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A Facile low temperature method for synthesis of $CoFe_2O_4$ nanoparticle possessing excellent microwave absorption property†

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$CoFe_2O_4$ nanoparticles, synthesized via a co-precipitation method at 120°C, exhibited excellent microwave absorption property, with minimum reflection loss of -55 dB (~99.99%) at 9.25 GHz. To the best of our knowledge, these synthesized $CoFe_2O_4$ nanoparticles are showing highest minimum reflection loss in comparison with the reported $CoFe_2O_4$ based materials.

In recent days, with the development of technology and modern life style, the problems caused by over exposure of electromagnetic waves have become more and more serious due to increasing applications of electromagnetic waves in mobile phone, local area network, personal computer, radar system, television image interference of high rise buildings, etc. Exposure of microwave radiation can be harmful to biological systems like increasing heart rate, DNA strand damage in brain cells, weakening immune responses, increasing possibility of cancer and so on.[1-3] To address these issues, the demands to develop efficient electromagnetic wave absorber with wider absorbing bandwidth and high absorbing property are increasing. Moreover, microwave absorbing materials also find applications in the stealth technology of military application and electronic devices. In last few decades, in the search of efficient radar absorbing materials (RAM), scientists are showing specific concern on the materials which exhibit microwave absorption in X-band region (8.2-12.4 GHz).

Use of ferrite based materials as micro-wave absorber has been reported by several scientists.[4-6] To achieve good radar absorbing materials (RAM) researchers have explored various compositions of pure ferrites[4-9] as well as variety of ferrite composites (such as ferrite- polymer,[10-13] ferrite-graphene,[10,13-17] metal-ferrite,[18] hard-soft ferrite nanocomposites,[19-21] ferrite-oxidenanocomposites[22-25] etc.). Various methods such as solid state, co-precipitation, sol-gel, hydrothermal, precursor etc. have been employed to prepare ferrite powders. We have recently reviewed several chemical methods which were reported for preparation of various types of ferrites and their applications and related references are cited there in.[26, 27] In the quest for a good microwave absorbing material, several researchers have investigated $CoFe_2O_4$ and $CoFe_2O_4$ based composites. $CoFe_2O_4$ nanoparticles are commonly prepared by co-precipitation,[8,10,22,28-32] sol-gel,[33-35] precursor,[11,36,37] reverse micelle,[38] micro-emulsion,[39] and hydrothermal technique.[7-9,14] Synthesis of $CoFe_2O_4$ hollow spheres have been reported by researchers using different solvothermal techniques,[7,40,41] vapour diffusion synthesis[15,42] and polymer templating method.[43] However, most of the synthetic methodologies suffer from at least one of the following limitations (i) requirement of high calcination temperature,[7, 8, 29-37,44] (ii) usage of organic reagents or solvents,[10,33-35,41] (iii) use of high pressure autoclave reactor.[7-9] Preparation of $CoFe_2O_4$ based composites is complicated in nature involving multiple steps.[7,15,32] In order to surmount these limitations, exploration of simple methods for preparation of $CoFe_2O_4$ nanopowder is of scientific importance.

Due to easy operational procedure and requirement of cheap starting materials co-precipitation method has been employed by some researchers to prepare $CoFe_2O_4$ nanopowders[8,10,22,28-32] Here, $CoFe_2O_4$ nanoparticles were synthesized by using an aqueous solution based co-precipitation method. In this method any calcination or annealing at higher temperature was not required. The structure, magnetic and microwave absorbing properties of the synthesized $CoFe_2O_4$ nanopowders were investigated. This material exhibited very high microwave absorption (~99.99%) property.

$CoFe_2O_4$ nanoparticles were synthesized by using $Fe(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ as starting materials. In a typical synthesis process, aqueous solutions of $Fe(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ were mixed keeping Fe^{3+} and Co^{2+} molar ratio 2:1. In this mixture an aqueous solution of NaOH (6M) was added drop wise at room temperature and pH of the reaction mixture became ~11. Then, this reaction mixture was refluxed at 120 °C for 12 h. After cooling this mixture at room temperature, the black precipitate thus obtained

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†Electronic Supplementary Information (ESI) available: Details of the characterization techniques used, Fig S1 Room temperature wide angle powder XRD pattern of the precipitates refluxed at 120 C at different time (0 h to 9h), Fig. S2EDAX analysis of the synthesized $CoFe_2O_4$ nanoparticles, Fig. S3 N_2 adsorption-desorption isotherms of the synthesized $CoFe_2O_4$ nanoparticles, Detail equations for calculation of reflection loss, Table S1: Methods of preparation of different $CoFe_2O_4$ and $CoFe_2O_4$ based composites and their microwave absorption property. See DOI: 10.1039/x0xx00000x

was collected by centrifugation and washed thoroughly by distilled water. This precipitate was then dried at 100 °C for 12 h to obtain $CoFe_2O_4$ nanoparticles (details of the techniques used for structural characterization are mentioned in ESI†).

To understand the growth mechanism of. $CoFe_2O_4$ nanocrystals a set of experiment were conducted, where the reaction mixtures of $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$ and NaOH solutions were refluxed at 120 °C for different times (0 h to 12 h). The precipitates thus formed were analyzed by XRD to identify the crystal phases formed with changing reflux time. The precipitate, formed soon after addition of NaOH solution at room temperature, (i.e. 0 h), was amorphous in nature. This brown precipitate was might be iron oxy-hydroxide (FeOOH), which is thermally stable at low temperature.[45] As pH of the reaction was high (pH 11-12), Co^{2+} ions were remained in solution due to the selective dissolution of $Co(OH)_2$.[46] Precipitate, formed after 1 h of reflux, was mostly amorphous in nature. However, formation of $CoFe_2O_4$ nanocrystals was started at this point as a small peak at 2θ = 35.65° (311) plane of $CoFe_2O_4$ was observed in its XRD pattern. XRD patterns of the precipitates, obtained till 9 h of reflux, showed only the peak at 2θ = 35.65°, but with increasing reflux time the intensity of this peak was increased indicating the progressive increase of crystallite size from ~ 5 nm to 7 nm (XRD patterns are provided in ESI† Fig. S1).In XRD pattern, of the precipitate produced after 12 h reflux, presence of diffraction peaks at 2θ= 30.35°, 35.72°, 37.83°, 43.32°, 53.94°, 57.20°, 62.89° corresponding to (220), (311), (222), (400), (422), (511) and (440) planes of $CoFe_2O_4$ (JCPDS card No. 22-1086) indicated the formation of single phase $CoFe_2O_4$ (Fig 1).

Formation of $CoFe_2O_4$ nanoparticles can be presented by the following equations:

$$Fe^{3+} + 3\,OH^- \longrightarrow FeOOH + H_2O \qquad (1)$$

$$2\,FeOOH + Co(OH)_2 \xrightarrow[12\,h]{120\,^0C} CoFe_2O_4 + 2\,H_2O \qquad (2)$$

It is important to note that, no impurity phase was detected. The crystallite size, of the final product was found to be ~8 nm. EDAX analysis of this sample also confirmed the formation of $CoFe_2O_4$ (Fig. S1 (ESI†)). Fig. 2(A) illustrates the HRTEM micrograph of the synthesized $CoFe_2O_4$ nanoparticles where average particle was found to ~7 nm. Average particle was also determined from dynamic light scattering technique and was found to be ~8 nm (Fig. 2(B)). BET surface area of these nanoparticles was ~143.32 m²/g (Fig. S2 (ESI†)).

Room temperature magnetic property measurement of synthesized $CoFe_2O_4$ nanopowders by vibrating sample magnetometer (VSM) showed that, saturation magnetization (Ms) and coercivity (Hc) values were 30.7 emu/g and 820 Oe respectively (Fig. 3). However, these values are lower than reported values of $CoFe_2O_4$ powders prepared by different reported methods.[8, 29-31, 35-37,44] This might be due to the fact that, the average particle size of the $CoFe_2O_4$ powders, prepared by this method, is very small (~7-8 nm) and magnetic properties are dependent on the size and shape of the particles. Size and shape anisotropy here played critical roles in determining magnetic properties.[47, 48]

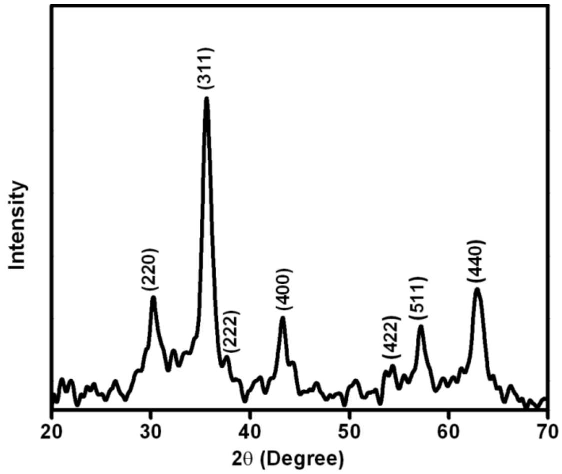

Fig. 1 Room temperature wide angle powder XRD pattern of synthesized $CoFe_2O_4$.

The electromagnetic parameters (relative complex permittivity $\varepsilon_r = \varepsilon' - j\varepsilon''$ and relative complex permeability $\mu_r = \mu' - j\mu''$) of the synthesized $CoFe_2O_4$ were measured at room temperature to determine its microwave absorption properties. It is well known that, the real permittivity (ε′) and real permeability (μ′) represent the storage ability of dielectric and magnetic energy, while the imaginary permittivity (ε′′) and imaginary permeability (μ′′) symbolize the electrical energy dissipation and magnetic loss respectively.[49,50]

The frequency dependence of real and imaginary permittivity and permeability of $CoFe_2O_4$ in the X-band region (8.2-12.4 GHz) are shown in Fig. 4. It was observed that, with increasing frequency ε′ declined from 15.3 to 14.12 whereas, ε′′ increased from 4.53 to 5.64. μ′ of the sample presented a flat trend (1.13-1.10 GHz) over the experimental frequency range; however slight fluctuation of the values were observed. μ′′ was found to be decreased from 0.035 to 0.0014.

The reflection loss (RL) was estimated from the complex relative permeability and permittivity at a given frequency and absorber thickness employing single layered plane wave absorber model, proposed by Naito and Sutake[51] (the detail information are provided in the ESI†).

Fig. 5 illustrates the reflection loss vs frequency of synthesized $CoFe_2O_4$ with different thickness of absorber. Important points observed from this plot are as follows:

i) The reflection loss (RL) was increased with increasing thickness of the sample till 2 mm.

ii) The frequency corresponds to maximum loss was shifted towards lower frequency with increasing thickness.

iii) With decreasing thickness of the absorber the effective band width (i.e. RL <- 10 dB and > 90% absorption) was increased. For example, when the absorber thickness was 2 mm effective bandwidth was 2.6 GHz (8.2 – 10.8 GHz).Whereas, with thickness 1.8 mm, the effective bandwidth was increased to 3.06 GHz (9.17 – 12.23 GHz).

iv) Minimum RL of -55 dB (~99.99% absorption) at 9.25 GHz. was observed when absorber thickness was 2 mm. From literature survey it was observed that, the minimum RL of the synthesized

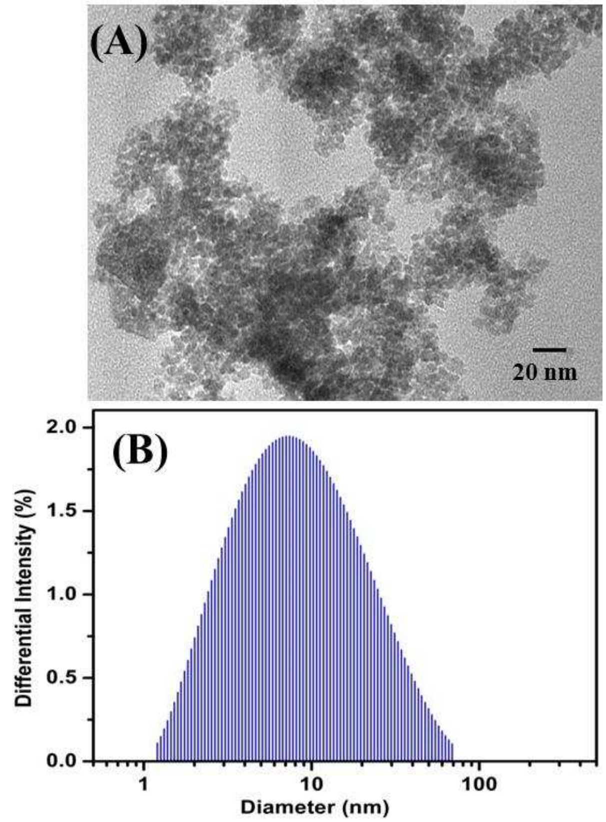

Fig. 2 (A) HRTEM micrograph and (B) Particle size distribution of synthesised $CoFe_2O_4$ nanoparticles.

$CoFe_2O_4$ nanoparticles is highest than that of so far reported values of $CoFe_2O_4$ and $CoFe_2O_4$ based composites.[6, 8-10, 11, 14, 15, 22, 24, 25, 28, 32, 33, 40, 41] A comparison of microwave absorption property of $CoFe_2O_4$ based materials, prepared by various methods has been listed in Table S1 (ESI†)

Many mechanisms have been proposed to explain microwave absorption of materials.[7,10] The optimum reflection loss can be achieved by impedance matching, when $Z_{in} = Z_0$, where $Z_0$and Z_{in} are free space impedance and absorber impedance respectively and corresponding frequency and absorber thickness are known as matching frequency (f_m) and matching thickness (t_m). In the present case, Z_{in} / Z_0 were ~1 (Z_0= 376.7 ohm[7] and Z_{in}= 376.65 ohm (calculated value)), when f_m was 9.25 GHz and tm was 2 mm. The microwave absorption properties of magnetic nanoparticles depend on several factors including domain wall resonance, spin rotational resonance, polarizability etc. $CoFe_2O_4$ possesses the highest anisotropy constant and moderate Ms value of all cubic ferrites.[7] Spin rotational resonance is sensitive to composition and structure of the materials. Here, very fine particle size (~ 8 nm) of the synthesized $CoFe_2O_4$ may also influence the resonance absorption effect because of the shape and size anisotropy and dipolar interaction effect between the individual magnetic domains. Hence, the high reflection loss exhibited by $CoFe_2O_4$ nanoparticles can be attributed to the synergistic effects derived from these factors.

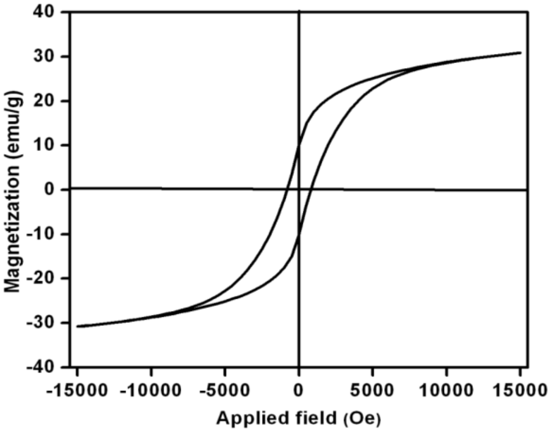

Fig. 3 Room temperature magnetic hysteresis loop of synthesized $CoFe_2O_4$ nanoparticles

Conclusions

In summary, $CoFe_2O_4$ nanopowders have been successfully synthesized by using a co-precipitation method. The method reported here offers several advantages over most of the reported methods such as (i) here, synthesis of pure $CoFe_2O_4$ nanoparticles was performed at relatively lower temperature (120 °C) whereas most of the reported methods require high calcination temperature (500 °C or higher),[8,29-37,44] (ii) in this method no organic solvent or organic reagent was required whereas most of the solvothermal or sol-gel based methods required organic solvent,[10,33-35,38,39,41] (iii) no high pressure autoclave was required for this synthesis route which is essential for hydrothermal or solvothermal technique.[7-9,14,40,41] Hence, this reported method provides a low temperature and cost effective alternative to the conventional synthetic routes for $CoFe_2O_4$ nanopowder preparation.

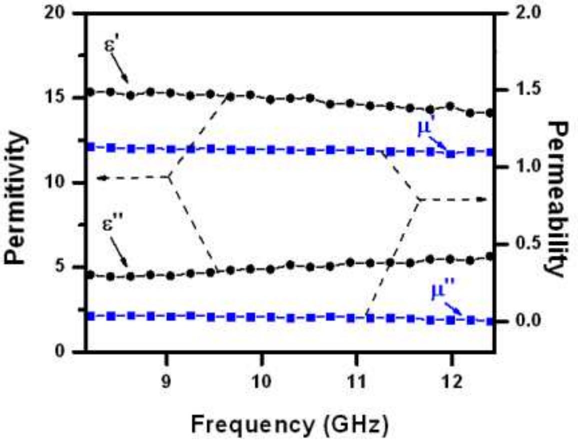

Fig. 4 Permittivity and permeability of synthesized $CoFe_2O_4$ nanoparticles.

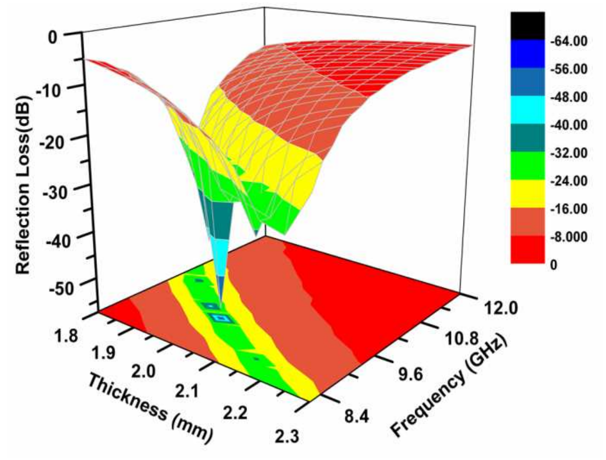

Fig. 5 Frequency dependence of reflection loss of synthesised $CoFe_2O_4$ nanoparticles by varying the thickness of the absorber.

Synthesized $CoFe_2O_4$ nanoparticles exhibit minimum reflection loss (RL) as high as -55 dB (correspond to > 99.99% loss) at 9.25 GHz and absorption band, (with RL under -10 dB), from 8.2-10.2 GHz when thickness is 2 mm. To the best of our knowledge, this is the first time $CoFe_2O_4$ nanoparticle exhibiting such a high RL is reported.

As the synthesized $CoFe_2O_4$ nanoparticles possess excellent microwave absorption property and also can be synthesized easily, they can be considered as promising radar absorbing material.

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