Improved structural and magnetic properties of cobalt nano ferrites: Influence of sintering temperature

Kush Rana, Preeti Thakur, Parul Sharma, M. Tomar, V. Gupta, Atul Thakur

School of Physics and Materials Science, Shoolini University, Solan 173212, H.P., India
Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

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Abstract

The influence of heat treatment on the structural, morphological and magnetic properties of CoFe$_2$O$_4$ nanopowder synthesised by a citrate precursor method is investigated. The studies were done using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Vibrating Sample Magnetometer (VSM). The results suggested that the specimen prepared by this method is purely crystalline having no other impurities and possessing improved magnetic properties. XRD analysis confirms the cubic spinel phase of CoFe$_2$O$_4$ nanoparticles with crystallite size is in the range 38–49 nm. SEM image confirms the formation of cubic grains with an average grain size of 80 nm. FTIR studies show the occurrence of the absorption bands between 470–420 cm$^{-1}$ and 590–530 cm$^{-1}$ corresponding to the strong metal oxide bonds in tetrahedral (A-site) and octahedral (B-site), respectively. M–H measurements verifies the strong influence of synthesis conditions and crystal size on the magnetic properties of ferrite nanocrystals. Specific saturation magnetization ($M_s$) value increases from 54 emu/g to 74 emu/g as sintering temperature increases from 900 to 1100 $^\circ$C.

Keywords: A. Powders: chemical preparation; B. Grain size; C. Magnetic properties; D. Ferrites

1. Introduction

Metal oxide nanoparticles provide a highly captivating field of research because of their extraordinary structural, optical, electrical and magnetic properties which frequently differ from bulk [1]. Spinel CoFe$_2$O$_4$ is a familiar class of ferrite and of particular interest due to its high coercivity, high anisotropy constant and reasonable saturation magnetisation [2–5]. These properties make this material a suitable candidate for magnetic recording media, high performance electromagnetic spintronic devices, cancer treatment, high frequency applications and also an ideal material for future magnetostrictive applications [6,7]. The magnetic behaviour of these nanoparticles is, therefore, strongly dependent on shape, size and the purity of nanoparticles [8]. CoFe$_2$O$_4$ forms partially inverse spinel structure and the degree of inversion depends upon the heat treatments [9]. The unit cell of the inverse spinel structure contains 32 oxygen atoms with 8 tetrahedral (A) sites and 16 octahedral (B) sites. The trivalent ions are distributed equally between the A and B-sites and all the divalent ions occupy B-sites [10]. The bulk saturation magnetization, Curie temperature, crystalline anisotropy, magnetostriction, etc. of CoFe$_2$O$_4$ depends on the cation distribution [11].

There are many conventional methods for the synthesis of cobalt nanoferrites like sol–gel method, ball milling process, co-precipitation, hydrothermal and many more [12–17]. Ayyappan et al. controlled the size and magnetic properties of CoFe$_2$O$_4$ nanoparticles by varying the solvent dielectric constant [18]. Cabuil et al. prepared ionic magnetic fluid based on cobalt ferrite nanoparticles and studied the influence of hydrothermal treatment...
on nanoparticle size [19]. Kumar et al. studied the effect of annealing on phase evolution, microstructure and magnetic properties of substituted cobalt nanoparticles prepared by evaporation and auto-combustion method [20]. Azhagushanmugam et al. studied the magnetic properties of zinc-substituted cobalt nanoparticles prepared by co-precipitation method and studied the correlation with annealing temperature [21]. Hence, selection of an appropriate synthesis process and conditions of nanoferrites will affect their crystal structure, size, morphology and cation distribution which influences the magnetic properties of cobalt nanoferrites [11].

Therefore, in the present work, a wet chemical method called citrate precursor method has been considered for production of homogeneous, fine and reproducible CoFe$_2$O$_4$ nano ferrites. As there is no precipitation at any stage, the problem of segregation of phases, which normally occurs in some other wet chemical methods, did not occur in this material [22]. Also, this technique offers advantages due to its low cost, high quality product and less time consumption. The present work emphasises on the improved structural, morphological and magnetic properties of the cobalt nano ferrites prepared by citrate precursor method.

2. Experimental details

Nanocrystalline cobalt ferrite powders were synthesized by a citrate precursor method. The starting materials Co(NO$_3$)$_2$·6H$_2$O (≥ 98% Merck, India), Fe(NO$_3$)$_2$·9H$_2$O (≥ 98% Merck, India) and C$_6$H$_8$O$_7$ (≥ 99.5% Merck, India) of AR grade were used without further purification. Double distilled water or deionised water was used as solvent. Complete synthesis process has been described elsewhere [23]. CoFe$_2$O$_4$ powder was pre-sintered at 700 °C and pressed to form pellets. These pellets and the powdered samples were sintered at 900 °C, 1000 °C and 1100 °C for further crystallisation. X-ray diffraction measurements were taken on a Rigaku Geiger Flex 3 kW diffractometer using CuKα source. MIRA 3 TESCAN model Field Effect scanning electron microscope was used to check the average grain size and the distribution of the cobalt nanoferrites. The sample was prepared in pellet form and coated with gold to make electrical contact. Perkin Elmer was used to record the Fourier Transform Infrared spectra of CoFe$_2$O$_4$ nanoferrites. Potassium bromide (KBr) is added as binder in small amount of CoFe$_2$O$_4$ samples to form a pellet. Microsens Model EV 9 Vibrating Sample Magnetometer was used to study the magnetic properties of CoFe$_2$O$_4$ nanoferrites at room temperature with a maximum applied field of 8000 Oe.

3. Results and discussion

3.1. Structural and morphological properties

The XRD pattern of cobalt nanoferrite pre-sintered at 700 °C and sintered at 900 °C, 1000 °C and 1100 °C is shown in Fig. 1. The planes at (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) confirmed the formation of spinel structured cubic cobalt nanoferrites (JCPDS No. 22.1086) [7,8]. At 2θ value of 33.06, α-Fe$_2$O$_3$ phase was found for presintered sample at 700 °C and sintered at 900 °C, which disappears at higher sintering temperatures. Acceptable matches are observed for samples sintered at 1000 °C and

1100 °C indicating the presence of only one crystalline phase. The average crystallite size of cobalt nanoferrites of the most prominent peak (3 1 1) is calculated by using Scherrer’s formula

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

where λ is the wavelength of Cu (Kα) and β is the full width at half maxima. The diffraction peaks become narrower and sharper, suggesting that there is an increase in the crystallite size upon annealing. Table 1 shows the increase in average crystallite size ‘D’, lattice constant ‘a’, interplaner spacing ‘d’ of CoFe$_2$O$_4$ nanoferrites with an increase in sintering temperature. The average crystallite size of cobalt nanoferrites is in the range 38-49 nm.

These results are better than those reported by Panda et al. (72 nm) [24]. There is a very small increase in the interplaner spacing ‘d’ and lattice parameter ‘a’ which is almost constant and not affected by the sintering temperature whereas the lattice strain decreases with an increase in sintering temperature. The obtained lattice parameter values of all the samples are lower than those reported by Manikandan et al. (8.434 Å) synthesized by a microwave combustion method [25] and the observed difference may be due to the preparation methods.

The Hall–Williamsons (H–W) plots of these samples are shown in Fig. 2. The increase in average crystallite size can be considered as a good indication of improved crystallinity and greater chemical homogeneity. Table 1 also shows the average

![Fig. 1. XRD patterns of CoFe$_2$O$_4$ nanoferrites pre-sintered at 700 °C and sintered at 900 °C, 1000 °C and 1100 °C for 3 h.](image)

<table>
<thead>
<tr>
<th>Sintering temperature (T) in °C</th>
<th>Average crystallite size D (nm)</th>
<th>Lattice constant a (Å)</th>
<th>Interplaner spacing d (Å)</th>
<th>Average crystallite size in nm calculated using Hall–Williamson plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>37.86</td>
<td>8.32</td>
<td>2.510</td>
<td>37.65</td>
</tr>
<tr>
<td>900</td>
<td>38.76</td>
<td>8.33</td>
<td>2.512</td>
<td>40.25</td>
</tr>
<tr>
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<td>42.60</td>
<td>8.35</td>
<td>2.518</td>
<td>44.38</td>
</tr>
<tr>
<td>1100</td>
<td>49.00</td>
<td>8.34</td>
<td>2.517</td>
<td>48.12</td>
</tr>
<tr>
<td>1100 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
crystallite size $D$ and lattice strain of CoFe$_2$O$_4$ nanoferrite as calculated from $H$–$W$ plot. The average crystallite size by $H$–$W$ plot is calculated using the formula

$$D = \frac{\lambda}{\text{Intercept}}$$  \hspace{1cm} (2)$$

where $\lambda$ is the wavelength of Cu ($K\alpha$) source and is in close agreement with the average crystallite size calculated by Scherrer’s formula. The strain in CoFe$_2$O$_4$ nanoferrite are calculated by using Hall–Williamson's plot using the formula

$$\varepsilon = \frac{\beta_{hkl}}{4 \tan \theta}$$  \hspace{1cm} (3)$$

where ‘$\varepsilon$’ is the strain [26] and ‘$\beta_{hkl}$’ is the full width at half maxima. The lattice strain is found to decrease from 12.8% to 1.0% as a function of sintering temperature. With an increase in sintering temperature, the lattice strain decreases and the slope of all the samples is positive which corresponds to the tensile strain in CoFe$_2$O$_4$ nanoferrites. This tensile strain on nanoparticles leads to a decrease in lattice strain and almost constant interplaner spacing as a function of sintering temperature.

Fig. 3 shows SEM images of products before and after annealing process (a) and (b-d), respectively. As can be seen size distribution of the samples was improved after annealing process and agglomerated particles were removed via the soft mechanical treatment. In Fig. 3(a) the particle distribution is

![Fig. 2. $H$–$W$ plot of CoFe$_2$O$_4$ nanoferrites pre-sintered at 700 °C and sintered at 900 °C, 1000 °C and 1100 °C for 3 h.](image)

![Fig. 3. SEM micrographs of CoFe$_2$O$_4$ nanoferrites as a function of sintering temperature.](image)
Gaussian (symmetric) and the average particle size found to be 80 nm for presintered sample at 700 °C; lesser than as reported by other researchers [3,25,27]. Some agglomerated particles and dispersed particles are also seen in the micrograph. In Fig. 3(b–d), the effect of sintering temperature is clearly seen as the particle/grain size increases from 90 nm to 100 nm with increasing sintering temperature from 900 to 1100 °C. Whereas agglomeration increases linearly as a function of sintering temperature; the porosity decreases. The SEM study also confirms the formation of nanostructured ferrite. In small sized grains, there is a possibility of re-oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) during cooling after the sintering process, as diffusion of oxygen advances more rapidly in smaller grains than in larger ones. Re-conversion of Fe\(^{2+}\) to Fe\(^{3+}\) improves the ferrite stoichiometry. Also, there is a slight difference in the particle size as calculated from XRD and SEM. This can be explained as the measured size is the result of an average weighed by a six power of the crystal radius because the intensity of the XRD is proportional to the square of the volume. Therefore, if the crystals are not perfectly monodisperse, the diffraction signals for bigger diameter are stronger than for the smallest one. As a result, the size measured by XRD should always be smaller than the one covered by electron microscopy [28].

FTIR spectra of CoFe\(_2\)O\(_4\) ferrites with formula MFe\(_2\)O\(_4\) where M designates a divalent metal, two absorption bands occur from interatomic vibrations for the stretching of bonds between octahedral or tetrahedral metal ions and oxide ions. The band with the higher wave number observed in the range 580–591 cm\(^{-1}\) corresponds to the intrinsic stretching vibrations of the metal at the tetrahedral site whereas the other band around the range 400–468 cm\(^{-1}\) is attributed to the octahedral-metal stretching confirming the formation of inverse spinel CoFe\(_2\)O\(_4\) ferrite. The characteristic bands at wave numbers around 3400 cm\(^{-1}\), 1500 cm\(^{-1}\) and 1380 cm\(^{-1}\) are due to O–H stretching vibration interacting through H bonds [30]. As the sintering temperature is increased, the intensities for the bands corresponding to O–H stretching vibration decrease drastically which may be due to the loss of residual water in the samples [21].

3.2. Magnetic properties

Fig. 5 shows the \(M–H\) loops of CoFe\(_2\)O\(_4\) ferrites. These curves highlight the effect of annealing temperature on magnetization. The values of magnetic parameters such as Saturation Magnetization \(M_s\), Magnetic Remnance \(M_r\), Coercivity \(H_c\) and Squareness ratio \(M_r/M_s\) are listed in Table 2. From the table, it is observed that with an increase in sintering temperature, the saturation magnetisation \(M_s\) is found to increase from 53.69 emu/g to 74.46 emu/g; lesser than the bulk value (90 emu/g) for CoFe\(_2\)O\(_4\) [31]. Our results for \(M_r\) are better at nano level; higher than reported by Sajjia et al. (62 emu/g) [16] and Kooti et al. (59.49 emu/g) [32]. This increase in the value of \(M_s\) strongly depends on the increase in particle size which increases with an increase in sintering temperature [20]. With an increase in sintering temperature, the saturation magnetisation \(M_s\) increases which may be attributed to the spin non collinearity at the surface of crystal whereas the coercivity have no similar orderliness. The net magnetisation in spinel ferrites is considered to be proportional to the difference between magnetic moment of tetrahedral (A) and octahedral (B) sites (\(M_s=M_B–M_A\)), therefore, \(M_s\) depends upon the cationic distribution. The interactions between tetrahedral and octahedral sub-lattices are in the form of exchange interaction of inter-sublattice. The magnetic moment of Co\(^{2+}\) is 2 \(\mu_B\) and for Fe\(^{3+}\) is 5 \(\mu_B\). In the inverse spinel structure of CoFe\(_2\)O\(_4\), half of the Fe\(^{3+}\) ions will occupy the octahedral site and half of the Fe\(^{3+}\) ions occupy the tetrahedral site. As the sintering temperature increases, most of the Fe\(^{3+}\) ions occupy the tetrahedral site.

![Fig. 5. M–H curves of CoFe\(_2\)O\(_4\) ferrites pre-sintered at 700 °C and sintered at 900 °C, 1000 °C and 1100 °C for 3 h.](image-url)

Table 2

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>(M_s) (emu/g)</th>
<th>(M_r) (emu/g)</th>
<th>(H_c) (Oe)</th>
<th>(M_r/M_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>53.69</td>
<td>21.81</td>
<td>257.40</td>
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<tr>
<td>900</td>
<td>57.91</td>
<td>24.64</td>
<td>304.99</td>
<td>0.42</td>
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<tr>
<td>1000</td>
<td>65.10</td>
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</tr>
<tr>
<td>1100</td>
<td>74.46</td>
<td>16.61</td>
<td>304.99</td>
<td>0.22</td>
</tr>
</tbody>
</table>
site which increases the net magnetic moment and hence the saturation magnetisation. The coercive field is a measure of magnetocrystalline anisotropy. The large coercive fields and low magnetizations observed are due to large magnetic anisotropy inhibiting alignment of magnetic moment in the magnetic field [33]. Fig. 6 shows Saturation magnetisation $M_s$ as a function of particle size at a maximum applied field of 8 kOe. Fig. 7 shows the room temperature variation of ratio of $M_r$ and $M_s$ called squareness with the sintering temperature. The squareness is strongly influenced by the magnetic anisotropy of the samples, particle size, shape density and synthesis techniques [32,34]. The squareness ratio of the CoFe$_2$O$_4$ nanoferrites decreases with an increase in sintering temperature which results in decrease in energy losses per unit cycle. In the presently investigated samples, $M_r/M_s$ is ranging from 0.22 to 0.42 which is well below the typical value $\sim 1$ for single domain isolated ferromagnetic particles. The squareness is $\sim 0.5$ for randomly oriented uniaxial anisotropic ferromagnetic particles [31]. The deviation of $M_r/M_s$ from typical single domain class value may be assigned to the interaction amongst the grains which may be affected by the grain size distribution in material. The observed ratio is well agreed to the values of single domain particles of other chemical routed CoFe$_2$O$_4$ samples [35].

4. Conclusions

Nanoferites of CoFe$_2$O$_4$ were successfully prepared by a citrate precursor method. The average crystal size is found to be in the range 38–49 nm. SEM confirmed the formation of uniform and crystalline inverse spinel CoFe$_2$O$_4$ nanoferites with an average grain size of 80 nm for presintered and 100 nm for sintered samples. The FTIR spectra showed bands in range 480–420 cm$^{-1}$ and 590–530 cm$^{-1}$ clearly indicating the formation of magnetic nanoparticles. The saturation magnetisation $M_s$ of CoFe$_2$O$_4$ nanoferites varies between 53.69 and 74.46 emu/g which is better than earlier reported values at nano level and is due to the spin non collinearity at the surface of crystal. The enhancement of magnetic properties of CoFe$_2$O$_4$ ferrites at nano level makes this material a suitable candidate for different applications.

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References