Influence of annealing process on the structure and magnetic behavior of Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ nanoparticles

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Abstract
The structure and magnetic properties of Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ nanoparticles were investigated for as-synthesized and for samples annealed at temperatures of 300 °C, 400 °C, 500 °C and 600 °C. The phase structure was studied by means of X-ray powder diffraction (XRD). The XRD results reveal that the annealing effect up to 500 °C decreases the sample microstrain and increases the crystallinity. Fe distribution and hyperfine parameters at tetrahedral (A) and octahedral (B) sites for the samples were studied using room temperature Mössbauer spectroscopy. The hyperfine fields increased with annealing temperature ($T_A$). The values of the isomer shifts show only existence of Fe$^{3+}$ cations on both A and B sites. We report magnetization measurements in the form of hysteresis loops in temperature range 4-300 K and magnetic fields up to 5 Tesla. The results show effects of spin freezing. The values of the remanence ($M_r$) at 4 K decreases as $T_A$ increases, whilst at 300 K, $M_r$ increases with increase in $T_A$. The measurement of $M_r$ at low temperature reveals evidence of cubic anisotropy.

Keywords: Nanoferrite; annealing temperature; hyperfine; interaction; spin freezing; anisotropy; reduced remanence

1 Introduction

The study of spinel ferrites ($M$Fe$_2$O$_4$ where $M$ is a divalent element) important due to several possible applications such as magnetic resonance imaging, microwave devices, photo-catalysis, high frequency transformers, adsorption technologies and high density data storage [1]. Recently, magnetic nanoparticles have been used in the field of biotechnology for DNA and RNA purification, magnetic hyperthermia for cancer treatments, cells separation and drug delivery [2]. CoFe$_2$O$_4$ for example has attracted a lot of attention to due to its magnetic properties such as high coercivity, strong anisotropy, moderate saturation magnetization and chemical stability [3], [4]. These unique properties allow
CoFe₂O₄ to be used in different applications [5], [6], [7]. In a previous work we synthesized Ba₀.₅Co₀.₅Fe₂O₄ nanoferrite used in the study of electrochemical activity of ciprofloxacin drug [8]. In the present work, we investigate the influence of annealing temperature on the structure and magnetic properties of Ba₀.₅Co₀.₅Fe₂O₄ ferrite nanoparticles.

2 Experimental details

Ba₀.₅Co₀.₅Fe₂O₄ nanoferrite was synthesized by glycol-thermal method. The starting materials were metal chlorides (BaCl₂·6H₂O: 99 %, CoCl₂·4H₂O: 98% and FeCl₂·6H₂O: 99 %) purchased from Sigma-Aldrich. The stoichiometric amounts of starting materials were reacted in a Watlow series model PARR 4843 stirred pressure reactor. The synthesis procedure is reported in detail elsewhere [8]. Different batches of the sample were annealed at different temperatures (300 °C, 400 °C, 500 °C, and 600 °C) under flowing argon gas (purity: 99.999 %). The phase and structural characterizations of the samples were performed on a Philips X-ray diffractometer Model: PANalytical, EMPYREAN using CuKα radiation. The morphology and micro-structure of the nanoparticles were investigated by high-resolution transmission electron microscopy (HRTEM) (Model: Jeol_JEM-1010) and high-resolution scanning electron microscopy (HRSEM) (Ultra Plus ZEISS-FEG HRSEM instrument). The ⁵⁷Fe Mössbauer spectra were obtained at room temperature on a conventional spectrometer using a ⁵⁷Co source sealed in Rh matrix and vibrated at constant acceleration. Magnetizations were obtained on a mini cryogen free measurement system (Cryogenic Ltd, UK) in the temperature range to 4 to 300 K in magnetic fields of up to 5 Tesla.

3 Result and discussion

Figure 1 shows the XRD patterns as a function of synthesis and annealing temperatures for Ba₀.₅Co₀.₅Fe₂O₄ nanoferrite samples. The peaks are indexed according to the spinel structure of CoFe₂O₄ (JCPDS file No. 22-1086) [8]. The peaks become sharper as the temperature increases up to 500 °C. This indicates an increase in the particle sizes and enhanced crystallinity. At 600 °C additional peaks appear which are suspected to be due a secondary phase of α-Fe₂O₄ [9]. The lattice parameters (a) were calculated using Bragg’s equation \( a = d(h^2 + k^2 + l^2)^{1/2} \) where d is the inter-planar spacing and hkl are the Miller indices. The lattice parameter changes as the annealing temperature increases and reaches a value of 8.389 Å at 500 °C. The increase of the lattice parameter is related to the increase in the particle sizes. The average XRD crystalline size (\( D_{XRD} \)) was calculated using Scherrer’s equation \( D = \frac{0.9\lambda}{\beta \cos \theta} \), where \( \beta \) is the full-width at half-maximum of the (311) XRD peak and \( \theta \) is the Bragg’s angle [10]. The XRD densities (\( \rho_{XRD} \)) were calculated using the formula \( \rho_{XRD} = \frac{8M_0}{N_a a^3} \), where \( M_0 \) is the molecular weight and \( N_a \) is the Avogadro’s number [11]. The microstrains (\( \varepsilon \)) were determined using the formula \( \varepsilon = \frac{W_{hkl}}{4\tan\theta} \). The calculated values of a, \( D_{XRD} \), \( \rho_{XRD} \), HRTEM particle sizes \( D_{HRTEM} \) and \( \varepsilon \) for as-prepared Ba₀.₅Co₀.₅Fe₂O₄ and the annealed samples at different temperatures are given in Table 1.
Table 1: Lattice parameters ($a$), XRD crystallite sizes ($D_{XRD}$), XRD densities ($\rho_{XRD}$), HRTEM crystallite sizes ($D_{HRTEM}$) and microstrains ($\varepsilon$) for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ nanoferrites.

<table>
<thead>
<tr>
<th>$T_A$ (°C)</th>
<th>$a$ (Å)</th>
<th>$D_{XRD}$ (nm)</th>
<th>$\rho_{XRD}$ (g/cm$^3$)</th>
<th>$D_{HRTEM}$ (nm)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>8.379</td>
<td>7.40</td>
<td>6.183</td>
<td>10</td>
<td>0.0016</td>
</tr>
<tr>
<td>300</td>
<td>8.366</td>
<td>7.68</td>
<td>6.212</td>
<td>13</td>
<td>0.0006</td>
</tr>
<tr>
<td>400</td>
<td>8.367</td>
<td>10.79</td>
<td>6.210</td>
<td>15</td>
<td>0.0005</td>
</tr>
<tr>
<td>500</td>
<td>8.389</td>
<td>27.05</td>
<td>6.161</td>
<td>21</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

After annealing at $T_A = 300$ °C, the lattice parameter decreased and then increased with further annealing up to 500 °C. This can be explained as a result of higher surface defects at low annealing temperature and subsequent increase in particle size and crystallinity expected at higher $T_A$ [12], [13], [14]. Since the Ba atom is relatively larger (atomic radius 2.78 Å) than Co atom (atomic radius 1.67 Å) therefore, the suspected defects in the sample could be caused by Ba atoms substituted at tetrahedral site. Figure 2 shows the variation of the crystallite size and the microstrain with annealing temperature. The crystallite size increases from 7.4 ± 0.1 nm to 27 ± 0.2 nm with increase in annealing temperature from 200 °C to 500 °C, respectively. The microstrain values decrease from 0.0016±0.0001 to 0.0004±0.0001 as $T_A$ increases which we attribute to the reduction of defects and internal strain relaxation [15].

Figure 1: XRD patterns for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ nanoparticle ferrites.

Figure 2: Variation of crystallite size and the microstrain with annealing temperature for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ nanoparticle ferrites.
enhancements of the nanoparticles defined by lattice fringes. The particle sizes calculated using HRTEM images also presented in Table 1 were found to increase with $T_A$.

Figure 5 shows room temperature Mössbauer spectra for the Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ samples which were fitted by two sextets corresponding to the presence of Fe$^{3+}$ ions at the A- and B-sites [10]. Significant changes in the hyperfine parameters given in Table 2 are observed. The isomer shift values obtained from the fitting curves confirm the presence of only Fe$^{3+}$ ions [16]. The orbital overlapping of Fe$^{3+}$ on B-site is smaller compared to A-site, thus, the bond separation is anticipated to be larger at B-site. Hence, the value of the isomer shift at B-site is expected to be greater than A-site [17]. The results in Table 2 shows that the isomer shift values that are higher at B-site. The changes on the isomer shift values with $T_A$ indicate that the s-electrons of the sample were affected by temperature [18]. The values of the hyperfine fields are due to the super-exchange between the atomic moments [19]. The higher values of the hyperfine field correspond to the B-site while the lower value is associated with A-sites. Hyperfine field values at A-site increase with increasing $T_A$ which we relate to the increase of the particle sizes [20]. The hyperfine fields increase and reach maximum values of 479 kOe and 514 kOe at A- and B-sites, respectively after annealing at 500 °C. The line widths are temperature dependent and show significant change with increasing $T_A$. The values of the line width broadening lie in the range of 0.60 – 0.17 mm/s. This also indicates presence of only Fe$^{3+}$ [21]. The calculated values of the isomer shift ($\delta$), hyperfine field ($H$), line width ($\Gamma$) and the Fe$^{3+}$ site fraction populations ($f$) are also given in Table 2.

![HRSEM images for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite nanoparticles.](image-url)

**Figure 3.** HRSEM images for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite nanoparticles.
Figure 4. HRTEM images $\text{Ba}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles.

The magnetization measurements consisted of isothermal initial magnetization curves and hysteresis loops. The saturation magnetization ($M_S$) were determined from initial magnetizations by fitting an empirical law of approach to saturation presented elsewhere [21]. In Figure 6 we show the influence of annealing temperature on the deduced $M_S$ and coercive fields ($H_C$) based on magnetization measurements at 300 K. The hysteresis loop measurements are presented in Figure 7. The results deduced from the hysteresis loops and initial magnetization curves at 300 K are presented in Table 3.

**Table 2.** Isomer shift ($\delta$), hyperfine fields ($H$), line width ($\Gamma$) and $\text{Fe}^{3+}$ fraction ($f$) on A site and B site for $\text{Ba}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$ (mm/s)</th>
<th>$H$ (kOe)</th>
<th>$\Gamma$ (mm/s)</th>
<th>$f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_A$</td>
<td>$H_A$</td>
<td>$\Gamma_A$</td>
<td>$f_A$</td>
</tr>
<tr>
<td></td>
<td>$\delta_B$</td>
<td>$H_B$</td>
<td>$\Gamma_B$</td>
<td>$f_B$</td>
</tr>
<tr>
<td>As-prepared</td>
<td>±0.03 ±0.02</td>
<td>±4 ±1</td>
<td>±0.06 ±0.02</td>
<td>±0.7 ±0.5</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.30 0.31</td>
<td>443 478</td>
<td>0.60 0.31</td>
<td>54.5 45.5</td>
</tr>
<tr>
<td>400 °C</td>
<td>0.14 0.32</td>
<td>457 469</td>
<td>0.34 0.22</td>
<td>42.8 57.2</td>
</tr>
<tr>
<td>500 °C</td>
<td>0.26 0.32</td>
<td>461 490</td>
<td>0.36 0.23</td>
<td>51.7 48.3</td>
</tr>
<tr>
<td></td>
<td>0.30 0.36</td>
<td>479 514</td>
<td>0.33 0.17</td>
<td>61.5 38.5</td>
</tr>
</tbody>
</table>
Table 3 Saturation magnetization ($M_s$), coercive field ($H_c$), remnant magnetization ($M_R$) and squareness of magnetization loops ($M_R/M_s$) for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ measured at 300 K.

<table>
<thead>
<tr>
<th>$T_A$</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
<th>$M_R$ (emu/g)</th>
<th>$M_R/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>±0.4</td>
<td>±2</td>
<td>±1</td>
<td>0.09</td>
</tr>
<tr>
<td>300°C</td>
<td>66.7</td>
<td>779</td>
<td>14</td>
<td>0.20</td>
</tr>
<tr>
<td>400°C</td>
<td>61.3</td>
<td>923</td>
<td>12</td>
<td>0.18</td>
</tr>
<tr>
<td>500°C</td>
<td>53.2</td>
<td>1642</td>
<td>21</td>
<td>0.39</td>
</tr>
<tr>
<td>600°C</td>
<td>39.6</td>
<td>802</td>
<td>8</td>
<td>0.01</td>
</tr>
</tbody>
</table>

In addition uncompensated surface spins for the smaller particles can cause reduction in the magnetization with increasing $T_A$ [23]. The coercivity on the other hand, increases as $T_A$ increases and reaches a maximum at 500 °C. This is in line with transformation from single to multi-domain structure for which $H_c$ may rise to a maximum value at a critical particle size. The decrease in $H_c$ for $T_A = 600$ °C can be associated with the onset of an impurity and bulk phases as indicated in the corresponding XRD pattern. The magnetization measurements also reveal the sensitivity of the properties on the measuring temperature. Figure 7 shows that the magnetizations measured at 4 K are much larger than at 300 K. This is attributed to contributions of the surface spins at low temperature which become less important with increase in $T_A$ or particle size [24]. The hysteresis loops also show significant increases in the $H_c$ and remanence magnetization ($M_r$) at 4 K which we associate with spin freezing effects. Some distortion of the hysteresis loops showing significant time dependence of

![Figure 5](image1.png)  
**Figure 5.** Room temperature Mössbauer spectra for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite nanoparticles.

![Figure 6](image2.png)  
**Figure 6.** Effect of $T_A$ on $H_c$ and $M_s$ at 300 K for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite nanoparticles.
Figure 7. $M-H$ loops at 4 K (in red) and 300 K (in black) for Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite nanoparticles. $M_r$ at 4 K. Distortions in the hysteresis loops can arise in a magnetic material with mixed soft and hard magnetic phases and surface spin canting can also cause loop distortions [25]. In Figure 8 we show the temperature dependence of the coercive fields $H_C(T)$ for the as-synthesized and annealed samples. The temperature dependence of the remanence $M_r(T)$ is shown in Figure 9.

In the Stoner–Wohlfarth model the squareness ratio $M_r / M_S$ is 0.5 for non-interacting single-domain particles with randomly oriented easy axes. The particles are assumed to interact via magnetostatic interaction when $M_r / M_S$ is less than 0.5. The exchange interaction is assumed to dominate the ratio $M_r / M_S$ exceeds 0.5 and $M_r / M_S = 0.83$ has been reported to represent particles with cubic anisotropy [27]. The inset in Figure 9 shows clearly that $M_r / M_S$ values for the present set of samples are greater than 0.5 at low temperatures which signifies tendency towards cubic anisotropy, and existence of exchange interactions.
Figure 8. Temperature dependence of coercive fields ($H_c(T)$) for as-prepared and annealed samples of Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite nanoparticles.

Figure 9. Temperature dependence of $M_r(T)$ for the Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ samples. The inset shows the variation of $M_r / M_S$.

4 Conclusion

Spinel Ba$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ nanoferrite was synthesized by glycol thermal method. The XRD patterns show no impurity peak indicating single phase structure of the sample. The influence of the annealing at different temperatures on the structure and the morphology of the samples was investigated by XRD, HRSEM and HRTEM. Increasing $T_A$ leads to enhanced sample crystallinity up to 500 °C. An additional phase appears at $T_A = 600$ °C. The hyperfine parameters obtained from Mössbauer spectrum show that the samples are sensitive to $T_A$. The magnetic measurement at 300 K revealed a decrease of the saturation magnetization with increasing $T_A$, whereas the coercivity increased as $T_A$ increased up to 500 °C. The magnetization as a function of measuring temperature shows evidence of spin freezing at low temperature. Thermal annealing appears to affect inversion of ions between on A and B sites, and leads to transformation from single domain to multi-domain structure.

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References