CoFe$_2$O$_4$-SiO$_2$ Composites: Preparation and Magnetodielectric Properties

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Received 27 April 2016; Accepted 22 August 2016

Academic Editor: Eric Guibal

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Cobalt ferrite (CoFe$_2$O$_4$) and silica (SiO$_2$) nanopowders have been prepared by the microwave hydrothermal (M-H) method using metal nitrates as precursors of CoFe$_2$O$_4$ and tetraethyl orthosilicate as a precursor of SiO$_2$. The synthesized powders were characterized by XRD and FESEM. The ($100-\chi$)CoFe$_2$O$_4$+$\chi$SiO$_2$ (where $\chi =$ 0%, 10%, 20%, and 30%) composites with different weight percentages have been prepared using ball mill method. The composite samples were sintered at 800°C/60 min using the microwave sintering method and then their structural and morphological studies were investigated using X-ray diffraction (XRD), Fourier transformation infrared (FTIR) spectra, and scanning electron microscopy (SEM), respectively. The effect of SiO$_2$ content on the magnetic and electrical properties of CoFe$_2$O$_4$/SiO$_2$ nanocomposites has been studied via the magnetic hysteresis loops, complex permeability, permittivity spectra, and DC resistivity measurements. The synthesized nanocomposites with adjustable grain sizes and controllable magnetic properties make the applicability of cobalt ferrite even more versatile.

1. Introduction

Spinel ferrites (MFe$_2$O$_4$; M = Co, Ni, Zn, Cu, Mg, etc.) with nanodimensions were recurrently studied because of their excellent magnetic, catalytic, and electrical properties and their potential applications for their extensive applications [1, 2]. They were also into research study because of their crystal chemistry offering tunable magnetic properties. Amongst all the ferrite materials, cobalt ferrite (CoFe$_2$O$_4$) nanostructures have revealed potential prospects for magnetic data storage [3], targeting drug delivery carriers [4], biosensors [5], and heating agents of magnetic hyperthermia [6]. All of them are credited to their significant mechanical hardness, exceptional chemical and structural stabilities, relatively high Curie temperature ($T_C \sim 520$ °C) and saturation magnetization, tunable coercivity ($H_c$), high magnetocrystalline anisotropy, and lower cost [7, 8]. In addition, it is essential to regulate and optimize the magnetic performance of CoFe$_2$O$_4$ nanostructures as strong magnetic candidates for numerous applications because the synthesized nanocrystals have a strong tendency to aggregate, which makes it very difficult to exploit the physicochemical properties. The dispersion of nanoparticles in amorphous, polymer, and inorganic matrices is an important method to avoid particle agglomeration and control of particle size [9]. Recently, it has been reported that the presence of nonmagnetic SiO$_2$ restrains the growth of CoFe$_2$O$_4$ nanoparticles and regulates their $H_c$ and $M_r/M_s$ ratio [10, 11]. Hence, in the present investigation, nanocomposites of ($100-\chi$)CoFe$_2$O$_4$+$\chi$SiO$_2$ (\$\chi = 0\%, 10\%, 20\%, and 30\%$) were prepared using microwave hydrothermal method. The structural and magnetic properties of composite samples were characterized via XRD, FTIR, and VSM, respectively. The changes in the structure, average grain size, and magnetodielectric properties of composite samples as a function of SiO$_2$ concentration have been discussed in detail.

2. Experimental Method

2.1. Synthesis of CoFe$_2$O$_4$ and SiO$_2$ Nanoparticles. CoFe$_2$O$_4$ nanoparticles were synthesized using pure chemicals of cobalt nitrate hexahydrate [Co (NO$_3$)$_2$ 6H$_2$O] (98.0%
Sigma-Aldrich) and iron nitrate nonahydrate [Fe(NO$_3$)$_3$
9H$_2$O] (98.0% Sigma-Aldrich). The molar ratios of the metal
nitrates were adjusted to obtain the composition CoFe$_2$O$_4$
and dissolved in 100 mL of distilled water. Similarly, SiO$_2$
nanopowders were prepared using tetraethyl orthosilicate as a
precursor of silica and were dissolved in 100 mL of deionized
water. Then the solutions were subjected to precipitation by
the slow addition of 4 M NaOH under constant stirring at
room temperature. The hydrolysis was controlled by the
addition of NaOH until reaction mixture attained pH value
between 9 and 10. The obtained suspensions were sepa-
rateley transferred into a Teflon microwave closed vessel and
then treated in the microwave hydrothermal (M-H) reactor
(MARS-5, CEM Corp., Mathews, NC) at 150 °C/60 min. After
the termination of microwave heating and cooling to room
temperature, the products were separated by centrifugation
and washed with deionized water and ethanol to remove the
residual nitrates present in the final compound. The final
slurry was dried at 60 °C for 12 h.

2.2. Preparation of CoFe$_2$O$_4$/SiO$_2$ Composite Samples.
CoFe$_2$O$_4$/SiO$_2$ composite nanoparticles were prepared by
mechanical mixing of CoFe$_2$O$_4$ and silica (SiO$_2$) nano-
particles in the weight percentages defined as (100 − x) CoFe$_2$O$_4$ + x(SiO$_2$), where the weight percentages are x =
0%, 10%, 20%, and 30%, followed by granulation using 2 wt%
polyvinyl alcohol (PVA) as a binder. Then the powders were
uniaxially pressed at a pressure of 150 MPa to form disc
samples with dimensions (diameter = 10 mm and thickness
= 2 mm) and toroidal samples (outer diameter = 8 mm, inner
diameter = 5 mm, and thickness = 3 mm). After the
binder had been burned out at 300 °C, the compacts were
microwave sintered at 800°C/60 min using a multimode
cavity of 2.45 GHz microwave oven [12].

2.3. Characterization. The phase identification of as-synthe-
sized CoFe$_2$O$_4$ and SiO$_2$ powders and sintered CoFe$_2$O$_4$/SiO$_2$
nanocomposite samples was carried out using X-ray diffrac-
tion (XRD), Philips PW 1830 and the grain distribution
of microwave sintered samples was identified using
scanning electron microscopy (SEM), Carl Zeiss EVO 18].
The bulk density of the present samples was measured via
the Archimedes principle. The Fourier transform infrared
spectra were recorded using a Brucker Tensor 7 spec-
trophotometer from 400 to 4000 cm$^{-1}$ with the KBr pellet
method in transmission mode. The room temperature DC
resistivity properties were measured by two-probe method.
The complex permittivity and permeability studies of sintered
samples were measured within the frequency range of
1 MHz–1.8 GHz using Agilent 4291B impedance analyzer.
The room temperature magnetic properties such as saturation
magnetization ($M_s$) and coercive field ($H_c$) were obtained
using the vibration sample magnetometer (VSM; Lakeshore,
Model 7400) at room temperature.

3. Results and Discussion

The XRD patterns of CoFe$_2$O$_4$ and SiO$_2$ nanoparticles syn-
thesized by microwave hydrothermal method are shown in

![Figure 1: XRD patterns of as-synthesized (a) CoFe$_2$O$_4$ and (b) SiO$_2$ powders.](image-url)

Figure 1 ((a) and (b)). The diffraction peaks related to Bragg’s
reflections from (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1
1), and (4 4 0) planes correspond to the standard structure
of CoFe$_2$O$_4$ (JCPDS card number 22-1086) which has spinel
cubic type with a space group of Fd3m, while the broad peak
in the diffraction pattern of SiO$_2$ confirms the amorphous
phase. Figures 2(a) and 2(b) show the FESEM pictures of as-
synthesized CoFe$_2$O$_4$ and SiO$_2$ powder, respectively. From
the FESEM images, the particle size was calculated and it was
found to be 21 nm and 16 nm, respectively.

Figure 3 shows the XRD patterns of microwave sintered
(100 − x) CoFe$_2$O$_4$ + x(SiO$_2$) nanocomposites with different
weight percentages of SiO$_2$. From the figure, it can be
observed that, for all the samples, the peaks have corre-
sponded to cubic spinel structure. However, there are not
any peaks of other phases except for CoFe$_2$O$_4$ found in the
XRD patterns of the all CoFe$_2$O$_4$/SiO$_2$ composites. No peaks
of expected SiO$_2$ have been traced which means that SiO$_2$
is present in the amorphous state. The average grain size of
the composite samples was calculated using Scherer formula
and it was found to be about 120 nm, 106 nm, 89 nm, and
77 nm. These results clearly show that the amorphous SiO$_2$
influences the microstructure of composites considerably and
it decreases gradually with the increase of SiO$_2$ concentration
from 0% to 30%, respectively. In general, the grain growth
of ferrites can be affected by the presence of pores or
inclusions at the grain boundaries. These represent a local
decrease of grain boundary energy, so they stay preferably
at the grain boundaries and they hinder the movement of
grain boundaries by impurity drag. Therefore, in the present
investigation, the grain growth inhibition by SiO$_2$ addition
is not only due to solid secondary phase particles situated at
planar grain boundaries but also due to the segregation of Si
at grain boundaries, where it impedes grain boundary motion
by impurity drag [13, 14].

The gradual shift in the peak positions towards higher 2θ
angles (Figure 3 inlet) is observed with increasing the SiO$_2$
concentration. In agreement with this observation, the lattice
Figure 2: FESEM patterns of as-synthesized (a) CoFe$_2$O$_4$ and (b) SiO$_2$ powders.

Figure 3: XRD patterns of $(100 - x)$ CoFe$_2$O$_4 + x$SiO$_2$ composite samples with different SiO$_2$ weight percentage.

The parameter is calculated using Nelson–Riley method with an accuracy of ±0.002 Å and it decreases with an increase of SiO$_2$ concentration. The bulk density ($d_B$) of the specimens was determined using Archimedes method and the densities of the present composites were increased with an increase of SiO$_2$.

Figure 4 shows the IR spectra of CoFe$_2$O$_4$/SiO$_2$ nanocomposite in the range 400–2000 cm$^{-1}$. The two absorption bands at about 3467 and 1618 cm$^{-1}$ were ascribed to the stretching modes of the O-H group and H-O-H bending vibration of the free and absorbed water. With increasing the SiO$_2$ content, the intensity of Si-O-Si absorption band of the SiO$_4$ tetrahedron of the silica network at 1080 cm$^{-1}$ slightly increases. The band due to metal-oxygen (Fe-O) (590 cm$^{-1}$) stretching vibration of the tetrahedral lattice of ferrite is greatly weakened compared with that in pure CoFe$_2$O$_4$ probably due to the modification of SiO$_2$ onto CoFe$_2$O$_4$. Figures 5(a)–5(d) show the SEM photograph of the CoFe$_2$O$_4$/SiO$_2$ nanocomposites. It can be seen from the figure that all the samples exhibit a compact arrangement of homogeneous nanoparticles with a spherical shape. The average grain size of sintered composite samples is calculated using a rectangular intercept procedure and the average grain size of the samples is in the range of 80 nm–140 nm.

In general, the electrical properties of the ferrite materials depend on chemical composition, homogeneity, synthesis method, sintering temperature, and grain size. The variation of room temperature DC electrical resistivity of the CoFe$_2$O$_4$/SiO$_2$ system as a function of SiO$_2$ is measured and the obtained results were depicted in Table 1. From the table, it can be observed that as the concentration of SiO$_2$ increases, the resistivity of the composite samples increases linearly by one order from $10^6$ to $10^7$ ohm-cm for $x = 0\%$–30\%. The increase in electrical resistivity with an increase in SiO$_2$ concentration is explained by Verwey’s hopping mechanism [15]. According to Verwey, the electronic conduction in ferrite is mainly due to hopping of electrons between ions of the same element present in more than one valence state, distributed randomly over crystallographically equivalent lattice sites. Therefore, with increase of SiO$_2$ content in the
Figure 4: FTIR spectra of $(100 - x) \text{CoFe}_2\text{O}_4 + x\text{SiO}_2$ samples with different SiO$_2$ weight percentages: (a) $x = 0\%$, (b) $x = 10\%$, (c) $x = 20\%$, and (d) $x = 30\%$.

Figure 5: SEM patterns of $(100 - x) \text{CoFe}_2\text{O}_4 + x\text{SiO}_2$ samples with different SiO$_2$ weight percentages: (a) $x = 0\%$, (b) $x = 10\%$, (c) $x = 20\%$, and (d) $x = 30\%$.

composites, it segregates at the grain boundaries and hinders the hopping process between Co$^{2+}$ + Fe$^{3+} \Leftrightarrow$ Co$^{3+}$ + Fe$^{2+}$ [16]. It can be seen from the figure that the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the permittivity of the composite samples measured in the frequency range of 1 MHz–1.8 GHz. Moreover,
Table 1: Structural, electrical, and magnetic properties of (100 − x) CoFe₂O₄ + x(SiO₂) composites.

<table>
<thead>
<tr>
<th>SiO₂ concentration</th>
<th>Lattice constant (Å)</th>
<th>ρ × 10⁴ (Ω·cm)</th>
<th>Mₛ (emu/g)</th>
<th>Hₑ (Oe)</th>
<th>ε’</th>
<th>ε’’</th>
<th>μ’</th>
<th>μ’’</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0%</td>
<td>8.391</td>
<td>1.46</td>
<td>68.0</td>
<td>920</td>
<td>21.5</td>
<td>1.5</td>
<td>906</td>
<td>2.7</td>
</tr>
<tr>
<td>x = 10%</td>
<td>8.383</td>
<td>3.52</td>
<td>60.2</td>
<td>980</td>
<td>19.0</td>
<td>1.1</td>
<td>726</td>
<td>1.9</td>
</tr>
<tr>
<td>x = 20%</td>
<td>8.370</td>
<td>7.70</td>
<td>54.9</td>
<td>1090</td>
<td>16.3</td>
<td>0.8</td>
<td>528</td>
<td>1.7</td>
</tr>
<tr>
<td>x = 30%</td>
<td>8.354</td>
<td>11.6</td>
<td>45.2</td>
<td>1020</td>
<td>13.5</td>
<td>0.5</td>
<td>406</td>
<td>1.4</td>
</tr>
</tbody>
</table>

![Figure 6: Complex permittivity spectra of (100 − x) CoFe₂O₄ + xSiO₂ composites.](image)

a considerable decrease in complex permittivity is observed with an increase of the SiO₂ content. The real permittivity (ε’) is reduced to 21.5, 19.0, 16.3, and 13.5 at 1 MHz, respectively, and the corresponding imaginary permittivity (ε’’) is decreased to 1.5, 1.1, 0.8, and 0.5 at 1 MHz. The decrement behavior of both ε’ and ε’’ with SiO₂ content may be due to the addition of SiO₂ that suppressed the grain growth and caused the grain size to decrease so that the proportion of the grain boundary was enhanced and this contributed to the reduction of the dielectric constant [17].

Figure 7 shows the complex (μ’ = μ’’ + iμ’’) permeability spectra for composite samples at room temperature. It can be seen that at low frequencies (1 MHz) the real part of complex permeability, μ’, is about 906, 726, 528, and 406 for x = 0%, 10%, 20%, and 30%, respectively. As the frequency increases, each measured complex permeability spectrum remains almost constant at first and then rises to a certain peak before falling rapidly to relatively low values. The imaginary part of permeability (μ’’) for presently investigated samples is found to be low and it gradually increases with an increase in frequency and took a maximum at a certain frequency, where μ’ rapidly decreased. It was also observed, from the figure, that the real and imaginary permeability change from cobalt ferrite to CoFe₂O₄/SiO₂ composites. Also, the critical frequencies (f_c) at which μ’’ has a maximum value change continuously and shift towards higher values with the increase in SiO₂ fraction. Since the composite contains nonmagnetic gaps, the demagnetizing field H_D is present along the circumference of the ring core. Hence, the μ’ value at low frequencies is reduced by H_D. On the other hand, the rotational frequency is related to the anisotropy field H_A antiparallel to the applied AC field and increases with H_D [18]. Thus, the value of H_A is also influenced by the change in SiO₂ ferrite fraction in the composite. The value of μ’ decreases and rotational frequency shifts higher due to the contribution of magnetocrystalline anisotropy field to H_A. As a result, the complex permeability spectra of composite samples were decomposed into the domain wall (DW) and rotational components. Consequently, the complex permeability can be controlled continuously between the composite structures. These materials seem to be good candidates for versatile applications in the microwave field.

Figure 8 shows the SiO₂ ratio dependence of magnetic parameters (Mₛ and Hₑ) of all samples. For the pure CoFe₂O₄ sample, the value of Mₛ is about 68 emu/g and Hₑ is about 914 Oe, which is much larger than 670 Oe of CoFe₂O₄ nanoparticles annealed at 1000°C reported by Chiu et al. [19]. This may be due to the fact that grain size plays an important role in assigning coercivity of sample as homogeneously distributed and small grains are required for high coercivity.

On one hand, Mₛ of all (1 − x) CoFe₂O₄ + xSiO₂ composites...
monotonically decreases with the SiO$_2$ ratio changing from 0% to 30%. The reduction in $M_s$ of composites is due to the presence of nonmagnetic SiO$_2$ and the reduction in grain size of composite samples. Moreover, $H_c$ rises initially and then goes down with an increasing SiO$_2$ ratio. The enhancement or reduction of $H_c$ is closely related to sintering temperature, crystalline size, lattice strain, and microstructure.

In the present investigation, pure CoFe$_2$O$_4$ and CoFe$_2$O$_4$/SiO$_2$ composites were prepared via the same route and they have a similar structure. Therefore, their improved $H_c$ value in the composites is mainly due to the reduction in the grain size. The decreasing grain size is getting closer to their single domains, and then they have higher $H_c$ than the pure CoFe$_2$O$_4$. And this also may be due to the local defect effect or the pinning effect in the interfaces between the magnetic CoFe$_2$O$_4$ and around nonmagnetic SiO$_2$. However, if the SiO$_2$ weight percentage equals 30% in $(100-x)$ CoFe$_2$O$_4$ + $x$SiO$_2$ composite system, then the grain size of system is smaller than their single domain and it causes a drop in anisotropy of the composite system. Then $H_c$ returns to decline again. Above all, the ideal $H_c$ and $M_s$ of the CoFe$_2$O$_4$-SiO$_2$ composite samples can be successfully achieved by changing the SiO$_2$ concentration. Therefore, the investigated composites with adjustable grain sizes and controllable magnetic properties make the applicability of cobalt ferrite even more versatile.

4. Conclusion

CoFe$_2$O$_4$/SiO$_2$ nanocomposites were prepared by using microwave hydrothermal synthesized CoFe$_2$O$_4$ and SiO$_2$ nanopowders. The structural, dielectric, and magnetic properties of the resultant composite samples as a function of SiO$_2$ concentration have been investigated. The XRD investigations have shown that silica plays a major role in controlling the grain size. The magnetic, dielectric, and electrical properties exhibit a strong dependence on the SiO$_2$ concentration. The values of saturation magnetization ($M_s$), real permittivity ($\varepsilon''$), permeability ($\mu''$), and dielectric and magnetic losses decrease whereas coercivity ($H_c$), DC resistivity ($\rho$), and operating frequency of the composite samples increase with increasing SiO$_2$ concentration. Although no specific practical examples are presented here, we believe that the presently investigated nanocomposites with adjustable grain sizes and controllable magnetic properties may improve a feasible thought and method for developing the fundamental research and potential applications of the CoFe$_2$O$_4$-based nanomaterials.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

Dr. T. Ramesh is thankful to the Principal Dr. K. V. N. Sunitha, BVRIT, Hyderabad, for her constant support.

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