Dielectric Properties of Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20 and its Dependence on Frequency and Temperature

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Abstract - Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20, Titanium Substituted new crystalline ceramic, is prepared by solid state reaction method involving mechanical mixing, ball milling, calcination and sintering with AR grade MnO, ZnO, TiO_2 and Fe_2O_3. Different samples are prepared at different temperatures. Much higher temperature is required for Solid-state reactions to take place which involves formation of product phase(s) at the interfaces of the reactants. Product sample undergoes measurement of various dielectric properties and its dependence on frequency and temperature. Measured parameters are dielectric constant, dielectric loss, conductivity and impedance.

Keywords

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

1. Introduction

Dielectric ceramics play a vital role in this new era of sophisticated technologies and applications. Both dielectrics with low and high dielectric constant find their on significance and importance in electronic industries. Insulators are made up of high dielectric constant materials. They are otherwise known as passivation materials. They find a wide range of applications from isolating signal-carrying conductors, fast signal propagation, interlayer dielectric to reduce the resistance-capacitance (RC) time delays, crosstalk and power dissipation in the high density and high speed integration. They are essential in very dense multi-layered IC's, where coupling between very close metal lines are necessary to be suppressed to obstruct degradation in device performance. This role includes both packaging and encapsulation. Regarding high dielectric constant dielectric ceramics, they are very significant now a days because, the current trends in electronics are directed toward reduced sizes, decreased voltages, and increased system complexity. This necessitates far greater filtering, noise, and decoupling requirements than higher voltage systems. As a result, there is an increased demand for high dielectric constant materials that can be used for filtering and decoupling applications. These materials should be stable over a wide temperature range, exhibit high dielectric constants, and be able to withstand high energy densities.

In this work the authors aimed to find out the dependence of most crucial dielectric parameters, viz, dielectric constant, impedance, conductivity and dielectric loss of a new crystalline dielectric ceramic material Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20 on temperature and frequency. The product sample is prepared by solid state reaction method involving mechanical mixing, ball milling, calcinations, attrition milling and sintering with AR grade MnO, ZnO, TiO_2 and Fe_2O_3. Ferrites are ferromagnetic semi conductors and the need for high resistivity ferrites led to the synthesis of various ferrites. The influence of various substituents like Ti, Zn etc considerably change in its electrical properties [1]. Polycrystalline ferrites have very good dielectric 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 is 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]. The study of dielectric constant, impedance, conductivity and dielectric loss factor, as a function of temperature and frequencies is one of the most important, convenient and sensitive methods of studying the ceramic and polymer structure [6]. The dielectric properties (dielectric constant, dielectric loss, conductivity and impedance) of a number of ceramics / polymers have been investigated in the last two decades [7-12].

2. Theory of dielectric properties

Dielectric constant

Dielectric constant can be defined as the ratio of the capacitance of a capacitor filled with the given dielectric material to the capacitance of an identical capacitor in a vacuum without the dielectric material.The definition for dielectric constant is related to the permittivity of the dielectric material. Permittivity means the ability of a material to polarise in an applied field. Dielectric constant of a material is the ratio of the permittivity of the dielectric to the permittivity of free space. The greater the polarisation developed by a material in an applied field of given strength, the greater the dielectric constant will be. Generally dielectric materials are made from inorganic substances.

Dielectric constant (ε) is given by

$\varepsilon = C / C_0$ -------------------[1]

$C_0 = A\varepsilon_0/d$-------------------[2] where

C = capacitance using the material as the dielectric in the capacitor

C_0 = capacitance using vacuum as the dielectric

ε_0= Permittivity of free space (8.85 x 10-12 F/m)

A = Area of the prepared sample

d = Thickness of the sample

Dielectric loss

Dielectric loss quantifies a dielectric material's inherent dissipation of electromagnetic energy (e.g. heat) [13]. It is the loss of power in a dielectric caused by the loss of energy in the form of heat generated by an electric field. For a capacitor formed from a loss dielectric material, the loss tangent is the ratio at any particular frequency between the real and imaginary parts of the impedance of the capacitor. A large loss tangent means you have a lot of dielectric absorption. It can be represented in two different ways. The first one is in terms of the loss angle δ and the second one is in terms of corresponding loss tangent tan δ. Both methods refer to the phasor in the complex plane whose real and imaginary parts are the resistive component of an electromagnetic field and its reactive counterpart. The loss tangent is then defined as the ratio (or angle in a complex plane) of the resistive reaction to the

electric field **E** in the curl equation to the lossless reaction.

$\mathrm{Tan}\delta = W\,\varepsilon'' + \sigma / W\,\varepsilon'$-------------------[3]where

W = angular frequency

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

Impedance spectroscopy

Dielectric spectroscopy (sometimes called impedance spectroscopy), and also known as electrochemical impedance spectroscopy (EIS), measures the dielectric properties of a medium as a function of frequency [14][15][16][17]. Impedance, denoted *Z*, is an expression of the opposition that an electronic component, circuit, or system offers to alternating and/or direct electric current. Impedance is a vector (two-dimensional) quantity consisting of two independent scalar (one-dimensional) phenomena: resistance and reactance. Resistance, denoted *R*, is a measure of the extent to which a substance opposes the movement of electrons among its atoms. The more easily the atoms give up and/or accept electrons, the lower the resistance, which is expressed in positive real number ohms. Resistance is observed with alternating current (AC) and also with direct current (DC). Reactance, denoted *X*, is an expression of the extent to which an electronic component, circuit, or system stores and releases energy as the current and voltage fluctuate with each AC cycle. Reactance is expressed in imaginary number ohms. It is observed for AC, but not for DC. When AC passes through a component that contains reactance, energy might be stored and released in the form of a magnetic field, in which case the reactance is inductive (denoted $+jX_L$); or energy might be stored and released in the form of an electric field, in which case the reactance is capacitive (denoted $-jX_C$). Reactance is conventionally multiplied by the positive square root of -1, which is the unit imaginary number called the j operator, to express *Z* as a complex number of the form *R* +. In Cartesian form, impedance is defined as

Z = R + jX -------------------[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*(ω) = (Z′- jZ″)----------------[6]

where Z′ =|Z|cosθ and Z″ =|Z|sinθ

Electrical conductivity

Electrical conductivity is an important intrinsic dielectric property. It is a measure which specifies how strongly a material allows the flow of electric current through it. A good conductor is a material which readily allows the flow of current. Conductivity is the inherent property of a material. Unit of conductivity is siemens per meter (S/m).Then there is conductance. Conductance is an expression of the ease with which electric current flows through a substance. In equations, conductance is symbolized by the uppercase letter G. The standard unit of conductance is the siemens (abbreviated S), formerly known as the mho. Conductance is not an intrinsic property. However higher conductivity yields a higher conductance. The formula that relates conductivity with conductance is:

G=σA/d------------------------[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

The simplest method for preparing the desired crystalline dielectric ceramic, Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20, is a solid-state thermo chemical reaction involving mechanical mixing, ball milling, attrition milling, calcination and sintering. The appropriate amounts of precursor powders (MnO, ZnO, TiO_2 and Fe_2O_3) are mixed thoroughly in Agate mortar followed by Ball milling for two months. For the prepared sample, the reagent grade chemicals of high purity (99.99%) are used. These powders are calcined for twelve hours at 700°C. The powders are cooled, reground and calcined again. This process is repeated several times to get homogeneous material. The powders are subsequently compacted to pellets and sintered for about 10 hours at 1150°C. The sintering environment such as temperature, annealing time, atmosphere and cooling rate play a very important role in getting good nano/micro crystalline dielectric material. Material is calcined at different treating temperatures. Control of temperature is necessary to ensure that the desired crystalline phase is formed with optimum particle size. Polyvinyl alcohol is used as the binder during pelletization. Finally the pellet is sintered for 20 hours followed by slow cooling to room temperature.

4. Results and Discussions

The fundamental dielectric properties of the prepared ceramic such as dielectric constant, dielectric loss, conductance and impedance are measured and their dependence on temperature and frequency are determined. For analyzing temperature dependence dielectric parameters are measured at 26°C, 120°C, 200°C, 300°C, 400°C, 500°C and 600°C. Frequency dependence properties are calculated in the frequency range 42 Hz to 5MHz.

A. Dielectric Constant

1. Effect of Frequency

Graphs describing frequency dependence of dielectric constant of the prepared ceramics are plotted with frequency (frequency range 42 Hz to 5MHz) against dielectric constant at various temperatures, viz, 26°C, 120°C, 200°C, 300°C, 400°C, 500°C and 600°C are given in fig.1. From the studies it is observed that dielectric constant decreases with increase in frequency and reaches a constant value.

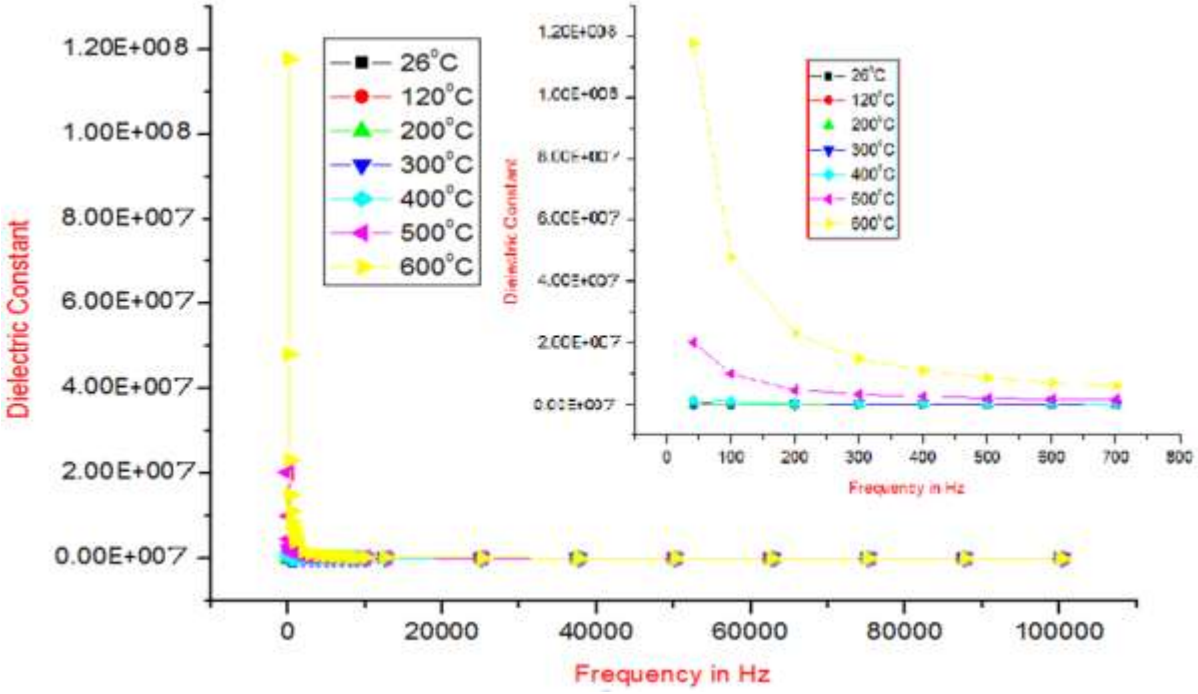


Fig.1 Variation of Dielectric constant with frequency and temperature of Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

2. Effect of Temperature

To find out the effect of temperature on dielectric constant, its variation with temperature (26⁰C, 120⁰C, 200⁰C, 300⁰C, 400⁰C, 500⁰C and 600⁰C) is plotted at different frequencies (i.e 42Hz to 5MHz) in the graph shown in Fig.2. From observations, Dielectric constant remains constant up to 300ᵒC, slight increment in between 300-400⁰C thereafter well increased with temperature, increment better for lower frequencies.

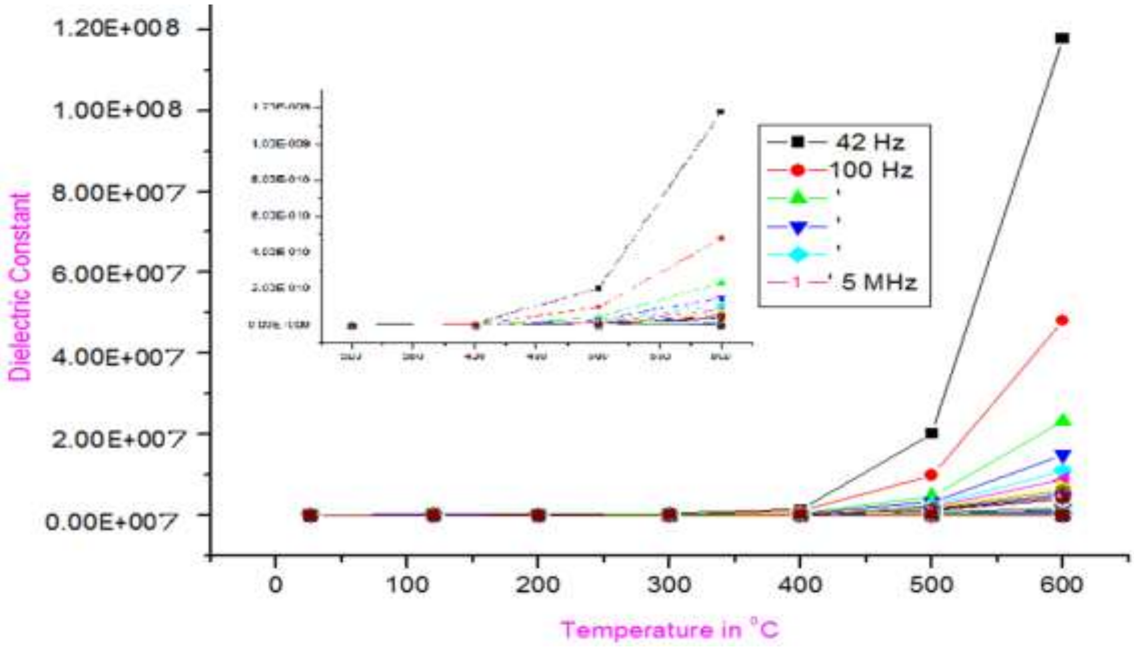


Fig.2 Variation of dielectric constant with temperature and frequencies of Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

B.Dielectric Loss

1. Effect of Frequency

Graphs illustrating the effect of frequency (frequency range 42 Hz to 5MHz) on dielectric loss at temperatures (26^{0}C, 120^{0}C, 200^{0}C, 300^{0}C, 400^{0}C, 500^{0}C and 600^{0}C) are given in Fig.3.

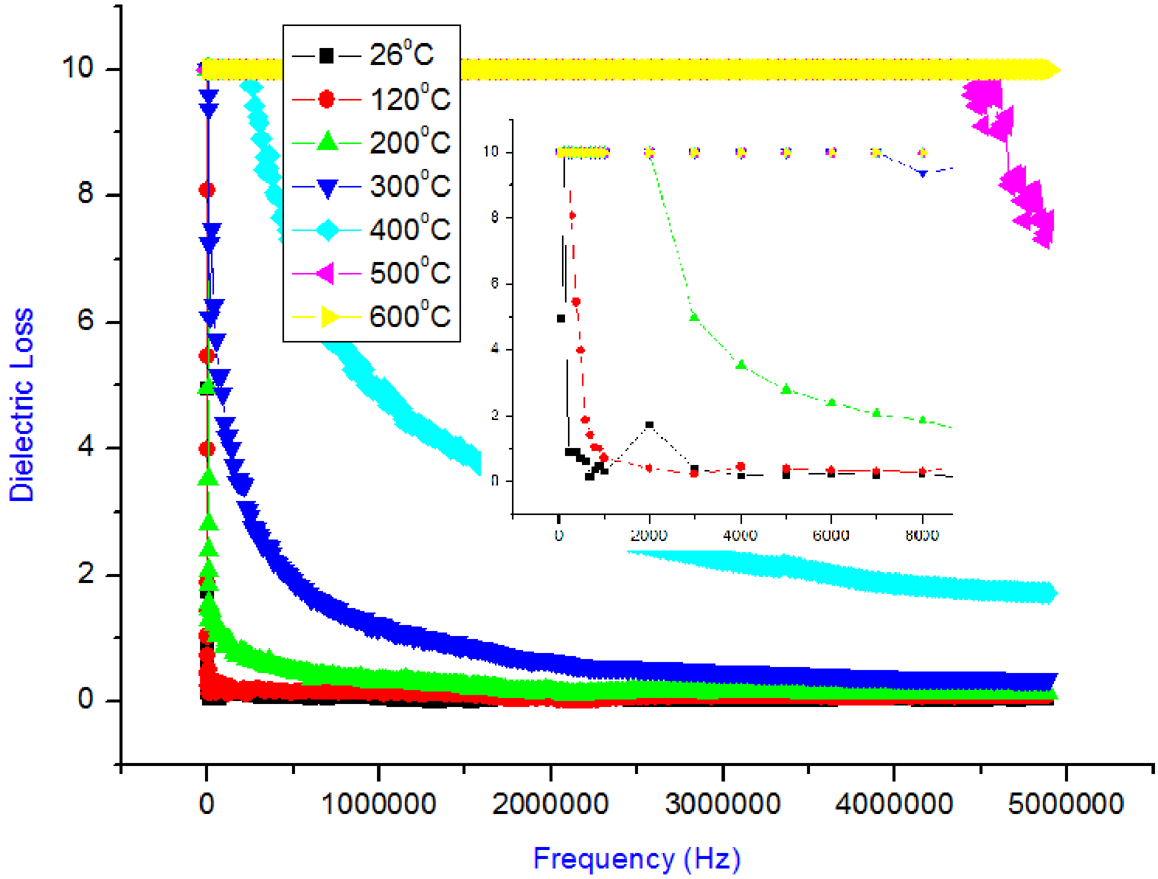


Fig.3 Variation of dielectric loss with frequency at various temperatures of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

Dielectric loss suddenly decreases thereafter become constant with increase in frequency for lower temperatures. For higher temperatures much variation is not observed.

2. Effect of Temperature

To illustrate temperature dependence of dielectric loss, its variation as a function of temperature (26^{o}C, 120^{o}C, 200^{o}C, 300^{o}C, 400^{o}C, 500^{o}C and 600^{o}C) is plotted at different frequencies (42Hz to 5MHz). Corresponding graph is presented in Fig.4.

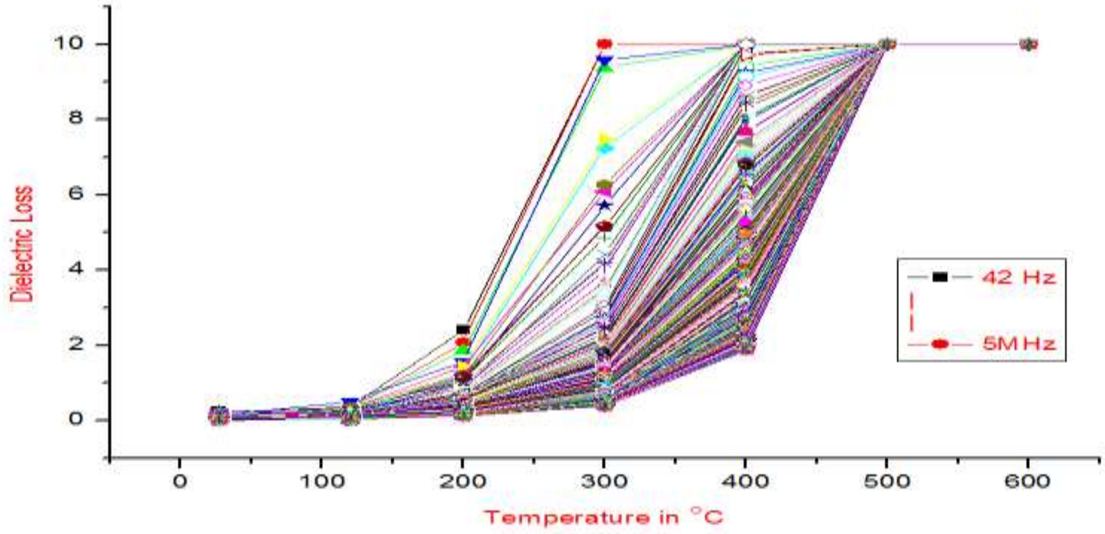


Fig.4 Variation of dielectric loss with temperature and frequency of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

It is evident from the graph that dielectric loss of all curves, increases with temperature up to 500 ^{0}C, after that almost constant up to 600 ^{0}C.

C. Impedance

1. Effect of Frequency

Frequency dependence of electrical impedance of the prepared ceramic sample is evident from the graphs plotted with frequency (frequency range 42 Hz to 5MHz) against dielectric constant at various temperatures, viz, 26°C, 120°C, 200°C, 300°C, 400°C, 500°C and 600°C. The graphs are plotted in Fig.5.

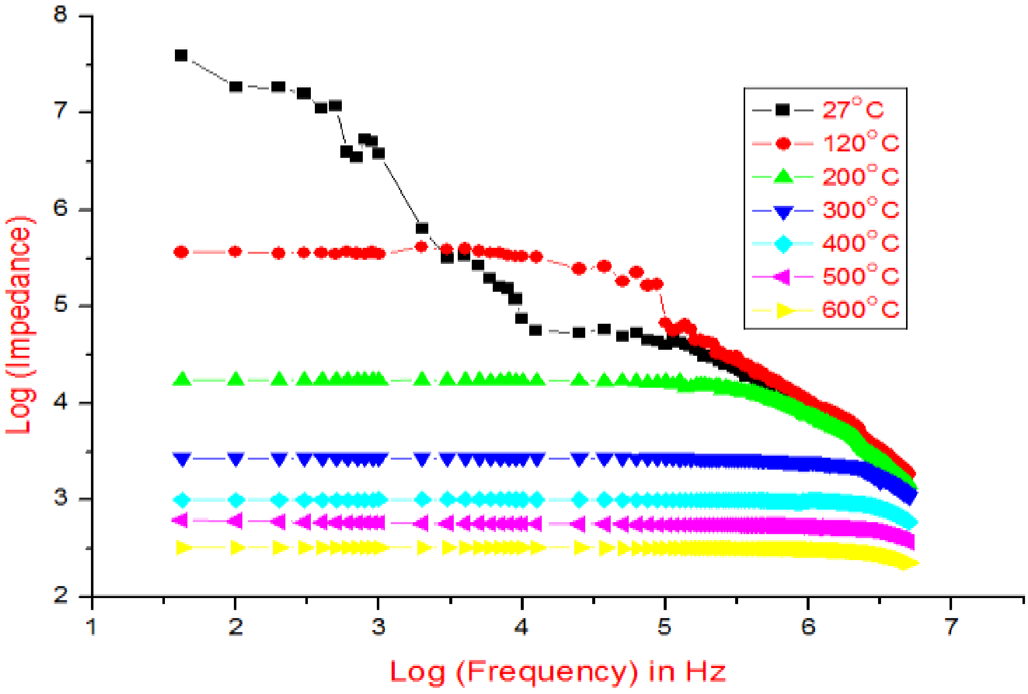


Fig.5 Variation of impedance with frequency at different temperatures of Titanium Substituted Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

Impedance curves of higher temperatures are almost straight lines parallel to X-axis except at very high frequency region where it slightly decreases. For 27^0C and 120^0C, impedance decreases with frequency. For 200^0C and 300^0C impedance retained almost constant at lower frequencies and decreases at higher frequencies.

We can observe the variation of the real part and the imaginary part of impedance with frequency at different temperatures from the graphs Fig. 6 and Fig.7. z' is the real part and z" is the imaginary part.

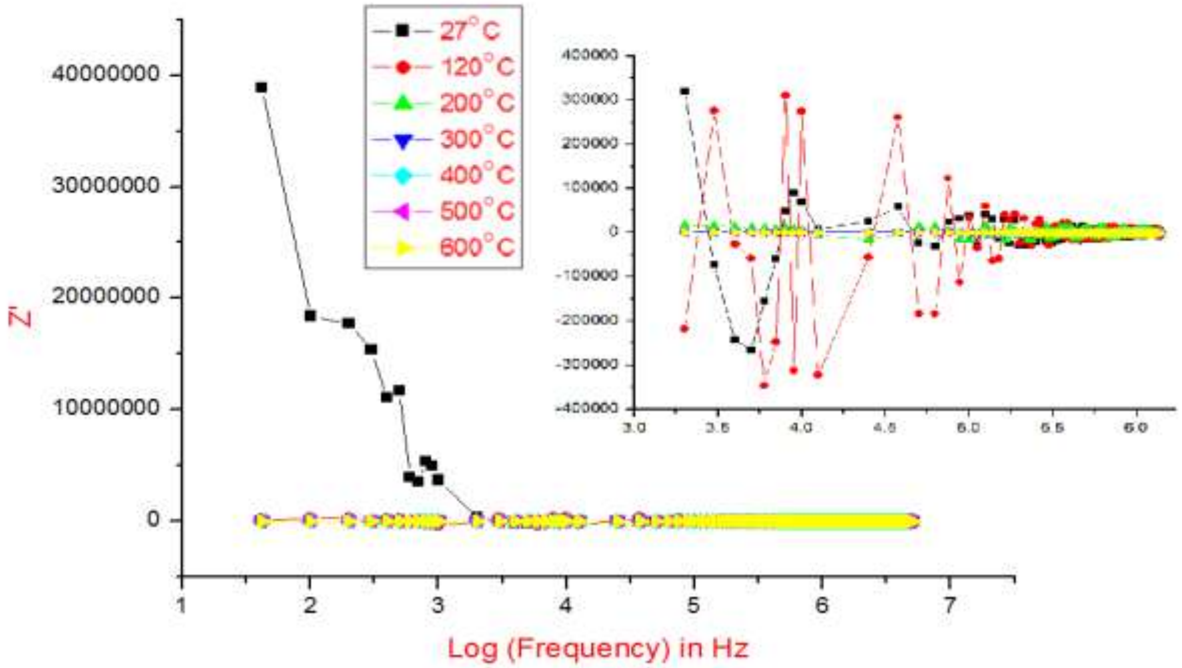


Fig.6 Variation of real part of impedence with frequency and temperature of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

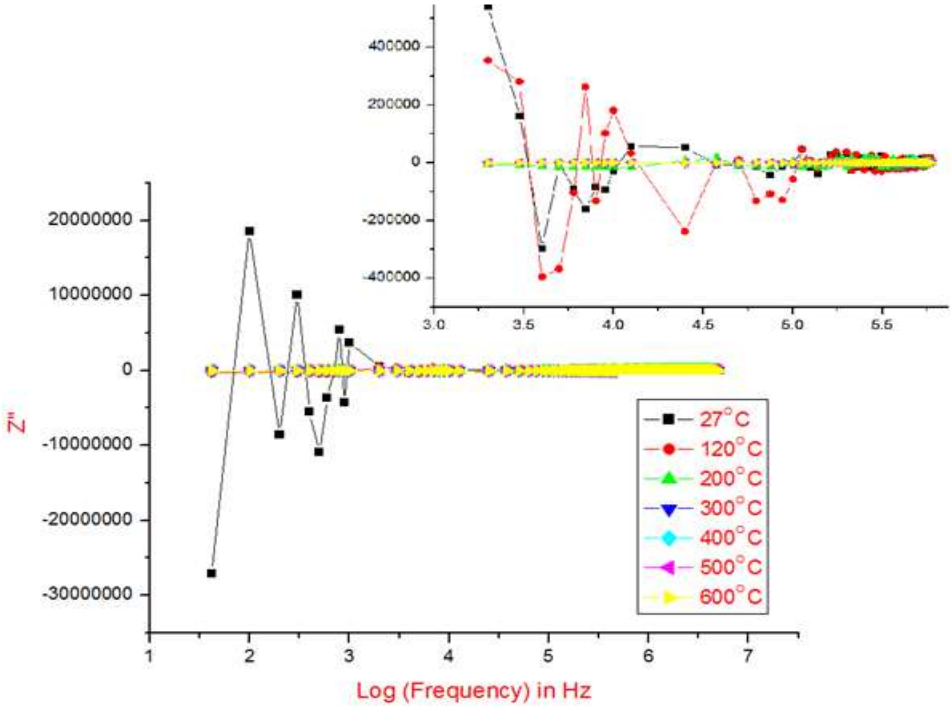
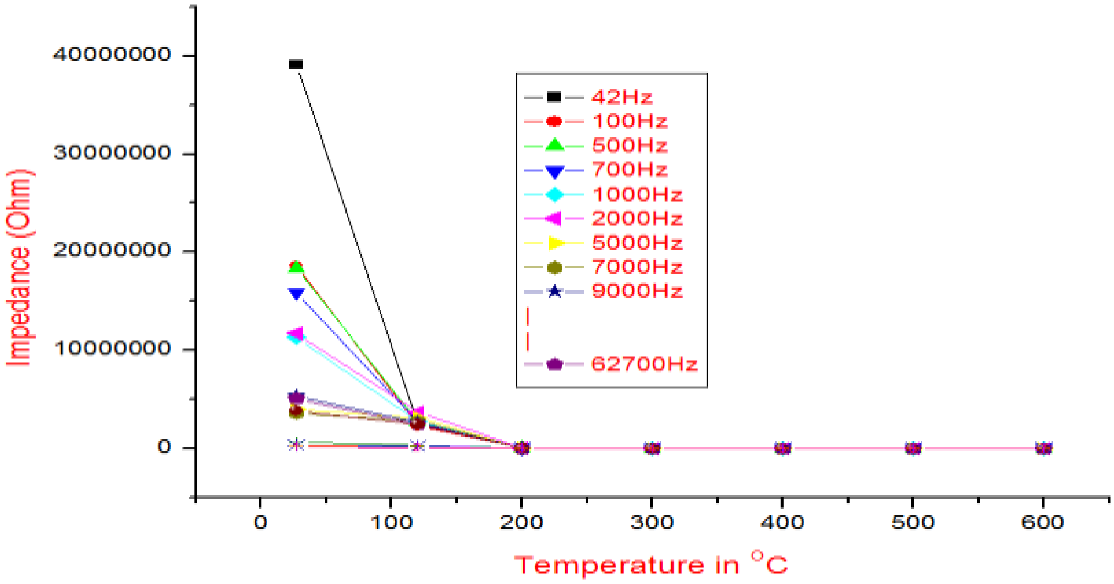


Fig.7 Variation of imaginary parts of impedance with frequency and temperature of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

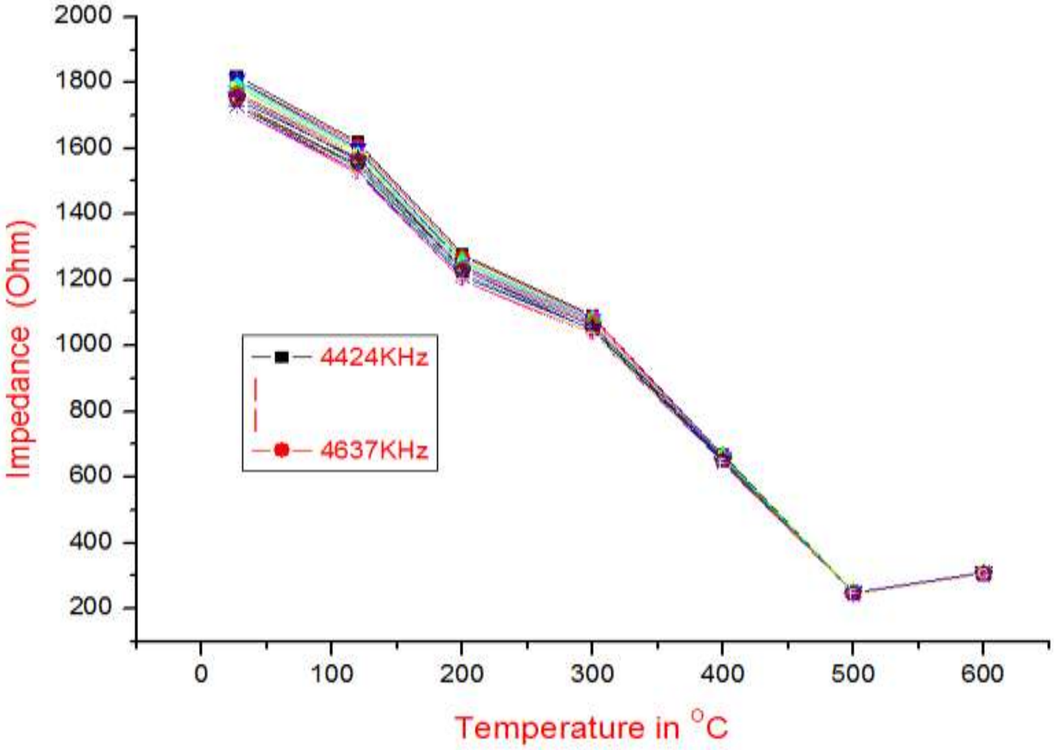
From figures 6&7, it is noted that the imaginary and real parts of impedance remain almost constant as frequency increases in high temperature region. But the variation in impedance with frequency is observed in low temperature regions.

2. Effect of Temperature

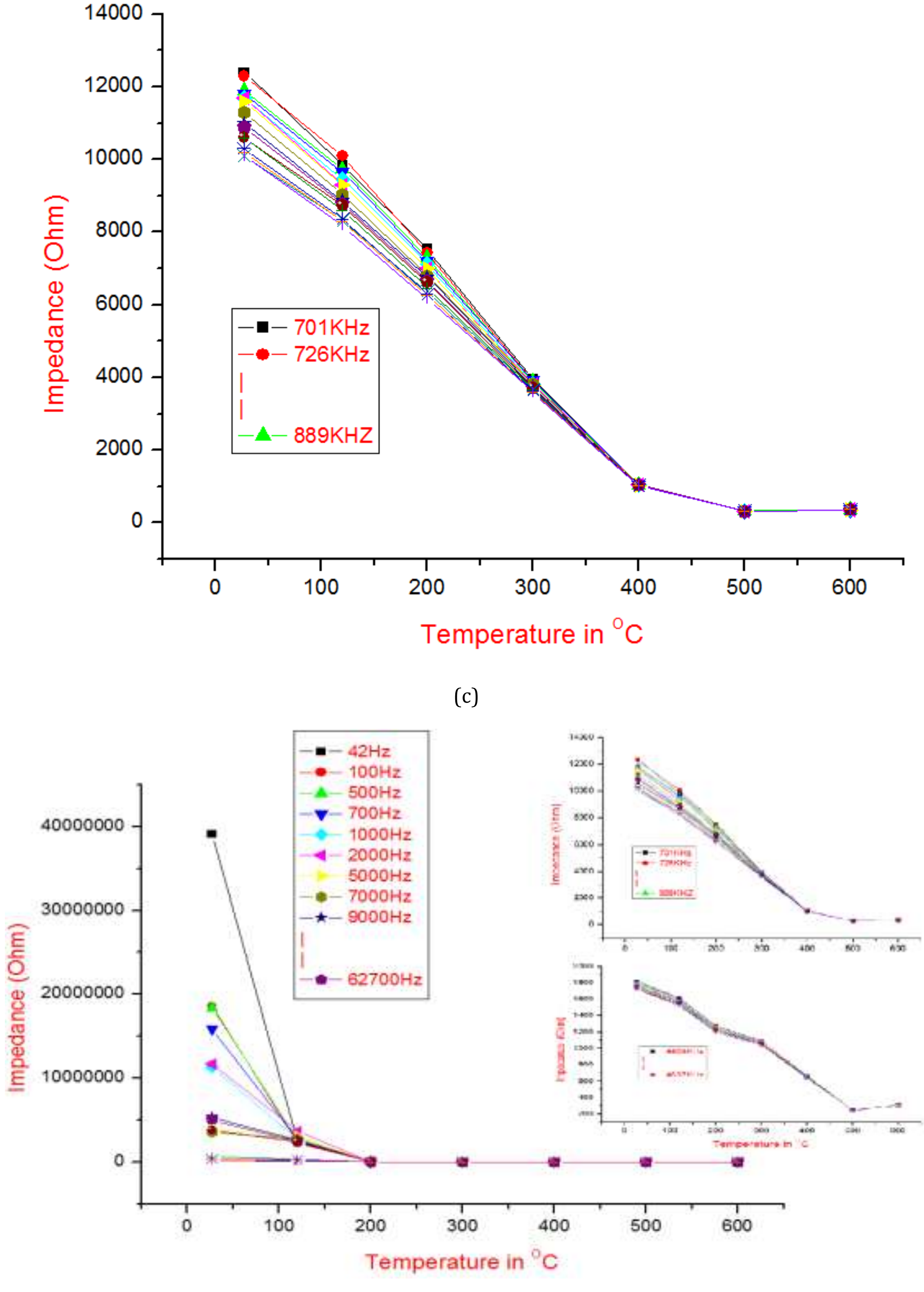
To find out the effect of temperature on impedance its change as a function of temperature (26°C, 120°C, 200°C, 300°C, 400°C, 500°C and 600°C) is plotted at different frequencies (i.e 42Hz to 5MHz).They are shown in the figures 8 (a,b,c,d).



(a)



(b)



(c)

(d)

Fig.8 Variation of impedance (in various ranges - a,b,c,d) with temperature of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

Variation of impedance for various ranges of frequencies are shown in the figures 8(a,b,c,d). Generally impedance decreases with increase in temperature upto 400/500ᵒC thereafter remains almost constant. Variation of impedance decrement is higher for lower frequencies.

D. Conductivity

1. Effect of Frequency

The frequency dependence (frequency range 42 Hz to 5MHz) of electrical conductivity at constant temperatures (27ᵒC, 120ᵒC, 200ᵒC, 300ᵒC, 400ᵒC, 500ᵒC and 600ᵒC) are plotted in Fig.9.

At all temperatures impedance remains almost constant at lower frequencies and slightly increased at higher frequency side.

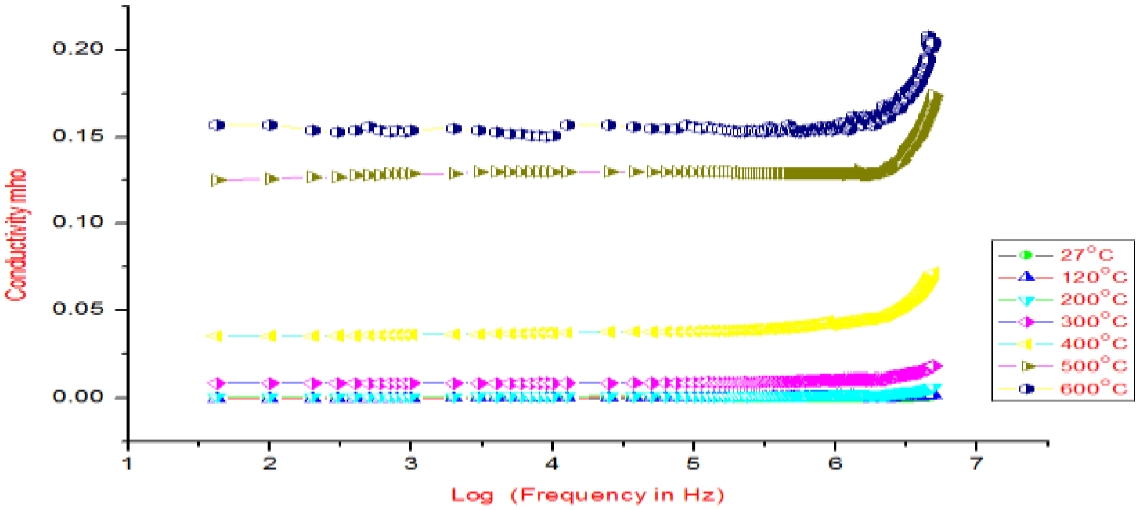


Fig.9 Variation of conductivity with frequency of Manganese -Zinc Ferrite System $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20

Joncher's power law, i.e. $\sigma_{ac} = \sigma_{dc} + A\omega^s$, can be applied to explain this figure. Conductivity remains constant except at very high frequencies. At higher frequencies conductivity increases exponentially.

The conductivity decreases with decrease of frequency at the low frequency region and it's attributed to the polarisation effects at the electrode-electrolyte interface [19-24]. In low frequency region, more charge accumulation occurs which exhibits the charge flow; and hence, drops the conductivity. In the intermediate plateau region, conductivity is almost independent of frequency and it is equal to the bulk or d.c conductivity of the sample. The high frequency dispersion region of the ac conductivity is fitted and explained using Jonscher's universal power law (JUPL) [25].

2. Effect of Temperature

To demonstrate the effect of temperature on conductivity its change as a function of temperature (27ᵒC, 120ᵒC, 200ᵒC, 300ᵒC, 400ᵒC, 500ᵒC and 600ᵒC) is plotted at frequencies ranging from 42Hz to 5000 KHz. They are plotted in Fig.10.

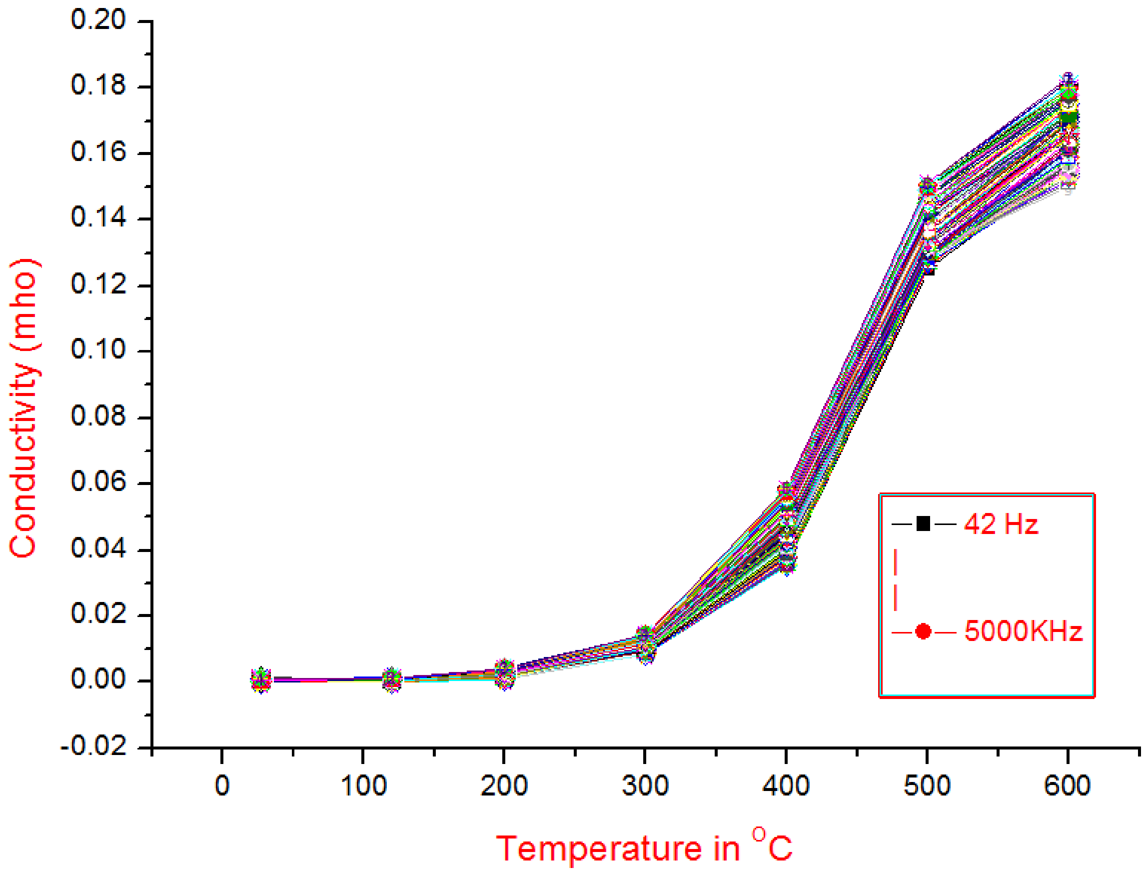


Fig.10 Variation of conductivity with temperature at different frequencis of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.20.

Conductivity remains almost a constant for all frequencies up to 100⁰C. Afterwards conductivity increases with increasing temperatures. This exponential increase is considerably large in the graph, but actually value is very small.

5. Conclusions

Dielectric properties of Titanium Substituted Manganese - Zinc Ferrite System Mn0.8+xZn0.2TixFe2-2xO4 with x=0.20, 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 upto300⁰C, slight increment in between 300-400⁰C 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 of all curves, increases with temperature up to 500⁰C, thereafter almost constant up to 600⁰C.

Impedance curves of higher temperatures are almost straight lines parallel to X-axis except at very high frequency region where it slightly decreases with increase in frequency.

Impedance steeply decreases first, then slightly decreases up to 200⁰C, after that remains almost constant together with increase in temperature. 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, real value is very small. The presence of some internal field within the dielectric composite material along with the external A C field is the implication of the variation of dielectric constant and dielectric loss with temperature and frequency.

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