Tailoring complex permittivity and permeability to enhance microwave absorption properties of FeCo alloy particles through adjusting hydrazine reduction process parameters

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Abstract
Owing to their high permeability, metallic soft magnetic materials exhibit high potential as microwave absorbers. The great challenge in designing desirable absorption properties from these materials is their large electrical permittivity at microwave frequencies. So, decreasing their permittivity within acceptable limits while keeping permeability at sufficiently high or improved levels is considered an important requirement for matching impedance and obtaining excellent electromagnetic (EM) absorption properties. In the present research, FeCo alloy particles produced employing a simple wet chemical reduction process with the intention of investigating dependence of their EM properties on synthesis parameters. The characterizations were done with the help of x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The intrinsic EM properties ($\varepsilon_r$, $\mu_r$) in a frequency range of 2–18 GHz were measured by a vector network analyzer (VNA) for the paraffin composites containing obtained products. The results indicated that the concentration of NaOH and metallic salts as the synthesis precursors can tune the permittivity and permeability. Under optimum conditions, bandwidths of 7.3 and 5.5 GHz with thicknesses of only 1.2 and 1.5 mm were obtained respectively. Also, Reflection loss (RL) of $-45$ dB was attained. The excellent EM absorption properties demonstrated that the synthesized FeCo alloy may be an ideal absorber having both a wide absorption bandwidth and a low thickness.

1. Introduction
A good number of recent researches focus on developing electromagnetic wave absorber materials [1–3]. The reason can be attributed to applications of these materials employed widely as radar absorbers in stealth technology, filters, and shielding [4, 5]. Absorption rate increases with matching impedance between the absorber and free space. The main impedance parameters are intrinsic electromagnetic properties, including complex permittivity ($\varepsilon_r = \varepsilon'_r + j\varepsilon''_r$) and permeability ($\mu_r = \mu'_r + j\mu''_r$). Thus, the ability to tune these parameters could lead to controlling the absorption properties in proportion to different applications. That is why designing and optimization of these electromagnetic features are among widely discussed issues in the field [6].

It is quite well-known that metallic soft magnetic materials are regarded as the best class of absorbers. These materials simultaneously display active dielectric and magnetic loss properties [7]. As the result, they are able to effectively attenuate the electromagnetic wave energy. According to Snoek’s law [8], these materials have most permeability in microwave frequencies as they exhibit high saturation magnetization as well as low static permeability. The microwave absorption potential of metallic soft magnetic materials has extensively been studied [9–14]. In working with these materials, researchers are faced with a major problem i.e. their large permittivity. This characteristic can bring about impedance mismatching and increased reflection. Accordingly, it is necessary to reduce permittivity in these materials while retaining their permeability at a high level. In order
to enhance the reflection loss (RL), researchers have improved the electromagnetic properties (\(\varepsilon, \mu\)) of the particles via modifying their structures and compositions. To take an example, some have concentrated on creating insulate shells on the metallic particles in the form of core–shell structures. To know more on this strategy, the interested reader can refer to FeCo@SnO\(_2\) [15], FeCo@C [16–18], Fe@SiO\(_2\) [19–21] and Ni@(SiO\(_2\), TiO\(_2\)) [22]. There are numerous works on the microwave absorption properties of metallic/(carbon based) composites. FeNi/CNTs [23], Ni/MWCNTs [24, 25], Fe50Ni50/functionalized graphene [26] and FeCo/graphite [27] are among the studies which follow the latter approach for increasing the microwave absorption properties. As well, the mechanical milling of metallic particles is a popular and convenient approach for attaining the high permeability [28–31].

One of the most important materials in this class is FeCo alloy as it displays highest saturation magnetization and lower static permeability compared with pure Fe [32]. The present research work is focused on investigating the dependence of electromagnetic properties on the synthesis parameters of the FeCo alloy. The FeCo alloy particles are produced through hydrazine reduction processing. Although the absorption properties of FeCo have been extensively studied, the main focus of this work is to modify and optimize the absorption properties by adjusting the processing parameters. The results indicate that it is possible to design optimum absorption properties per microwave frequencies bands (S, C, X and Ku bands) in this way. According to the literature review, it seems this is a novel approach that can be applied to extend performance of an absorber material.

2. Experimental

FeCo particles were prepared in an N\(_2\) atmosphere through wet chemical reduction processing inside a three-necked round-bottomed flask. Briefly, equal amounts of FeSO\(_4\), 7H\(_2\)O and CoSO\(_4\), 7H\(_2\)O as cationic sources were dissolved in 200 ml of water accompanied by vigorous stir at about 700 rpm. The reaction temperature was fixed by means of a water bath at 70 °C. Next, 32 ml solution of Hydrazine (50% v/v) and NaOH were added to that. After 30 min, the deposited particles were separated magnetically and washed with the help of water and acetone. The products were then dried in an oven at a temperature of 60 °C. The synthesis reaction can be described according to the following chemical equation:

\[
\text{Fe}^{2+} + \text{Co}^{2+} + \text{N}_2\text{H}_4\cdot4\text{OH}^{-} \rightarrow 2\text{FeCo} + \text{N}_2 + 4\text{H}_2\text{O}
\]  

Five samples were obtained per table 1 by making changes in the metallic source concentration and the sodium hydroxide concentration. The samples phase purity was characterized by x-ray diffraction (XRD) with CuK\(_\alpha\) radiation. The morphology and the microstructure of the samples were determined using Field Emission Scanning Electron Microscopy (FESEM). Complex permeability and permittivity features were measured on paraffin composite samples containing 80%wt of the synthesized FeCo particles. To prepare composites, FeCo particles were introduced into a solution of toluene and paraffin. The resulting homogenous mixture was placed in an oven at 60 °C for 3 h to evaporate the toluene content. Next, the prepared composites were pressed in the form of disks respectively having 7 mm and 3 mm dimensions for the outer and inner diameters. Measurements were performed by means of a vector Network Analyzer (VNA) in 2–18 GHz frequency ranges.

3. Results and discussion

The XRD patterns of the synthesized samples are shown in figure 1. All the diffraction peaks belong to FeCo pure phase containing no impurity. Figure 2 demonstrates the FESEM images of the synthesized samples. It is well known that under high supersaturating conditions the precipitation process in the solution takes place during a synthesis process. Meanwhile, the growth process for the particles nuclei continues in a way so as to preserve the thermodynamic equilibrium state [33]. For that reason, all parameters of a chemical reaction e.g. temperature, PH, reactants concentration play their own parts in the growth process. Thus, the final morphology and microstructure of the resultant products can be attributed to the reaction parameters. According to FESEM images (figure 2), sample A contains particles having average sizes of about 350 nm. On the other hand, in other samples, the particles with a size of about 1–3 micrometers and irregular surface is seen. As is revealed by the

**Table 1. Concentration of metallic salts and NaOH in synthesis of samples (all quantities are in molar unit).**

| Sample | A   | B   | C   | D   | E   |
|--------|-----|-----|-----|-----|-----|
| Metallic salts | 0.10 | 0.10 | 0.10 | 0.05 | 0.15 |
| NaOH    | 3.75 | 2.50 | 1.25 | 1.25 | 1.25 |
images no specific shape is produced in the prepared samples, but a hypothesis is whether the microstructure and consequently the inherent properties may vary according to the different synthesis conditions.

Figure 3 indicates the frequency dispersions of the complex permittivity and permeability of samples A, B and C. In these samples, only the concentration of NaOH is changed while other processing conditions remain unchanged (table 1). As is evident, compared with sample A, the real and imaginary parts of permittivity drop significantly simultaneously with a decrease in the concentration of NaOH in samples B and C. In general, permittivity depends upon relaxation polarizations and conductivity. Using Maxwell’s equations, $\varepsilon''$ could be expressed as follow [34]:

$$\varepsilon''(\omega) = \varepsilon''_p(\omega) + \sigma_{dc}/\varepsilon_0\omega$$

(2)

Where $\varepsilon''_p(\omega)$ is the portion of polarization relaxation, $\sigma_{dc}$ is the dc conductivity of the composite, $\varepsilon_0$ and $\omega$ are respectively the free space permittivity and the angular frequency. As can be seen, the $\varepsilon''$ dispersion in sample A (figure 3) is proportional to the inverse of frequency ($\propto 1/\omega$). This behavior verifies the significant contribution of conductivity in the dielectric permittivity of the sample. On the other hand, in the $\varepsilon''$ spectrum of samples B and C, simultaneous with changes in the NaOH amount, the conductivity portion is notably suppressed. The high conductivity in sample A can be attributed to smaller size of particles. In composites, small particles having chain connections in the matrix can increase the conductivity whereupon the percolation threshold of volume fraction of filler can change. It is a well-known fact that in the percolation threshold, there occurs a sharp increase in conductivity. Percolation threshold is a critical value of volume fraction of filler contents in absorber composites. To further confirm the matter, the sample A composites and their intrinsic electromagnetic properties are investigated at the lower volume fraction. Figure 4 shows the real and imaginary parts of 60%wt, 70%wt and 80%wt composites containing the sample A. As can be seen, with decrease in the filler contents of the composites, the permittivity decreases dramatically. The decrease is attractive in the imaginary part of permittivity. So, a logical conclusion is that in the 80%wt composites, volume fraction exceeds the percolation threshold. On the other hand, this behavior in the real and imaginary parts of permeability is quite the reverse. In these samples, the real and imaginary parts of permeability increase along with a decrease in the NaOH amount in samples B and C compared with the permeability of sample A. The lower permeability in sample A can be attributed to the presence of eddy currents arising from high conductivity. When magnetic fluxes change in a ferromagnetic, loops of electrical currents perpendicular to applied magnetic field lines are created according to Faraday’s law of induction. By Lenz’s law [35], an eddy current loop produces an induced magnetic field that opposes the change in applied magnetic field [36]. Thus, simultaneously with a decrease in the effectiveness of the applied field, there occur a decreasing in permeability, too. The magnitude of the current in a given loop is proportional to the conductivity of the material. So, if conductivity is large, the eddy currents produced can be large as well. As a result, the induced magnetic field is larger in the opposite directions and a lower permeability is observed in sample A. Figure 5 shows the complex permittivity and permeability dispersions in samples C, D and E. Only the cation concentrations were changed in the samples, as decreased in D and increased in E compared with C (table 1). Accordingly, there occur an increase in both the real and imaginary parts of the permittivity of samples D and E. This increase is more noticeable in sample E. On the other hand, least changes are observed in the real and imaginary parts dispersion of the permeability.

Figure 1. XRD patterns of synthesized samples A, B, C, D and E.
To gain a deep understanding of the absorption mechanisms, the Cole-Cole plots and $\mu'' / \mu' - 1/f$ plots of the samples are shown in Figure 6. Based on the Debye theory [34, 37], the electric dipole relaxation appears as a circle form in the $\varepsilon'' - \varepsilon'$ plot. On the other hand, it is proved that if the magnetic loss is originated from the
**Figure 3.** Complex permittivity and permeability of samples A, B and C versus frequency in 2–18 GHz range: (a) real permittivity, (b) imaginary permittivity, (c) real permeability and (d) imaginary permeability.

**Figure 4.** Complex permittivity and permeability of composites containing 60%wt, 70%wt and 80%wt of samples A versus frequency in 2–18 GHz range: (a) real permittivity, (b) imaginary permittivity, (c) real permeability and (d) imaginary permeability.
Figure 5. Complex permittivity and permeability of samples C, D and E versus frequency in 2–18 GHz range: (a) real permittivity, (b) imaginary permittivity, (c) real permeability and (d) imaginary permeability.

Figure 6. Cole–Cole plots of the samples (a) A, (b) B, (c) C, (d) D and (f) the $\mu''/\mu' - j\omega f$ variation against frequency for the samples.
eddy current loss, the \( \mu'' \mu' - 2f^{-1} \) against frequency remains constant [38]. As shown in figures 6(b, d, e), the circles in Cole-Cole plots confirm the presence of the polarization relaxation in the samples B, D, and E. On the other hand, the behavior is not seen in the \( \varepsilon'' - \varepsilon' \) plots of samples A and C (figures 6(a, c)). As discussed ago, the conduction is dominant mechanism in the electrical loss of sample A and for sample C the electrical loss is very weak, hence the polarization relaxation is not observed in these samples.

The figure 6(f) shows the \( \mu'' \mu' - 2f^{-1} \) against frequency. As can be seen, its variation is very insignificant at >6 GHz frequencies and it indicates that the main magnetic loss mechanism in all samples originates from eddy current loss.

As discussed above, the synthesis conditions changes changes have a significant effect on the intrinsic parameters of the obtained samples. In the following, the effect of the permittivity and permeability behaviors on the absorption properties are investigated. According to transmission line theory, the reflection loss of the metal backed composite samples can be calculated as follows (RL) [39]:

\[
RL = -20 \log|\Gamma| = -20 \log\left|\frac{Z_{in}/Z_0 - 1}{(Z_{in}/Z_0 + 1)}\right| 
\]  

(3)

Figure 7. Calculated optimum Reflection loss for absorber composites containing (a) sample A, (b) sample B, (c) sample C, (d) sample D and (e) sample E in 2–18 GHz frequencies.
According to equation 3, maximum absorption occurs if the reflection coefficient is reached to zero. In this case, impedance of the absorber layer is equal to the air impedance mismatch. According to equation 4, the reflection coefficient can be attributed to the large permittivity of the sample. The large permittivity has given rise to impedance mismatch. Therefore, impedance properties can be designed. As discussed, in the prepared composites of synthesized samples, along with controlling permeability and permittivity, the proper impedance for the desired microwave absorption parameters are the outcome of electric and magnetic properties of an absorber when affected by wave. By controlling permeability and permittivity, the proper impedance for the desired microwave absorption properties can be designed. As discussed, in the prepared composites of synthesized samples, along with the changes of the synthesis parameters, considerable changes occur in the intrinsic EM properties. Figure 7 shows the RLs in optimum thicknesses for S (2–4 GHz), C (4–8.2 GHz), X (8.2–12.4 GHz) and Ku (12.4–18 GHz) bands. The optimum RLs are obtained through calculating maximum area between the RLs plot and frequency axis in different thicknesses [40]. Tables 2 and 3 display microwave absorption properties of the samples in all frequency bands. A desired absorber has a wide bandwidth, a thin thickness and deep absorption rate. In these tables, \( \Delta f/d \) is calculated for all the designed absorbers. A large \( \Delta f/d \) means more bandwidth and thinner thickness. So, it can be considered as a comparison parameter. According to the imaginary part of the permittivity, although sample A is an intensive lossy media, its reflection loss is quite insignificant. This behavior can be attributed to the large permittivity of the sample. The large permittivity has given rise to impedance mismatch. According to equation 3, maximum absorption occurs if the reflection coefficient is reached to zero. In this case, impedance of the absorber layer is equal to the air impedance \( (Z_{in} = Z_0) \) and matching impedance is created. Figure 8 shows a map chart of absolute values of \( (Z_{in}/Z_0 - 1) \) in different thicknesses and all frequency bands. As can be seen, at the zones that values of \( (Z_{in}/Z_0 - 1) \) are near to zero (matching impedance zone), is expected an increase in absorption. The two-dimensional absorption plots in figure 7 fit well with these maps. According to tables 2 and 3, and the permittivity plots in figures 3 and 5, a decrease in the permittivity promotes absorption. Samples with higher bandwidth and thinner thickness or larger \( \Delta f/d \) are bolded. In the S band, the most absorption rate belongs to sample D. This sample has a 1.3GHz bandwidth in the 3.4 mm thickness. In addition, its \( RL_{max} \) is calculated −36 dB at 3.2 GHz frequency. The optimum absorption in the C band is for sample B. Its bandwidth is 3.1 GHz with a thickness of 2.1 mm. For this sample the absorption depth reaches a \( -35 \) dB at 6.5 GHz frequency. In the X and Ku bands, sample C has the most absorption rate. The designed absorber for this sample has 5.5 GHz bandwidth that, in addition all frequency range related to the X band, it covers parts of the Ku band at thickness of only 1.5 mm. Furthermore, the absorption intensity rate is

| Sample | \( \Delta f \) (GHz) | \( RL_{max} \) (dB) | \( f_{max} \) (GHz) | \( d \) (mm) | \( \Delta f/d \) (GHz/mm) |
|--------|-----------------|-----------------|-----------------|-----------|-----------------|
| A      | 0               | −18             | 9.7             | 1.3       | 6.6             |
| B      | 3.7             | −45             | 10.7            | 1.5       | 7.3             |
| C      | 5.5             | −45             | 10.7            | 1.5       | 7.3             |
| D      | 5.5             | −45             | 10.7            | 1.5       | 7.3             |
| E      | 0               | −11             | 9.2             | 1.1       | 0               |

Table 2. Microwave absorption properties of optimum RLs for the samples at S and C bands.

| Sample | \( \Delta f \) (GHz) | \( RL_{max} \) (dB) | \( f_{max} \) (GHz) | \( d \) (mm) | \( \Delta f/d \) (GHz/mm) |
|--------|-----------------|-----------------|-----------------|-----------|-----------------|
| A      | 0               | −18             | 9.7             | 1.3       | 6.6             |
| B      | 3.7             | −45             | 10.7            | 1.5       | 7.3             |
| C      | 5.5             | −45             | 10.7            | 1.5       | 7.3             |
| D      | 5.5             | −45             | 10.7            | 1.5       | 7.3             |
| E      | 0               | −11             | 9.2             | 1.1       | 0               |

Table 3. Microwave absorption properties of optimum RLs for the samples at X and Ku bands.
−45 dB at 10.7 GHz frequency, which is the highest $RL_{\text{max}}$ among all designed absorbers in the present work. For the ku band, this sample has able to absorb 7.3 GHz bandwidth in a thin thickness of 1.2 mm contain all frequencies of the band. Also $RL_{\text{max}}$ is −22 dB at 14.1 GHz frequency.

### 4. Conclusion

In order to enhance microwave absorption properties, the reaction parameters effect is investigated in synthesizing FeCo alloy particles. The obtained results indicate that the concentration of the cations and NaOH are effective parameters in controlling the absorption properties. In samples with high permittivity would create an impedance mismatch and no absorption whatsoever is observed. By changing the effective synthesis parameters, the permittivity was reduced significantly and the permeability was increased. Accordingly, a matching impedance is produced and the absorption properties in the samples are enhanced. The optimally
designed absorber with a thickness of 1.5 mm displayed a 5.5 GHz bandwidth covering the whole range of the X band and parts of the Ku band. Also, its maximum absorption intensity rate ($R_{\text{max}}$) reaches $-45$ dB at 10.7 GHz frequency.

The final conclusion reached is that synthesis parameters are effective in the EM properties ($\varepsilon_r$, $\mu_r$) of the produced FeCo alloy particles. Also, with tailoring these parameters this compound can be attractive candidates for microwave absorption.

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