This chapter puts forward the effect of Ag$^{15+}$ ion irradiation on the properties exhibited by La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ thin films. Modifications have been probed using XRD, AFM, frequency and temperature dependent dielectric response, temperature dependent and isothermal magnetization, XAS and XMCD studies.
Chapter 7

7.1 Introduction

Multiferroic materials are of special interest because of their potential applications [1, 2]. It has been reported that the buffer layer of conductive oxide electrodes, such as LaNiO$_3$ [3] can induce a preferred oriented growth and may also improve the properties of thin films. Details of LNO as buffer layer have been discussed in previous chapter [4]. Practical way of search for new multiferroics is preparing composite material system which is also adopted in present thesis work. Results have already been discussed in Chapters 4-6. They demonstrate that proper Bi and Mn ions substitution for La and Fe site in La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (0.0 ≤ x ≤ 0.4) multiferroic samples and use of proper electrode in La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$/LaNiO$_3$/LaAlO$_3$ (LBFMO3/LNO/LAO) thin film form can improve the magnetic, ferroelectric and magneto-electric properties simultaneously.

Synthesis of these materials in thin film form and tailoring their properties with SHI is an important study in itself. The physical properties of oxide materials are highly dependent on charge transfer energy, Coulomb repulsion and these entire parameters are then dependent on bond length, bond angles and local disorders. SHI irradiation is known to introduce structural and electronic alteration, and further, can modify the strain electrical and magnetic properties in the films depending on the extent of fluence values in film [5]. The impact of SHI in single phase LBFMO3/LNO thin film on LAO substrates may enhance its transport and magnetic properties. Ag$^{15+}$ beam of 200 MeV has been selected for irradiation owing to the nature of statistical energy deposition process, stopping and range of ions in matter (calculation based on Monte Carlo simulation) [6]. Particularly LBFMO3/LNO/LAO has been selected to study in thin film form, since a detailed study on bulk series suggest that this gives the best results as far as multiferroic properties are concerned amid the presence of magneto-capacitive coupling (details in Chapter 5). Prospects to tailor the electronic properties offers the various possibility of engineering the transport and magnetic property of this material using ion beam irradiation. Mixed valence states in oxide materials play a key role in determining the electrical and magnetic properties since they are directly related with the exchange interaction due to different hybridization states. To the best of my knowledge, very few reports [7] have been available on such type of studies.

Present study has been undertaken to explore the modification introduced in LBFMO3/LNO/LAO thin films after irradiation with Ag$^{15+}$ SHI beam of 200 MeV having fluence values 5x10$^{11}$ and 5x10$^{12}$ ions/cm$^2$. Changes brought into film due to irradiation have
been examined by means of structural, surface morphology, dielectric and magnetic studies. NEXAFS and XMCD measurements in LBFMO3/LNO/LAO multiferroic thin films have been performed since the deeper understanding of the electronic structure of material is enviable to understand their complex magnetic ordering and also help in growth and design of new materials. Results suggest almost favorable effect of SHI irradiation on its properties. Moreover, magnetization results are also found to be correlated with electronic distribution of ions present in the system.

7.2 Experimental details

Bulk targets of LBFMO3 and LNO were prepared by standard solid state reaction technique. The details of thin film synthesis together with structural, magnetic and ferroelectric studies are presented in Chapter 6 of the thesis. Before irradiation, thin films were cut into four pieces, each of size 5 mm × 5 mm. One piece of film was kept pristine while the other three pieces were used for irradiation and further study in order to keep the growth conditions uniform for all the samples. Thin films were irradiated at 300 K with Ag$^{15+}$ ion beam of 200 MeV using the 15 UD tandem accelerator [8] at the IUAC, New Delhi with different fluence value (5×10$^{11}$ and 5×10$^{12}$ ions/cm$^2$). The irradiation was performed under high vacuum condition (base pressure 2×10$^{-6}$ torr). Beam current was kept at ~0.1 pnA to avoid heating and beam was focused to a spot of 1 mm diameter. Film was scanned over the entire film area using a magnetic scanner. The fluence values were determined by measuring the charge falling over the sample surface under the well designed secondary electron suppressed geometry (discussed in Chapter 2). The ladder current was measured with a digital current integrator and a scalar counter. Details of rest of the measurements performed have been already discussed in Chapter 4 - 6. The XMCD experiments at different temperatures (10 and 300 K) were performed at the ESRF’s ID08 beamline, which uses an APPLE II type undulator giving ~100% linear/circular polarization. All scans were collected simultaneously in both total electron yield (TEY) and total fluorescence yield (TFY) modes, ensuring both surface (TEY) and bulk (TFY) sensitivities. The spectra were normalized to incident photon flux and the base pressure of the experimental chamber was better than 3×10$^{-10}$ torr. The sample was aligned at an angle of 45° between the surface normal and the incident beam.

7.3 Results and discussion

7.3.1 X-ray diffraction

XRD data are collected using Bruker D8 X-ray diffractometer with Cu K$_\alpha$ radiation at 300 K.
in standard 0/20 mode for identification of phase and orientation of thin films. XRD spectra for unirradiated LBFMO3/LNO/LAO thin film and films irradiated at different fluence values (5 x 10^{11} and 5 x 10^{12} ions/cm^2) is shown in Fig 7.1 (a-c). It is clearly evident from the XRD analysis that all the films exhibit single phase oriented (101) growth and reveals no structural transformation even after irradiation. All the peaks present in case of unirradiated and irradiated thin films match well either with bulk LBFMO3 sample or with LAO substrate [9]. Peaks indicated by asterisk (*) are identified as the Kβ reflections from LAO substrate. Shift in peaks towards lower 2θ values with increase in irradiation dose values [Fig. 7.1 (b, c)] indicate the augment in lattice. It is also apparent from Table 7.1 that parameters a and c calculated within orthorhombic symmetry and sp.gp. Pnma are continuously increasing leading to distortion in Fe/MnO\textsubscript{6} octahedra and increase in unit cell volume. This may be ascribed to energy transfer from the energetic incoming Ag\textsuperscript{15+} ion beam to the LBFMO3/LNO/LAO target in Se regime. Due to the electron-phonon coupling, the ion’s energy is transferred to lattice resulting in increase of temperature in localized regime around trajectory of itinerant ion path inside the target. As a result, the temperature of target increases far above its melting temperature. This heating is followed by rapid thermal quenching at the rate of ~ 10^{13} to 10^{15} K/sec. Therefore, the phenomenon accountable to bring about the augment in lattice constant may be the thermal spike model [10]. This rapid annealing and quenching of the target material lead to the formation of latent tracks or columnar defects and play vital role in properties exhibited by material under study [11, 12].

**TABLE 7.1 Calculated lattice parameters and unit cell volume for La_{0.8}Bi_{0.2}Fe_{0.7}Mn_{0.3}O_3/LaNiO_3/LaAlO_3 thin films.**

<table>
<thead>
<tr>
<th>Thin film</th>
<th>Symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>Orthorhombic</td>
<td>5.5911</td>
<td>7.8325</td>
<td>5.5902</td>
<td>244.80</td>
</tr>
<tr>
<td>5 x 10^{11} ions/cm\textsuperscript{2}</td>
<td>Orthorhombic</td>
<td>5.6041</td>
<td>7.8325</td>
<td>5.6381</td>
<td>247.47</td>
</tr>
<tr>
<td>5 x 10^{12} ions/cm\textsuperscript{2}</td>
<td>Orthorhombic</td>
<td>5.6381</td>
<td>7.8325</td>
<td>5.6506</td>
<td>249.53</td>
</tr>
</tbody>
</table>

Another important thing to be noticed is that, after irradiation the intensity of peaks corresponding to LBFMO3/LNO/LAO thin film with respect to the buffer layer is increased [Fig 7.1 (c)] with slight variation in FWHM profile, confirming the enhanced crystalline
Fig 7.1 (a) XRD pattern of pristine LBMO3/LNO/LAO thin film. (b-c) XRD pattern of irradiated \(\text{La}_{0.8}\text{Bi}_{0.2}\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_3\) thin films at respective dose of \(5 \times 10^{11}\) and \(5 \times 10^{12}\) ions/cm\(^2\).
nature of films after irradiation, despite retaining the oriented growth of thin films.

### 7.3.2 Surface studies

To further understand the effect of 200 MeV Ag$^{15+}$ SHI irradiation on the surface morphology of LBFMO3/LNO/LAO thin films compared to that of unirradiated films, systematic AFM measurements were performed on the thin films at fluence of 5 x 10$^{11}$ and 5 x 10$^{12}$ ions/cm$^2$ which are shown in Fig 7.2 (a - d). Fig 7.2 (a, b) demonstrate the two dimensional (2D) and three dimensional (3D) images of films irradiated at fluence of 5 x 10$^{11}$ ion/cm$^2$ while Fig 7.2 (c, d) show 2D and 3D views at a fluence value of 5 x 10$^{12}$ ions/cm$^2$ respectively. After irradiation, the rms values of the surface roughness got enhanced as being evaluated from the AFM data and found to increase from 1.964 nm to 2.664 nm for 5 x 10$^{11}$ and 5 x 10$^{12}$ ions/cm$^2$ irradiated thin film respectively. After irradiation, the average grain size also exhibit slight increase from 20 nm in case of unirradiated sample [see Chapter 6] to 28 nm at highest dose value (5 x 10$^{12}$ ions/cm$^2$) along with almost spherical grains shape as is also clear from Fig 7.2 (d). Slight enhancement in the grain size may be due the fact that during irradiation, energy is transferred to the electrons in 10$^{-17}$ sec and they reach an equilibrium state in a time of 10$^{-15}$ sec. Within this thermodynamic system, the excess produced heat increases the local temperature of the system. This heat may get confined within the grain volume and give rise to a non-equilibrium process, resulting in raised grain sizes.

### 7.3.3 Dielectric analysis

To look into the modification in dielectric properties due to SHI irradiation, frequency and temperature dependent measurement of $\varepsilon'$ have been also studied. Frequency (75 kHz – 3 MHz) dependence of $\varepsilon'$ for the unirradiated LBFMO3/LNO/LAO thin film and films irradiated at different fluence values 5 x 10$^{11}$ and 5 x 10$^{12}$ ions/cm$^2$ at room temperature (300 K) is shown in Fig 7.3 (a). For all samples, the $\varepsilon'$ decreases with the increase in frequency. Enhancement in the value of $\varepsilon'$ after irradiation, is a substantial feature being noticed. Maximum value of $\varepsilon'$ ($\sim$ 119) is observed corresponding to the fluence value of 5 x 10$^{12}$ ions/cm$^2$. This enhancement can be understood in terms of the defects generated due to the irradiation. Increased $\varepsilon'$ with irradiation at a fluence of 5 x 10$^{12}$ ions/cm$^2$ is also found to be in accordance with the increased grain size as calculated from AFM data. Fig 7.3 (b) reveals the variation in $\tan \delta$ with $f$ at 300 K for unirradiated LBFMO/LNO/LAO thin films amid the films irradiated at different fluence values 5 x 10$^{11}$ and 5 x 10$^{12}$ ions/cm$^2$. It is evident...
Fig 7.2 (a, b) Show the two dimensional (2D) and three dimensional (3D) view of \( \text{La}_{0.8}\text{Bi}_{0.2}\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_3/\text{LNO/LAO} \) thin film irradiated at fluence value of \( 5 \times 10^{11} \) ions/cm\(^2\) and (c, d) display the 2D and 3D images of film irradiated with \( 5 \times 10^{12} \) ions/cm\(^2\).
Fig 7.3 (a) Dielectric constant ($\varepsilon'$) of unirradiated $La_{0.8}Bi_{0.2}Fe_{0.7}Mn_{0.3}O_3$/LaNiO$_3$/LaAlO$_3$ thin film and thin film irradiated at $5 \times 10^{11}$, $5 \times 10^{12}$ ions/cm$^2$ as a function of frequency (75 kHz – 3 MHz) at 300 K. (b) Variation of tan $\delta$ with frequency at 300 K.
that $\tan \delta$ also decreases with the increase in $f$. Also $\tan \delta$ illustrates a decrease in magnitude with irradiation and found to be minimum in case of film irradiated at highest dose value ($5 \times 10^{12}$ ions/cm$^2$) which is a good indication for application point of view. Figure 7.4 (a-c) displays the $\varepsilon'$ as a function of temperature for both unirradiated and irradiated LBFMO3/LNO/LAO thin film at various fixed frequencies (100 kHz–1 MHz). It clearly demonstrates that $\varepsilon'$ increases slightly in film irradiated with $5 \times 10^{11}$ ions/cm$^2$ but show considerable change on irradiation at dose value of $5 \times 10^{12}$ ions/cm$^2$. This may be because of increased contribution from Bi 6$s^2$ lone pair of electrons as is depicted from the XAS data (details discussed in section 7.3.5). Polarization of the Bi 6$s^2$ lone pair of electrons is also found to be in accordance with results of bulk sample of LBFMO series [13]. Thin film irradiated with $5 \times 10^{12}$ ions/cm$^2$ exhibit almost temperature independent behavior up to ~294 K and increases sharply beyond it. Range of independent region is found to increase with increase in $f$, being maximum at high $f$ (1 MHz) which is an intriguing feature. For better comparison between the results of unirradiated and Ag$^{15+}$ irradiated thin films, values of $\varepsilon'$ at 100 kHz and 350 K for all films are displayed in Table 7.2.

Temperature dependence of the $\tan \delta$ of the unirradiated and irradiated LBFMO3/LNO/LAO thin film is presented in Fig 7.5. Dielectric loss illustrates a decrease in magnitude with the application of SHI irradiation [see Fig 7.5 (b, c)] which is another most noticeable feature observed in these materials for their application in high frequency region. Values of $\tan \delta$ at 100 kHz and 350 K for all films are presented in Table 7.2. $\tan \delta$ for thin film irradiated with $5 \times 10^{12}$ ions/cm$^2$ exhibit almost temperature independent behavior up to ~250 K and increases beyond it which is similar to that exhibited in temperature dependent behavior of $\varepsilon'$ (Fig 7.4). Overall, it is concluded that thin films irradiated with 200 MeV Ag$^{15+}$ ions at different fluence ($5 \times 10^{11}$ and $5 \times 10^{12}$ ions/cm$^2$) exhibit improvement in the dielectric properties compared to the unirradiated film.
Figure 7.4 Temperature variation of dielectric constant ($\varepsilon'$) of unirradiated $La_{0.8}Bi_{0.2}Fe_{0.7}Mn_{0.3}O_3/LaNiO_3/LaAlO_3$ thin film and irradiated at a fluence of $5 \times 10^{11}$, $5 \times 10^{12}$ ions/cm$^2$ in frequency range of 100 kHz – 1 MHz.
Fig 7.5 Thermal variation of \( \tan\delta \) of unirradiated La\(_{0.8}\)Bi\(_{0.2}\)Fe\(_{0.7}\)Mn\(_{0.3}\)O\(_3\)/LaNiO\(_3\)/LaAlO\(_3\) thin film and irradiated at \( 5 \times 10^{11}, 5 \times 10^{12} \) in frequency range of 100 kHz – 1 MHz.
7.3.4 Magnetization

Variation in magnetization with temperature ($M$ vs $T$) measured in presence of an applied magnetic field of 5 kOe in the field cooled (FC) condition for LBFO3/LNO/LAO thin film irradiated at different fluence values ($5 \times 10^{11}$ and $5 \times 10^{12}$ ions/cm$^2$) is shown in Fig 7.6 (a, b). Precipitous increase in value of $M$ is observed at low temperatures which are demonstrating ferrimagnetic behavior. It has been found that irradiated thin films obey the Curie– Weiss law with value of $\theta_N$ varing from -155 to -128 K for $5 \times 10^{11}$ and $5 \times 10^{12}$ ions/cm$^2$ irradiated thin films respectively. Variation of inverse of susceptibility with temperature has been presented in the respective insets of Fig 7.6 a and b. It is clear from Fig 7.6 (a, b) that magnetization is growing with increase in dose of SHI irradiation. Magnetic properties of films have been enhanced considerably with SHI specially after irradiation with fluence of $5 \times 10^{12}$ ion/cm$^2$ whereas lower dose i.e $5 \times 10^{11}$ ions/cm$^2$ does not progress much compared to unirradiated film. LNO being Pauli paramagnetic and LAO diamagnetic in nature has an insignificant effect on the exchange interactions in these films. Therefore, the enhanced magnetization in samples may be due to the distortion in the Fe/MnO$_6$ as is established from XRD results or it is because of the presence of mixed valence states of the Mn/Fe ions (details in section 7.3.5) that may bring in the double exchange interaction.

Hysteresis loop ($M$ vs $H$) measurement performed at 5 K for LBFO3/LNO/LAO thin films irradiated at fluence of $5 \times 10^{11}$ and $5 \times 10^{12}$ ions/cm$^2$ is displayed in Fig 7.7 (a, b) and Fig 7.7 (c) shows the $M$ vs $H$ behavior of film with highest fluence ($5 \times 10^{12}$ ions/cm$^2$) value at 300 K. Insets of Fig 7.7 (a, b) demonstrate the asymmetric behavior and indicates the presence of EB phenomenon. EB is also demonstrated in bulk form of similar (LBFO3) composition (Chapter 4).

**TABLE 7.3 Parameters calculated from magnetization hysteresis ($M$ vs $H$) curves for $La_{0.8}Bi_{0.2}Fe_{0.7}Mn_{0.3}O_3/LaNiO_3/LaAlO_3$ films.**

<table>
<thead>
<tr>
<th>Thin film</th>
<th>$M_{R1}$ (emu/ cc Oe)</th>
<th>$M_{R2}$ (emu/ cc Oe)</th>
<th>$H_{c1}$ (Oe)</th>
<th>$H_{c2}$ (Oe)</th>
<th>$H_{EB}$ (Oe)</th>
<th>$M_{EB}$ (emu/ cc Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>+2.46</td>
<td>- 1.79</td>
<td>+140.20</td>
<td>-198.24</td>
<td>-29.20</td>
<td>0.34</td>
</tr>
<tr>
<td>$5 \times 10^{11}$ ions/cm$^2$</td>
<td>+10.14</td>
<td>-5.96</td>
<td>+296.22</td>
<td>-448.84</td>
<td>-76.31</td>
<td>2.09</td>
</tr>
<tr>
<td>$5 \times 10^{12}$ ions/cm$^2$</td>
<td>+20.72</td>
<td>-13.85</td>
<td>+318.08</td>
<td>-476.78</td>
<td>-79.35</td>
<td>3.44</td>
</tr>
</tbody>
</table>
EB come into existence in thin film with fluence of $5 \times 10^{11}$ ions/cm$^2$. It is further noticed that the considerable EB effect is observed for film irradiated with $5 \times 10^{12}$ ions/cm$^2$ while it was not present in unirradiated thin film as discussed in previous Chapter. Taken as a whole, one may say that the thin films of LBFMO3/LNO/LAO are exhibiting good multiferroic properties after SHI irradiation to facilitate its candidature for future device application.
Fig 7.7 (a,b) $M$ vs $H$ hysteresis curve of LBFMO3/LNO/LAO thin films irradiated at 5 x $10^{11}$ and 5 x $10^{12}$ ions/cm$^2$ at 5 K. Inset: enlarged view showing $H_{EB}$. (c) $M$ vs $H$ curve for thin film irradiated with 5 x $10^{12}$ ions/cm$^2$ at 300 K.
7.3.5 Electronic structure

To look into the changes introduced in the electronic structure of LBFMO3/LNO/LAO thin film due to irradiation, NEXAFS at the O K-edges is performed to gain information regarding the hybridization of O 2p orbitals with 3d orbitals of the neighbouring transition metal ions [14]. Figure 7.8 presents the normalized O K-edge NEXAFS spectra of LBFMO3/LNO/LAO thin film unirradiated and films irradiated at fluence of $5 \times 10^{11}$ and $5 \times 10^{12}$ ions/cm$^2$ along with the spectra of compounds MnO$_2$, MnO, Fe$_2$O$_3$ and Bi$_2$O$_3$ for coparision [see inset Fig 7.8].

![Normalized O K-edge NEXAFS spectra](image_url)

*Fig 7.8* Normalized O K-edge NEXAFS spectra of unirradiated and irradiated $La_{0.8}Bi_{0.2}Fe_{0.7}Mn_{0.3}O_3$/LaNiO$_3$/LaAlO$_3$ thin films at a fluence of $5 \times 10^{11}$, $5 \times 10^{12}$ ions/cm$^2$. Inset shows the Spectra of MnO$_2$, MnO, Fe$_2$O$_3$ and Bi$_2$O$_3$ as reference compounds.
O K-edge spectra of thin film irradiated with $5 \times 10^{12}$ ions/cm$^2$ is found to consist of four spectral features namely $a, a'$ at $\sim 529.77$ and $530.84$ eV and $b, b'$ at $\sim 534.84$ and $536.35$ eV, respectively. Features $a$ and $a'$ are attributed to the transitions from O $1s$ core levels to the $2p$ states which are hybridized with Mn/Fe $3d$ orbitals. A slight shift in peak position towards the lower energy region with respect to unirradiated and film irradiated at fluence of $5 \times 10^{11}$ ions/cm$^2$ suggests the possibility of the presence of mixed valence states of Mn or Fe ions in the system which is in good agreement with the shift of peak in bulk LBFMO sample (Chapter 5). Feature marked by arrow at $\sim 532.88$ eV is assigned to the hybridization of O $2p$ with the Bi $6s/6p$ orbitals. It is also noted that this peak is not well defined except in film with fluence of $5 \times 10^{12}$ ions/cm$^2$. It may be due to behavior of highly polarizable $6s^2$ lone pair electrons of the Bi$^{3+}$ ion. The orientation of the $6s^2$ electrons lone pair toward the surrounding anion (O$^{2-}$) can produce a local distortion and hybridization between $6s$ Bi and O $2p$ orbitals which is also responsible for enhanced dielectric and magnetic properties of LBFMO3/LNO/LAO thin films. However, the broad feature in the higher energy region beyond $\sim 536.35$ eV is due to the mixing of higher energy metal states of Mn $4sp$, Fe $4sp$ and La $5sp$ orbitals. In order to confirm these facts and to understand the valence states of the transition metal ions (Mn/Fe) $L_{3,2}$ spectra have been also studied.

In order to investigate the cause of enhanced magnetization (discussed in section 7.3.4), we have performed the XAS measurements at Mn $L_{3,2}$-edges of LBFMO3/LNO/LAO thin films. Figure 7.9 shows the normalized Mn $L_{3,2}$ edge NEXAFS spectra of the unirradiated and irradiated ($5 \times 10^{11}$ and $5 \times 10^{12}$ ions/cm$^2$) thin films at 300 K. Spectra of unirradiated and irradiated (at fluence of $5 \times 10^{11}$ ions/cm$^2$) films exemplify the existence of mixed valence states (+3 / +4) and with SHI. Owing to the spin–orbit interaction, Mn $2p$ core states split the spectrum into two broad multiplets, namely the $L_3$ ($2p_{3/2}$) and $L_2$ ($2p_{1/2}$) which are $\sim 11$ eV apart. This value is consistent with those reported in detail for bulk LBFMO samples of LBFMO ($0.0 \leq x \leq 0.4$) series [15]. Mn $L_{3,2}$ spectra of $5 \times 10^{12}$ ion/cm$^2$ film contains four spectral features, $a$ ($640.8$ eV), $a'$ ($641.5$ eV), $b$ ($642.05$ eV), $b'$ ($642.8$ eV) and $c$ ($643.62$ eV) which may be directly compared with the three valence states of Mn ions (2+, 3+ and 4+). These structural and valent features will definitely influence the electronic and magnetic behavior of thin films. Increased Mn$^{2+}$ at the expense of Mn$^{3+/4+}$ after SHI with dose of $5 \times 10^{12}$ ion/cm$^2$ is perceptibly displayed in the inset of Fig 7.9 which may in turn favors the multichannel double exchange mechanism (Mn$^{2+}$ – O – Mn$^{3+}$, Mn$^{3+}$ – O – Mn$^{4+}$). This leads to the considerable enhancement in net magnetization of
Fig 7.9 Normalized Mn L\textsubscript{2,3}-edge NEXAFS spectra of unirradiated and irradiated La\textsubscript{0.8}Bi\textsubscript{0.2}Fe\textsubscript{0.7}Mn\textsubscript{0.3}O\textsubscript{3}/LaNiO\textsubscript{3}/LaAlO\textsubscript{3} thin films at a fluence of $5 \times 10^{11}$, $5 \times 10^{12}$ ions/cm\textsuperscript{2}. Inset shows the enlarged view of peaks from a-c.

To investigate the valence state of Fe ions in the LBFMO3/LNO/LAO thin film due to SHI irradiation, the Fe L\textsubscript{3,2}-edge spectra have been also evaluated. Figure 7.10 displays the normalized NEXAFS spectrum of the Fe L\textsubscript{3,2}-edge for the unirradiated and
Fig 7.10 Normalized Fe L$_{3,2}$-edge spectra of unirradiated and irradiated La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$/LaNiO$_3$/LaAlO$_3$ thin films at a fluence of $5 \times 10^{11}$, $5 \times 10^{12}$ ions/cm$^2$ along with the spectra of reference compound Fe$_2$O$_3$ spectra. Inset shows the enlarged view of peaks.

Irradiated LBFMO3/LNO/ALO thin films. L$_3$ edge of film irradiated at fluence of $5 \times 10^{11}$ ions/cm$^2$, the peaks marked with arrow (↓) and $a'$ are found to be similar to that of unirradiated film (i.e. ~ at 708.32 eV and ~709.92 eV) but film irradiated at highest dose exhibit different features with decrease in the intensity of peak marked by ↓ [inset Fig 7.10]
amid slight shift in main peak marked as ‘a’ towards lower energy. It may be attributed to severe distortion in the FeO$_6$ octahedra from tetrahedral towards octahedral symmetry or it may be due to some contribution from Fe$^{2+}$ ions as was also reported in MnFe$_2$O$_4$ system by Lee et al [16]. Further, the lower intensity of peak marked with ↓ also reflects that Fe ions occupy tetrahedral sites. In other words, Fe ions in film with 5 x 10$^{12}$ ions/cm$^2$ fluence value occupy both tetrahedral and octahedral sites.

The normalized NEXAFS spectra of the La M$_{4,5}$- edge for the unirradiated and SHI irradiated (5 x 10$^{11}$ and 5 x 10$^{12}$ ions/cm$^2$) LBFMO3/LNO/LAO thin films are presented in Fig 7.11. This spectra has been taken to probe the changes introduced due to SHI in valence state of La present in the system. M$_{4,5}$-edge spectra are dominated by the spin–orbit splitting where M$_5$-edge is related to the $^3$D$_1$ state and M$_4$- edges with the $^1$P$_1$ state [17].

![Figure 7.11](image)

**Fig 7.11** Normalized La M$_{4,5}$- edge spectra of unirradiated and irradiated La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$/LaNiO$_3$/LaAlO$_3$ thin films at a fluence of 5 x 10$^{11}$, 5 x 10$^{12}$ ions/cm$^2$. **
It is clear from the spectra that M₅ edge occurs at ~ 835.32 and ~ 851.59 eV, respectively, with the difference ~ 16.3 eV in peak position which matches well with earlier reports [17]. It shows that La remains in +3 state even after irradiation. Thus, all the above NEXAFS results suggest that SHI irradiation on LBFMO₃/LNO/LAO thin films modifies the electronic structure. The existence of mixed valence states of Mn ions as complemented by magnetization studies is also confirmed by the Mn L₃,2⁻ and Fe L₃,2⁻ edge spectra. However, in order to acquire in depth information about magnetic contribution from Mn/Fe ions in irradiated LBFMO₃/LNO/LAO thin films, XMCD is performed at Mn L₃,2 edge [18].

**Fig 7.12** Mn L₃,2 edge XMCD spectra at 10 and 300 K for LBFMO₃/LNO/LAO thin film irradiated at fluence of 5 x 10¹¹ ions/cm² (a, b) and Film irradiated with 5 x 10¹² ions/cm² (c, d).
Therefore, to further investigate the source of magnetism and the role of Mn and Fe ions in the LBFMO3/LNO/LAO films, XMCD spectra were collected at the Mn L\textsubscript{3,2}-edge at 10 and 300 K with applied magnetic field of 5 tesla. Figure 7.12 (a-d) present the normalized XMCD spectra for thin films irradiated at different fluence values (5 x 10\textsuperscript{11} and 5 x 10\textsuperscript{12} ions/cm\textsuperscript{2}). One may separate the spin and the orbital part of the magnetic contribution using...
the sum rules but in the present scenario it is not worth since Mn ions are in mixed valence states as is confirmed from XAS data [18, 19]. XMCD spectra of irradiated sample demonstrate the considerable increase in magnetic signal with decrease in temperature compared to unirradiated thin film. However, substantial signal has been obtained in XMCD performed at room temperature as well. Interestingly, magnetism is found to increase [Fig 7.12. (c, d) when irradiated at higher dose (i.e. 5 x 10^{12} ion/cm^{2})]. This is in accordance with the magnetic hysteresis measurement done on film as discussed in section 7.3.4 that divulges the presence of enhanced ferrimagnetism after SHI irradiation. This improvement in magnetic property with SHI supports the fact that irradiation may be employed to modify the properties of thin film. Figure 7.13 (a-d) presents the normalized XMCD spectra for thin films irradiated at different fluence values (5 x 10^{11} and 5 x 10^{12} ions/cm^{2}) collected at the Fe L_{3,2}-edge at 10 and 300 K with applied magnetic field of 5 tesla. Film irradiated at dose of 5 x 10^{11} ions/cm^{2} [Fig 7.13 (a, b)] exhibits almost similar magnetic signal as that of unirradiated sample with no change in spectral feature. Further, 5 x 10^{12} ion/cm^{2} irradiated thin film illustrates the minimal increase in magnetic signal with increase in dose value [Fig 7.13 (c, d)].

7.4 Conclusions

The results of the comparative study on, 200 MeV Ag^{15+} ion beam irradiations lead to following conclusions. From the analysis of the XRD data, it is found that with increasing irradiation fluence, the unit cell parameters also increase compared to that of unirradiated LBFMO3/LNO/LAO thin films. In addition, after irradiation intensity of peaks corresponding to thin film irradiated at highest fluence increases. AFM results are also found to be in harmony with XRD results and show increase in RMS surface roughness value with irradiation amid increase in grain size. Irradiated thin films at fluence of 5 x 10^{12} ions/cm^{2} exhibit improvement in the ferroelectric properties compared to the unirradiated film. Temperature dependent magnetization in FC mode confirms the ferrimagnetic nature of thin film. Isothermal magnetization measurement done at 5 and 300 K exhibit hysteresis loops along with unsaturated behavior even up to 1 tesla. Interestingly, irradiation induced EB phenomena in LBFMO3/LNO/LAO thin film which is not present prior to irradiation. Element specific observations, NEXAFS done at Mn L_{3,2} edge illustrates the evolution of Mn^{2+} in a network of Mn^{3+}/Mn^{4+}. Fe L_{3,2} edge gives the signature of distortion in FeO_{6} octahedra. XMCD measurement further show considerable contribution to magnetization from Mn ions in irradiated films with minimal contribution from Fe ions. These findings
encourage the fact that the preparing the multiferroic thin films followed by irradiation with heavy fluence on conducting layer of LNO might be used to tailor the properties and for developing films with improved properties for technological application.

References