Structural and FTIR Spectroscopic Studies of Mg-Zn Ferrite Nanoparticles Synthesized by Co-Precipitation Technique

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Abstract: *A series of co-precipitated $Mg_xZn_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) ferrite nanoparticles have been synthesized followed by annealing at a temperature of 200 °C. The results obtained from XRD and IR analysis are reported. XRD patterns confirm the formation of cubic spinel phase of ferrite samples along with secondary phase of α-Fe_2O_3 and MgO. Both lattice parameter and crystallite size decreased with the substitution of Mg^{2+}. FTIR spectra present the characteristic peaks of spinel structure. This paper reports the structural results obtained from XRD and FTIR studies and the results are analyzed presuming core-shell interactions and cation redistribution.*

Keywords: XRD; FTIR; ferrites; nanoparticles.

1. Introduction

Synthesis and characterization of spinel ferrites at nanoscale have drawn much attention because nanoparticles with large surface to volume ratios have enhanced magnetic, electrical, optical properties which in turn found potential applications in magnetic fluid, high density data storage, medical diagnostics, etc. [1]. Mg-Zn ferrite is one of the promising candidates which has been used in electronics applications. Besides that, due to low magnetic anisotropy this can be suitable for cancer treatment by hyperthermia [2]. Mg-Zn ferrite is a mixed ferrite of Mg-ferrite and Zn-ferrite. Mg occupies octahedral (B) sites and Zn occupies tetrahedral (A) sites in the spinel structure with the formula unit $(Zn^{2+}_{1-x}Fe^{3+}_x)[Mg^{2+}_xFe^{3+}_{2-x}]O_4$. [3].

Spinel ferrites at nanoscale have been synthesized employing various chemical routes such as sol–gel [4], reverse micelle method [5], ultra sound irradiation [6], hydrothermal method, etc. [7]. Among all these methods co-precipitation method is highly preferable for preparation of ferrites because of easy preparation, composition flexibility, homogeneity, etc. [8].

In the present study a series of $Mg_xZn_{1-x}Fe_2O_4$ (x =0.5, 0.6, 0.7) ferrite nanoparticles have been synthesized using co-precipitation method and the samples were annealed at 200 °C. X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were employed for characterization. In the present paper the results of structural and FTIR analysis are reported and are incorporated presuming core-shell interactions and cation redistribution.

2. Experimental

High purity magnesium chloride ($MgCl_26H_2O$), zinc chloride ($ZnCl_2$) and ferric chloride ($FeCl_36H_2O$) were taken as starting materials to prepare ferrite nanoparticles by co-precipitation technique [9]. Each material was weighed separately in stoichiometric ratio and dissolved in a suitable quantity of de-ionized water to obtain 0.5 M solutions. The cationic solutions were mixed thoroughly using a magnetic stirrer for complete dissolution and heated to 60 °C. A NaOH solution of 0.4 M concentration was prepared and heated to 60 °C and quickly transferred into the hot cationic solution while maintaining the stirring and heating till complete precipitation was occurred. Heating of the precipitate in its alkaline condition was continued at a soaking temperature of 100 °C for 1 h. Stirring was further continued for 12 h for complete aging. The precipitated particles were washed several times and dried at 80 °C for 2 days. The ferrite powders were pressed under a pressure of 50 MPa into pellets of uniform diameter of 1.5 cm and a varying thickness of 2 mm to 3 mm. The pellets were heat treated at 200 °C in air for 2 h and were ground into fine powder in an agate mortar. The powders were characterized by XRD, SEM and FTIR techniques.

An INELXRG 3000 powder diffractometer was employed to obtain the X-ray diffraction patterns of the samples using Co K_α (1.78901Å) radiation.

A Carl Zesis EVOMA15 scanning electron microscope was employed to check the morphology of the samples.

IR spectra were recorded in the range 400 cm^{-1} to 4000 cm^{-1} using Perkin Elmer spectrometer.

3. Results and Discussion

X-ray diffraction analyses have been performed on the series of $Mg_xZn_{1-x}Fe_2O_4$ (x =0.5, 0.6, 0.7) ferrite samples to study their structural phase and the respective XRD patterns are given in Fig.1. The XRD patterns reveal the cubic spinel structure of samples along with secondary phases of

Paper ID: NOV161491   1524

α-Fe_2O_3 and MgO. These secondary phases were also observed in other ferrites at low annealing temperatures [10, 11]. The diffraction planes are analyzed with powder software and the planes are indexed as (220), (311), (400), (422), (511) and (440) which are well matched with the earlier reports [12]. The broadening and low intensity of diffraction peaks is attributed to presence of ultrafine particles in the samples. The structural and microstructural parameters were calculated using the following relations. The average lattice constant values (a) were obtained using 2θ values of the most intense peaks using Bragg's diffraction [13] condition, given by

$$a = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin\theta} \qquad (1)$$

The average crystallite sizes are calculated with full width at half maximum of most intense peaks using Debye–Sherrer's [13] equation, given by

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (2)$$

where K is shape factor taken as 0.89, λ is the X-ray wavelength used and β is full width at half maximum intensity taking into account of instrumental broadening.

The X-ray density [13] has been calculated using the relation

$$\rho_x = \frac{8M}{N_A a^3} \qquad (3)$$

where M is molecular weight of the ferrite sample, N_A is Avogadro's number and a is experimental lattice constant.

The lattice strain was estimated from the following derived relation modifying the Williamson and Hall equation [14]

$$\eta = \frac{2d\left|K-1\right|}{D} \qquad (4)$$

where d is lattice spacing for (311) planes, D is average crystallite size and K (0.89) is shape factor.

The calculated values of lattice parameter (a), crystallite size (D), X-ray density (ρ_x) and lattice strain (η) are summarized in Table.1. The values of lattice parameter are in between the reported values of lattice parameters of $MgFe_2O_4$ [15] and $ZnFe_2O_4$ [16] and it was observed that the lattice parameter increases monotonically with the substitution of Mg^{2+}, which is attributed to smaller ionic radius of Mg^{2+} (0.67Å) compared to Zn^{2+} (0.74Å). The similar observations were reported for other spinel ferrites [17, 18]. The crystallite size decreases with increase of Mg^{2+} ion concentration, resulting in the increase of lattice strain. The variations in lattice parameter and crystallite size follow the Vegard's law [19] as shown in Fig 2. It was observed that the experimental density decreases with increase of Mg^{2+} ion concentration. The variation of experimental density depends upon molecular weight of ferrite in spite of decrease in lattice parameter. In the present study the substitution of low atomic mass of Mg^{2+} ion (24.3g) substantially decrease the molecular weight of ferrite which was resulted in the decrease of density.

The SEM micrographs of annealed ferrites of $Mg_xZn_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) at 200 $^{\circ}$C are shown in Fig.3. The nature of SEM micrographs reveals the small sizes of ferrite

Figure 1: XRD patterns of $Mg_xZn_{1-x}Fe_2O_4$ (x =0.5, 0.6, 0.7)

Figure 2: Plot of lattice parameter and crystallite sizes.

Table 1: Lattice parameter (a), crystallite size (D), experimental density (ρ_x) and lattice strain (η).

x	a(Å)	D(nm)	$\rho_x(g/cm^3)$	η ($\times 10^{-3}$)
0.5	8.442	8.4	4.869	6.65
0.6	8.425	5.1	4.807	10.86
0.7	8.420	2.3	4.724	26.69

nanoparticles. These small particles are agglomerated into large clusters as observed from SEM micrographs. Similar observations were also reported by other researchers [20]. The close examination reveals the distribution of particles in different sizes which is ascribed to the nature of grain boundaries of particles that requires different surface energies needed for grain growth.

Fourier transform infrared spectroscopy has been employed to observe the structural variations and spinel phase of ferrite systems. The two vibrational bands, one is higher vibrational frequency (ν_1) in the range of600-500 cm^{-1} and the other one is lower vibrational frequency (ν_2) in the range of 450-350 cm^{-1}, are the characteristic bands of cubic spinel structure [21]. The higher vibrational frequency (ν_1) is assigned to Fe^{3+}- O^{2-} stretching vibrations at tetrahedral site (A) and the lower vibrational frequency (ν_2)
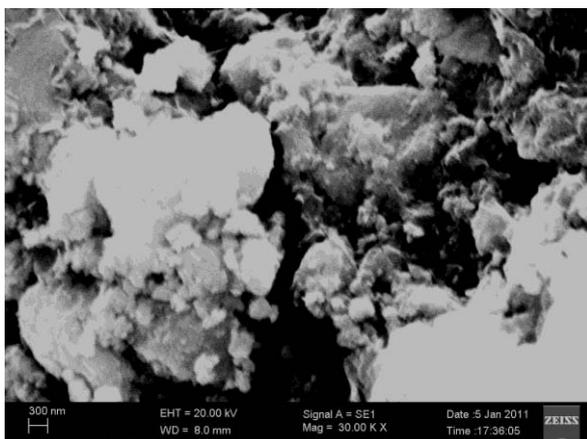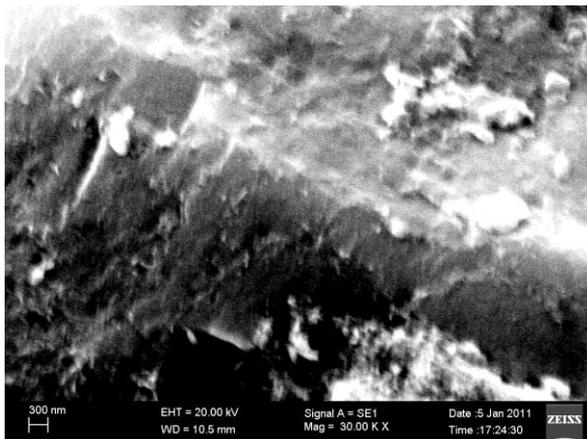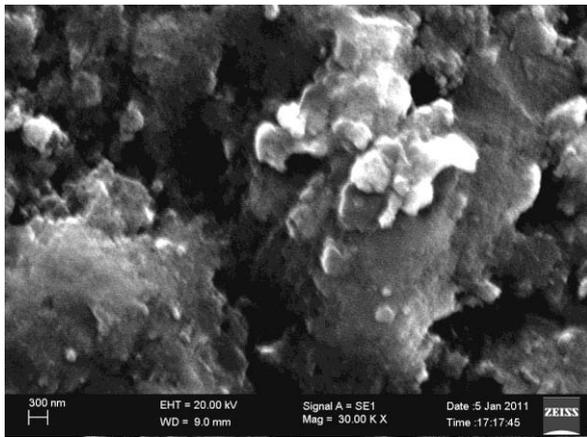
Figure 3: SEM micrographs of $Mg_xZn_{1-x}Fe_2O_4$ (x =0.5, 0.6, 0.7)

is assigned to Fe^{3+}- O^{2-} stretching vibrations at octahedral site (B).

The FTIR spectra of $Mg_xZn_{1-x}Fe_2O_4$ (x =0.5, 0.6, 0.7) are shown in Fig.4. The tetrahedral and octahedral vibrational frequencies (v_1 and v_2) along with tetrahedral and octahedral force constants (K_T and K_O) are listed in Tab.2. It was observed that the both tetrahedral and octahedral vibrational frequencies are shifted towards the higher frequencies with increase in Mg^{2+} ion concentration, which are ascribed to increase in force constants and contraction of Fe^{3+} - O^{2-} bond lengths at both A and B sites. This supports the observed decrease in lattice constant. T. Slatineanu et al [22] observed similar variation in Zn ferrites substituted with Ni. M.A. Gabal et al [23] reported the increase in v_1 and random
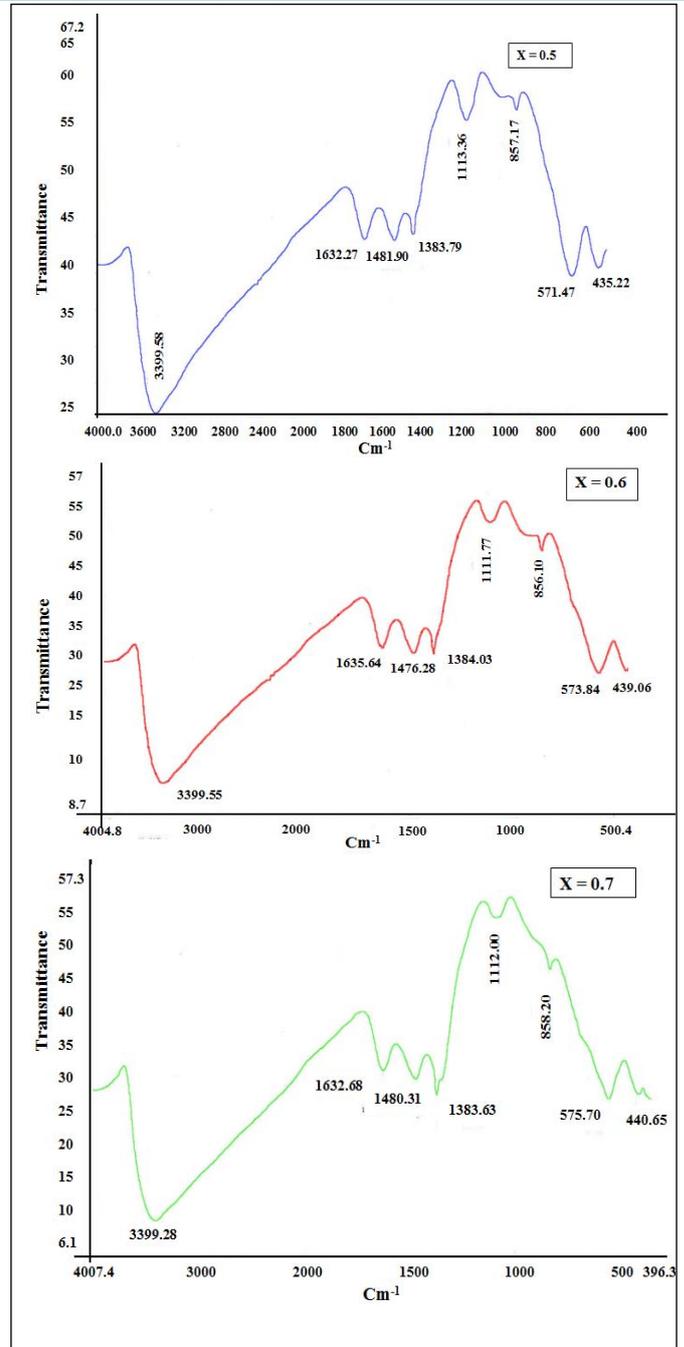
Figure 4: FTIR spectra of $Mg_xZn_{1-x}Fe_2O_4$ (x =0.5, 0.6, 0.7)

Table 2: Tetrahedral, octahedral vibrational frequencies (v_1 and v_2) and force constants (K_T and K_O)

x	$v_1 (cm^{-1})$	$v_2 (cm^{-1})$	$K_T(dyne/cm^2)$	$K_O(dyne/cm^2)$
0.5	571.47	435.22	239.25	138.76
0.6	573.84	439.06	241.24	141.19
0.7	575.70	440.65	242.81	142.25

variation in v_2. The increase in v_1 and v_2 in the present series is attributed to random distribution of cations in tetrahedral (A) and octahedral (B) sites against their normal preference. The broad band around 3400 cm^{-1} can be assigned to hydroxyl group and the bands around 1630–1384 cm^{-1} and 970–880 cm^{-1} are assigned to in-plane and out-plane of O–H vibration [24, 25]. The remaining bands are probably due to combinational frequencies or overtones.

Paper ID: NOV161491

1526

4. Conclusions

$Mg_xZn_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) ferrite nanoparticles were prepared successfully using co-precipitation technique. XRD patterns confirm the formation of spinel phase of ferrite samples along with secondary phases. Both crystallite sizes and lattice parameters are decreased with increase in Mg^{2+} ion concentration. The variation in ν_1 and ν_2 is ascribed to random variation of cations in the spinel structure. The method of preparation and nature of additives influence the cation distribution affecting the structural parameters.

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1527

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