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

S. B. Singh¹, Ch. Srinivas²

¹Department of Physics, Government Polytechnic, Tadepalligudem 534101, India,
²Department of Physics, Sasi Institute of Technology and Engineering, Tadepalligudem 534101, India,

Abstract: A series of co-precipitated MgₓZn₁₋ₓFe₂O₄ (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-Fe₂O₃ and MgO. Both lattice parameter and crystallite size decreased with the substitution of Mg²⁺. 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 (Zn²⁺₋ₓFex⁺)₂₋ₓ[Fe³⁺ₓFe²⁺₋ₓ]O₄. [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 MgₓZn₁₋ₓFe₂O₄ (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 (MgCl₂·6H₂O), zinc chloride (ZnCl₂) and ferric chloride (FeCl₃·6H₂O) 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 Kα (1.78901 Å) 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 MgₓZn₁₋ₓFe₂O₄ (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
The lattice strain was estimated from the following derived equation, given by

\[ \eta = \frac{2d[K - 1]}{D} \]  

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

The lattice strain was estimated from the following derived equation, given by

\[ \eta = \frac{2d[K - 1]}{D} \]  

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 \(\rho\) and lattice strain \(\eta\) are summarized in Table 1. The values of lattice parameter are in between the reported values of lattice parameters of MgFe\(_2\)O\(_4\) [15] and ZnFe\(_2\)O\(_4\) [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\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) (x = 0.5, 0.6, 0.7) at 200 °C are shown in Fig.3. The nature of SEM micrographs reveals the small sizes of ferrite 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 \(v_1\) in the range of 600-500 cm\(^{-1}\) and the other one is lower vibrational frequency \(v_2\) in the range of 450-350 cm\(^{-1}\), are the characteristic bands of cubic spinel structure [21]. The higher vibrational frequency \(v_1\) is assigned to Fe\(^{3+}\) - O\(^2-\) stretching vibrations at tetrahedral site (A) and the lower vibrational frequency \(v_2\)
Figure 3: SEM micrographs of Mg$_x$Zn$_{1-x}$Fe$_2$O$_4$ (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$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x =0.5, 0.6, 0.7) are shown in Fig.4. The tetrahedral and octahedral vibrational frequencies ($\nu_1$ and $\nu_2$) 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 Mg ferrites substituted with Ni.

M.A. Gabal et al [23] reported the increase in $\nu_1$ and random variation in $\nu_2$. The increase in $\nu_1$ and $\nu_2$ 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.

Table 2: Tetrahedral, octahedral vibrational frequencies ($\nu_1$ and $\nu_2$) and force constants ($K_T$ and $K_O$)

<table>
<thead>
<tr>
<th>x</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$K_T$ (dyne/cm$^2$)</th>
<th>$K_O$ (dyne/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>571.47</td>
<td>435.22</td>
<td>239.25</td>
<td>138.76</td>
</tr>
<tr>
<td>0.6</td>
<td>573.84</td>
<td>439.06</td>
<td>241.24</td>
<td>141.19</td>
</tr>
<tr>
<td>0.7</td>
<td>575.70</td>
<td>440.65</td>
<td>242.81</td>
<td>142.25</td>
</tr>
</tbody>
</table>
4. Conclusions

Mg$_x$Zn$_{1-x}$Fe$_2$O$_4$ (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 v$_1$ and v$_2$ 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.

References


[7] Zhongzhuo Wang, Yanyu Xie, Peihong Wang, Yongqing Ma, Shaowei Jin, Xiansong Liu, Microwave anneal effect on magnetic properties of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles prepared by conventional hydrothermal method” J. Magn. Magn. Mater. 323(2011) 3121–3125.


[21] Kumar Mohit, Vibha Rani Gupta, Nisha Gupta, S. K. Rout “Structural and microwave characterization of Ni$_{0.5}$Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ for antenna applications” Ceram. Int 40 (2014) 1575-1586.


Author Profile

Volume 5 Issue 2, February 2016

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

1527
S. B. Singh received the B.Sc. and M.Sc. degrees in Physics from Andhra University. He published research papers in national and international journals. At present working as Senior Lecturer in Physics, A. P. Technical Education Services, A. P., India.

Dr. Ch. Srinivas received the B.Sc. and M.Sc. degrees in Physics and Ph. D in Magnetic Materials from Andhra University. He published research papers in national and international journals. At present working as Professor in Physics, Sasi Institute of Technology and Engineering, A.P., India.