Measurement and Analysis of Temperature Dependent resistance of $Li_xCu_{0.5}Zn_{0.5-2x}Fe_{2+x}O_4$

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Declaration

It is hereby declared that

1. The thesis submitted is my/our own original work while completing a degree at Brac University.

2. The thesis does not contain material previously published or written by a third party, except where this is appropriately cited through full and accurate referencing.

3. The thesis does not contain material which has been accepted, or submitted, for any other degree or diploma at a university or other institution.

4. I/We have acknowledged all main sources of help.

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Approval

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ABSTRACT

The DC electrical property of $Li_xCu_{0.5}Zn_{0.5-2x}Fe_{2+x}O_4$ (x=0.00, x=0.05, 0.10) samples prepared by solid state reaction method was investigated. The samples were calcined at $800℃$ and sintered at $1000℃$ and $1050℃$ respectively in air for 5 hours. The samples were placed in an electric oven and the corresponding resistance and temperature measurement were taken using 2 probe method by keithley 2450 and 6517b respectively. The resistance was found to decrease as the value of x increased and also increasing temperature showed semiconductor behaviour of the samples.

Acknowledgement

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Chapter 1

Introduction

Ferrite is a type of ceramic material with a chemical composition consisting of iron oxide (Fe_2O_3) and other metallic oxides, such as zinc oxide or nickel oxide. Ferrites are widely used due to their magnetic properties and their ability to conduct direct current (DC).

Ferrites' DC conductivity is a crucial characteristic since it establishes the material's capacity to carry electrical charges steadily in the absence of alternating current. The type of metallic oxide utilised in the material and the size of the ferrite particles are two parameters that have an impact on the DC conductivity of ferrites.

Ferrites are employed as the magnetic cores of microwave filters, inductors, and transformers in electronic applications. They also serve as microwave absorbers and magnetic data storage devices. Ferrites are perfect for these applications due to their high DC conductivity, which enables the quick movement of electrical charges.

As a result of their unique mix of magnetic and electrical characteristics, ferrites are adaptable materials that are useful in a variety of electronic applications.

One of the main factors contributing to their widespread use in the electronics sector is their excellent DC conductivity.

Ferrites; has many significant characteristics such as high permeability and saturation magnetization in the radio frequency region, high electrical resistivity, etc make ferrite a superior material.

Lithium ferrites like other ferrites, have high magnetic properties and high DC conductivity. The high DC conductivity of lithium ferrite makes it ideal for use in electronic applications where efficient transport of electrical charges is required.

One of the unique characteristics of lithium ferrite is its high dielectric constant, which is a measure of the material's ability to store electrical charges. This makes lithium ferrite a promising material for use in capacitors, where it can store large amounts of electrical energy. In addition to its high DC conductivity and dielectric constant, lithium ferrite also has a high thermal stability, making it suitable for use in high-temperature applications. This combination of physical and electrical properties makes lithium ferrite a versatile material that can be used in a variety of applications in the electronics industry.

Lithium and mixed Lithium ferrite have a significant role, especially as replacement of garnets because of their low cost [1]. Lithium ferrites are used as microwave devices like circulators, isolators and phase shifters [2].

Lithium ferrite can be prepared by sol gel technique, ball milling, micellar reactions, solid state reaction, sucrose method,coprecipitation method and combustion synthesis. Substitution with metals ions like cobalt (Co^{2+}), zinc (Zn^{2+}), etc. different experiments can be performed. [2]

In this experiment we performed Zinc substituted Li-Cu ferrite polycrystalline synthesis by solid state reaction method.

<h1 style="text-align:center">Objective of the research</h1>

High permeability and stability in high frequency range makes particular ferrite material to be used in many electronic devices. Having high resistivity , low power and eddy current losses, Furthermore, ferrites are good filters as it reduces high frequency electrical disturbances making it a good candidate for low pass filters. Therefore, investigating the DC electrical property of the ferrite samples can provide insights into the potential applications of lithium ferrite as a material for electronic devices and can contribute to the development of new and improved ferrite materials with desired properties and further our knowledge about lithium doped ferrites.

Possible outcome of the research

Due to Li and Fe substitution the ferrite's resistance decreases and increasing temperature will also cause resistance to decrease due to the semiconducting behaviour of the material.

Spinel structure

Ferrite has a spinel structure[3] similar to that of MgO. Al_2O_3 which is also known as cubic spinel. It usually consists of cubic close packed oxides and two tetrahedral and four octahedral sites per unit formula. The formula being AO. B_2O_3 or AB_2O_4

Where A and B represent the divalent (A^{2+}) and trivalent (B^{3+}) cations respectively [4].

All B^{3+} ions occupy the octahedral sites and the A^{2+} ions occupy the tetrahedral sites. The B site is surrounded by 6 nearing oxygen neighbours who form an octahedral site and A site is surrounded by 4 oxygen atoms in a tetrahedral structure shown in Fig 1 below. The total structure consists of 2 tetrahedral and four octahedral sites in a repeating array of lattices. In total a single unit consists of eight sub cells with 8 A sites, 16 B sites and 32 oxygen ions. Metal ions enter site A when chemical bonding happens whereas site B is occupied by the trivalent ions. Whether a bigger or smaller ion will be accommodated is determined by the void in between the oxygen ions. Metal cations occupy the A-site and B-site crystallographic

positions in the spinel structure. In this instance(x=0), the B-site cations are iron (Fe) atoms, whereas the A-site cations are a mixture of copper (Cu) and zinc (Zn) in equal amounts.Inside the crystal lattice, the iron cations occupy the octahedral B-sites, while the copper and zinc cations share the tetrahedral A-sites. The remaining spaces are taken up by oxygen (O) ions, which cluster closely around the metal cations. When Lithium and iron is doped; the value of x is 0.05 or 0.1. Lithium replaces Zinc from the tetrahedral A site and more iron is added in the octahedral B-site.[10,11]. Fe ions occupy the larger octahedral B-sites [11]. Under certain conditions and depending on the composition of the ferrite material, a small proportion of Fe ions can occupy the tetrahedral sites (site A) in the spinel structure, although they typically prefer to occupy the octahedral sites (site B) due to their coordination number.[12]

The A sites are occupied with smaller cations, usually with tetrahedral coordination , whereas the B sites are occupied by the larger cations. Lithium being a small cation with a much lesser radius than that of Fe prefers the tetrahedral A site and is unable to occupy the larger octahedral B site
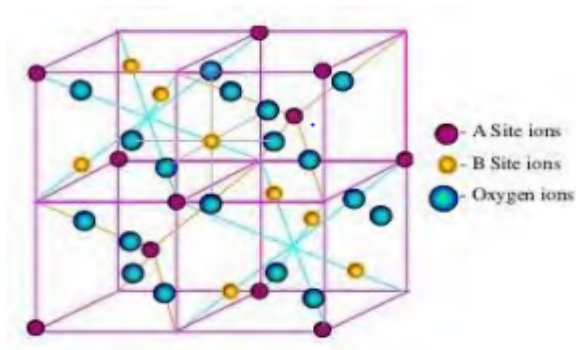

Fig 1:Crystal structure of spinel ferrite

Chapter 2

Sample preparation

Ferrites and their compositions are analysed using a variety of methods[3]. Among these, ferrite powder is usually produced using the traditional ceramic technique and solid state reaction method. Additional approaches are [13,14]:

1) Sol-gel synthesis

2) Co-precipitation

3) Organic precursors

4) Freeze dying

5) Spray dying

6) Combustion synthesis

7) Glass crystallisation

The solid state reaction method was used for the preparation of your samples. The method is discussed below.

Solid state reaction method:

To produce the final researched products, the solid state reaction process goes through a number of steps. It is required to heat solids to higher temperatures to encourage the reaction since solids normally do not perform chemical reactions at room temperature in a decent length of time. The structural properties of the reactants, the surface area of the solids, the reaction circumstances, and the reaction's thermodynamics are only a few of the variables that affect whether the reaction is successful [13]

To obtain the desired composition, raw materials consisting of oxides or carbonates are ground, crushed, and milled in the appropriate proportions. Once the powders have been finely ground, they are subjected to calcination in air at temperatures exceeding 500 degrees celsius for a duration of 5 hours. The specific temperature required for calcination may vary

depending on the specific needs of the process. Calcination serves to remove impurities from the powders. Following calcination, the powders are once again hand-milled to ensure that they are smooth and uniform. Using a die punch assembly or hydrostatic/isostatic pressure, the necessary pellets and toroid samples are prepared from the calcined powder, as needed. Sintering is then carried out in various atmospheres at temperatures ranging from 950 to 1150 degrees celsius for a typical period of 1 to 10 hours.[13,14]

The general solid state which leads to the formation of the ferrite may be represented as

$$MeO + Fe_2O_3 \xrightarrow{\text{Heat treatment}} MeFe_2O_4$$
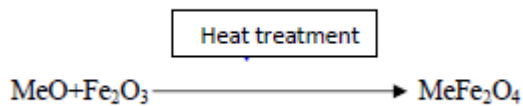
Where Me is the metal ion. The 4 basic steps for the preparation of ferrites are as follows:

1) Preparing the components to make a close combination with the metal ions in the proportions that the finished product will have.

2) Calcinating the combination to create ferrite.

3) Grinding and pressing the calcined powders to get the desired form.

4) Sintering to create a product that is considerably densified.

Details for Sintering, Pressing and Calination:

The process of calcination involves heating mixed powders to a specific temperature for a designated duration, followed by a gradual cooling process, in order to attain a uniform and pure composition. This method can be repeated multiple times to achieve a high level of uniformity. Once calcined, the powders are once again pulverised.

Prior to compaction, a binder is often applied at a concentration lower than 5wt%. Binders, which might be polymers or waxes, help the particles move during compacting and strengthen the link between them. Polyvinyl acid is the most often used binder for ferrites. Binders break down and are removed from the ferrite during sintering. Various pressures,

often many tons per square inch, are employed for compacting. (i.e. to desired toroid and pellet forms at up to 108 nm^{-2}).

By heating a compacted powder for a fixed amount of time at a temperature high enough to encourage diffusion but definitely below the melting point of the basic element, the sintering process creates a sample with a denser, more durable body.

The flow chart below shows the entire process:

Raw materials
⇓
Weighing by different mole
⇓
Hand milling
⇓
Calcination
⇓
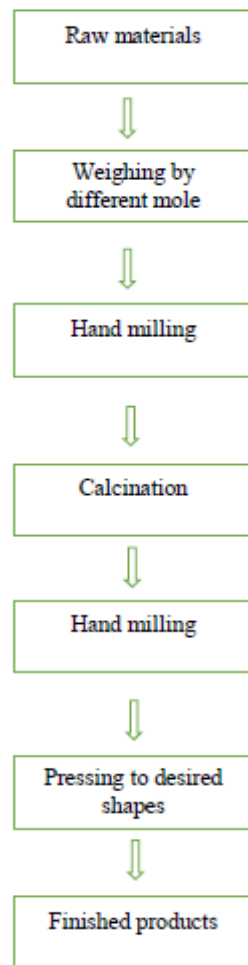Hand milling
⇓
Pressing to desired shapes
⇓
Finished products

Fig 2: The entire process for obtaining ferrite samples

Sintering is an important process with three main objectives. Firstly, it helps to bind the particles together, giving the final product the strength it requires. Secondly, it works to eliminate any pores and increase the density of the material. Finally, sintering aids in achieving homogeneity by completing any unfinished reactions from the calcination stage.

$Li_xCu_{0.5}Zn_{0.5-2x}Fe_{2+x}O_4$ (with x=0.00, 0.05, 0.10) To prepare this material, the solid state reaction method was employed with the required amount of raw material. The pure powder (99.9%) of Li_2CO_3, Cu_2O, ZnO, Fe_2O_3 are weighed out according to the required composition and hand milled for about 5 hours for chemical reaction to happen using a clean pistol and mortar. The process is further facilitated by calcination which is undertaken for 5 hours in air at a temperature of about 950℃. The calcined powder was then granulated using polyvinyl acid as a binder and pressed into desired pellet and toroid shapes. In the final stages it was sintered at temperatures of 1000℃ and 1050℃ in air for about 5 hours. The temperature ramps for sintering were 5℃ /min for heating and 10℃ /min for cooling.

Chapter 3

Results and discussion

The conductivity of electrical charges in ferrites is due to both electron and hole conduction. While the electrons in ferrite materials are not completely free, they can move through the material and participate in the flow of electrical charges[15]. This movement of electrons is influenced by the electronic structure of the material, including the density of states and the bandgap, which determines the material's conductivity[15].

Conduction in ferrites is primarily due to Verwey's hopping mechanism. Principally it is due to the hopping of electrons from one valence state to another of the same element for example Fe^{2+}/Fe^{3+}. The hopping probability depends upon the ion pairs present at the octahedral B sites [5] Therefore as x increases the chances of ion hopping in the octahedral site increases. Hence reducing resistivity.

Sintering temperature 1000℃:

Value of x	Resistance(ohm)
x=0.00	5.02E+07
x=0.05	4.24E+07
x-0.10	3.96E+07

Table 1**:** Room temperature resistance(304.97K) of the samples sintered at 1000℃
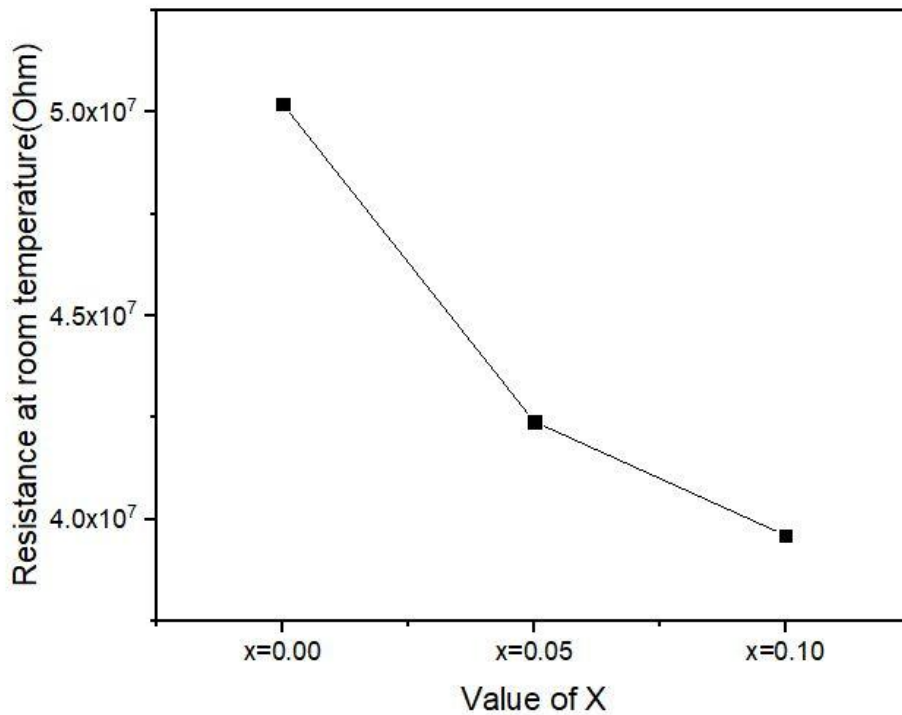
The values are represented below in the graph.

Fig 3: Resistance Vs value of X at room temperature for samples sintered at 1000℃

Increasing temperature showed an decrease in resistance. The increase in conductivity of ferrites can be linked to the increase of the drift mobility of charge carriers with increase in temperature.[6]

Drift mobility is a measure of the average velocity of a charge carrier (electron or hole) in a material in response to an applied electric field. It is defined as the ratio of the drift velocity of a charge carrier to the applied electric field. The drift velocity is the velocity of the charge carrier in the direction of the electric field, and it is proportional to the strength of the electric field.
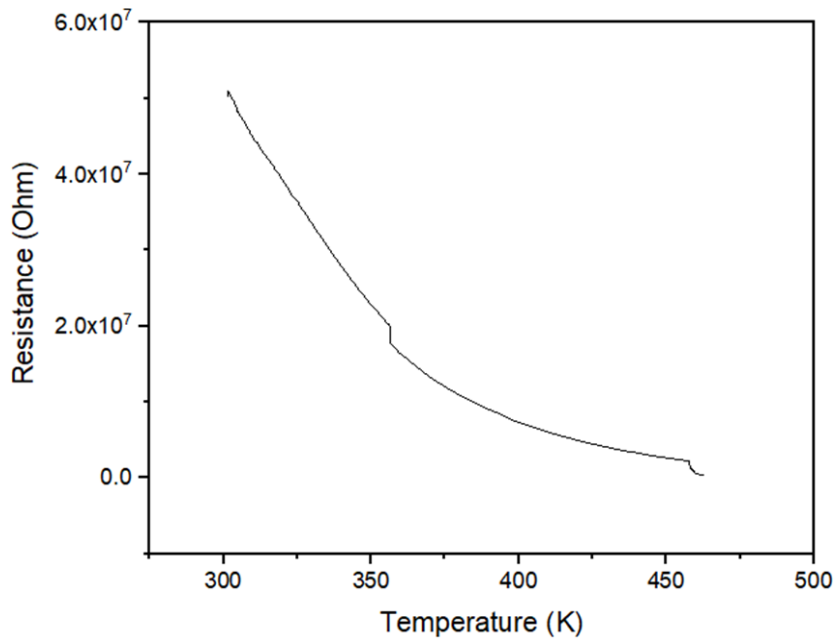
Graph for x=0.0

Fig 4: Resistance Vs temperature graph for sample x=0.00 sintered at 1000℃
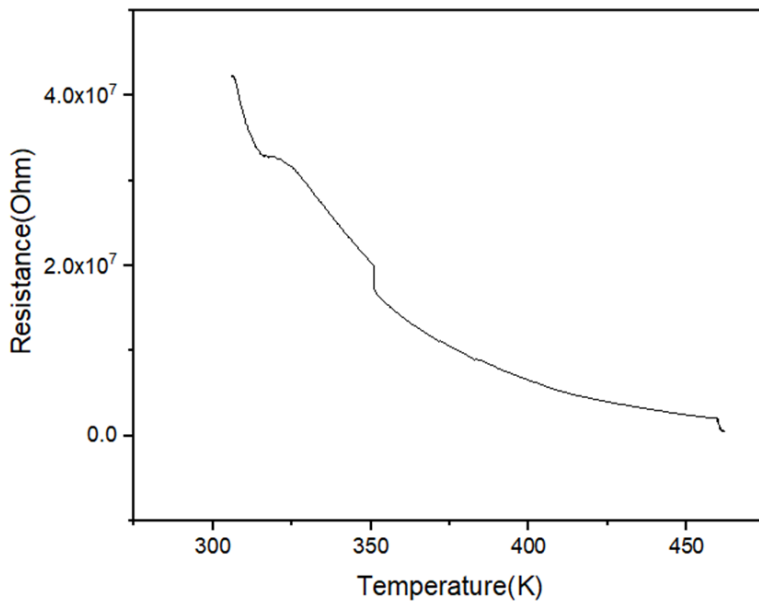
Graph for x=0.05

Fig 5: Resistance Vs temperature graph for sample x=0.05 sintered at 1000℃
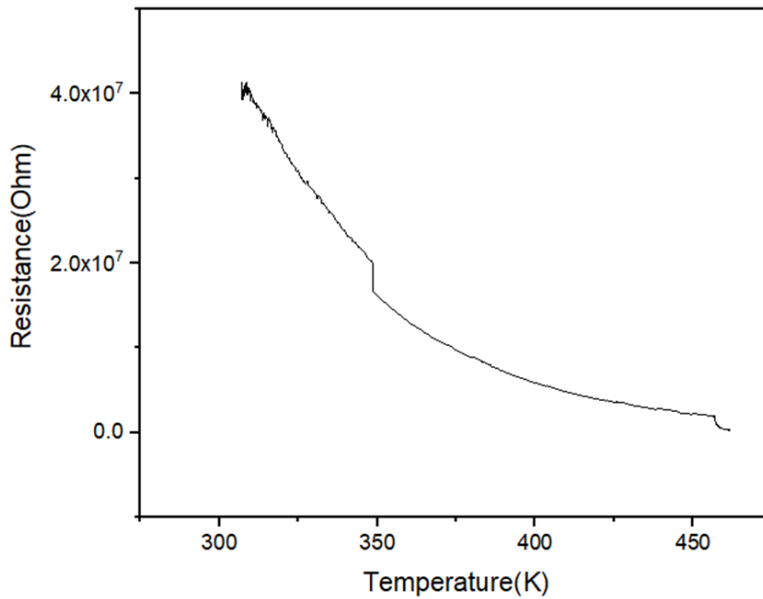
Graph for x=0.1

 Fig 6: Resistance Vs temperature graph for sample x=0.10 sintered at 1000℃

Sintering temperature 1050 ℃

The sample sintered at 1050℃ also shows a similar decrease in resistance when the value of

x increases at room temperatures and can be linked to similar reasoning just like before.

Value of x	Resistance(Ohm)
x=0.00	5.01E+07
x=0.05	2.96E+07
x-0.10	9.97E+06

Table 2: Room temperature resistance(301.97K) of the samples sintered at 1050℃
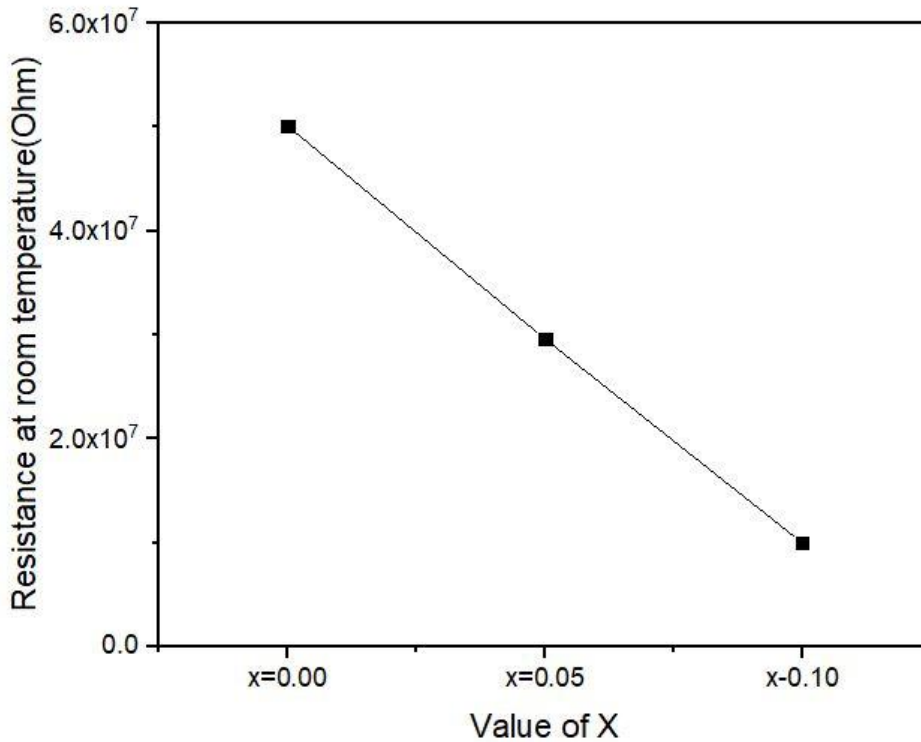
The values are represented below in a graph:

Fig 7:Resistance Vs value of X at room temperature for samples sintered at 1050℃

The increase in conductivity of ferrites can be linked to the increase of the drift mobility of charge carriers with temperature[6]. Increasing temperature increases the thermal energy of the charge carriers which allows much efficient movement of these charge carriers through the material. Decreasing resistance with increasing temperature confirms semiconductor behaviour, which works according to Arrhenius relation[8]:

$\rho = \rho_{\theta} \exp (E_a /kT)$; where k is the Bolztman constant. ρ resistivity at temperature T, E_a is the activation energy and ρ_{θ} resistivity at 0K. Moreover, most probably a change in slope can be associated with the change in conduction mechanism or phase transition from ferromagnetic to paramagnetic[9].

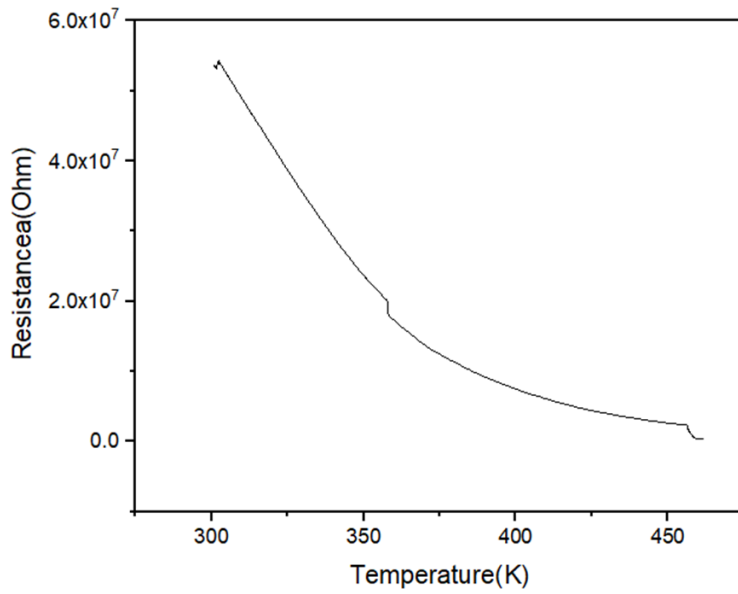Therefore, increasing temperature decreases resistance.

Graph for x=0.0

Fig 9:Resistance Vs temperature graph for sample x=0.00 sintered at 1050℃
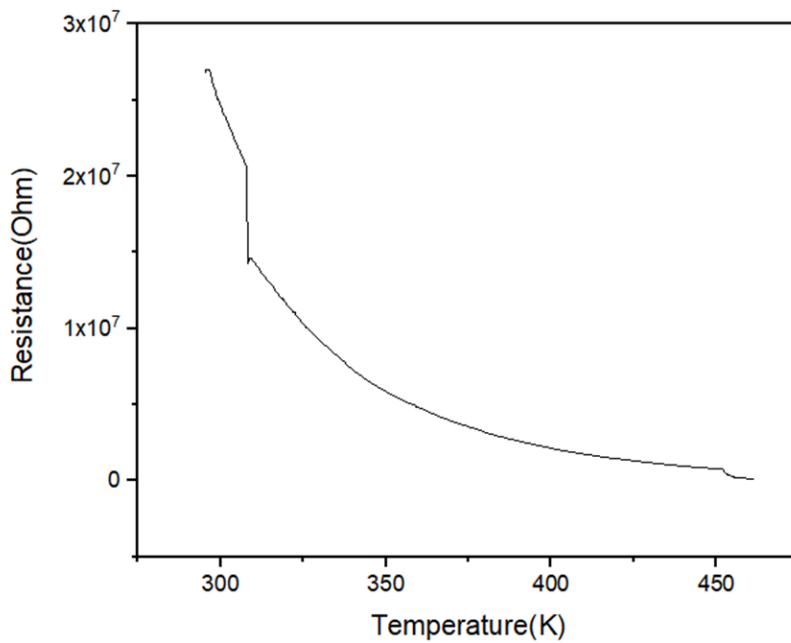
Graph for x=0.05

Fig: 10 Resistance Vs temperature graph for sample x=0.05 sintered at 1050℃

Graph for x=0.10
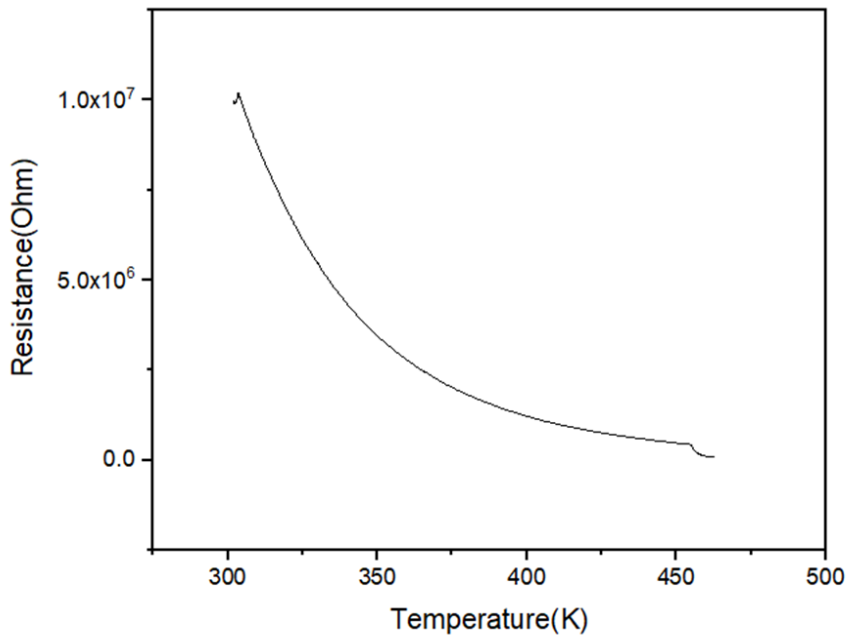

Fig 11: Resistance Vs temperature graph for sample x=0.10 sintered at 1050℃

A higher sintering temperature causes the crystal structure to change from disorder to ordered structure [7]. Ultimely, enabling the possibility for the hopping of electrons to be higher. Hence, the same value of x sintered at higher temperatures shows lower resistance. The following phenomena is provided below in the form of a graph.
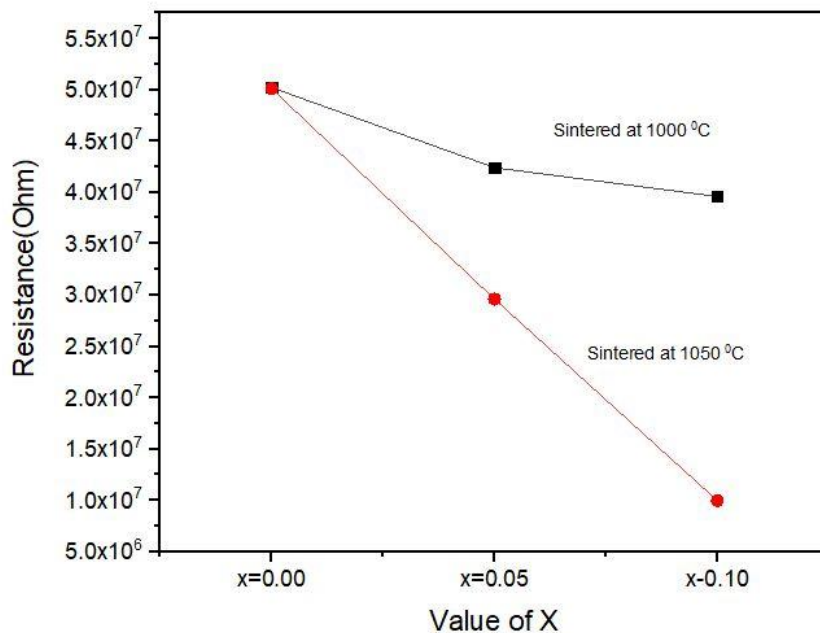

Fig 12: Room temperature resistance Vs value of X for both the sample sintered at 1000℃ and 1050℃.

Graph plotted from table 1 and table 2.

Even at higher temperatures the effect of sintering temperature is the same. Where a higher sintering temperature shows a decrease in resistance for the same value of x.

Value of x	Temperature(K)	Resistance (Ohm)
Sintered at 1000℃ x=0.00	402.2	7.34018E+06
x=0.05	402.2	6.3254E+06
x-0.10	402.2	5.60791E+06
Sintered at 1050℃ x=0.00	402.2	7.15021E+06
x=0.05	402.3	2.02989E+06
x-0.10	402.3	1.1612E+06

Table 3:Higher temperature resistance for different values of x sintered at 1000℃ and 1050℃
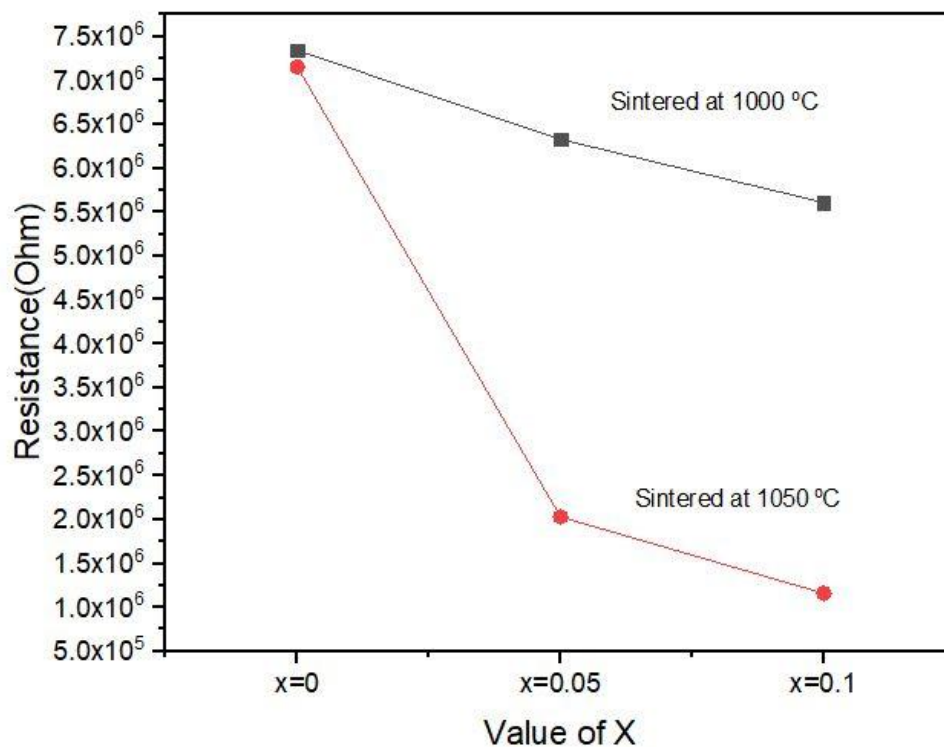
The data is displayed below in the form of a graph

Fig:13 Higher temperature resistance Vs value of x for both the sample sintered at 1000℃ and 1050℃

Conclusion

In conclusion, the study of the properties of lithium ferrite has revealed important knowledge about its electrical behaviour. According to the study, the material behaves like a semiconductor and resistance decreases as temperature increases due to increase in drift mobility of charge carriers at higher temperature . Furthermore, it has been noted that the resistivity decreases as x increases due to the higher probability of ion hopping in octahedral B sites, showing a considerable impact of doping concentration on the substance's electrical properties. The usage of lithium ferrite in semiconductor applications may prove to be a promising choice as a result of these findings, which have significant implications for the creation of innovative electronic devices. Overall, this study has improved our understanding of lithium ferrite's electrical characteristics and offered up new directions for future research in the area.

Reference

[1] Baba, P.D., Argentina, G., Courtney, W., Dionne, G. and Temme, D. (1972). Fabrication and properties of microwave lithium ferrites. IEEE Transactions on Magnetics, 8(1), 83-94.

[2] Adarakatti, S. N., Pattar, V. S., Korishettar, P. K., Grampurohit, B. V., Kharabe, R. G., Kulkarni, A. B., ... & Pujar, R. B. (2018). Synthesis, Structural and Electrical Studies of Li-NiCu Nano Ferrites. Acta Chemica Iasi, 26(1),

[3] Mustafa, Anjum. (2019). Influence of Li+ Substitution on Magnetic and Electrical Properties of $Li_xCu_{0.5}Zn_{0.5-2x}Fe_{2+x}O_4$. [Doctoral dissertation, BRAC University]. Retrieved from http://dspace.bracu.ac.bd/xmlui/handle/10361/13517

[4]AdiChemistry. (2017, October 20). Spinel and Inverse Spinel Structures. Retrieved from http://www.adichemistry.com/inorganic/cochem/spinels/spinel-structures.html

[5] Naeem, M. A., & Saleemi, M. A. (2017). Electrical Resistivity and Mössbauer Studies of Cr Substituted Co Nano Ferrites. Journal of Magnetism and Magnetic Materials, 425, 73-78. doi: 10.1016/j.jmmm.2016.10.072

[6] Hemeda, O. M., Said, M. Z., & Barakat, M. M. (2001). Spectral and transport phenomena in Ni ferrite-substituted Gd2O3. Journal of Magnetism and Magnetic Materials, 224(2), 132-142. doi: 10.1016/S0304-8853(00)00578-3

[7] Shirsath, S. E., Kadam, R. H., Gaikwad, A. S., Ghasemi, A., & Morisako, A. (2011). Effect of sintering temperature and the particle size on the structural and magnetic properties of nanocrystalline Li0.5Fe2.5O4. Journal of Magnetism and Magnetic Materials, 323(23), 3104-3108. doi: 10.1016/j.jmmm.2011.06.065

[8] Akhter, S., Paul, D. P., Hakim, M., Saha, D. K., Das, H. N., Parveen, A., & Anjuman, B. (2018). Transport Properties of Polycrystalline Mixed Copper-Zinc Ferrites. Materials Research, 21, e20170655. doi: 10.1590/1980-5373-mr-2017-0655

[9] Anupama, M. K. (2015). Synthesis and studies on Structural and electrical properties of Ni-Zn Ferrites. [Master's thesis, Mahatma Gandhi University]. http://mgutheses.in/wp-content/uploads/2015/07/24._ANUPAMA_M_K.pdf

[10] Buschow, K. H. J., Cahn, R. W., Flemings, M. C., & Kramer, E. J. (2003). Magnetic Oxides and Composites. Elsevier Science.

[11] Yadav, B. S., Chauhan, M. S., Chauhan, N. S., & Singh, M. (2012). Structural and magnetic properties of $Li_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles prepared by co-precipitation method. Journal of Alloys and Compounds, 539, 174-179. doi: 10.1016/j.jallcom.2012.05.042.

[12] Singh, K., Gope, J., & Singh, M. (2017). Recent developments in the structural, magnetic and electrical properties of Li-Cu-Zn-Fe ferrite nanoparticles. Journal of Materials Science:Materials in Electronics, 28(6), 4716-4731. doi:10.1007/s10854-016-6129-9

[13] Goldman, A. (1999). Handbook of Modern Ferromagnetic Materials. Kluwer Academic Publishers.

[14] Valenzuela, R. (1994). Magnetic Ceramics. Cambridge University Press, Cambridge.

[15]Kittel, C. (2005). Introduction to solid state physics (8th ed.). Wiley.