INVESTIGATION OF TEMPERATURE SENSITIVE ELECTRICAL PROPERTIES OF MANGANESE-ZINC FERRITES

By

S. N. PATIL * B. P. LADGAONKAR ** S. K. TILEKAR ***

D. DESHPANDE **** A. M. PAWAR *****

*,****,***** Department of Electronics, Tuljaram Chaturchand College, Baramati, District, Pune, Maharashtra.
-*Department of Electronics Shankarrao Mohite Mahavidyalaya, Akluj, District, Solapur, Maharashtra.

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ABSTRACT

Keeping pace with facets of nanotechnology and its applications in the field of development of smart instrumentation to cater present day needs and future requirements of various sectors, sensor is the key portion of measurement system that, responds directly to the physical variables to be measured. Therefore, one should opt for proper sensor of better characteristics, nanoparticle spinel Manganese-Zinc ferrites have been synthesized by co-precipitation method. The formation of the materials is confirmed by X-ray powder diffraction & FTIR absorption technology. From the results of X-ray diffraction investigation confirm the formation of single phase composition with the average particle size from 40 nm to 48 nm. Temperature dependent electrical properties of the compositions of $Mg_xZn_{1-x}Fe_2O_4$ *nano ferrites were investigated for suitability of these materials as the sensing element for designing of sensors. The sensors are developed, employing thick film technology. Measure the D. C electrical resistivity of the pelletized compositions and shows semiconducting behavior, which is attributed to the electron hopping mechanism. This electrical conductivity exhibit the influence of magnetic ordering at and about curie temperature. The curie temperature values depict the compositional dependence. The electrical resistivity shows negative temperature coefficient with temperature and hence the materials could be used to design temperature sensors. Results of implementation are interpreted in this paper.*

Keywords: Electrical Properties, Sensing Element, D. C Electrical Resistivity, Electron Hopping.

INTRODUCTION

During recent days, the state-of-art is to develop smart instrumentation to cater present day needs and future requirements of various sectors, such as industrial parameters measurement and controlling, biomedical, agriculture, food processing domestic appliances, R & D instrumentation, textile industries etc. Modern instrumentation exhibits the deployment of an ubiquitous and most pervasive technologies to enhance the reliability and preciseness in the results. To achieve these goals, instead of traditional sensor system, the use of intelligent sensor system is recommended for dedicated applications. The traditional sensor systems are based on early days` technologies. Therefore, the designers have to put rather more efforts in development of instrumentation. Deployment of the ferrites for sensor based applications is the novel field for the researchers (Patil & Ladgaonkar, 2013; Patil et al., 2017). Electrical properties of the polycrystalline spinel ferrites reveal the materials` suitableness for sensor based applications. The possibility of preparing ferrites in the form of nanoparticles has open a new and exciting research field, with revolutionary applications in the electronic technology. Polycrystalline ferrites exhibit interesting electrical properties, wherein the semiconducting behavior is realized. Measurement of dc conductivity is essentially important technique to explore the transport process in ferrites. The electrical properties such as dc resistivity, dielectric polarization, mobility etc are the intrinsic properties and these properties are found to be dependent on the chemical compositions, preparation conditions, substitution of divalent or trivalent cations in the parent lattice, temperature, environmental conditions etc. These ferrite materials are highly resistive and its resistivity is mostly sensitive to the microstructure of the compositions. The microstructure usually develops at the sintering stage. Therefore, sintering conditions play significant role on the electrical properties of the ferrites. Thus, by controlling preparation condition, the electrical properties can be optimized. It is also reported that, the electrical properties are sensitive to the distribution of cations among tetrahedral (A) and octahedral (B) sites of the spinel structure (Patil & Ladgaonkar, 2013). Development of Smart Sensor Module is the major objective of present research work. For this purpose, it is also proposed to design own sensors of required characteristics. To develop the sensor, the sensing materials play vital role. Therefore, the polycrystalline spinel nano ferrites have been synthesized, and used to develop the sensors.

1. Review of Literature and Mechanism of Temperature Dependent Electrical Conduction

The exponential dependence of electrical conductivity of ferrites with temperature can be attributed to the semiconducting nature. However, the semiconducting nature of spinel ferrites is quite different than that of semiconductors. Because, in semiconductor the conductivity is because of thermally generated charge carriers. However, in case of the ferrites the electrical conductivity is due to thermally activated charge carriers in the ionic lattice, which can be explained on the basis of hopping model (Patil et al., 2017; Shinde et al., 2008). The activation energy for electrical conduction is considerably reduced if the crystallattice intrinsically contains cations of one element in more than one valence state. According to Verway et al, the conduction in the ferrite composition is due to electron hopping between Fe^{3+} and Fe^{2+} ions localized at crystallographic octahedral (B) site (Fu & Hu, 2010). During this electron exchange the valence states of two cations are exchanged. However, this conductivity is very low, which can be attributed to the lower mobility of the charge carriers. The cations are not free to leave the lattice sites. However, due to lattice vibrations, these cations come enough close together to transfer the electrons as $Fe^{2+} \Leftrightarrow Fe^{3+} + e$-. The number of electrons contributing the conduction process depends upon the concentration of the Fe^{2+} ion of octahedral site. Therefore, in ferrous ferrite the concentration of Fe^{2+} ions is same as that of Fe^{3+} ions on octahedral site. Therefore, it favours the conduction process and results into low resistivity. Moreover, on substitution, the nickel ion is also contributing electron hopping mechanism as $Ni^{2} + Fe^{3+} \Leftrightarrow Ni^{3+} + Fe^{2+}$(El-Shabasy, 1997). However, this is also featured with low mobility. Because of the thermal energy, the mobility of charge carriers increases significantly. Hence, electrical conduction significantly depends upon temperature. In addition to electron hoping model, other models are also suggested by the investigators (Abbas & Chaudhry, 2002; Chavan et al., 2010). Polaron, electron with strain field, hopping mechanism is suggested by (Abbas & Chaudhry, 2002; Chavan et al., 2010) to explain the conduction phenomenon, due to thermally activated mobility (Murthy & Sobhanadri, 1976; Gopalan et al., 2009). Thus, the electrical conductivity of the ferrite compositions strongly depends upon the temperature.

The temperature dependence of electrical resistivity obeys Wilson`s relations (Shinde et al., 2010),

$$\rho = \rho_o \exp(DE/KT) \qquad (1)$$

where DE is the activation energy and K is the Boltzman constant. An expression 1 depicts the fact that, the ferrite compositions reveal semiconducting nature with negative temperature coefficient of resistance. The graph of logr against 1/T is the straight line with discontinuities in the slope at certain temperatures, which can be attributed to the Curie points. Thus, the electrical conductivity is strongly influenced by the magnetic ordering as well (Bhise et al., 1996).

The temperature dependence of dc resistivity of the Mg-Zn-Cu ferrites was studied by (Bachhav et al., 2013) and reported three significant regions in the graph of logr against 1/T. The nature of graph is attributed to the effect of magnetic interaction on electrical conduction. Temperature dependent electrical resistivity of CuNi nanoferrites, synthesized by using citrate gel auto combustion technique, was investigated by (Kumar et al., 2014) and reported that, electrical conduction is due to electron hopping for lower temperature. Moreover, the behaviour of resistivity for elevated temperature is attributed to the polaron hopping conduction mechanism. They reported that the activation energy at paramagnetic region is more than that of at ferrimagnetic region (Vasambekar et al., 1999). The variations in the logr against 1/T curve depict the semiconducting nature with two regions referred as ferri region and para region. They reported that, the substitution of Mg results into decrease in the Curie temperature, which could be attributed to the decrease in the magnetic interaction. The substitution of rare earth element in spinel ferrites causes to increase in the resistivity (Gopalan et al., 2009; Gopalan et al., 2009; Rama et al., 2012). This may be due to stable valence of the rare earth ions.

Thus, it is found that, to decide applicability of the nanoferrites, the study of dc electrical properties and its temperature dependence is essential (Chaudhari & Ghatage, 2013). Therefore, electrical properties of the $Mg_xZn_{1-x}Fe_2O_4$ ferrites under investigation are studies and results are reported in this paper.

2. Experimental

Present investigation emphasizes the synthesis of polycrystalline ferrites materials suitable for typical sensor based applications using co-precipitation method. The materials can be characterized by X-ray diffraction and FTIR to explore the structural details of the compositions. X-ray diffractograms of $Mg_xZn_{1-x}Fe_2O_4$ ferrite compositions were x =0.20, 0.40, 0.60 and 0.80 depicts in Figure1. From X-ray diffractogram information, structural details for composition under investigation are calculated (Patil et al., 2018; Patil et al., 2016). The particle size, for all compositions under investigation is estimated for employing Scherrer Equation obtain and it is within the range of 40 nm to 48 nm. The FTIR spectra of the compositions $Mg_xZn_{1-x}Fe_2O_4$, ferrites were obtained in the range from 400 cm-1to 4000 cm^{-1}. The significant absorption bands revels the confirmation of structural details and suitability of ferrite material for sensor base applications (Patil et al., 2018; Ladgaonkar et al., 2013). Figure 2 show the IR absorption spectra of the composition x=0.60.

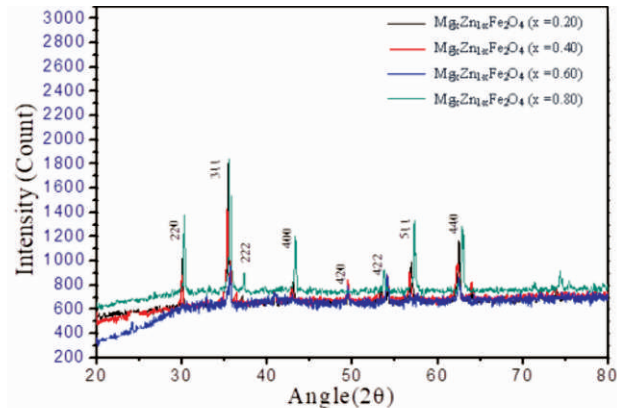


Figure 1. X-ray Diffract Grams of $Mg_xZn_{1-x}Fe_2O_4$ (x=0.20, 0.40, 0.60 and 0.80)

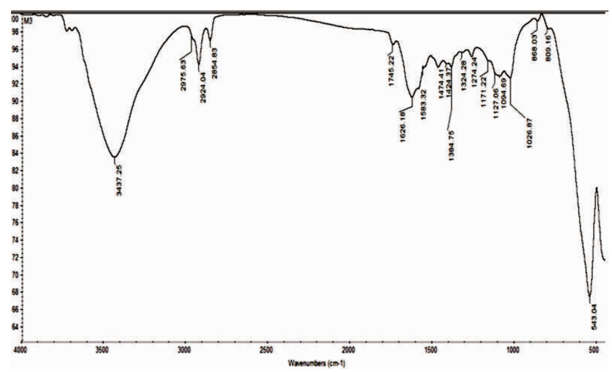


Figure 2. IR Absorption Spectra of the Composition $Mg_xZn_{1-x}Fe_2O_4$ (x=0.60)

The measurement of electrical resistance (R) of the pelletized composition of the polycrystalline, MgxZn1-xFe2O4 (x= 0.20, 0.40, 0.60 and 0.80) spinel ferrites were carried out from room temperature to 600 K using two probe method. An experimental arrangement is shown in Figure 3. The measurements are carried out using samples in pellet (disk) form. The electrode designed in the laboratory and is depicted in Figure 3 and mention schematic of electrode. A silver paste is used to achieve Ohmic contacts. Highly precise digital meter, Tektronix Make model DMM4050, 10 Ω to 1.2 GΩ Range, with 10 μΩ Resolution is used for resistance measurement. Automatic controlled electric furnace is used and temperature of the furnace is measure by Cromel-Alumel thermocouple.

3. Results and Discussion

3.1 Investigation of DC Electrical Resistivity of Pelletized Compositions:

The DC electrical resistance 'R', of the pelletized

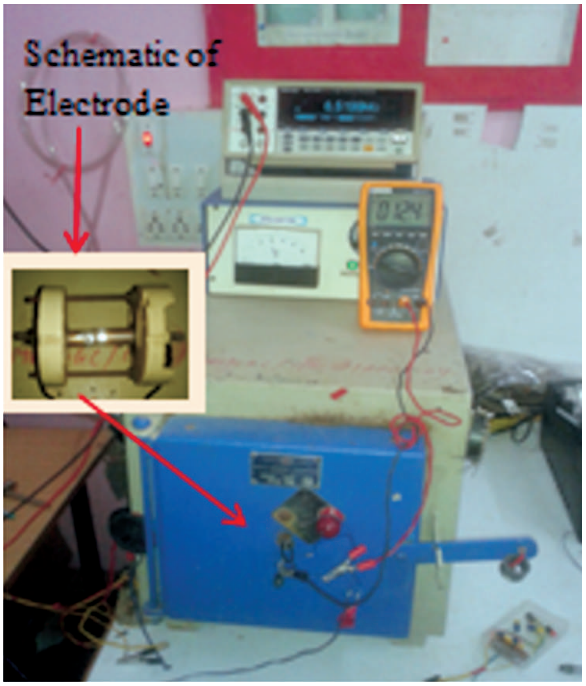
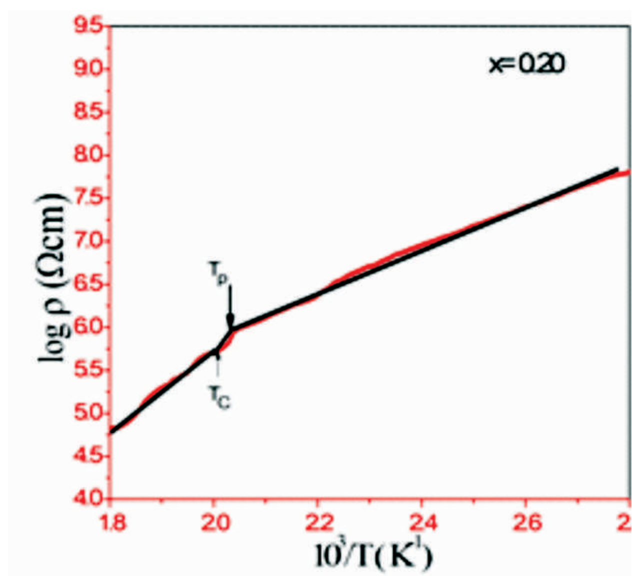


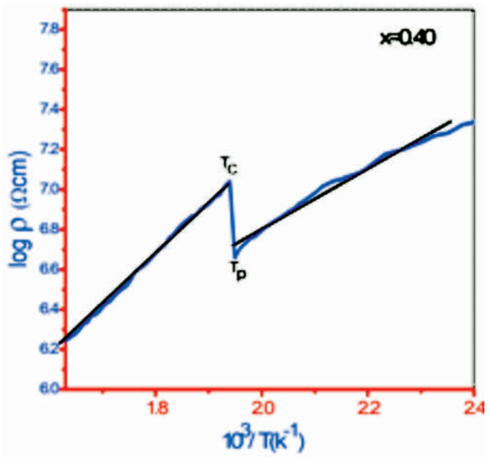
Figure 3. Experimental Set up to Measure Temperature Dependent Electrical Resistance.

compositions under investigation, is measured in range from 300K to 675K. To explore the details regarding conduction mechanism the values of resistivity 'r', in Wcm, are obtained from resistance data and values of logr are plotted against inverse temperature (1000/T) and presented in Figures 4 (a-d) for the compositions polycrystalline, $Mg_xZn_{1-x}Fe_2O_4$, spinel nanoferrites. On inspection of these figures, it is found that, the graphs of logr against 1/T are almost linear obeying Wilson relation. The figures reveal semiconducting nature by exhibiting decrease of resistivity due to increase in the temperature. As depicted in the Figure 4 the compositions of $Mg_xZn_{1-x}Fe_2O_4$ ferrites exhibit decrease in the resistivity with increase in the temperature. The graphs of logr against inverse temperature (1000/T) are almost linear with two significant breaks at distinct temperatures. This decrease in the resistivity with increase in the temperature can be attributed to the conduction mechanism, wherein conductivity due to thermally activated mobility of the charge carriers is ensured. It is known that, the zinc ions prefer to reside on a site, whereas magnesium ions preferentially distribute among A and B site. Moreover, valency of Mg ion remains stable. Therefore, the conduction is due to hopping of electrons between Fe^{3+} and Fe^{2+} ions on octahedral site (Gopalan et al., 2009). On inspection of Figure 4 (a-d), it is found that, the linear relationship of logr against 1/T graph shows two significant breaks Tp and Tc for the compositions for x = 0.20, 0.40 and 0.60. Moreover, the composition for x = 0.80 depicts one break at a temperature Tc. Such two breaks are also reported by (Bachhav et al., 2011; Varalaxmi & Sivakumar, 2010). These two temperatures, Tp and Tc, are called magnetic phase transition temperature and Curie temperature, respectively. The magnetic interaction is sensitive to the thermal energy and hence at a typical temperature, the disordering of interaction begins. Due to this disorder an amount of energy required for activation of the hopping is increased and hence the graph depicts the change in the slope. Moreover, at Curie temperature, the magnetic interaction vanishes. Therefore, the compositions become paramagnetic at which more amount of disorder is realized. This results into increase in the slope of the graph of log r against inverse of temperature (T). This reveals the fact that, the electrical conductivity is strongly influenced by magnetic interaction. Therefore, the region of the graph before Curie temperature is called ferri region and that of after Curie temperature is called Para region. Thus, the graphs of logr against 1000/T, Figure 4 (a-d) clearly depict the ferri and para magnetic nature of the compositions.

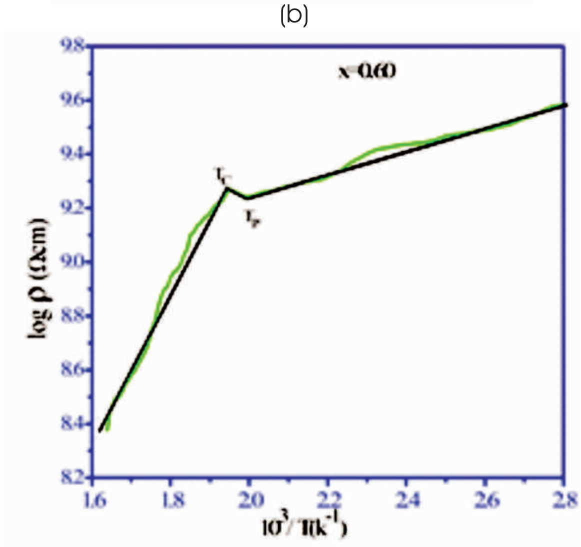
The Curie temperature values are obtained from



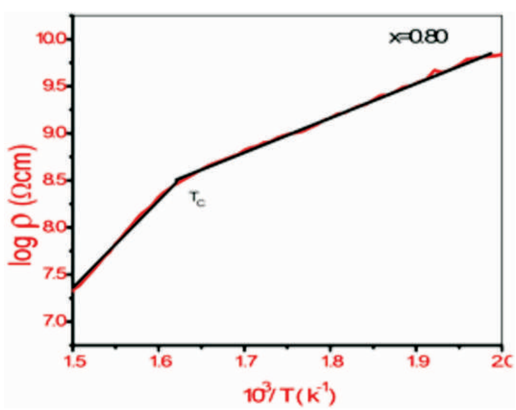
(a)



(b)



(c)



(d)

Figure 4. (a) Graph of Log ρ Against (1000/T) for $Mg_xZn_{1-x}Fe_2O_4$ (x = 0.20)
(b) Graph of Log ρ Against (1000/T) for $Mg_xZn_{1-x}Fe_2O_4$ (x = 0.40)
(c) Graph of Log ρ Against (1000/T) for $Mg_xZn_{1-x}Fe_2O_4$ (x= 0.60)
(d) Graph of Log ρ Against (1000/T) for $Mg_xZn_{1-x}Fe_2O_4$ (x = 0.80)

temperature dependent electrical resistivity data and presented in Table 1. On inspection of this table, it is found

X	Activation Energy DE (eV)		Curie Temperature
	Ferri Region	Para Region	(Tc)K
0.20	0.084	0.095	499
0.40	0.024	0.102	515
0.60	0.010	0.135	602
0.80	0.135	0.377	626

Table 1. The Curie Temperature and Activation Energy Values for the Composition $Mg_xZn_{1-x}Fe_2O_4$

that, the Curie temperature values reveal compositional dependence. Pure zinc ferrite is paramagnetic in nature (Totagi et al., 2015). Moreover, occupancy of magnesium ion on B site displaces proportional amount of iron ion from B site to A site, which causes to increase in the magnetic interactions (Choudary et al., 2014). Therefore, increase in concentration of magnesium ion (x), the concentration of Zinc ion decreases. Therefore, magnetic interaction becomes more favorable. Thus, increase in the Curie temperature, due to increase in the magnesium ion, can be attributed to the increase in the magnetic interactions (Ladgaonkar et al., 2000). Activation energies for both ferri region as well as para region are estimated from the slope of log r against inverse temperature graphs and presented in the Table 1. On inspection of the Table 1, it is found that, the activation energies observed for present investigation found close match with that of earlier reports (Li et al., 2007). From, this Table, it is also found that, the activation energy for para region is more than for ferri region. This supports the statement that electrical properties are strongly influenced by magnetic ordering.

Conclusion

The MgZn polycrystalline ferrite materials were successfully synthesized by chemical routh and confirm the nature of material using X-ray diffraction and FTIR. The diffracto grams show the formation of single phase compositions. Using Debye-Scherer relation, the particles size of compositions is estimated and it is in the range from 40 nm to 48 nm. Temperature dependent electrical properties of the composition of $Mg_xZn_{1-x}Fe_2O_4$ nano ferrite were investigated for suitability of these materials as the sensing element for designing of sensor. The D. C electrical resistivity of the pelletized compositions shows, semiconducting behavior, which is attributed to the electron hopping mechanism. This electrical conductivity exhibit the influence of magnetic ordering at and about Curie temperature. The Curie temperature values depict the compositional dependence. Keeping pace with the objectives of present research, the compositions of the ferrite under investigation, it is attempted to design the sensors on different substrates, Such as epoxy resin, glass and ceramic as sensing elements, employing thick film technology. The resistance of sensing element shows negative temperature coefficient within the range of investigation.

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ABOUT THE AUTHORS

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