

Preparation and Characterization of Nano-Sized $(\text{Mg}_{(x)}\text{Fe}_{(1-x)}\text{O}/\text{SiO}_2)$ ($x = 0.1$) Core-Shell Nanoparticles by Chemical Precipitation Method

Mohsen Ahmadipour, Mozhgan Hatami, Kalagadda Venkateswara Rao

Center Nano science and Technology, Institute of Science and Technology, Jawaharlal Nehru

Technological University Hyderabad, Hyderabad, India

Email: Mohsenxm@gmail.com, omrah.h486@gmail.com, kalagadda2003@gmail.com

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ABSTRACT

Magnetic core-shell nanoparticles have been widely studied because of their excellent and convenient magnetic and electrical properties. In this present work core-shell magnetic nanoparticles (MNPs) were synthesized by simple chemical precipitation method. Firstly $\text{Mg}_{(x)}\text{Fe}_{(1-x)}\text{O}$ (magnesiowuestite) nano powder samples were synthesised by low temperature chemical combustion method. Secondly the as synthesised $\text{Mg}_{(x)}\text{Fe}_{(1-x)}\text{O}$ nanoparticles are used to synthesis magnetic core-shell Nano particles by using 2-propanol, poly ethylene glycol (PEG), ammonia solution 30 wt%, tetraethyl orthosilicate (TEOS). Separation of the core-shell magnetic nanoparticles from the aqueous suspension using a centrifuge. The synthesised MNPs and core shell MNP were characterized by X-ray diffraction (XRD), Thermal gravimetric-differential thermal analyzer (TG-DTA), Transmission electron microscopy (TEM), scanning electron microscopy (SEM), (EDAX) for structural, thermal and morphological respectively. It is observed that the particle size of spherical samples is 32.5 nm.

Keywords: Magnetic Nanoparticle; Core-Shell; TG-DTA; SEM; TEM

1. Introduction

In the past decades, considerable attention has been devoted to the preparation of magnetic nanoparticles because of unique magnetic properties microwaves devices, noise filters, recording heading [1-3] and sensors [4].

The core-shell type magnetic nanoparticles can be broadly defined as comprising a core (inner material) and a shell (outer layer material). These are able to consist of a wide range of different combinations in close interaction, including inorganic/inorganic, inorganic/organic, organic/inorganic, and organic/organic materials which the inorganic/inorganic interaction has utilized in this paper. For these types of particle core and shell both are made of metal, metal oxide, semiconductor, any other organic compound, or silica. The silica coating used on a core particle has several advantages. The Most basic advantage of silica shell compares to other inorganic compounds, it reduces bulk conductivity, increase the suspension stability of the core particle, it can block the core surface without interfering in the redox reaction at the core surface.

In recent years, various chemical techniques have been successfully employed for the synthesis of inorganic/

inorganic interaction ($\text{Mg}_{0.1}\text{Fe}_{0.9}\text{O}/\text{SiO}_2$) such as sol-gel [5], hydrolysis [6], stober method [7-8].

The choice of shell material of the core-shell nanoparticle is generally strongly dependent on the end application and use. The Developing new synthesis techniques make it possible to synthesize not only the symmetrical (spherical) shape nanoparticles but also a variety of other shapes such as cube, hexagon [9], prism [10], octahedron [11], disk [12], wire, rod and tube [13] etc. magnetic core-shell NPs are also used in important bio applications, including magnetic bio separation and detection of biological entities (cell, protein, nucleic acids, enzyme, bacterial, virus, etc.), clinic diagnosis and therapy (such as MRI (magnetic resonance image) and MFH (magnetic fluid hyperthermia), targeted drug delivery and biological labels [14].

Preparation of core-shell nanoparticle involves multistep synthesis procedure. But the most important step during synthesis is to maintain uniform coating and controls the shell thickness such as precipitation [15], polymerization [16], microemulsion [17], sol-gel condensation [18]. The overall size and shell thickness can be controlled by varying the reactant concentration both the core and shell material.

2. Experimental

2.1. Preparation of $Mg_{(x)}Fe_{(1-x)}O$ Nano Powder

A number of techniques have been used for the preparation of nanoparticles, such as sol-gel [19], micro emulsion method [20], ball milling [21], microwave hydrothermal method [22].

In the present research paper low temperature glycine based chemical combustion synthesis [23] is used to prepare $Mg_{(x)}Fe_{(1-x)}O$ nanoparticles. The iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) were dissolved in a beaker with sufficient deionized water with Glycine in appropriate amount and the solution was placed under thermal stirring with the temperature of $60^\circ C$; at this temperature, different molar amounts of the fuel were added. The precursor solutions were maintained under thermal stirring for few minutes to ensure homogeneity subsequently these solutions were placed in a hot plate, as the temperature reached $100^\circ C$, water started to boil and evaporate from the solution, which increased solution viscosity substantially, during which the compound caught fire. Precursor is annealed for 2 hrs at $300^\circ C$ the as-obtained precursor and annealed precursor were both characterized.

2.2. Preparation of Core-Shell $Mg_{(x)}Fe_{(1-x)}O/SiO_2$

Appropriate amount of $Mg_{(x)}Fe_{(1-x)}O$ Nano powder was added to 120 ml of 2-propanol and sonicated for about 1 hr. Under continuous stirring, 2.0 g of PEG (poly ethylene glycol), 10 ml of deionized water, 10 ml of ammonia solution (30 wt%) and 0.2 ml of TEOS (tetraethyl orthosilicate) as source of silica were consecutively added into the above suspension, the reaction was allowed to continue for 24 h under stirring. After the reaction was completed, the products were collected through centrifugation at 4000 rpm, followed by washing with deionized water and ethanol several times, and dried at $80^\circ C$ overnight in an oven. The core-shell ($Mg_{(x)}Fe_{(1-x)}O/SiO_2$) magnetic nanoparticles were obtained. The shell and core thickness were controlled by experimental parameters such as coating time, feed concentrations, catalyst and other precursor.

The core-shell magnetic nanoparticle and $Mg_{(x)}Fe_{(1-x)}O$ nanoparticles also was characterized by X-ray diffraction (Bruker D8 Advance, Germany), Thermal gravimetric analysis, (SII EXSTAR 6300R, Japan), Scanning Electron Microscope and Energy-dispersive X-ray spectroscopy, S-3400N-hitachi-Japan), Transmission Electron Microscope (JEM-2100, Jeol).

3. Result and Discussion

3.1. X-ray Diffraction Analysis

The powder x-ray diffraction measurements (XRD) of

the samples were obtained on a Bruker D8 Advance systems were taken from 20° to 80° (2θ value) using Cu-K α ($\lambda = 0.154$ nm) radiation. The crystallite size (D) of the synthesized nanoparticles was measured using the Scherrer's formula [24]

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystallite size, λ is the x-ray wavelength, the β equal to full width half maximum, and θ is the Bragg angle.

The existence of a peak around the diffract ion angle (2θ) equal to $35.66^\circ C$ corresponding to (311) plane confirms the formation of spinel ferrites. The calculated average crystallite size (D) is 52 nm. **Figure 1** shows the XRD pattern of the synthesized Nano powder. It is clear that a cubic structure of $Mg_{(x)}Fe_{(1-x)}O$ that is described in JCPDS 89-4924 is detected in all samples. Seven peaks centered at $2\theta = 30.28^\circ C$, $35.66^\circ C$, $43.33^\circ C$, $53.77^\circ C$, $57.31^\circ C$, $62.93^\circ C$ and $74.44^\circ C$, which correspond to diffraction planes of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) respectively are detected. According to JCPDS 89-4924, the obtained phase has a cubic structure. In the X-ray diffraction pattern of $Mg_{(x)}Fe_{(1-x)}O/SiO_2$ five peaks at 24° , 33° , 41° , 49° and 64° appeared. The first three peaks were from crystalline SiO_2 , and next two peaks might be from α - Fe_2O_3 . In addition to these peaks, the diffractogram of showed a sharp peak of crystalline SiO_2 at 33° . It can be concluded that not pure $Mg_{(x)}Fe_{(1-x)}O$ nano crystals were formed and the silica matrix could be crystallized.

3.2. Thermal Gravimetric Analysis (TGA)

Decomposition path of $Mg_{(x)}Fe_{(1-x)}O$ and $Mg_{(x)}Fe_{(1-x)}O/SiO_2$ core-shell magnetic nanoparticle were studied by TGA. **Figure 2** shows the weight loss percentage for the magnetic particles during heat treatment under constant air flow which is placed on the graph. Thermo gravimetric measures the mass of a sample as the temperature increases. This method is useful for determining sample purity, moisture content of sample, carbonate, organic content and for studying decomposition reaction.

3.3. Fourier Transform Infrared Spectroscopy Analysis (FTIR)

The formation of Nano crystalline $Mg_{(x)}Fe_{(1-x)}O$ and $Mg_{(x)}Fe_{(1-x)}O/SiO_2$ core-shell nanoparticle are supported by FT-IR spectra. The FT-IR spectra for variable G/N^{-1} ratios were recorded in the range $400 - 3000$ cm^{-1} (**Figure 3**). A broad absorption spectrum is seen around 3430 cm^{-1} (**Figures 3(a)** and **(b)**) which is a characteristic stretching vibration of hydroxylate group (O-H). Peaks localized at 1560 cm^{-1} and 1411 cm^{-1} are assigned to asymmetrical

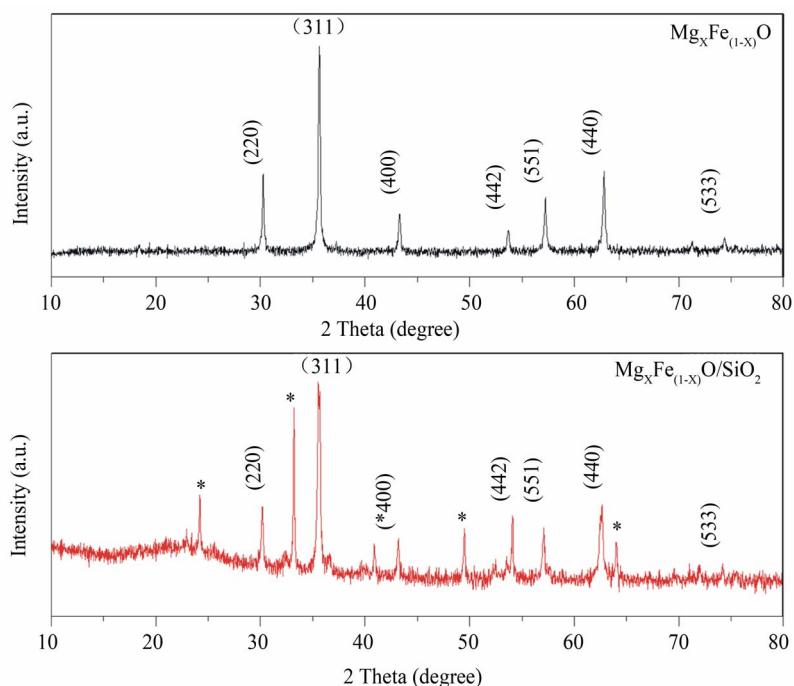


Figure 1. XRD patterns of $Mg_xFe_{(1-x)}O$ nanoparticles and $Mg_xFe_{(1-x)}O/SiO_2$ core-shell.

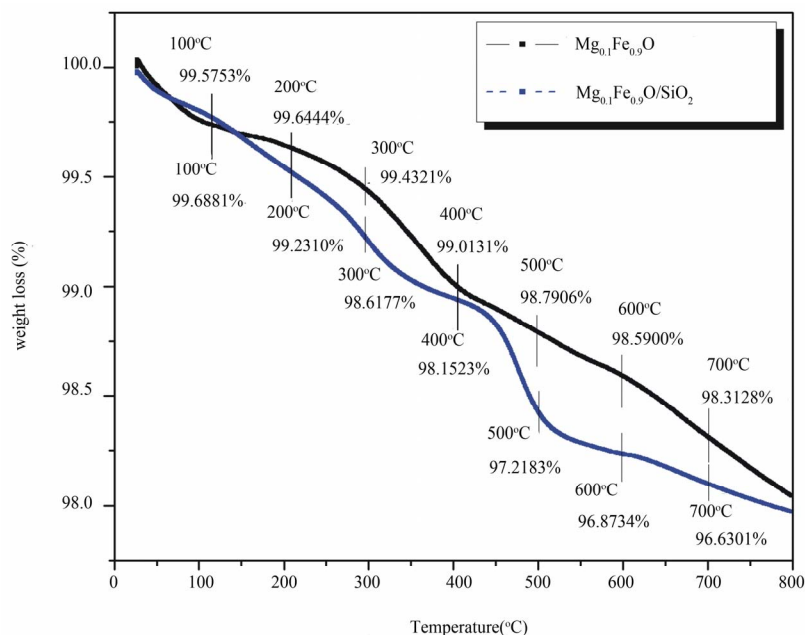


Figure 2. TGA curve for Nano crystalline $Mg_xFe_{(1-x)}O$ and $Mg_xFe_{(1-x)}O/SiO_2$ core-shell nanoparticle.

and symmetrical stretching vibration of carboxylate (O-C-O) respectively (Figures 3(a) and (b)). The peak around 1400 cm^{-1} (broad) characterizes the formation of surface sulfate species with S=O bond (Figures 3(a) and (b)). Absorption bands due to the iron-oxygen (Fe-O) are observed in the $450 - 550\text{ cm}^{-1}$ (Figures 3(a) and (b)). The band at 955 cm^{-1} (Figure 3(b)), Probably caused by Si-O-H stretching vibrations [25,26]. The high fre-

quency band is around 1561 cm^{-1} (Figure 3(a)) which is common feature to all the ferrites [27] and 1095 cm^{-1} (Figure 3(b)) which is characteristic of the silica [28].

3.4. SEM, TEM and EDAX Analysis

Figures 4-6, shows the detailed morphology and crystalline structure of the $Mg_xFe_{(1-x)}O$ nano powder and

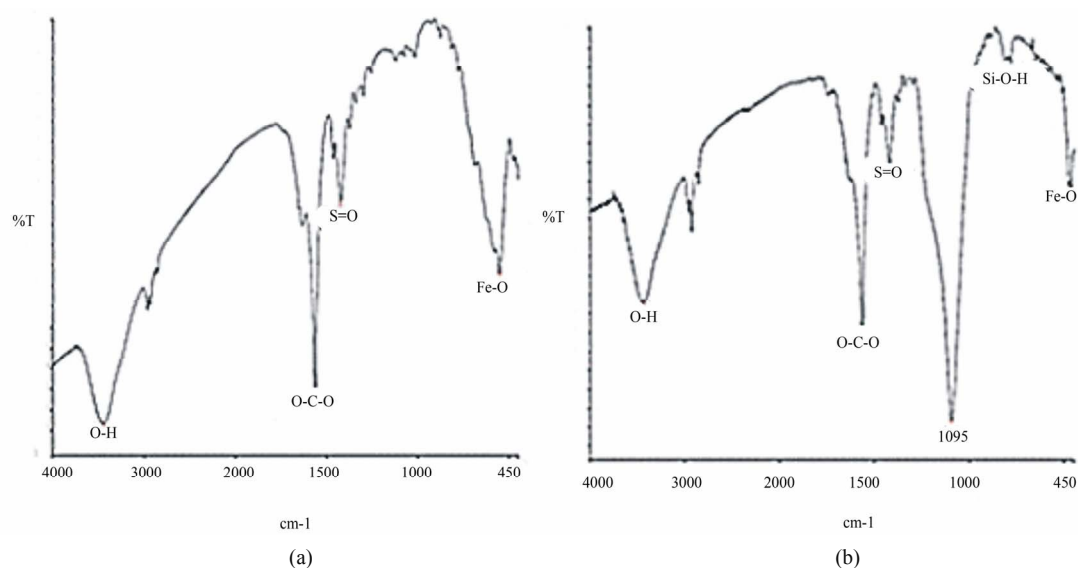


Figure 3. (a) FT-IR spectra of the $Mg_xFe_{(1-x)}O$ powders produced by combustion method at $300^\circ C$; (b) FT-IR spectra $Mg_xFe_{(1-x)}O/SiO_2$ core-shell nanoparticle.

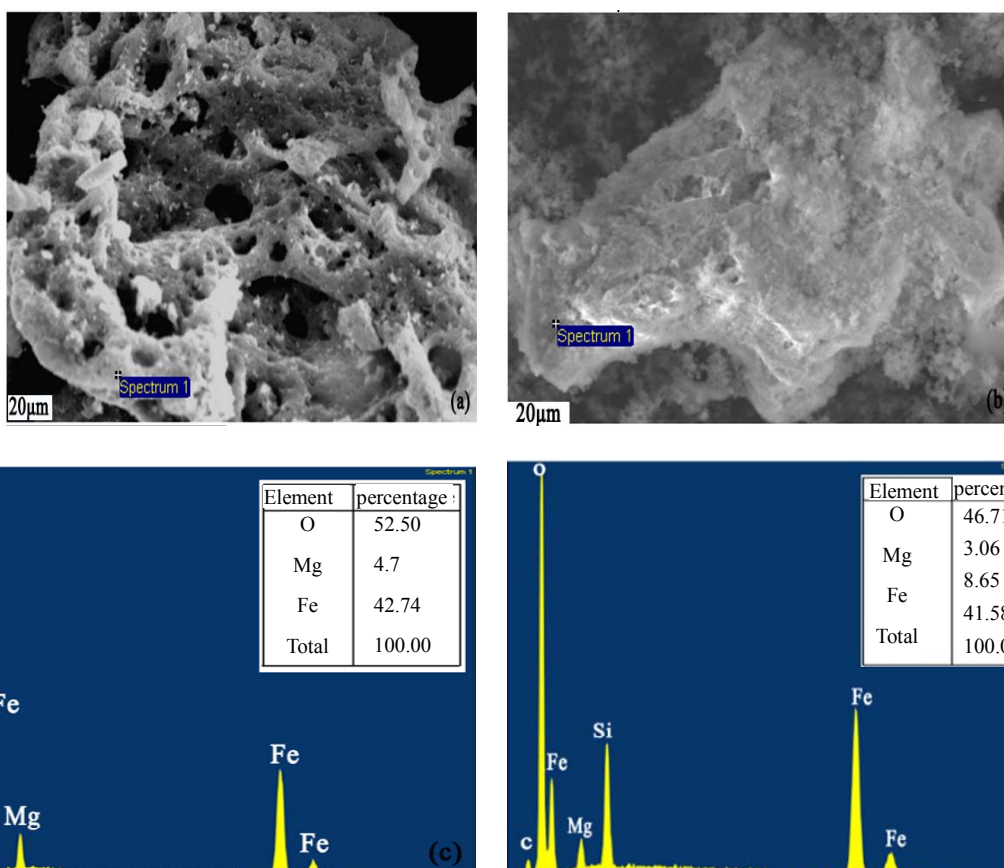


Figure 4. (a-d) SEM micrograph and EDAX of sample; (a) $Mg_xFe_{(1-x)}O$; (b) $Mg_xFe_{(1-x)}O/SiO_2$ core-shell, scale bar $20 \mu m$.

$Mg_xFe_{(1-x)}O/SiO_2$ core-shell nanoparticle, then they were further investigated by SEM, TEM and selected-area electron diffraction (SAED).

It can be seen, $Mg_xFe_{(1-x)}O$ have high porous structure

which was shown in (Figure 4(a)) and also can be seen the structure of $Mg_xFe_{(1-x)}O/SiO_2$ core-shell magnetic nanoparticle in (Figure 4(b)). Energy dispersive x-ray spectroscopy (EDAX) equipped within the SEM was

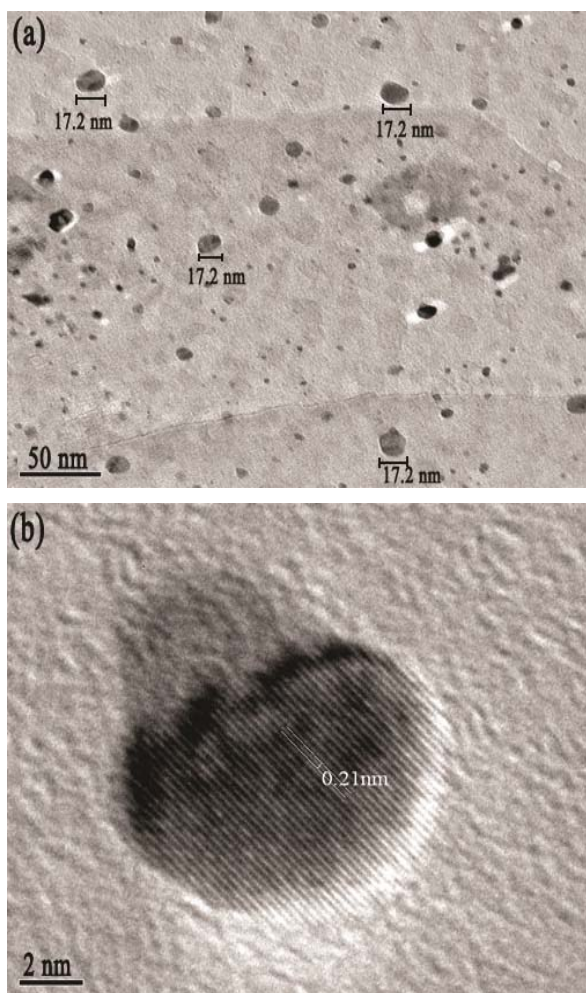


Figure 5. (a) TEM image with scale bar 50 nm; (b) d spacing with scale bar 2 nm (High resolution TEM (HRTEM)); (c) SAED patterns of the $Mg_xFe_{(1-x)}O$ with scale bar 21nm

used to determine the chemical composition of the synthesized nanoparticles. EDAX revealed the chemical composition of synthesized nanoparticles, as shown in **Figures 4(c) and (d)**. No contaminating elements from re

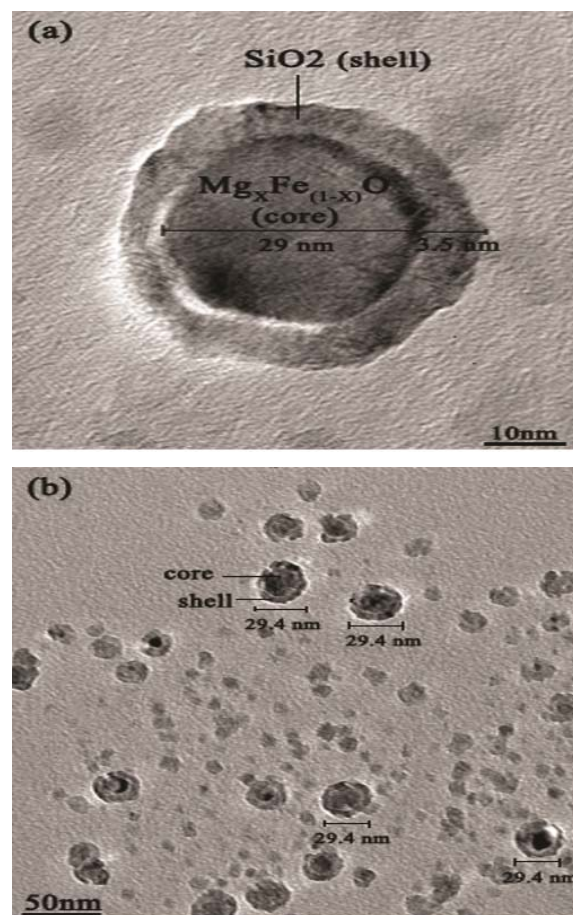


Figure 6. (a) TEM image of $Mg_xFe_{(1-x)}O/SiO_2$ core-shell; (b) high resolution TEM (HRTEM) of core-shell.

agents were detected Transmission electron microscopy (TEM) shows the particle's morphology, distribution and its size **Figure 5(a)**. **Figure 5(c)** is selected-area electron diffraction (SAED) showing (h k l) values which are exactly matching with XRD pattern which is put on white ring in SAED and good uniform dispersion also we observed from **Figure 5(b)** says $Mg_xFe_{(1-x)}O$ has Nano sphere shape with d spacing of 0.21nm. **Figure 6(a)** shows high magnification TEM images of average SiO_2 shell thickness of nanoparticle is 3.5 nm and $Mg_xFe_{(1-x)}O$ core diameter is 29nm. The darker core and the lighter shell of the particles in routine transmission electron microscopy (TEM) images suggest the core-shell structure as shown in **Figure 6(b)** in which the contribution of the atomic number to TEM contrast is also important.

4. Conclusion

Magnetic Core-shell nanoparticle with pure $Mg_{0.1}Fe_{0.9}O$ that is coated with silica has successfully been prepared by chemical precipitation method. The average crystallite size of $Mg_{0.1}Fe_{0.9}O$ nanoparticles were estimated from the full width half maximum of the X-ray diffraction

peaks. XRD pattern showed that $Mg_{0.1}Fe_{0.9}O$ have cubic spinel Fd-3m structure with average crystalline size 52 nm. The weight loss percentage of the synthesized particles is calculated with TG-DTA. FTIR conform formation of the $Mg_{0.1}Fe_{0.9}O/SiO_2$. It is observed from SEM that the core is porous in nature with uniform dispersion. From TEM it is very clear that core-shell MNPs $Mg_{0.1}Fe_{0.9}O/SiO_2$ formation with uniform shell thickness. The results reported in this study could be applied for establishing a simple method for the preparation of $Mg_{0.1}Fe_{0.9}O/SiO_2$ Magnetic Core-shell nanoparticle.

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