Temperature Dependent Dielectric, Conductivity and Electric Modulus of CuO-Mn$_2$O$_3$ Composites

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ABSTRACT

$_{1-x}$CuO-$_x$Mn$_2$O$_3$ where x = 0.05, 0.10, 0.15 & 0.20 ceramic composites have been successfully synthesized by adopting conventional mixing method using ball milling machine. Composites mentioned above in appropriate stoichiometric proportion prepared by mixing of CuO and Mn$_2$O$_3$ oxides and ball milled for 12 hours using zirconia ball and non-reacting solvent (water). The temperature dependent dielectric, conductive properties as well as electric modulus of prepared composites have been investigated. Both ε' & ε" increases with increase in temperature whereas decrease in value of M´ results for reduction in resistive behavior. The shifts in maxima in M" with temperature as well as frequency reveals presence of frequency as well as temperature dependent dielectric relaxation. The increase in conductivity directly reveals enhancement in conductive behavior due to increase of Mn$_2$O$_3$ concentration in CuO-Mn$_2$O$_3$ ceramic composites.

Keywords: Composites material; Metal Oxide; Electric Modulus; Conductivity, Dielectric Relaxation,

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INTRODUCTION

Due to their excellent response in semiconducting properties, metal oxides from transition metal category attracts major attention of researchers in materials science, technologists and engineers from various sectors of semiconducting industries in past few years. Due to vast usage of transition metal oxide in many component of semiconducting devices such as p-type semiconductor made these oxide materials potential candidates for various industrial applications in various technological domains such as magnetic storage, electrode materials, catalysts, noble cathode materials in dye solar cell etc(1–8). The creation of superior nanostructures with regulated, sized and morphological characteristics is essential for the development of nano devices and various other applications such as sensing, pharmaceutical, catalyst etc. CuO belongs to transition metal oxide group and has a small bandgap of p type. Along with its monoclinic structure, it possesses a number of intriguing qualities, including high stability, photovoltaic capabilities, super thermal conductivity, and antibacterial activity. CuO has unique qualities that make it useful in a wide range of technical applications. Active catalyst gas sensors, high-efficiency thermal conducting materials, data storage etc. Due to its monoclinic crystal form and high electrical conduction, copper oxide (CuO) may have certain physical characteristics. Because crystalline CuO nanoparticles have a narrow energy band gap, they can be used for photovoltaic and photocatalytic processes. Copper oxide (CuO) has become a key material in technology due to the physicochemical properties of the nanocomposites that contain CuO NPs incorporated into them (9–13). These properties include great chemical stability, low toxicity, and semiconducting characteristics. Furthermore, it is now a viable choice for energy storage system applications. Super-capacitors, an additional device that sits between batteries and ordinary capacitors, have also drawn a lot of interest due to their beneficial characteristics.

In this paper, we report temperature dependent dielectric, electric modulus and conductivity (σ_{ac}) properties of $_{1-x}$CuO-$_x$Mn$_2$O$_3$ (x = 0.05, 0.10, 0.15 & 0.20) ceramic composites. The temperature dependent dielectric response (variation of ε' & ε") vs. frequency has been studied. Apart from dielectric behavior, dielectric relaxation and resistive behavior has also be

studied from temperature dependent electric modulus response. Effect of Mn_2O_3 on conductivity properties has also be explored as temperature increases.

EXPERIMENTAL DETAILS

Preparation of Cuo and Mn_2O_3 Composites
Ceramic composites of $_{1-x}CuO-_xMn_2O_3$ (x = 0.05, 0.10, 0.15 & 0.20) have been successfully synthesized using mechanical mixing approach. For mechanical milling approach, planetary ball milling machine has been used. Pristine CuO and Mn_2O_3 of analytical grade purchased from Sigma Aldrich have been mixed in above-mentioned stoichiometric proportion using mechanical mixing approach. The as prepared CuO and Mn_2O_3 weighed in above-mentioned proportion by wt% and ball milled in presence of non-reacting solvent (water). For this, powder and non-reacting solvent transferred into bottles along with circular shaped zirconia ball and milled for 24 hours. After completion of milling process, powder taken out from bottles and let for dried. The dried powder mixed of 2 wt% polyvinyl alcohol act as binder. For this, weighed polyvinyl alcohol dissolved in water and stirring until clear solution obtained. The ball milled powder in mentioned stoichiometric proportion thoroughly mixed with solution of polyvinyl alcohol & water. The mixed powder pressed in disc of roughly 10 mm in diameter and thickness about 0.5 mm. The disc sintered at 900 °C for densification. The sintered pallets have been characterized for electric modulus, dielectric and conductivity properties. For this, circular electrode has been deposited on both side of circular shaped disc for making parallel plate like capacitor across which external ac signal has been applied.

Characterisation Techniques
Complex Impedance Spectroscopy:
The real and imaginary components of electrical impedance as well as dielectric permittivity has been studied using complex impedance spectroscopy. Contribution of grain and grain boundaries to electrical properties through the analysis of Nyquist plots and conduction mechanism from universal Johncher's power fitting of conductivity data at different temperatures has been studied using complex impedance spectroscopy (CIS). This is valuable and important characterizing technique in material science. These electrical properties were ascertained using Keysight Technologies (E4990A) using impedance analyzer. All of these characteristics were calculated from empirically acquired Z versus θ at various temperatures using recognized equations.

$$\text{Complex Impedance}, Z^* = Z' - jZ''$$
$$\text{Complex dielectric constant}, \varepsilon^* = \varepsilon' - j\varepsilon''$$
$$\text{Complex electric modulus}, M^* = M' + jM''$$
$$\text{Also}, \tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Where Z', ε', M' and Z'', ε'', M'' denote the real and imaginary parts of the impedance, dielectric constant and electric modulus respectively and $j = \sqrt{(-1)}$.

RESULTS & DISCUSSION

Dielectric Spectroscopy
Temperature dependent Real part of dielectric permittivity ε' vs. frequency analysis
Real part of dielectric permittivity ε' vs. frequency (Hz) of $_{1-x}CuO-_xMn_2O_3$ (x = 0.05, 0.10, 0.15 & 0.20) ceramic composites in temperature 298K-548K range has been shown in figure 1. It has been clear visualize from graphs that value ε' exhibits maximum value in lower frequency region and as frequency increases; value starts decreases and after some particular frequency, shows almost linear variance w.r.t. frequency. Such type of behavior represent general behavior of dielectric materials. In such kind of behavior, value of dielectric constant depends upon contribution of various polarization like Ionic, Dipolar, electronic & Space Charge with frequency variation. In lower frequency range, maximum value of ε' may results due to contribution of all polarizations (Ionic, Dipolar, electronic & Space Charge) whereas smaller value shows elimination of some polarizations at higher frequencies.

In higher frequency range, diploe orientations of dipoles lags behind than the electric field. This causes a filtration of various polarizations, which lowers material's net polarization and, as a result, resulting in low values of ε' in higher frequency region and beyond certain maximum value of frequency, dielectric constant become almost constant and this may only due to contribution of space charge polarization only. It has also depicted from graph that real component of dielectric constant (ε') continuously increases as temperature increases (14–19). The increased dielectric constant with increasing temperature increase mobility of charge carriers with rising temperatures causes dielectric constant increased. Interfacial polarization, not dipolar polarization, is responsible for this effect. Thermal vibrations are the main cause for dispersion loss increase with temperature and frequency. Interfacial polarization has no more effect in value of ε'.
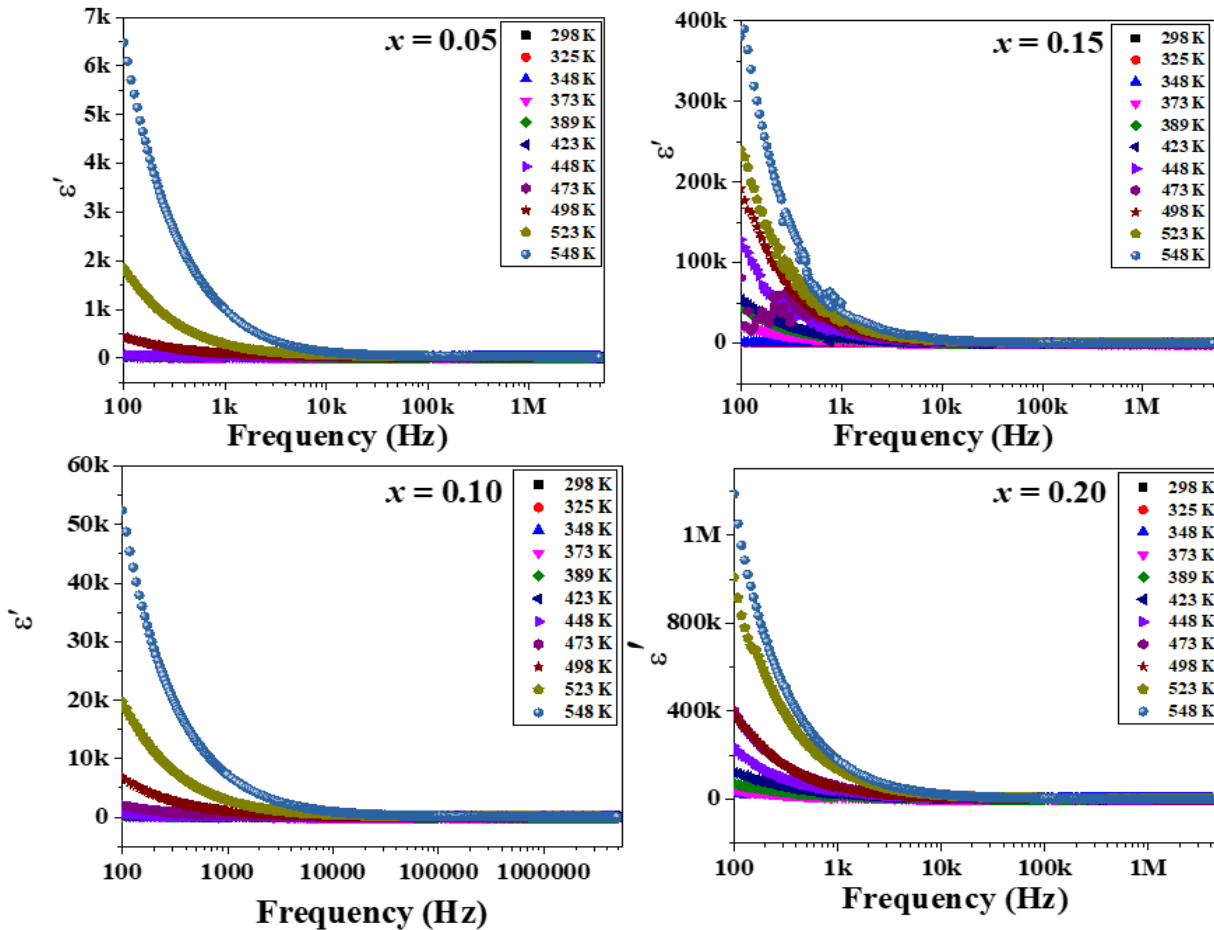
Figure 1: ε' vs. Frequency (Hz) at Different Temperature of $_{1-x}$CuO-$_x$Mn$_2$O$_3$ (x = 0.05, 0.10, 0.15 & 0.20)

Temperature dependent Imaginary part of dielectric permittivity ε" vs. frequency analysis

Temperature-dependent ε" vs. frequency of $_{1-x}$CuO-$_x$Mn$_2$O$_3$ (x = 0.05, 0.10, 0.15 & 0.20) ceramic composites in temperature 298K-548K range has been shown in figure 2 in fill frequency range ~ 1 MHz. Graphs show that imaginary parts of dielectric permittivity (ε") reach their maximum value prior to 1 kHz, indicating a lower frequency regime. Thereafter, value of dielectric constant (Imaginary part ε") continuously decrease with increasing frequency, confirming that the prepared samples behave in a simple manner consistent with that of normal dielectrics. The existence of all polarizations (ionic, dipolar, electronic, and space charge polarization) results in the maximum value of the real and imaginary parts of dielectrics (ε"). A continuous decrease followed by a linear variation may result from the elimination of some polarizations (space charge polarization) at higher frequency region and almost constant value of dielectric constant (Imaginary part) may results only due to contribution of space charge polarization among all various type of polarizations that paly significant role in value of dielectric constant.

The graphs clearly show that the dielectric permittivity values (ε") continuously increases with increasing temperature achieved maximum value. Such a trend can be explained by theory that increased dielectric constant with simultaneous increasing of temperature may be the result easy orientation of dipoles with respect to applied field in presence of given temperature because they have received enough energy to do so, either from external heat sources or from enough energy to overcome thermal barriers. Temperature-dependent dielectric relaxation occurs when a dipole unable to respond appropriately outside of this temperature range (16,17,19). This kind of behavior can be explained by thermal energy that heating provides to dipoles. As a result, dipoles' response to applied fields becomes easier, which raises their dielectric permittivity (Imaginary part). The increased dielectric constant with increasing temperature increase mobility of charge carriers with rising temperatures causes dielectric constant increased. Interfacial polarization, not dipolar polarization, is responsible for this effect. Thermal vibrations are the main cause for dispersion loss increase with temperature and frequency. Interfacial polarization has no more effect in value of ε'.
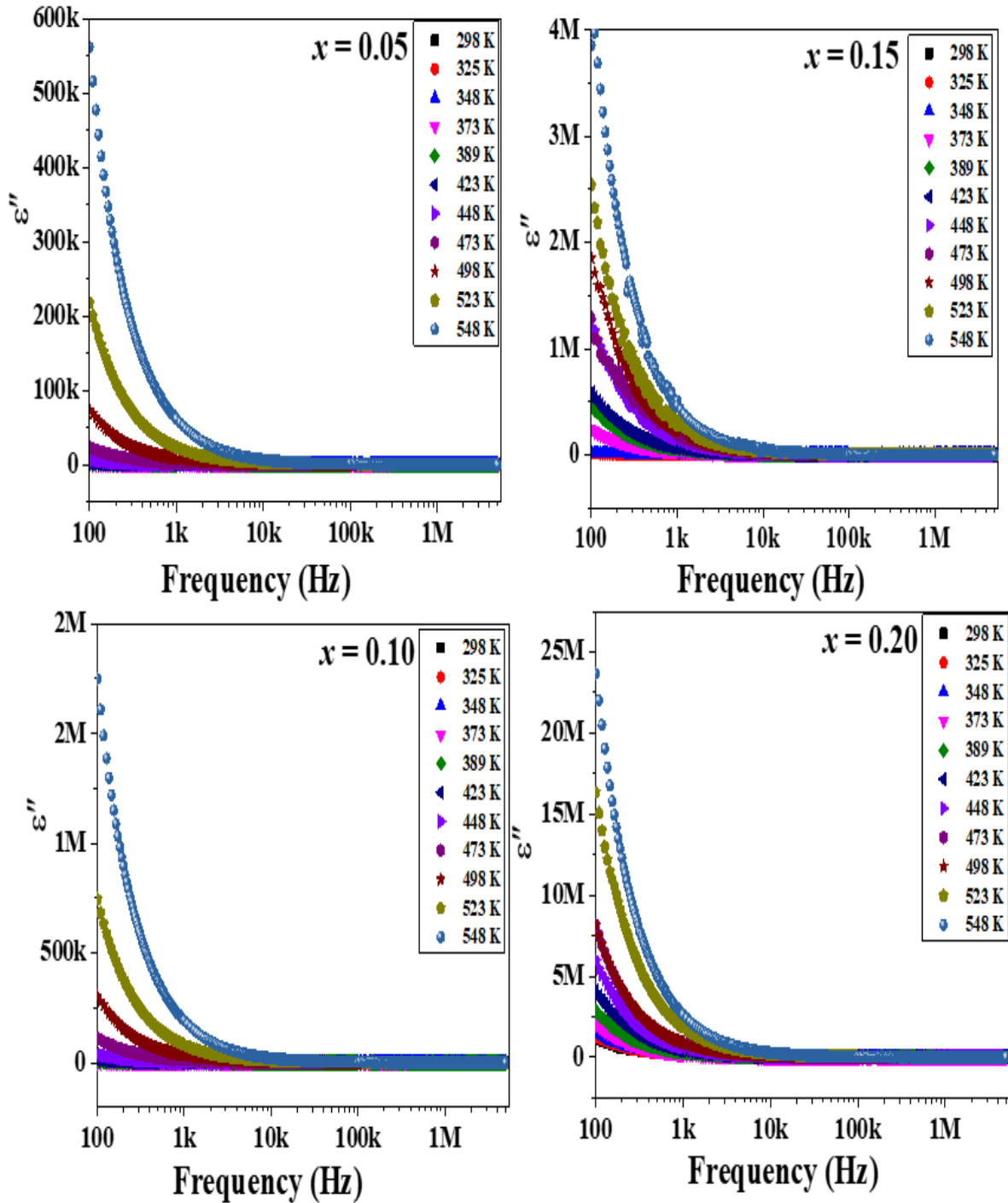
Figure 2: ε" vs. Frequency (Hz) at Different Temperature of $_{1-x}CuO-_xMn_2O_3$ (x = 0.05, 0.10, 0.15 & 0.20)

Conductivity Spectroscopy
ac conductivity σ_{ac}vs Frequency analysis
Figure 3 shows σ_{ac}vs Frequency (Hz) of $_{1-x}CuO-_xMn_2O_3$ (x = 0.05, 0.10, 0.15 & 0.20) ceramic composites in temperature 298K-548K range has been shown in figure 3 over entire frequency range (up to 1 MHz). Graphs show that there are two segments (a) frequency independent, which represents dc conductivity (σ_{dc}) & (b) frequency variable, whichmay higher frequency regime, referred to as ac conductivity (σ_{ac}).
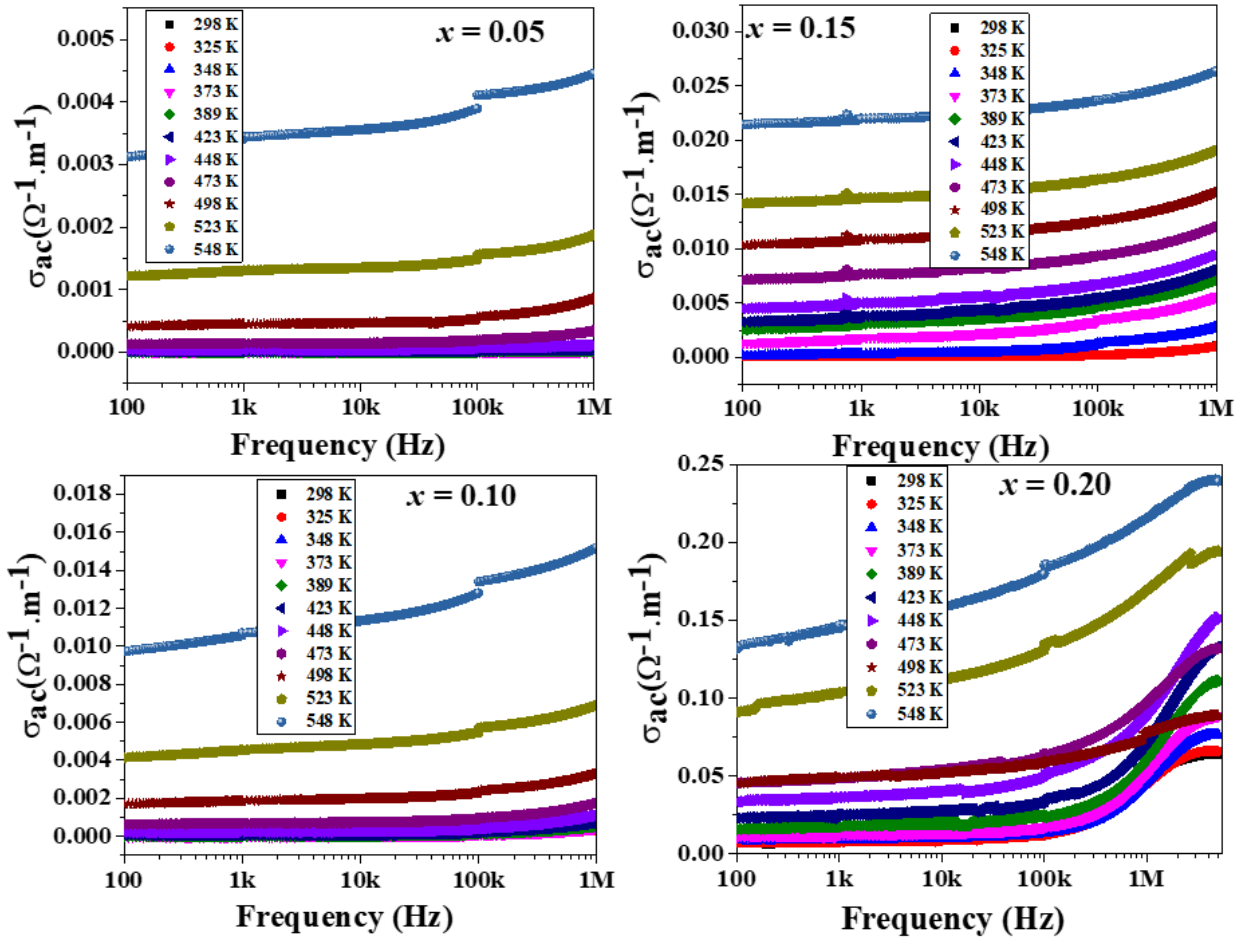
Figure 3: $\sigma_{ac}(\Omega^{-1}m^{-1})$ vs. Frequency (Hz) at Different Temperature of $_{1-x}CuO-_xMn_2O_3$ (x = 0.05, 0.10, 0.15 & 0.20)

To further study type of conduction mechanism in prepared, the experimentally collected ac conductivity has been used to analyse the conduction mechanism using the universal Johnson's power law:

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

In this case, "n" is a dimensionless parameter, A is the dispersion parameter that represents the strength of polarizability, and σ_{ac} and σ_{dc} are the ac and dc conductivities, respectively. Graphs make it abundantly evident that conductivity rises with temperature. It has been clearly perceived from graphs that conductivity increases with increasing temperature. The increase of oxygen vacancies due to temperature may results for uninterrupted increase in electrical conductivity.

The rise of oxygen vacancies as a result of results in an increase in conductivity with both increasing temperature as well as Mn_2O_3 concentration in composites (20–23).

Electric Modulus M´and M"
Electric Modulus M´ vs frequency analysis
M´vs. frequency in temperature range varies from RT 323K-548K of prepared ceramic composites of $_{1-x}CuO-_xMn_2O_3$ (x = 0.05, 0.10, 0.15, & 0.20) in entire frequency range from 100 Hz-10^6 Hz has been shown in figure 4. It has been clearly depicted from graphs that value of M´ starts reducing with continuous increment of both frequency as well as temperature simultaneously directly manifest that in prepared composite samples, prepared samples exhibit negative temperature coefficient of resistance (NTCR) (15) which can also be verified from reduction in value of Z´ (real part of impedance) as well as regular increased in value of conductivity discussed in above section. The reduction in value of M´ with increasing temperature clearly evident for reduction in resistive characteristics of prepared ceramic composites with continuous increase in temperature. This reduction in resistive response may also results in an increased conductive behavior. The increasing concentration of Mn_2O_3 in prepared ceramic composite in above mentioned stoichiometric proportion may also results due to increasing concentration of oxygen vacancies formed when sample get heated. The decreased resistive response or barrier properties can also be explained from temperature dependent conductivity response (15,16).
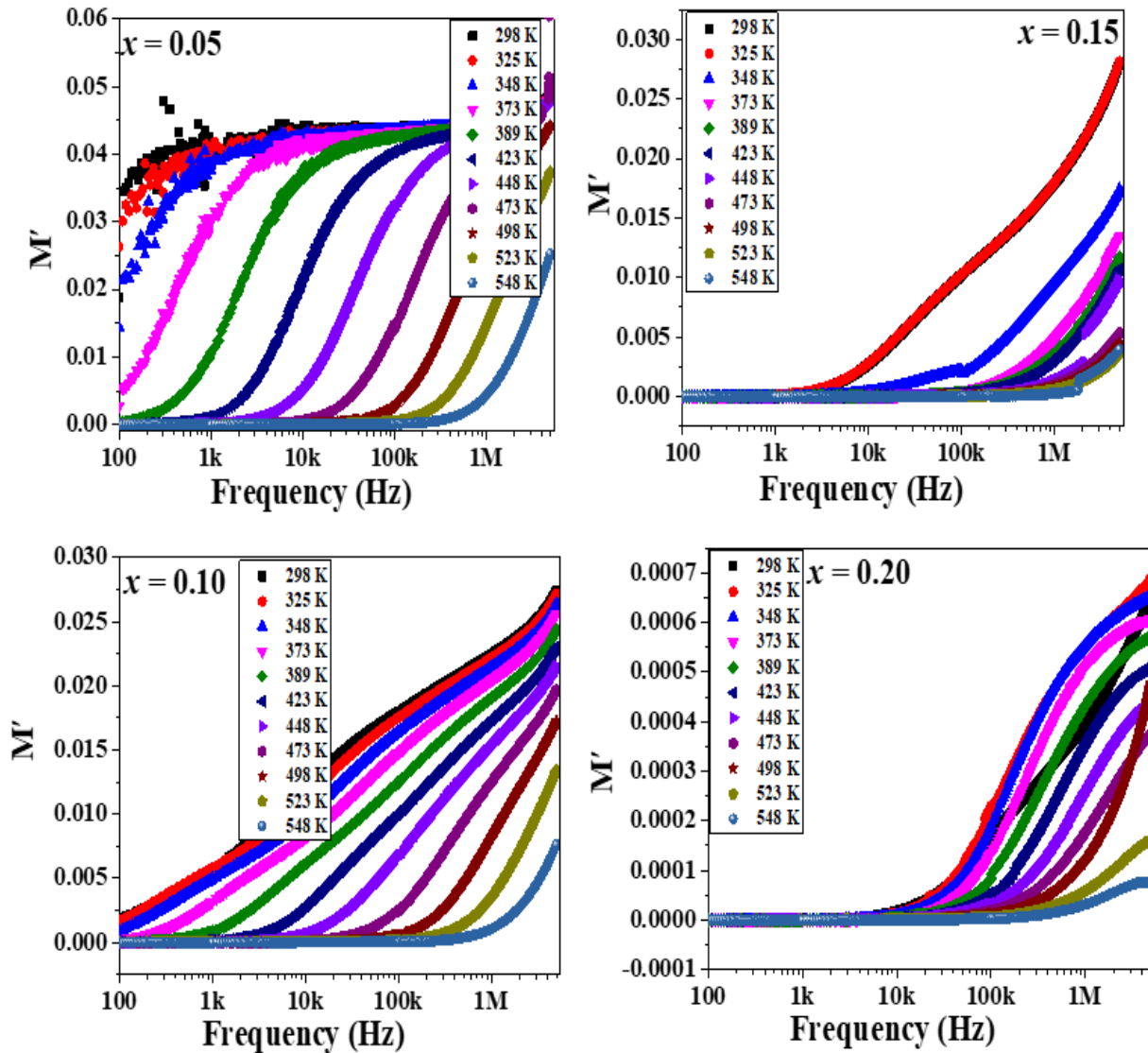
Figure 4: M' vs. Frequency (Hz) at Different Temperature of $_{1-x}CuO$-$_xMn_2O_3$ (x = 0.05, 0.10, 0.15 & 0.20)

Electric Modulus M" vs frequency analysis

M"vs. frequency in temperature range varies from RT 323K-548K of prepared ceramic composites of $_{1-x}CuO$-$_xMn_2O_3$ (x = 0.05, 0.10, 0.15, & 0.20) in entire frequency range from 100 Hz-10^6 Hz has been shown in figure 5. It has been clearly depicted from graphs that the value of M"continuously decreases with increasing both frequency as well as temperature continuously   clearly evidence for presence dielectric relaxations. In sample for x = 0.20, absence of maxima reveals absence of dielectric relaxation whereas in samples x = 0.05, 0.10 & 0.15, maxima represents confirmation of presence of frequency dependent dielectric relaxations.

The maxima also shifts towards maximum region of frequency as temperature increases continuously, also responsible for temperature dependent dielectric relaxation and this relaxation continuously disappeared as concentration of Mn_2O_3 increases in above mentioned stoichiometric proportion for preparation of ceramic composites. In sample x = 0.20, sample does not exhibits maxima results for absence of frequency as well as temperature dependent dielectric relaxation. The continuous shift in maxima of M" vs. Frequency with temperature accounted for presence of temperature dependent dielectric relaxation (13–15) and merging at higher temperatures reveals for elimination of space charge polarization (16,17).
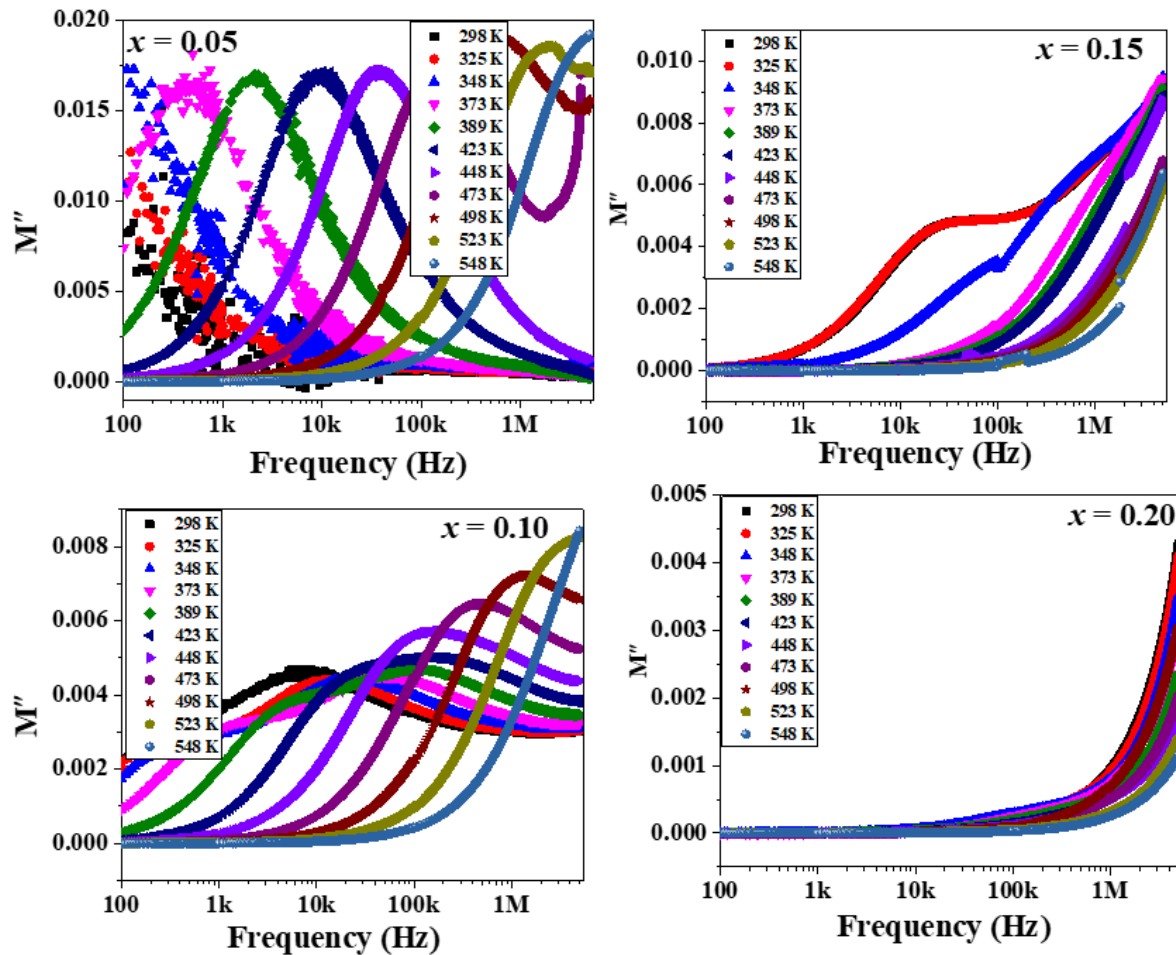
Figure 5: M" vs. Frequency (Hz) at Different Temperature of $_{1-x}CuO-_xMn_2O_3$ (x = 0.05, 0.10, 0.15 & 0.20)

CONCLUSION

$_{1-x}CuO-_xMn_2O_3$ where x = 0.05, 0.10, 0.15 & 0.20 ceramic composites have been successfully synthesized using conventional mixing method using ball milling machine. The both real and imaginary part of dielectric constant (ε' & ε") increases with simultaneous increase in temperature and frequency, suggesting that materials dipoles responds maximum to applied external signal and results in maximum orientation due to easily overcome of thermal barrier of dipoles by gaining enough energy from external temperature during measurement. The decreased in value of real part of electric modulus (M') confirms for reduction of resistive behavior of prepared ceramic composites along with increased conductive behavior. The enhanced conductive response may results due to increased no. of oxygen vacancies due to simultaneous increase in temperature as well as concentration of Mn_2O_3 in ceramic composites according to above mentioned stoichiometric proportion. The absence of maxima in imaginary part of electric modulus responsible for absence of dielectric relaxation (Both frequency as well as Temperature Dependent) in sample x = 0.20 whereas in sample x = 0.05, 0.10 & 0.15, shifts in position of maxima towards maximum range of frequency with both increasing frequency as well as temperature evidence for presence of frequency as well as temperature dependent dielectric relaxations

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