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Dielectric and ac conductivity of ilmenite-type $CdTiO_3$ ceramic

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Abstract: Cadmium titanate $CdTiO_3$ powder sample was prepared using the sol-gel route and calcined at 900°C. The dependence of the permittivity, loss tangent (tan δ) on the temperature in the range 40–600°C, and frequency in the range 10^3–2.10^6 Hz for the pure hexagonal ilmenite is reported. The ln(σac) versus T plots suggest that the conduction mechanism is of ionic hopping nature. The evolution of ln(σac) as a function of frequency suggests that the ionic hopping conduction decreases with the rise in temperature. The complex impedance plots revealed two depressed semicircular arcs indicating the bulk and interface contributions. The bulk resistance was found to increase with a decrease in temperature exhibiting typical semiconductor-like behavior.

Keyword: $CdTiO_3$ crystals; ilmenite; Dielectric characteristics; ac conductivity.

Introduction

Cadmium titanate ($CdTiO_3$) belongs to a large family of the titanium-based oxides with perovskite and ilmenite-type structures which have intensively studied for their ferroelectric and electro-optical applications [1]. The ilmenite $CdTiO_3$, obtained by sol-gel method [1] has been reported to show the rhomboedrique ilmenite structure with the space group R-3 at room temperature, and a dielectric anomaly [2] appeared near 77 K. In the present paper, we have investigated the dependence of permittivity, loss tangent and conductivity on frequency and temperature.

Experimental

The CdTiO3 sample was synthesized by the sol-gel method using titanium isopropoxide (Ti(OCH(CH3)2)4, 97% Aldrich), cadmium acetate (Cd(CH3COO)2 > = 97% Aldrich) as a precursor, and distilled water, acetic and lactic acids were used as solvents. The obtained powder was annealed in static air for 2hrs at 900, with a heating rate of 5 oC/min. Details of the procedure of preparation of titanium sol are given in ref. [1]. In order to investigate dielectric properties of the $CdTiO_3$ sample, the latter was prepared under the form of a disc with a diameter of about 12 mm and a thickness of about 1 mm and sintered at 950°C for 4 hours.

The permittivity was calculated using the formula ε =C/C0, C0= ε0S/e where C is the capacitance (F), e is the thickness(m), S the cross-sectional area (m2) of the sample and ε0 is the absolute permittivity of the free space having a value of 8.854×10^{-12} F.m-1. The imaginary dielectric constant (εi) of the capacitor was calculated using the relation εi = ε0 tanδ where tanδ is the loss tangent.

Results and Discussion

Dielectric characteristics

The dependence of the permittivity and dielectric losses (tan δ), of the as-prepared $CdTiO_3$ sample on temperature and frequency were studied in the temperature range of 40–600°C and frequency range of 10^3–2.10^6 Hz. Fig. 1 shows the thermal variation of loss tangent (tan δ) of the sample in the range 103–2.10^6 Hz. From these plots, it can be seen that the values of tan δ are temperature independent up to 350°C. Above 350°C, tan(δ) increases with the rise in temperature up to 600°C. Above this temperature, the loss parameter tangent has higher values at low frequency and hence behaves as other materials [3]. In our material, the increase in the loss tangent can be explained by the space charge polarization due to ions immobilization of part of the free ions [4] (which could be oxygen vacancies due to volatilization of CdO during the process of preparation [1]).

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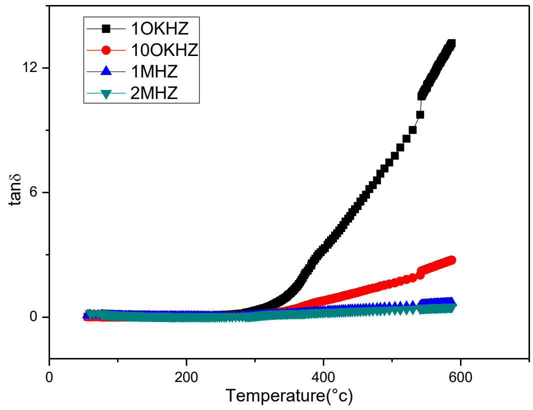

Figure 1. Loss tangent (tan δ) vs. frequency (ν) plots at different temperatures (40°C–600°C) for ilmenite $CdTiO_3$ ceramic

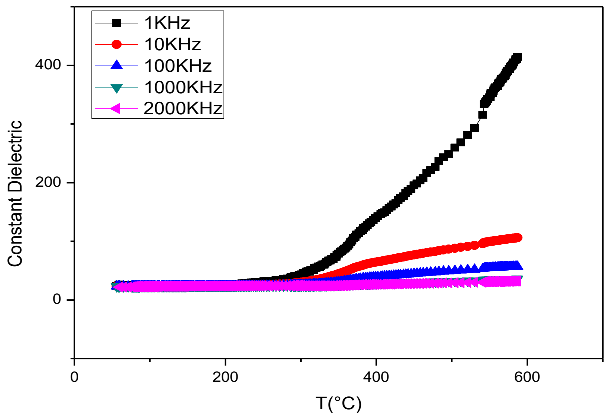

Figure 2. Dielectric constant (ε) as a function of temperature (T) at different frequencies (10^3-2.10^6Hz) for ilmenite $CdTiO_3$ ceramic

From Fig.1, it can also be seen that the values of tan δ decrease with increase in frequency, which is a characteristic of a dipole mechanism. Fig. 2 shows the variation of the real part of the permittivity (ε) versus temperature at different frequencies for the ilmenite ($CdTiO_3$) ceramic sample. The observed behavior is invariant with the rise in temperature up to 300°C. Above 300°C, ε increases with the rise in temperature. However, this increase is more pronounced at lower frequencies. It can be seen that no Ferro-to-paraelectric transition in the temperature range of 40–600°C [5,6] is observed, as this temperature was reported to occur at around 77K [2]. It is well known that the electronic and ionic polarization contribute to the permittivity at higher frequencies, while the other mechanisms (space charge or interfacial and dipolar polarization) contribute at lower frequencies. The ionic and electronic polarization decrease with an increase in temperature. With the increase in temperature, ionic distances increase, which affects both the ionic as well as the electronic contributions to polarization as they both decrease as the temperature rises [7,8]. It is also well known that the dipolar and space charge polarization contribute at low frequency, and they are both temperatures dependent [9]. When the temperature rises, the interfacial polarization increases due to the creation of crystal defects [10]. The increase in dielectric constant with an increase in temperature may be due to an increase in contribution from space charge polarization. At higher frequencies, ε should vary less with temperature. The sharp increase in dielectric constant versus temperature at 10^3 Hz is due to the major contribution from space charge polarization.

Fig. 3. Shows the variation of the real part of the dielectric constant (ε) versus frequency at various temperatures. From this figure, it can be seen that the values of ε decrease with rising in frequency as due to dipoles that are not able to follow the high vibrating field.

However, with the increase in frequency values of the dielectric constant remain almost constant and weak that are typical of the space charge polarization [11].

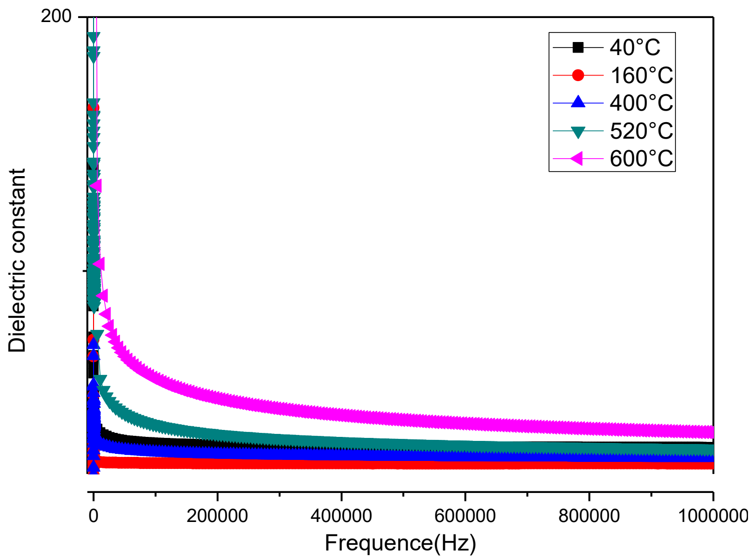

Figure 3. Dielectric constant (ε) as a function of frequency (ν) at different temperatures (40°C–600°C) for ilmenite $CdTiO_3$ ceramic

Fig. 4 shows the variation of the imaginary part of the permittivity (εi) with the temperature at various frequencies and Fig. 5 describes the variation of (εi) with frequency at different temperatures. From these graphs, it is worth noting that the variations of ε with temperature and frequency are similar to those of the thermal variation of tan δ. The ilmenite $CdTiO_3$ ceramic has the same dielectric behavior with some materials [12].

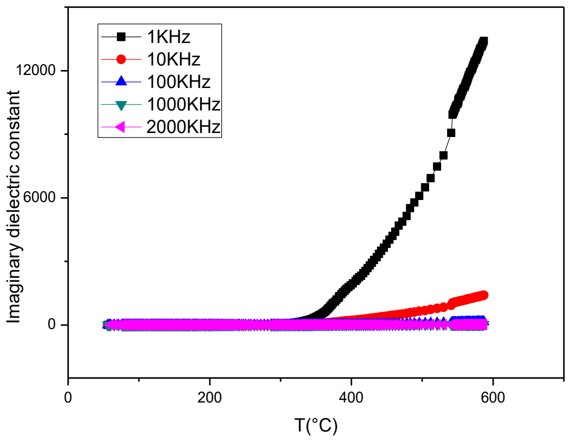

Figure 4. Imaginary dielectric constant (ε) vs. temperature (T) curves at different frequencies (10^3–2.10^6 Hz) for ilmenite $CdTiO_3$ ceramics

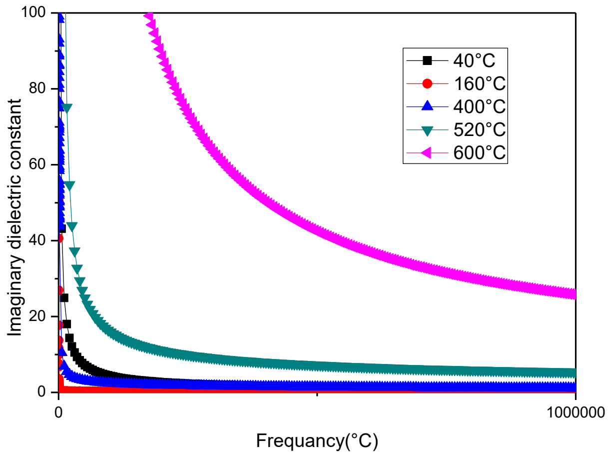

Figure 5. Imaginary part of dielectric constant vs. frequency (ν) at different temperatures (40–600°C) for ilmenite $CdTiO_3$ ceramic

Measurements of the impedance by the capacitor must be less than Zmax. Nevertheless, the losses with this device will be noisy around Zmax. This result is illustrated in Fig. 6; one can observe that for low frequencies, the value of the capacity is slightly noisy. This is mainly because the impedance of the low-frequency capacitance approaches the measurable limit impedance Zmax. Thus with this type of device to optimize measurements in the low frequencies, it is important to maximize the value of the capacity.

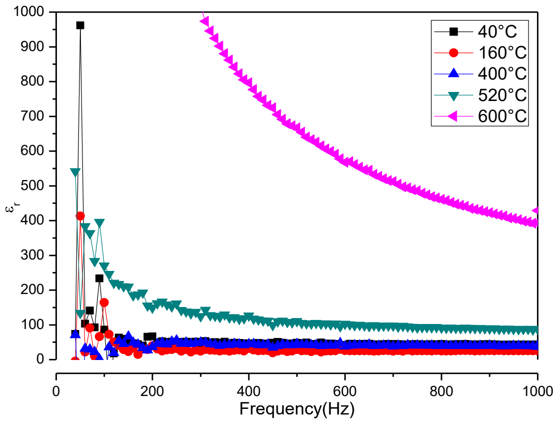

Figure 6. Dielectric constant as a function of frequency at different temperatures

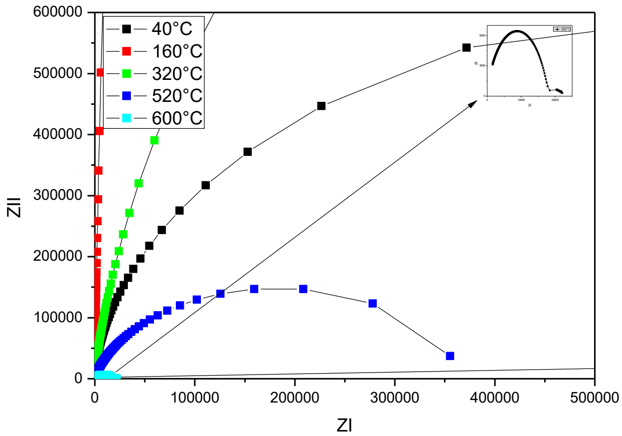

Figure 7. Z " as a function of Z ' for the ceramics $CdTiO_3$

Complex impedance studies

The main mode of charge transport in the ilmenite system is a multiple jump process. This jumping process occurs, especially through the potential barriers that occur within the structure and the local atoms/ions environment. In order to better understand the nature of conduction, we studied the complex impedance spectra of $CdTiO_3$ sample. Fig.7 shows the impedance spectra (Z" = f (Z')) of $CdTiO_3$ sample. For each temperature, the corresponding curves appear under the form of two depressed semicircles, suggesting the presence of both bulk and grain boundary effects in the sample. Results from impedance spectra have been approached by an equivalent circuit composed of two parallel elements (R, C) connected in series with other resistances, as shown in Fig. 8. Values of these parameters have been obtained from impedance data (Table 1). The high-frequency arc is related to the grain and the low-frequency arc to the grain boundary contribution.

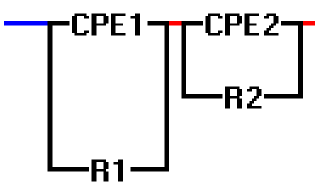

Figure 8. Equivalent circuit of the $CdTiO_3$ ilmenite structure

Table 1. Estimated values of equivalent circuit parameters.

T	$R_1(\Omega)$	$R_2(\Omega)$	CPE1(F)	CPE2(F)
600°C	437E3	9.78E5	7.77E-6	5.35E-5
500°C	1.01E6	1.01E6	6.75E-7	6.75E-7
400°C	2.50E5	1.00E6	4.87E-5	4.87E-5
160°C	2.00E5	3.00E6	5.00E-5	6.00E-6
40°C	3.64E5	1.00E6	3.78E-11	6.44E-11

The frequency dependence of Z' at different temperatures is shown in Fig. 9. It is observed that Z' decreases with increasing frequency and temperature, indicating the increase in ac conduction (σac) in the sample. This increase in conduction may be explained as due to the contribution of defects such as oxygen deficiencies, and consequently, at high temperature, the contribution due to the latter is more dominant. For high frequency, the value of Z' appears to be frequency independent for all temperatures, indicating that there is an increase in the concentration of defects with the rise of temperature leading to an increase of conductivity of the samples [13,14]. The merging of the Z' curves in the higher frequency region is probably due to the release of space charges due to the reduction of the barrier properties of the samples.

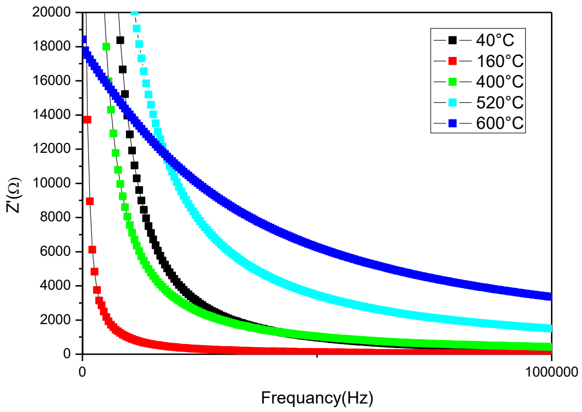

Figure 9. variation of Z' as a function of the frequency for ceramics $CdTiO_3$

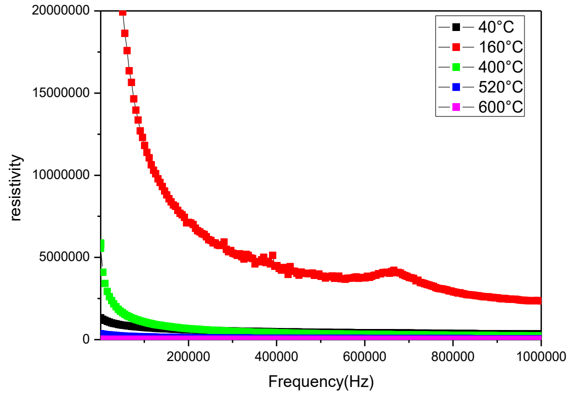

Figure 10. Thermal variation of resistivity of the sample

Resistance

The bulk resistance decreases with rising in temperature (Fig. 10). The resistance has the opposite evolution compared with conductivity; it has a saturation value (near the 0) at a higher frequency, which is important for an industrial application like sensor and capacitor.

Conductivity studies

In order to better understand the transport mechanism in the ilmenite $CdTiO_3$ ceramic, the electrical conductivity behavior was investigated. The electrical conductivity can be determined from the dielectric data with the help of the following relation:

$$\sigma = \varepsilon_0 \varepsilon_r \omega \tan\delta$$

Where f is the frequency (Hz), ε0 is the permittivity of vacuum (8.854×10^{-12} F/m), and εr is dielectric constant. Fig. 11, shows the variation of the conductivity as a function of frequency.

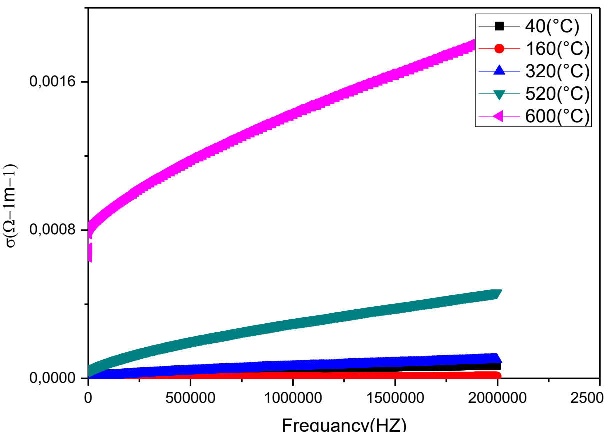

Figure 11. Variation of conductivity as a function of frequency for ilmenite $CdTiO_3$ ceramics

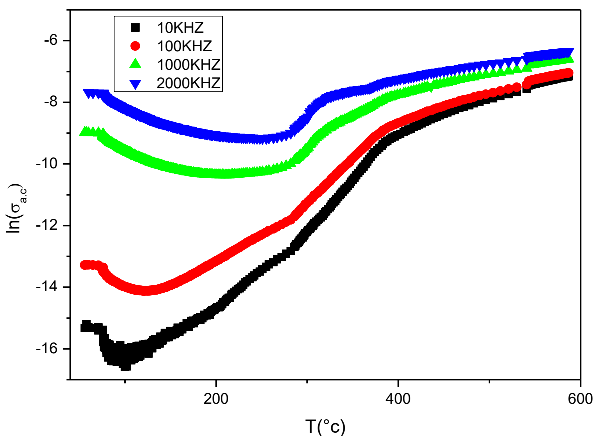

Figure 12. lnσac vs. temperature T plots at different frequencies (10^4–2.10^6 Hz) for $CdTiO_3$ crystals

The conduction in this material may be due to the migration of charge carriers over a long distance or to the relaxation mechanism over a short distance. In dielectric materials, which is our case of, the electrical conductivity is attributed to the jump of polarons in the material.

Fig.12 displays the dependence of conductivity on the temperature at different frequencies. The ac conductivity is temperature independent in the frequency range (40°C–400°C), this ac conductivity is interpreted by proposing that ac conductivity due to hopping conduction increases with increasing frequency. The mechanism of conduction in this region may be attributed to ionic hopping conduction by the charge carriers, which in the present case may include mobile ions [14-16]. Above 400°C, the ac conductivity is temperature and frequency independent. The influence of temperature on ac conductivity has been explained by considering the mobility of charge carriers responsible for hopping. The increase in conductivity is due to the increase in mobility, which is caused by the elevated temperature.

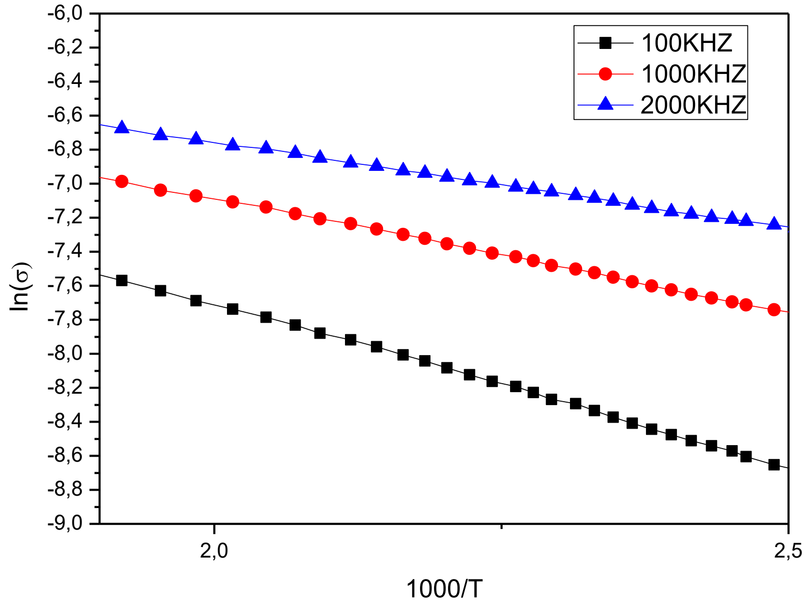

Figure13. Conductivity vs. 1000/T

Fig.13 suggests a thermally activated process in the sample and follows the Arrhenius law σ = σ0exp(-Ea/KbT), where Ea is the activation energy of conduction which is calculated from the slope of ln σ with 1000/T curve and reported in Table 2.

Table 2. The activation energy of conduction at different frequencies.

Frequency(Hz)	100KHz	1000KHz	2000KHz
Ea(ev)	0,16	0,11	0,05

Modulus spectra

Analysis and interpretation of the dynamic aspects of electric transport phenomena may be carried out with the help of complex modulus. The complex electrical modulus (M*) is defined as a function of complex dielectric permittivity (ε*) by the following relation:

$$M^*=M'+iM'' \qquad \text{Avec} \quad M'=\frac{\varepsilon'^2}{\varepsilon'^2+\varepsilon''^2} \quad \text{and} \quad M''=\frac{\varepsilon''^2}{\varepsilon'^2+\varepsilon''^2}$$

Alternatively, M' and M" are respectively the real and imaginary part of the complex electric modulus M* Fig. 15a shows the variation of the real part of the electric modulus (M') as a function of frequency, at high temperatures (between 40°C and 600°C). Low values of M' are observed in the low-frequency region, followed by a continuous dispersion with increasing frequency. Fig. 14b, shows the frequency dependence of the imaginary part, M'', of the electric modulus at different temperatures. M'' exhibits a maximum which shifts to higher frequencies with an increase in temperature. This peak observed in the plot of M'' as a function of frequency corresponds to a relaxation process. The frequency region below this maximum of M'' gives the extent to which charge carriers are mobile on long distances (Jump conduction process). At the frequency above this maximum, the carriers are confined to potential wells and hence are mobile on short distances [17]. Moreover, the widening of the observed asymmetric peak Fig. 14a may be related to the existence of a distribution of relaxation times.

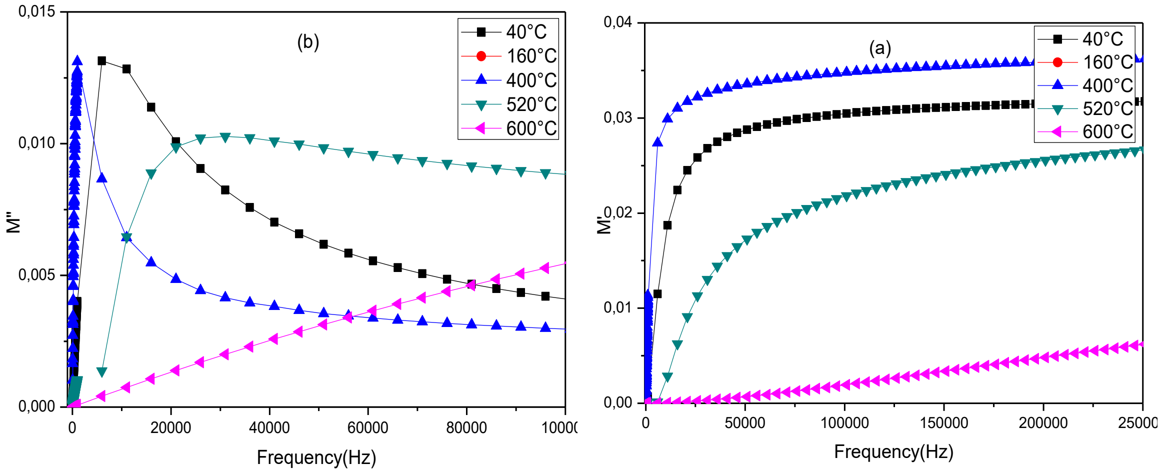

Figure 14. Variation of (a) M' and (b) M'' as a function of frequency for $CdTiO_3$ ceramics

Fig. 14b shows that M" approaches to zero at low frequency and continuous increase at high frequency. This shows the tendency to saturate at a maximum asymptotic value (i.e., $M\infty = 1/\varepsilon\infty$), for all the temperatures. A sigmoidal shape curve is observed where the transition from low to high values of M is clear.

Conclusions

The present work reports the dielectric properties and ac conductivity of polycrystalline $CdTiO_3$ Ilmenite structure prepared by sol-gel technic. The loss tangent (tan δ), dielectric constants (ε' and ε''), and conductivity (σac) of flux grown $CdTiO_3$ single crystals are dependent on temperature and frequency of the applied ac field, the variation depending on the ranges of temperature and frequency. The behaviour of $CdTiO_3$ showing dependence of dielectric constant on temperature is almost similar at all the frequencies. The values of ε increase slightly with an increase in temperature up to 350°C. Above 350°C, ε increases with the rise in temperature up to 600°C, the increase being more pronounced at lower frequencies. The values of ε decrease with a rise in frequency. The values of loss tangent (tan δ) are almost invariant with the rise in temperature up to 350°C. Above 300°C, tanδ begins to increase with the rise in temperature; the rate of increase of tan δ is higher for lower frequency. The values of tanδ decreases with increase in frequency. The conductivity σac is almost temperature independent and strongly frequency dependent in the temperature range of 40–400°C. However, beyond 400°C σac is temperature dependent and less frequency dependent. The influence of temperature on the conductivity is explained by considering the mobility of charge carriers (maybe mobile ions) responsible for hopping.

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