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Effect of sintering conditions on resistivity of nanoparticle Mn–Zn ferrite prepared by nitrilotriacetate precursor method

Rudraji B. Tangsali · Satish H. Keluskar ·
Ganpat K. Naik · J. S. Budkuley

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Abstract Mn–Zn spinel ferrites are most important class of magnetic materials owing to their high saturation magnetization, high permeability, low loss and interesting applications in various fields. The magnetic as well as electrical properties of these ferrites depend on relative distribution of cations at different sites, grain size, sintering conditions as well as preparative conditions. Nanoparticle Mn–Zn ferrite material having general formula $Mn_xZn_{1-x}Fe_2O_4$ with $x = 0.35/0.4/0.45/0.5/0.55/0.6/0.65$ were synthesized using nitrilotriacetate precursor method and characterized using standard techniques. The resistivity measurements of all these samples were carried out after sintering the same in nitrogen atmosphere at 1,050 °C/1,150 °C/1,250 °C/1,350 °C, respectively. High resistivity values obtained for the system of materials would provide a low eddy current loss material for wide ranging applications in electronics and telecommunications. Semiconductor like behavior of the material with resistivity variation over large range of temperature is ideal characteristic essential for materials in sensor applications.

Introduction

Research in nanomaterials is on growth as the reduced grain dimensions drastically alter the properties of materials. Nano sized magnetic oxides are becoming important materials due to their unique micro magnetic properties such as superparamagnetism, magneto optic, magneto caloric effect, colossal and giant magnetic resistance etc. These materials are useful in a variety of applications in the electronic industry due to their high permeability, high saturation magnetization, high resistivity and low loss as these formed the key impediments in downsizing of transformer cores deflection yokes, antenna rods in the world of miniaturization. The most important parameter for high performance is small grain size. Resistivity of bulk Mn–Zn Ferrite obtained by sintering ultra fine particle Mn–Zn ferrite material is different from the one obtained by sintering material prepared by conventional methods like ceramic method and other wet chemical methods which yields large particle size. The performance of these materials is greatly influenced not only by its composition but also by the method of preparation and conditions at preparations. These factors are responsible for controlling the grain size of the material. The power loss per unit volume P_V for a Mn–Zn ferrite material can be divided into the hysteresis loss P_H, the eddy current loss P_E, and the residual loss P_R. The eddy current loss is dependent on the resistivity of the sample. The eddy current loss is given by $P_E = cL^2B_m^2f^2/\rho$; f is frequency, L^2 is equal to the A dimension of the circuit, B_m is the maximum flux density, ρ is the electrical resistivity of the bulk, and c is a coefficient related to the dimension of the circuit of the eddy current. Eddy currents in the core are related to material microstructure as the

R. B. Tangsali (✉)
Department of Physics, Goa University, Taleigao Plateau, Panjim, Goa 403206, India
e-mail: rbtangsali@unigoa.ac.in

S. H. Keluskar
Department of Physics, P. E. S. College of Arts and Science, Ponda, Goa, India

G. K. Naik · J. S. Budkuley
Department of Chemistry, Goa University, Taleigao Plateau, Panjim, Goa 403206, India

parameter L^2 may be replaced by D^2 the average diameter of the individual grains [1, 2].

Fine particle Mn–Zn ferrites were synthesized using nitrilotriacetate precursor method. Samples were characterized using standard techniques. The resisitivity of the bulk material obtained on sintering the nanoparticles at different temperatures was found to be very high which can account for sizable reduction in eddy current losses.

Experimental

Mn–Zn ferrites samples in form of ultra fine powders having general formula $Mn_xZn_{1-x}Fe_2O_4$ with $x = 0.35/0.4/0.45/0.5/0.55/0.6/0.65$ were synthesized using nitrilotriacetate precursor method [3]. The advantage of this method is that it produces nanoparticle Mn–Zn Ferrite material at much lower temperature. The decomposition of the complex precursor takes place at around 250 °C, which proceeds via auto-combustion method. XRD pattern for the samples were obtained on microcomputer controlled Siemens Diffractometer using Cu Kα (λ = 1.54183 AU). FTIR absorption spectra were recorded Shimadzu FTIR 8900 Spectrometer. Estimation of metal ions was carried out by titrimetry. Analysis for estimation of Mn, Zn, Fe and O by EDAX was also carried out by using Joel Model 840(SEM). Average grain size estimation was done using Scherrer Formula. TEM photographs were taken on Philips model CM200 Transmission electron Microscope with resolution 0–23 nm to confirm formation of ultra fine particle size of the samples. SEM photographs of sintered samples were obtained on Joel Model 840(SEM), which gave information on the microstructure of the materials under investigation. Fine powders of $Mn_xZn_{1-x}Fe_2O_4$ were pressed into pellets of the size 10 mm diameter and of thickness ranging between 2 and 3 mm under a pressure of 75 KN applied for 3 min. Four sets of pellets were sintered in nitrogen atmosphere at temperatures, 1,050, 1,150, 1,250 and 1,350 °C, respectively, for 3 h by setting heating and cooling rate at 5 °C per minute. The pellets were silver painted on either side for establishing good Ohmic contacts with the electrodes. Resistivity measurements on these samples were then made using standard two-probe method.

Results and discussion

A typical XRD pattern obtained for the sample is shown in Fig. 1. Similar patterns were recorded for all the samples. The d values, 2θ values and the values of lattice constants a calculated from these was verified and is found to be in excellent agreement with reported values. Formation of cubic spinel structure was thus confirmed by XRD data analysis. The particle size of these fine powders, as calculated from Scherrer formula using XRD data, was found to range between 10 and 80 nm.

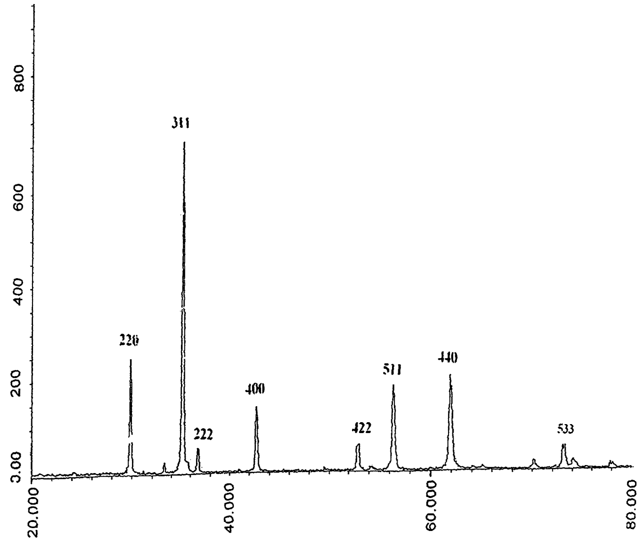

Fig. 1 XRD pattern obtained for as prepared powdered sample $Mn_{0.6}Zn_{0.4}Fe_2O_4$

Analysis of IR spectra gave the information about product structure transformation. The study of far-infrared spectrum is an important tool to get information about the positions of the ions in the crystal through the crystal's vibrational modes [4]. It also helps in identifying the spinel structure as well as a presence

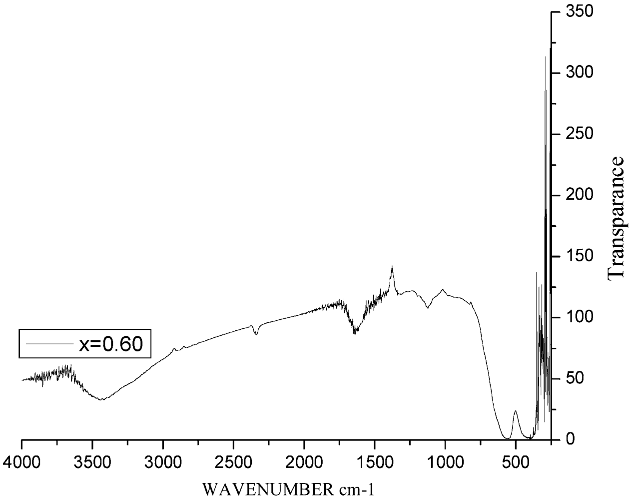

Fig. 2 IR spectra obtained for as prepared powdered sample $Mn_{0.6}Zn_{0.4}Fe_2O_4$

of certain types of chemical substances adsorbed on the surface of particles. In the IR spectra of the mixed oxides the following vibrations, with a corresponding wavenumber are possible.

$$\mathrm{Me_T} - \overset{\leftrightarrow}{\mathrm{O}} - \mathrm{Me_O}\ \text{stretching vibration}\ 600 - 550\,\mathrm{cm}^{-1} \tag{1}$$

$$\mathrm{Me_O} \overset{\leftrightarrow}{-} \mathrm{O}\ \text{stretching vibration}\ 450 - 385\,\mathrm{cm}^{-1} \tag{2}$$

$$\mathrm{Me_T} \overset{\leftrightarrow}{-}\ \mathrm{Me_O}\ \text{stretching vibration}\ 350 - 330\,\mathrm{cm}^{-1}, \tag{3}$$

where O is oxygen, $\mathrm{Me_O}$ is metal in the octahedric site and $\mathrm{Me_T}$ in the tetrahedric site. The metal–oxygen absorption bands (1) and (2) are pronounced for all spinel structures and essentially for ferrites. Usually the band (3) is less intense than bands (1) and (2), and sometimes found to merge with the band (2) resulting in a singlewide band at 420–330 cm^{-1}. In the IR absorption spectra recorded for the powdered samples (Fig. 2), two broad bands (1) and (2) are observed in addition to a small narrow less intense third band in the range 350–330 cm^{-1} that has almost merged with band (2).

The grain size of the sample as seen from TEM photograph of Fig. 3 is in excellent agreement with values obtained for particle size using Scherer formula. . Preservation of stoichiometry was confirmed on analyzing the EDS results.

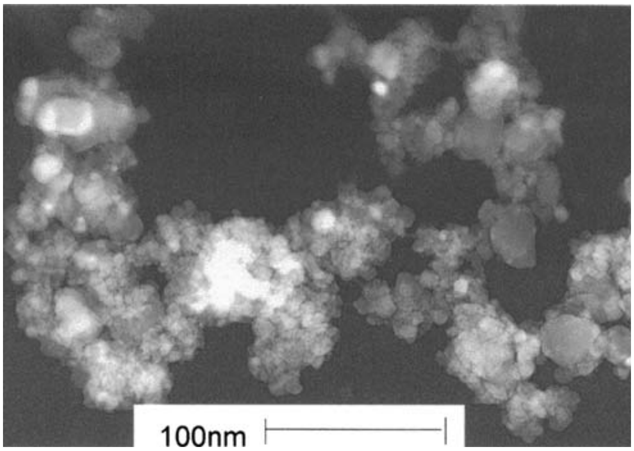

Fig. 3 TEM photograph of as prepared powdered sample $\mathrm{Mn_{0.6}Zn_{0.4}Fe_2O_4}$

Table 1 Table showing density of unsintered samples and density of samples sintered at 1,050, 1,150, 1,250 and 1,350 °C

Mn Conc. (x)	Unsintd. density (g/cc)	Sintd. 1,050 °C density (g/cc)	Sintd. 1,150 °C density (g/cc)	Sintd. 1,250 °C density (g/cc)	Sintd. 1,350 °C density (g/cc)
0.65	2.3941	3.1825	4.1127	4.0287	4.1824
0.6	2.7779	3.6226	3.7624	3.6477	4.0999
0.55	2.696	3.7536	3.9285	3.9909	4.1401
0.45	2.396	3.2007	3.9833	3.8674	3.9251
0.4	2.3273	3.5169	3.8471	3.5923	3.7124
0.35	3.0324	3.7512	4.0987	4.2953	3.9222

The density values of the samples (Table 1) are found to show abrupt changes on changing sintering temperature from 1,050 to 1,350 °C. The density of sintered $\mathrm{Mn}_x\mathrm{Zn}_{(1-x)}\mathrm{Fe_2O_4}$ ferrite material where $x = 0.65$, 0.6, 0.45 and 0.4 is found to be high when sintered at 1,150 and 1,350 °C whereas these values are low when these samples are sintered at 1,050 and 1,250 °C. The density for sample with $x = 0.55$ is found to increase with sintering temperature whereas the same is observed to be lower for sample with $x = 0.35$ sintered at 1,350 °C. Although density depends on the concentration of Mn in the sample the present unusual behavior observed in the density may be attributed to the existence of phase transitions which occur during the crystal formation process while sintering, as evident from SEM photographs depicted in Fig. 4. The investigation on fine structure of $\mathrm{Mn}_x\mathrm{Zn}_{(1-x)}\mathrm{Fe_2O_4}$ ferrite clearly indicates the influence of sintering conditions on the grain growth [5], density of the sample and crystalline phase of the sample [6]. The unusual trend in the density values is also observed in the resistivity trends of the samples. Figure 5a–d shows plots of log ρ v/s $1{,}000/T$ (K) for $\mathrm{Mn}_x\mathrm{Zn}_{(1-x)}\mathrm{Fe_2O_4}$ ferrite. A semiconductor like general behavior is seen for all the samples as the samples undergo a second order ferrimagnetic to paramagnetic phase transition. Although the trends depend on the concentration of Mn in the sample these are more strongly dependent on the sintering temperature of the sample. Resistivity values at 300 K are seen to vary between 3.789×10^7 ohm-cm and 1.898×10^6 ohm-cm for samples sintered at 1,050 °C the highest and the lowest being observed for $\mathrm{Mn_{0.35}Zn_{0.65}Fe_2O_4}$ and $\mathrm{Mn_{0.4}Zn_{0.6}Fe_2O_4}$, respectively. A considerable variation in the resistivity is observed for samples sintered at 1,150 °C. The resistivity at 300 K is found to vary between 7.5×10^8 ohm-cm and 2.832×10^6 ohm-cm with the highest for $\mathrm{Mn_{0.65}Zn_{0.35}Fe_2O_4}$ sample. These values are found to be much lower for samples sintered at 1,250 °C and are found to range between 2.285×10^6 ohm-cm and 6.08×10^5 ohm-cm. A large variation in the resistivity values is observed for samples sintered at 1,350 °C both at 300 K and at higher temperatures with the highest being 1.624×10^9 ohm-cm for $\mathrm{Mn_{0.6}Zn_{0.4}Fe_2O_4}$ at 300 K. It

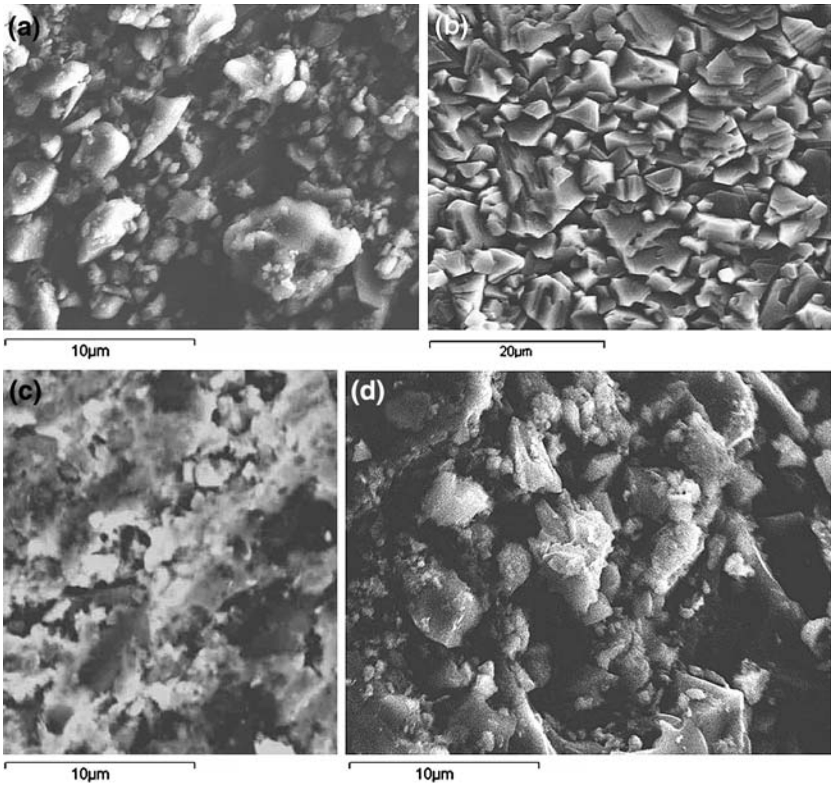

Fig. 4 SEM photographs of $Mn_{0.45}Zn_{0.55}Fe_2O_4$ sintered in nitrogen atmosphere for 3 h at (**a**) 1,050 °C, (**b**) 1,150 °C, (**c**) 1,250 °C and (**d**) 1,350 °C

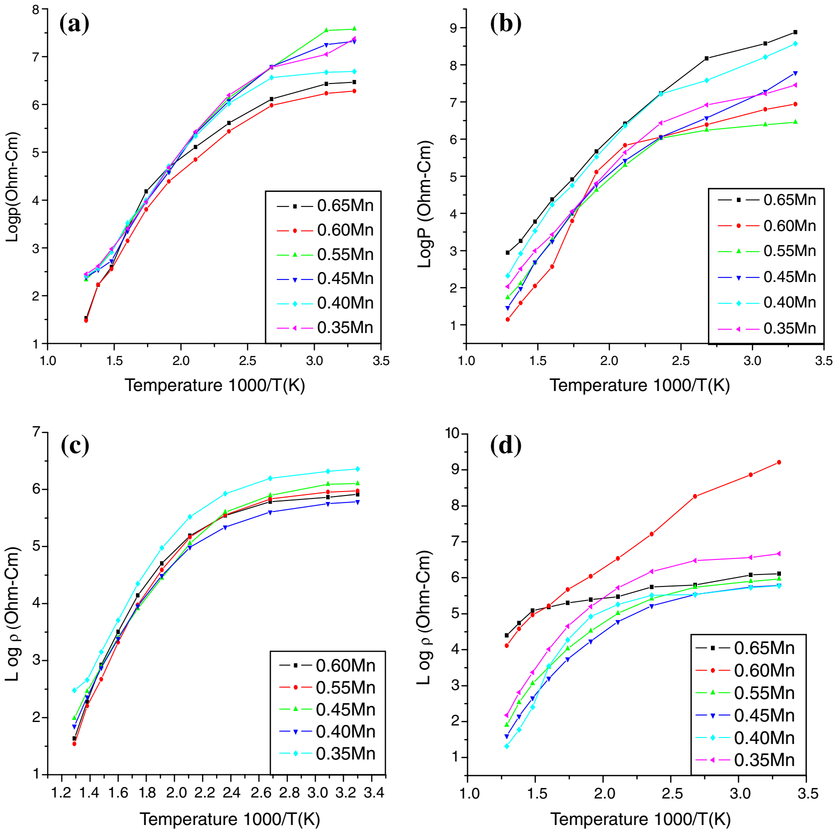

Fig. 5 Resistivity variation for the samples of different compositions, sintered at (**a**) 1,050 °C, (b) 1,150 °C, (**c**) 1,250 °C and (**d**) 1,350 °C

may be seen that large variations in resistivity at 300 K are observed for samples sintered at 1,150 and 1,350 °C. This may be due to formation of definite small grain shapes with high resistive boundaries in between any nearby neighbors and is evident from the SEM photographs (b) and (d) of Fig. 4.

In ferrites electron conduction mechanisms have been studied by many investigators and reviewed by Klinger et al. [7]. 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 (Fe^{2+}) ion requires little energy to move to an adjacent (Fe^{3+}) 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 (Fe^{2+}) 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 [2].

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. It is evident from Fig. 4 that due to phase transitions samples sintered at 1,150 and 1,350 °C show small grain sizes with large non-ferrimagnetic grain boundaries more over the total surface area of the sample also increases due to formation of fine crystals which results in high resistivity for the samples. The samples sintered at 1,050 and 1,250 °C do not show formation of perfect crystals or small grain shapes which results in low surface area and less high resistivity non-ferrimagnetic grain boundaries which accounts for low value of resistivity at 300 K for this samples as compared to samples sintered at 1,150 and 1,350 °C. The resistivity values obtained are much higher as compared to the reported resistivity values of 10^5 ohm-cm [8, 9].

Conclusion

The present investigations on the resistivity of the Mn–Zn ferrite developed by sintering nanoparticle Mn–Zn ferrite, prepared by nitrilotriacetate precursor method in an inert atmosphere, show existence of phase transitions thus contributing 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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