Effect on Properties of ZnFe$_2$O$_4$ Ferrites on Doping with Manganese Ions

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Abstract: In the present study, a series of Zn ferrites doped with Mn having compositions of Mn$_x$ Zn$_{(1-x)}$ Fe$_2$O$_4$ (x = 0.4, 0.5, 0.6, 0.7 and 0.8) were synthesized from metal salts and succinate hydrazinate ligand precursors, by drying on a hot plate, which automatically got decomposed into the ferrite powders. The chemical interaction of ferrite powders was investigated by Fourier transform infra red spectroscopy (FTIR). The crystal structures and morphologies of these compounds were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The single phase spinel cubic structure formation was confirmed by XRD and FTIR results. The magnetic properties of nanoparticles were measured at room temperature and indicate that the Mn content has a significant influence on the magnetic properties such as saturation magnetization and Curie temperature.

Keywords: Doped, ligand, precursors, nanoparticles, magnetic properties

1. Introduction

Ferrites are synthesized by many techniques such as ceramic, co-precipitation, hydrothermal, sol-gel, etc., also ball milling or mechanical alloying. However, most of these techniques have complicated synthesis steps, requires sophisticated instruments and take a long processing time [1]. Synthesis of ferrite using fuels such as urea, citric acid, glycine etc., in combustion method is well known [2, 3]. However, using a hydrazine based ligand to form a precursor with metal salts is tried in this synthesis. The technique involved is simple involving conventional heating using a hot plate and time required for synthesis is short and the product are obtained at a lower temperature. Among the spinel ferrites, zinc ferrite is being studied because of its unique properties such as chemical and thermal stability and the particle size dependence of magnetic properties [4]. Zinc ferrite in bulk state has a normal spinel structure with the Zn$^{2+}$ ions without magnetic moment in the tetrahedral sites, and it behaves as antiferromagnetic. It is observed that method of preparation as well as crystallite size affects the magnetic properties of nanocrystalline zinc ferrite. Nickel and manganese ferrites are kind of soft ferrimagnetic materials which have high saturation magnetization, high initial permeability, high resistivity, high dielectric constant and low power losses. As a result these materials have many applications such as electronic and computer devices, communication, space exploration and in the medical field [1,5]. Mn ions were doped in the zinc ferrite and the nanoparticles obtained were studied for their changes in structural, magnetic and electrical properties as mixed metal ferrites.

2. Experimental

Manganese Acetate, Zinc Nitrate, Ferric Nitrate chemicals of analytical grade were used in the synthesis. Manganese Acetate, Zinc Nitrate and Ferric Nitrate in stoichiometric amount were dissolved in minimum quantity of distilled water to obtain aqueous solution of metal ion. To this solution a calculated amount of Succinate hydrazinate ligand solution was added and it was thoroughly mixed to obtain a precursor. The mixture was then kept for drying on a hot plate. The solution dried to a solid mass, which automatically got decomposed into the powdered form and this powders were used for characterization and study of electrical and magnetic properties.

The phase formation of ferrite materials was investigated by X-ray diffraction (XRD). The chemical vibrational mode of ferrite samples was studied by Fourier transform infrared spectroscopy (FTIR). The morphology analysis of the samples was carried out by scanning electron microscopy (SEM). The saturation magnetization measurements of all the samples were carried out at room temperature using Pulse Field Magnetic Hysteresis Loop Tracer. Magnetization, coercivity and remanence magnetization were calculated from the hysteresis loops.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of Mn$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ samples

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3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of samples Mn$_x$Zn$_{(1-x)}$ Fe$_2$O$_4$, where x = 0.4, 0.5, 0.6, 0.7 and 0.8. All the peaks of all samples show the characteristic reflections of spinel cubic crystal structure of ferrite. The crystallite size (T), and lattice parameter (a) of all ferrite samples were calculated from the X-ray peak broadening of the characteristic (311) diffraction peak. Formation of single phase cubic spinel structure of Mn$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ with x =
0.4/0.5/0.6/0.7/0.8 was confirmed with the help of XRD patterns obtained for all the samples. As shown in Table 1. The values of lattice constants ‘a’ calculated from these were found to increase with increasing Mn concentration [6] and are in excellent agreement with reported values.

Table 1: Variation of lattice constant

| Composition               | a in Å  |
|---------------------------|---------|
| Mn_{0.4}Zn_{0.6}Fe_{2}O_{4} | 8.4219  |
| Mn_{0.5}Zn_{0.5}Fe_{2}O_{4} | 8.4431  |
| Mn_{0.6}Zn_{0.4}Fe_{2}O_{4} | 8.4628  |
| Mn_{0.7}Zn_{0.3}Fe_{2}O_{4} | 8.4704  |
| Mn_{0.8}Zn_{0.2}Fe_{2}O_{4} | 8.4826  |

Infra red (IR) absorption spectroscopy helps to identify the spinel structure. The three typical vibrational bands associated with spinel structure [7] are at (1) 600-550 cm^{-1} (2) 450-385 cm^{-1} (3) 350-330 cm^{-1} for metal-oxygen band. Fourier transformed infra red (FTIR) spectroscopy studies of the nano particle ferrite samples were carried out between 1000 - 400 cm^{-1} as shown in figure 2. Out of the two bands the high frequency (υ₁) band is attributed to the tetrahedral metal-oxygen bond and second frequency (υ₂) band to the octahedral metal-oxygen bond corresponding to:

(1) Me\_T - O - Me\_O stretching vibration 600-550 cm^{-1}  
(2) Me\_O ↔ O stretching vibration 450-385 cm^{-1} here O is oxygen, Me\_O is metal in the octahedral site and Me\_T in the tetrahedral site. The metal-oxygen absorption bands (1) and (2) are pronounced for all spinel structures and essentially for ferrites, which are also seen in these samples. IR spectral data of all the ferrite samples prepared by these methods are found to show two peaks in the range 578-564 cm^{-1} and 472-443 cm^{-1} which are in agreement with the reported value [8].

Average crystallite sizes were calculated by using XRD data by measuring the full-width at half maximum (FWHM) for most intense characteristic (311) peak for each sample with the help of the Scherer formula as given in equation 1, and are in the range 20.4–41.1 nm for different Mn concentrations.

\[
T = 0.9 \frac{\lambda}{D_p \cos \theta}
\]  

Where, T is the average crystallite size, λ is the X-ray wavelength, Dp is the angular line width of half maximum intensity and θ is the Bragg angle in degrees. The particle size of Mn\_xZn\_{1-x}Fe\_2O\_4, where x = 0.4, 0.5, 0.6, 0.7 and 0.8 with Mn concentration is given in Table 2. The crystallite sizes are found to increase with increasing Mn content in the range 20.4-41.1 nm for different compositions. It is observed that minimum crystallite size of 20.4 nm is observed for the ferrite sample with Mn concentration of x=0.4 which may be due to the lower concentration of Mn ions and as the concentration of manganese increases which have higher ionic radii (0.91Å), compared to zinc ions (0.82Å) the lattice constant increases and also crystallite size increases.

Table 2: Variation of particle size in nm

| Concentration of Mn | Particle size in nm |
|---------------------|---------------------|
| 0.4                 | 20.4                |
| 0.5                 | 21.9                |
| 0.6                 | 34.1                |
| 0.7                 | 38.6                |
| 0.8                 | 41.1                |

From the figures 3(a), (b) and (c), the microstructure of Mn-Zn ferrites reveals that the nanoparticles are porous and are agglomerated due to the presence of magnetic interactions.
The Curie temperature was found to increase with increase in manganese content in the samples Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ to Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ from 232 °C to 384 °C as given in Table 4, in these ferrites [12]. This is attributed to the substitution of non-magnetic Zn$^{2+}$ ions by the magnetic Mn$^{2+}$ ions in the samples. The value of Tc is found to be higher in the case of the nanoparticles than that in bulk ferrites. This is due to the deviation of cation distribution in a nano-sized particle as in comparison with its bulk counterparts [13]. In general, magnetic properties are controlled by exchange interaction of the metallic ions on the two interactive sub-lattices A and B. It is also possible that Tc may decrease due to some unknown surface effect. For small particles a significant fraction of atoms are on the surface, and therefore their magnetic interactions are expected to be different. It is observed to give rise to a different average Curie temperature [14].

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### Table 3: Variation of saturation magnetization

| Composition | Saturation Magnetization (emu/g) |
|-------------|----------------------------------|
| Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ | 21.74 |
| Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ | 36.52 |
| Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 45.17 |
| Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ | 38.91 |
| Mn$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ | 33.11 |

### Table 4: Variation of curie temperature

| Composition | Curie temperature in °C |
|-------------|-------------------------|
| Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ | 232 |
| Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ | 257 |
| Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 289 |
| Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ | 341 |
| Mn$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ | 384 |

The samples Mn$_x$Zn$_{1-x}$Fe$_2$O$_4$ with x=0.4, 0.5, 0.6, 0.7 and 0.8 prepared by using Succinate hydrazinate ligand with metal ions to produce a precursor, which undergoes auto combustion- self decomposition, were found to have spinel structure. This was confirmed using XRD and IR spectroscopy. The particle sizes were estimated using Scherer formula and were found to be in nano range, confirmed by SEM. Nano-materials produced by this method show high values of saturation magnetization. Tc increases with Mn content and was found to be higher than for the bulk material.