Journal of Materials Science and Chemical Engineering, 2020, 8, 14-23
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

The Influence of Cu on the Dielectric Properties of $NiZnFe_2O_4$ Synthesized by Solid State Reaction Method

Sozie Y. Ali[1], Omer I. Eid[2,3*], Mohamed A. Siddig[1,4]

[1]Department of Physics, AL Neelain University, Khartoum, Sudan
[2]Department of Physics, Faculty of Science, University of Khartoum, Khartoum, Sudan
[3]Faculty of Science, Northern Border University, Arar, Saudi Arabia
[4]Department of Physics, Al Baha University, Al Baha, Saudi Arabia
Email: suzyphysics@gmail.com, *omereid@gmail.com, omer.hussien@nbu.edu.sa

How to cite this paper: Ali, S.Y., Eid, O.I. and Siddig, M.A. (2020) The Influence of Cu on the Dielectric Properties of $NiZnFe_2O_4$ Synthesized by Solid State Reaction Method. *Journal of Materials Science and Chemical Engineering*, **8**, 14-23.
https://doi.org/10.4236/msce.2020.89002

Received: June 24, 2020
Accepted: September 8, 2020
Published: September 11, 2020

Abstract

The phase pure Copper Ferrite, Zinc Ferrite, and Nickel Ferrite were prepared from oxides of Ni, Cu, Zn, and Fe using traditional ceramic method. X-ray diffraction data were collected and the formation of the spinal phase structure was found. The lattice parameter was found to be 8.441 Å for $ZnFe_2O_4$, 8.35 Å for $NiFe_2O_4$, and 8.349 Å for $CuFe_2O_4$. The $Ni_{0.4}Zn_{0.6}Fe_2O_4$ ferrite was sintered at three different temperatures: namely 1100˚C, 1200˚C, and 1300˚C and similar temperature control was applied to $Cu_{0.2}Ni_{0.2}Zn_{0.4}Fe_2O_4$ ferrite group. The energy band gap was calculated for $Ni_{0.4}Zn_{0.6}Fe_2O_4$ and $Cu_{0.2}Ni_{0.2}Zn_{0.4}Fe_2O_4$ and was found to be 3.657 eV and 4.889 eV, respectively. The dielectric properties were investigated over a wide range using impedance spectroscopy and were found to decrease with the increase of frequency. Similar behavior was observed with the sintering temperature. In the same manner, the electric conductivity was found to decrease with the increase of frequency and sintering temperature as well. On the other hand, the electric resistivity was found to increase with both frequency and the sintering temperature.

Keywords

Conductivity, Dielectric, Impedance, Polarization, Resistivity, XRD, UV-Vis

1. Introduction

The oxides of the cube crystals whose formula is AB_2O_4 make a big percentage of the inorganic materials which have many applications in industry since they

showed physical and chemical properties that depend on their internal ions, their charges, and their distribution. Magnetite had been known since early times and it has a formula similar to AB_2O_4, but it was used only in electronics due to its high electric conductivity that reaches $10^6\ \Omega^{-1}\cdot m^{-1}$, with magnetic saturation that reaches 4.75×10^5 m/h, Curie temperature of 585˚C and very weak eddy currents, which makes it widely applicable in engineering fields [1] [2].

Magnetite Fe_3O_4 is considered as the only spinel ferrite to be found in nature which has formula as $FeOFe_2O_3$. It is also possible to substitute FeO for any one of the transition elements, as will be seen later in this study. Ferrite is formed by the reaction of ferric (iron oxide or rust) with any of a number of the metals including magnesium, aluminum, barium, manganese, copper, nickel, cobalt, zinc and even iron itself [3]. Ferrite is also known as alpha iron with a body-center cubic B.C.C. crystal structure [4] [5]. Ferrites are hard, brittle, stable, and have a dark-grey or black color, with other properties, such as small size, light weight and cubic crystal structure. The most common properties of ferrites include high magnetic permeability, high electrical resistance, high permeability to magnetic fields and high resistance to electrical fields [2] [6].

These materials have potential applications in numerous different industries, such as the use of ferrite as an alternative to plates, which has become very common in constituting transformers, magnetic coils, as well as telecommunications filters, amplifiers, flash memories, digital cameras, and many other electrical and power applications. Due to the importance of ferrite and its excellent electrical and magnetic properties, it has recently become the focus of scientists' attention [7] [8].

The spinel type with cubic crystal structure is used in transformers or electromagnetic cores which contain nickel, zinc and/or manganese compounds [9]. They have low coercive force, which means that the materials' magnetization can easily reverse direction without dissipating much energy (hysteresis losses), while the materials' high resistivity prevents source of energy loss which is the eddy current in the core. Because of their comparatively low energy loss at high frequencies, they are used in the cores of transformers and inductors in applications, such as switched-mode power supplies and loop stick antennas used in AM radio [9].

The most common soft ferrites are: Manganese-Zinc ferrite (Mn/Zn, with the formula $Mn_aZn_{1-a}Fe_2O_4$) [10] which have a higher permeability and saturation induction than NiZn, and Nickel-Zinc ferrite (Ni/Zn, with the formula $Ni_aZn_{1-a}Fe_2O_4$). The latter exhibits higher resistivity than Mn/Zn and it is more suitable for frequencies above 1 MHz. The Ferrite used for applications below 5 MHz is MnZn, but NiZn is usually chosen for frequencies above that. The exception is with common mode inductors where the threshold of choice is at 70 MHz [2]. Motivated by the technological applications in variety fields, Zinc-Nickel ferrite was considered in the current study. Structural and electrical properties of Zinc-Nickel ferrite were studied. Furthermore, the effect of adding copper to Zinc-Nickel ferrite was investigated and the effect of different temperatures on

the structure and properties was explored.

2. Experimental

Materials and Method

The basic materials including ZnO, NiO, CuO, and Fe_2O_3 with a high percentage purity of 99% were purchased from ALFA AeSar [11]. The sample was prepared from these materials using the conventional solid state reaction which is widely used for solid materials due to its simplicity and direct reaction of a mixture of those materials.

An electrical blender was used to get rid of the oxalate root. The prepared samples were given the temperate treatment starting from room temperature to 800˚C, and kept in the furnace for 2 hours. The temperature was slowly reduced to room temperature at the rate of 10˚C/min., ground in a mortar, and then compressed as tablets. It was then taken out to be ground until it became a homogenous powder.

X-ray diffraction technique is used to explore the structure of the resulting materials; namely; $ZnFe_2O_4$, $NiFe_2O_4$, and $CuFe_2O_4$. This is an X-ray Diffractometer system with Cu-kα radiation (λ = 0.15418 nm) with X–ray source at 40 kV and 30 mA. The spectra were obtained in the scanning angle (2θ) from 20˚ to 50˚ for the preparation of $NiZnFe_2O_4$, with values of thickness as 13 mm and about 5 - 6 mm of diameter. The samples $ZnFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$ are compressed into tablets with the same compressor 4 ton/cm^2, and then heated up to 1100˚C, 1200˚C and 1300˚C for 2 hours at the rate of 10˚C/min. and left at each heating round to cool down at the same rate. The Band gap is found with the UV-visible spectrometer and finally taken to the L. C. R. meter KEithley 590 CV ANALYZER for dielectric measurement.

3. Results and Discussion

3.1. Structural Characterizations

Powder XRD is widely used to identify the crystal structure of a substance that gives the fingerprint image of the crystal structure of this substance [12]. This technique is mainly used for the identification of phase formation and crystal structure of the different materials, which is done by matching the obtained peak pattern with that of the standard pattern of the same substance. In addition, information about the structural parameters such as lattice constant, cell volume, crystallite size and X-ray density of the desired phase were determined. The X-ray diffraction data for the sample are recorded using Cu Kα radiation (0.15404 nm). The XRD pattern of the powder is studied with the diffraction angle range between 20˚ - 50˚. MDI jade 0.5 program [13] is used to investigate the structure and the calculation of the lattice parameters, the structure is found to be cubic phase.

Figure 1 shows the XRD data of samples for $NiFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$. The Miller indices of $NiFe_2O_4$ are (220), (311), (222), and (400) when 2θ equals

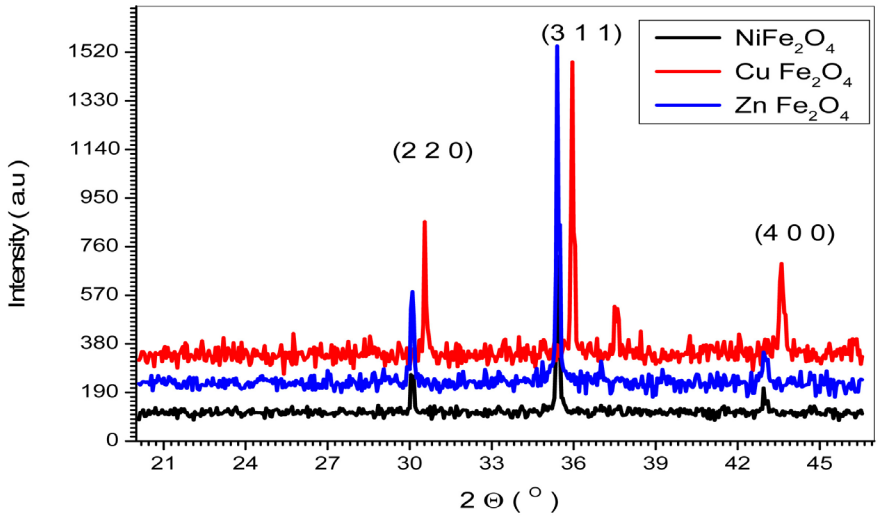

Figure 1. XRD patterns of ($NiFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$) samples synthesized by solid state reaction.

28.563, 35.958, 37.546, and 44.009 respectively. For $CuFe_2O_4$, they are (220), (311), (222), and (400) when 2θ equals 30.091, 35.415, 36.85, and 42.965 respectively. For $ZnFe_2O_4$ they are (220), (311), (222), and (400) when 2θ equals 29.915, 35.234, 36.855, and 42.816 respectively.

Table 1 shows that all the samples prepared through the solid state reaction method are single phase of a face center cubic (FCC) spinel.

3.2. UV-VIS Spectroscopy

The band gap may be estimated by using the Tauc formula equation [14].

$$(\alpha h\nu)^{2/y} = A^{*}\left(h\nu - E_g\right) \tag{1}$$

where α is the absorption coefficient, A^{*} is a constant, y is an integer that defines the Sort of transition, for $y = 1$ (direct transition) and $y = 4$ (indirect transition). The energy magnitude is determined by extrapolation for the linear range of the experimental curve $(\alpha h\nu)^2$ to x axis.

Figure 2 and Figure 3 show the energy band gap for Zinc Nickel and Copper Zinc Nickel Ferrite. It can be observed from the figures that the energy band gap is increased when Copper Ferrite is added to Zinc Nickel Ferrite. This leads to increase in the dielectric properties of the material and in resistivity as well. The opposite behavior was observed in the case of conductivity. The energy band gap was found to be 4.889 eV and 3.657 eV for Copper Zinc Nickel and Zinc Nickel Ferrite, respectively.

3.3. Dielectric

The Dielectric constant is calculated by using formula

$$\varepsilon_r = Cd/\varepsilon_0 A \tag{2}$$

where d is the thickness of the pellet in meters, A is the cross-sectional area of

Table 1. The crystal structure of $NiFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$.

No	samples	$a = b = c$ (Å)	density (nm)	$\Upsilon = \beta = \alpha$
1	$ZnFe_2O_4$	8.441	2.54	90˚
2	$CuFe_2O_4$	8.349	2.532	90˚
3	$NiFe_2O_4$	8.352	2.492	90˚

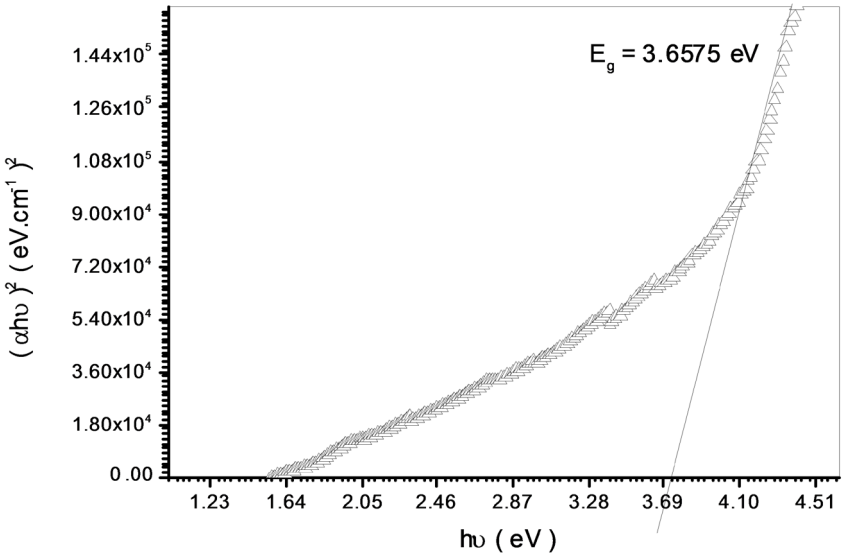

Figure 2. Energy band gap of Zinc Nickel Ferrite.

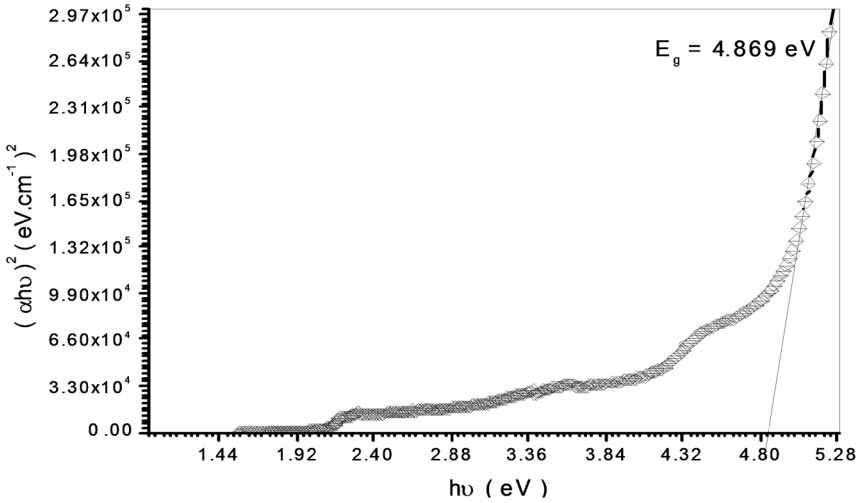

Figure 3. Energy band gap of Copper Zinc Nickel Ferrite.

the flat surface of the pellet, C is the capacitance of the material, ε_0 is the permittivity of the free space (8.858×10^{-12} F/m).

Figure 4 shows the change in the dielectric constant with the frequency at three temperatures: 1100˚C, 1200˚C, and 1300˚C. It can be observed that the dielectric constant suddenly drops at the low frequencies. Afterward, the drop becomes gradual with the increase of frequency. It is also remarkable that the values

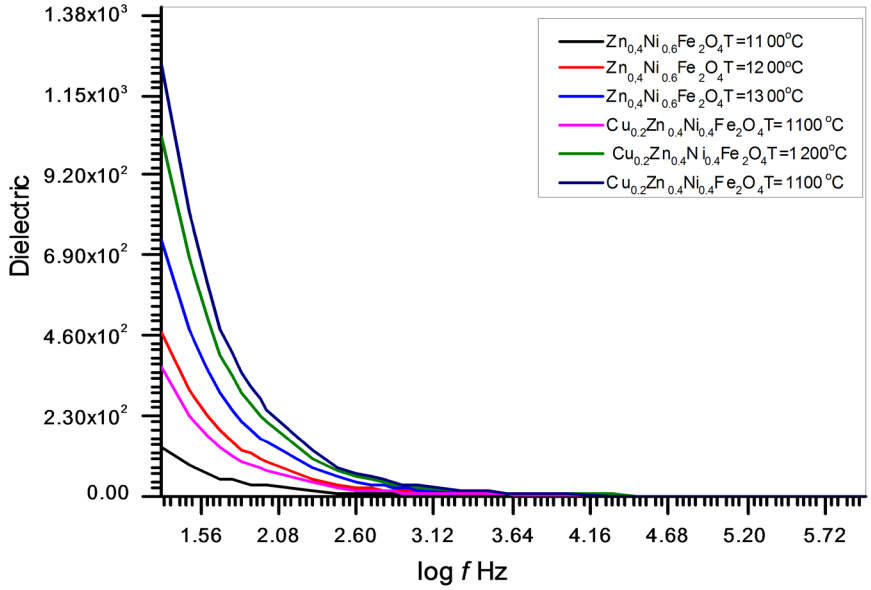

Figure 4. Dielectric constant of Copper Nickel Zinc Ferrite with the frequency at three temperatures: 1100˚C, 1200˚C, and 1300˚C.

of the dielectric constant rise with the increase of the sintering temperature. It was observed that the dielectric constant increases as a result of adding Copper Ferrite to the Nickel Zinc Ferrite and it reaches the highest value in the case of the sample with the Copper Zinc Ferrites at 1300˚C [15]. In order to interpret this behavior of the dielectric constant, it is necessary to relate that to the mechanism of polarization, which refers to its four types. This means that the range of the frequencies used in this research is that of all types; namely electronic polarization, ionic polarization, orientation polarization and interfacial polarization (the space-charge polarization) [16].

At frequencies less than 10^4 Hz, the total value of polarization will be considered for all types, *i.e.* the value of the dielectric constant is very high. This makes the high values of the dielectric constant move to the interfacial polarization because of its large mass in comparison with the other types as it is a large group of charges accumulated at the points of crystal defects or the spaces, which leads to create a localized accumulation of the charges. This generates opposing charges in the opposite direction, which leads to the emergence of dipolar materials [17]. This is not limited to atoms or molecules, but it extends to other areas. This type of polarization requires a low frequency of not more than 10^4 Hz. It stops soon, so the relaxation time almost approaches the zero [17]. Moreover, it was observed that there is an increase in the values of the dielectric constant with the increase of the sintering temperature. This is attributed to the increase of the density and the existence of heterogeneous areas in the material, which promotes the growth of the space charge. This in turn leads to an increase in the value of the interfacial polarization which in turn increases the dielectric constant.

The dielectric constant is found to increase when Copper is added to Nickel

Zinc Ferrite and this is attributed to the optical properties of CuO which is the basic component of Copper Ferrite, as it has a large reflection factor. The dielectric constant is increased according to the direct relationship between the dielectric constant and the reflection factor as follows [18]:

$$\varepsilon = \left(n + iK\right)^2 \tag{3}$$

where ε is the dielectric constant, n is the reflection factor, K is the extinction coefficient.

3.4. Conductivity

Conductivity has a direct relationship with frequency, which is clear from the following equation [9]:

$$\varepsilon = \sigma / i\varepsilon_0 \omega \tag{4}$$

where ε is the dielectric constant, ε_0 is permissibility, and ω is the angular frequency of the applied current.

Equation (4) shows that the values of conductivity are determined by the imaginary dielectric constant and the frequency, as other values are constants, and the values of the dielectric constant are small when compared to the frequency. Therefore, frequency plays an important role in determining the increase in conductivity which is also a measure of the lost power, *i.e.* it is a measure of the temperature that might be generated as a result of the spinning of the dipolar in its positions or the vibration of charges with the change in range. This is the reason why frequency is considered as the basis on which studying the conductivity depends [19].

Figure 5 shows conductivity as a function of frequency for Copper Nickel Zinc Ferrite and Nickel Zinc Ferrite. From **Figure 5**, it can be observed that conductivity increases with temperature and this may be attributed to the increase in density with temperature. On the other hand, it was found that conductivity decreases when Copper Ferrite is added to Nickel Zinc Ferrite, which could be attributed to the increase in the energy band gap of Copper Zinc Nickel Ferrite.

3.5. Resistivity

The following equation shows the relationship between conductivity and resistivity [9].

$$\sigma = 1/\rho \tag{5}$$

where σ is conductivity and ρ is resistivity

Figure 6 shows the electrical resistivity as a function of frequency. It can be observed that electrical resistivity is very high at low frequencies and it decreases gradually with the increasing frequency for three patterns at three different sintering temperatures: 1100˚C, 1200˚C, and 1300˚C. This may occur because the increase in frequency possibly leads to particle mobility, and the increase in the temperature leads to the increase in the crystal growth. Moreover, the resistivity

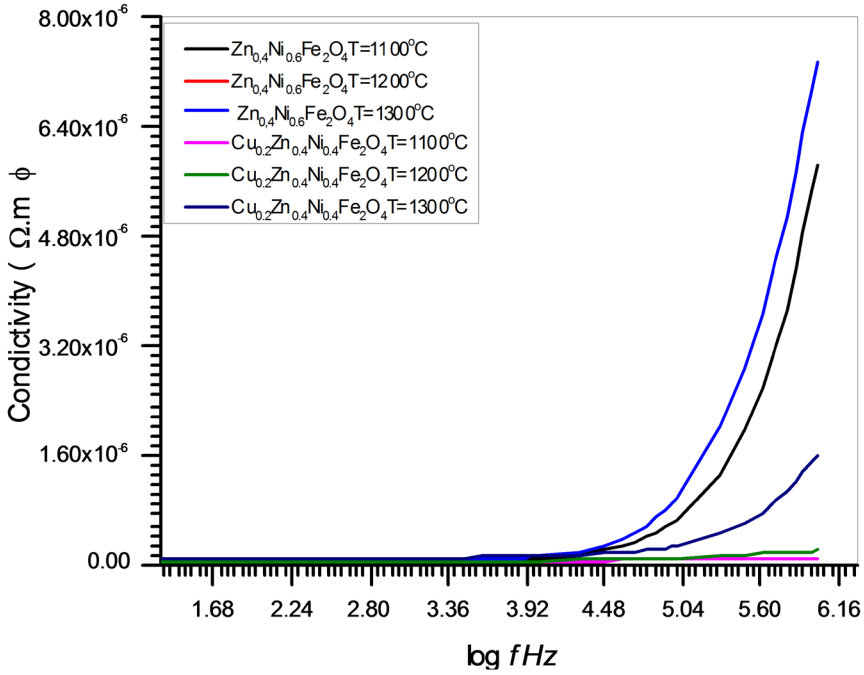

Figure 5. Conductivity of Copper Nickel Zinc Ferrite and Nickel Zinc Ferrite with the frequency at three temperatures: 1100˚C, 1200˚C, and 1300˚C.

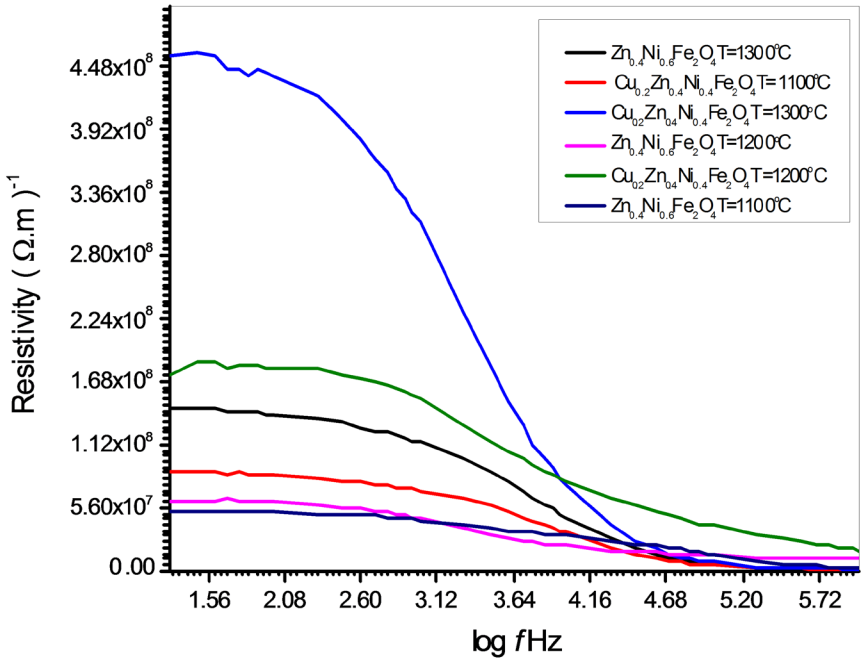

Figure 6. Electrical resistivity of Nickel Zinc Ferrite and Copper Nickel Zinc Ferrite with the frequency at three temperatures: 1100˚C, 1200˚C, and 1300˚C

of Ferrite also depends on the purity of the used primary materials and the preparation details such as the sintering temperature [20]. Since electrical resistivity is the reciprocal of electrical conductivity, this may explain the increase of resistivity with Copper Zinc Ferrite which could be attributed to the increase in

the energy band gap.

4. Conclusion

In this study, the dielectric properties of two Ferrite groups were investigated: namely, the Zinc Ferrite, and Nickel Ferrite. The effect of Copper ferrite and the three sintering temperatures 1100˚C, 1200˚C, and 1300˚C was explored. It was found that the dielectric constant increases with the frequency and temperature to a limited value. This increase was attributed to polarization. In the same way, the electric conductivity was found to increase with the frequency and temperature, while the opposite behavior was observed in resistivity. The results revealed that the groups of Copper Ferrite, Zinc Ferrite, and Nickel Ferrite have better dielectric properties than those groups without Copper Ferrite and that was explained by the good electric properties of Copper.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Goev, G., Masheva, V., Ilkov, L., Nihtianova, D. and Mikhov, M. (2003) Magnetic Properties of Ni-Cu-Zn Ferrites. BPU-5 August, 25-29.

[2] Sindhu, S., Anantharaman, M.R., Thampi, B.P., Malini, K.A. and Kurian, P. (2002) Evaluation of ac Conductivity of Rubber Ferrite Composites from Dielectric Measurements. *Bulletin of Materials Science*, **25**, 599-607. https://doi.org/10.1007/BF02707892

[3] Khine, P.P., Myint, M.S. and Kyaw, W. (2018) Study on Characterization of $MgO{\cdot}5CuO{\cdot}5Fe_2O_4$ Ferrite Compound.

[4] Rama, K., Vijaya, K. and Dachepalli, R. (2012) Structural and Electrical Conductivity Studies in Nickel-Zinc Ferrite. *Advances in Materials Physics and Chemistry*, **2**, 185-191. https://doi.org/10.4236/ampc.2012.23028

[5] Rezlescu, E., Sachelarie, L., Popa, P.D. and Rezlescu, N. (2000) Effect of Substitution of Divalent Ions on the Electrical and Magnetic Properties of Ni-Zn-Me Ferrites. *IEEE Transactions on Magnetics*, **36**, 3962-3967. https://doi.org/10.1109/20.914348

[6] Tilley, R. (2004) Understanding Solids: The Science of Materials. John Wiley & Sons, Ltd., Hoboken, 374-375. https://doi.org/10.1002/0470020849

[7] Nam, J.H., Jung, H.H., Shin, J.Y. and Oh, J.H. (1995) The Effect of Cu Substitution on the Electrical and Magnetic Properties of NiZn Ferrites. *IEEE Transactions on Magnetics*, **31**, 3985-3987. https://doi.org/10.1109/20.489838

[8] Spaldin, N.A. (2010) Magnetic Materials: Fundamentals and Applications. Cambridge University Press, Cambridge. https://doi.org/10.1017/CBO9780511781599

[9] Ahmed, M.A.A. (2017) A Review on the Properties and Uses of Ferrite Magnet. PhD Dissertation, Sudan University of Science and Technology, Khartoum.

[10] Zahoor, N. (2017) Influence of Yb Substitution of the Properties of W-Type Hexagonal Nano-Sized Ferrites Synthesized by Micro-Emulsion Technique. PhD Dissertation.

[11] https://www.alfa.com/en/catalog/014680

[12] Rajeswaran, M., Blanton, T.N., Giesen, D.J., Whitcomb, D.R., Zumbulyadis, N., Antalek, B.J. and Misture, S.T. (2006) Azine Bridged Silver Coordination Polymers: Powder X-Ray Diffraction Route to Crystal Structure Determination of Silver Benzotriazole. *Journal of Solid State Chemistry*, **179**, 1053-1059. https://doi.org/10.1016/j.jssc.2006.01.022

[13] https://materialsdata.com

[14] Von Blanckenhagen, B., Tonova, D. and Ullmann, J. (2002) Application of the Tauc-Lorentz Formulation to the Interband Absorption of Optical Coating Materials. *Applied Optics*, **41**, 3137-3141. https://doi.org/10.1364/AO.41.003137

[15] Jahanbin, T., Hashim, M. and Mantori, K.A. (2010) Comparative Studies on the Structure and Electromagnetic Properties of Ni-Zn Ferrites Prepared via Co-Precipitation and Conventional Ceramic Processing Routes. *Journal of Magnetism and Magnetic Materials*, **322**, 2684-2689. https://doi.org/10.1016/j.jmmm.2010.04.008

[16] Allen, J.A. (1968) An Outline of Polymer Chemistry (Vol. 25). Oliver & Boyd, Edinburgh.

[17] Omar, M.A. (1993) Elementary Solid State Physics: Principles and Applications. Addison-Wesley, New York.

[18] Meyers, H.P. and Myers, H.P. (1997) Introductory Solid State Physics. CRC Press, Boca Raton. https://doi.org/10.1201/9780429320286

[19] Cullity, B.D. (1978) Elements of X-Ray Diffraction. Addison and Wesley Publishing Company Inc., Reading, 32-106.

[20] Hossain, A.A., Mahmud, S.T., Seki, M., Kawai, T. and Tabata, H. (2007) Structural, Electrical Transport, and Magnetic Properties of $Ni_{1-x}Zn_xFe_2O_4$. *Journal of Magnetism and Magnetic Materials*, **312**, 210-219. https://doi.org/10.1016/j.jmmm.2006.09.030