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Frequency and Temperature Dependence on Dielectric and Impedance Properties of Titanium Substituted Manganese-Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

Satheesh D. J. [1], **Jayakumari Isac** [2]

[1, 2]Centre for Condensed Matter, Department of Physics, CMS College, Kottayam, India

Abstract: ***A nano/micro crystalline ceramic, Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15 is synthesised by solid state reaction route using high quality raw materials, MnO, ZnO, TiO_2 and Fe_2O_3 which are mixed, milled in a ball mill, calcined at suitable temperature, pelletized and sintered. Various dielectric parameters which define the dielectric properties of the material such as dielectric constant, dielectric loss, conductivity and impedance of the material are measured at different temperatures (25–600 °C) for a frequency range of 100 Hz to 5 MHZ using HIOKI 3532-50 LCR Hi tester. Frequency and temperature dependence of the so mentioned parameters are evaluated.***

Keywords: Crystalline ceramic, Titanium Substituted Manganese -Zinc Ferrite System, Dielectric constant, Impedance, Dielectric loss, Conductivity

1. Introduction

The quest of human beings for developing better and more efficient materials is never ending. Dielectric ceramics are highly desirable in this technological era because of its flexibility with its comparatively low processing temperature, high dielectric constant, low dielectric loss and high dielectric strength. These materials offer a very high resistance to the passage of electric current under the action of the applied voltage and therefore sharply differ in their basic electrical properties from conductive materials. Layers of such substances are commonly inserted into capacitors to improve their performance. Research in the area of Ferroelectrics is driven by the market potential of next generation memories and transducers. Thin films of ferroelectrics and dielectrics are rapidly emerging in the field of MEMS applications. Ultrasonic micro-motors utilizing PZT thin films and pyroelectric sensors using micro-machined structures have been fabricated. MEMS are finding growing application in accelerometers for air bag deployment in cars, micro-motors and pumps, micro heart valves, which have reached the commercial level of exploitation in compact medical, automotive, and space applications. Extremely sensitive sensors and actuators based on thin film and bulk will revolutionize every walk of our life with Hi-Tech gadgets based on ferroelectrics.

Here the authors prepared a nano crystalline ceramic Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15 by solid state reaction route using high quality raw materials, MnO, ZnO, TiO_2 and Fe_2O_3 which are manually mixed, milled in a ball mill, attrition milled, calcined at suitable temperature, pelletized and sintered. Most important dielectric parameters which define the dielectric properties of the material are measured and their frequency and temperature dependence are evaluated. The impedance, dielectric permittivity, electrical conductivity and loss factor are very crucial quantities in the designing of a practical device. Ferrites are ferromagnetic semi conductors and the need for high resistivity ferrites led to the synthesis of various ferrites. Polycrystalline ferrites have very good dielectric properties [1]. The influence of various substituents like Ti, Zn etc considerably change in its electrical properties [2]. Ferrites having very high dielectric constants are useful in designing good microwave devices such as isolators, circulators etc. Manganese-Zinc Ferrite $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ in the spinel structure are a low cost material which is generally useful for microwave - devices and memory-core applications. Due to Ti substitution electrical and magnetic properties changes and hence have much technological merits [3,4,5]. One of the most important and sensitive methods of studying the polymer structure is the study and analysis of dielectric constant, impedance, conductivity and dielectric loss factor, as a function of temperature and frequencies [6]. The dielectric properties (dielectric constant, conductivity, dielectric loss and impedance) of a number of ceramics and polymers have been studied in the last two decades [7-12].

2. Theory of Dielectric Properties

2.1 Dielectric Constant

Dielectric constant at different temperatures and frequencies were calculated using the common equation used in parallel plate capacitor. Dielectric constant can be defined as the property of an electrical insulator which is equal to the ratio of the capacitance of a capacitor filled with the given electrical insulator to the capacitance of an identical capacitor in a vacuum without the dielectric material.

Dielectric constant (ε) is given by

$$\varepsilon = C / C_0 \text{ -------------------[1]}$$

$$C_0 = A\varepsilon_0/d \text{-------------------[2]}$$

where

C = capacitance using the material as the dielectric in the capacitor
A = Area of the prepared sample
d = Thickness of the sample
ε_0= Permittivity of free space (8.85 x 10-12 F/m)
C_0 = capacitance using vacuum as the dielectric

2.2 Dielectric Loss

Dielectric loss quantifies a dielectric material's inherent dissipation of electromagnetic energy (e.g. heat) [13]. In other words it is the loss of energy that goes into heating a dielectric material in a varying electric field. For example, a capacitor which is used in an alternating-current circuit undergoes alternate charging and discharging in each half cycle. During this alternation of polarity of the plates of the capacitor, the charges will be displaced through the dielectric material first in one direction and then in the other direction, and defeating the opposition that they face leads to the production of heat through dielectric loss. Dielectric loss is dependent on the frequency and nature of the dielectric material. Dissipation of heat through dielectric loss is widely employed in various industrial applications. Dielectric loss can be expressed in terms of loss tangent tan δ. The loss tangent can be defined as the ratio of the lossy reaction to the electric field **E** in the curl equation to the lossless reaction.

$$\tan\delta = \omega\varepsilon'' + \sigma / \omega\varepsilon' \text{-------------------[3]}$$

where
ω = angular frequency
σ = conductivity. For dielectrics with small loss, this angle is $\ll 1$ and $\tan\delta \approx \delta$.

2.3 Impedance spectroscopy

Dielectric spectroscopy (sometimes called impedance spectroscopy), measures the dielectric properties of a medium as a function of frequency and also known as electrochemical impedance spectroscopy (EIS) [14-17]. **I**mpedance can also be defined as the measure of the opposition that a circuit presents to a current when a voltage is applied. In quantitative terms, it is the complex ratio of the voltage to the current in an alternating current (AC) circuit. Impedance extends the concept of resistance to AC circuits, and possesses both magnitude and phase, unlike resistance, which has only magnitude. When a circuit is driven with direct current (DC), there is no distinction between impedance and resistance; the latter can be thought of as impedance with zero phase angle. In Cartesian form, impedance is defined as

$$Z = R + jX \text{ -------------------[5]}$$

where the real part of impedance is the resistance R and the imaginary part is the reactance X [18].

Impedance is represented as a complex quantity Z and the term complex impedance may be used interchangeably Complex impedance:

$$Z^*(\omega) = (Z' - jZ'')\text{----------------[6]}$$

where $Z' = |Z|\cos\theta$ and $Z'' = |Z|\sin\theta$

2.4 Electrical conductivity

Electrical conductivity (specific electrical conductance, or volume conductivity also known as conductivity) is an intrinsic property that quantifies how strongly a given material allows the flow of electric current. A low conductivity indicates a material that strongly opposes the flow of electric current. Every material has its own characteristic resistivity. Conductivity σ (Greek: sigma) is defined as the inverse of resistivity. Conductivity has SI units of siemens per meter (S/m).

When conductivity is defined in such a way that it makes conductivity an intrinsic property, conductance is not. All wires of a certain material, irrespective of their shape and size, have approximately the same conductivity, but a long, thin wire has a much smaller conductance than a thick, short wire. However higher conductivity yields a higher conductance. The formula that relates conductivity with conductance is:

$$G = \sigma A/d \text{-----------------------[7]}$$

where G is the conductance, σ the conductivity, A the total surface area and d the thickness of the conductor.

3. Materials and Experimental Methods

Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15, the nanocrystalline ceramic, is prepared by solid state reaction route using high quality raw materials, MnO, ZnO, TiO_2 and Fe_2O_3. The solid-state reaction technique is the most popular and a convenient method for the preparation of polycrystalline solids from a mixture of solid starting materials. Normally solids do not undergo reactions at room temperature. We have to heat them to very higher temperatures, for the solid state reaction to take place. Carefully selected reactant chemicals are weighed manually according to their stoichiometric formula. After the reactant chemicals are weighed out in required amounts, they are mechanically mixed. Mechanical mixing is adopted using an agate mortar, the mixture is grounded for ten hours. It was followed by ball milling for 2 months. Then the mixture is dried in air and presintered for 10 hours at 700°C. A platinum-Rhodium thermocouple is included within the furnace to control temperature. The pre sintered mixture is again grounded for two to three hours. The granulated powder was pelletized at a pressure of $1N/M^2$ in a hydraulic press. Polyvinyl alcohol is used as the binder. Finally the pellet is sintered for 20 hours at 1150°C followed by slow cooling to room temperature.

4. Results and Discussions

The most important dielectric properties of the pelletized ceramic such as dielectric constant, dielectric loss, conductance and impedance of Titanium Substituted Manganese - Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15 is determined at temperatures 27°C, 120°C, 200°C, 300°C, 400°C, 500°C and 600°C in a range of frequency 42Hz to 5MHz. The observed results are analyzed using existing theories.

4.1 Dielectric Constant

1) Effect of Frequency

Graphs describing frequency dependence of dielectric constant of the ceramic, are plotted with frequency (frequency range 42 Hz to 5MHz) against dielectric constant at various temperatures, viz, 27^0C, 120^0C, 200^0C, 300^0C, 400^0C, 500^0C and 600^0C are given in Fig.1. From the studies it is observed that dielectric constant decreases with increase in frequency and reaches a constant value.

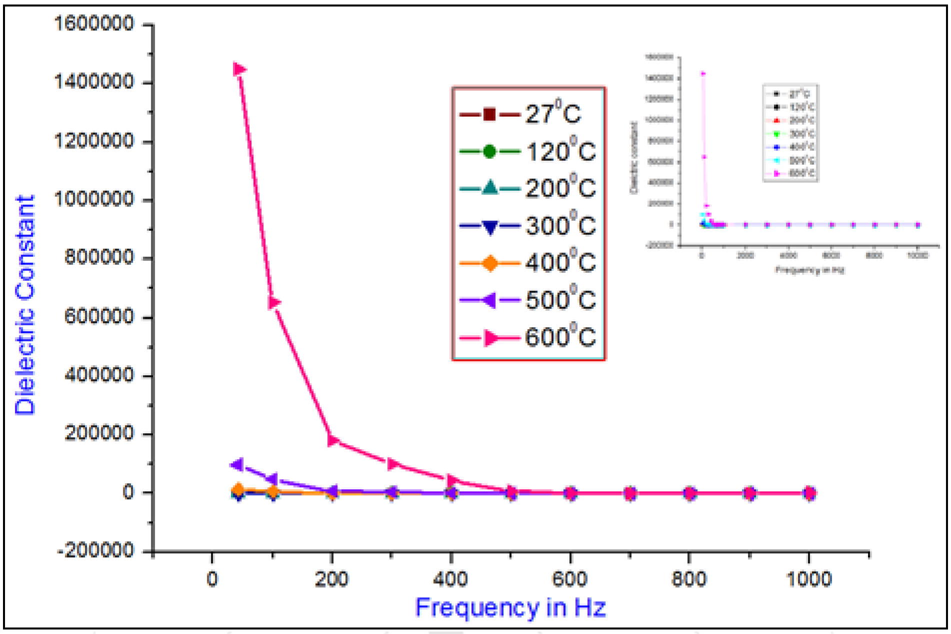

Figure 1: Variation of Dielectric constant with frequency at different temperatures of Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

2) Effect of Temperature

To find out the effect of temperature on dielectric constant, its variation with temperature (27^0C, 120^0C, 200^0C, 300^0C, 400^0C, 500^0C and 600^0C) is plotted at different frequencies (i.e 42Hz to 5000KHz).The graphs are shown in Fig.2. Dielectric constant remains constant up to 300^oC, slight increment in between 300-400^0C thereafter well increased with temperature, increment better for lower frequencies.

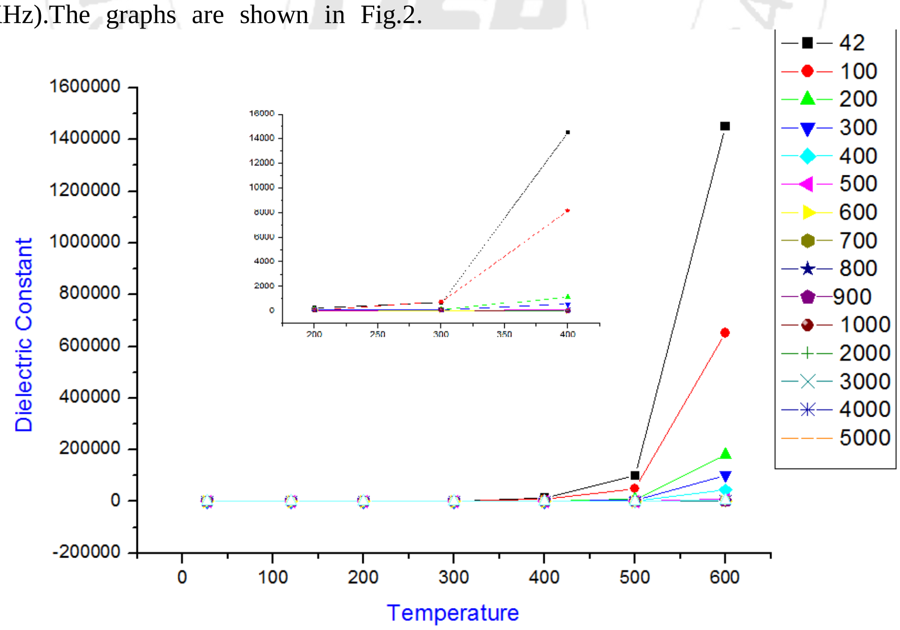

Figure 2: Variation of dielectric constant with temperature at various frequencies of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

4.2 Dielectric Loss

1) Effect of Frequency

Graphs illustrating the effect of frequency (frequency range 42 Hz to 5MHz) on dielectric loss at temperatures (30^0C, 110^0C, 200^0C, 300^0C, 400^0C, 500^0C and 600^0C) are given in Fig.3.

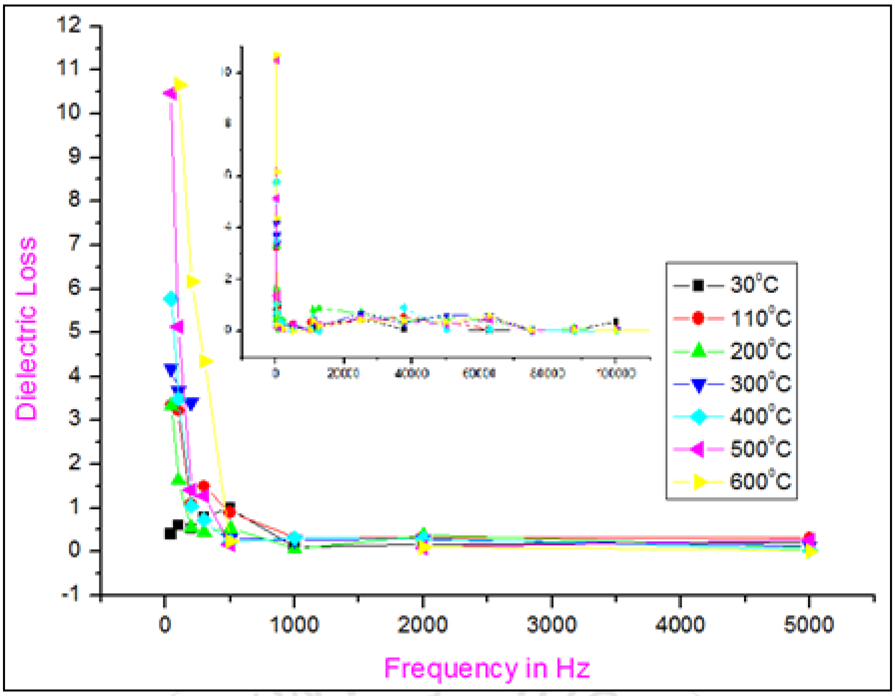

Figure 3: Variation of dielectric loss with frequency at different temperatures of Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

It is observed that dielectric loss, decreases rapidly in the lower frequency region (say up to 800 kHz), for lower temperatures, with rapidness increasing with fall in temperature and remains a constant thereafter. The dielectric loss reaches the instrumental saturation value (tan δ = 9.9999) in the low frequency range, but at higher frequencies the value drops down drastically. Due to the low value of dielectric loss at higher frequencies, all the samples possess superior crystalline quality. For higher temperatures dielectric loss is a constant in the lower frequency region and then its value decreases gradually.

2) Effect of Temperature

To illustrate temperature dependence of dielectric loss, its variation as a function of temperature (30^0C, 110^0C, 200^0C, 300^0C, 400^0C, 500^0C and 600^0C) is plotted at different frequencies (42Hz to 5MHz). Corresponding graph is shown in Fig.4.

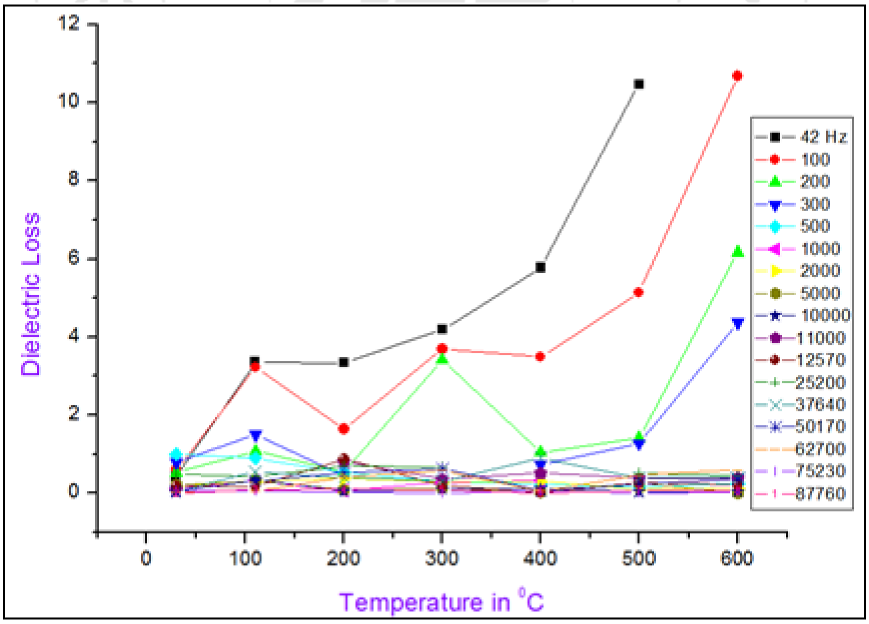

Figure 4: Variation of dielectric loss with temperature at varied frequencies of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

It is evident from the graph that dielectric loss of all curves, except the one at 42-300 Hz, is constant up to say 125^0C, increases with temperature in the case of 42-300Hz, for other higher frequencies tends to remain almost constant. Curve at 42 Hz gradually increases.

4.3 Impedance

1) Effect of Frequency

Impedance spectroscopy is a non-destructive technique and it provides the dynamic properties to understand the microscopic nature of the materials [19-27]. It is used to study the electrical properties of materials. Frequency dependence of electrical impedance of the prepared ceramic sample, is evident from the graphs plotted (Fig.5) with frequency (frequency range 42 Hz to 5MHz) against dielectric constant at various temperatures, viz, 30^0C, 110^0C, 200^0C, 300^0C, 400^0C, 500^0C and 600^0C. The graphs are plotted in figure 5.

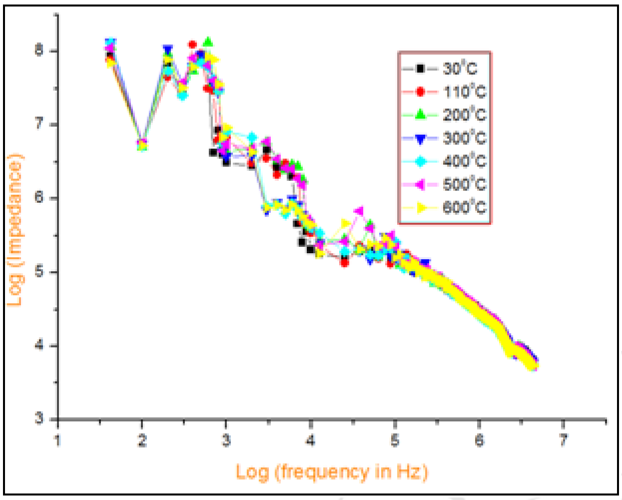

Figure 5: Variation of impedance with frequency at different temperatures of Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

Impedance values of higher temperatures are comparatively less. Impedance decreases with increase in frequency.

The variation of the real part and the imaginary part of impedance with frequency at different temperatures can be observed from the graph, Fig.6 & Fig.7. z' is the real part and z" is the imaginary part.

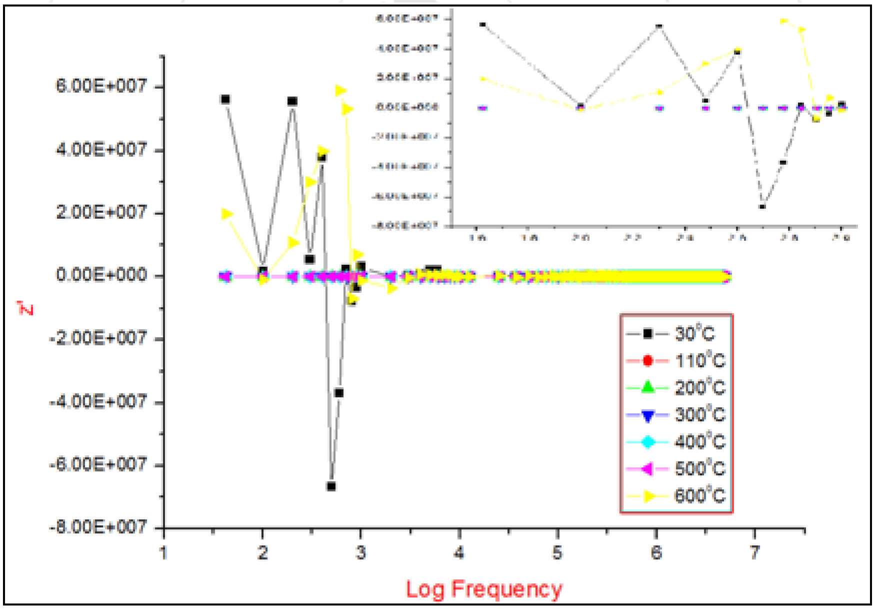

Figure 6: Variation of real part of impedance with frequency at diferent temperatures of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

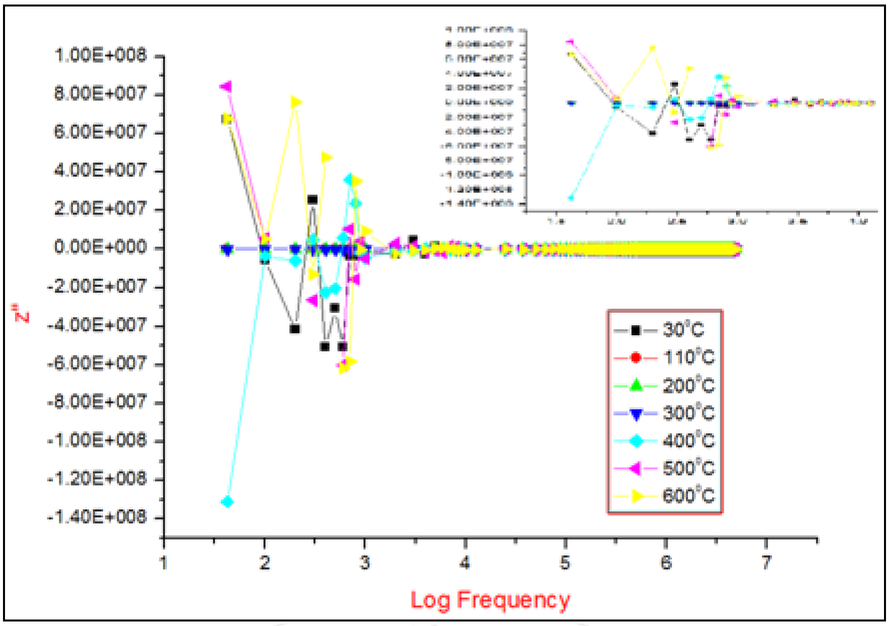

Figure 7: Variation of imaginary parts of impedance with frequency at different temperatures of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

From figure 6 & 7 the relationship between real and imaginary parts of impedance along with frequency can be learnt. It is noted that the imaginary and real parts of impedance remain almost constant as frequency increases in high temperature region. But variation in impedance with frequency is observed at low temperature regions.

2) Effect of Temperature

To find out the effect of temperature on impedance its change as a function of temperature (30^0C, 110^0C, 200^0C, 300^0C, 400^0C, 500^0C and 600^0C) is plotted at different frequencies (i.e 42Hz to 5MHz). They are shown in the figure 8a. Log. of impedance against temperature along with variation of log of frequency is plotted in figure 8b.

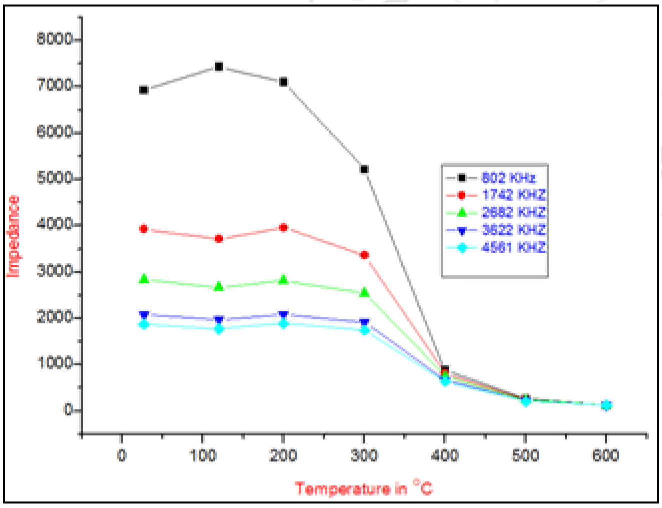

Figure 8 (a): Variation of impedance with temperature and frequency of Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

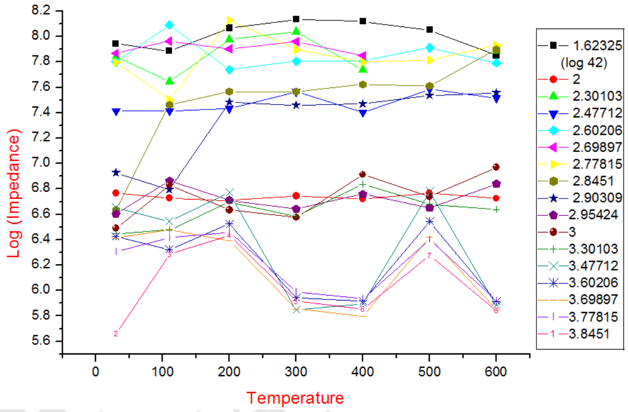

Figure 8 (b): Variation of log. impedance with temperature and frequency along with log (frequency) of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15.

From figure 8a, for higher frequencies, up to 400^0C impedance decreases, then slightly decreases up to 500^0C, then remains almost constant. For lower frequencies impedance decreases up to 400 ^{0}C, then decreases slightly up to 500^0C, then remains constant together with other frequencies.

In figure 8b, higher values of impedance for lower frequencies and have slight variation with temperature. At higher frequencies much fluxuations are observed.

4.4 Conductivity

1) Effect of Frequency

The frequency dependence (frequency range 42 Hz to 5MHz) of electrical conductivity at constant temperatures (30^0C, 110^0C, 200^0C, 300^0C, 400^0C, 500^0C and 600^0C) are plotted in fig.9.

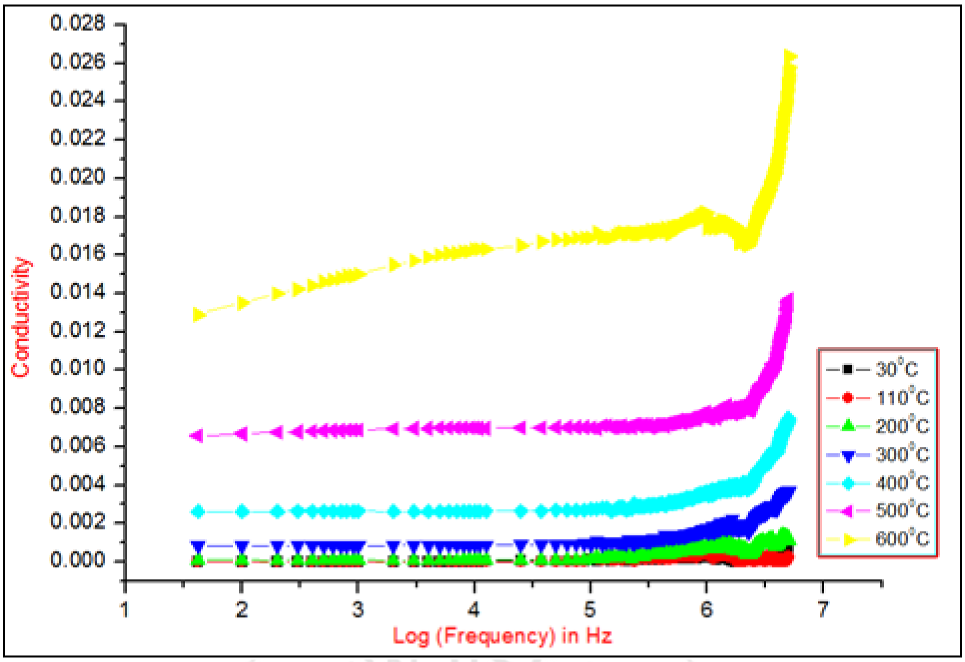

Figure 9: Variation of conductivity with Log (frequency) at different temperatures of Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

At higher frequencies conductivity increases exponentially. Conductivity remains constant except at very high frequencies. This can be explained according Joncher's power law.

i.e. $\sigma\ ac = \sigma\ dc + A\omega^s$.

2) Effect of Temperature

To demonstrate the effect of temperature on conductivity its change as a function of temperature (30^{0}C, 110^{0}C, 200^{0}C, 300^{0}C, 400^{0}C, 500^{0}C and 600^{0}C) is plotted at frequencies ranging from 42Hz to 5MHz. They are plotted in Fig.10.

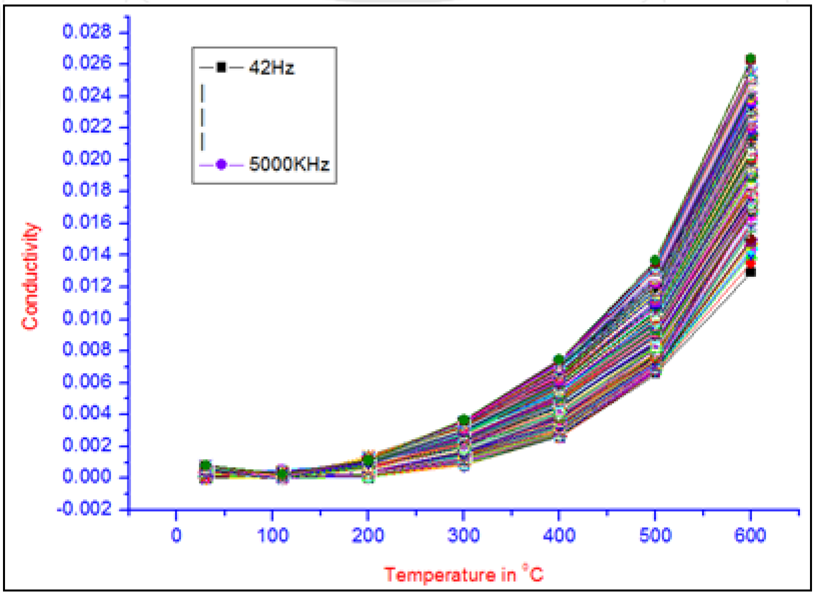

Figure 10: Variation of conductivity with temperature and frequency of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15

Conductivity remains almost a constant for all frequencies up to 100^{0}C. Afterwards conductivity increases with increasing temperatures. This increase is considerably large in the graph, but actually value is very small.

5. Conclusion

Dielectric properties of Titanium Substituted Manganese - Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.15, viz, dielectric constant, dielectric loss, electrical conductivity and impedance varies with frequency and temperature. Dielectric constant decreases with increase in frequency and reaches a constant value. Dielectric constant remains constant up to 300°C, slight increment in between 300-400^{0}C thereafter well increased with temperature, increment better for lower frequencies. Due to the low value of dielectric loss at higher frequencies, all the samples possess superior crystalline quality. Dielectric loss increases with temperature in the case of lower frequencies, for other higher frequencies tend to remain almost constant. Impedance decreases with increase in frequency, for higher/ lower frequencies impedance decreases, then slightly decreases up to 500^0C, after that remains almost constant together. Conductivity remains constant except at very high frequencies, can be explained according Joncher's power law. i.e. σ ac = σ dc + Aωs . Conductivity increases with increasing temperatures, value is very small. The presence of some internal field within the dielectric composite material along with the external AC field is the implication of the variation of dielectric constant and dielectric loss with temperature and frequency.

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