and bulk densities of the samples as follows [21]:

$$P\% = \left(1 - \frac{ρ_b}{ρ_x}\right) \times 100 \tag{5}$$

The average nanoparticle size is determined using Jeol transmission electron microscope JEM- 2100, carried out at 200 kV through dispersing the powders in diluted HCl on a copper grid. The elemental compositions of barium hexaferrites are studied by scanning electron microscopy (SEM/ EDS; JSM-7200F). The estimated value of lattice parameters for sample B-1000 are consistent with published values [22,23].

3. Results and discussion

In order to study the effect of annealing temperature on phase formation, the percentage, the type of impurities formed and crystallite size were determined. XRD analysis was applied on the samples. Figure 1 shows XRD pattern of the barium hexaferrite, BaFe$_{12}$O$_{19}$, samples annealed at different temperatures 700°C (B-700), 800°C (B-800), 900°C (B-900) and 1000°C (B-1000). The estimated values of crystallite size and lattice parameters at different annealing temperature are listed in Table 1. Table 1 clarifies that with increasing temperature, the percentage of intermediate phase Fe$_2$O$_3$ decreases, while the percentage of barium hexaferrite increases until reached to single phase at annealing temperature 1000°C. The crystallite size increases with increasing annealing temperature as a result of the tendency of particles, where they are collected together and form large particles. The estimated value of lattice parameters for samples B-700, B-800 and B-900 are inconsistent with the reported values as a result of the presence of impurities beside the basic phase. On the other hand, the lattice parameters for sample B-1000 are consistent with published values [22,23].

Figure 2 shows XRD patterns of hexaferrite BaFe$_{12−x}$Hg$_x$O$_{19}$ nanoparticles annealed at 1000°C for 4 h,
Figure 1. XRD patterns of BaFe$_{12}$O$_{19}$ nanoparticles annealed at different temperatures.

Table 1. Barium hexaferrite and intermediate impurity phase percentages, lattice constants and average crystallite size for BaFe$_{12}$O$_{19}$ nanoparticles prepared at different annealing temperature.

| Sample  | BaFe$_{12}$O$_{19}$ (%) | Fe$_2$O$_3$ (%) | $a$ (Å) | $c$ (Å) | $L$ (nm) |
|---------|------------------------|----------------|--------|--------|--------|
| B-700   | 69.7                   | 31.3           | 5.870  | 23.239 | 32.88  |
| B-800   | 82.2                   | 17.8           | 5.875  | 23.206 | 34.76  |
| B-900   | 91.0                   | 9.0            | 5.809  | 23.234 | 35.45  |
| B-1000  | 100                    | 0.0            | 5.893  | 23.132 | 36.08  |

Figure 2. XRD patterns of BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles annealed at 1000°C for 4 h.

$x = 0.00, 0.05, 0.10, 0.20$ and 0.30. All diffraction peaks in the pattern were belonging to those of M-type barium hexaferrite BaFe$_{12}$O$_{19}$ with space group P63/mmc (194) from JCPDS card number 01-084-0757. From the diffraction patterns, they show the crystallite as single phase of the prepared samples, with no impurity phases. The calculated lattice parameters for undoped sample, $a = 5.893$ Å and $c = 23.132$ Å, are consistent with JCPDS card number 01-084-0757 [24]. Figure 3 shows the lattice parameters variation versus $x$. It is seen that the lattice parameter $c$ increases with increasing $x$, while the lattice parameter $a$ slightly decreases. The increase in $c$ can be attributed to the partial substitution of the smaller ionic radius Fe$^{3+}$ ions (0.64 Å) by larger ionic radius Hg$^{2+}$ ions (1.02 Å). More variation is observed for lattice parameter $c$ because of $c$-axis is easy axis which the spins can freely rotate around this axis, comparing with $a$-axis. The ratio $c/a$ has been calculated for all the prepared samples and found to be in the range 3.925–3.983, confirming with Vegard’s law as the ratio $c/a$ should be less than 3.98 for M-type hexaferrite [24]. Moreover, the unit cell volume decreases from 695.688 Å$^3$ for $x = 0.00$–688.106 Å$^3$ for $x = 0.30$ (Table 2). This decrease is due to the strongly dependence of unit cell volume on $a (V \propto a^2)$ more than $c$. The calculated values of X-ray density ($\rho_x$), bulk density ($\rho_b$) and percentage of porosity ($P\%$) are listed in Table 2 versus Hg$^{2+}$ ions content. It is displayed the increase of ($\rho_x$) and ($\rho_b$) with increasing $x$, which is attributed to the larger atomic weight and density of Hg 200.59 g mol$^{-1}$ and 13.56 g cm$^{-3}$, respectively, comparing with Fe of
Figure 3. The variation of the lattice parameters $a$ and $c$ versus Hg$^{2+}$ ions content.

density $7.87 \text{ g cm}^{-3}$ and atomic weight $55.84 \text{ g mol}^{-1}$. It is observed that $\rho_x$ is higher than $\rho_b$ due to the presence of pores which affected by sintering temperature [25] and the syntheses conditions [26]. The results showed that porosity follows the inverse behaviour of $\rho_x$, it is found to increase as the Hg$^{2+}$ ion content increases. The increase in porosity may be attributed to the diminution of oxygen vacancies or the formation of a solid solution [27].

The average crystallite size ($L$) for the prepared samples is estimated by taking the average value of the most intense diffraction peaks using the Debye Scherrer formula [28] and their values are tabulated in Table 2. The average crystallite size is calculated from Scherrer equation and is found to increase from 36.077 nm at $x = 0.00$ to 37.544 nm at $x = 0.10$ and then it decreases to minimum value 26.971 nm at $x = 0.30$. The decreasing trend of crystallite size may be due to the high concentration of Hg$^{2+}$ ions content which reduces the grain growth because of isolation on or close to the grain boundary which impedes its movement.

The morphologies of hexaferrite BaFe$_{12-x}$HgxO$_{19}$ nanoparticles are shown in Figure 4. It is clear that the samples are composed of approximately lamellar grains. There are agglomerations between the particles which may be due to the high magnetization and the magnetic interaction between the particles [29] or related to particles chemical reaction at the time of calcination procedure. The particle size ($w$) of BaFe$_{12-x}$HgxO$_{19}$ nanoparticles obtained at 1000°C, is mainly between 41.86 and 53.29 nm. Table 2 shows that the values of $w$ are slightly higher than those obtained from XRD ($L$). This is because of X-rays can detect the individual crystallite parts into the nanoparticle, as TEM deals with the grain which might consist of a number of crystallites. As present in Table 2, it is clear that $w$ has the same behaviour of $L$ with Hg$^{2+}$ ions content.

The elemental analysis of BaFe$_{12-x}$HgxO$_{19}$ nanoparticles is investigated by Energy dispersive X-ray analysis (EDS). The results indicate the presence of Ba, Fe, Hg, and O peaks as seen in Figure 5, affirming the formation of BaFe$_{12-x}$HgxO$_{19}$ solid solution and indicates Hg$^{2+}$ ions incorporation in the BaFe$_{12}$O$_{19}$ host lattice. Experimental and theoretical atomic percentages (%) of BaFe$_{12-x}$HgxO$_{19}$ nanoparticles, $x = 0.00$, 0.10 and 0.30, are inserted in the EDS Figs. It is clear the rapprochement between the calculated and experimental values of the atomic percentages for all elements. FTIR absorption spectra of M-type hexaferrite BaFe$_{12-x}$HgxO$_{19}$ nanoparticles recorded in range of 400–4000 cm$^{-1}$ are seen in Figure 6(a). Two main absorption bands $\nu_1$ and $\nu_2$ in the ranges 560–590 cm$^{-1}$ and 430–450 cm$^{-1}$ are observed which are characteristic to M-type barium hexaferrite. The band $\nu_1$ is attributed to the stretching vibrations of the tetrahedral A-site and $\nu_2$ to the octahedral B-site vibrations [12]. It is observed that the values of $\nu_1$ are higher than $\nu_2$, indicating that the vibration normal mode for A-sites is larger than that of B-sites. This is attributed to shorter bond length of the A-site clusters than that of the B-site clusters [30]. Also, the band $\nu_A$ shows up in the spectra
Table 2. XRD parameters of BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles annealed at 1000°C for 4 h.

| Hg$^{2+}$ ions content (x) | a (Å)  | c (Å)  | c/a   | V(Å$^3$) | $\rho_{x}$(g/cm$^3$) | $\rho_{b}$(g/cm$^3$) | $P_%$ | L (nm) | w (nm) |
|--------------------------|--------|--------|-------|----------|----------------------|----------------------|--------|--------|--------|
| 0.00                     | 5.893  | 23.132 | 3.925 | 695.688  | 5.31                 | 3.76                 | 28.94  | 36.077 | 46.955 |
| 0.05                     | 5.883  | 23.138 | 3.933 | 693.512  | 5.36                 | 3.89                 | 27.20  | 37.294 | 48.835 |
| 0.10                     | 5.876  | 23.239 | 3.955 | 694.883  | 5.38                 | 4.08                 | 24.14  | 37.544 | 53.296 |
| 0.20                     | 5.860  | 23.257 | 3.969 | 691.639  | 5.48                 | 4.35                 | 20.47  | 32.784 | 47.921 |
| 0.30                     | 5.852  | 23.261 | 3.974 | 689.871  | 5.56                 | 4.67                 | 15.82  | 26.971 | 41.860 |

Figure 4. TEM images of BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles.

at around 880 cm$^{-1}$ and is attributed to increment in the concentration of divalent ions among the A-sites [30]. The appearance of this band confirms the represents the divalent metal- oxygen vibrations and may assign to the existence of Hg$^{2+}$–O$^{2-}$ or/and Fe$^{2+}$–O$^{2-}$ among A-sites. Carbonyl group (C = O) with asymmetric stretching is detected at 1633 cm$^{-1}$. The detection of band around 3438 cm$^{-1}$ is assigned to the O–H bond
Figure 5. EDX spectra and elemental mapping images of BaFe$_{12-x}$HgxO$_{19}$ nanoparticles, x = 0.00, 0.10 and 0.30.
Figure 6. (a) FTIR spectra of BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles and (b) The variation of Debye temperature against Hg$^{2+}$ ions content.
The thermal properties of M-type hexaferrite can be discussed in terms of mean value of wave number $\nu_{av}$ of the characteristic peaks $\nu_1$ and $\nu_2$ as follows [32], and their values are listed in Table 3 versus Hg$^{2+}$ ions content.

$$T_D = \frac{\hbar C \nu_{av}}{K}$$  \hspace{1cm} (6)

where $T_D$ is Debye temperature in Kelvin and $C$ is the velocity of light.

The variation of $T_D$ versus Hg$^{2+}$ ions content is shown in Figure 6(b). It is demonstrated that $T_D$ values show increment behaviour against $x$. The variation of $T_D$ is attributed to the variation of the mean value of the characteristic wave number $\nu_{av}$ of IR bands [33]. For n-type materials, according to specific heat theory, the conduction electrons can absorb part of the heat resulting in a decrease in Debye temperature. And therefore, the increasing trend of $T_D$ confirms the reduction of conduction electrons (i.e. n-type) and increment of the holes contribution (i.e. p-type) by increasing Hg$^{2+}$ ions [34].

The magnetic hysteresis loops, at room temperature for BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles are shown in Figure 7. The magnetic measurements are carried out under an applied field of $\pm$20 kG. It is displayed wide hysteretic behaviour curves (large coercivity $H_c$) which distinguish the hard magnetic materials [35,36]. The saturation magnetization values ($M_s$) are estimated from the approximation of Stoner-Wohlfarth (S-W) using the following equation [37]:

$$M = M_s \left[ 1 - \frac{\alpha}{H^2} \right]$$  \hspace{1cm} (7)

According to eq. (7), the plot of $M$ versus $1/H^2$ (Figure 8) leads to a straight line with slope = $M_s \times \alpha$. The intersection of this straight line with $y$-axis gives the values of saturation magnetization $M_s$. The estimated values of $M_s$ and $\alpha$ are displayed in Table 4 versus Hg$^{2+}$ ions content. It is observed that $M_s$ and remnant magnetization $M_r$ rise with increasing $x$ and attained the maximum value at $x = 0.10$, beyond which they decrease. The increase in $M_s$ is mainly attributed to the strengthening of super-exchange interactions among nanoparticles due to the partial substitution of Fe$^{3+}$ ions by the Hg$^{2+}$ ions. The ions radii Hg$^{2+}$ ions (1.02 Å) is larger than that Fe$^{3+}$ ions (0.64 Å). This leads to decrease the different magnetic ions distances and subsequently enhance the strength of the super-exchange interactions [38]. On the other hand, the Fe$^{3+}$ ions in barium hexaferrite have five sites are up-spins ($\uparrow$), whereas two sites are down-spins ($\downarrow$) [24]. The increase in $M_s$ is attributed to the occupation of Hg$^{2+}$ ions in the down-spin states. The net spin in upward direction consequently increases, leading to enhance $M_s$ up to $x = 0.10$. While the decreasing of $M_s$ and $M_r$ at high Hg$^{2+}$ ions content may be resulting...
Figure 8. The plots of $M$ versus $1/H^2$ for BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles.

Table 3. The distinguishing wave number $\nu_1$, $\nu_2$ corresponding to different vibrations and Debye temperature of BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles.

| Hg$^{2+}$ ions content ($x$) | $\nu_1$ (cm$^{-1}$) | $\nu_2$ (cm$^{-1}$) | $\nu_{av}$ (cm$^{-1}$) | $T_D$(K) |
|-----------------------------|---------------------|---------------------|-------------------------|----------|
| 0.00                        | 590.307             | 438.362             | 514.335                 | 739.613  |
| 0.05                        | 591.834             | 443.095             | 517.465                 | 744.114  |
| 0.10                        | 592.052             | 444.524             | 518.288                 | 745.298  |
| 0.20                        | 593.012             | 445.116             | 519.064                 | 746.414  |
| 0.30                        | 593.893             | 446.208             | 520.051                 | 747.833  |

from the enhancement of nonmagnetic Hg$^{2+}$ ions concentration and existing of spin canting due to magnetic collinearity loss.

The magnetic moment ($m_B$) per formula unit in Bohr magneton ($\mu_B$) can be calculated through the following equation [39]:

$$m_B = \frac{M_w \times M_s}{5585},$$  \hspace{1cm} (8)

where $M_w$ is the molecular weight of each composition. The obtained values of magnetic moment are presented in Table 4 versus $x$. It is observed that $m_B$ has the same trend with $x$ as $M_s$. The increase in the crystallite size $L$ and the decrease in spin canting angle lead to enhance $M_s$, $m_B$ and the strength of A–B super-exchange magnetic interactions [39].

The magneto crystalline anisotropy constant ($K_{mag}$) and the intrinsic coercivity ($H_I$) can be deduced from the following relations [40,41]:

$$K_{mag} = M_s \left( \frac{15\alpha}{4} \right)^{0.5},$$  \hspace{1cm} (9)

$$H_I = \frac{2K_{mag}}{M_s},$$  \hspace{1cm} (10)

The estimated values of $K_{mag}$ and $H_I$ are also presented in Table 4 versus $x$. It is obvious that $H_I$ slightly decreases as Hg$^{2+}$ ions content increases till $x = 0.10$, and then increases with further increase in $x$, and become close to that of $x = 0.00$. The reduction in $H_I$ may be attributed to the non-magnetic Hg$^{2+}$ ions which make the intersublattice interactions weak, leading to decrease the anisotropy energy and $H_I$ [30]. Coercivity $H_I$ also decreases from 4943 G at $x = 0.00$ to 4345 G at $x = 0.10$ and then increases to 4900 G at $x = 0.30$. The variation of $H_I$ is associated with the extrinsic effect which related to porosity and the distribution of grain size, as well as the intrinsic effect which directly related to the anisotropy field [42]. From the results listed in Table 2, it is observed that $H_C$ decreases with increasing the grain size and with decreasing the porosity which improves the inter grain connectivity across the crystal lattice. The other reason of the decrease in $H_C$ may be ascribed to the decrease in magneto crystalline anisotropy. Frequently, we can use the variations in $H_I$ values to explain the $H_C$ variations [43]. The high values of $H_I$ indicate the hard magnetic behaviour of the samples. Figure 9 shows that $H_I$ of the samples is proportional to $H_C$ and depends on crystallite size. Usually, the values range of coercivity determines the application in which nanomaterials are used, for example the substances that have $H_C < 1200$ G is applicable in the field of perpendicular magnetic recording media [44]. Moreover, as-prepared hexaferrites nanoparticles of $H_C$ in the range (4943–4345 G) with $H_C > M_s/2$, are known as permanent magnets which have a potential candidate for numerous applications.
Table 4. Magnetic parameters of BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles.

| Hg$^{2+}$ ions content (x) | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (G) | $m_B$ ($\mu_B$) | $K_{mag}$ (erg/G) | $H_i$ (G) |
|---------------------------|----------------|----------------|------------|----------------|-------------------|------------|
| 0.00                      | 56.38          | 25.254         | 4943       | 11.22          | 448167.10         | 15898.09   |
| 0.05                      | 57.93          | 26.529         | 4682       | 11.60          | 442169.37         | 15265.64   |
| 0.10                      | 62.17          | 30.647         | 4345       | 12.57          | 440594.50         | 14128.64   |
| 0.20                      | 59.99          | 28.707         | 4645       | 12.25          | 474298.17         | 15812.84   |
| 0.30                      | 59.91          | 28.306         | 4900       | 12.34          | 497120.46         | 16593.58   |

Figure 9. The variation of $H_c$ and $H_i$ with the crystallite size $L$.

Figure 10. First-derivative absorption spectra for BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles versus the magnetic field.

The study of EPR of ferrites is very important for investigation high frequency magnetic properties as the resonance originates from the spins-electromagnetic waves interaction [45]. Figure 10 shows the first-derivative electron paramagnetic resonance absorption spectra at room temperature for BaFe$_{12-x}$Hg$_x$O$_{19}$ samples with $0.00 \leq x \leq 0.30$. EPR spectra contain an isotropic with relative narrow EPR line, characterizing Ba ferrite samples [46]. The isotropic behaviour of EPR line, for all substituted samples, reflects its symmetry about the central position. This indicates the absence of skin effect [47]. In ferrites, Fe$^{3+}$ ions are the main responsible
for EPR spectra as EPR signal for Fe$^{2+}$ ions can be only observed at very low temperature ($\sim$ 4K) because of their very short spin–lattice relaxation time [48]. On the other hand, the two main sources which are responsible for the EPR signal linewidth for any ferrite material are the interaction between magnetic dipoles among particles and the super-exchange interactions between magnetic ions through the ions of oxygen [49].

The strong EPR intensity display slightly shift for the point of maximum derivative with increasing Hg substitution. This makes a slight change in g-factor. The g-factor was calculated from knowing the g-factor of CuSO$_4$·5H$_2$O [50]. The g-factor variation with x for BaFe$_{12-x}$Hg$_x$O$_{19}$ samples is shown in Figure 11. The g-factor is near $\approx$ 2, corresponding to barium ferrite sample [46]. There is a slight increase in g-factor with increasing Hg$^{2+}$ ions content up to x = 0.10, followed by a decrease with further increase in x. The slight reduction of g-factor for x $\geq$ 0.20 reflect the decrease in the magnetic interaction. Reverse behaviour for the resonance field $H_r$ versus x is plotted in Figure 11. The EPR line intensity of peak-to-peak amplitude $Y^*$ increases with increasing Hg substitution up to 0.10, beyond which it decreases as represented in Figure 11. This enhancement indicates the enhancement of unpaired electrons in BaFe$_{12-x}$Hg$_x$O$_{19}$ samples. Moreover, the variation of peak-to-peak line width $\Delta x_{pp}$ with Hg$^{2+}$ ions content is also shown in Figure 11. It is clear that $\Delta x_{pp}$ increases with increasing Hg$^{2+}$ ions content up to x = 0.10, beyond which it decreases. The increase in $\Delta x_{pp}$ reflects the strengthening of the dipolar interaction and indicates the existence of critical grain size with 0.00 $\leq$ x $\leq$ 0.10 as the crystalline size increases up to x = 0.10. On the other hand, the decrease in $\Delta x_{pp}$ for x $\geq$ 0.20 can be interpreted as the reduction of magnetic interaction effect, according to the reduction of magnetic ions (Fe$^{3+}$ ions), confirming with the model of solidsolutions with magnetic dilution; $\Delta x_{pp}$ $\propto$ $(1 - x)^{1/2}$ [51]. The number of spins N participating in the resonance are estimated from comparing the area under the absorption curve with that for CuSO$_4$·5H$_2$O [50]. N enhances as Hg$^{2+}$ ions content increases up to x = 0.10, beyond which it decreases as listed in Table 5. This enhancement of N, as well as g-factor and $\Delta x_{pp}$ reflects the increase of the crystalline degree for BaFe$_{12-x}$Hg$_x$O$_{19}$ samples as x increases up to 0.10, which improve the dipole interaction that in turn give large $\Delta x_{pp}$, g-factor and N [52].

The spin–spin relaxation time constant $T$ can be calculated through the following relation [54]:

$$\frac{1}{T} = \frac{g_\beta \Delta x_{1/2}}{h}, \Delta x_{1/2} = \sqrt{3} \Delta x_{pp}$$  \hspace{1cm} (12)

where $\beta$ is Bohr magneton, $\Delta x_{1/2}$ is the linewidth at half height of absorption peak. The values of spin–spin

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
x & N x 10$^2$ (spin/g) & $\chi$ x 10$^{-3}$ (emu/g) & $\tau$ x 10$^{-9}$ (s) \\
\hline
0.00 & 1.94 & 5.01 & 1.30 \\
0.05 & 3.14 & 8.26 & 1.26 \\
0.10 & 4.15 & 11.14 & 1.21 \\
0.20 & 2.41 & 6.30 & 1.36 \\
0.30 & 1.57 & 3.97 & 1.43 \\
\hline
\end{tabular}
\caption{Variation of N, $\chi$ and $\tau$ versus x for BaFe$_{12-x}$Hg$_x$O$_{19}$ nanoparticles.}
\end{table}
relaxation time constant versus Hg\(^{2+}\) ions content for BaFe\(_{12-x}\)Hg\(_x\)O\(_{19}\) samples are also listed in Table S. One can notice that \(T\) decreases with increasing Hg\(^{2+}\) ions content up to \(x = 0.10\), followed by a decrease for further increase in \(x\). The behaviour could be explained according to the change in electron motion and the strength of super-exchange interaction between magnetic ions through oxygen.

4. Conclusion

Barium hexaferrite nanoparticles were prepared at different temperature through a co-precipitation method. XRD diffraction patterns revealed that the annealing temperature played an important role in the crystallization of barium hexaferrite. A series of BaFe\(_{12-x}\)Hg\(_x\)O\(_{19}\) nanoparticle, 0.00 \(\leq x \leq 0.30\) were successfully prepared at the optimum annealing temperature 1000°C. XRD and FTIR analysis confirmed the single phase formation and the absence of impurities. Lattice parameter \(c\) increased with the increase in \(x\), whereas \(a\) slightly decreased. M-H curves displayed wide hysteretic behaviours with higher coercivity which is characteristic of the typical hard magnetic materials, leading to recommend these materials to be a potential candidate for numerous applications such as recording media applications. M-H curves indicated the enhancement in saturation magnetization values (\(M_s\)) and remnant magnetization \(M_r\) up to \(x = 0.10\) followed by a decrease up to \(x = 0.30\). On the other hand the intrinsic coercivity (\(H_c\)) and coercivity \(H_c\) diminished as Hg\(^{2+}\) content increased till \(x = 0.10\), beyond which they enhanced. The decrease in \(H_c\) might be ascribed to the increase in the grain size and the decrease in magnetic crystalline anisotropy. The increase of Hg\(^{2+}\) content up to 0.10 for BaFe\(_{12-x}\)Hg\(_x\)O\(_{19}\) nanoparticle improved the dipole interaction that in turn made an enhancement for the values of g-factor, peak-to-peak line width, number of spin and paramagnetic susceptibility. The enhancement of these EPR parameters confirmed the improvement of the crystalline degree as Hg\(^{2+}\) content increased up to 0.10, reflecting the existence of critical grain size with 0.00 \(\leq x \leq 0.10\).

Disclosure statement

No potential conflict of interest was reported by the author(s).

ORCID

M.ME. Barakat  http://orcid.org/0000-0003-3730-3710  
D. El-Said Bakeer  http://orcid.org/0000-0002-8456-5134  
Abdel-Hamed Sakr  http://orcid.org/0000-0003-0095-5774

References

[1] Mosleh Z, Kameli P, Ranbar M, et al. Effect of annealing temperature on structural and magnetic properties of BaFe12O19 hexaferrite nanoparticles. Ceram Int 2014;40:7279–7284.
[2] Pullar RC. Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics. Prog Mater Sci. 2012;57(7):1191–1334.
[3] Harris VG, Geller A, Chen Y, et al. Recent advances in processing and applications of microwave ferrites. J Magn Magn Mater 2009;321:2035–2047.
[4] Chen D, Liu Y, Li Y, et al. Microstructure and magnetic properties of Al-doped barium ferrite with sodium citrate as chelate agent. J Magn Magn Mater 2013;337:338:65–69.
[5] Almessiere MA, Slimani Y, El Sayed HS, et al. Investigation of Microstructural and magnetic properties of BaVxFe12−xO19 Nanohexaferrites. J Supercond Nov Magn. 2019;32:1437–1445.
[6] Maria Lumina Sonia M, Anand S, Maria Vinosel V, et al Effect of lattice strain on structure, morphology and magneto-dielectric properties of spinel NiGd x Fe 2−x O 4 ferrite nano-crystallites synthesized by sol-gel route. J Magn Magn Mater 2018;466:238–251.
[7] Elayakumar K, Dinesh A, Manikandan A, et al. Structural, morphological, enhanced magnetic properties and antibacterial bio-medical activity of rare earth element (REE) cerium (Ce3+) doped CoFe2O4 nanoparticles. J Magn Magn Mater. 2019;476:157–165.
[8] Rai GM, Iqbal MA, Kubra KT. Effect of Ho3+ substitution on the structural and magnetic properties of BaFe12O19 hexaferrites. J Alloy Compd. 2010;495:229–233.
[9] Chen W, Wu W, Mao M, et al. Improvement of the magnetization of barium hexaferrites Induced by substitution of Nd3+ ions for Fe3+ ions. J Supercond Nov Magn. 2017;30:707–714.
[10] Slimani Y, Baykal A, Manikandan A. Effect of Cr 3+ substitution on AC susceptibility of Ba hexaferrite nanoparticles. J Magn Magn Mater 2018;458:204–212.
[11] Topkaya R. Effect of Zn substitution on temperature dependent magnetic properties of BaFe12O19 hexaferrites. J Alloy Compd. 2017;725:1230–1237.
[12] Amer MA, Meaz TM, Attallah SS, et al. Structural and magnetic studies of Ti4+ substituted M-type BaFe12O19 hexa-nanoferrites. Mater Sci Semicond Process 2015;30:374–382.
[13] Ali I, Islam MU, Ashiq MN, et al. Investigation of the magnetic properties of nanometric Sr5SmCoNi ferrite/PST matri. Ceram Int. 2015;41:8748–8754.
[14] Kaur T, Kaur B, Bhat BH, et al. Effect of calculation temperature on microstructure, dielectric, magnetic and optical properties of Ba0.7La0.3Fe11.7Co0.3O19 hexaferrites. Physica B. 2015;456:206–212.
[15] Khan HM, Islam MU, Xu Y, et al. Structural and magnetic properties of TbZn-substituted calcium barium M-type nano-structured hexa-ferrites. J Alloys Compd 2014;589:258–262.
[16] Sharma R, Agarwala RC, Agarwala V. A study on the heat-treatments of nanocrystalline nickel substituted BaW hexaferrite produced by low combustion synthesis method. J Magn Magn Mater. 2007;312:117.
[17] Yu H. Bafe12O19 powder with high magnetization prepared by acetone-aided coprecipitation. J Magn Magn Mater. 2013;341:79–85.
[18] Tang X, Hong RY, Feng WG, et al. Ethylene glycol assisted hydrothermal synthesis of strontium hexaferrite nanoparticles as precursor of magnetic fluid. J Alloys Compd 2013;562:211–218.
[19] Ghoneim AI, Amer MA, Meaz TM, et al. Dielectric properties of Th⁺ substituted BaFe₁₂O₁₉ nanoparticles. Physica B. 2017;507:1–12.
[20] Catellanos PAM, Jarque JCS, Rivera JA. Magnetic and microstructural properties of the BaFe₁₂₋₄(3x)SnₓO₁₉ ceramic system. Physica B. 2005;362:95–102.
[21] Safaan SA, Abo El Ata AM, El Messeery MS. Study of some structural and magnetic properties of Mn-substituted SrCu hexagonal ferrites. J Magn Magn Mater. 2006;302:362–367.
[22] Kumar S, Manglam MK, Supriya S, et al. Lattice strain mediated dielectric and magnetic properties in L doped barium hexaferrite. J Magn Magn Mater. 2019;473:312–319.
[23] Kaur P, Chawla SK, Narang SB, et al. Effect of Cu-Co-Zr Doping on the properties of Strontium hexaferrites synthesized by Sol-Gel Auto-combustion method. J Supercond Nov Magn. 2017;30:635–645.
[24] Almessiere MA, Slimani Y, Tashkandi NA, et al. The effect of Nb substitution on magnetic properties of BaFe₁₂₀⁻SnO₉₁₉₁ oxide ferrites. Ceram Int 2019;45:1691–1697.
[25] Islam MU, Ahmad I, Abbas T, et al. pp. 19–23, 155–158. Proceedings of 6th International Symposium on Advanc ed Materials, Islamabad (1999).
[26] Deraz NM, Alarif A. Int J Electrochem Sci 2012;7:4585.
[27] Verma A, Thakur OP, Prakash C, et al. Temperature dependence of electrical properties of nickel–zinc ferrites processed by the citrate precursor technique. Mater Sci Eng B. 2005;116:1–6.
[28] Cullity BD. Powder photographs, Debye Scherrer Method, 150–151, Elem. of X-ray Diff., Addision Wesley Publishing Company Inc., Reading, Massachusetts, M. Cohen, Printed in U.S.A.; 1956.
[29] Kumar ER, Jayaprakash R, Kumar S. The role of annealing temperature and bio template (egg white) on the structural, morphological and magnetic properties of manganese substituted MnFe₂O₄ nanocrystalline ferrites. J Magn Magn Mater 2014;351:70–75.
[30] Amer MA, Meaz TM, Mostafa AG, et al. Time effect of annealing on phase transformations of Cu–Al–Cr ferrites synthesized by a ceramic method. Mater Sci Semicond Process 2015;32:68–75.
[31] Singh J, Singh C, Kaur D, et al. Elucidation of phase evolution, microstructural, mòssbauer and magnetic properties of Co₂⁺–Al₃⁺ doped M-type Ba Sr hexaferrites synthesized by a ceramic method. J Alloys Compd 2017;695:1112–1121.
[32] Patange SM, Shirsath SE, Lohar KS, et al. Infrared spectral and elastic moduli study of NiFe₂₋ₓCrₓO₄ nanocrystalline ferrites. J Magn Magn Mater 2013;325:107–111.
[33] Patange SM, Shirsath SE, Jadhav SP, et al. Elastic properties of nanocrystalline aluminum substituted nickel ferrites prepared by co-precipitation method. J Mol Struct 2013;1038:40–44.
[34] Mazen SA, Mansour SF, Dhahi E, et al. The infrared absorption and dielectric properties of Li–Ga ferrite. J Alloy Compd. 2009;470:294–300.
[35] El-Sayed SM, Meaz TM, Amer MA, et al. Magnetic behavior and dielectric properties of aluminum substituted M-type barium hexaferrite. Physica B. 2013;426:137–143.
[36] Teh GB, Nagalingam S, Jefferson DA. Preparation and studies of Co(II) and Co(III)-substituted barium ferrite prepared by sol–gel method. Mater Chem Phys 2007;101:158–162.
[37] Amir M, Gungunes H, Slimani Y, et al. Mössbauer Studies and magnetic properties of Cubic CuFe₂O₄ nanoparticles. J Supercond Nov Magn. 2019;32:557–564.
[38] Almessiere MA, Slimani Y, Baykal A. Structural and magnetic properties of Ce-doped strontium hexaferrite. Ceram Int 2018;44:9000–9008.
[39] Bobade DH, Rathod SM, Mane ML. Sol–gel auto-combustion synthesis, structural and enhanced magnetic properties of Ni2⁺–Fe₃O₄ substituted nanocrystalline Mg–Zn spinel ferrite. Physica B. 2012;407:3700–3704.
[40] Slimani Y, Baykal A, Amir M, et al. Substitution effect of Cr³⁺ on hyperfine interactions, magnetic and optical properties of Sr-hexaferrites. Ceram Int 2018;44:15995–16004.
[41] Almessiere MA, Slimani Y, Baykal A. Structural, morphological and magnetic properties of hard/soft SrFe₁₂₋ₓVₓO₁₉/(Ni₀.5Mn₀.5Fe₂O₄) nanocomposites: effect of vanadium substitution. J Alloys Compd. 2018;767:966–975.
[42] Ali I, Islam MU, Awan MS, et al. Effect of Tb₃⁺ substitution on the structural and magnetic properties of M-type hexaferrites synthesized by sol–gel auto-combustion technique. J Alloys Compd 2013;550:564–572.
[43] Slimani Y, Gunguneý H, Nawaz M, et al. Magneto-optical and microstructural properties of spinel cubic copper ferrites with Li-Al co-substitution. Ceram Int 2018;44:14242–14250.
[44] Ali I, Islam MU, Awan MS, et al. Effects of Ga–Cr substitution on structural and magnetic properties of hexaferrite (BaFe₁₂₀) synthesized by sol–gel auto-combustion route. J Alloys Compd 2013;547:118–125.
[45] Gazeeu F, Bacri JC, Gendron F, et al. Magnetic resonance of ferrite nanoparticles. J Magn Magn Mater 1998;186:175–187.
[46] Koksharoy VA, Pankratov DA, Gubin SP, et al. Electron paramagnetic resonance of ferrite nanoparticles. J Appl Phys 2001;89:2293–2298.
[47] Bejjit L, Haddad M. EPR study, in the normal and superconducting states, of GdBa₂Cu₃O₇ single crystal before and after grinding. Physica C. 2002;371:339–343.
[48] Sastry MD, Nagar YC, Bhushan B, et al. An unusual radiation dose dependent EPR line at gₑffective = 2.54 in fieldspars: possible evidence of Fe⁵⁺−O₂⁻ ↔ Fe³⁺−O− and exchange coupled Fe³⁺−Fe³⁺−nO⁻. J Phys Condens Matter. 2008;20:025224.
[49] Singh JP, Dixit G, Srivastava RC, et al. Magnetic resonance in superparamagnetic zinc ferrite. Bull Mater Sci 2013;36:751–754.