STRUCTURAL,MAGNETIC AND SURFACE MORPHOLOGICAL FEATURES OF Mn^{2+} DOPED $CoFe_2O_4$ NANOPARTICLES SYNTHESIZED BY SOL-GEL AUTO COMBUSTION METHOD

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ABSRACT

Mn^{2+} dopped $CoFe_2O_4$ ferrite nanoparticles were synthesized by sol-gel auto combustion method XRD pattern confirms the presence of single phase cubic spinel structure from 42nm to 56 nm VSM study indicates increase in saturation magnetization (Ms) and decrese in coervitty(Hc) FE-SEM images exhibit particles with spherical shape and size ranges is found from 37.5 nm to 59.5nm the two main metal vibrations of ferrite observed in FT-IR

Keywords

Mn^{2+} dopped $CoFe_2O_4$ -sol-gel auto combustion method,structure-magnetic properties

SYNTHESIS OF MANGANESE DOPED $CoFe_2O_4$ NANOPARTICLES

INTRODUCTION

Cobalt ferrite nanoparticles have high coercivity and moderate saturation magnetization.Cobalt ferrite nanoparticles have been widely used in manyapplications due to high electromagnetic properties, good chemical stability andmechanical hardness. Due to these properties of cobalt ferrites are used in video andaudio tapes, high density digital recording media in spintronics, solar cells, sensorsand catalysis. Cobalt ferrites are used as application in magnetic resonanceimaging (MRI), magnetic fluid hyperthermia (MFH), biosensors, ferrofluids,magnetic separations, storage magnetic materials, targeted and controlled drug delivery [21].

Saturation magnetization (Ms) of cobalt ferrite nanoparticles is smaller thanthat of the bulk and Ms decreasing with decrease in size. When the crystallite size isapproximately equal to the single domain size then the coercivity reaches to itsmaximum value.Cobalt ferrite nanoparticles have an inverse spinel structure. In this O^{2-} form FCCclose packing, and Co^{2+} and Fe^{3+} occupy either tetrahedral or octahedral interstitialsites. In this inverse spinel cobalt ferrite structure half of Fe^{3+} ion and Co^{2+} ionsoccupy the octahedral sites and rest of Fe^{3+} ions occupy the tetrahedral sites [22].

Magnetic materials are used in a variety of applications. Magnetic spinel ferrites possess excellent magneticproperties like high magnetocrystalline anisotropy, largecoercivity and ideal saturation magnetization. They possessgood structural and chemical stability at elevated temperatures.Substitution of divalent ions like $Mn^{2+}$of ferrites has been made to vary the structural, magneticand electrical properties [23, 24]. Though several methods are available to synthesize ferrites, chemical methods are preferreddue to their simplicity and chemical homogeneity.A fine particle size is required for uniform sintering and densification which can be obtained easily by chemicalmethods [25]. Materials synthesized by sol-gel auto combustionmethod have high purity, chemical homogeneityand uniform particle size. Cobalt ferrite doped with Mn^{2+}ion using sol-gel auto combustionmethod, and their magnetic, structural and morphological features were examined and reported in this work.

Manganese ion doped cobalt ferrite of chemical composition $Mn_{0.5}Co_{0.5}Fe_2O_4$sampleswere synthesized by sol-gel auto combustion methodat room temperature.Cobaltferrite ($CoFe_2O_4$)nanoparticleswere synthesized by sol-gel auto combustion method at room temperature. The chemicals used were analytical reagent grade manganese nitrate ($Mn(NO_3)_2.6H_2O$),, ferric nitrate ($Fe(NO_3)_3.9H_2O$), Cobalt nitrate ($Co(NO_3)_2.6H_2O$), citric acid ($C_6H_8O_7.H_2O$) and ammonia (NH_3) solution. Citric acid was employed as the chelating agent.

Stoichiometric ratio of nitrates/chelating agent is 1:2. Nitrates and citric acid were dissolved in de-ionized water. This solution was kept in continuous stirring for 24 hrs at 60 °C. The solution become dehydrated and transform into gel. This gel was heat treated in the hot air oven at 250 °C for 8 hrs. This leads to the formation of a dark loose powder. The powder was heated at a rate of 5 °C/min in a muffle furnace and kept at 800 °C for 3 hrs. Finally it was grained finely using mortar and pestle for further analysis. The following instruments were used to synthesis of Mn-$CoFe_2O_4$ nanoparticles.

Result and Discussion

1) Powder X-ray diffraction (XRD) analysis

Structural and phase analysis of Mn^{2+}ion doped cobalt ferrite nanoparticles were conducted with powder XRDpatterns obtained from an X'Pert-PRO Pan Analytical X-raydiffractometer operated at 45 kV and 30 mA, Cu K$\alpha$and wavelength 1.5406 Å. These are shown in Fig. 1. Thesepatterns confirm the presence of a single-phase cubic spinelstructure. The prominent *hkl*planes (220), (311), (222),(400), (422), (511) and (440) are identified and indexed. Theresults are in good agreement with literature values [26–28].

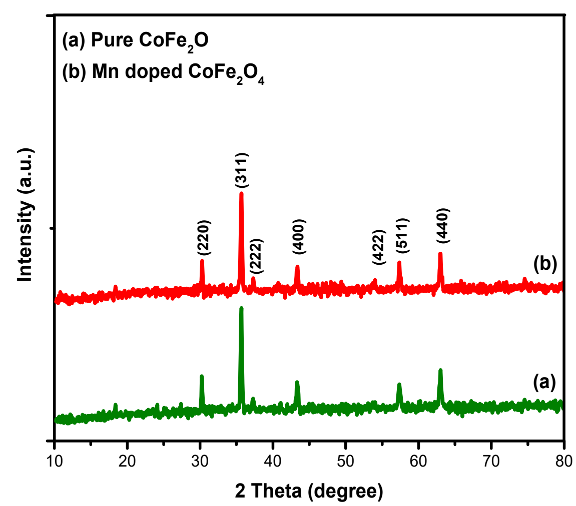


Fig. 1: XRD patternsof (a) Pure $CoFe_2O_4$ (b) Mn-$CoFe_2O_4$nanoparticles

The lattice parameters were calculated using the formula,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where*d* is the inter-planar distance and *h*, *k*, and *l* are theMiller indices [29].These values slightly change with doping of Mn^{2+} ion in cobalt ferrite nanoparticles.It is also observed that the crystallite size changes due to the mixing of Mn^{2+} ion. This variation may beattributed to the changes in the ionic radii of Mn^{2+} (0.67Å),Co^{2+} (0.65Å) ions [30].

X-ray density (ρ_x) of Mn^{2+} ion doped nickelferrite nanoparticles was calculated using the following equation:

$$\rho_x = \frac{8M}{Na^3}$$

where 8 denotes the number of atoms in a unit cell of thespinel lattice, *M* is the molecular mass of the particularferrite samples, *N* is Avogadro's number (6.02252×10^{26}kmol^{-1}) and *a* is the lattice constant. The calculated valuesof X-ray density are 5.415 g/cm^3 for cobalt ferrite, 5.358g/cm^3 for Mn-Co ferrite nanoparticles respectively. The X-ray density values slightly decrease due tothe difference in the radius of Mn^{2+} ion whichis doped in the cobalt ferrite nanoparticles. This is in accordancewith previous reported studies [31].

The average crystallite size (D) were calculated from the XRD pattern with the help of Scherer equation,

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Here, λ is wavelength of the X-ray radiation used, β is full width at half maximum (FWHM) measured in radians and θ is Bragg angle. The crystallite sizes were found to vary from 42 nm to56 nm.

2)Vibrating Sample Magnetometer (VSM) analysis

Magnetization measurements of manganese doped $CoFe_2O_4$nanoparticles were done using vibrating sample magnetometer (VSM-Lake Shore model 7404, operated at a maximum applied field of 10 kOe at room temperature). The observed hysteresis (M-H) curves are presented in Figs. 2 and 3. From the plotted M-H curves, the saturation magnetization (Ms), coercivity (Hc) and remanent magnetization (Mr) values are measured.

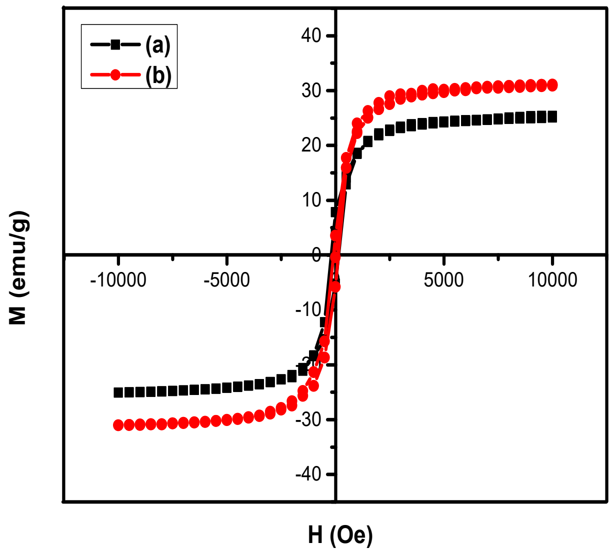


Fig. 2: M-H curves of (a) Pure $CoFe_2O_4$ (b) Mn-$CoFe_2O_4$nanoparticles

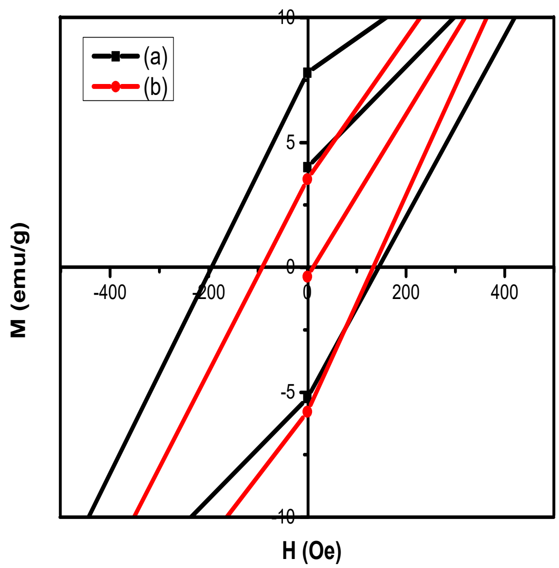


Fig. 3:M-H enlarged curves of(a) Pure $CoFe_2O_4$ (b) Mn-$CoFe_2O_4$nanoparticles

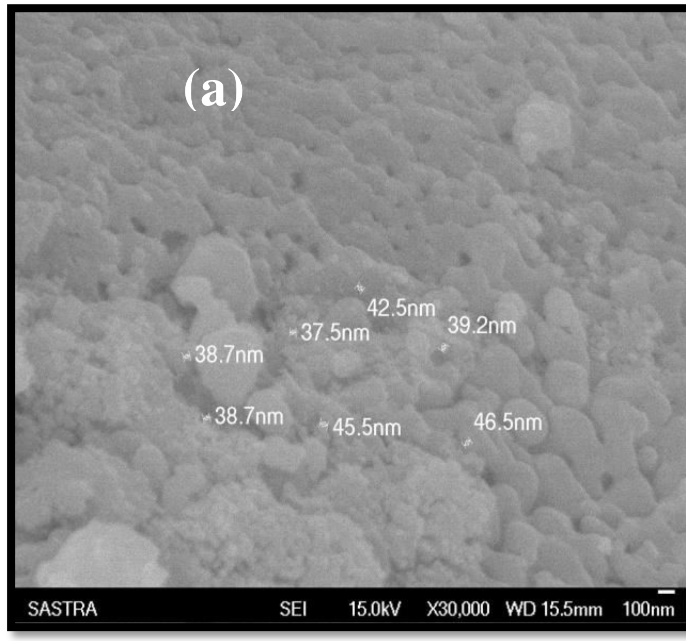
The experimental magnetic moment per formula unit in Bohr magneton (μ_B) was calculated from the saturation magnetization values using the equation,

$$\mu_B = \frac{M_S M_W}{5585}$$

where, M_S is saturation magnetization, M_W is molecular weight of the $CoFe_2O_4$nanoparticles and 5585 is magnetic factor. The M-H curves revealed that the magnetic properties of the nanoparticles are affected by composition and different cation distribution. Various cation can be occupied in tetrahedral sites and octahedral sites to change the magnetic properties [32, 33]. All the hysteresis curves indicate soft ferromagnetic nature of the samples. The saturation magnetization value of $CoFe_2O_4$ferrite nanoparticles is 25.37 emu/gand Mn^{2+} ion doped $CoFe_2O_4$ferrite nanoparticles is 30.86 emu/g with maximum applied field 10 kOe at room temperature. The saturation magnetization isslightly higher than that of the unsubstituted cobalt ferrite (25.37 emu/g) sample. It may be due to the replacement of Co^{2+} ionby Mn^{2+} ion in the octahedral sites Co^{2+}ion having a high magnetic moment (3 μ_B) compared with Mn^{2+} ion (1μ_B). The increase in grain size of ferrite nanoparticlesdecreases the surface area to volume ratio and surfaceanisotropy of the crystal. The coercivity property of the samplesoriginates from a multidomain structure, which theseferrite samples may have due to their large grain size. Inthe multidomain region, the increase in particle size maydecrease the coercivity.This is good agreement with already reported values [34-38].

3)Field Emission Scanning Electron Microscopy (FE-SEM) analysis

The morphological features of pure and Manganese doped $CoFe_2O_4$ ferrite nanoparticles were analyzed by FE-SEM analysis (Model-JEOL/JSM-5610 NE instrument) and are shown in Fig. 28 (a) and (b). FE-SEM images reveal that the grain size of the heat treated undoped $CoFe_2O_4$nanoparticlesis found to be from 37.5 nm to 46.5 nm and 37.6 nm to 59.5 nm for Manganese doped cobalt ferrite nanoparticles. FE-SEM images revealed the spherical nature of the particles. Observed particle size closely matches with the values obtained from XRD measurement.



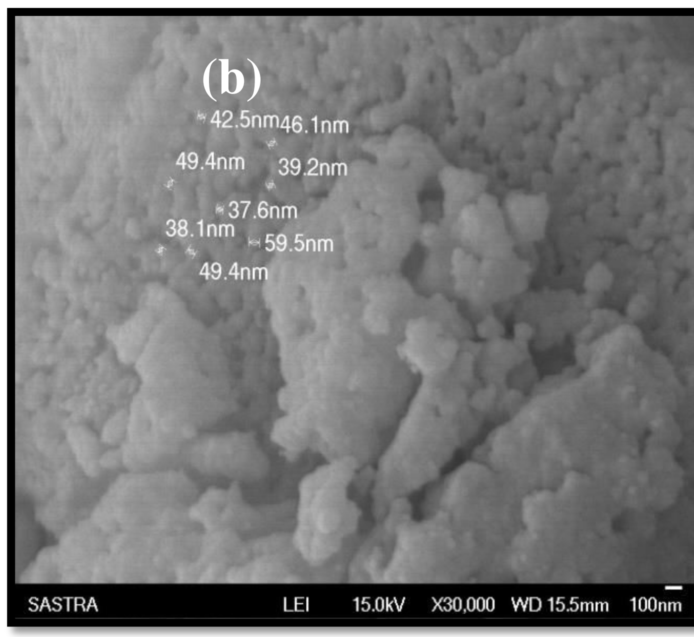


Fig.4: FE-SEM images of (a) Pure $CoFe_2O_4$ (b) Mn-$CoFe_2O_4$nanoparticles

4)FT-IR spectral study

FT-IR spectra of pure and Manganese doped $CoFe_2O_4$ ferrite nanoparticles were recorded using Perkin Elmer FT-IR spectrometer in the range 4000 to 400 cm^{-1} and are shown in Fig.29. The unit cell of nickel ferrite contains 8 molecules. There are 32 divalent oxygen ions, 16 trivalent iron ions and 8 divalent nickel ions in the unit cell. 32 oxygen atoms arrange themselves in fcc structure and this leads to 8 tetrahedral voids (A-sites) and 16 octahedral voids (B-sites). The manganese ions occupy half of the B-sites. The remaining B-sites and A-sites are occupied by iron ions. Co^{2+} ion is expected to occupy B-sites. This divalent metal ion may also occupy A-sites and B-sites which results in the movement of iron ions from A-sites to B-sites [39-41].

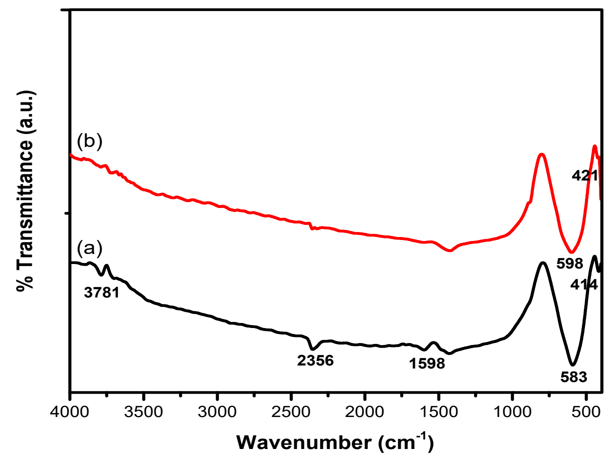


Fig. 5: FT-IR spectra of (a) Pure $CoFe_2O_4$ (b) Mn-$CoFe_2O_4$nanoparticles

FT-IR spectra reveal that the two main vibrations of tetrahedral (A-sites) and octahedral (B-sites) metal-oxygen bonds will be observed in the range of 800cm^{-1}– 400 cm^{-1}. The band observed around 583cm^{-1}– 598 cm^{-1} and 414cm^{-1}– 421 cm^{-1} is due to tetrahedral sites and octahedral sites respectively. In $CoFe_2O_4$, the tetrahedral M-O vibration occurs at 583 cm^{-1} and the octahedral M-O vibration of $CoFe_2O_4$ occurs at 414 cm^{-1}. The occurrence of two metal-oxygen (M-O) vibrations at two different wavenumbers is due to the change in metal-oxygen bond length for tetrahedral and octahedral sites. The observed absorption bands closely match with earlier literature values [42, 43].

CONCLUSIONS

Manganese doped $CoFe_2O_4$nanoparticles were synthesized at room temperature by sol-gel auto combustion method.They synthesized nanoparticles crystallized in cubic spinel phase from the XRD pattern.The lattice parameter and average crystallite size values are calculated.The magnetic properties such as saturation magnetization (M_s), coercivity (H_c) and remanence magnetization (M_r) values are calculated from the plotted M-H loop.FE-SEM image shows the synthesized $CoFe_2O_4$and Mn-$CoFe_2O_4$nanoparticles are spherical in shape and size of the particles was in the range from 37.5 nm to 59.5 nm, which is confirmed by the XRD pattern.Presences of two main metal (M-O) ion vibrations of tetrahedral (A-sites) and octahedral (B-sites) sites were observed in FT-IR spectra. From this results, the substitution manganese ions slightly modify the structural, magnetic and surface morphology of thecobalt ferrite nanoparticles.

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