Chapter 5

Effect of tensile strain on the magnetoelectric coupling of YMnO₃ thin films

Abstract

Multiferroic materials provide an opportunity to use electric field and/or strain to control the magnetism and vice-versa. In this chapter we demonstrate the effect of strain on multiferroic properties of single phase YMnO₃ thin film grown on sapphire (0001) substrate with conducting Zn₀.₉₉Ga₀.₀₁O buffer contact layer. High quality epitaxial films prepared by pulsed laser deposition technique were characterized using XRD, SEM, EDAX and magnetic field dependent dielectric measurement techniques. Both the real ($\varepsilon$) and imaginary (tan$\delta$) part of dielectric constant indicate an anomaly in the vicinity of 30 K, well below the bulk YMnO₃ Néel temperature ~ 65 K. The shift of anomaly in dielectric measurement is attributed to lattice mismatch of YMnO₃ film and Zn₀.₉₉Ga₀.₀₁O substrate. We also observed a substantial enhancement in the magnetoelectric coupling for magnetic field parallel to ab plane as compare to bulk YMnO₃. The results emphasize that it is possible to tune the multiferroic property of YMnO₃ via ferroelastic route, particularly through lattice mismatched tensile strain.
5.1 Introduction

Thin film processing is important for development of electronic devices with low consumption of energy i.e. low operating voltage. Multiferroic materials offer the possibility of manipulating the magnetic (electric) state by an electric (magnetic) field and/or strain or vice versa [5, 6, 7, 8, 9, 10, 11, 12]. Although these materials are known for a long time, there has been a revival in research on multiferroic thin films primarily due to three reasons:

1. Fast development in different sample preparation techniques, and technology for making good quality epitaxial thin films [13].
2. The discovery of improper ferroelectricity in spin frustrated systems [14, 15, 16].
3. Observation of strain induced enhancement in ferroelectric Curie temperature and polarization in thin films of complex oxides [17, 18, 19, 20].

Various techniques such as chemical solution deposition (CSD) [21], sol-gel, and metal-organic chemical vapor deposition (MOCVD) [22], molecular beam epitaxy (MBE) [23], sputtering [24] and pulsed laser deposition (PLD) [25] etc. have been employed successfully to fabricate high quality epitaxial thin films. The major advantage in thin film technology is the ability to stabilize the metastable structure and to tune material properties by varying the lattice mismatch between the film and the substrate, thereby introducing epitaxial strain in the thin film. It is observed that substantial elastic tensile or compressive stress can be introduced by lattice mismatch between the materials of interest and the substrate [17]. Among all the known multiferroic materials YMnO₃ (YMO) has been used as a model system to study the effect of lattice strain along with other external perturbation viz. electric and magnetic field. The immense emphasis on YMnO₃ also lies in the fact that the microscopic origin of multiferroicity in this model system is better understood [26, 27, 28].

YMnO₃ belongs to a class of materials having general formula RMnO₃ with hexagonal crystal structure. A detailed study of crystal and magnetic structure of YMnO₃ is presented in chapter 6. Bulk YMnO₃ shows antiferromagnetic ordering T_N ~ 65 K and ferroelectric transition T_E ~ 900 K. The dielectric constant (ε) and loss factor (tanδ), that reflect the electric ordering, show magnetic field dependence across the antiferromagnetic transition...
and thus establish multiferroicity near 65 K [10]. Due to this, MnO$_2$ blocks tilt, leading to displacement of Y$^{3+}$ ions along $c$ axis and causes ferroelectric polarization [26, 27]. Thin films and single crystals of YMnO$_3$ show that these materials are highly anisotropic in terms of magnetic and electrical properties [10].

However, the potential application of YMnO$_3$ film lies in crystal orientation, as the ferroelectric polarization is along the $c$ axis [30]. Impurities and oxygen vacancies also play an important role in thin film application as they are known to artificially enhance the leakage current. Minimizing these factors require careful tuning of thin film growth parameters [31]. Moreover, from the standpoint of fabricating actual multi-functional devices, it is required to attach top and bottom conducting electrodes to these films. Though the fabrication of the top contact is quite straightforward, the fabrication of the bottom contact requires a buffer layer of conducting properties. To maintain the high crystal quality of the YMnO$_3$ film, the bottom contact layer itself need to be epitaxial with the YMnO$_3$ as well as with the sapphire substrate (Al$_2$O$_3$). It is observed by Eerenstein et al. that magnetic, resistive, and magnetoelectric effects can be changed due to the strain induced coupling at the interface [32].

5.1-1 Motivation

A significant amount of strain is always present in thin film grown on heteroepitaxial substrates. The effect of strain on the ferroelectric properties of conventional ferroelectric materials is a topic of current interest. It can lead to a substantial increase of the spontaneous polarization and Curie temperature, and even drive paraelectric materials such as SrTiO$_3$ into the ferroelectric phase [17, 18]. Since the mechanism for ferroelectricity in multiferroic materials is often different from that of conventional perovskite ferroelectrics, the question arises is whether similar strain effects will be observed in multiferroic materials also. Magnetic behaviour can also be strongly affected by strain, mainly due to large changes in anisotropy. Strain can also affect the saturation magnetization and Curie temperature. An open question that is of current interest is whether this onset temperature can be increased or decreased by introducing strain into multiferroic system. What role strain can play in determining the magnetic and electric ordering temperature and how magnetoelectric coupling
is affected due to tensile/compressive strain in lattice mismatched multiferroic thin films? Particularly in case of YMnO₃ epitaxial thin films, is it possible to alter the tilting of MnO₅ polyhedra controllably by lattice strain?

5.2 Experimental Section

5.2-1 Target preparation

The bulk target of YMnO₃ for thin film deposition was prepared by using low temperature sol-gel technique. The steps involved in sol-gel processing of YMnO₃ target are as follows:

1. Manganese (II) nitrate hydrate and Yttrium (III) nitrate hexahydrate, used as Y and Mn precursors, are dissolved in distilled water and mixed in a 1:1 molar ratio.

2. Citric acid is dissolved in water and added to the Y and Mn solution in a 1:1(Citric acid) to 1(Y or Mn) molar ratio. Then the solution is diluted to 750 ml and refluxed for \( \sim 12 \) hours.

3. The refluxed solution is heated on a hot plate to evaporate solvent (water). After the solvent is evaporated a gel remains and the gel is heated to \( \sim 160 \) °C where the gel to powder reaction occurs.

4. Synthesized powders are calcined at 500 °C for 4 hours in air. From the calcined powders 1 inch deposition targets are pressed using a uniaxial hydraulic press. The pressure used was 33 MPa. The pressed targets are sintered in air at \( \sim 850 \) °C for 8 hours.

5.2-2 Thin film preparation

For ablating the targets, a KrF pulsed excimer laser having wavelength of 248 nm and pulsed width of 25 ns was used. In the first step of the deposition, the deposition chamber was evacuated to a base pressure of \( 10^{-6} \) torr and a 100 nm thick epitaxial layer of Zn₀.⁹⁹Ga₀.₀₁O (ZnGaO) was deposited on (0001) sapphire. During the above deposition process, temperature of the substrate was kept at 600 °C, energy density was 2 J/cm² and a pulse repetition rate of 10 Hz was used. In the second step of deposition, YMnO₃ film was deposited on
ZnGaO coated sapphire (0001) substrates with an energy density 3 J/cm² at a pulse repetition rate of 10 Hz and with a substrate temperature of 65 °C. Approximately 200 nm thick films were obtained after a deposition time of 10 min. In order to perform the optical measurements, a thin film of YMnO₃ was deposited on transparent sapphire under the identical conditions. To characterize the dielectric properties, gold electrode of nominal dimension 3×2 mm² was deposited at room temperature on top of the film using an appropriate shadow mask. The schematic diagram of YMnO₃ thin film is shown below (Fig 5.1). It is to be noted that 1 % Ga doped ZnO substrate is highly conducting (room temperature resistivity ~ 1.44×10⁻⁴ Ω-cm) and that formed the second terminal for the dielectric measurements [33].

![Schematic diagram of YMnO₃ thin film deposited on Sapphire substrate with Zn₀.₉₉Ga₀.₀₁O as bottom electrode and Au as top electrode.]

Figure 5.1: Schematic diagram of YMnO₃ thin film deposited on Sapphire substrate with Zn₀.₉₉Ga₀.₀₁O as bottom electrode and Au as top electrode.

### 5.2-3 Measurement techniques

The structural properties and crystallographic orientation of YMnO₃ thin films were characterized using Philips X-pert X-ray diffraction (XRD) system. Composition analysis was performed using an electron diffraction energy dispersive absorption X-ray spectroscopy (EDAX). The optical transmission measurements were performed using a DU 730 UV/visible scanning spectrophotometer in wavelength scanning mode. The capacitance (C) and the loss factor (tan δ) were measured with a QUADTECH 1920 precision LCR meter. Capacitance-voltage (C-V) measurement has been done using Agilent HP 4285A Precision LCR meter at the frequency of 100 kHz. The resistivity of the insulating film was measured by using a constant voltage source in a two-probe configuration. The magnetic DC susceptibility (χ) was determined by Quantum Design Magnetic property measurement system (MPMS) SQUID.
5.3 Result and discussion

5.3-1 XRD and EDAX measurement

Figure 5.2 shows the XRD pattern of Y\textsubscript{Mn}O\textsubscript{3} thin film on Ga doped ZnO substrate.

Figure 5.2: X-ray diffraction pattern of $c$ axis oriented hexagonal Y\textsubscript{Mn}O\textsubscript{3} thin film grown on Zn\textsubscript{0.99}Ga\textsubscript{0.01}/sapphire substrate.

Figure 5.3: Energy dispersive spectrograph (EDAX) of Y\textsubscript{Mn}O\textsubscript{3} film.
In the 2θ range from 20 to 100, we could see only the peaks corresponding to (0006) and (000 12) planes of sapphire, (0002) and (0004) planes of ZnGaO and (0002) plane of YMnO₃ indicating the highly c axis aligned nature of the film. EDAX spectrum of YMnO₃ thin film grown on Zn₀.₉₉Ga₀.₀₁O/sapphire substrate is shown in Fig 5.3. Only the peaks corresponding to elements of the YMnO₃ film and sapphire/Zn₀.₉₉Ga₀.₀₁O are observed indicating the high phase-purity of the material. It confirms that these peaks correspond to metal elements Y, Mn, Zn, Ga and O. No other peaks corresponding to other metal peaks are present.

### 5.3-2 Optical Measurement

Figure 5.4 shows the optical transmission spectrum of YMnO₃ thin film in the wavelength range of 200 - 1100 nm. The film exhibits high optical transparency over the entire portion of the visible spectrum with transmittance values exceeding 85% for wavelengths above 500 nm. Over the wavelength range of 500 - 1100 nm, transmission spectrum of YMnO₃ film remained quite flat without any sign of absorption bands. The absorption coefficient (α) was calculated from transmittance measurement using the relation $\alpha = -\log\left(\frac{T}{100}\right)$ and wavelength was converted into energy using $E = h\nu = \frac{1240}{\lambda(nm)} eV$. The plot of $\alpha^2$ versus $h\nu$ is shown in the inset of Fig 5.4.

![Optical Transmission Spectrum](image_url)

Figure 5.4: Optical transmission spectra of YMnO₃ thin film deposited on transparent sapphire. Inset shows the square of absorption spectra over the range of 4.3 - 6.3 eV.
In order to determine the nature of band gap (direct or indirect) associated with the absorption bands, optical absorption coefficient data near these points were fitted to relation \( \alpha = C(h\nu - E_g)^t \), where \( t = \frac{1}{2} \) corresponds to direct band gap and \( t = 2 \) corresponds to indirect band gap. In the linear region, fitting was done to both the exponents corresponding to \( t = \frac{1}{2} \) and \( t = 2 \). The \( \chi^2 \) values of the fitting were \( 2.27 \times 10^{-4} \) and \( 1.17 \times 10^{-3} \) corresponding to \( t = \frac{1}{2} \) and \( t = 2 \) respectively. Here \( \chi^2 \) is a measure of the goodness of fitting data to an equation. By comparing \( \chi^2 \) values for both \( t = \frac{1}{2} \) and \( t = 2 \), we conclude that YMnO\(_3\) is a direct band gap material. \( \alpha^2 \) varied linearly with \( h\nu \) in the high energy region of the absorption edge. A straight line behavior of the \( \alpha^2 \) versus \( h\nu \) plot in the high energy region is taken as the evidence for a direct band gap. The band gap energy of about 4.7 eV was determined for hexagonal YMnO\(_3\) by extrapolating the linear portion of the plot to \( \alpha^2 = 0 \), as shown in the inset of Fig 5.4.

### 5.3-3 Capacitance - Voltage Measurement

To characterize the ferroelectric properties of the \( c \) axis oriented YMnO\(_3\) films, a ZnGaO-YMnO\(_3\)-Au capacitor was prepared by the deposition of a top gold electrode. Figure 5.5 represents C-V measurement at room temperature.

![Figure 5.5: Room temperature capacitance - voltage (C-V) characteristics of YMnO\(_3\) film at 100 kHz. The butterfly nature of C-V curve suggests a weak ferroelectric behavior at room temperature.](image)

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The C-V measurements were accomplished in the voltage range of -5 to 5 V, sweeping at 0.1 V/s from a negative bias to a positive bias and reversing it again. These measurements were done by applying small alternating voltage of amplitude 10 mV at a frequency of 100 kHz. This C-V characteristic has a hysteretic nature, which shows that the ferroelectric polarization is switching its behaviour but the memory retention property is very poor. These results show that remnant polarization of YMnO$_3$ film possibly induces positive charge compensation on the ZnO substrate surface.

5.3-4 Magnetization Measurement

According to neutron diffraction experiments, hexagonal YMnO$_3$ is antiferromagnetic and the Mn$^{3+}$ magnetic moments lie in the $ab$ plane. The Mn$^{3+}$ moments in $z = 0$ and $z = 1/2$ planes are coupled antiferromagnetically with each other. In our film YMO(001)/ZnGaO(001), the atomic spins are located in the plane of the film (i.e. $ab$ plane).

![Magnetization Measurement](image)

Figure 5.6: Temperature dependence of magnetization of YMnO$_3$ film. The zero field cooled data are taken in the warming cycle with an external magnetic field of 0.1 T parallel to $c$ axis.

The magnetic moment ($m$) was determined as a function of the temperature and with the magnetic field applied perpendicular to $ab$ plane. Figure 5.6 shows the zero field cooled (ZFC) M versus T data taken in the warming cycle at an external field of 1000 Oe using SQUID
magnetometer. It is to be pointed out that the signal from such measurement is extremely weak and generally shrouded by large paramagnetic contribution from the background. As expected, $M(T)$ rises while lowering the temperature and a clear downturn, which is a characteristic of AFM ordering, is observed at $T \sim 30$ K.

### 5.3-5 Magnetoresistance Measurement

In magnetoelectric materials both magnetic and electric order parameters are coupled with each other i.e., magnetic field is coupled to polarization and to dielectric constant as well. To detect the multiferroic state it is a common technique to measure $\epsilon(T)$ and look for deviation around magnetic transition. However the problem with this approach is that magnetoelectric coupling is not the only way to produce magnetocapacitance, but magnetoresistive (MR) artifacts can also give rise to an apparently large magnetodielectric effect [34]. It is also important to mention that giant MR can yield giant magnetocapacitance and the sign of the magnetocapacitance depends on whether material has positive MR or negative. Finally, the MR directly affects the dielectric loss that is present in the material.

![Figure 5.7: Temperature dependence of resistivity ($\rho$) at $\mu_0 H = 0$ T (o) and 3 T (Δ). No trace of magnetoresistance is observed.](image-url)
To check whether the observed anomaly in the dielectric constant is coming from magnetoresistance, resistivity measurements in zero field as well as in presence of 3 T magnetic field were performed. The DC resistivity ($\rho$) was found to increase exponentially as temperature decreased (Fig 5.7). Even in the presence of 3T magnetic field no magnetoresistance is observed that confirms that any anomaly appearing in the dielectric constant measurement is dominantly of capacitive origin.

5.3-6 Dielectric Measurement

Magnetoelectric coupling in YMnO$_3$ film was studied in the broad temperature range of 1.6 - 100 K at various frequencies and magnetic fields. The temperature dependence of real and imaginary part of dielectric constant measured at frequency 123 Hz is plotted in Fig 5.8.

Figure 5.8: Capacitance and tan$\delta$ as a function of temperature at 123 Hz. An inverse S-shape anomaly in tan$\delta$ which is signature of AFM ordering in YMnO$_3$ is observed.
The dielectric constant, shown in the upper panel of Fig 5.8, increases with temperature and shows a sharp upturn at $T \sim 30$ K. Whereas in $\tan \delta$, shown in the lower panel, there is a clear evidence of an inverse S-shaped anomaly around the same temperature range. As ferroelectric transition temperature is very high for YMnO$_3$ $\sim 900$ K, the deviation in dielectric measurements correspond to magnetic transition. In previous reports such anomaly in dielectric constant has been identified as the signature of the onset of antiferromagnetic transition in a multiferroic system [35]. This inverse S-shape anomaly in polycrystalline samples of YMnO$_3$ is observed near $T_N \sim 65$ K. Therefore the decrease in the magnetic transition (i.e., inverse S-shape anomaly) from $\sim 65$ K to $\sim 30$ K is attributed to lattice mismatch of ZnGaO/sapphire substrate and YMnO$_3$ film. It is important to note that substrate as well as YMnO$_3$ has hexagonal crystal structure and lattice parameters for YMnO$_3$ and ZnO are $a = 3.06 \ \text{Å}$ and $a = 3.25 \ \text{Å}$ respectively which provides a basal lattice mismatch of 5.8 % in the system.

![Figure 5.9: Capacitance as a function of temperature and magnetic field. The data were taken at 123 Hz and $\mu_0 H = 0$ T (■), 3 T $\perp$ to ab plane (●) and 3 T $\parallel$ to ab plane (▲).](image)

The magnetic field dependent real and imaginary part of dielectric constant for the YMnO$_3$ film is shown in Fig 5.9 and 5.10. One can clearly see that in the presence of 3 T magnetic field both $\varepsilon$ and $\tan \delta$ decreases. The effect of magnetic field both in parallel and perpendicular directions to the $ab$ plane are studied. From this study it is observed that the change in dielectric constant is more pronounced when applied field is parallel to $ab$ plane.
and no significant changes are observed in perpendicular configuration. These measurements point out that the dielectric properties of YMnO$_3$ films are highly anisotropic. The magnetodielectric properties were also studied on randomly oriented grains i.e. the polycrystalline samples of YMnO$_3$ and observed a clear dielectric anomaly and magnetoelectric coupling near $T_N$ i.e. $\sim 65$ K. After the application of 4 T magnetic field, this anomaly is suppressed as shown in Fig 5.11. A detailed study of dielectric measurement on polycrystalline YMnO$_3$ sample is presented in chapter 6.

![Figure 5.10: tanδ as a function of temperature and magnetic field. The data were taken at 123 Hz and $\mu_0H = 0$ T (■), 3 T ⊥ to ab plane (●) and 3 T || to ab plane (▲).](image)

Magnetocapacitance is defined as $(MC = \epsilon (H, T) - \epsilon (0, T)/ (0, T)) \times 100$. MC for randomly oriented YMnO$_3$ pallets is calculated to be $\sim 0.3$ at 4 T, whereas for epitaxial YMnO$_3$ film this increases significantly to $\sim 5.5$ even at 3 T. This order of magnitude enhancement in strained thin film has substantial ramification for device applications. The frequency dependent study of loss ($\tan\delta$) as a function of temperature for the YMnO$_3$ film is shown in Fig 5.12. At the lowest frequency i.e., 31 Hz the inverse S anomaly is clearly evident. As the frequency increases the magnitude of anomaly in $\tan\delta$ decreases and at 10023 Hz the anomaly is barely visible. With the increase of frequency the dielectric constant decreases and the shoulder in $\tan\delta$ broadens and shifts toward higher temperature. The loss data in Fig 5.12 reveal the occurrence of a transition over a broader temperature range i.e. 22-30 K.
5.3-6 Dielectric Measurement

Figure 5.11: Dielectric constant ($\varepsilon$) a function of temperature for a polycrystalline YMnO$_3$ pellet in zero field (△) and at 4 T (●) magnetic field.

Figure 5.12: Frequency and temperature dependence of tanδ. Symbols a-h represents data taken at 31, 53, 73, 123, 523, 1023, 5023, and 10023 Hz respectively.

The microscopic origin of strain induced lowering of antiferromagnetic transition temperature requires more study but qualitatively one can understand the origin of these effects. In general, a broad transition in dielectric measurement, for normal ferroelectrics, is assigned to the presence of grains and it is termed as “relaxor behaviour”. The frequency dependent dielectric property arises because of presence of oxygen vacancies, and short polar regions
5.4 Conclusion

within a single film [36]. Another possible cause for this broad transition is the movement of domain walls. It is possible that our thin film is ferroelectrically ordered but it contains multiple magnetic domains. In multiferroic materials, these electric and magnetic domains interact with each other and as temperature is lowered below magnetic ordering temperature, both ferroelectric and antiferromagnetic domains coexist and coincide with each other [30].

When external perturbation (such as electric or magnetic field) is applied, these domains start moving. The movement of domains happens at the cost of energy and because of this reason the magnitude of dielectric constant ($\epsilon$) as well as loss (tanδ) decreases when magnetic field is switched on [37]. In strained ferromagnetic films, the variation of Curie temperature has been attributed to change in the bond lengths and bond angles of Mn-O octahedral and splitting of $e_g$ levels [17, 18, 38]. In this case too a similar behavior can be expected leading to change in magnetic ordering temperature as indicated in the magnetization and field dependent dielectric measurements.

5.4 Conclusion

Thin films of epitaxial and highly oriented YMnO$_3$ were deposited on Ga doped ZnO buffer on top of (0001) sapphire using pulsed laser deposition technique. The results show that the magnetic and dielectric properties of the film depend on the lattice strain between the substrate and YMnO$_3$ film. The inverse S-shape anomaly in loss factor, accompanying AFM ordering, shifts to lower temperature ($\sim 30$ K) as compared to bulk YMnO$_3$, which is at $\sim 65$ K. The magnetodielectric measurements parallel and perpendicular to $ab$ plane confirms that the dielectric properties of YMnO$_3$ are highly anisotropic. The magnetodielectric coupling in case of thin films of YMnO$_3$ are an order of magnitude higher as compared to bulk YMnO$_3$ which is of great advantage for device fabrication. The results elucidate that it is possible to tune multiferroic properties by lattice strain in case of hexagonal YMnO$_3$. 
References


