Synthesis of Ni doped iron oxide nanoparticles and their dielectric properties

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Abstract: Sol-gel method was adopted for the formation of magnetite and metal doped nanoparticles. The synthesized nanoparticles were confirmed by using XRD, FE-SEM, FTIR and UV-Vis spectroscopic techniques. The X-ray diffraction results confirm crystalline structure and the size of the synthesized nanoparticles. IR data reveals the characteristic absorption bands for oxide formation. Dielectric properties of the prepared composite were determined by impedance analyser. Significant improvement of dielectric properties can be obtained when we incorporated polymer matrix in metal oxide nanoparticles.

Key words: Sol-gel method, nanoparticles, polymer matrix, Dielectric properties

1. Introduction:

Wide applications of the nanomaterials, its promising area for today’s research. Due to large surface to volume ratio, and size nanoparticles used in several applications.[1-4] These Metal oxide nanoparticles show special electronic properties as compared to those of bulk materials. Cost effective and simple method should be adopt for the formation of nanoparticles. The metal oxide-based conducting polymer nanocomposites also exhibit both electrical and magnetic functions with their potential applications. Magnetic dependent applications such as EMI shielding, sensors and magnetic hypothermia are most prominenting thrust area of now the days research.

Ferrimagnetic $\text{Fe}_3\text{O}_4$ (Magnetite) is widely used as a magnetic material. But for some technical application its saturation magnetization could not meet the requirements. According to some research it was proved that the magnetic performance of $\text{Fe}_3\text{O}_4$ could be improved by doping $\text{Fe}_3\text{O}_4$ with transition metals such as (M=Mn,Co,Ni). Doping of these metals are responsible for raised the saturation magnetisation of the metal oxide based nanocomposite.
We used Ni for doping because Ni doped nanoparticles exhibit super magnetic behaviour at room temperature as compared to other transition metals.[5]

When Ni doped with in $Fe_3O_4$, there would be a formation of spinel structure compound called Nickel ferrites. It consists of a cubic structure of oxoanions where tetrahedral & octahedral sites are occupied at different positions. The structural formula is $MY_2O_4$ having different oxidation state where M and Y are the different metal cations. The spinel structure is $[M^{2+}Y^{3+}]_A [M^{2+}_i Y^{2+}_i Y^{3+}]_B O_4$ where A and B suffixes represents for the tetrahedral and octahedral sites, respectively, and i is a parameter called inversion grade or rate. Thus, if $i=0$ means normal spinel[2], if $i=1$ inverse spinel and for $0<i<1$ mixed spinel. For nickel ferrites, the inverse spinel is usually obtained $2^+$, where the $Ni^{2+}$ ions possess the octahedral sites and the $Fe^{3+}$ ions are distributed among the A and B sites equally. As a result, we observed that the structure (inversion grade) and composition of the nickel ferrites nanoparticles determine the final properties of the material, in particular, their magnetic behaviour (i.e., saturation magnetization). Opting the sol-gel method the role of different percentage of nickel doped iron oxide was synthesized and their effects on structural, magnetic and morphological properties on thin films of PVA dispersed polymer.[5]

Some of the scientists came up with various methods for the preparation of Ni doped $Fe_3O_4$ in aqueous medium by hydrothermal reaction at low temperature (200 °C).[6] Magnetic nanoparticles were prepared by the aqueous co-precipitation method by Mohammad Yousefi and Paransa Alimard.[7] Ni-doped Fe$_3$O$_4$/ppy nanocomposite was prepared by in situ polymerisation of a pyrrole monomer in an aqueous solution by X. Shen et al.[8]

Here we were using sol-gel method for the synthesis of Nickel doped Iron oxide nanoparticles due to its cost effectiveness, relevant, require easily available chemicals and most importantly gives maximum yield of product.

2.Experimental:

Materials-
Ferric Nitrate, Nickel Nitrate, DDW, Ethanol, Sodium Hydroxide, Citric acid, Polyvinyl alcohol were of analytical grade and used from properly sealed boxes. No contamination of chemicals was there. DDW was used for the preparation of all the solutions.

2.1 Formation of Fe$_3$O$_4$

Ferric nitrate (2.00 gm) was dissolved in 50 ml distilled water. Sodium hydroxide solution was prepared in another beaker and added dropwise in iron nitrate solution. After addition the sodium hydroxide solution feeric hydroxide solution was prepared after 30 minutes. Prepared solution was kept overnight for clear solution. After decantation of clear solution centrifuged it for 5 min and ultra-sonication (5 min) was done. A slurry type solution was obtained by the addition of ethanol and then dried in oven and iron oxide was formed.[9]

2.2. Formation of Ni doped Fe$_3$O$_4$

Different concentration (1 wt %, 2 wt %, 3 wt %) of nickel nitrate was dissolved in 3.00 gm of ferric nitrate in 50 ml distilled water respectively. 4.00g of sodium hydroxide a small amount of citric acid was dissolved in 30 ml of water in another beaker. This prepared solution was added in nickel doped iron nitrate solution dropwise and prepared solution was stirring vigorously for 30 minutes at room temperature. The colour of the solution was changed from greenish to brown when we were added the citric acid solution in nickel doped iron oxide solution. The formed slurry was kept in furnace at 500°C for for 4 hr after that nickel doped iron oxide nanoparticles was obtained,

2.3. Preparation of Thin films

Sol-gel methodology was adopted for the synthesis of Ni doped transparent thin films, different concentration of nickel doped iron oxide (0.8, 1.2, 1.5, 2.0) wt% was disperse in methanol and sonicate it to make solution A. In another beaker, solution B was prepared using 0.4 g of PVA in 20 ml deionized water for 30 min. Solution A was added slowly in a solution B with continuous stirring for obtaining the clear solution and transferres to Petri dish, and kept in an oven for 48 hr at 60°C. Thin films of composite
2.4. Characterization

Synthesized nanoparticles were confirmed by different spectroscopic techniques such as XRD, FTIR, FESEM, and EDS. For X-Ray diffractogram PANanalytical Empyrean with CuKa(λ = 1.5406 Å) was used, and SEM images were capture by a Zeiss-Sigma300.

Results and discussion –

FTIR Analysis -

FTIR spectroscopy analysed the interaction between the Particles after doping Ni with Iron oxide. The spectrum for iron oxide should show a strong band within the region (4000–500 cm\(^{-1}\)) due to iron oxide structure, which is reliable with magnetite (\(Fe_3O_4\)) IR spectrum. In Fig (1) For \(Fe_3O_4\), two characteristics peaks at 580 and 498 cm\(^{-1}\) credited to Fe–O stretching modes in \(Fe_3O_4\) nanoparticles. Due to the doping of nickel the wave number of rion oxide is slightly shifted but the doping percentage of nickel is less hence it was not effected the wavenumber. [9]

Figure 1: FTIR spectrum of \(Fe_3O_4\) and nickel doped \(Fe_3O_4\) nanoparticles
XRD Measurements-

The X-ray diffraction spectrum (XRD) gave accurate measurement of atomic spacing and determined the strain state in the thin films. The XRD diffraction of Ni-doped Fe$_3$O$_4$/PVA nanocomposite is given in Figure (5). The obtained peaks in XRD for Ni doped Iron oxide/PVA thin films are at planes (012), (104),(110),(113),(024),(116),(214) and (300) which was determined from the diffraction angle $2\theta = 23.50^0$, $32.82^0$, $35.67^0$, $40.84^0$, $49.89^0$, $53.53^0$, $62.06^0$, $63.61^0$ respectively.[10] The size of crystallite (D) of Fe$_3$O$_4$ nanoparticles can be calculated with the help of Scherrer’s equation

$$D = \frac{K\lambda}{\beta\cos\theta}$$

![Figure 2. XRD image of Ni doped iron oxide](image)

FESEM & EDS Study-

Ni doped iron oxide nanoparticles SEM images were shown in Figure (3) respectively. On the variation of the percentage of the nickel in nickel doped iron oxide the morphology of the nanoparticles was changed. The particle density with increase in the concentration of ratio of [Ni]: [Fe]. Also, we observed that with increase in concentration of Ni the compactness of the sample increases and the structures became more smoother and the orientation of the microparticles would depend on the Ni-doped iron oxide content. Thus, there would be an increase in conductivity with Ni-doped Fe$_3$O$_4$ content which was directly proportional to the improved compactness of the PVA when the Ni-doped Fe$_3$O$_4$ content was relatively high.[11]

EDS (Energy Dispersive X-ray spectroscopy) gave information about the elemental
composition of a desired sample taking into account the high-resolution images obtained from FESEM analysis. From this we analysed the presence of elements such as Ni, Fe, O which determined any impurity was present or not. Figure 6 shows the presence of Ni, Fe, O.

Figure 3(a), (b) and (c) Ni doped Fe3O4/PVA thin films (0.8, 1.5 and 2.0 %)
Magnetic properties: Magnetic properties of Fe$_3$O$_4$ and Ni doped Fe$_3$O$_4$ were measured at room temperature by using Vibrating Sample Magnetometer (VSM). No hysteresis curve has been obtained in iron oxide and nickel doped iron oxide nanoparticles. Hence both the nanoparticles were shown the paramagnetic nature. It is noticed that when the nickel is doped in Fe$_3$O$_4$ nanoparticles the saturation magnetization is reduced from 93 emu g$^{-1}$ to 55 emu g$^{-1}$. The reason behind that the existence of the nickel nanoparticles on the surface of the Fe$_3$O$_4$ superfine powders. The other reason behind the phenomena is that the non-collinear spin structure is originated on the surface of iron oxide nanoparticles due to that saturation magnetization is reduced.[12]
Electrical properties: Figure 6(a) & (b) shown the electric properties of Fe$_3$O$_4$ and Ni doped Fe$_3$O$_4$ nanoparticles. The dielectric properties $\varepsilon$ and $\varepsilon'$ is slightly increased from Fe$_3$O$_4$ nanoparticles. The reason behind that the due to the electric dipole and polarization which is created by doping of nickel nanoparticles in iron oxide nanoparticles integration the grain boundary and enhance the conductivity of the nanoparticles. Imaginary part of the permittivity is also raised due to high conductivity of the nickel doped iron oxide nanoparticles. [14]

![Figure 6](image.png)

Figure 6 (a) & (b) permittivity curve of iron oxide and nickel doped iron oxide nanoparticles

Conclusions-

Using sol-gel method, first, we prepared $Fe_3O_4$, then Ni doped $Fe_3O_4$ and lastly thin films of Ni-$Fe_3O_4$/PVA nanoparticles. Ni-doped $Fe_3O_4$/PVA nanocomposites had a better and more magnetic property that we observed. The results of analysis obtained by IR, XRD, FESEM, EDS showed that Ni-doped $Fe_3O_4$/PVA nanoparticles gave core shell type of structure. Increase in the concentration of Ni-doped Fe3O4 content in the composites, also there is an increase in saturation magnetisation. As a result, we found that by applying sol-gel method for the synthesis of nanoparticles we get maximum yield of product as it is easy and cost-effective.
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