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Effect of Sintering Temperature on Electrical Properties of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ Nanoscale Particles Prepared by Co-Precipitation Method

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Abstract

Magnetic Nano particles of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ have been synthesized using Co-precipitation technique. During the experimental investigation, MnZn ferrites exhibited interesting structural, electrical and magnetic properties. Formation of spinel phase was identified using X-Ray diffraction (XRD) technique. The ferrite compound prepared in the laboratory exhibited cubic spinal symmetry. The Lattice constant of the compound was determined to be 8.324 A^0. The morphology and size of the crystallite was found by Transmission Electron Microscopy (TEM). The magnetic properties were studied using Vibration Sample Magnetometer (VSM) and the saturation magnetization (Ms), remenant magnetization (Mr) and the Coercivity force (Hc) values were evaluated. Electrical properties of the samples were quantified using standard two-probe method.

Keywords: Nano particles, Co-precipitation, morphology, Hysteresis curves, soft ferrites.

Introduction

There is an intense demand for high performance and miniaturization of many electronic devices, which exclusively need soft magnetic materials with high permeability. AB_2O_4 type of compounds with spinel structure shows interesting structural, electrical and magnetic properties, which vary with the nature of the ions, their charge and site distribution amongst tetrahedral and octahedral sites [1, 2].

Various cations can be placed in A site and B site to tune its magnetic properties. Depending on A site and B site cations it can exhibit ferromagnetic, antiferromagnetic, spin (cluster) glass, and paramagnetic behaviour [3]. The general composition of such ferrites is MFe_2O_4, where M represents one or several of the divalent metals. These types of ferrites have been extensively used in many electrical devices because of their high permeability in the radio frequency region, high electrical resistivity, mechanical hardness, and chemical stability [4- 6]. Among them, manganese ferrite, nickel ferrite, zinc ferrite and copper ferrite are most popular and versatile as investigated by many researchers. In this paper, magnetic and electrical properties of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ are discussed thoroughly. The performance of any ferrite is greatly influenced by its synthesizing technique [7- 13]. The conventional ceramic method of preparation which involves solid state reaction between oxides at high temperatures is cumbersome, time consuming and does not always result in pure reproducible product. Therefore, various non-conventional processing techniques [7-9], which are mainly solution techniques are reported. In the present work non-conventional preparation method, known as co-precipitation method, was used for preparation of Mn Zn ferrite. Main advantages of this method are that it is inexpensive, time saving and results in superior properties of ferrites processed at much lower temperature. The absence of ball milling in this method leads to stoichiometric composition as there is no possibility of loss or gain of material during milling, as in case of conventional ceramic method. In the present work magnetic and electrical properties of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite synthesized by co-precipitation method were considered.

Experimental

In the present work, nano scale particles were prepared by co-precipitation method. The materials - manganese chloride (98.0% Merck, India), zinc chloride (99.1% Merck, India) and iron III chloride (99 % Merck, India) in required stoichiometric proportions were dissolved in distilled water. To this, NaOH (97 % Merck, India) solution was added with continuous stirring at constant speed. The reaction temperature was maintained constant, by manipulating with alkaline aqueous solution. The precipitation occurred immediately and the color of suspension changed from brown to dark brown. It was kept stirred for 2h at constant temperature and then washed with distilled water to remove sodium and chloride ions. The washed sample was dried in air and the dried sample was examined by X- Ray diffraction, Transmission Electron Microscope and Vibration Sample Magnetometer. X-Ray powder diffraction was achieved using Cu-Kα source and the mean crystallite size was estimated using Debye-Scherer formula applying to the FWHM of the (311) peak of X- ray diffraction [14]. The morphological properties of specimens were observed by TEM. The magnetization loop for the sample was measured at room temperature using a vibrating sample magnetometer (VSM, JDM-13). Fine powders of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ were mixed with 5% P.V.A binder and pressed into pellets of the size 10mm diameter and thickness range between 2 and 4 mm under a pressure of 50 KN applied for 3 min. The pellets were sintered in air at temperatures 900, 1000, 1100, 1200, 1300^{O}C respectively, for 2h, by setting heating and cooling rate at 5^{O}C per minute. The pellets were coated with silver paste on either side to establish good ohmic contacts with the electrodes. Resistivity as a function of temperature was measured using standard two-probe method.

Result and Discussion

X- ray diffraction pattern of the ferrite sample is shown in the fig (1). The observed diffraction lines were found to correspond to those of standard pattern of manganese ferrite with no extra lines, indicating there by that the samples have single phase spinal structure and no unreacted constituents were present in the sample. Lattice constant “a” for the sample was calculated from the observed “d” values and found to be 8.324 A^{0}. The crystallite size of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ sample for the most intense peak (311) plane was determined from the x-ray diffraction data using the Debye-Scherer formula.

$d_{RX} = k\lambda/ \beta \cos\theta$

where d_{RX} is the crystalline size, k= 0.9 is a correction factor to account for particle shapes, β is the full width at half maximum of the most intense diffraction peak (311) plane, λ is the wave length of cu target= 1.5406 A^{o} and θ is the Bragg angle. The average crystallite size of the prepared sample at preparation temperature is 19 nm.

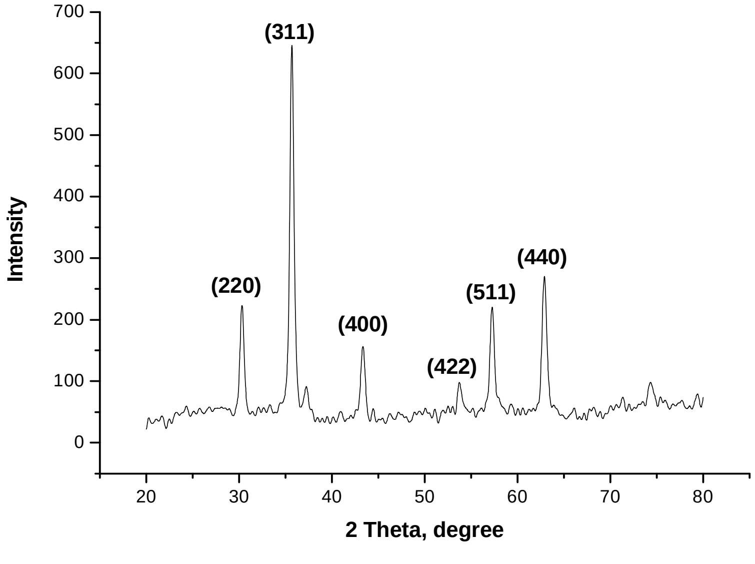

Figure 1: X-ray diffraction pattern of powder sample $Mn_{0.5}Zn_{0.5}Fe_2O_4$.

Fig (2) shows (TEM) Transmission Electron Micrograph of the sample at preparation temperature. There is good agreement with the theoretical XRD results. The densities of the sintered pellets were measured and shown in the table (1). The density of sintered $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite is found to be increasing with the sintering temperature. The density may be attributed to the existence of phase transition which occurs during the crystal formation process while sintering. The investigation on fine structure of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite clearly indicates the influence of sintering conditions on the growth [15], density of the sample and crystalline phase of the sample [16]. The usual trend in the density values is also observed in the resistivity trends of the samples. Fig: 3 shows plots of Temperature V/s Resistivity for $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite. A semiconductor like general behavior is observed as the sample undergoes a second order ferrimagnetic to paramagnetic phase transition. The trend depends on the sintering temperature of the sample. Resistivity values at $27^{O}C$ (300K) are seen to vary between2.12 $x10^6$ ohm-cm and 1.898 $x10^6$ ohm-cm for samples sintered at different temperatures, the highest and the lowest being observed at 900^0C and 1300^0C, respectively.

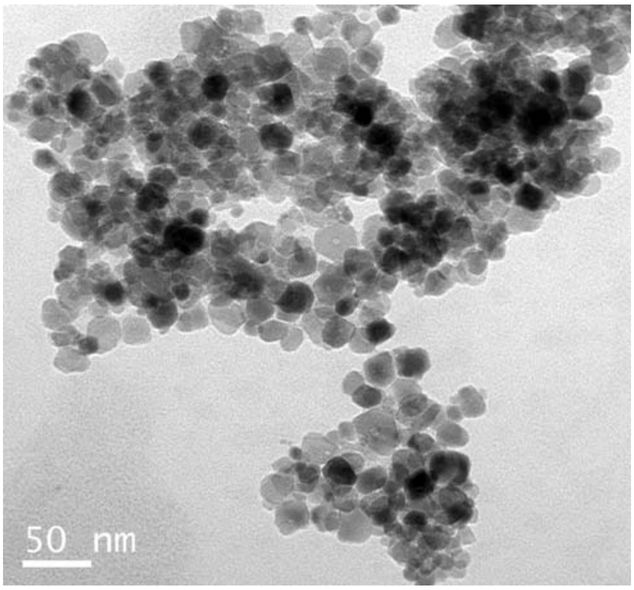

Figure 2: TEM photograph of powder sample $Mn_{0.5}Zn_{0.5}Fe_2O_4$.

Table 1: Density Values according to Sintering Temperatures.

Sintering Temperature (^{O}C)	Density (gm / cc)
Un Sintered	2.7512
900	2.982
1000	4.1854
1100	4.3020
1200	4.3893
1300	4.4562

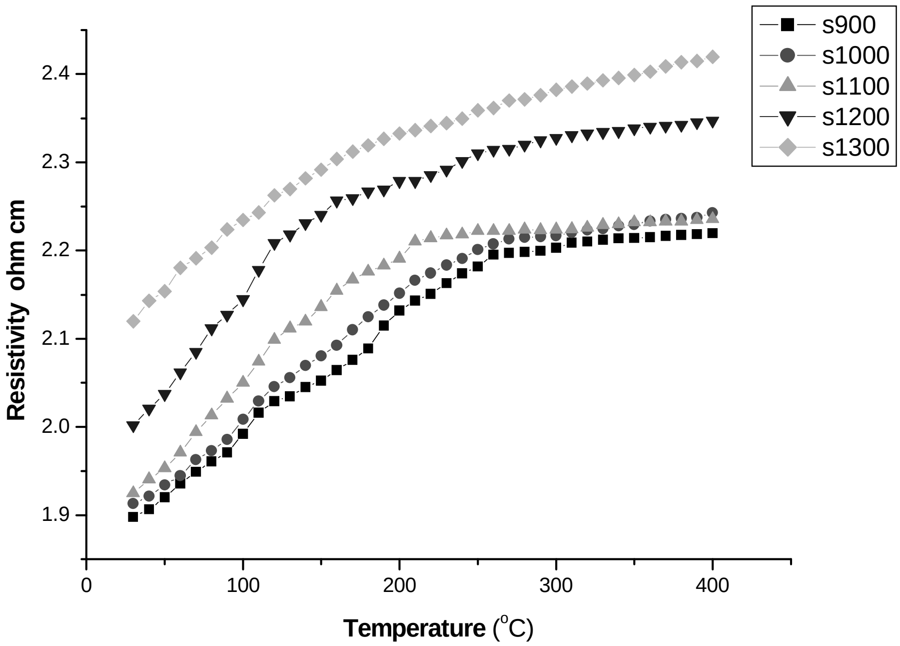

Figure 3: Temperature Vs Resistivity plots of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite at different sintering Temperature.

In ferrites, electron conduction mechanisms have been studied by many investigators and reviewed by Klinger et al. [19]. Various models were proposed. However, the thermally activated hopping model is found to be more appropriate in explaining qualitatively the electrical behavior of Mn–Zn ferrites. In the hopping process the additional electron on a ferrous (Fe2+) ion requires little energy to move to an adjacent (Fe3+) on the equivalent lattice sites (B sites). In presence of the electric field, these extra electrons hopping between iron ions give rise to the electrical conduction. Therefore, any change in the (Fe2+) ion content in the spinel ferrite lattice and/or the distance between them is crucial to the intrinsic resistivity of Mn–Zn ferrite grains, including the intrinsic grain boundaries. If the introduction of another cation into the lattice causes a change in the valency distribution on the B sites, then the number of electrons potentially available for transfer will be altered. On the other hand, the incorporation of foreign (addition of impurity) ions can change the distance between the B lattice sites, which is crucial for the conduction mechanism. Thus, the formation of an intrinsic grain boundary in doped samples by the segregation of aliovalent ions must increase the resistivity. This gives rise to polycrystalline Mn–Zn ferrite with non-ferrimagnetic grain boundary, ferrimagnetic outer grain region and ferrimagnetic conductive core. Thus the contribution to the bulk resistivity may be considered as resistivity contribution coming from three different regions. To establish a relation between the power loss due to eddy currents and the average grain diameter a hypothetical brick wall model is applied. As per the model each layer can be represented by a resistance–capacitance (R–C) lumped circuit of high Ohmic layers. When the resistivity of the bulk is much lower than the grain boundary layers, the equivalent circuit of the ferrite can be represented by a series of lumped R–C circuits of the grain boundary layers [17]. As the samples under investigation are sintered from nanoparticle Mn–Zn ferrite in a reducing atmosphere with no additives there is no possibility of formation of high resistivity ferrimagnetic outer grain boundary. Thus the total contribution should come only from the non-ferrimagnetic grain boundaries and ferrimagnetic conductive core.

The magnetic properties of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ powder prepared at preparation temperature were measured using Vibrating Sample Magnetometer. Magnetization was performed at room temperature. The hysteresis loop of the ferrite powder was obtained and given in the Fig: 4. Apparent superparamagnetic behavior was observed for the sample at the room temperature. The coercive force Hc = 70 Oe, saturation magnetization Ms = 20.66 emu/g, remenant magnetization Mr = 1.629 emu/g and the ratio of remenant magnetization to saturation magnetization Mr/Ms = 0.0788 were the experimental results. The low value of Mr/Ms ratio indicates an appreciable fraction of superparamagnetic particles.

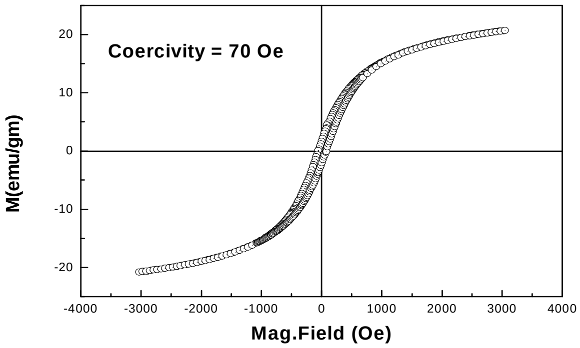

Figure 4: Hysteresis loop of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite powder.

Conclusion

In the present work $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles were prepared using co precipitation. The average crystallite size of the sample was 19.42 nm. The experimental values had excellent agreement with TEM image. The saturation magnetization (Ms), remenant magnetization (Mr), and coercive force (Hc) were found to be 20.66emu/g, 1.629emu/g and 70Oe respectively. And the investigations on the resistivity of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite developed by sintering nanoparticle $Mn_{0.5}Zn_{0.5}Fe_2O_4$ ferrite, prepared by co – precipitation method, showed existence of phase transitions that contributed to amazingly high electrical resistivity in comparison to the reported values. This is a very important parameter in minimizing the eddy current losses in power applications. It is evident that the material prepared by sintering nanomaterial Mn–Zn ferrite not only gives low loss material but also produces material with small grain size with large surface area as the grain growth is suppressed due to phase transitions. This feature can have remarkable effect on the other properties of the material. The semiconductor like behavior of the resistivity shown by this material makes it a favorable material for sensor applications.

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