Research Article

CoFe₂O₄-SiO₂ Composites: Preparation and Magnetodielectric Properties

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Cobalt ferrite (CoFe₂O₄) and silica (SiO₂) nanopowders have been prepared by the microwave hydrothermal (M-H) method using metal nitrates as precursors of CoFe₂O₄ and tetraethyl orthosilicate as a precursor of SiO₂. The synthesized powders were characterized by XRD and FESEM. The (100 - x) (CoFe₂O₄) + xSiO₂ (where x = 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 SiO₂ content on the magnetic and electrical properties of CoFe₂O₄/SiO₂ 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 (MFe₂O₄; 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 (CoFe₂O₄) 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 ($T_c \sim 520^\circ\text{C}$) 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 CoFe₂O₄ 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 SiO₂ restrains the growth of CoFe₂O₄ nanoparticles and regulates their H_c and M_r/M_s ratio [10, 11]. Hence, in the present investigation, nanocomposites of (100 - x) (CoFe₂O₄) + xSiO₂ (x = 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 SiO₂ concentration have been discussed in detail.

2. Experimental Method

2.1. Synthesis of CoFe₂O₄ and SiO₂ Nanoparticles. CoFe₂O₄ nanoparticles were synthesized using pure chemicals of cobalt nitrate hexahydrate [Co (NO₃)₂ · 6H₂O] (98.0%

Sigma-Aldrich) and iron nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (98.0% Sigma-Aldrich). The molar ratios of the metal nitrates were adjusted to obtain the composition CoFe_2O_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 separately transferred into a Teflon microwave closed vessel and then treated in the microwave hydrothermal (M-H) reactor (MARS-5, CEM Corp., Mathews, NC) at $150^\circ\text{C}/60$ 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 $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ Composite Samples. $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ composite nanoparticles were prepared by mechanical mixing of CoFe_2O_4 and silica (SiO_2) nanoparticles in the weight percentages defined as $(100 - x)\text{CoFe}_2\text{O}_4 + x(\text{SiO}_2)$, 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 $800^\circ\text{C}/60$ min using a multimode cavity of 2.45 GHz microwave oven [12].

2.3. Characterization. The phase identification of as-synthesized CoFe_2O_4 and SiO_2 powders and sintered $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanocomposite samples was carried out using X-ray diffraction [(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 Bruker Tensor 7 spectrophotometer 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_2O_4 and SiO_2 nanoparticles synthesized by microwave hydrothermal method are shown in

FIGURE 1: XRD patterns of as-synthesized (a) CoFe_2O_4 and (b) SiO_2 powders.

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_2O_4 (JCPDS card number 22-1086) which has spinel cubic type with a space group of $\text{Fd}3\text{m}$, 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_2O_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 $(100 - x)\text{CoFe}_2\text{O}_4 + x(\text{SiO}_2)$ nanocomposites with different weight percentages of SiO_2 . From the figure, it can be observed that, for all the samples, the peaks have corresponded to cubic spinel structure. However, there are not any peaks of other phases except for CoFe_2O_4 found in the XRD patterns of the all $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ 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 Scherrer 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 inset) is observed with increasing the SiO_2 concentration. In agreement with this observation, the lattice

FIGURE 2: FESEM patterns of as-synthesized (a) CoFe_2O_4 and (b) SiO_2 powders.

FIGURE 3: XRD patterns of $(100 - x) \text{CoFe}_2\text{O}_4 + x\text{SiO}_2$ composite samples with different SiO_2 weight percentage.

parameter is calculated using Nelson–Riley method with an accuracy of $\pm 0.002 \text{ \AA}$ 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 $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanocomposite in the range $400\text{--}2000 \text{ cm}^{-1}$. 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_2O_4 probably due to the modification of SiO_2 onto CoFe_2O_4 . Figures 5(a)–5(d) show the SEM photograph of the $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ 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 $80\text{--}140 \text{ nm}$.

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 $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ 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 $x = 0\text{--}30\%$. 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 ferrites 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 $\text{Co}^{2+} + \text{Fe}^{3+} \rightleftharpoons \text{Co}^{3+} + \text{Fe}^{2+}$ [16].

Figure 6 shows the frequency dependence of real (ϵ') and imaginary (ϵ'') parts of the permittivity of the composite samples measured in the frequency range of 1 MHz–1.8 GHz.

It can be seen from the figure that the real (ϵ') and imaginary part of the permittivity (ϵ'') values remain almost constant up to a frequency of 700 MHz and increase further with an increase in frequency. In all the samples, a resonance peak was found to be above 1 GHz (Figure 6 inset). Moreover,

TABLE 1: Structural, electrical, and magnetic properties of $(100 - x) \text{CoFe}_2\text{O}_4 + x(\text{SiO}_2)$ composites.

SiO_2 concentration	Lattice constant ($\text{\AA}$)	$\rho \times 10^6$ ($\Omega\text{-cm}$)	M_s (emu/g)	H_c (Oe)	ϵ'	ϵ''	μ'	μ''
$x = 0\%$	8.391	1.46	68.0	920	21.5	1.5	906	2.7
$x = 10\%$	8.383	3.52	60.2	980	19.0	1.1	726	1.9
$x = 20\%$	8.370	7.70	54.9	1090	16.3	0.8	528	1.7
$x = 30\%$	8.354	11.6	45.2	1020	13.5	0.5	406	1.4

FIGURE 6: Complex permittivity spectra of $(100 - x) \text{CoFe}_2\text{O}_4 + x\text{SiO}_2$ composites.

a considerable decrease in complex permittivity is observed with an increase of the SiO_2 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 SiO_2 content may be due to the addition of SiO_2 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 ($\mu^* = \mu' + i\mu''$) 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

FIGURE 7: Complex permeability spectra of $(100 - x) \text{CoFe}_2\text{O}_4 + x\text{SiO}_2$ composites.

change from cobalt ferrite to $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ 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 SiO_2 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 SiO_2 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 SiO_2 ratio dependence of magnetic parameters (M_s and H_c) of all samples. For the pure CoFe_2O_4 sample, the value of M_s is about 68 emu/g and H_c is about 914 Oe, which is much larger than 670 Oe of CoFe_2O_4 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, M_s of all $(1 - x) \text{CoFe}_2\text{O}_4 + x\text{SiO}_2$ composites

FIGURE 8: M_s and H_c values of the $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ composite samples as a function of SiO_2 weight percentage.

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_2O_4 and $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ 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_2O_4 . And this also may be due to the local defect effect or the pinning effect in the interfaces between the magnetic CoFe_2O_4 and around nonmagnetic SiO_2 . However, if the SiO_2 weight percentage equals 30% in $(100 - x)\text{CoFe}_2\text{O}_4 + x\text{SiO}_2$ 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 $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ 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

$\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanocomposites were prepared by using microwave hydrothermal synthesized CoFe_2O_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 (ϵ'), permeability (μ'), and dielectric and magnetic losses decrease whereas coercivity (H_c), DC resistivity (ρ), 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_2O_4 -based nanomaterials.

Competing Interests

The authors declare that they have no competing interests.

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