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LOW TEMPERATURE SYNTHESIS OF NI-ZN FERRITE BY CERAMIC METHOD MODIFICATION WITH A PRECURSOR

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ABSTRACT

Nickel zinc ferrite with general formula $Ni_xZn_{(1-x)}Fe_2O_4$ where X= 0.2, 0.4, 0.6, and 0.8, was prepared by modifying the ceramic method at a lower temperature. The temperature is much lower than those used in the conventional ceramic method for the preparation of ferrites (~1000^{0}C). The structural, magnetic and electrical properties were investigated. The lattice constant is in the range of 8.3564 X 10^{-8}-8.4178 X 10^{-8}. The lattice parameter decreased with increase nickel content. The SEM revealed formation of nano size particles The dc resistivity of the sintered specimens was observed to be ~10^8 ohm cm which is greater, by at least two orders of magnitude, than that for specimens prepared by the conventional ceramic method.

KEYWORDS: ceramic method, low temperature, lattice parameters, nano size, dc resistivity

1. INTRODUCTION:

There is a constant efforts by different researchers to synthesis and characterize nano-crystalline ferrites due to their enhanced structural, magnetic, and electrical properties, when compared with their bulk counterparts [1]. Nickel–Zinc ferrites are most versatile soft magnetic ferrites having low coercivity, high electrical resistivity, high curie temperature and low dielectric loss which makes them an excellent material for use in different industrial areas with multiple applications as radio-frequency applications, magnetic cores of read–write heads for high-speed digital tape or disk recording, power transformer in electronic and Telecommunication applications, rod antennas, radar-absorbing materials, also as a catalyst

[2-4]. The performance of the spinel ferrite is strongly dependent on its synthesizing technique, also on the ionic radii and concentration of the substituted divalent metal ions. The conventional ceramic method of preparation involving reaction between oxides at high temperatures is cumbersome, time consuming, and has a drawback of causing chemical inhomogenity due to evaporation of some component, formation of bigger particle with larger pore size material, lack of reproducibility of products. Attempts are made towards improving the technological performance of ferrites by the development of various non-conventional methods involving mainly solution techniques. The advantages of these techniques are the appreciable reduction in the synthesizing temperature and the resulting ferrite being of improved microstructure. These techniques are auto-combustion [5], co-precipitation [6], hydrothermal [7], precursor [8, 9], reverse micelle [10], sol–gel [11], etc.

In the present investigation an attempt is made to overcome the disadvantages of a conventional ceramic method by coupling it with a non conventional method like precursor to produce nickel zinc ferrites at a lower temperature. The oxides of nickel, zinc and iron are ball milled for homogenous mixing and then treated with a ligand to produce a precursor, which on decomposition produce the ferrite material.

2. EXPERIMENTAL PROCEDURES:

The stoichiometric amounts of pure 99.9% nickel oxide (Thomas Baker make), zinc oxide (Thomas Baker make) and ferric oxide (Thomas Baker make) was taken as starting materials. The mixture was then ball-milled with ball to material ratio of 10 at 80 rpm speed for 10 hrs in Acmas Technocracy Ball Mill (model Acm - 8203) to obtain a powdered mixture. This mixture was then treated with calculated amount of aqueous oxalate hydrazinate ligand to produce a precursor and homogenized to a thick paste. The resulting paste was dried slowly by the conventional heating which on drying gets ignited to form a finely divided solid powder which was found to be magnetic in nature. This powder was used for characterization as well as to study the structural, magnetic and electrical properties.

The structural characterization of the prepared Ni-Zn ferrite nanoparticles was carried out using XRD, IR, and SEM. The phase and crystal structure analysis was carried out by an X-ray

diffraction technique using Rigaku, X-ray advance Power diffractometer using Cu Kα radiation (λ = 1·54183 Å). The step size employed was 0·02°, in the range of 20^0–80^0. The IR absorption spectra for the samples were recorded in the wavelength range 700$cm^{-1}$to 400 cm^{-1} by using FTIR Shimadzu Model IR prestige 21 series spectrophotometer. The average crystallite size was calculated by Debye–Scherer's equation using data obtained from X-ray diffractograms. The morphology and microstructure of obtained powders were examined using a scanning electron microscope (SEM) Model JEOL 5800LV. The DC electrical resistivity helps in understanding conductivity mechanism in ferrite samples. The DC resistivity of the samples was carried out by two probe method using the instrument supplied by Pushpa Scientific Hyderabad [12]. The instrument consists of a muffle type furnace, which can give temperature up to 800^0C. It has a stable D. C. source of 10 volts (D. C. voltmeter 0 to 10 volts range), a D. C. microammeter (0 to 500 μA range) and ionic conductivity cell with two brass electrodes. In a typical experiment, the Ni-Zn ferrite powder sample was pressed under 75 KN pressure applied for about 5 minutes to make pellets of 1.0 cm diameter and 2-3 mm thickness. The pellet was silver pasted on either side for establishing good ohmic contacts with the electrodes. It was then placed between the two brass electrodes of the conductivity cell. At constant voltage, the current at various temperatures was recorded while cooling from 500^0C to room temperature. By knowing the value of current and voltage across the sample, resistivity of the sample could be calculated by using the relation.

$$\rho = RA/t \quad \Omega \cdot cm \qquad (1)$$

Where R: Resistance of the sample; A: Surface area of the sample = πr^2; r: Radius of the sample; t: Thickness of the sample.

3. RESULTS AND DISCUSSION:

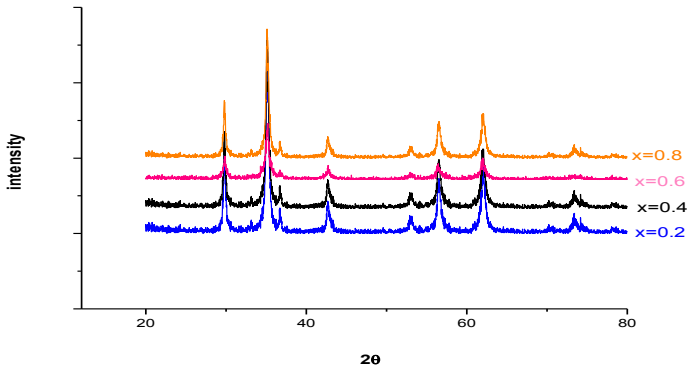


Figure 1: XRD pattern of $Ni_xZn_{(1-x)}Fe_2O_4$ samples

Formation of single phase cubic spinel structure of $Ni_xZn_{(1-x)}Fe_2O_4$ (X=0.2, 0.4, 0.6, and 0.8) samples was confirmed with help of XRD patterns obtained for all the samples as shown in Figure 1.

Table 1: Variation of lattice constant

Samples	Lattice constant "a" in cm.
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	8.4178 X 10^{-8}
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	8.3824 X 10^{-8}
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	8.3645 X 10^{-8}
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	8.3564 X 10^{-8}

The values of lattice constants 'a' estimated from XRD peaks were found to decrease with increase in Ni concentration and are in the range of 8.3564 X 10^{-8}-8.4178 X 10^{-8} shown in table 1. This decrease is attributed to the lower ionic radii of Ni (0.78A^o) as compared to Zn (0.82A^o), and is in agreement with reported values [13].

Table 2: Variation of X-Ray density

Samples	X-Ray density
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	5.2898
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	5.3189
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	5.3258
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	5.3383

The X-ray density calculated for the samples synthesized using oxide method are shown in table 2, it lies in the range of 5.2898 g/cc for $Ni_{0.2}Zn_{0.8}Fe_2O_4$ to 5.3383 g/cc for $Ni_{0.8}Zn_{0.2}Fe_2O_4$ as the lattice constants decreases the X-ray density is found to increase as it is inversely proportional to the lattice constant

IR Spectroscopy allows us to identify the spinel structure. The three typical vibrational bonds associated with spinel structure are at (1) 600-550 cm^{-1} (2) 450-385 cm^{-1} for metal oxygen bonds. IR spectra were obtained for all the samples under investigation confirming formation of spinel ferrite.

The infrared spectra for $Ni_xZn_{(1-x)}Fe_2O_4$ where X= 0.2, 0.4, 0.6, and 0.8 ferrite sample is shown in Fig.2 recorded in the range of 700-400 cm^{-1}

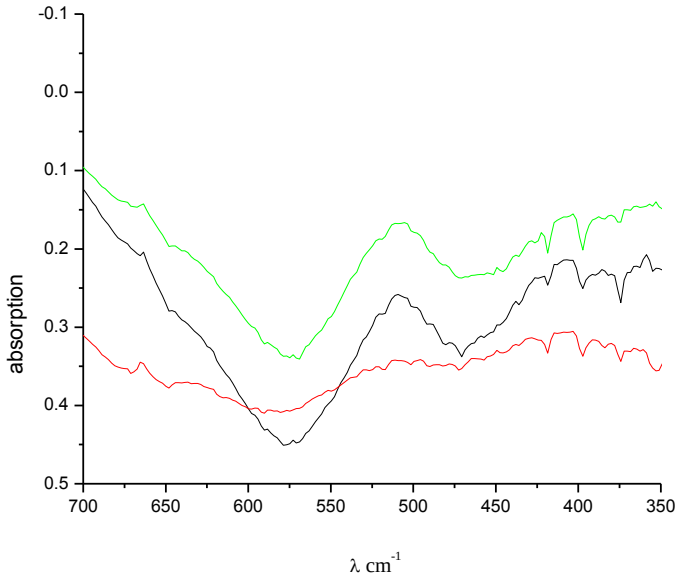
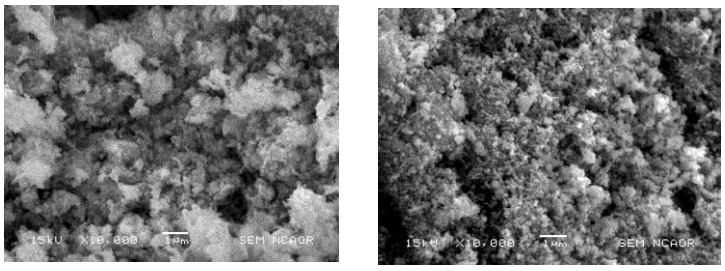


Figure 2: IR spectra of $Ni_xZn_{1-x}Fe_2O_4$samples

The IR spectra of samples show two peaks, one in the range 600-550 cm^{-1} for tetrahedral stretching vibration and the other 450-385 cm^{-1} for octahedral stretching vibration corresponding to spinel structure. For $Ni_xZn_{(1-x)}Fe_2O_4$ where X= 0.2, 0.6, and 0.8 sample synthesized by this modified method two bands in the range at 570-581 cm^{-1} and 469-476 cm^{-1} are observed. IR spectral data of all the ferrite samples are in agreement with the reported value [14].



(a) (b)

Figure 3: SEM micrograph of (a) $Ni_{0.4}Zn_{0.6}Fe_2O_4$ and (b) $Ni_{0.8}Zn_{0.2}Fe_2O_4$.

As can be seen from the SEM micrograph Fig 3(a) and (b) $Ni_xZn_{(1-x)}Fe_2O_4$ samples synthesized reveals that the particles are in nano range and are found to decrease with increasing

nickel content. This may be attributed to the lower lattice constants therefore smaller crystallite size

Table 3: Variation of particle size

Concentration of Nickel	Particle size in nm
0.2	38.4
0.4	30.2
0.6	27.3
0.8	20.1

The particle size of samples is calculated using the Scherer formula, indicated in table 3 is in the range from 38.4 nm to 20.1 nm. , which also confirmed by the SEM micrograph shown in Figure 3.

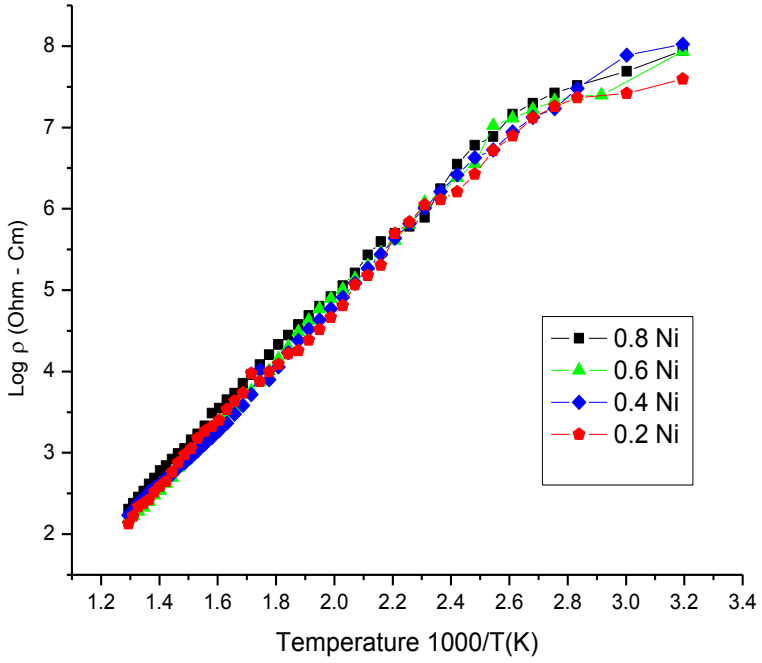


Figure 4: Variation of resistivity (logρ) with 1000/T (K) for $Ni_xZn_{(1-x)}Fe_2O_4$ samples.

The temperature dependence of DC electrical conductivity measured in the temperature range 300 K - 873 K is shown in the Figure 4. It follows the Arrhenius plot. This graph shows

that by increasing temperature conductivity increases hence resistivity decreases. This confirms that the ferrite under investigation has semi conductor behavior. Wherein initially the conductance is low and it increases with the temperature and also undergoes ferrimagnetic to paramagnetic transition. The curve has two distinct broad parts; initial parts of curve indicating low conductance at lower temperature and later on sharp increase with steep slope when conductance increases or resistivity decreases. The samples show resistivity value in the range 5.5022 X 10^6 ohm cm to 0.6551 X 10^8 ohm cm with low value for $Ni_{0.2}Zn_{0.8}Fe_2O_4$ and high for $Ni_{0.8}Zn_{0.2}Fe_2O_4$ sample, with increasing Ni^{2+} from $x = 0.2$ to $x = 0.8$. The reason for increase in ρ on increasing Ni composition is because Zn^{2+} ions prefer the occupation of tetrahedral sites (A) and Ni ions prefers the occupation of octahedral sites (B). But Fe ions partially occupies A and B sites. On increasing Ni concentration at B sites, Zn ions concentration at A sites will decrease. This leads to migration of some Fe ions from B site to A site to balance the reduction in Zn ions concentration at A sites. As a result the number of ferric and ferrous ions at B sites which are responsible for electrical conductivity in ferrites decreases consequently resistivity increases by increasing Ni ion concentration. [15, 16]. Similar trend of resistivity have been reported by the other researchers [17]. Electronic conduction mechanisms in ferrites have been studied by many and various models have been proposed; however, the thermally activated hopping model is found to be more appropriate in explaining quantitatively the electrical behavior of Ni–Zn ferrite. In the hopping process the additional electron on ferrous (Fe^{2+}) ion requires little energy to move to an adjacent (Fe^{3+}) ion on the equivalent lattice sites (B sites). In the presence of the electric field, these extra electron hopping between iron ions give rise to the electrical conduction. Therefore any change in the (Fe^{2+}) ion content in spinel ferrite lattice and/or the distance between them is crucial to the intrinsic resistivity of Ni–Zn ferrite. It is also affected by impurities. The introduction of another cation into the lattice causes a change in the valence distribution on the B sites, then the number of electrons potentially available for transfer will be altered. This is crucial for the conduction mechanism.

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