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Characterization of Polycrystalline Zinc Ferrite ($ZnFe_2O_4$) by XRD, SEM, IS and Resistivity Measurements

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ABSTRACT

Polycrystalline Zinc Ferrite having spinel structure has been prepared at 1200˚C by solid state reaction method. Low cost oxide powders, Fe_2O_3 and ZnO, were used as raw materials. Zinc Ferrite has been characterized using X-ray diffraction and scanning electron microscopy for its phase analysis and microstructure properties. Electrical behavior has been studied by using impedance spectroscopy in the frequency range of 1Hz-100 kHz. Resistivity and conductivity has been calculated by using Nyquist plot in the frequency range 1 Hz-100 kHz with variation of temperature i.e. from room temperature to 350 °C. Resistance measured by high resistance meter shows that volume resistance depends on the applied voltage. On increasing the voltage beyond a certain value, volume resistance decreases. SEM micrographs show that the grains are not homogenously developed and some of them have relatively larger grain boundary area. The micrographs also indicate high porosity of these samples.

1. INTRODUCTION

Magnetic ceramics or ferrites are quite well-established group of magnetic materials (Su 2009, Zhao 2009). The ferrites have applications in electronics, engineering and telecommunication, owing to its wide diversity of properties and compositions (Naeem 2009). Ferrites have become a reference material as the developments associated with new magnetic materials, such as the extra-hard rare-earth intermetallics, or the extra-soft amorphous ribbons are often assessed by comparison with ferrites (Viriani 1997). Zinc ferrite has attracted the interest of researchers since long because of its intriguing magnetic properties compared with other spinel ferrites.

Ferrites are complex to understand due to combination of two areas; ceramic microstructures and magnetic phenomena. Ceramic microstructures, formed as a result of physio-chemical processes such as solid-state sintering. These are affected by a large number of interacting variables. The quantum mechanical nature of magnetic properties of ferrites makes them very difficult to comprehend, since they are entirely different to macroscopic view point. The approach to ferrites; the synthesis; the relationship between crystal structure, texture and physical properties;

the modeling of magnetic interactions, is quite essential in interdisciplinary reserach (Wang 2009).

One of the most important attributes or advantages of ferrites is their high degree of compositional variability. Some fundamental developments of the theory and applications of ferrites included simple systems, like MFe_2O_4, where M = Mn, Co, Ni. However, commercially important ferrites of appropriate compositions consist of wide range of solid solutions (Ghasemi 2008).

Ferrites have a low value of conductivity, which is one of the considerations for microwave applications (Martha 2000, Jun 2010). The hopping mechanism is mainly dominant for conduction in ferrites (Charanjeet 2011), which is associated with the easy electron shift between di- and trivalent iron ions. This conduction mechanism is impossible to eliminate without eliminating the iron, the basic ingredient of ferrites, or the Fe^{2+}. Thus, additional barriers to conduction must be formed through the controlled deposition (segregation) of SiO_2, CaO, TiO_2 on the grain boundaries of super fine grained ferrites through controlled sintering process (Shelar 2010).

The aim of this research work is to explore the influence of temperature on conductivity. $ZnFe_2O_4$ was chosen because they usually show a high grain boundary resistance, which allows a clear resolution of impedance contributions from grain (bulk) and grain boundaries.

2. EXPERIMENTAL PROCEDURES

Polycrystalline samples of zinc ferrite ($ZnFe_2O_4$) have been prepared using well-recognized solid state reaction. The host ZnO and Fe_2O_3 used were of analytical grade purity. The reagents were mixed homogenously in a required proportion in an agate mortar and pestle. The powders were pressed into pellets of 15.876 mm diameter under a pressure of 5 tons using an Apex hydraulic press. The samples in powder form were sintered in a muffle furnace. The sintering process was carried out in two steps and each process was repeated after re-grinding and re-pelletizing the samples. Sintered pellets change their color during sintering and also show reduction in their respective volume.

X-ray diffraction (XRD) patterns were obtained to explore the phase formation and to determine the completion of the reaction using Rigaku XRD-D/Max-11A diffractometer with CuK_α radiation. Afterwards, sample was analyzed for electrical properties using a Solatron-1260 impedance gain/phase analyzer (FRA) with extended probe assembly by two electrode methods and a Eurotherm-815 controller/programmer was used to control the temperature. For impedance analysis, the sample was mechanically polished with SiC abrasive papers to remove any contamination from the surface of electrodes. Electric connections to the sample were made by using pure copper wires using conducting silver paste.

Microstructure of Zinc Ferrite was obtained by Jeol-JSM-6480 scanning electron microscopy (SEM) operated at 15 kV. Samples were mounted on brass stubs using conducting paste and were coated in (JEE-4X/5B) coating unit. Micrographs were obtained at different magnifications.

3. RESULTS AND DISCUSSION

The crystal structure of the prepared samples was investigated using XRD. The diffraction pattern of the sample was obtained after first heating at 1200 °C, for 24 hours. It was observed that all the major diffraction peaks were matched with JCPD card no. 22-1012, belonging to the zinc ferrite ($ZnFe_2O_4$). However, some minor peaks were also present in the pattern which were found to belong to ZnO and one minor peak of Fe_2O_3. The pattern also contained two other small impurity peaks. Therefore, a second heat treatment was carried at 1200 °C for another 24 hours, in order to develop the exact phase of zinc ferrite. The diffraction pattern obtained after second heat treatment showed more intense and sharp peaks belonging to $ZnFe_2O_4$, well-matched with the reference card no. 22-1012. The unknown impurity peaks vanished in the pattern and the intensity of the peaks due to ZnO and Fe_2O_3 was much reduced. The pattern also revealed some doublets in the peaks and it was found that those doublets were due to the $CuK_{\alpha1}$ and $CuK_{\alpha2}$ radiations. The XRD pattern indicated that the product after second heating at 1200 °C mainly belonged to zinc ferrite having cubic spinel structure, with some minor impurities. The estimated crystallite size was evaluated using Scherrer's equation (Saleem 2011) and was found to be 7±0.05 nm, well-matched with the value reported earlier (Fresno *et al*. 2010). Lattice parameters of the sample were evaluated using the software "CELL", and found to be 8.4375 Å. The X-ray densities were evaluated from XRD patterns and was found to be ρ = 5.33 g/cm^3. The bulk density was calculated by measuring bulk volume and mass of the samples. The unit cell volume for $ZnFe_2O_4$ is 600.677 × 10^{-24} cm^3. The bulk density of the sample was evaluated to be 3.372 g/cm^3. Density measurement showed that the bulk density was less than that of X-ray density, indicating that the prepared material was porous.

In order to understand the mechanism that controls the electrical properties in polycrystalline zinc ferrite sample, the bulk and grain boundary properties must be convoluted to enable the analysis of each component. This objective can be achieved by measuring the frequency dependent complex impedance. The impedance spectra have been obtained for zinc ferrite ($ZnFe_2O_4$) in frequencies range (1 Hz -100 kHz) at room temperature to 350 °C. The data obtained has been used to draw Nyquist plot (Z_{real} – Z_{img}), as shown in the Figs. 1 to 7. The complex plane impedance spectrum shows that the resistive and capacitive properties of the material are broadly attributed to the mechanism related with the bulk and grain boundaries. These plots clearly show the existence of two semi-circles. From the Nyquist plot, the grain boundary resistance (R_{gb}) and bulk resistance (R_b) can be evaluated, separately using the values of the first R_1 and second intercepts R_2 on the real axis Z. The conductivity of the $ZnFe_2O_4$ can be calculated using the equation:

$$\sigma = t / R.A. \quad (\Omega\text{-cm})^{-1} \qquad (1)$$

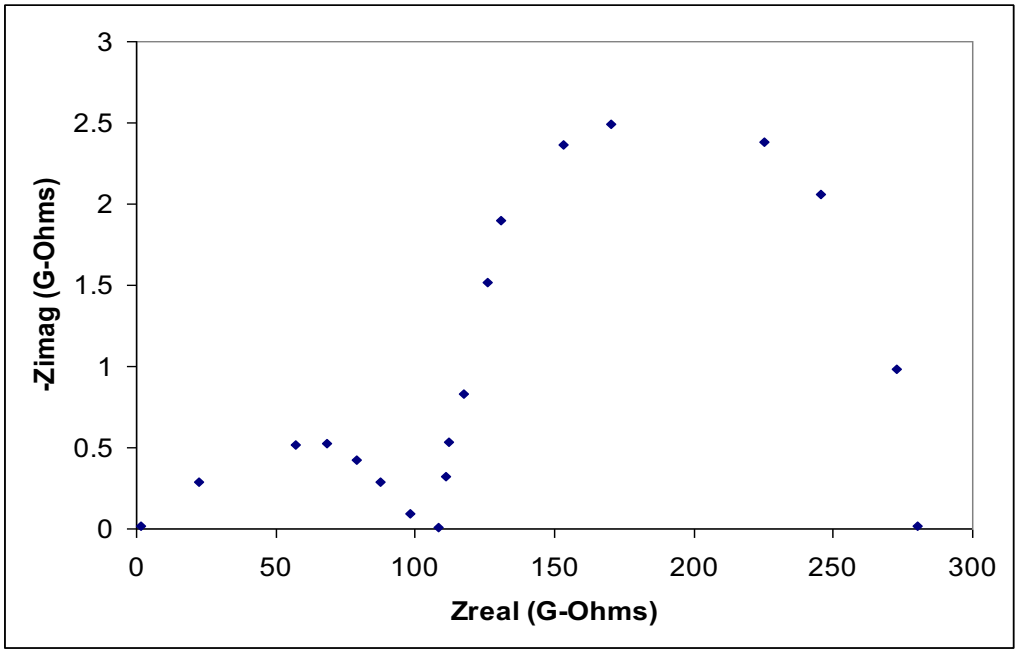

Fig. 1 Complex impedance data at room temperature plotted as Nyquist plot

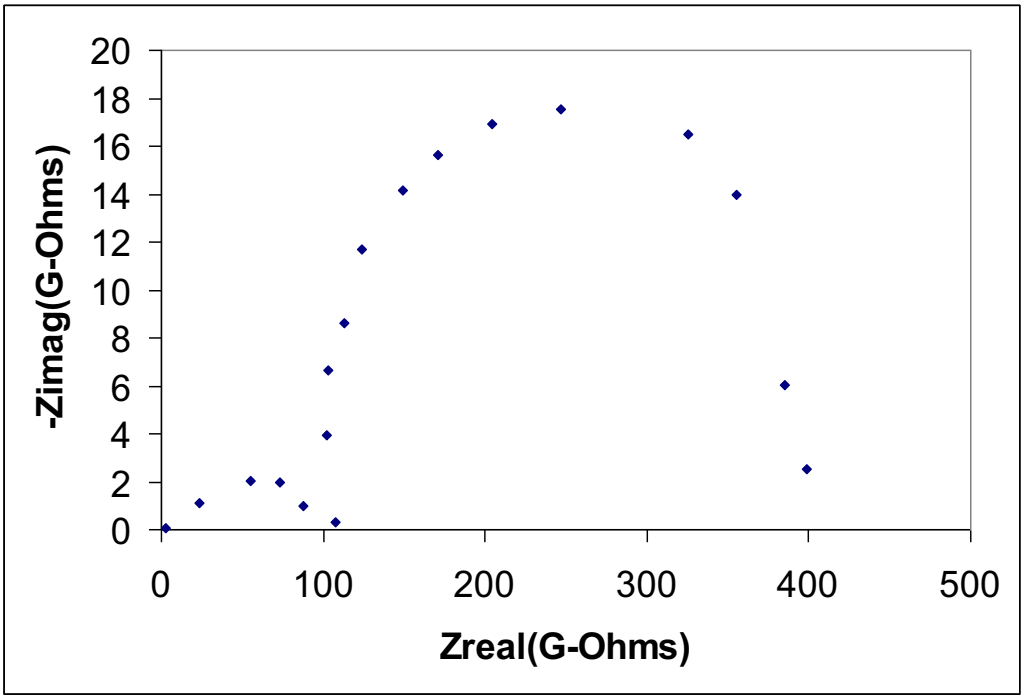

Fig. 2 Complex impedance data at 100 °C plotted as Nyquist plot

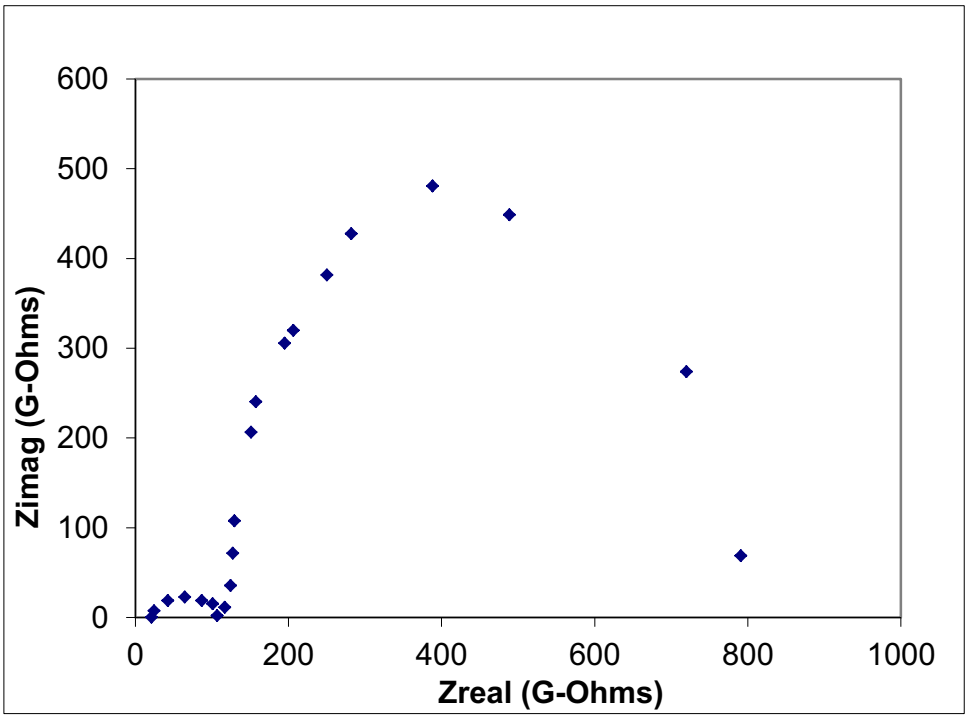

Fig. 3 Complex impedance data at 150 °C plotted as Nyquist plot

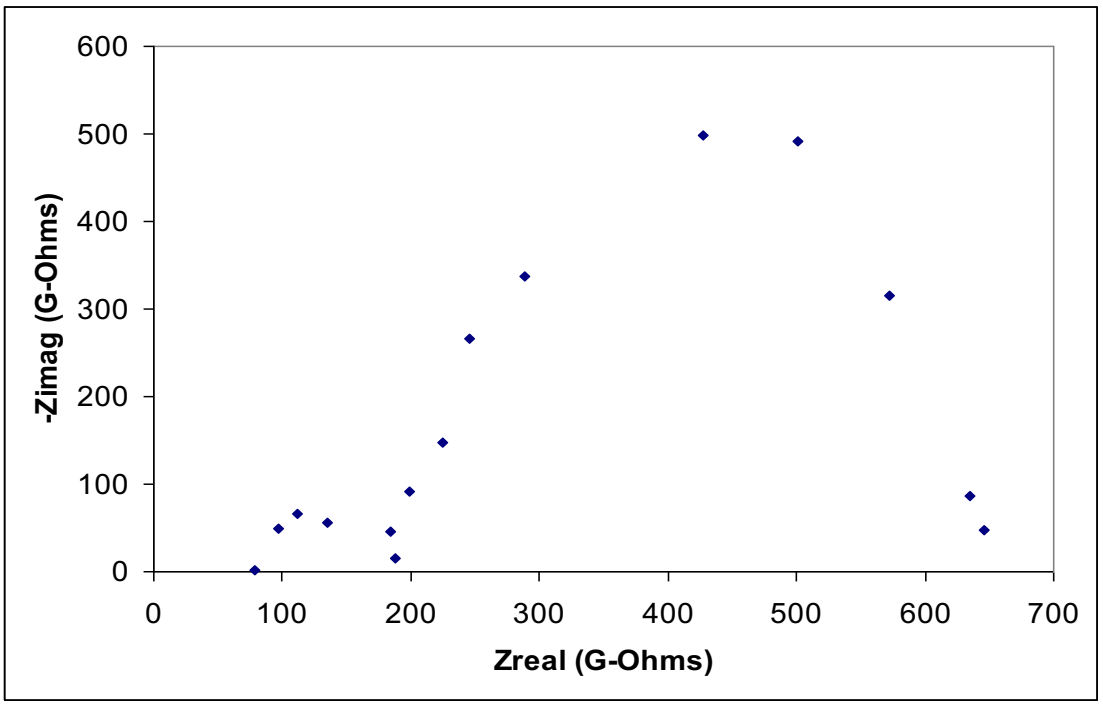

Fig. 4 Complex impedance data at 200 °C plotted as Nyquist plot

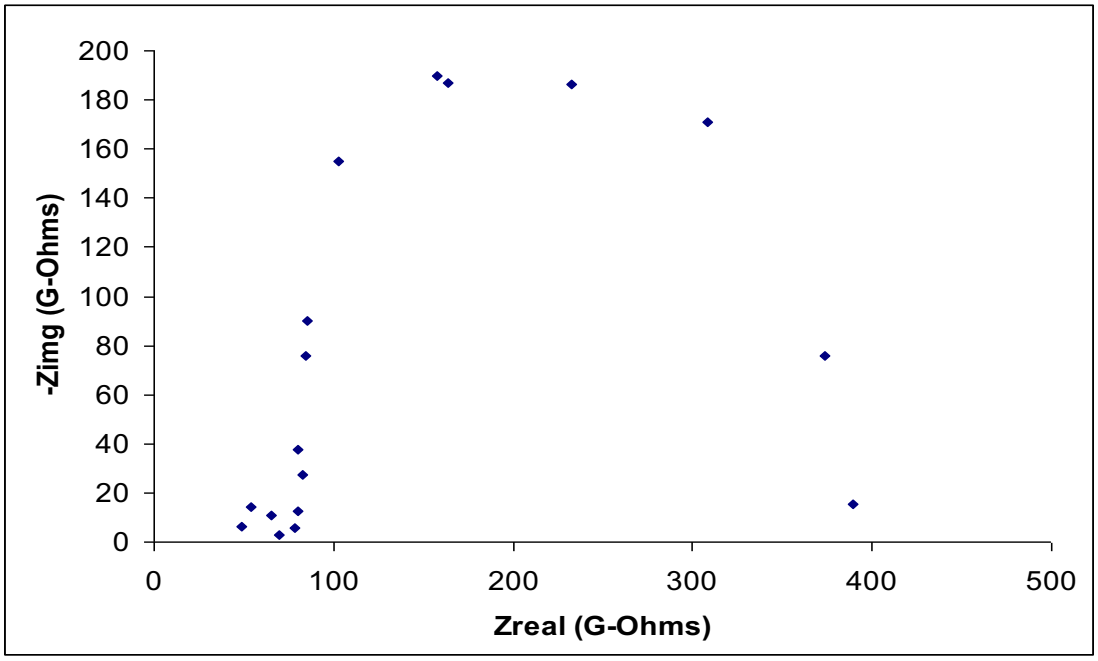

Fig. 5 Complex impedance data at 250 °C plotted as Nyquist plot

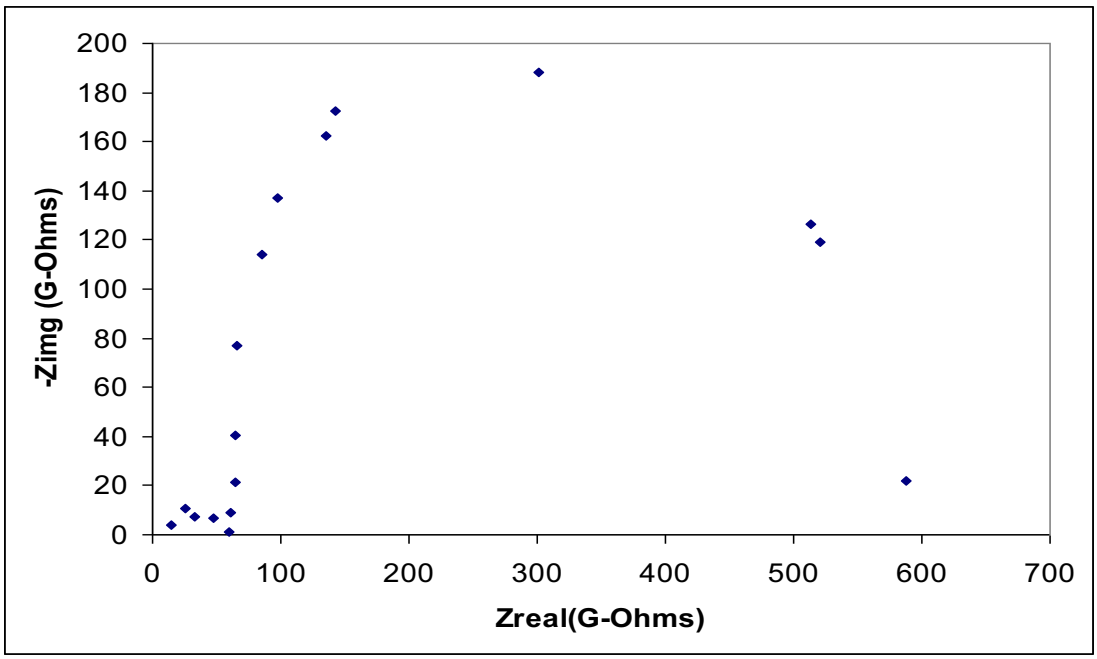

Fig. 6 Complex impedance data at 300 °C plotted as Nyquist plot

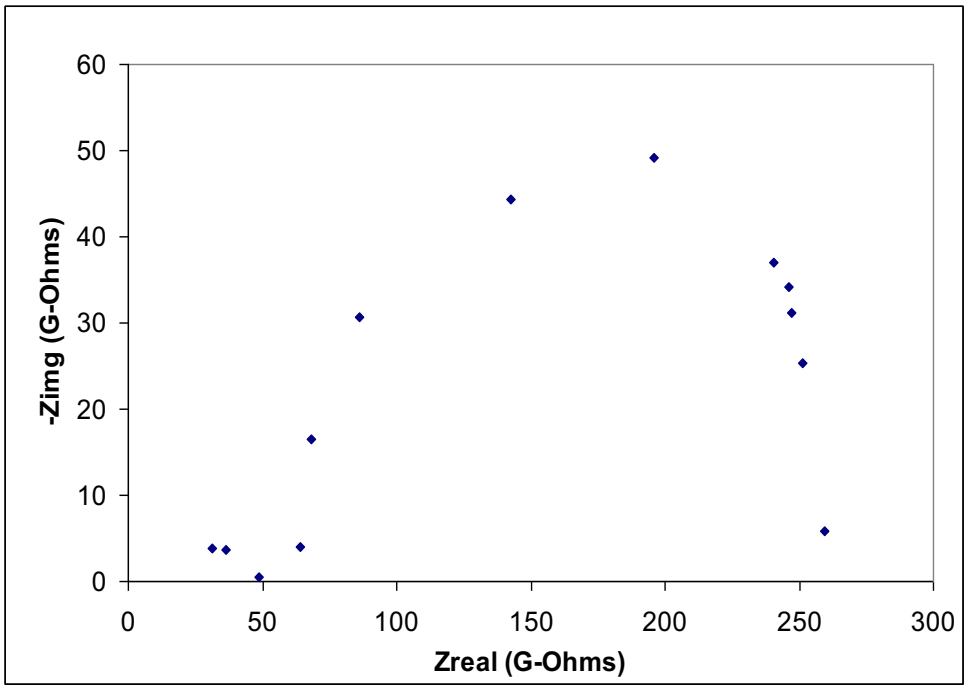

Fig. 7 Complex impedance data at 350 °C plotted as Nyquist plot

It was observed that the conductivity of the samples varies between (1.572×10^{-12} – 3.480×10^{-12}) Ω-cm^{-1}, for the temperatures from room temperature to 350 °C. Previous investigations have shown that rise of conductivity in ferrites is mainly associated with electron hopping from and to Fe^{2+} and Fe^{3+}, being simultaneously present at octahedral sites of the spinel lattice. It was observed that the conductivity increased with the rise of temperature. This trend of electrical conductivity can be associated with the mobility of charge carriers, mainly responsible for hopping mechanism. The mobility of hopping ions thereby increases the conductivity with rise of temperature. The carriers (electrons) involved in the hopping mechanism are mainly responsible for polarization in ferrites (Navneet 2011). The electrical resistivity of ferrites at room temperatures depends on their chemical composition and the method of preparation. Resistivity of the sample is calculated by using equation;

$$\rho = t/\sigma \ (\Omega\text{-cm}) \qquad (2)$$

It is obvious that small grain size implies large number of insulating grain boundaries and hence greater energy barrier for the electron conduction resulting thereby in higher resistivity. Resistivity is normally represented by the combined effect of various factors like Fe^{2+} concentration, crystal structure, grain size, perfection and micro-structural homogeneity. Volume resistivity of $ZnFe_2O_4$ has been measured at different applied voltages (10-1000 V) are given in Table 1 and plotted in Fig. 8.

Table 1 Volume resistivity For $ZnFe_2O_4$

No.of Obs.	Test Voltage Applied (V)	Volumr Resistance $R_v(\Omega)$	Volume Resistivity $\rho = 19.6 \times R_v/t$ (Ω-cm)
1	10	2.87×10^{13}	1.669×10^{15}
2	25	3×10^{13}	1.774×10^{15}
3	50	4.1×10^{13}	2.384×10^{15}
4	100	9.5×10^{13}	5.525×10^{15}
5	250	13.4×10^{13}	7.793×10^{15}
6	500	12.8×10^{13}	7.444×10^{15}
7	1000	7.2×10^{13}	4.187×10^{15}

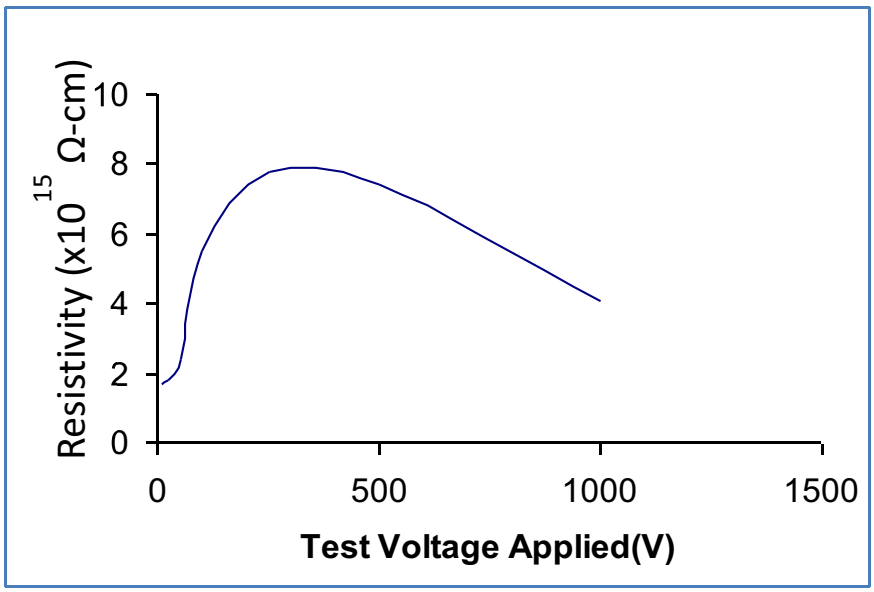

Fig. 8 Volume resistivity of $ZnFe_2O_4$

Measurement shows that volume resistivity depend on the applied voltage. On increasing the applied voltage from 10 to 250 V, the volume resistivity increases because trap charges are tightly bound to the nucleus making no contribution to the conductivity of the sample. Whereas, on further increasing the applied voltage

ranging from 500-1000 V, the volume resistivity of the sample decreases. When the applied voltage is increased beyond a certain value, the trap charges become mobile resulting in decrease of the volume resistivity of the sample. Therefore, above 250 V the volume resistivity decreases against the applied voltage up to 1000 V. The microstructure analysis of $ZnFe_2O_4$ sample was carried out by using SEM, as shown in the Fig. 9.

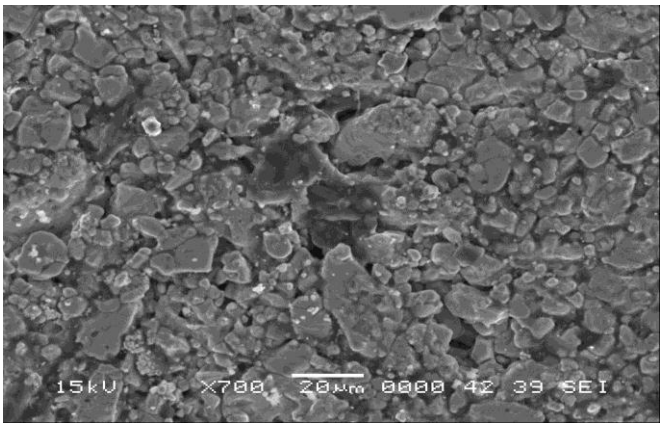

Fig. 9 (a) SEM Micrograph of $ZnFe_2O_4$ at X = 700 Magnification.

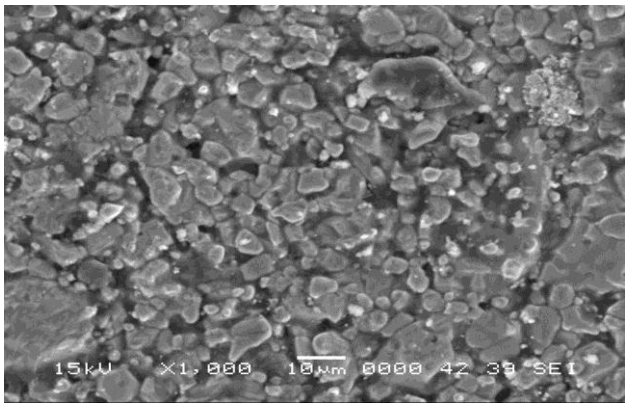

Fig. 9(b) SEM Micrograph of $ZnFe_2O_4$ at X = 1000 Magnification.

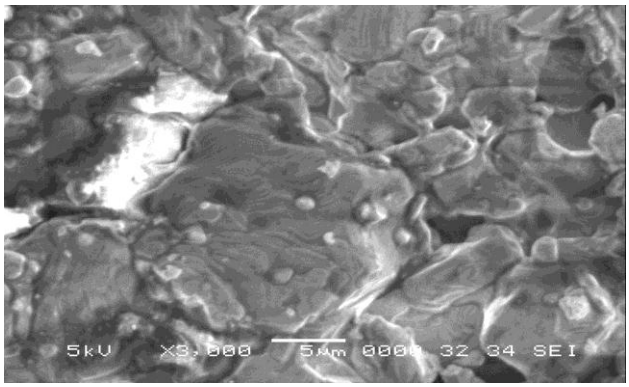

Fig. 9**(c)** SEM Micrograph of $ZnFe_2O_4$ at X = 3000 Magnification.

These micrographs show that grains are not homogeneously well developed. Grain boundaries are not inter-connected indicating that material is highly porous and having high resistivity. Further, it is also revealed that the material has layered structure and is not fully densified, although, some of the grains are interconnected. The micrograph shown in Fig. (c) shows a selected area of the sample representing relatively large sized grains (~ 15 μm). Layered structure is evident from the set of parallel lines contained in individual grains. Secondly, large grains also have inclusions of small particles. In short, one can infer the granular microstructure of $ZnFe_2O_4$ in the form of varying grain sizes (0.2 μm to 25 μm). However, large size grains are small in number and contain inclusions of small sized grains.

4. CONCLUSIONS

Polycrystalline zinc ferrite has been prepared by using low cost ZnO and Fe_2O_3 powders, employing solid state reaction method. The powder sample was sintered, palletized and characterized for its structural, electrical and morphological investigations using XRD, IS and SEM, respectively. The structural analysis revealed the sample as zinc ferrite having cubic spinel phase with the cell dimensions of 8.4375 Å. Bulk density was found less than the x-ray density, attributable to the porous structure of the sample. Impedance analysis showed two distinct semicircles, as plotted using the impedance data. Bulk and grain boundary resistances have been obtained from the first and second intercepts on the real axis. High frequency semicircle corresponds to the bulk response and low frequency semicircle corresponds to the grain boundary response. The analysis showed that the conductivity increases with the rise of temperature. The micrographs confirmed that the sample is not completely densified and bears high porosity.

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