Chapter 4

Effect of Swift Heavy Ion Irradiation on the Properties of BiFeO$_3$ / SrNb$_{0.002}$Ti$_{0.998}$O$_3$ (SNTO) Multiferroic Films

Chapter IV is dedicated to the studies on thickness dependent swift heavy ion irradiation effects on PLD grown BFO films for understanding the modifications in structural strain and surface morphology on their properties. It also explains role of structural defects and internal annealing effect in the transport, dielectric, ferroelectric and magnetic properties of 50, 100 and 200nm BFO films studied.
Chapter 4: Effect of Swift Heavy Ion Irradiation on the Properties of BiFeO$_3$ / SrNb$_{0.002}$Ti$_{0.998}$O$_3$ (SNTO) Multiferroic Films

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4.1 Introduction

Multiferroics, having two or more ferroic orders have been extensively studied in the last decade owing to their applicability in various SPINTRONIC devices for data storage, in multiple state memories, non-volatile memory devices, etc. BiFeO$_3$ (BFO) is most widely studied multiferroic, having large polarization (~100µc/cm$^2$) and magnetization (~1µB/Fe) at room temperature [1 - 3]. The usefulness of BFO in device applications is hindered by the factors, such as leakage current due to oxygen vacancies, weak magnetic behaviour due to inhomogeneous cycloidal spin spiral arrangement, Bi-volatility, high coercive field, etc [4 - 7]. Earlier studies, to overcome, one or many of these factors, were focused on the synthesis of BFO in polycrystalline bulk or thin film form using different synthesis routes or by iso-or aliovalent chemical doping at either Bi or Fe - sites [8, 9]. It is reported that, the electrical and magnetic properties of BFO films are highly strain dependent [10] which prompts, one, to modify the strain in film, leading to the suppression of leakage currents and hence better multiferroic behaviour [11].

It is well established fact that, the material properties can be successfully tailored by using swift heavy ion (SHI) irradiation technique [12]. Low energy ion bombardment on the oxide thin film results in controlled ion - doping or implantation, while using swift heavy ion (SHI) irradiation, it is possible to modify the structural strain in films which in turn, alter the structure, electrical and magnetic properties [13, 14]. In addition, SHI irradiation with different ion fluencies, leads to the creation of point or columnar defects, amorphization and magnetic anisotropy in the material [15, 16]. Very few studies are reported, on the effect of SHI irradiation on the electrical and magnetic properties of BFO films [17, 18]. Further, the defect created in BFO films, due to SHI irradiation, would result in the trapping of charges which in turn will help to suppress the leakage current leading to enhanced multiferroicity.

Keeping in mind, the above mentioned aspects and possibilities, an attempt is made, in this study, to investigate the role of 200MeV Ag$^{+15}$ - ion irradiation (ion fluencies ~ $5 \times 10^{10}$, $5 \times 10^{11}$, $1 \times 10^{12}$ and $5 \times 10^{12}$ ions/cm$^2$) on the modifications in the structural, microstructural, electrical and magnetic properties of 50, 100 and 200nm BFO films grown on conducting single crystalline SrNb$_{0.002}$Ti$_{0.998}$O$_3$ (SNTO) substrates. The
results have been discussed in the light of defect formation and oxygen vacancy migration.

BFO films having 50, 100 and 200nm thicknesses, were deposited onto single crystalline, n-type conducting SrNb_{0.002}Ti_{0.998}O_{3} (SNTO) (100) substrates by ablating the polycrystalline bulk BFO target using 248nm KrF excimer laser with ~250mJ energy at 5Hz repetition rate. Deposition parameters are given in Table 4.1. All the BFO/SNTO films, of size, 10×10mm², were irradiated with 200MeV Ag^{+15} ions with ~ 5 × 10^{10}, 5 × 10^{11}, 1 × 10^{12} and 5 × 10^{12} ions/cm² ion fluence, using 15 UD Tandem Accelerator facility at Inter University Accelerator Centre (IUAC), New Delhi. Ion beam was focused onto a spot of ~ 1mm diameter and was continuously scanned over a complete area of the film, using a magnetic scanner, to ensure uniform irradiation. Irradiation was performed at low angle with respect ion beam direction, to avoid channeling effect. Films irradiated with ~ 5 × 10^{10}, 5 × 10^{11}, 1 × 10^{12} and 5 × 10^{12} ions/cm² will be referred, hereafter as 5E10, 5E11, 1E12 and 5E12, respectively.

Structural and microstructural properties of the pristine and irradiated BFO films were studied using XRD (θ - 2θ), XRD reciprocal space map (RSM) and atomic force microscopy (AFM) measurements, respectively. I–V measurements were performed using two - probe technique, in current perpendicular to plane (CPP) geometry at RT (fig. 4.1). Au-contacts (0.5mm diameter) were deposited on to the film using D.C. coating unit. Dielectric and P-E loop measurements were carried out using Agilent L-C-R meter and Radiant technologies precession ferroelectric loop tracer, respectively. M - H data was obtained on all the films at RT using Quantum design 7 Tesla SQUID–VSM systems.

Using SRIM simulation program [19], the calculated values of electronic energy loss (S_e) and nuclear energy loss (S_n) were ~ 14.05keV/nm and 42.76eV/nm, respectively and projectile range of 200MeV Ag^{+15} ions (ion fluencies ~ 5 × 10^{10}, 5 × 10^{11}, 1 × 10^{12} and 5 × 10^{12} ions/cm²) was ~ 22.86µm which is very large as compared to film thicknesses, ensuring that all the ions striking the films, completely pass through them. According to thermal spike model, highly energetic ions, on passing through the thin
samples, it deposits their energy on to the material resulting in large electronic excitation leading to structural modification evident from the change in unit cell dimensions [20].

Table 4.1: Thin film deposition parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser used</td>
<td>KrF Excimer</td>
</tr>
<tr>
<td>Targets</td>
<td>BFO Polycrystalline bulk</td>
</tr>
<tr>
<td>Substrates</td>
<td>SrNb_{0.002}Ti_{0.998}O_3; Single crystalline (100)</td>
</tr>
<tr>
<td>Laser energy</td>
<td>~ 250mJ</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>5 Hz</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>670°C</td>
</tr>
<tr>
<td>Oxygen Partial Pressure</td>
<td>100 mTorr</td>
</tr>
<tr>
<td>Substrate to target distance</td>
<td>5.5 cm</td>
</tr>
<tr>
<td>Thickness</td>
<td>50, 100 and 200nm</td>
</tr>
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</table>

Figure 4.1: CPP geometry of transport measurements on BFO/SNTO films (Schematic view)

4.2 Structure

XRD patterns of the pristine and irradiated BFO films shows (h00) oriented growth of the film along (h00) peaks of the SNTO substrate (fig.4.2).
Figure 4.2: XRD patterns of pristine and irradiated (a) 50nm (b) 100nm and (c) 200nm BFO films
Lattice mismatch between the film and substrate can be clearly seen from the separation between the film and substrate XRD peaks, resulting in the strain $\delta$, which can be quantified as $\delta (%) = \left[ \frac{(a_{\text{substrate}} - a_{\text{film}})}{a_{\text{substrate}}} \right] \times 100$, where ‘a’ is the lattice parameter of film / substrate. Table 4.2 lists the value of ‘$\delta$’, suggesting the compressive strain in all the film studied.

Figs. 4.2 (a), (b) and (c) shows the XRD patterns of 50, 100 and 200nm pristine and irradiated BFO/SNTO film, respectively. It can be seen from fig. 4.2 (a) that, 50nm pristine and 5E11 films are strained while in 5E12 film, BFO (200) peak almost merges with SNTO (200) peak suggesting the suppression in structural strain.

It can be seen from the XRD patterns of 100 and 200nm BFO films [figs. 4.2 (b) and (c)] that, with increasing ion fluence up to $5 \times 10^{11}$ ions/cm$^2$, BFO (200) peak shifts towards lower angle (more separation between BFO and SNTO peaks) indicating an increase in strain while in 1E12 film, BFO (200) peak shifts towards higher angle, suggesting a decrease in strain. In 5E12 film, BFO peak almost merge with SNTO substrate peak suggesting a decrease in strain in films irradiated with higher fluence. Observation of hump like BFO (200) and (300) peaks in 5E11 film [figs. 4.2 (b) and (c)] suggest defect induced pressure in lattice. Values of structural strain ($\delta$), calculated from the mismatch between the BFO and SNTO XRD peaks, in pristine and irradiated BFO / SNTO films (50, 100 and 200nm) are tabulated in Table 4.2. The variation in $\delta$ with ion fluence and its effect on the properties of BFO / SNTO film is discussed at the end of this chapter.

For understanding the structural strain state of pristine and irradiated BFO films, XRD RSM measurements were carried out around symmetric (100) and asymmetric (311) peaks of BFO and SNTO substrate using high resolution PIxcel3D detector. Fig. 4.3 (a) shows the RSM of pristine 100nm BFO film in which, relative positions of symmetric peaks of BFO and SNTO, clearly indicate highly epitaxial growth of BFO onto SNTO substrate. It can be observed from fig. 4.3 (b, c and d) that, the separation of asymmetric (311) peaks of BFO and SNTO of pristine 50, 100 and 200nm films, decreases with increases thickness suggesting reduction in structural strain. On irradiating 50nm film with 5E11 fluence [fig. 4.3 (e)], separation between BFO and SNTO (311) peaks
Effect of Swift Heavy Ion Irradiation on the Multiferroic Films decreases, suggesting reduction in strain while in 5E12 irradiation, 50nm BFO (311) peak gets merged with the SNTO peak but observed dense background in fig.4.3 (f), gives clear image of increased defects due to 5E12 fluence irradiation resulting in amorphization. Interestingly, fully relaxed phase is observed for 5E12 irradiated 100nm film, evident from, overlapping of (311) asymmetric peak of BFO and SNTO [fig. 4.3(g)].

Effect of SHI irradiation on the 100nm BFO - SNTO film lattice mismatch leading to structural strain has been explained pictorially in fig. 4.4 by showing the inclination of lattice vector. It can be seen that, pristine BFO/SNTO film has a structural strain which increases with ion fluence up to $5 \times 10^{11}$ ions/cm$^2$. Further increase ion fluence ($1 \times 10^{12}$ ions/cm$^2$) results in the decrease in strain while 5E12 film is having minimum strain in it.
Figure 4.3: Reciprocal Space Maps of (a) symmetric \((100)\) planes of BFO and SNTO 100nm pristine film, asymmetric \((311)\) planes of BFO and SNTO for Pristine (b) 50nm, (c) 100nm, (d) 200nm, (e) 50nm \(5\times10^{11}\), (f) 50nm \(5\times10^{12}\) and (g) 100nm \(5\times10^{12}\) films
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4.3 Microstructure

Modifications in the surface morphology observed using AFM (2D and 3D) images of different 50 and 100 BFO films irradiated with various ion fluencies are shown in fig. 4.5 (a - h) while fig. 4.5 (i - m) shows the AFM micrograph of pristine and irradiated 200nm films, respectively.
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It can be seen from fig. 4.5 (a - c) that, 50nm pristine BFO film exhibit, homogeneous rectangular grain structure which gets modified into hillock like defects onto surface after irradiation with $5 \times 10^{11}$ and $5 \times 10^{12}$ ions/cm$^2$ fluencies. Values of rms surface roughness (RSR) increase with ion fluence are given in Table 4.2.

Pristine 100nm BFO film shows larger rectangular grains as compared with 50nm films with few structural defects possibly due to the grain agglomeration [fig. 4.5 (a &
d). After irradiation, small hillocks originating out on the surface of 5E10 film get modified in bigger hillocks in 5E11 film whereas 1E12 film shows columnar track like formation and 5E12 film becomes granular without any defect (hillock or columnar track) formation due to energy minimization [fig. 4.5 (e - h)]. From Table 4.2, it can be seen that, the RSR increases from pristine to 1E12, mainly due to the creation of defects on the surface of the films, while decreases in 5E12, may be attributed to the energy deposition created due to higher fluence. Similar to the strain variation, RSR is also small in 5E12 as compared to the pristine one.

In case of pristine and irradiated 200nm BFO films [figs. 4.5 (i - m)], it can be seen that, surface modification, differs from that of 50 and 100nm films. After irradiation, columnar track like defects observed onto the surface of 5E10 film gets modified in bigger hillocks in 5E11 and 5E12 films while 1E12 film shows barely smooth surface with few small hillock formations. From Table 4.2, it can be seen that, the RSR increases from pristine to 5E11, due to the creation of defects onto the surface of the films, while decreases in 1E12, which may be attributed to the energy deposition due to irradiation. 5E12 film shows higher value of RSR as compared to pristine and irradiated BFO films studied, due to higher fluence irradiation results in increase in defect density and hence dead layer formation.

### 4.4 Dielectric

Plots of variation in dielectric constant and loss in the frequency range (1 KHz – 1 MHz) for pristine and irradiated BFO films obtained at RT are shown in figs. 4.6 (a - c). In order to avoid the contribution from conducting SNTO substrate, the dielectric measurements were carried out using one contact probe on BFO film and another on the step made on SNTO substrate, so that, the interfacial polarization only contribute to the dielectric behaviour. All films show the higher value of dielectric constant \((\varepsilon')\) at lower frequency, which is due to higher relaxation time.

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Figure 4.6: Plots of variation in dielectric constant and loss for (a) 50nm, (b) 100nm and (c) 200nm pristine and irradiated BFO films
From the plots of $\varepsilon'$ and loss (tan$\delta$) for 50nm pristine and irradiated BFO films [fig. 4.6 (a)], it can be seen that, $\varepsilon'$ decreases from pristine to 5E11 and 5E12 irradiated films, suggesting that, energy deposited due to irradiation leads to the formation of oxygen vacancies and hence increase in film conductivity. Variation in tan$\delta$ vs. frequency plots, show that relaxation behaviour is observed at $\sim 10^4$ Hz for pristine and 5E12 irradiated films which may be attributed to presence of few oxygen vacancies in pristine film which increases after irradiation, suggesting the hopping of electron through Fe$^{3+}$ - oxygen vacancy - Fe$^{2+}$. 5E11 film exhibit lower value of tan$\delta$ possibly due to formation of structural defects resulting in the suppression in electron hopping.

$\varepsilon'$ and tan$\delta$ behaviour of 100nm pristine and irradiated films is shown in fig. 4.6 (b), depicting, higher $\varepsilon'$ value for 5E11 film while other irradiated films show decrease in $\varepsilon'$ compared with pristine film. This can be understood as the defect formation due to $5 \times 10^{11}$ ions/cm$^2$ fluence become prominent for 5E11 film while other films possesses more oxygen vacancies. These results can be correlated with XRD analysis in which strain increases for 5E11 film due to increase in defects.

Fig. 4.6 (c) shows the $\varepsilon'$ and tan$\delta$ behaviour of 200nm pristine and irradiated BFO films. It can be observed that, the irradiated films show the enhancement in $\varepsilon'$ due to defect induced reduction in conversion of Fe$^{3+}$ - oxygen vacancy - Fe$^{2+}$. 5E12 show the highest $\varepsilon'$ value, due to the formation of dead layer at film - substrate interface resulting in the suppression in conductivity, as compared to other films. The observed plateau like behaviour in $\varepsilon'$ and Debye like relaxation in tan$\delta$ behaviour of 5E10 and 5E12 films may be due to defect induced reduction in migration of charge carriers released from the oxygen vacancies under applied frequency while other films show linear behaviour in tan$\delta$, possibly due to the direct hopping of Fe$^{3+}$ to Fe$^{2+}$. The similar results have been observed in temperature dependent dielectric studies on La and Mg co-doped BFO [21].
Table 4.2: Values of strain ($\delta$), rms surface roughness (RSR), saturation voltage ($V_C$), saturation polarization ($P_S$), coercive electric field ($E_C$), saturation magnetization ($M_S$), coercive magnetic field ($H_C$) and Dielectric constant ($\varepsilon'$) for pristine and irradiated BFO / SNTO films

<table>
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<tr>
<th>BFO Films</th>
<th>Strain ($\delta$) (%)</th>
<th>RSR (nm)</th>
<th>$V_C$ (V)</th>
<th>$P_S$ (µC/cm$^2$)</th>
<th>$E_C$ (kV/cm)</th>
<th>$M_S$ (emu/cc)</th>
<th>$H_C$ (Oe)</th>
<th>$\varepsilon'$</th>
</tr>
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<tbody>
<tr>
<td>50nm Pristine</td>
<td>-4.46%</td>
<td>03.09</td>
<td>4.9</td>
<td>5.78</td>
<td>248</td>
<td>25</td>
<td>63</td>
<td>2.12</td>
</tr>
<tr>
<td>50nm-5E11</td>
<td>-4.20%</td>
<td>05.67</td>
<td>3.2</td>
<td>2.68</td>
<td>43</td>
<td>23</td>
<td>62</td>
<td>0.61</td>
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<tr>
<td>50nm-5E12</td>
<td>-1.52%</td>
<td>09.72</td>
<td>4.0</td>
<td>1.93</td>
<td>92</td>
<td>15</td>
<td>43</td>
<td>1.44</td>
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<td>100nm Pristine</td>
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<td>05.44</td>
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<td>0.80</td>
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<td>3.4</td>
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<td>124</td>
<td>06.52</td>
<td>50</td>
<td>2.33</td>
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<td>200nm Pristine</td>
<td>-3.25%</td>
<td>4.87</td>
<td>2.9</td>
<td>0.78</td>
<td>19</td>
<td>05.20</td>
<td>61</td>
<td>4.46</td>
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<td>0.72</td>
<td>17</td>
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<td>200nm-1E12</td>
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<td>01.11</td>
<td>3.6</td>
<td>0.86</td>
<td>43</td>
<td>06.49</td>
<td>70</td>
<td>15</td>
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<tr>
<td>200nm-5E12</td>
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<td>--</td>
<td>2.88</td>
<td>70</td>
<td>09.06</td>
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</table>
4.5 Transport (I - V)

To understand the possible role of leakage currents in pristine and irradiated BFO films, I-V measurements were performed by sweeping bias voltages $0V \rightarrow +6V \rightarrow 0V \rightarrow -6V \rightarrow 0V$ with delay time of 200ms for avoiding joule heating effect. Currents measured from 0.5mm Au - top electrode on BFO surface are shown in fig. 4.7 (a - l). All films exhibit rectifying I - V behaviour with hysteresis. I - V measurements repeated for 1V, 2V and 3V bias voltages using same path $(0V \rightarrow +V \rightarrow 0V \rightarrow -V \rightarrow 0V)$, showed large fluctuation in currents without rectifying behaviour with current values in the range of $\sim nA$ suggesting highly insulating nature of all the films under low applied voltages. Hysteresis in I - V behaviour observed for BFO/SNTO films, under 6V bias can be understood as - application of +6V results in the release of electron from oxygen vacancies which leads to the formation of conducting channels during cycle - 1, whereas during $+6 \rightarrow 0V$ (voltage cycle - 2), electron move more easily through already formed conduction channels resulting in high currents. This results in the hysteresis in I - V, with cycle 1 (high resistance state, HRS) and cycle 2 (low resistance state, LRS) across the films. It is reported that, at lower bias voltages, oxygen vacancies acting as donor impurities, do not move freely but, at higher bias voltages, they release one or two electrons, leading to conduction [22].

From I - V plots of 50, 100 and 200nm BFO/SNTO films (pristine and irradiated) [fig. 4.7 (a - l)] the following observations along with the possible cause for them are given below –

- Pristine 50nm film exhibit higher saturation voltage ($V_C$) as compared to irradiated 50nm films (Table 4.2) due to lower oxygen vacancies.

- 50nm 5E11 film show the reduction in $V_C$, may be due to energy deposition during irradiation, resulting in formation of oxygen vacancies which release additional charge carrier under applied bias voltages.

- 50nm BFO film irradiated by $5 \times 10^{12}$ ions/cm$^2$ fluence, show slight increase in $V_C$ and reduction in hysteresis in I - V due to increase in defects and amorphization which can be correlated with the RSM results.
100nm and 200nm pristine films, display lower value of $V_C$ as compared with 50nm pristine film, possibly due to prolonged time required for deposition resulting in increased oxygen vacancies.

Enhancement in $V_C$ and hysteresis in I - V for 100nm irradiated films (5E10, 5E11 and 1E12) as compared to pristine film, may be due to defect formation which hinder the conduction path for charge carriers.
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Figure 4.7: I - V behaviour of pristine and irradiated BFO (a - c) 50nm, (d - h) 100nm and (i - l) 200nm films
Interestingly, lower value of $V_C$ and hysteresis nature has been observed for 5E12 100nm film, possibly due to the increase in oxygen vacancies by energy deposition at higher fluence irradiation.

5E10 200nm film show higher value of $V_C$ as compared to the 5E11 and 1E12 200nm films which may be due to the lower ($\sim 5 \times 10^{10}$ ions/cm$^2$) fluence irradiation, creating defects while for fluence $\sim 5 \times 10^{11}$ and $1 \times 10^{12}$ ions/cm$^2$, larger irradiation time is required, resulting in increase in local temperature and hence oxygen vacancies.

Observation of very low current (non-measurable) and absence of rectification in 5E12 200nm film may be attributed to increase in defect at the interface due to higher fluence irradiation resulting in the formation of dead layer and suppression in conduction. Interestingly, lower value of $V_C$ and hysteresis nature has been observed for 5E12 100nm film, possibly due to the increase in oxygen vacancies by energy deposition at higher fluence irradiation.

The possible mechanism of charge conduction in pristine and irradiated 100nm BFO films, due to the formation of defects and release of electrons by neutral oxygen vacancies, has been pictorially shown in a schematic manner in fig. 4.8. Pristine BFO film possess fewer oxygen vacancies formed during the film growth, which takes part in conduction under higher applied bias voltage $> \pm 3$V [fig. 4.8(a)]. Irradiation induced defects are responsible for hindrance to the flow of charge carriers in conducting channels, resulting in the increase in $V_C$ up to 5E11 film, as shown in fig. 4.8 (b) and (c) whereas formation of oxygen vacancies with defects in 1E12 film, slightly increases the conductivity resulting in reduction in $V_C$, as shown in fig. 4.8 (d). However, in 5E12 film, the local annealing effect due to prolonged duration of irradiation, results in the creation of more oxygen vacancies leading to enhanced conduction and lower $V_C$ [fig. 4.8 (e)]. This is corroborated with the observation of reduction in structural strain [fig. 4.2, XRD and fig.4.3, RSM results] and formation of highly granular microstructure [fig. 4.5, AFM results] in 5E12 film.
4.6 Ferroelectric (P - E loop)

For understanding the ferroelectric behaviour of pristine and irradiated BFO / SNTO films, P - E loops were obtained at RT and 50Hz by using bias voltages well below $V_C$ (obtained from I - V measurements). P - E loop measurements under voltages $> V_C$ ($\sim$3V), do not show any significant P - E loops, mainly due to conducting nature of the film at higher bias voltages. Figs. 4.9 (a), (b) and (c) show the P - E loops of 50, 100 and 200nm BFO films (pristine and irradiated), respectively.
Figure 4.9: P - E hysteresis loop of pristine and irradiated (a) 50nm, (b) 100nm and (c) 200nm BFO films
It can be seen that, in 50nm film [fig. 4.9(a)], polarization decreases with increase in ion fluence which may be correlated with the formation of oxygen vacancies due to ion irradiation resulting in enhanced conductivity. In 100nm films, 5E11 exhibit highly saturated P - E loop (maximum $P_S$ and $E_C$) [fig. 4.9 (b)], possibly due to the increase in defects due to irradiation which is corroborated with the observed large values of structural strain and rms roughness [fig. 4.2, XRD and fig.4.5, AFM]. Interestingly, in 200nm BFO films, irradiation with $5 \times 10^{10}$, $5 \times 10^{11}$, $1 \times 10^{12}$ ions/cm$^2$ fluencies result in the increase in polarization at low bias voltages as compared to pristine 200nm film, which may be attributed to the formation of defects and trapping of electron released from oxygen vacancies. 5E12 film exhibit highest polarization, because, under large fluence and higher thickness (200nm), passage of ions for longer duration, creates more defects forming dead layer at the film - substrate interface resulting in increase in insulating nature of film. However, the values of $P_S$ obtained for BFO/SNTO film (pristine and irradiated) are comparatively lower than those reported for BFO films grown on highly conducting Pt/TiO$_2$/SiO$_2$/Si and other substrates [23] which may be due to the lower conductivity of SNTO substrate ($\sim 5.21 \times 10^{-6}$Ω$^{-1}$cm$^{-1}$) and lower measurement frequency ($\sim$50Hz) used.

To know the effect of applied electric field (bias voltage) on the P - E loop behaviour of BFO / SNTO films, measurements were carried out on 200nm film irradiated with different ion fluencies, as shown in figs. 4.10 (a - d). It can be seen that, all the films exhibit well developed P - E loops at low applied bias voltages ($\sim$2V), whereas, under higher applied voltage ($> 2V$), leakage increases due to the released charge carrier from oxygen vacancies. Also, 1E12 film show almost square P - E loop which may be possibly due to defect induced enhanced dipolar polarization with large $E_C$, useful for device application.
Effect of Swift Heavy Ion Irradiation on the Multiferroic Films

Further investigations on the ferroelectric properties of BFO pristine and irradiated films, capacitance ($C_p$) vs. voltage (V) measurements were carried out under 1MHz frequency with sweeping bias -5 to +5V at RT and the $C_p$ - V plots are shown in figs. 4.11 (a - c). It can be seen that, all the films possesses butterfly shape of $C_p$ - V behaviour, similar to one observed in typical ferroelectric materials. It can be seen from fig. 4.11 (a) that, $C_p$ - V behaviour of 50nm pristine and irradiated films shows the good
butterfly shape $C_p$ - V loop for pristine film, which gets suppressed slightly after irradiation similar to observed in P - E behaviour. Irradiation induced enhancement is observed in $C_p$ - V behaviour as compared to pristine 100nm film [shown in fig. 4.11 (b)]. 5E11 100nm film shows the improved butterfly loop and higher value of $C_p$, which may be due to the increase the defects resulting in suppression of conductivity, leading to insulating nature. 5E12 irradiated film shows very low value of $C_p$ due to formation of oxygen vacancies due to internal annealing effect (discussed in I - V and P - E behaviour). Fig. 4.11 (c) depicts the $C_p$ - V behaviour of 200nm pristine and irradiated films which shows good butterfly like $C_p$ - V of 1E12 and 5E12 irradiated films which may be due to increase in the defects and formation of dead layer due to higher fluence.
Figure 4.11 $C_p - V$ characteristic of pristine and irradiated (a) 50nm, (b) 100nm and (c) 200nm BFO films
4.7 Magnetic (M - H)

For understanding the ion irradiation effects on the modifications in BFO / SNTO films, M - H measurements were carried out at RT under ±3T.

![M - H hysteresis curve of pristine and irradiated films](image_url)

Figure 4.12: M – H hysteresis curve of pristine and irradiated (a) 50nm, (b) 100nm and (c) 200nm BFO films
M - H plots obtained after subtracting the diamagnetic contribution (linear part of fitted data at higher field region) of the SNTO substrate from the measured data are shown in fig. 4.12 (a - c). It can be seen that all the pristine and irradiated films display a weak ferromagnetic behaviour. Values of saturation magnetization ($M_S$) and coercive magnetic field ($H_C$) of pristine and irradiated films are listed in Table 4.2. It can be observed from the fig. 4.12 and Table 4.2 that, $M_S$ and $H_C$ of pristine and irradiated BFO films vary according to the changes in lattice strain. It has been theoretically proved that, the epitaxial strain modifies the spiral spin structure resulting into the canting of spins and weak ferromagnetism in multiferroic BFO compounds [24].

50nm pristine BFO film exhibit the higher value of $M_S$ ($\sim 25$emu/cc) which decreases with increasing ion fluence due to irradiation induced decrease in the structural strain. In 100nm pristine and irradiated films, 5E11 irradiated film display higher value of $M_S$, which may be possibly due to formation of defects resulting into increase in lattice pressure and strain value, whereas 5E12 film shows the decrease in $M_S$ which may be attributed to the local annealing induced improvement in the interface crystallinity and hence reduced strain at the film - substrate interface. 200nm irradiated films, depict different mechanisms as compared with 50 and 100nm irradiated films, in which, 5E12 irradiated film shows higher $M_S$ value which may be due to increase in defects resulting in dead layer formation.
4.8 Conclusions

SHI irradiation studies performed using 200MeV Ag\textsuperscript{15} ion with ion fluencies \(\sim 5 \times 10^{10}, 5 \times 10^{11}, 1 \times 10^{12}\) and \(5 \times 10^{12}\) ions/cm\textsuperscript{2} on 50, 100 and 200nm BFO films, show that, irradiation induces structural defects and oxygen vacancies created are responsible for the modifications in the multiferroic properties of BFO films. As a result of structural, microstructural, electrical and magnetic property measurements, the following conclusions have been drawn -

Structural studies show that, compressive strain decreases from pristine to 5E12 irradiated film in 50nm BFO while it increases from pristine to 1E12 fluence and decreases in 5E12 film in 100 and 200nm BFO films. Depending on ion fluence and film thickness, defects are created and local annealing effect is observed which results in modification in structural strain. RSM measurements show the epitaxial nature of 100nm pristine film and strain modifications observed along \((311)\) plane in 50 and 100nm pristine and irradiated films.

Microstructural investigations using AFM, shows irradiation induced formation of hillock like defect and granular grain morphology in BFO / SNTO films. 50nm irradiated BFO films show the increase in surface roughness with ion fluence with hillock like defect formation at surface while in 100nm BFO film, it is observed that, under higher ion fluence (1E12), columnar track like defects are generated. Further increase in ion fluence (> 1E12), results in the decreases in the surface roughness and more granular grain morphology, possibly due to local annealing effect. In 200nm BFO films, surface roughness increases up to 5E11 while in 1E12 film, it gets reduced appreciably due to local annealing effect. Irradiation with higher fluence (5E12) in 200nm film, results in to the formation of dead layer at the film - substrate interface due to the increased number of defects generated due to prolonged duration of irradiation.

Modification in the I - V behaviour of BFO film irradiated with different ion fluencies show that defects formed help to reduce the conductivity resulting in increase in \(V_C\) and hysteresis behaviour of 100nm (5E10, 5E11, 1E12) and 200nm (5E10, 1E12) BFO films while formation of oxygen vacancies, increases the conductivity resulting in
reduction in \( V_C \) and hysteresis behaviour in 50nm (5E11 and 5E12), 100nm (5E12) and 200nm (5E11) films.

Investigation on the ferroelectric behaviour (P - E, dielectric and C - V) of pristine and irradiated BFO films (50, 100 and 200nm) show that, 50nm films exhibit reduction in ferroelectric behaviour with increase in ion fluence while in 100nm film ferroelectricity gets improved up to 5E11, due to defect formation, whereas, it decrease in 1E12 and 5E12 films due to oxygen vacancy formation. In 200nm films, higher polarization is observed for 5E12 film due to increased number of defects formed results in dead layer.

In conclusion, as a result of present studies on irradiation effects on various properties of BFO / SNTO films, the role of oxygen vacancies and defects formed due to various ion fluencies has been understood to modify the multiferroic properties of film. An interesting outcome of the present studies is, the observation of modification in multiferroic property of BFO / SNTO films which depends on the film thickness and ion fluencies. This has been shown in a schematic manner, by plotting the variation in structural strain, polarization and magnetization as a function of ion fluencies in 100nm BFO / SNTO films (fig. 4.13). Further irradiation studies on similar multiferroic based thin film and devices will help to engineer the properties for possible device applications.

![Schematic diagram of fluence dependent ion irradiation effects in the properties of 100nm BFO film](image.png)

**Figure 4.13:** Schematic diagram of fluence dependent ion irradiation effects in the properties of 100nm BFO film

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References:


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