Synthesis, characterization and Transport properties of $Co_xZn_{1-x}Fe_2O_4$ Nanoparticles

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Abstract. Spinel ferrites are commercially important materials due to their excellent electrical and magnetic properties. Mixed metal spinel ferrites, essentially with low hysteresis loss and small particle sizes, have found new applications in areas like biosensors, drug delivery systems, and hyperthermia. The electrical conductivity, which gives credible information about conduction mechanism, is one of the important properties of ferrites. The order of magnitude of conductivity greatly influences the dielectric and magnetic behavior of the ferrites and depends on the preparative method. The present work deals with investigations into electrical, dielectric and thermo power parameters of **$Co_xZn_{1-x}Fe_2O_4$** ferrite nano particles synthesized by co-precipitation method. The effect of variation of the cobalt concentration in the sample on transport properties of nano ferrites has been analyzed.

1. Introduction

Nano spinel ferrites are becoming important candidates as far as newer high end technological applications are concerned in fields such as microwave devices, high speed digital storage systems, ferro-fluids, catalysis, and magnetic refrigeration [1-3]. Mixed spinel ferrites, essentially with low hysteresis loss and small particle sizes, have found new applications in areas like drug delivery systems and hyperthermia [4]. Apart from magnetic applications of Co ferrites, they are used in thermistors [5] where resistivity plays an important role. The electrical conductivity, which gives credible information about conduction mechanism, is one of the important properties of ferrites. The order of magnitude of conductivity greatly influences the dielectric and magnetic behavior of the ferrites and depends on the type of preparation method [1,5]. This has provided the motivation to synthesize, characterize and carry out electrical, dielectric as well as thermo power measurements on **$Co_xZn_{1-x}Fe_2O_4$** ferrite nano particles. The nanoparticles under investigation were synthesized by co-precipitation method, which were then analyzed to study various transport properties.

2. Experimental

Nanoparticle **$Co_xZn_{1-x}Fe_2O_4$** ferrite material with (x=0.2, 0.4, 0.6) were prepared in our laboratory by co-precipitating aqueous solutions of $ZnSO_4$, $CoCl_2$ and $FeCl_3$ mixtures in alkaline medium. $ZnSO_4:7H_2O$, $CoCl_2:6H_2O$ and $FeCl_3:6H_2O$ were taken in their respective stoichiometry dissolved in distilled water and heated up to 65^0C. The respective metal ions were precipitated by adding a suitable precipitating reagent in boiling solution state within 10 seconds under constant stirring. After maintaining the solution along with the precipitate at 80^0C for one hour, the precipitate was filtered

and dried at 100^0C. The dried powder was pelletized and sintered at 1000^0C for 15 hours, resulted in formation of **$Co_xZn_{1-x}Fe_2O_4$** nanoparticles

The three powdered samples were characterized using high intensity rotating anode Rigaku X-ray diffractometer (XRD). FT-IR absorption spectra of the samples were recorded on a Shimadzu 8900 FT-IR spectrometer. The resistivity measurements were carried out by two probe method using Keithley's electrometer (model 6514), by maintaining a constant supply voltage across the sample. The frequency dependent dielectric measurements were carried out on Wane Kerr 6440B LCR-Q meter at room temperature. Thermo electric power (TEP) measurements were carried out on an indigenously built, lab based set up with variations in ΔT ranging from 0^0C to 150^0C.

3. Results and Discussion

The X-ray diffraction peaks shown in figure 1, indicative of single phase spinel crystal structure were identified and indexed in all three samples. The lattice parameter is found to vary between $8.32A^o$ and $8.34 A^o$ with increasing Co content in the sample. This variation can be ascribed to the difference in ionic sizes of the component ions. The Co2+ ions have larger ionic radius (0.82 A°) than Zn 2+ (0.74 A°), and Fe3+ (0.67 A°) ions. The average particle size calculated from XRD line width of (311) peak using Debye Scherrer's formula, $t = 0.9\lambda/\beta\cos\theta$, where t = particle size, λ = wavelength of X-ray, β=full width at half maxima(FWHM) and θ is Bragg angle works out to 44nm,which indicate formation of nano particle material.
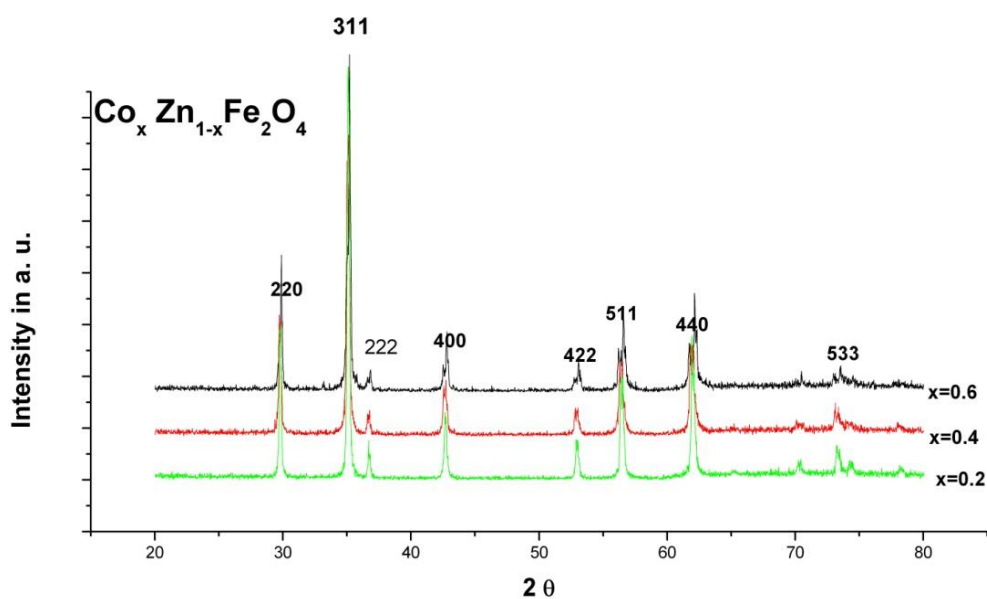

Figure 1. XRD pattern of $Co_xZn_{1-x}Fe_2O_4$

FT-IR absorption spectrum shown in figure 2,with two broad absorption bands (610-550cm^{-1}) which corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site and (450-375 cm^{-1}) due to octahedral metal stretching, confirmed spinel phase formation [6]. The absorptions noticed at higher wave numbers are due to the presence of water molecules and traces of other contaminating molecules present in air.

The temperature-dependent dc resistivity measured from room temperature till 550^0C is as shown in Figure 3. It can be seen that for all the samples variation of resistivity with increasing temperature follow the same trend. The change in slope indicates change in conduction mechanism. The prominent change in slope occurs at 426 K for sample x=0.6, at 393K for sample x=0.4 and at 473K for sample x=0.2. Mild slope change indicative of shift in conduction behavior is noticed at 743K, 683K and 643K for sample x=0.6. The trend is repeated for samples x=0.4 and x=0.2 for temperatures 773K,743K,683K and 803K,763K,663K respectively.
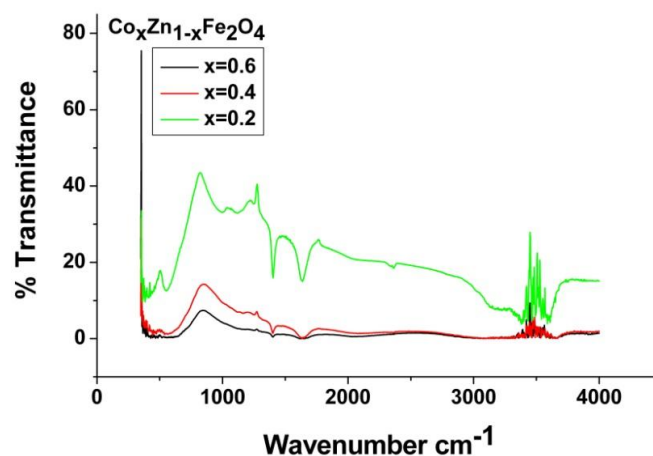
Figure 2. FT- IR spectrum of $Co_xZn_{1-x}Fe_2O_4$

The first low-temperature region (up to about 423 K) is attributing to the conduction due to impurities, voids, defects, etc. The second temperature region (up to Curie temperature) is attributed to ferrimagnetic region. Third temperature region (above Curie temperature) is attributed to paramagnetic region [7–9]. With respect to increase in Co concentration a systematic decrease in temperature at which the change in conduction mechanism occurs is also noticed at higher temperatures.
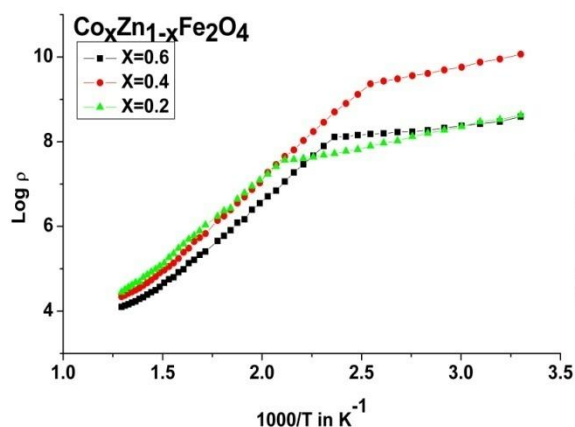

Figure 3. DC resistivity of $Co_xZn_{1-x}Fe_2O_4$

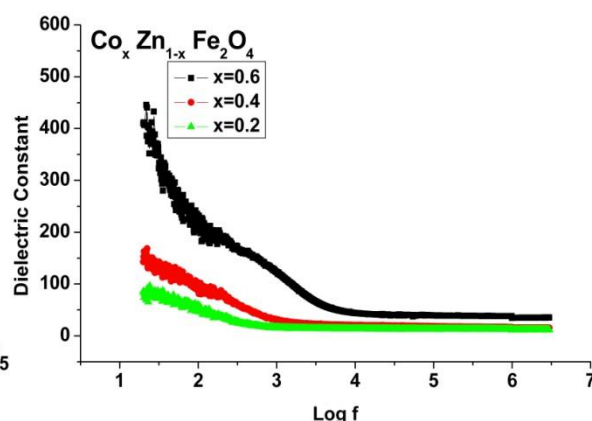**Figure 4.** Dielectric constant of $Co_xZn_{1-x}Fe_2O_4$

Figure 4 shows variation of dielectric constant ($Є$) with frequency for the three samples. Initially $Є$ decreases nearly exponential with increasing frequency and reaches constant value for all the three compositions. According to the model based on dispersion due to Maxwell–Wagner [10,11] type interfacial polarization, which is in agreement with Koop's phenomenological theory [12], a heterogeneous dielectric material is considered containing well conducting grains, separated by highly resistive thin grain boundaries. In such situation, the applied voltage on the sample drops mainly across the grain boundaries resulting in creation of a space charge polarization. According to Koop the effect of grain boundaries is prominent at lower frequencies and the grain boundary thickness is inversely proportional to the dielectric constant value. The observed decrease of $Є$ with increase in frequency can be attributed to the fact that the electron exchange between Fe^{+2} and Fe^{+3} ions cannot follow the change of the external applied filed beyond a certain frequency [13,14].It may be seen from Figure 4 that, an enhancement of dielectric constant occurs with the corresponding increase of Co ions concentration in the matrix.

Thermo electric power (TEP) measurements carried out on the samples are as shown in Figure 5.
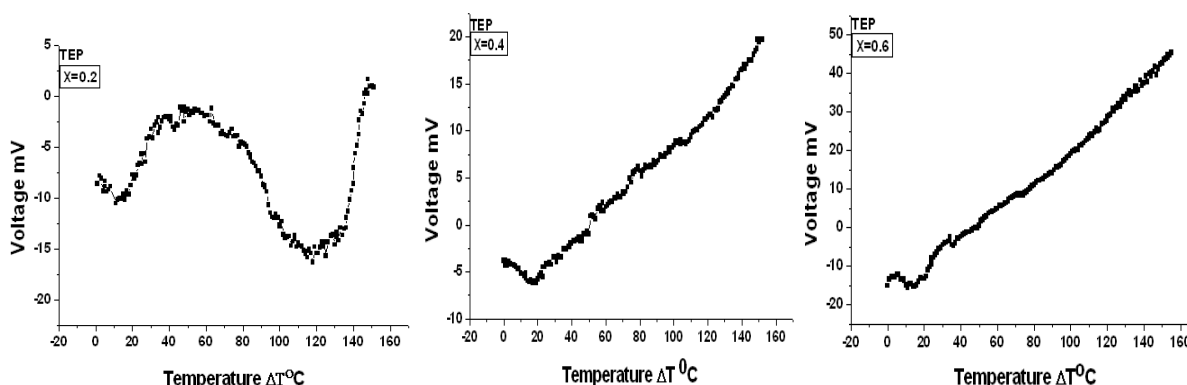
Figure 5. Thermo Electric Power measurements of $Co_xZn_{1-x}Fe_2O_4$

TEP analysis confirm semiconducting nature of the material, with the presence of n-type charge carriers for x=0.4 and 0.6 at lower values of ΔT ^0C, which shifts to p-type at larger values of ΔT ^0C. However for sample with x=0.2, n-type charge concentration is predominant with large amplitude fluctuations of the charge concentration as ΔT ^0C approaches 150^0C.

4. Conclusion

The $Co_xZn_{1-x}Fe_2O_4$ nanoparticles with (x=0.2, 0.4, 0.6) were synthesized by Co-precipitation method and characterized using (XRD) & FT-IR spectroscopy. The decrease in resistivity with increase in temperature indicates semi conductor-like behaviour. The changes observed in dc resistivity at various measuring temperatures provide adequate testimony to the idea of the changing conduction behaviour or mechanism in the samples with rising ambient temperature. An increase in dielectric constant with increasing Co concentration in the sample suggests that the addition of cobalt is responsible for introduction of more dipoles in the sample.TEP analysis confirm semiconducting type behaviour of the samples, with generation of n-type charge carriers in the sample with x=0.2 and dual type, n-type at low temperature difference ΔT ^0C and p-type subsequently for higher values of ΔT ^0C in samples with x=0.4 and x=0.6.

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