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Transport Properties of Polycrystalline Mixed Copper-Zinc Ferrites

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Polycrystalline mixed Cu-Zn spinel ferrites with general formula $Cu_{1-x}Zn_xFe_2O_4$ (x = 0.0, 0.1, 0.3, 0.5 and 0.7) have been prepared by solid-state reaction method. The effect of Zn^{2+} ions on transport properties such as DC and AC resistivity, dielectric constant and dielectric loss tangent has been presented in this paper. The resistivity increases with Zn content and decreases with frequency which have been explained by Verway's hopping mechanism. Decrease of DC electrical resistivity with increasing temperature has been observed and activation energy has been found to increase with increasing Zn content. The dielectric constant is found to decrease with increasing Zn content as well as increasing of frequency has been explained on the basis of space charge polarization. In this communication, an attempt has been made to explain the conduction mechanism of Cu-Zn ferrites on the basis of electronic hopping frequency between Fe^{2+} and Fe^{3+} ions.

Keywords: *Ferrites, Solid-state reaction, DC resistivity, Activation energy, Dielectric constant.*

1. Introduction

Polycrystalline ferrites are a class of materials from ferromagnetic group which have great importance for both the fundamental and applied research points of view. They have many application ranges from simple function devices to sophisticated devices in the electro-electronic industry. The technical importance of ferrites is due to their high electrical resistivity, low dielectric constant, high magnetization, high permeability and low cost. These properties make the ferrites suitable for microwave devices, transformers and electric generator storage devices[1,2]. They are good dielectric materials having low conductivity which is one of the major consideration in many technological applications from microwave to radio wave frequencies[3]. The electrical transport properties gives valuable information about the selection of these materials for specific applications and they are widely used in the interpretation of the conduction mechanism in semiconductor. The electrical and dielectric properties of spinel ferrites are governed by the cation distribution among the tetrahedral (A-site) and octahedral (B-site) as well as the method of preparation, sintering temperature and sintering time, chemical composition and types of substitution[4-6]. Among all the ferrites, Cu-ferrites considered as good dielectric materials, having very high dielectric constants which are useful in designing good microwave devices as insulators, circulators, etc. By introducing non-magnetic Zn^{2+} ions in Cu-ferrite, the significant influence on several of its transport properties such as electrical and dielectric phenomena as a function of composition, frequency and temperature has been presented in this paper.

2. Materials and Methods

Samples having chemical formula $Cu_{1-x}Zn_xFe_2O_4$ (x= 0.0, 0.1, 0.3, 0.5 and 0.7) were prepared by the solid state reaction method. Analytical reagents of CuO, ZnO, and Fe_2O_3 were mixed in stoichiometric proportion using agate mortar and pestle. Then the mixture was ball milled for 4 hours with acetone and the slurry was dried and was pressed into disc shape pellets. The disc shaped pellets were pre-sintered at 850ºC for 4 hours to form ferrite. The pre-sintered material was again crushed into powder and wet milled for another 4 hours in distilled water to reduce it to small crystallites of uniform size. The mixture was dried and mixed with polyvinyl alcohol as a binder for granulation. The resulting powders were pressed uniaxially under a pressure of (20 kN/cm^2) in a stainless steel dies to make pellets. The pressed pellets were then finally sintered at 1050ºC for 2 hours. Single phase cubic spinel structure of all samples were found by X-ray Diffraction using Philips X'pert PRO X-rat diffractometer which is shown in Figure 1 (x=0.5). The samples were painted with conducting silver for providing good electrical contact. The DC resistivity was measured using Keithley electrometer and its variation with temperature was carried out using two-probe method over temperature range of 30-250ºC.

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The AC resistivity and dielectric constant measurement as a function of frequency was carried by WAYNE KERR 6500B Impedance Analyzer at Materials Science Division of Atomic Energy Centre, Dhaka.

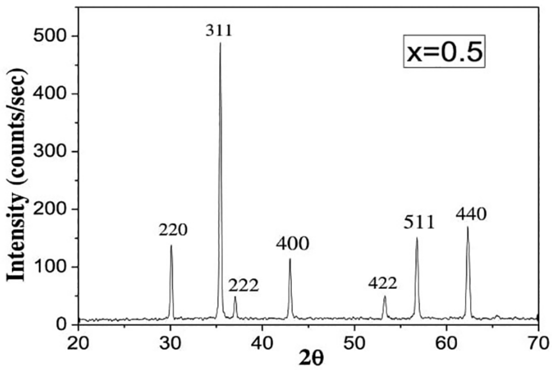


Figure 1. XRD pattern of sample x=0.5.

3. Results and Discussion

3.1 Effect of composition on resistivity

Figure 2 (a) shows the variation of DC resistivity as a function of Zn content in Cu-Zn ferrites. From Figure, it is noticed that DC resistivity increases from 2×10^3 to 7×10^3 Ω-cm with the increase of Zn content which can be explained by Verway's hopping mechanism[7]. According to Verway's, the electric conduction in ferrites is mainly due to hopping of electrons between ions of the same element present in more than one valance state, distributed randomly over the crystallographically equivalent lattice sites. The distance between B-B sites is smaller than B-A sites so the electron hopping between B-A sites has a very small probability than that for B-B sites. Without Zn content (x= 0.0), Fe concentration is maximum at B-site which is responsible for electrical conduction in ferrites[8]. On increasing Zn content in A-site, a decrease of Cu ion concentration observes at B-site. This will lead to the migration of some Fe^{3+} ion from A to B site to accommodate the increased number of Zn ions at the A-sites. As a result, electron hopping between Fe^{2+} and Fe^{3+} is greater at B-site. As Fe^{2+} ion lowers the conduction and subsequently an increase in resistivity is observed. The DC resistivity is also influenced by microstructural factors such as grain size, porosity and grain boundary. Kim and Kwan[9] reported a relation between resistivity and grain size which confirms that resistivity is inversely proportional to grain size. The decrease of grain size with Zn content in Cu-Zn ferrite was clearly evident in our earlier micrographs measurement[10]. So resistivity of Cu-Zn ferrite is expected to increase with increase of Zn content. Similar increase of resistivity has been observed by Mangalaraja et al.[11] in Ni-Zn ferrite and by Gul et al.[12] in Co-Zn ferrite.

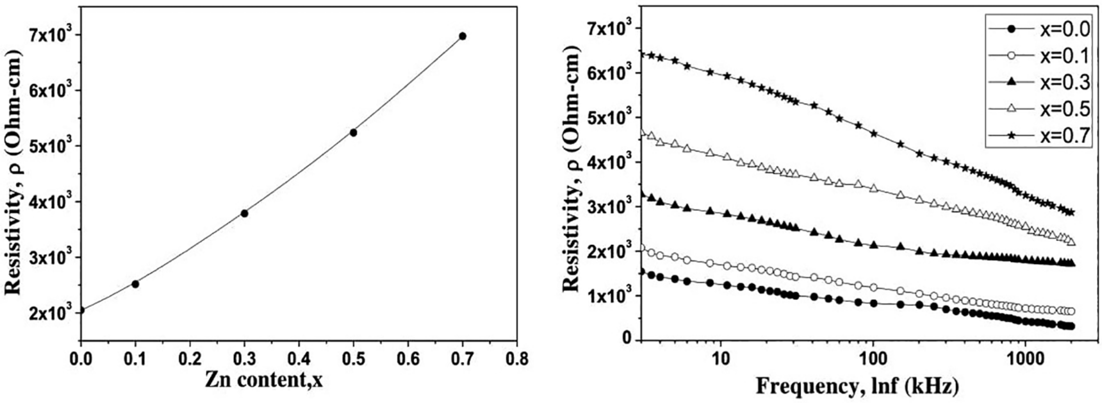
3.2 Effect of frequency on resistivity

The variation of AC resistivity with frequency is shown in Figure 2 (b). All the samples show a decrease of resistivity with increase of frequency which is the normal ferromagnetic behavior of ferrites. This can be explained on the basis of hopping of charge carriers between the Fe^{2+} and Fe^{3+} ions on octahedral site. The increase in frequency enhances the hopping frequency of charge carriers which results an increase in the conduction process thereby decreasing the resistivity. At higher frequencies, AC resistivity decrease and remains constant at lower frequencies because of the fact that hopping frequency can no longer follow the frequency of the applied external field leading to lower the values of AC resistivity. Such type of behavior has been reported by Shaikh et al.[13] in Li-Mg-Zn ferrite and by Watawe[14] in Li-Cd ferrite.

3.3 Effect of temperature on resistivity

Temperature dependence resistivity is measured in the temperature range 30-250ºC has been illustrated in Figure 3. This graph shows that by increasing temperature, resistivity decreases which confirms the semi-conductor behavior of ferrites. The decrease of resistivity with increasing temperature occurs according to Arrhenius relation[15]: $\rho = \rho_0 \exp(E_a/kT)$, where E_a activation energy, k Boltzman constant, ρ resistivity at temperature T and ρ_0 resistivity at 0 K. Figure 4 shows the plot between logρ and $10^3/T$ for samples x=0.0, 0.3 and 0.5. In few ferrites samples, a change in slope is found in the curve, which points to two parallel conductivity mechanisms with different activation energies. This change in slope generally occurs at a temperature range approaching the Curie temperature value of samples[16]. In most ferrites, a straight line is found in a wide temperature range, with a slope corresponding to activation energy. In this work, straight line are drawn using least square fit in which break-up of straight line at Curie temperature (T_C) was not found as T_C of the samples are greater than the present range of measured temperature[17].

The activation energy of each sample in the measured temperature range can be determined from the slope of linear plots (Figure 4) of resistivity. The value of activation energy was found in the range 0.21-0.32 eV and presented in Figure 5. Similar range of activation energy was obtained for Mn-Zn ferrite[18]. Activation energy behaves in the same way of as DC resistivity. Since the resistivity has been found to increase with Zn content, a rise in activation energy with the Zn composition is expected. According to the theory of magnetic semiconductors, a change in activation energy is due to the splitting of the conduction band and the valence bands below T_c. The higher value of activation energy at higher concentration of Zn indicate the strong blocking of the conduction mechanism between Fe^{3+} and Fe^{2+} ions.



(a) with Zn contant (b) with frequency

Figure 2. Variation of resistivity with (a) Zn content and (b) frequency.

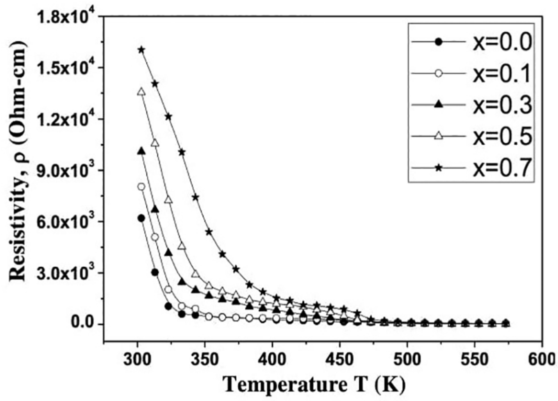


Figure 3. Temperature dependence resistivity of Cu-Zn ferrites.

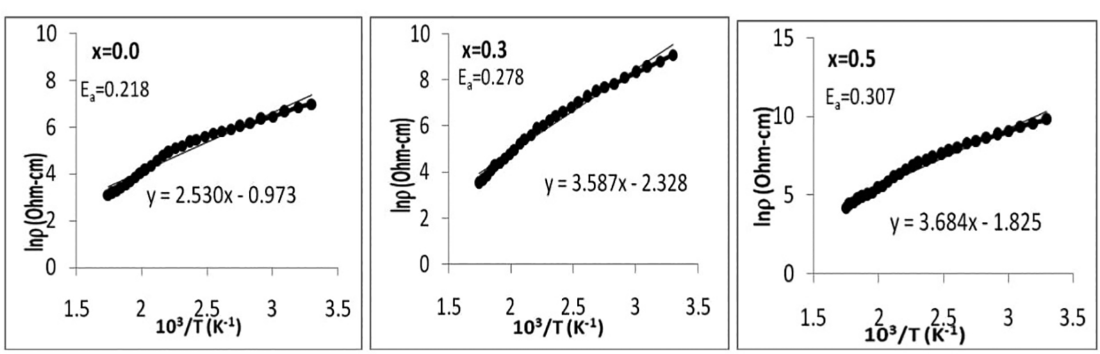


Figure 4. Arrhenius plot between log(and 10^3/T for samples x=0.0, 0.3 and 0.5

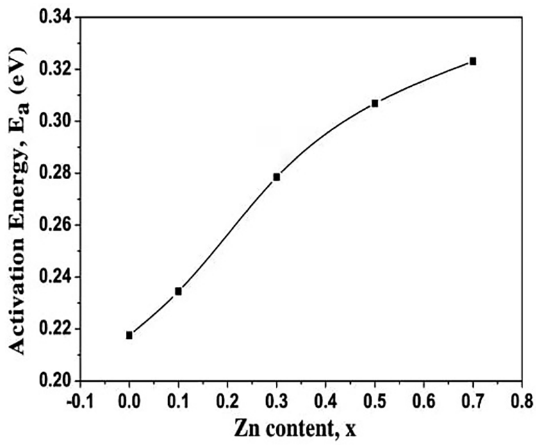


Figure 5. Activation energy as a function Zn content.

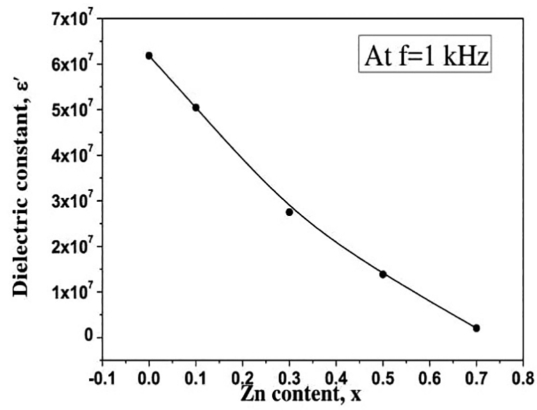


Figure 6. Variation of dielectric constant with Zn content.

3.4 Effect of composition on dielectric constant

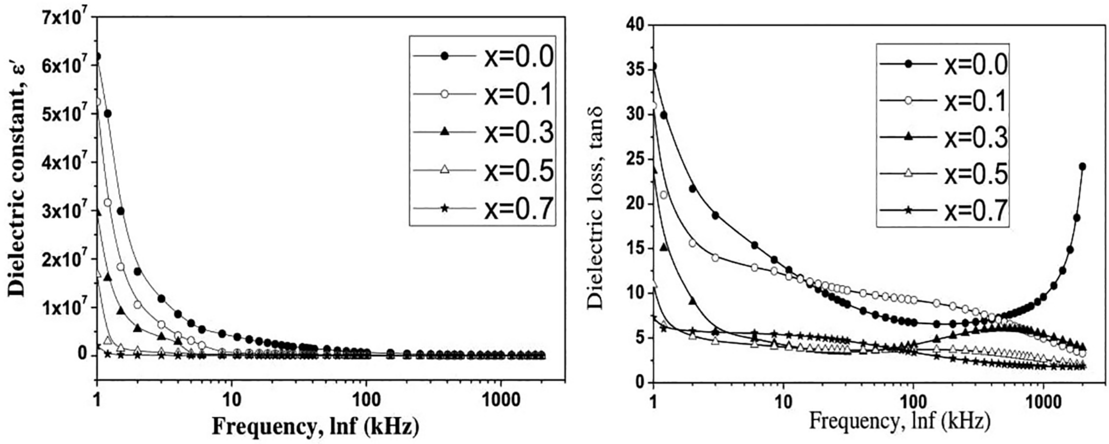
The dielectric measurements reveal an insight into the behavior of electrical charge carriers. The variation of dielectric constant (ε′) with Zn content at frequency of 1 KHz is shown in Figure 6 in which dielectric constant decreases with increasing Zn content. A sample with high DC resistivity acquires low value of dielectric constant and vice-versa[19]. The observed variation in dielectric constant may be understood on the basis of space charge polarization which is due to an inhomogeneous dielectric structure governed by (1) the number of space charge carrier and (2) resistivity of the sample[20]. The increase of resistivity obstructs the flow of space charge carriers and therefore impedes the build-up of space charge polarization. Since the resistivity is observed to increase with Zn content in the present Cu-Zn ferrite, the dielectric constant is thus expected to decrease as a result of space charge polarization. Reslescu[21], while studying the composition, temperature and frequency dependence of copper containing mixed ferrites of Cu-Mn and Cu-Zn ferrites, assumed that the mechanism of dielectric polarization is similar to that of conduction mechanism by Robinkin[22] in order to explain the composition dependence of dielectric constant. They assumed that the electron exchange interaction $Fe^{2+} \leftrightarrow Fe^{3+}$ results in local displacement of electrons in the direction of the field, which determines the polarization of the ferrites. According to this model, compositional dependence of the dielectric constant in Cu-Zn ferrite may be attributed to the hopping of charge carrier from Fe^{2+} to Fe^{3+} at octahedral site.

3.5 Effect of frequency on dielectric constant

The effect of frequency on dielectric constant is illustrated in Figure 7 (a). The dielectric constant is found to decrease at lower frequencies and remains constant at higher frequencies, showing the usual dielectric dispersion. This type of dielectric behavior was also observed by several investigators in case of Co-Zn[23], Ni-Zn[24] and Mn-Zn[25] ferrites. The dispersion of dielectric constant with frequency is due to Maxwell-Wagner[26] type interfacial polarization in agreement with Koop's[27] phenomenological theory. According to this theory, the displacement of electrons in the direction of applied electric field occurs due to electronic exchange $Fe^{2+} \leftrightarrow Fe^{3+} + e^{-1}$. These displacements determine the polarization in the ferrites. The decrease of polarization of dielectric constant with the increase of frequency is due to the fact that beyond certain frequency in the electric field, the electronic exchange between Fe^{2+} and Fe^{3+} ion cannot follow the alternating field. An assembly of space charge carriers in a dielectric requires finite time to line up their axes parallel to an alternating electric field, if the frequency of the field reversal increases, a point will reach when the space charge carriers cannot keep up with the field and the alternation of their direction lags behind the field. As the frequency of the field reversal further increases, at some stage the space charge carriers will have started to move before the field reverses and make no contribution to the polarization of the dielectric. Therefore, dielectric constant of a material may decrease substantially as the frequency is increased. As very low values of dielectric constants are observed, so these samples are appropriate to use them at higher frequencies.

3.6 Effect of frequency on dielectric loss

Dielectric loss (tanδ) is an important part of total core loss in ferrites. The value of loss tangent (tanδ) depends on stoichiometry, Fe^{2+} content and structural homogeneity which in turn depend on the composition and sintering temperature of the samples[28]. The dielectric loss tangent as a function of frequency for all compositions is depicted in Figure 7 (b). The behavior of loss tangent shows a decreasing at lower frequency and almost constant at higher frequency which is similar to those of dielectric constant. The dielectric loss is due to the increase in hopping electrons which leads to an increase in electric polarization. The slight increase of dielectric loss occurs for sample x=0.0 at 2MHz. This increase occurs when the jump frequency of electrons between



(a) Dielctric constant (b) Dielectric loss

Figure 7. Variation (a) dielectric constant and (b) dielectric loss as a function of frequency.

Fe^{2+} and Fe^{3+} is equal to frequency of the applied field[29]. Other samples are not showing this increasing behavior of dielectric loss as those samples are outside the frequency range studied here. The present samples with relatively lower losses might be useful at frequencies higher than those of the individual ferrites.

3.7 Relation between ε' and ρ

From Figure 2 and 6, we found a relation between resistivity (ρ) and dielectric constant (ε'). From combination of these two Figures, it is observed an inverse trend of variation of the ρ and ε' with composition is due to their inverse interdependence. As the dielectric constant is roughly inversely proportional to the square root of resistivity such variation is expected[30]. The changes in the dielectric constant and electrical conductivity is due to the exchanges of electrons between Fe^{2+} and Fe^{3+} ions which is also responsible for this inverse variation. Such type of similar relationship was found by Koop for Ni-Zn ferrite, Ravinder[31] for Li-Zn ferrite and Shaikh[13] for Li-Zn ferrite. Thus the high electrical resistivity along with low dielectric constant is expected to fulfill the requirement of microwave applications.

4. Conclusion

On the basis of the results, it is revealed that the substitution of Zn ion in $Cu_{1-x}Zn_xFe_2O_4$ ferrites produce a great appreciable changes in electrical and dielectric properties. The decrease of DC resistivity increase with increasing temperature ensures the semiconductor like behavior of the samples. DC resistivity and activation energy have been observed an increasing trend with Zn content. The value of dielectric constant and dielectric loss are higher at lower frequencies and their values become independence at higher frequencies. This is a good agreement with the conclusion that the higher activation energy is associated with lower dielectric constant and vice-versa which make these ferrites to be used in higher frequency applications. The decrease in dielectric constant and dielectric loss has been explained on the basis of space charge polarization resulting from electron displacement which is a major contribution of these ferrites.

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