Chapter 5

SHI Irradiation Induced Effects
After discussing the gamma and UV irradiation induced effects on optical, electrical and structural properties of PVA–Ag nanocomposites in Chapter 3 and Chapter 4, respectively, the present chapter is devoted to the similar studies after Swift Heavy Ion (SHI) irradiation on these nanocomposites. To accomplish this, the synthesized PVA–Ag nanocomposites were irradiated to 150 MeV Si\(^{12+}\) ions at fluences of \(1\times10^{11}\), \(3\times10^{11}\) and \(1\times10^{12}\) ions/cm\(^2\), as already discussed in Chapter 2, Section 2.2. Afterwards, these irradiated samples were characterized through UV–Visible spectroscopy for optical studies, transmission electron microscopy for size, shape and concentration of embedded nanoparticles, I–V measurements to analyze the conductivity behaviour and XRD, FTIR & Raman spectroscopy for structural modifications. The results of these studies and their interpretation are presented in the following sections.

5.1 UV–Visible Studies

Figure 5.1 presents the absorption spectra for PVA–Ag nanocomposite films before and after 150 MeV Si\(^{12+}\) ion irradiation at different fluences. It is clearly observable from this figure and as already discussed in Chapter 3, Section 3.1 that the observed absorption band around 425 nm for unirradiated PVA–Ag nanocomposite film (spectrum 'a') corresponds to the surface plasmon resonance (SPR) of Ag nanoparticles embedded in PVA matrix (Keirbig & Vollmer, 1995; Link & El-Sayed, 1999; Carotenuto et al., 2001; Heilman, 2003; Kelly et al., 2003; Gautam & Ram, 2009; 2010; Garcia, 2010) which arises due to the collective oscillations of conduction band electrons of metal nanoparticles, when interacted with the incident electromagnetic radiation.

After irradiation to 150 MeV Si\(^{12+}\) ion beam, the intensity of surface plasmon absorption band increases with increase in the ion fluence. Such an increase in intensity of surface plasmon absorption band may be due to the increase in the concentration of Ag nanoparticles with increasing ion fluence which can be understood in the following manner. As the ion passes close to the embedded nanoparticles, these may be fragmented to smaller nanoparticles depending upon the energy loss by the incident ion (Biswa et al., 2004; Mohanta et al., 2004; Singh et al., 2009; Avasthi et al., 2010;
Avasthi & Pivin, 2010; Kuiri et al., 2010; Avasthi & Mehta, 2011). Also, the interaction of the ion with the polymer chains results in the electronic excitation and ionization which helps in the reduction of Ag\(^+\) into the metallic silver (Wilks et al., 2005; Abargues et al., 2008; Liu et al., 2009; Avasthi and Metha, 2011). Both the fragmentation of the embedded nanoparticles and reduction of Ag ions into metallic Ag as a result of ion irradiation, are responsible for the increased concentration of Ag nanoparticles in the host matrix which in turn causes the increase in intensity of surface plasmon absorption band after ion irradiation. Further, a noticeable decrease in FWHM of SPR peak on account of SHI irradiation follows similar trend as for gamma and UV exposure, as already explained in Chapter 3, Section 3.2.1 and Chapter 4, Section 4.1, respectively.

![UV–Visible absorption spectra of PVA–Ag nanocomposite films before and after SHI irradiation.](image)

**Figure 5.1:** UV–Visible absorption spectra of PVA–Ag nanocomposite films before and after SHI irradiation.
In addition to the above, a continuous red shift in the absorption edge corresponding to PVA–Ag nanocomposites has been observed with increase in SHI fluence. Such a shift in the absorption edge is a result of generation of trap levels between HOMO and LUMO of the nanocomposites on SHI irradiation and is responsible for the change the optical energy gap (Devi et al., 2002; Shah et al., 2010; Mahendia et al., 2011; 2011; Sharma et al., 2013), as discussed in the preceding Section.

5.1.1 Optical Energy Gap

In order to study the change in optical energy gap of PVA–Ag nanocomposites with SHI irradiation at different fluences, the values of \( (\alpha h\nu)^{1/2} \) are plotted as a function of \( h\nu \) corresponding to the fundamental absorption edge in respective UV–Visible spectra (figure 5.1) in light of the Tauc’s relation (Tauc et al., 1966; Tauc, 1974; Fink, 2004; Migahed & Zidan, 2006; Sharma et al., 2007) and are presented in figure 5.2.

![Figure 5.2: Plots of \((\alpha h\nu)^{1/2}\) vs energy \((h\nu)\) for PVA–Ag nanocomposite films before and after \( \text{Si}^{12+} \) ion irradiation.](image-url)

Figure 5.2: Plots of \((\alpha h\nu)^{1/2}\) vs energy \((h\nu)\) for PVA–Ag nanocomposite films before and after \( \text{Si}^{12+} \) ion irradiation.
The corresponding values of optical energy gap have been determined by extrapolating the linear fitted lines in these plots on the $h\nu$ axis (Tauc et al., 1966; Fink, 2004). The observed values of $E_g$ for nanocomposite films before and after SHI irradiation at varying fluences are listed in Table 5.1.

**Table 5.1** Values of optical energy gap for PVA–Ag nanocomposite films before and after SHI irradiation.

<table>
<thead>
<tr>
<th>PVA–Ag nanocomposite films</th>
<th>Optical energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiated at fluence (ions/cm$^2$)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.57±0.02</td>
</tr>
<tr>
<td>$1\times10^9$</td>
<td>3.20±0.05</td>
</tr>
<tr>
<td>$3\times10^9$</td>
<td>2.50±0.03</td>
</tr>
<tr>
<td>$1\times10^{10}$</td>
<td>2.25±0.01</td>
</tr>
</tbody>
</table>

The table clearly depicts that the value of optical energy gap, which is found to be 4.57 eV for PVA–Ag nanocomposite without irradiation, reduces continuously with increasing fluence of SHI irradiation and attains a value of 2.25 eV for the fluence of $1\times10^{12}$ ions/cm$^2$. Such a decrease in optical energy gap may be explained on the basis of the fact that the ion beam irradiation causes chain scission, cross–linking, rupture of ionic bonds, release of ions, electrons & free radicals, etc. thus, enhancing metal–polymer interaction (Singh et al., 2008) and thereby, increasing the localized states between the HOMO and LUMO bands of PVA, which makes the lower energy transistion feasible and leads to the observed changes in the optical energy gap (Ramu et al., 1994; Devi et al., 2002; Mahendia et al., 2010), like that for gamma and UV irradiated samples.
5.1.2 Refractive Index

The refractive index behaviour of PVA–Ag nanocomposites before and after SHI irradiation has been analyzed using the same procedure, as discussed in Chapter 3, Section 3.2.3. Figure 5.3 presents the variation in the value of refractive index \( n(\lambda) \) as a function of wavelength for PVA–Ag nanocomposites before and after SHI irradiation at varying fluence.

![Graph of Refractive Index Behaviour](image)

**Figure 5.3:** Refractive index behaviour of PVA–Ag nanocomposites before and after SHI irradiation for different fluences.

It is clear from the figure that the value of refractive index decreases continuously with wavelength for all the samples. It is also evident from the figure that with increase in dose of SHI to such nanocomposites, refractive index increases consistently. The value of refractive index, which was found to be 1.68 for PVA–Ag nanocomposite, has been found to be increased to 1.86 after irradiation at fluence of
1x10^{12} \text{ ions/cm}^2, at the wavelength 632 nm. Such an enhancement in refractive index may be attributed to the increase in the intermolecular hydrogen bonding between Ag with the adjacent OH group of PVA resulting in the change in packing density, molecular weight distribution (Kumar et al., 2011), etc., as a result of ion irradiation, on the similar lines as that after gamma irradiation.

### 5.2 Transmission Electron Microscopy

Figure 5.4 presents the TEM photographs of PVA–Ag nanocomposite films before (images ‘a’ & ‘b’) and after irradiation to SHI at fluence 1x10^{12} \text{ ions/cm}^2 (images ‘c’ & ‘d’).

![Figure 5.4: TEM images of PVA–Ag nanocomposite before (‘a’ & ‘b’) and after Si^{12+} ion beam irradiation at fluence of 1x10^{12} \text{ ions/cm}^2 (‘c’ & ‘d’).](image)
These images clearly show the enhanced uniformity in particle size and distribution of Ag nanoparticles in PVA matrix after SHI irradiation. From the TEM images, size of the embedded Ag nanoparticles was determined. The size of the Ag nanoparticles, which was found to be 13 ± 5 nm for the sample without irradiation (Chapter 3, Section 3.1.2), has been decreased to 6 ± 1 nm after SHI irradiation at the fluence of 1x10^{12} ions/cm^2. Further, on exposure to SHI, the increase in concentration of nanoparticles is also evident. This increase in concentration of Ag nanoparticles in PVA matrix may be explained on the basis of reduction of Ag ions into metallic Ag, as already discussed.

**5.3 Current–Voltage (I–V) Measurements**

In order to study the DC conduction behaviour and associated conduction mechanism in PVA–Ag nanocomposites before and after SHI irradiation at different fluences, the I–V measurements of these samples were carried out in the voltage range 0–100 V (figure 5.5), following the procedure as already explained in Chapter 2, Section 2.8.

![Figure 5.5: Current–Voltage (I–V) curves for PVA–Ag nanocomposite films before and after ion beam irradiation at different fluences.](image-url)
It is clear from the figure that the value of current increases with increasing voltage for all the samples, however, the linear behaviour of I–V plots observed in PVA-Ag nanocomposite prior to irradiation (inset) is found to be no longer valid after being irradiated with SHI at different fluences.

Further, there is a continuous increase in the value of current with increasing ion beam fluence in the entire voltage range (curves ‘b’–‘d’). This may be due to further reduction of remaining Ag ions into metallic silver as an effect of ion irradiation as already discussed.

### 5.3.1 D.C. Conductivity

The DC conductivity of PVA–Ag nanocomposite films before and after ion beam irradiation at different fluences were determined following the same procedure, as already discussed in Chapter 2, Section 2.8. Figure 5.6 presents the variation of dc conductivity with ion irradiation dose at different voltages.

![Figure 5.6: DC conductivity of PVA–Ag nanocomposite films at different voltages plotted as a function of ion fluence.](image)

Due to non-linear behaviour of I–V plots for SHI irradiated PVA–Ag nanocomposites (figure 5.5); dc conductivity is observed to have an increasing trend with voltage. It can be seen clearly from the figure that the conductivity increases with increase in ion fluence at all voltages, however, this increase is more pronounced at higher voltages. At the applied voltage of 100 V, conductivity of the nanocomposite, irradiated at the fluence of 1x10^{12} ions/cm^2, increases by two orders of magnitude. The values of dc conductivity for PVA-Ag nanocomposites at various fluences are tabulated in table 5.2.

### Table 5.2: Value of DC conductivity for PVA–Ag nanocomposite films before and after ion beam irradiation at different fluence.

<table>
<thead>
<tr>
<th>PVA–Ag Nanocomposite films Irradiated at fluence (ions/cm^2)</th>
<th>Conductivity at Voltage (S/cm)</th>
<th>30 V</th>
<th>60 V</th>
<th>100 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>3.58x10^{-10}</td>
<td>3.71x10^{-10}</td>
<td>3.82x10^{-10}</td>
</tr>
<tr>
<td>1x10^{11}</td>
<td></td>
<td>2.62x10^{-10}</td>
<td>8.39x10^{-10}</td>
<td>2.94x10^{-9}</td>
</tr>
<tr>
<td>3x10^{11}</td>
<td></td>
<td>5.38x10^{-10}</td>
<td>1.87x10^{-9}</td>
<td>5.43x10^{-9}</td>
</tr>
<tr>
<td>1x10^{12}</td>
<td></td>
<td>1.42x10^{-9}</td>
<td>4.061x10^{-9}</td>
<td>1.01x10^{-8}</td>
</tr>
</tbody>
</table>

### 5.3.2 Charge Conduction Mechanism

Figure 5.7 presents the plots of ln (I) versus ln (V) for PVA–Ag nanocomposite films before and after ion beam treatment at different fluences. The charge conduction process can be identified by determining the value of ‘m’ in light of the power law, i.e. I \( \propto V^m \). It is clear from the inset of this figure that the ln (I) varies linearly with ln (V) with m = 1, thus, predicting the charge conduction mechanism to be ohmic in nature for PVA–Ag nanocomposite. This linear dependence of current on voltage is no longer sustained after the ion beam treatment, as discussed earlier. The slope (m) of ln (I) versus ln (V) plots for ion beam irradiated PVA–Ag nanocomposite films was obtained and found to be \( \sim 2 \), thus, predicting the space charge limited conduction (SCLC)
mechanism (Dissado, 1962) as the dominant charge transportation mechanism for ion irradiated samples.

![Graph](image)

**Figure 5.7:** Plots for $\ln(I)$ versus $\ln(V)$ for PVA–Ag nanocomposite films without and with ion beam irradiation at different fluences.

From the above discussion, it can be concluded that optical and electrical properties of PVA–Ag nanocomposites are modified considerably as a result of ion beam treatment. Optical properties of the nanocomposites show the similar, whereas electrical properties exhibit somewhat different rather more pronounced variations in comparison of those for gamma and UV irradiations, explained in Chapter 3 and 4, respectively. These changes are the result of induced structural rearrangements produced as an effect of ion beam treatment. The proceeding section highlights the results and interpretation of structural analysis, as revealed through various techniques.
5.4 Structural Analysis

In order to analyse the induced structural changes in PVA–Ag nanocomposites as a result of ion beam irradiation at different fluences, the same were subjected to XRD, FTIR and Raman analysis.

5.4.1 X-ray Diffraction

Figure 5.8 presents the XRD patterns for PVA–Ag nanocomposites before and after ion beam treatment at different fluences.

![X-ray diffraction pattern for PVA–Ag nanocomposite films before and after ion beam treatment at different fluences.](image)

The diffraction pattern for PVA–Ag nanocomposite without irradiation (inset) shows the same diffraction peaks, as already explained in Chapter 3, Section 3.4.1 (Bhat et al., 2005; Ram & Gautam, 2007; Sadjadi et al., 2008; Gautam & Ram, 2010; Rao et al., 2010; Eisa et al., 2011).
With increasing ion beam irradiation, intensity as well as FWHM of the peaks at 36.3° and 45.8° is found to increase continuously indicating the increase in concentration and decrease in particle size \((Vij et al., 2009)\) of embedded Ag nanoparticles. The position, FWHM and intensity of the characteristic peaks of Ag before and after ion beam treatment have been tabulated in Table 5.3.

**Table 5.3**: Position, Intensity and FWHM of Ag diffraction peaks before and after ion beam irradiation at different fluences.

<table>
<thead>
<tr>
<th>PVA–Ag Nanocomposite films at fluence (ions/cm²)</th>
<th>2θ (deg)</th>
<th>FWHM (deg)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>36.301</td>
<td>0.356</td>
<td>10.27</td>
</tr>
<tr>
<td></td>
<td>45.746</td>
<td>0.376</td>
<td>20.27</td>
</tr>
<tr>
<td>1x10¹¹</td>
<td>36.484</td>
<td>0.376</td>
<td>15.24</td>
</tr>
<tr>
<td></td>
<td>45.864</td>
<td>0.382</td>
<td>24.73</td>
</tr>
<tr>
<td>3x10¹¹</td>
<td>36.376</td>
<td>0.384</td>
<td>21.65</td>
</tr>
<tr>
<td></td>
<td>45.845</td>
<td>0.388</td>
<td>23.08</td>
</tr>
<tr>
<td>1x10¹²</td>
<td>36.454</td>
<td>0.456</td>
<td>23.92</td>
</tr>
<tr>
<td></td>
<td>45.902</td>
<td>0.576</td>
<td>25.99</td>
</tr>
</tbody>
</table>

Further, a new peak has been found to be originated at 32.1° on ion beam treatment of PVA–Ag nanocomposite film at a fluence of 1x10¹¹ ions/cm², intensity of which increases with increase of ion beam fluence. The appearance of this new peak may be due to some disorder produced in host matrix after ion beam treatment and this disorder increases with increase in ion beam fluence. These observations indicate that ion beam irradiation causes the structural rearrangements in a significant manner in the nanocomposite films.
5.4.2 Fourier Transform Infra-Red Spectroscopy

Figure 5.9 presents the FTIR spectra of PVA–Ag nanocomposite films before and after ion beam irradiation at different fluences, in the wavenumber range 4000–700 cm\(^{-1}\). The FTIR spectrum for unirradiated PVA–Ag nanocomposite (curve ‘a’) shows the same vibrational absorption peaks (dips in transmission spectrum), as already mentioned and explained in Chapter 3, Section 3.4.2 (Mbhele et al., 2003; Bhat et al., 2005; Khanna et al., 2005; Bai et al., 2007; Raju et al., 2007; Sun et al., 2010).

![FTIR spectra of PVA–Ag nanocomposite films without and with ion beam irradiation at different fluences.](image)

Figure 5.9: FTIR spectra of PVA–Ag nanocomposite films without and with ion beam irradiation at different fluences.

The decrease in the intensity of absorption band in the 3500–3200 cm\(^{-1}\) region (curves ‘b’–‘d’) after ion beam irradiation indicates the structural rearrangements of...
silver nanoparticles with the chains of PVA molecules. Further, after ion beam treatment, the decrease in intensity of bands at 2928 & 1720 cm\(^{-1}\) and generation of new peaks in region 1250–1450 cm\(^{-1}\) indicate the decoupling between O–H and C–H vibrations due to the increase in interaction of embedded Ag nanoparticles with O and H atoms of PVA chains (Mbhele et al., 2003; Zidan, 2003; Khanna et al., 2005). The effect becomes more enhanced with increasing ion fluence. The appearance of small absorption band around 1637 cm\(^{-1}\), corresponding to C=C stretching, indicates the formation of carbonaceous structure in host matrix after ion beam irradiation (Shah et al., 2009). The decrease in intensity and broadening of band at 837 cm\(^{-1}\), assigned to out of plane vibrations of C–H group, signifies the increase in interaction of embedded Ag nanoparticles with PVA chains at higher fluence. These observations indicate that ion beam irradiation substantially causes the structural rearrangements in PVA–Ag nanocomposite films.

5.4.3 Raman Spectroscopy

Figure 5.10 presents the Raman spectra for PVA–Ag nanocomposite films before and after ion beam treatment at different fluences. The inset in the figure shows the peaks/bands for unirradiated PVA–Ag nanocomposite film, as already explained in detail in Chapter 3, Section 3.4.3 (Thomas & Stuart, 1997; Lin & Yang, 2005; Yu et al., 2007; Tripathi et al., 2012).

On irradiating the nanocomposites by SHI, the bands in the region 600–1300 cm\(^{-1}\) are observed to be almost disappeared. The disappearance of the bands in this region is a signature of structural rearrangements between PVA chains and embedded Ag nanoparticles. The presence of Raman signal at 1365 and 1576 cm\(^{-1}\) corresponds to D and G bands. The appearance of these bands may be attributed to the SERS effect of embedded Ag nanoparticles. Further, the intensity of these bands increases with increase of ion beam fluence (curve ‘c’ & ‘d’). For the present case, the observation of the enhancement in the Raman signal of D and G bands may be assigned to the formation of chemical bonding between Ag nanoparticles and PVA molecules.
Figure 5.10: Raman spectra of PVA–Ag nanocomposites films without and with ion beam irradiation at different fluences.

These significant changes in the Raman vibrational bands may be associated with the breaking of PVA intra or inter–molecular bonds with simultaneous inclusion of new bonds between PVA and Ag nanoparticles. Further, increase in intensity of band at 1576 cm\(^{-1}\) with increasing dose of ion beam irradiation suggests the increase in the carbonaceous phase of PVA, in agreement with the results of FTIR and XRD studies and thus, corroborating towards the change in optical and electrical behaviour.

5.5 Conclusions

It can be concluded that swift heavy ion beam irradiation in PVA–Ag nanocomposites causes significant reduction in size and more uniform distribution of embedded Ag nanoparticles in PVA matrix. A significant change in the optical
parameters i.e. optical energy gap and refractive index has been observed after swift heavy ion beam irradiation. Considerable increase in DC conductivity has been noticed on swift heavy ion beam irradiation. These results are tried to be understood in terms of induced structural changes revealed through XRD, FTIR and Raman analysis.
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