Chapter 5
On the Multiferroic Behaviour of Gadolinium Based Manganites

5.1 Introduction

Ferroelectric and magnetic materials are a time-honored subject of study and have led to some of the most important technological advances [1-4]. Magnetism and ferroelectricity are involved with local spins and off-center structural distortions, respectively. These two seemingly unrelated phenomena can coexist in certain unusual materials, called "multiferroics". Multiferroics, sometimes called "magnetoelectrics", possess two or more switchable states such as polarisation, magnetisation or strain. Multiferroics are of particular interest recently both to understand the fundamental aspects of the novel mechanism that gives rise to this magnetic-ferroelectric coupling, as well as because of the intriguing possibility of using these coupled order parameters in novel device applications. The understanding of the physics of multiferroics will be crucial to design smarter multiferroic materials and control their functionality for practical applications, such as electric-field-controlled ferromagnetic resonance devices, actuators, transducers, and storage devices with either magnetically modulated piezoelectricity or electrically modulated piezomagnetism. The multiferroic nature of manganites Pr$_{0.6}$Ca$_{0.4}$MnO$_3$, Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ and Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ is recently reported and the effect is explained by using the mixing of site centered or bond centered charge ordering mechanisms [5-7]. There is a possibility of obtaining the ferroelectric behaviour for the Gd doped (comparable ionic radius with Pr and Nd) manganite. This chapter deals with the dielectric studies of Gd based manganites along with the a.c conductivity and capacitance-voltage (CV) studies.
5.2 Dielectric permittivity studies of GSMO

The dielectric permittivity studies on the Gd based manganite sample were carried out by using a dielectric cell and an HP 4285 LCR meter in the frequency range 100 kHz- 8 MHz from 145K to 300K. High frequencies are used in the measurement to avoid strong contact contribution at the sample electrode interface, which dominate at low frequencies. The dielectric cell was standardized by using Teflon. The fabrication details of the dielectric cell are cited elsewhere [8]. In the dielectric cell, a capacitor is created by placing the pellet in between two copper discs of the same diameter of the pellet. The temperature was recorded with a Cryocan temperature controller with platinum resistance (PT-100) temperature sensor. The dielectric permittivity is calculated using the following relation from the capacitance data obtained from the LCR meter.

\[ \varepsilon_r = \frac{C d}{\varepsilon_0 A} \]  

(5.1)

where C is the capacitance of the sample, A is the surface area of the sample, \( \varepsilon_0 \) is the permittivity of free space. The acquisition of data was automated by interfacing HP 4285A with a computer using a virtual instrumentation package LabVIEW. The variation of dielectric permittivity with frequency at different temperatures for the GSMO sample is given in figure 5.1.

The dielectric permittivity decreases with increase of frequency in the case of all compositions of GSMO sample. The dielectric spectra reveal a quasi-Debye relaxation, which can be explained satisfactorily with the help of a two-or tri layer Maxwell-Wagner capacitor [9]. Considering the compositional dependence on permittivity from figure 5.1, it is clear that there is an increase of dielectric constant with Sr concentration. It is due to the increase of hopping polarisation with increase of Sr doping. The temperature variation of dielectric constant at different frequencies is shown in figure 5.2.
From the figure it is clear that as temperature increases dielectric constant also increases, attains a maximum value and then decreases. The dielectric peak is very close to $T_{CO}$, which is an evidence of the link between electronic state and increase of dielectric response [9]. The anomaly in dielectric constant at the charge ordering temperature was earlier observed in Pr-Ca manganites [10, 11]. The peak height at the transition temperature was observed to decrease with increase in frequency and the dielectric constant peak get shifted to higher temperature with increase in frequency, which is indicative of the relaxational behaviour of the
material [12]. The word relaxor is used because there is only broad peak instead of sharp peak as in the case of conventional ferroelectric materials.

![Graphs showing the variation of dielectric permittivity with temperature for different samples of Gd$_{1-x}$Sr$_x$MnO$_3$. (a) x = 0.3, (b) x = 0.4, and (c) x = 0.5) at selected temperatures.]

Figure 5.2: The variation of dielectric permittivity with temperature for the samples Gd$_{1-x}$Sr$_x$MnO$_3$ [(a) x = 0.3, (b) x = 0.4 and (c) x = 0.5] at selected temperatures.

In the case of manganites the ferroelectric nature can be explained by using intermediate charge ordering state. Charge ordering is usually considered as an ordering of transition metal ions with different valencies (e.g. Mn$^{3+}$/Mn$^{4+}$ in manganites and Fe$^{2+}$/Fe$^{3+}$ in ferrites). This charge ordering state is called Site-centered Charge Ordering (SCO). Recently another type of charge ordering is discovered and is called Bond-centered Charge Ordering (BCO). This state is
actually an oxygen centered charge ordering state as oxygen ions are located on the TM-TM bonds in the typical perovskite crystal structure. With in such a dimmer spins are aligned ferromagnetically due to Zener double exchange mechanism. It is referred to as Zener polaron state. In SCO Mn ions have unequal valencies but in BCO they have the same valency. The superposition of these two states results into a ferroelectric intermediate state. The CE structure (SCO) has a center of inversion symmetry and consequently there are no electric dipole moments present in the ground state. This is also the case in the pure Zener polaron structure (BCO) as both the Mn ions in each dimmer are equivalent. But the intermediate state has a magnetic structure in which the inversion symmetry is lost and the dimmer attains a dipole moment. Thus there is a net polarisation which leads to a ferro-electric ground state [6, 13]. The three states are depicted in figure 5.3.

![Figure 5.3](image)

**Figure 5.3** (a) Site centered Charge Order (SCO) (b) Bond centered Charge Order (BCO) or Zener Polaron state (c) Intermediate ferroelectric state

The frequency variation of dielectric loss tangent for the GSMO sample is depicted in the figure 5.4 and the variation of dielectric loss tangent with temperature is shown in figure 5.5. As frequency increases dielectric loss tangent decreases. The high frequency decrease of dielectric loss tangent can be explained
by considering the RC equivalent circuit of a lossy dielectric material. In the parallel combination of resistor and capacitor, the decrease of capacitive reactance

![Graph A](image1.png)

![Graph B](image2.png)

![Graph C](image3.png)

**Figure 5.4** Frequency variation of dielectric loss tangent for GMSO sample Gd$_{1-x}$Sr$_x$MnO$_3$

[(a) $x=0.3$, (b) $x=0.4$ and (c) $x=0.5$] at selected temperatures.

at high frequency causes a decrease of charge flow across the resistor, which in turn reduces the energy dissipation across the resistor. The temperature variation of dielectric loss tangent has the same behaviour as that of the dielectric permittivity except the shifting of the peak temperature towards 255K and 260K for Gd$_{0.8}$Sr$_{0.4}$MnO$_3$ and Gd$_{0.5}$Sr$_{0.3}$MnO$_3$ respectively. This shift of dielectric loss peak is due to the fact that it usually appears at certain temperature where the dielectric constant varies quickly [14]. The quick decrease of dielectric
permittivity at 220K for Gd_{0.5}Sr_{0.5}MnO_3 resulted into the occurrence of dielectric loss peak at the same temperature. But in the case of Gd_{0.6}Sr_{0.4}MnO_3 and Gd_{0.7}Sr_{0.3}MnO_3 dielectric permittivity peak is very broad and a quick decrease occurs at comparatively higher temperatures.

![Graphs showing dielectric loss tangent vs. temperature for various frequencies and compositions of Gd_{1-x}Sr_xMnO_3 samples.](image)

Figure 5.5 Temperature variation of dielectric loss tangent for GSMO sample Gd_{1-x}Sr_xMnO_3 [(a) x=0.3, (b) x=0.4 and (c) x=0.5] at selected frequencies.

The dielectric loss of the material was measured by using the equation

\[ \varepsilon'' = \varepsilon' \tan \delta \]  \hspace{1cm} (5.2)
where \( \tan \delta \) is the dielectric loss tangent. The frequency and temperature variations of dielectric loss (imaginary permittivity) for the GSMO samples are shown in figure 5.6 and figure 5.7. The sample exhibits the same behaviour as in the case of loss tangent.

**Figure 5.6** Frequency variation of dielectric loss for GSMO sample \( \text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3 \) [(a) \( x=0.3 \), (b) \( x=0.4 \) and (c) \( x=0.5 \)] at selected temperatures.
Figure 5.7 Temperature variation of dielectric loss for GSMO sample $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ [(a) $x=0.3$, (b) $x=0.4$ and (c) $x=0.5$] at selected frequencies.

5.3 Capacitance Voltage (CV) measurements in GSMO

In order to confirm the ferroelectric property of GSMO sample, the capacitance versus voltage (CV) measurements were carried out using an HP 4192 A impedance analyser. The sample in the form of pellet was placed in between two copper plates in the dielectric cell and the capacitance values were measured by varying bias voltage from -8 V to +8 V in a step of 1 V. The variation of capacitance with applied bias voltage at room temperature is presented in figure 5.8. The butterfly nature of the figure is an indication of ferroelectricity in GSMO
sample [15]. The change in capacitance with applied bias voltage is pronounced in the case of Gd_{0.5}Sr_{0.5}MnO_{3} which confirms the role of charge ordering in the multiferroic behaviour of the manganite sample.

![Graphs showing variation of capacitance with bias voltage](image)

**Figure 5.8** Variation of capacitance with bias voltage for GSMO sample Gd_{1-x}Sr_{x}MnO_{3} [(a) x=0.3, (b) x=0.4 and (c) x=0.5] at frequency 1MHz.

### 5.4 A.C conductivity studies in GSMO

A.C conductivity values of GSMO samples were obtained from the dielectric permittivity ($\varepsilon'$) and dielectric loss tangent ($\tan\delta$) using the equation

$$\sigma_{ac} = 2\pi f \varepsilon_{0} \varepsilon' \tan\delta$$  \hspace{1cm} (5.3)

where $f$ is the frequency of ac applied field and $\varepsilon_{0}$ is permittivity of free space.
Figure 5.9 Frequency variation of ac conductivity for GSMO sample Gd$_{1-x}$Sr$_x$MnO$_3$ [(a) $x=0.3$, (b) $x=0.4$ and (c) $x=0.5$] at selected temperatures. (d) frequency variation of ac conductivity in the temperature range (145K-160K) for the GSMO sample $x=0.3$.

The variation of the ac conductivity with frequency at different temperatures for the samples Gd$_{1-x}$Sr$_x$MnO$_3$ ($x=0.3$, $x=0.4$ and $x=0.5$) is plotted in a semi log plot (figure 5.9). In the case of GSMO with $x=0.3$ and $x=0.4$, at lower frequencies, there is a small increase in ac conductivity for temperatures lower that the relaxor ferroelectric transition temperature and above that particular temperature the ac conductivity is frequency independent. But for higher frequencies the ac conductivity decreases with increase of frequency. For $x=0.3$, the appearance of frequency independent behaviour at low temperatures in the diagram is due to the large Y-axis scale value which can be confirmed from figure 5.9 (d). But for
GSMO with x=0.5, as frequency increases the ac conductivity increases, attains a maximum and then decreases. The increase in ac conductivity is due to the hopping mechanism of bound charges back and forth between well defined bound states [16]. But at higher frequencies the hopping of charge carriers could not follow the applied field, resulting in the decrease of ac conductivity. From figure 5.9 it is clear that the ac conductivity value decreases with increase of Sr doping. This behaviour may be due to the increase in number of Mn$^{4+}$ ion sites at the expense of Mn$^{3+}$ site with increase of Sr doping. As a result the available Mn$^{3+}$-Mn$^{4+}$ pairs for hopping decreases and hence the ac conductivity due to the jumping between bound states decreases.

In general ac conductivity power law is given by

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

where $\sigma(0)$ is the frequency independent contribution from dc conductivity, $A$ is constant, $\omega$ is angular frequency of the applied field and $n$ is the power law exponent [17,18]. From the equation it is clear that the variation of $\log \sigma$ with $\log \omega$ is a straight line and the slope of the straight line graph is the power law exponent ‘$n$’. The log-log plot of ac conductivity with angular frequency of the applied electric field in the low frequency region (where ac conductivity increases with frequency) for all the three GSMO compositions are presented in figure 5.10.

All the plots are straight lines and the slopes of the straight lines are calculated using linear fitting. The power law exponents thus obtained are plotted against temperature and the variation is presented in figure 5.11. The different mechanisms for ac conduction are overlapping large polaron tunneling (OLPT) and correlated barrier hopping (CBH) [19]. The OLPT model predicts a minimum value of ‘$n$’ followed by an increase. A decrease of $n$ with increase of temperature is according to the correlated barrier hopping (CBH). For the compositions $x=0.3$
and $x=0.4$, as temperature increases the power law exponent ‘$n$’ decreases and at around 210 K it becomes almost constant.

Figure 5.10 Log log plot of frequency variation of ac conductivity for GSMO sample

Thus for the above mentioned compositions the ac conduction mechanism is CBH below the ferroelectric transition temperature. Above the transition temperature the steady value of $n$ indicates the frequency independent nature of ac conductivity. The frequency dependence of conductivity is a characteristic of hopping conduction. The decrease of $n$ value with temperature indicates that as temperature increases hopping conduction decreases. Deepam Maurya et al. reported a similar behaviour in the case of ferroelectric Na doped potassium...
titanate ceramics [20]. The temperature variation of power law exponent of the composition x=0.5 has different behaviour. With increase in temperature, the power law exponent ‘n’ decreases, attains a minimum and then increases. Therefore the possible ac conductivity mechanism is overlapping large polaron. This is due to the fact that large concentration of Sr can reduce the number of Mn$^{3+}$-Mn$^{4+}$ pairs and consequently hopping gets reduced. In such case the spatial extend of polaron covers several inter atomic distances resulting into formation of overlapping large polaron [21].

![Graph](image)

**Figure 5.11** Temperature variation of power exponent of ac conductivity for GSOMO sample Gd$_{1-x}$Sr$_x$MnO$_3$ (x=0.3, 0.4 and x=0.5)

### 5.5 Conclusion

The frequency and temperature dependence of the dielectric parameters of the Sr doped Gadolinium manganites were studied. The frequency dispersion of the dielectric parameters was explained using a two-or tri layer Maxwell-Wagner capacitor. The temperature variation of dielectric permittivity shows a broad peak near the charge ordering temperature. This dielectric anomaly is due to the relaxational behaviour of the GSOMO sample. The ferroelectric behaviour is explained by inversion symmetry loss in the intermediate charge ordering state.
between site centered charge ordering (SCO) and bond centered charge ordering (BCO). The ferroelectric behaviour of the GSMO samples was verified by capacitance voltage measurement, where butterfly curves appear. The increase in ac conductivity is attributed to the hopping mechanism of bound charges back and forth between well defined bound states. The decrease of ac conductivity value with Sr doping may be due to the increase in number of Mn$^{4+}$ ion sites at the expense of Mn$^{3+}$ sites with increase of Sr doping, which results in shortage of Mn$^{3+}$-Mn$^{4+}$ pairs. The frequency dependent term of ac conductivity was analyzed using power law and the power law exponents (n) were evaluated. Based on the variation of n with temperature, appropriate conduction mechanisms were proposed for different compositions.

References


