

Approval Sheet

This thesis entitled “**Lead-free piezoelectric material – Ag(Ta_{0.5}Nb_{0.5})O₃**” by Biswajit Dutta is approved for the degree of Master of Science from IIT Hyderabad.

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Dielectric studies of $\text{AgTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$

A Project Report Submitted
as part of the requirements for the degree of

MASTER OF SCIENCE

By

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Under the supervision of

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to the

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY HYDERABAD


INDIA

APRIL, 2014

Declaration

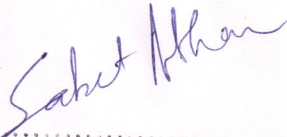
I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Physics, Indian Institute of Technology Hyderabad under the supervision of Dr. Manish K. Niranjana and Dr. Saket Asthana.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



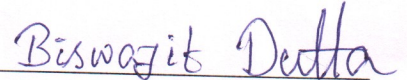
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Abstract

The complex perovskite oxide $\text{AgNb}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (ATN) synthesized by solid state reaction technique has single phase with monoclinic structure. The scanning electron micro graph of the sample shows that grains and grain boundary are there but grain size is not definable from there. The field dependence dielectric response and loss tangent were measured in the temperature range from 30°C to 430°C and in the frequency range from 100Hz to 1MHz. An analysis of the dielectric constant (ϵ') and loss tangent ($\tan \delta$) has done and concluded that at high temperature in low frequency region space charge contribution are dominant contribution in polarization. Conductivity study shows that at low frequency conductivity is almost constant at a particular frequency but at high frequency increase very sharply at high frequency value.

Table of Contents:-

1. Introduction	3
2. Experimental		
2.1. Preparation of pellets of ATN	4
2.2. Microstructure of ATN	4
2.3. XRD	4
2.4. SEM	4
3. Complex permittivity & Loss tangent	5-8
4. Impedance spectroscopy	9-10
5. Results and discussions	11
• List of figures		
1.1. Room temperature XRD pattern of ATN	11
2.1. SEM image of ATN ceramic	12
2.2. EDX image ATN ceramic	12-13
3.1. Raman scattering spectra	14
4.1. Temperature dependent dielectric constant of ATN ceramic	15
4.2. Frequency dependence of ϵ' at different temperatures	16
4.3. Frequency dependence of $\tan\delta$ at different temperatures	17
4.4. Temperature dependence of loss factor ($\tan\delta$)	18
4.5. Imaginary part of permittivity	20
5.1. Cole- Cole plot	21
5.2. Conductivity at different frequency	22
6. Conclusions	23
7. References	24

Introduction :-

Perovskite material with high dielectric constant have been used for technological application. Such as wireless communication, cellular phones, capacitor, resonator, filter etc [3].

Higher dielectric constant in a very tiny region will increase higher charge storage property, so for this reason electrical component is becoming smaller in size.

So my goal in this experiment is to increase the dielectric property of ATN material and measure all the property by dielectric spectroscopy. I choose Ta doped AgNbO_3 because the ionic radius of Ta and Nb is very nearly equal and also the value of bond length of Ta-O and Nb-O is supposed to be same, but due to electronegativity of Ta the bond length of Ta-O become lesser and as result of this the Tolerance factor of the system become higher and the octahedral will tilt is less than AN material ,and as result of this the total polarization of ATN at room temperature will not be zero like AN. Dielectric spectroscopy is a very power full and versatile technique to analyze the electrical property of complex perovskite oxide as it distinguishes between intrinsic and extrinsic (grain boundary, surface layer and electrode) contribution. To know more about dielectric real part and imaginary part we have plotted (ϵ' & ϵ'' versus frequency) graph. To know about various relaxation time or various dielectric constant with time we have plotted cole-cole plots well as scaling behavior has suggested that the relaxation describes the same mechanism at various temperature in ATN system. The high value of dielectric constant over a very wide range of temperature is due to the disorder in the of B-site ion in perovskite unit shell [3]. Her we choose the composition $x=0.5$ because in this composition the value of the dielectric constant is high than other composition [9]. Various relaxation process are coexist in a real perovskite unit shell, which contain number different energy barrier due to point defects which are appearing mainly technological process [2]. Therefore the departure of response from the ideal Debye model in the solid sample resulting from the interaction between dipoles and cannot be discarded.

In this paper we investigate the electrical relaxation properties of $(\text{AgNb}_{0.5}\text{Ta}_{0.5}\text{O}_3)$ in the temperature range from (30-430) & frequency range from (100Hz-1MHz) by means of dielectric spectroscopy. Dielectric spectroscopy Dielectric spectroscopy allows measurement of the capacitance and conductance over a wide range of frequency and temperature. Impedance (Z^*), permittivity (ϵ^*), electrical modulus (M^*). Studying electrical data at different condition allow

different features of the material to be recognize. Study of electrical properties, such as dielectric constant, loss tangent, Ac conductivity will help us I assessing its insulating character for potential application [1]. The electrical modulus representation has been used to provide comparative analysis of ion transport properties in different ion-conducting materials [1]. This studies are necessary for understanding structural and electrical property of the sample.

A recent microwave sub millimeter-to-infrared spectroscopic study showed that ATN could be used for microwave devices [11]. ATN shows an interesting dependence of its physical properties, such as the phase transition and the dielectric permittivity on the Ta/Nb combination. Also, ATN was found to have a weak dielectric dispersion over a very wide frequency range from 1kHz to 100 GHz [12]. According to Kania, the perovskite ATN ceramics showed high dielectric permittivity and low loss tangent with temperature-stable dielectric properties [13]. Therefore, ATN can be a potentially useful material for wireless communications, microwave technologies, and miniaturization of components [14]. The electrical properties, including the leakage current and the dielectric dispersion were found to be greatly influenced by the composition.

Experimental procedure :-

A modified solid-state reaction method was applied to prepare " $AgNb_{1-x}Ta_xO_3$ " (ATN) solid solution. " $(Nb_{1-x}Ta_x)_2O_5$ " precursor was synthesized first by grinding " Nb_2O_5 " and " Ta_2O_5 " and then heating them at a temperature of 1200°C for 12 hrs. Then " Ag_2O " was added to the precursor in appropriate amount, then grind the mixture again for 3 hours, then the mixture were sintered again in an oxygen atmosphere at temperatures of 970°C for 10 hrs. Then again the prepared solid solution is grinded for 3 hours, then filled the solid solution in the "Ball mill" for 6 hrs. Then the "BALL MILLED" and calcined sample are palletized into disc using polyvinyl alcohol as binder. Finally the discs were sintered at an optimized temperature of 1100°C for 5 hrs in O_2 atmosphere. We are doing it in O_2 atmosphere because to delay the decomposition process and we will get a very good high density [9]. The X-ray powder diffraction pattern of the sample at room temperature and the scanning electron micrograph are shown in the figure (1) & (2). The high-resolution diffraction pattern of " $AgTa_{0.5}Nb_{0.5}O_3$ " was indexed by a monoclinic unit cell and was consistent with the literature data and space group is $P2_1/m$. For the dielectric characterization, the sintered disc of (Diameter= $3.92 \times 10^{-3}\text{m}$, Area= $1.206874234 \times 10^{-5}$, thickness= 2.15mm) was polished. From the measurement we have obtained capacitance(C) and tangent loss ($\tan \delta$). By using "C" and ($\tan \delta$), we have computed dielectric constant (ϵ') and conductivity (σ) as follows

$$(\epsilon') = \epsilon_0 \frac{C}{C_0}$$

$$\sigma = \omega \epsilon_0 \epsilon''$$

ϵ_0 = dielectric permittivity in air.

$\frac{C}{C_0}$ = the ratio of capacitance measure with dielectric and without dielectric.

ω = angular frequency of the incident signal.

Theory:-

Complex Permittivity:-

When a time-varying electric field is applied across a parallel plate capacitor with the plate area of one unit and a separation of d between the plates [7], then the total current is given by

$$J_T = J + \epsilon^* \frac{dD}{dt}$$

J = conduction current

D = displacement vector

ϵ^* = complex permittivity, which is introduced to deal with dielectric losses due to the friction accompanying polarization and orientation of electric dipoles. This may be written as

$$\epsilon^* = \epsilon' - j\epsilon''$$

ϵ' = real part of dielectric permittivity,

ϵ'' = imaginary part of dielectric permittivity.

By considering the applied field to be monochromatic and sinusoidal function of angular frequency can be expressed as

$$E = E_m \exp^{j\omega t}$$

Put it in the above equation, it will come like

$$\begin{aligned} J_T &= \sigma E + j\omega(\epsilon - j\epsilon')E \\ &= (\sigma E + \omega\epsilon'E) + j\omega\epsilon E \end{aligned}$$

σ = electrical conductivity of the material

The first term on the right is a loss component due to the inelastic scattering of conducting charge carriers with scatters during their migration, which is present at all frequencies, including $\omega = 0$

(DC fields), the second term is also a loss component due to the friction in the polarization processes, which disappears when $\omega = 0$ and increases with ω , and the third term is a lossless component which is in fact the displacement current. For dielectric polymers “ σ ” is normally extremely small, and in most cases the contribution of the first term can be neglected. By ignoring the first term, the “ $\tan\delta$ ” is given by

$$\tan\delta = \frac{\epsilon''}{\epsilon'}$$

It is generally known as loss tangent,

$$\text{If } \frac{\epsilon''}{\epsilon'} \ll 1$$

$\tan\delta = \delta$ this is known as loss angle. This picture is representing an overall view of the given theory [8].

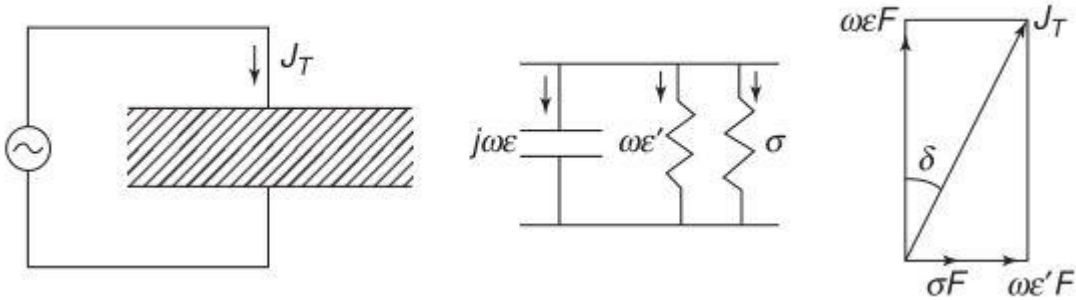


Figure -1 [8]

Conductivity:-

If the **DC conductivity** “ σ ” is not negligibly small, then “ σ ” will contribute to the imaginary part of complex permittivity (ϵ^*) [8]. The total complex permittivity become

$$\epsilon^* = \epsilon - j \left(\epsilon'' + \frac{\sigma}{\omega} \right)$$

Putting this value in "DEBYE" equation and when the

"Time period of the applied field" ($T = \frac{1}{\omega}$) \gg "DEBYE" relaxation time (τ_0) Then the dipoles cannot follow the field variation $\epsilon' = \frac{\sigma}{\omega}$

Impedance and modulus spectroscopy :-

Back ground theory-

Complex impedance is a well-known powerful tool which has been effectively used for probing into the dielectric material. This analysis enable one to resolve the contribution of various process, such as electrode effect bulk effect and interfaces the grain the grain boundary effect etc, in the frequency domain. In general the data in the complex plane could be represented in any of our basic formalism. These are complex impedance (Z^*), complex admittance(Y^*), complex modulus (M^*) which are related [3]. When the relaxation time of various process differs, so this means various capacitive components, the material have in it. In the complex impedance plot like as “Cole-Cole” plot (e'' vs e'). Depending on various values of relaxation time we will get three semicircular arc. The arc at high frequency is corresponds to grain or bulk electrical conduction. Just the arc before that corresponds to grain boundary conduction and arc at low frequency than grain boundary corresponds to electrode process. This depressed semicircle whose center lies below the real axis suggested that departure from the ideal “DEBYE” condition. The semicircle passes through a maximum frequency f_0 and satisfy the condition

$$\omega\tau = 1$$

On the other hand complex modulus and complex permittivity plot represent the response of the dielectric material [1].

Debye's classical model says that,

$$Z^* = Z' - iZ''$$

$$= \frac{R}{1 + i\omega RC}$$

This equation implies a simple parallel “RC” circuit, which give rise to a semicircle which center lies on the real axis of the complex plane (Z'' VS Z')

$$Z^* = Z' - iZ'' = \frac{R}{1 + i\omega RC} = \frac{R}{1 + (\omega RC)^2} - i \frac{\omega R^2 C}{1 + (\omega RC)^2}$$

$$Z' = \frac{R}{1+(wRC)^2} \quad , \quad Z'' = \frac{wR^2C}{1+(wRC)^2}$$

Now complex modulus is

$$M^* = iwC_0Z^*$$

W = angular frequency

$$C_0 = \text{Capacitance in vacuum} = \epsilon_0 \frac{A}{d}$$

But in most of the cases we will get a depressed semicircle which is described by the following equation

$$Z^* = \frac{R}{1+(i\omega\tau)^n}$$

$$n = (1-\beta)$$

β = It is angle of deviation from ideal semicircular arc, when " $\beta=0$ " then $n=1$ it is ideal "DEBYE" equation.

Now complex impedance plot of Z' vs Z'' are useful to determine the dominant resistance of a sample at a particular frequency. But it is insensitive for smaller value of resistance. Similarly complex Modulus plot are useful to determine the smallest value of capacitance. So we can combine this two consequence from here that the combined usage of impedance and modulus spectroscopy plot to recognize the dielectric property. The peak height of for Z'' vs f will give me the value of resistance(R) and " M " vs f will give the value of " C^{-1} " [4].

Result and discussion:-

Structural studies :-

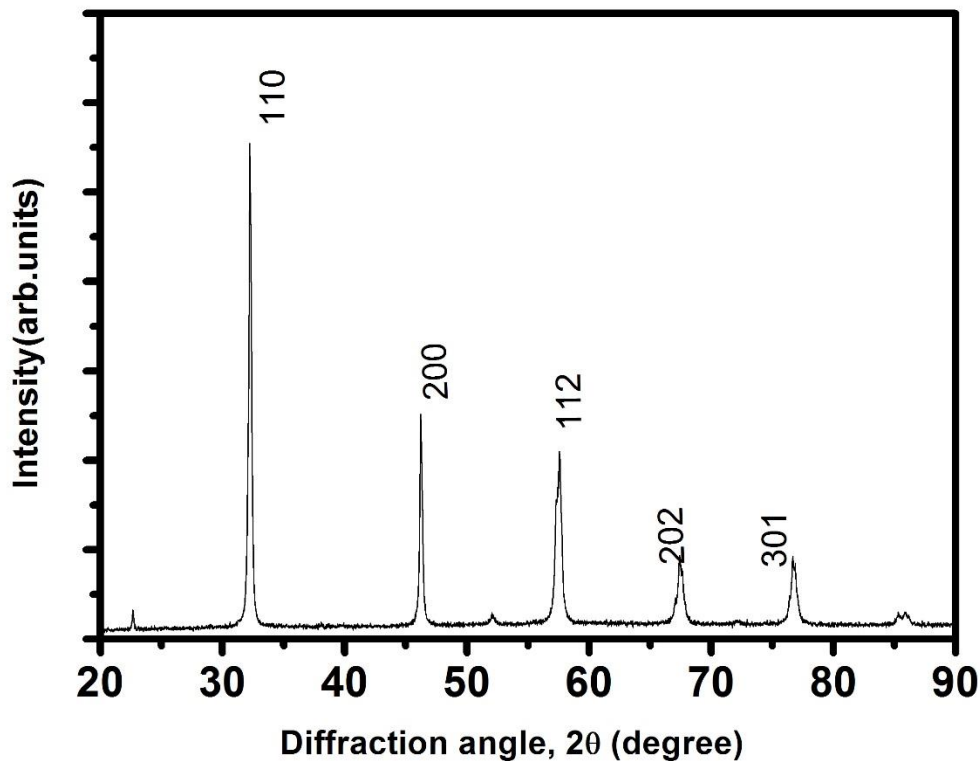


Figure-1.1

The crystalline structures of the ATN ceramics were investigated by using X-ray diffraction (XRD) patterns (Intensity vs 2θ scans with Cu-K α source). The XRD pattern shows that it has a perovskite structure with “P2/m” space group and monoclinic structure comparing with JCDs no- 510373. The values of lattice parameters (a ,b and c) can be calculated from the position of “Bragg” reflection by using “Bragg’s” law of diffraction ($2d\sin \theta = n\lambda$). The calculated lattice parameters “a ,b and c” of “AgNb_{0.5}Ta_{0.5}O₃” ceramics are (considering n=1) given below

a(Å)	b(Å)	c(Å)
2.1333	1.9611	2.6977

Microstructural studies of $\text{AgTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$:-

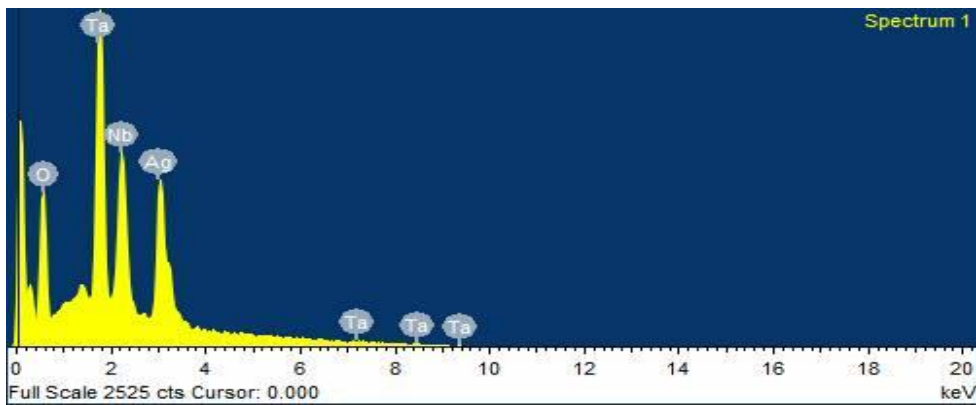
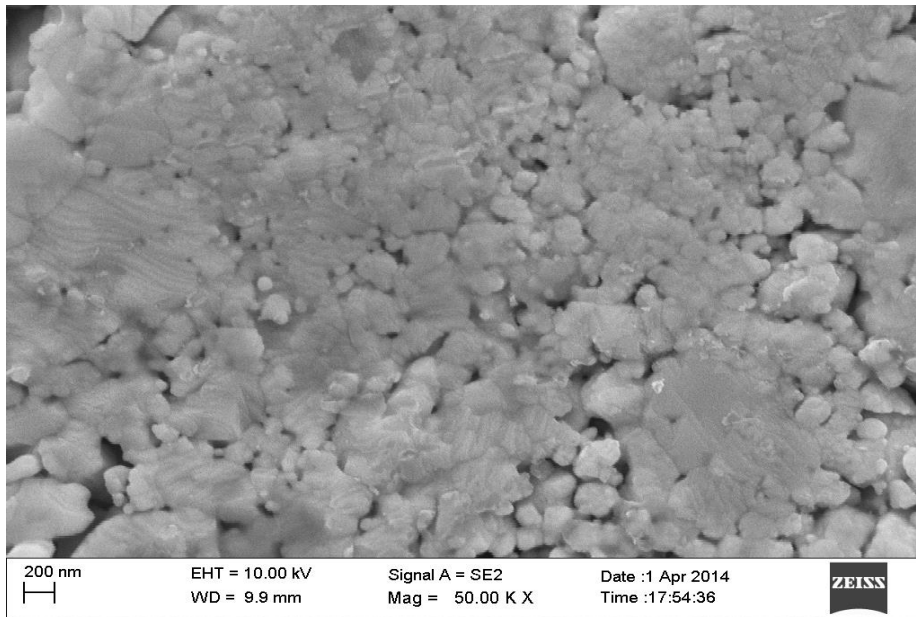


Figure-2.1 FE-SEM micro graph of ATN , Figure-2.2 Energy dispersive spectrum of a selected ATN sample

The above figure is showing the scanning electron micrograph record of polished surface of “ATN” sample to check the proper compactness of the sample. It shows that the density of the sample is good. In figure 3-b peaks at different position is showing the energy dispersive spectrum of “ATN” and confirm the presence of “Ta” in Nb, Ag, and O in the ATN sample.

Percentage of elements in the sample:-

Element	Expected Atomic %	Actual Atomic %
O	60	61.59
Nb	10	11.89
Ag	20	16.29
Ta	10	10.23
Total	100	100

From the percentage of Ta and Nb is nearly same from the figure so we can say that our stoichiometric calculation was right when we prepare our solid state method.

Raman scattering spectra:-

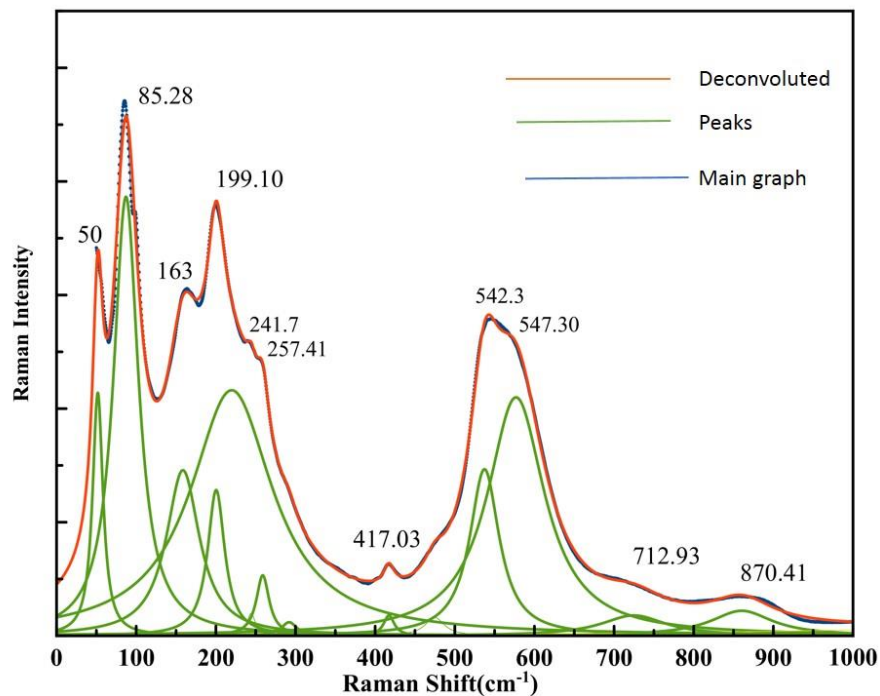


Figure- 3.1 Raman scattering spectra

The following graph is deconvoluted Raman spectra of ATN. Here various peaks are corresponds to various vibrational mode of different bond. Raman spectroscopy is based on the principle of scattering of light. In Raman spectroscopy they just occur as the difference in the frequency of incident and scattered light, respectively .Raman lines go along with a change in polarizability during the vibration .Therefore the selection rule for Raman transition are widely used to interpret the vibrational spectra and to derive the geometrical structure of the underlying molecules and cluster.

Permittivity formalism:-

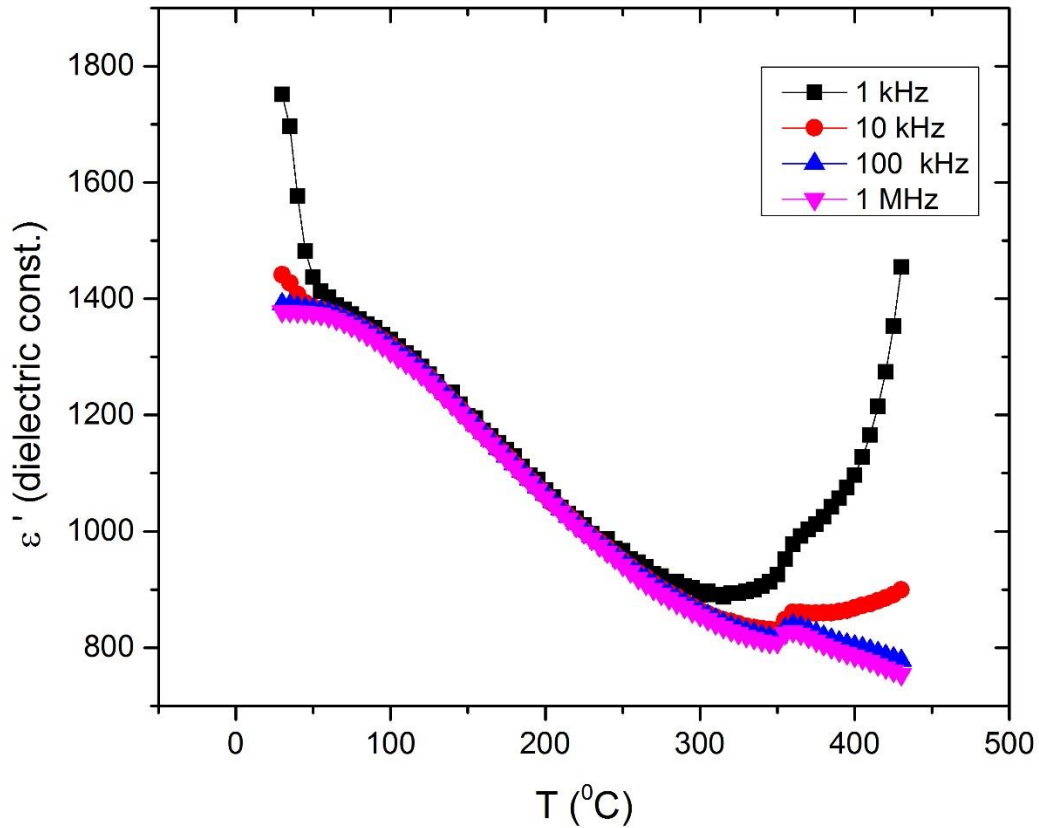


Figure- 4.1

Figure shows two peaks at nearly 50°C and 325°C, 375°C. It is also showing that ϵ' is decreasing with increasing temperature and another thing is that after 10 KHz the decreasing rate of ϵ' with temperature is same. This two peak indicates, there is a discontinuity of ϵ' , which indicates phase transition at this two Temperature (50°C and 375°C).

If we look at the graph of 1 kHz then we will see that there is also a phase transition near about 325°C. Which will be clear in ϵ' vs T graph.

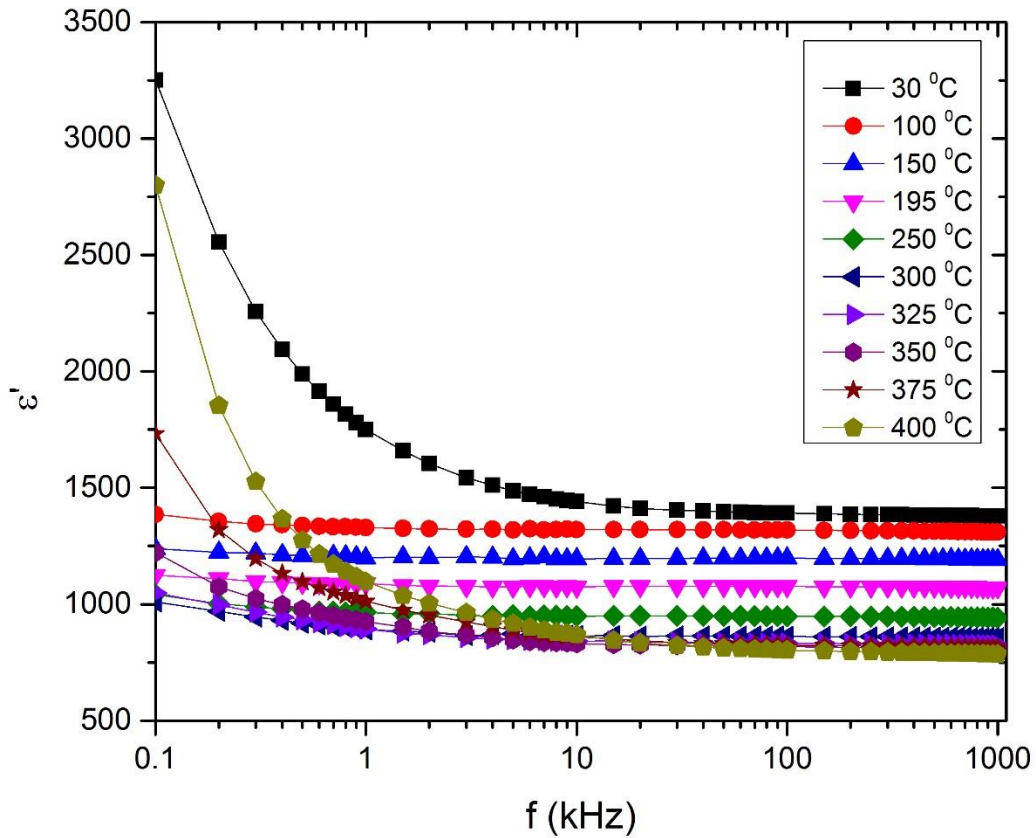


Figure -4.2

The relation of angular frequency (ω) with dielectric constant (ϵ') and tangential loss ($\tan\delta$) at various temperature of ATN is described in figure-3 and figure-5. The variation of (ϵ') with frequency explains the relaxation phenomena of the material, which are associated with the frequency dependent orientation polarization. The value of (ϵ') is remaining constant with increase of the frequency, so it is showing the fact that at low frequency the dipoles orient themselves to the field direction and contribute to the total polarization of the material. But at high frequency the dipoles cannot follow the field so they will not align in the same direction so as a result of this the polarization of the material will be less and as a result of this the dielectric permittivity will decrease. So as a result of this (ϵ') will decrease [2-5].

Another thing that we are observing that is phase transition. Because with the increase of temperature dielectric constant is decreasing up to 300 °C (it is because of with increase in temperature space charge will increase), but after 325 °C it starts to increase and again at 375 °C it is showing some increase. So we can conclude that there are two phase transition one is nearly at 325 °C and another is at nearly 375 °C.

Loss tangent formalism:-

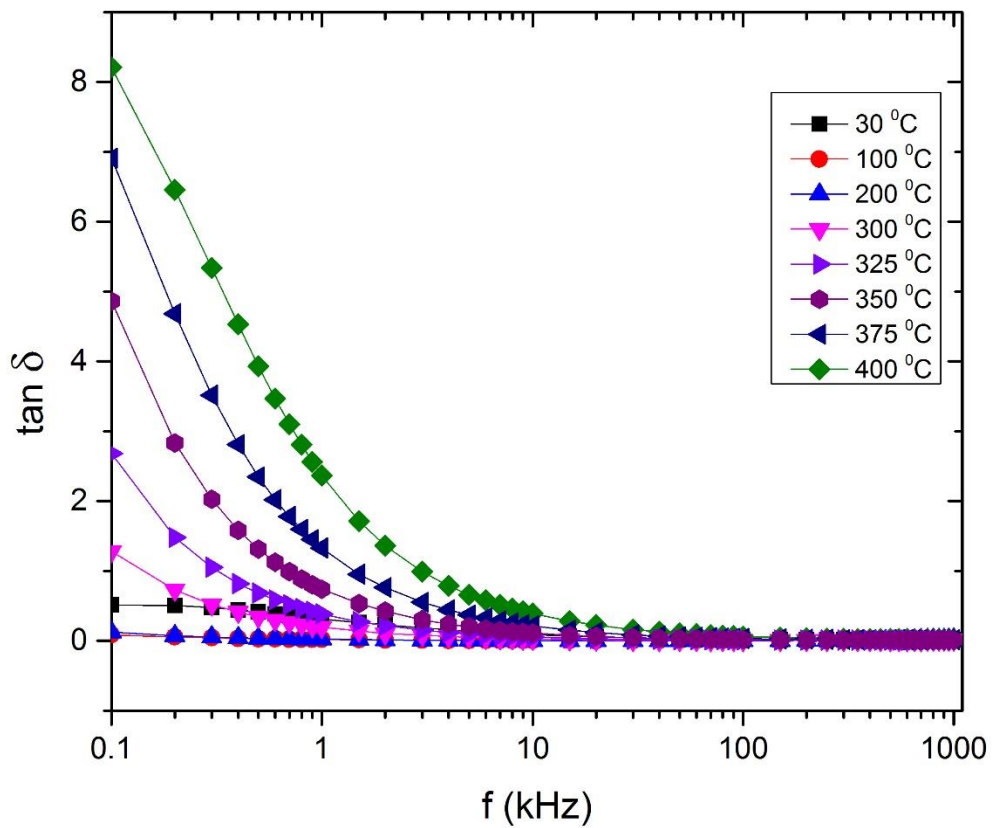


Figure-4.3

Figure- 5a- logarithmic angular frequency of loss tangent ($\tan \delta$) vs frequency (kHz)

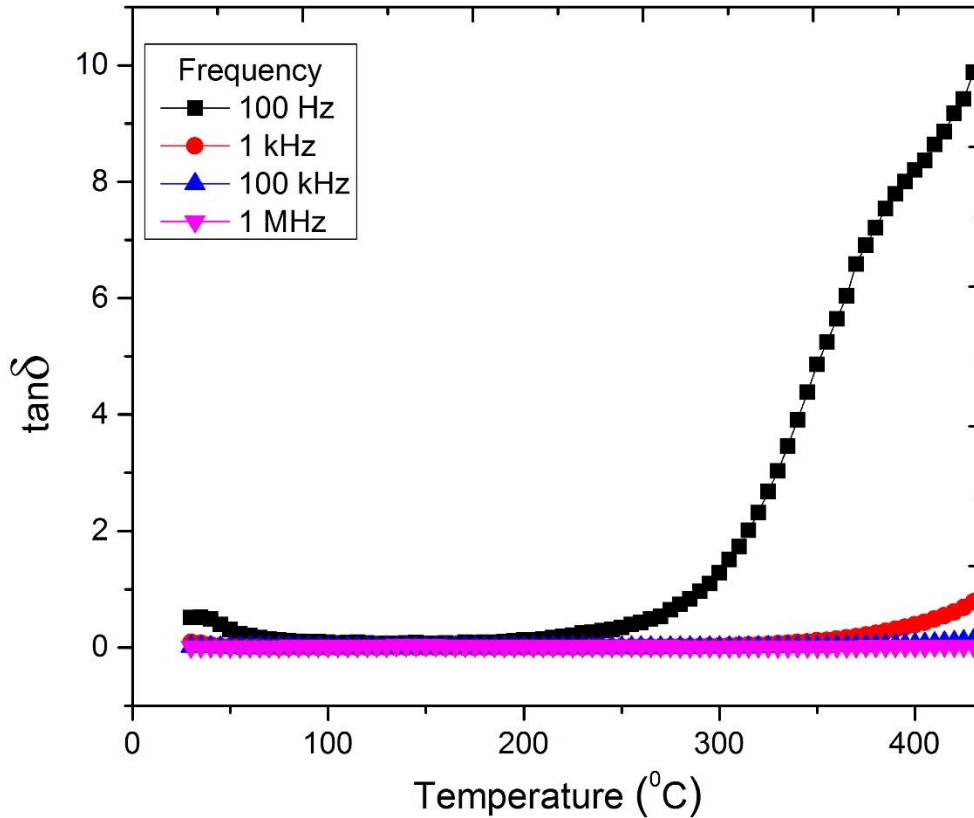


Figure - 4.4 Temperature dependence of loss tangent ($\tan \delta$) vs Temperature (T °C)

Dielectric loss is the electrical energy loss as heat in the polarization process in the presence of an applied ac field. So the dipoles are absorbing energy from the field and converted into heat during polarization. Dielectric loss is a function of frequency and temperature and it is also related with relaxation polarization, in which the dipole cannot follow the frequency variation of field without a measurable lag because of the frictional force of the rotating dipoles. Also the change in polarization of the dielectric causes a polarization current (from Maxwell law the polarization or bound current is $\epsilon \frac{dE}{dt}$) to flow, which is induced by the relaxation rate. This induced current will mainly create loss at high frequency. So there is always a phase difference between the polarization and the applied field, which will give rise a dissipation factor $\tan \delta$ [8].

The dielectric loss tangent $\tan \delta = \frac{\epsilon''}{\epsilon'}$ of ATN at different temperature is plotted in figure.

From (30° C – 200° C) is almost constant with the change in frequency. But from (300° C - 400°C) it is changing abruptly, so a strong dispersion of $\tan \delta$ exist from 10Hz to 10KHz in this temperature range. It shows that number of charge carriers are increasing with the increase in temperature, describing the thermally activated nature of the material. The first increasing nature in $\tan \delta$ at low frequency is due to DC conductivity. Figure-4b is depicting that at high temperature low frequency loss is more that is due to the number of space charge is increasing with the increase in temperature ,and the space charge effect is dominant at low frequency, so at low frequency and high temperature the loss is mainly due to space charge effect which are thermally generated [2-6].

If we compare our system with a system which consists a parallel plate capacitor and a resistance is connected parallel with it. So at low frequency capacitive path will be closed due to high impedance and all loss will be there is due to Joule heat loss in resistance. But at high frequency the capacitive path become open to flow current and all loss at that time is due to the dielectric loss of the material in between the plate of the capacitor. This loss will occur because at high frequency the dipole will not get enough time to relax, then it can't follow the applied field and as discussed in the theory of loss tangent the loss angle “ δ ” will increase, so loss will increase.

Imaginary part of permittivity (ϵ'') vs frequency:-

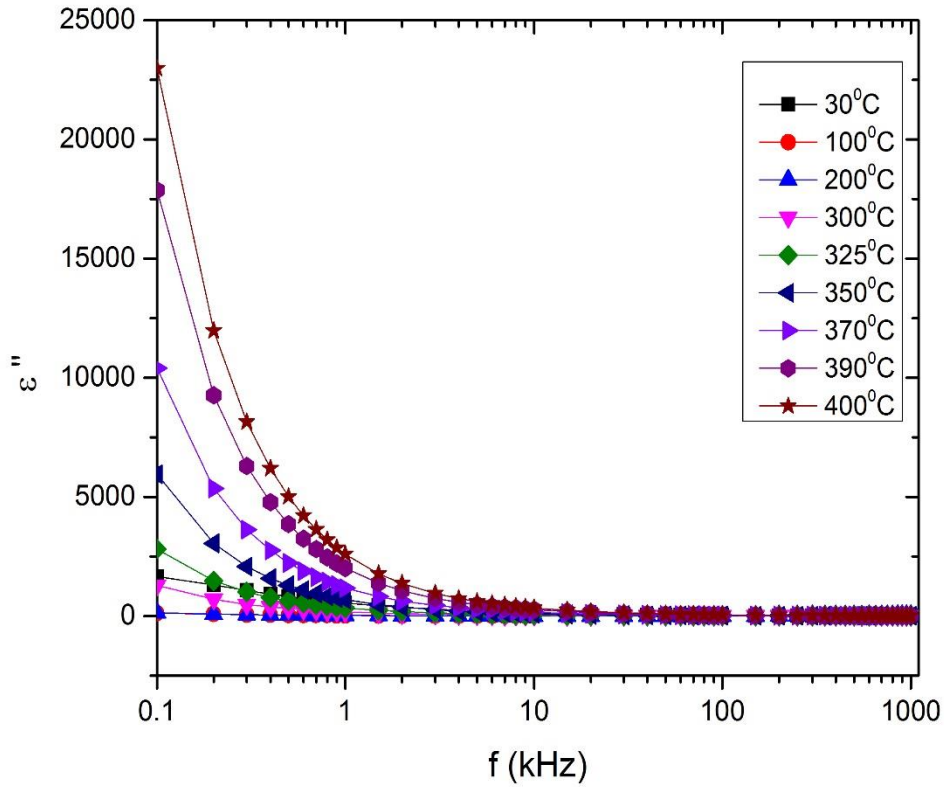


Figure-4.6

From this graph also one can conclude that Dielectric loss at low frequency is higher when temperature is higher. Mainly near the transition temperature the values of (ϵ'') is higher than other temperature at low frequency. This is happening because of space charge. At higher frequency the loss is zero because the field cannot follow the field and space charge cannot causes loss at high frequency because space charge polarization is dominant in lower frequency range.

Cole-Cole plot:-

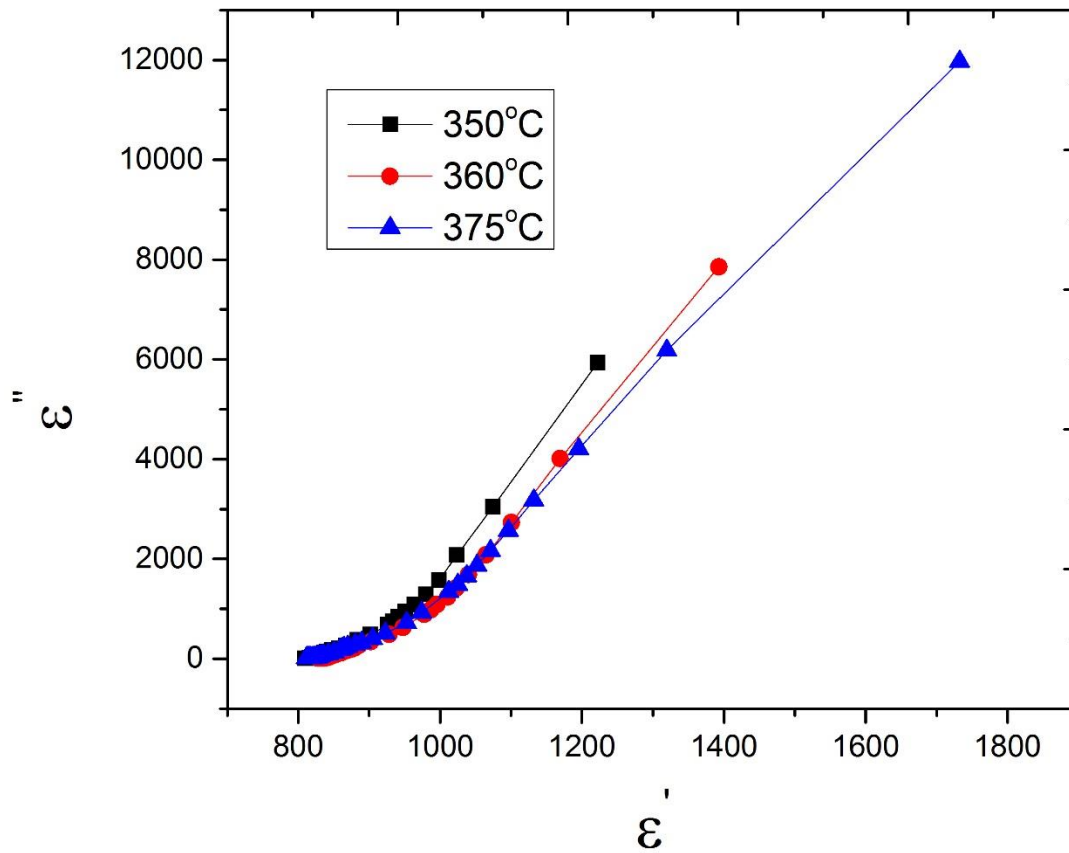


Figure-5.1

If we will fit it then we will get two semicircle one is due to grain and another is due to grain boundary. The relative position of the two arcs in the complex plane can be identified by frequency. The arc of bulk generally lies in the frequency range higher than that of interfacial boundary science the relaxation time $\tau_m = 1/\omega_m$ for the interfacial boundary is much larger than that for bulk crystal. When the bulk resistance is much lower then and the resistance of the equivalent circuit is dominate by interfacial boundary resistance then the arc due to bulk may not be visual in that limited frequency range.

Conductivity formalism:-

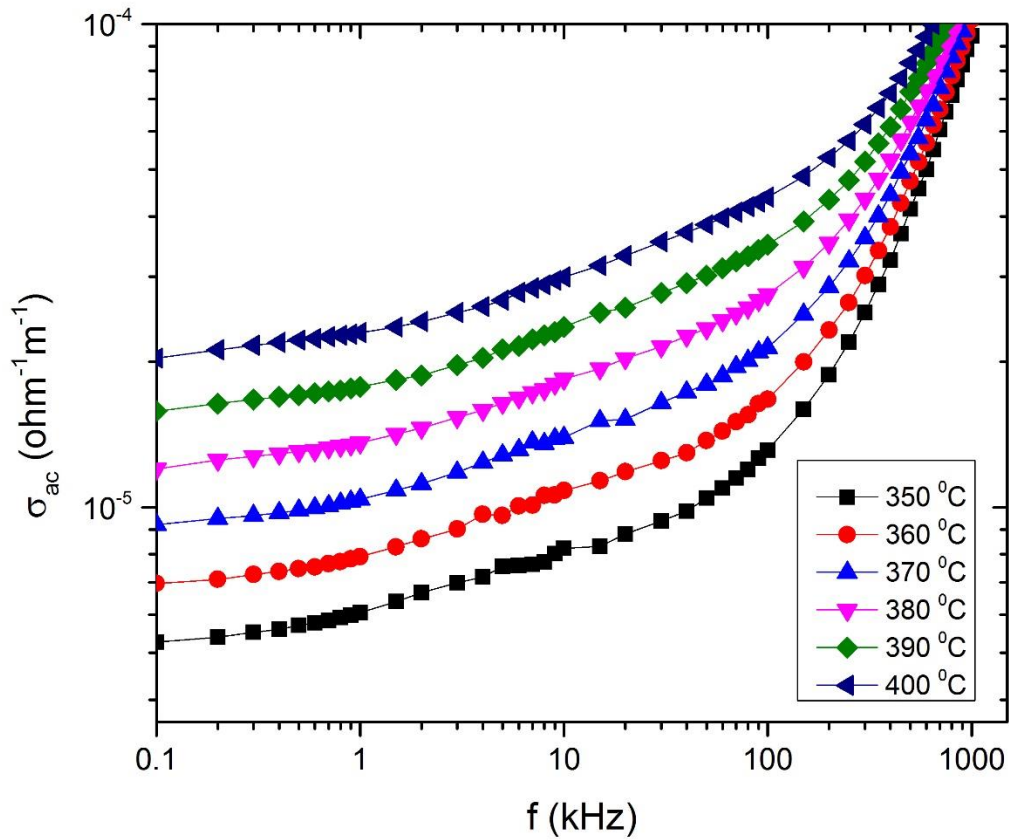
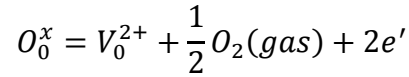


Figure- 5.2

Figure-7 is showing log- log plot of frequency dependence of ac conductivity for ATN at various temperatures. The conductivity increases with the increase of frequency. At higher temperatures, a plateau is observed in the plots in the low frequency region, that is a region where conductivity “ σ ” is independent on frequency. the plateau region extends to high frequency with the increase in temperature. It is concluded from here is that at low frequency region the random diffusion of charge carrier via hopping give rise to a frequency independent conductivity. At high frequency $\sigma(\omega)$ exhibits dispersion, it is increasing in power law fashion and at last become almost linear.

It is to be mentioned that the sample ATN is synthesized at high temperature(=1100°C), so a slight amount of oxygen loss can occur and may be expressed as “Kroger-Vink” notation [7]:



O_0^x =loss of lattice oxygen, V_0^{2+} =presence of oxygen ion vacancy, e' = is the electron released or capture. This Oxygen vacancies facilitate the appearance of dipole formed with the an adjacent host ion and enlarge the rattling space available for dipole vibration, so as a consequence of this leads to the short range hopping of ions and give rise to a relaxation. The O_2 ion jumps from one vacancy to another vacancy to give rise to a transportation of ion and give rise to conductivity in the material.

Joncher power law [10] can be written as

$$\sigma(\omega) = \sigma(0) + A\omega^n$$

$\sigma(\omega)$ = total conductivity

$\sigma(0)$ = dc conductivity

So it is observed from the figure that at low frequency “n” is nearly equal to zero. But at high frequency region “n” has some value. For this reason at high frequency region there exist a strong dispersion of conductivity.

Conclusion:-

Our aim is to improve the dielectric property of AN sample. The dielectric property of a complex perovskite oxide Silver Tantalum Niobate (ATN) is synthesized by the solid state reaction technique is investigated in the temperature range from 30°C to 430 °C. The capacitance and conductance of ATN are measured in a frequency range from 100Hz to 1MHz at various temperature 30 °C to 430 °C. The X-Ray diffraction analysis shows that the compound is orthorhombic structure. The micro graph of ATN shows the expected atomic percentage. The Raman spectra is showing various modes but to conclude about which modes are coming from which bond . The increasing dielectric constant (ϵ') with increasing in temperature is attributed to the conductivity which is directly related with increase in mobility of localized charge carriers. The frequency dependence conductivity spectra follow the Jonscher power law.

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