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Characterization of Ni-Zn nanocrystalline ferrites prepared by chemical method

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ABSTRACT

Nanocrystalline $Ni_xZn_{1-x}Fe_2O_4$ with x = 0.1 to 0.5 mixed ferrites were prepared by Sucrose process. The samples were characterized by high resolution TEM, XRD and IR spectroscopy. The dielectric behavior was studied in the frequency range 20 Hz to 1MHz. Dielectric constant shows dispersion in lower frequency region. XRD patterns confirm the formation of spinel cubic structure. The IR spectra show two prominent absorption bands.

KEYWORDS

Nanocrystalline ferrites;
TEM;
XRD;
IR;
Dielectric etc.

INTRODUCTION

Nanocrystalline ferrite systems are being intensively studied, both theoretically and practically, due to their interesting electric, dielectric, magnetic and optical properties that are sensibly different from their bulk materials. In recent years number of physical and chemical techniques has been developed to prepare nanosized magnetic materials. The widely used chemical methods are electro deposition[1], sol gel route[2], co-precipitation[3], micro emulsion technique[4], Glyoxylate precursor method[5], hydrothermal method[6], reverse micelle technique[7], sucrose method[8,9].

Among them sucrose method is cumbersome, more versatile and cost effective solution based method for preparation of fine oxide ceramic powders at lower processing temperatures. It can avoid three major problems – diffusion, impurities and agglomeration. This improves homogeneity. The chemical precursors used can be easily refined to increase the purity and careful control of solvent removal from the precursors will lead production of crushable agglomerates.

Due to their remarkable magnetic properties and low production cost Ni- Zn ferrite being intensely studied in nanocrystalline form. Ni –Zn ferrites with nanosized particles show unique electrical, mechanical, optical and catalytic properties. They also exhibit superior magnetic properties[10] as compared with their bulk counter part.

EXPERIMENTAL

Preparation

Initially stoichiometric amounts of the individual metal nitrates viz. Ni $(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3$, were thoroughly mixed in desired composition in distilled H_2O to form mixed cation solution. A 10% aqueous solution of PVA and aqueous solution of sucrose were added and mixed together with thorough stirring and heating at 80 ^{0}C. The resultant solution was evaporated at about 200^{0}C. Complete evaporation of solution with liberation of brown fumes of NO_2 occurred and highly viscous liquid was formed. Further heating of this liquid caused decomposition to voluminous, black, organic based floppy mass which was ground to fine powder. It forms precursor material. Proper heat treatment in air at 2 h to the precursor material results into nanocrystalline ferrites. The powder was pelletized using a pressure of 5 – 10 tons /cm^2 using hydraulic press. It was presintered at 800 ^{0}C for 9hr and final sintered at 900 ^{0}C for 12 h[9,11].

Characterization

The samples were characterized by using x-ray diffractometer (XRD) Phillips Model PW- 3710 using CuK_α radiation with λ =1.541^{0}A

Particle size was determined by using TEM (Model JEOL- 1200 EX).

The IR spectra were recorded using Perkin Elmer IR spectrometer (Model 783) in KBr medium in frequency range 200-800 cm^{-1} to study IR absorbtion.

The dielectric measurements were carried out in the frequency range from 100 Hz to1 MHz and with temperature at fixed frequency by using LCR Meter Bridge (Model HP 4284A).

RESULTS AND DISCUSSION

Structure and microstructure

The XRD patterns of $Ni_xZn_{1-x}Fe_2O_4$ with x = 0.1 to 0.5 ferrite powders are as shown in Figure 1. The pattern match well with Ni-Zn ferrite pattern from ASTM data[12] showing no extra peaks establishing the formation of single phase cubic spinel structure. The lattice parameter 'a' increases with Zn composition by obeying Vegard's law[13] as shown in Figure 2 Figure 3 represents TEM micrographs of samples sintered at 900^{0}C for `12 h having different compositions. The average grain size was observed to vary from 30 nm to 70 nm. The grain size is lower than those obtained for ferrites prepared by ceramic methods.

IR spectra

Figure 4 shows IR spectrographs of all samples. It provides information about positions of ions in crystal lattice through crystal vibrations. It shows two prominent absorption bands with vibrations υ_1 and υ_2 around

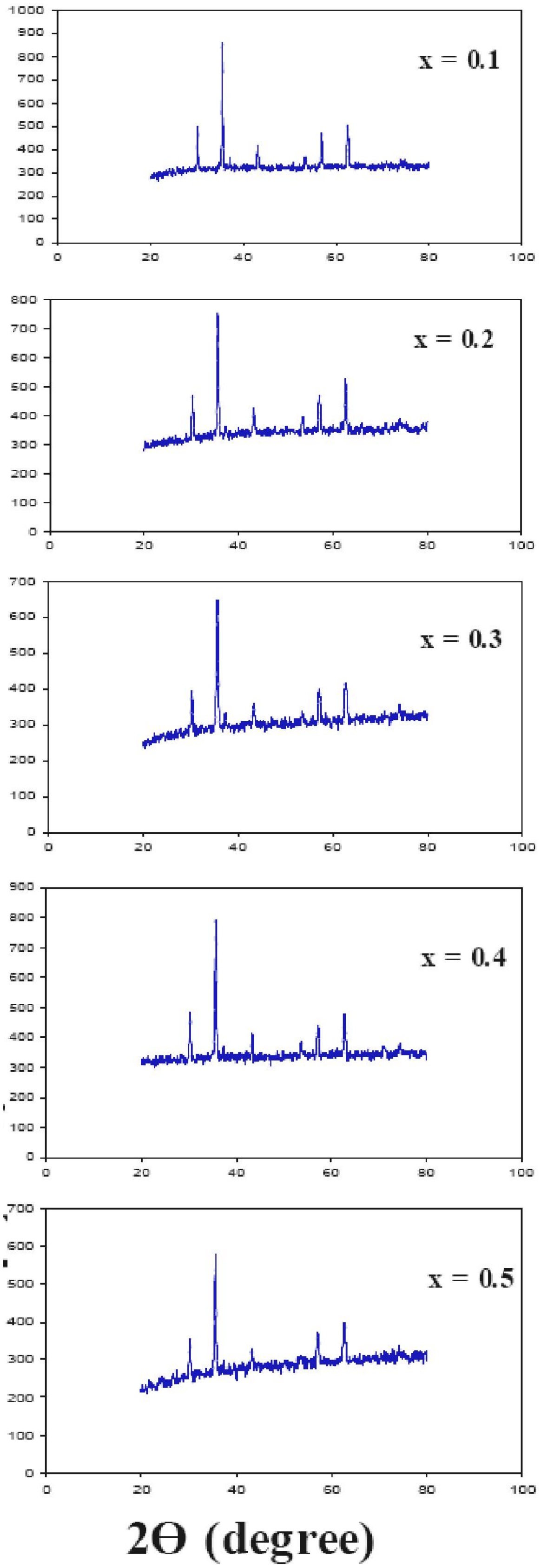

Figure 1 : XRD patterns of NixZn 1-xFe2O4 ferrites

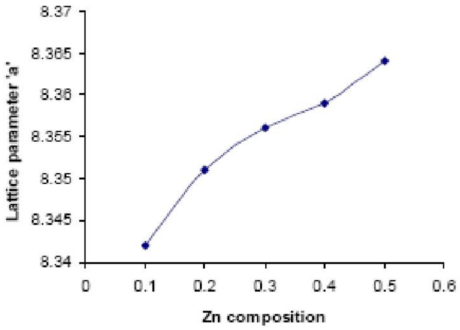

Figure 2 : Variation of lattice parameter with 'Zn' composition

600 cm^{-1} and 400cm^{-1} respectively

Murthy et al[14] have studied the IR absorption in Ni-Zn ferrites. The vibrations in band positions are due to change in Fe^{3+}- O^{2-} bond distance in two crystal sites. Waldron[15] has attributed the band υ_1 around 600 cm^{-1} to the vibrations of tetrahedral complexes corresponding to highest restoring force causes stretching of Fe^{3+}-O^{2-} bonds where as bond υ_2 around 400 cm^{-1} is attributed to vibrations of octahedral complexes which are bond bending vibrations.

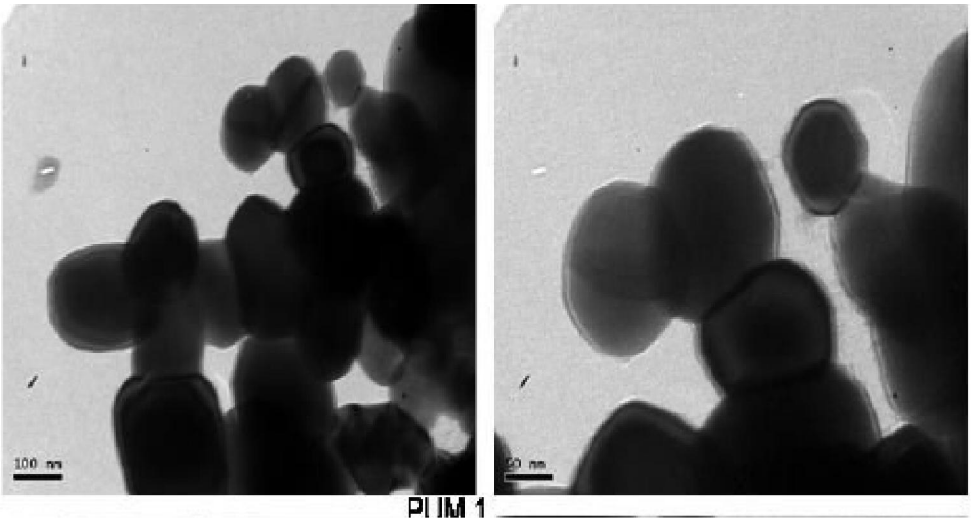

Figure 3 : TEM micrographs $Ni_xZn_{1-x}Fe_2O_4$ ferrites

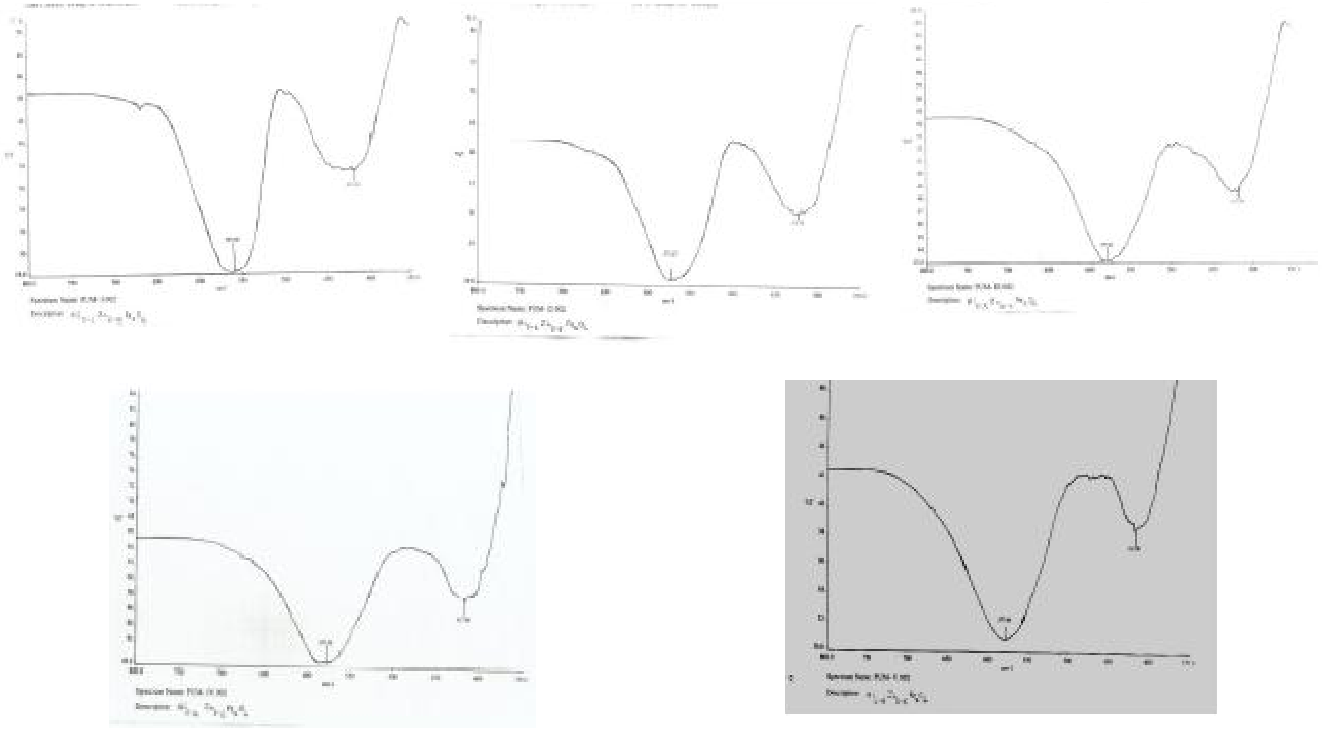

Figure 4 : Position of IR bands in NixZn 1-xFe2O4

Dielectric properties

Dielectric constant is calculated by using the relation

$$\acute{\varepsilon} = c\, d/\varepsilon_o A$$

where, c is capacitance of pellet in Farad, d is the thickness of pellet, A is the cross-sectional area of the flat surface of the pellet and εo is permittivity of free space (8.85×10^{-12} F/m).

The variation of dielectric constant and loss tangent as a function of frequency at room temperature is as shown in Figure 5 and Figure 6 respectively.

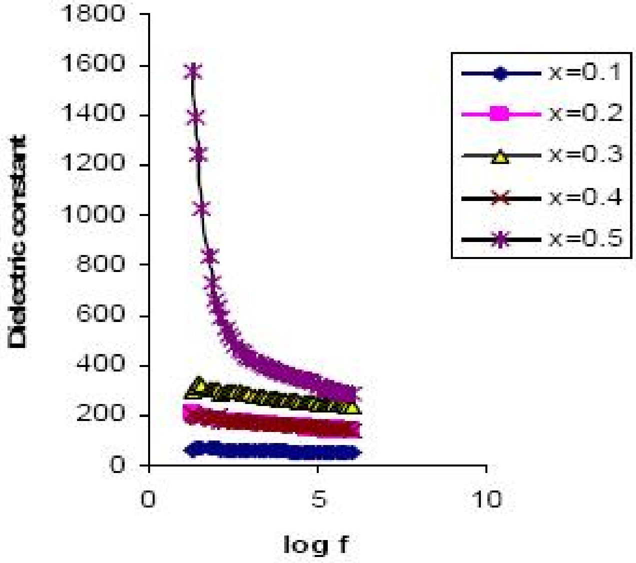

Figure 5 : Variation of dielectric constant with frequency

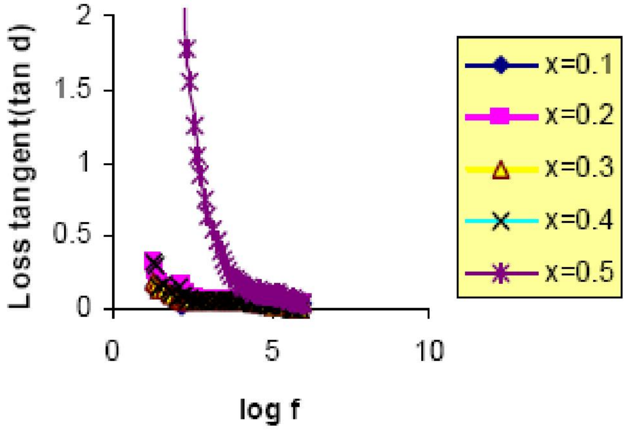

Figure 6 : Variation of tan δ with frequency

The dielectric constant decrease rapidly at lower frequencies and remain constant at higher frequencies was observed earlier for Ni-Zn ferrite. The decrease in both values for the dielectric loss as frequency increases can be related to electron exchange interaction between Fe^{2+} and Fe^{3+} which can allow alternation of applied electric field beyond certain critical frequency[14] The dielectric loss in ferrites originates from two mechanisms – electron hopping and charged defect dipoles. The former contribute to dielectric loss mainly in low frequency range. In high frequency range dielectric loss mainly results from response of defect dipoles to the field. These dipoles in ferrites are formed due to change of cation valance state such as Fe^{3+}/Fe^{2+}, Ni^{3+}/Ni^{2+} during sintering under oxygen partial pressure. The relaxation of dipole under electric field is decreased with increase in frequency resulting in decrease in dielectric loss in high frequency range.

AC conductivity

The frequency dependence of ac conductivity was measured at room temperature in frequency range 20 Hz to 1 MHz to study the mechanism of conduction. It is illustrated in Figure 7

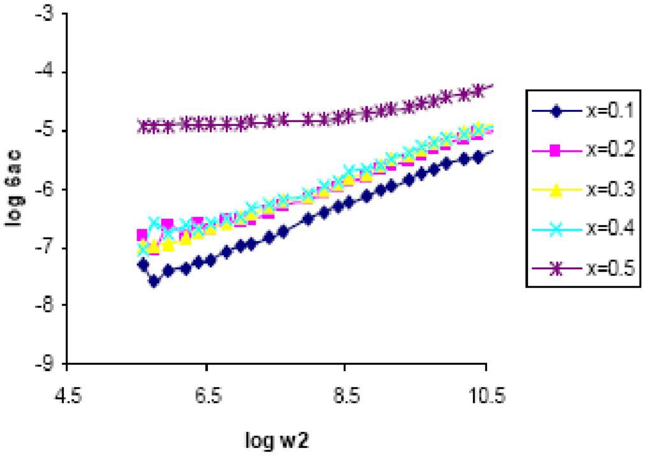

Figure 7 : Variation of ac conductivity with frequency

The ac conductivity was calculated by using the relation -

$$\sigma_{ac} - \sigma_{dc} = \varepsilon' \varepsilon_0 \omega \tan\delta$$

The ac conductivity is observed to increase with increase in frequency for all compositions. The nature of the plots indicates that conduction occurs by hopping of charge carriers between localized states.

CONCLUSIONS

Nanocrystalline, single phase ferrite powder was prepared by sucrose process. All compositions show formation of single phase cubic spinel structure. The dielectric constant and dielectric loss decrease with frequency of applied electric field. The ac conductivity increases with increase in frequency. IR spectra of the ferrites show two prominent absorption bands ν_1 and ν_2 in the range 570-600 cm^{-1} and 410-425 cm^{-1} respectively.

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