

Research Article

A Comparison of Modifications Induced by Li^{3+} and Ag^{14+} Ion Beam in Spectroscopic Properties of Bismuth Alumino-Borosilicate Glass Thin Films

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Ion irradiation effects on the glass network and structural units have been studied by irradiating borosilicate glass thin film samples with 50 MeV Li^{3+} and 180 MeV Ag^{14+} swift heavy ions (SHI) at different fluence rates ranging from 10^{12} ions/cm² to 10^{14} ions/cm². Glass of the composition $(65-x)\text{Bi}_2\text{O}_3-10\text{Al}_2\text{O}_3-(65-y)\text{B}_2\text{O}_3-25\text{SiO}_2$ ($x = 45, 40$; $y = 20, 25$) has been prepared by melt quench technique. To study the effects of ionizing radiation, the glass thin films have been prepared from these glasses and characterized using XRD, FTIR, and UV-Vis spectroscopic techniques. IR spectra are used to study the structural arrangements in the glass before and after irradiation. The values of optical band gap, Urbach energy, and refractive index have been calculated from the UV-Vis measurements. The variation in optical parameters with increasing Bi_2O_3 content has been analyzed and discussed in terms of changes occurring in the glass network. A comparative study of the influence of Li^{3+} ion beam on structural and optical properties of the either glass system with Ag^{14+} ion is done. The results have been explained in the light of the interaction that SHI undergo on entering the material.

1. Introduction

Ion irradiation is a novel technique for the modification of materials at molecular and electronic level. Ion interactions with materials can result in enhancement in their performance as well as properties such as conductivity, chemical stability, sensitivity, crystallinity, and density [1]. Ion beam effects have been studied for various materials such as insulators [2–4], semiconductors [5], metals [2, 6] and metallic alloys in their crystalline [7], and amorphous phases [8].

Energetic ions lose their energy in matter predominantly via two mechanisms. First, there is a direct transfer of kinetic energy to target atoms by elastic collisions between a projectile nucleus and target nuclei. This mechanism is commonly referred to as nuclear energy loss " S_n " and is mainly responsible for atomic displacements in material. Secondly, the energy of the incident ion is also transferred to target electrons by the generation of excited or ionized target

atoms. This mechanism in the form of inelastic collisions is known as electronic energy loss " S_e " and has a major contribution to the deceleration of fast ions of kinetic energy ≥ 1 MeV/u. The electronic energy loss is relatively low for light ions, so that electronic excitations and ionizations are sparsely distributed mainly along the ion's path. However, for fast heavy ions, the density of electronic excitations and ionizations becomes so high that new and collective effects arise. It has also been found that these electronic excitations (above a certain threshold of S_e which varies from material to material) are capable of provoking structural changes in materials, particularly in insulators [9]. The interaction between SHI and bulk materials leads to specific effects because of the huge amounts of energy being deposited on the target electrons by incident ions [10]. The deposited energy may then be converted to atomic motion and finally leads to the structural and even chemical modifications (such as in polymers) within the cylindrical zone of several nanometers in diameter resulting in the emergence of altogether new

structural arrangements [11]. The energy distribution of heavy ions in matter has been explained with the help of both experimental and theoretical models such as ion explosion, thermal spike [12], and Track core and penumbra models by many workers [13–16].

The changes which take place in materials on interacting with fast heavy ions depend on the irradiation conditions such as irradiation temperature, irradiation angle, and the corresponding projected range and also on the irradiation dose, atomic number, and energy of the ion beam used [10]. Glasses have been found to be sensitive to the effects induced by electronic energy loss “ S_e ” of swift heavy ions [10, 17]. All glassy materials during swift heavy ion irradiation are known to exhibit nonsaturating anisotropic plastic deformation, known as ion hammering effect [18] and have been explained successfully by the viscoelastic model for ion hammering. In metallic glasses effects like phase transformation [19, 20], damage creation [20, 21] and even dimensional changes both in width and length [9] have been observed as a result of an electronic energy loss introduced by ion irradiation.

Glasses are the materials of excellent radiation-resistance provided crystallization can be avoided [22]. This opinion is based on the intuitive argument that a random regrouping or realignment of atoms in an almost perfectly disordered solid would leave its structure nearly unchanged and, consequently, its macroscopic properties. However, in addition to a radiation-insensitive structure, for a material to be technologically useful it must also be stable in macroscopic shape. Therefore, the radiation-induced structural instability of amorphous materials and particularly of glasses provides a new access to the question concerning the way in which an intense electronic excitation can induce atomic rearrangements in solids [23, 24]. Among various types of glasses, borosilicate glass is considered to be one of the most suitable materials for radiation shielding design [25]. On the other hand, glasses based on heavy metal oxide Bi_2O_3 have interesting physical properties such as high density, high thermal stability, and high linear and nonlinear refractive index enabling their extensive applications in the field of optics and opto-electronics [26–32]. Therefore, in the present work we choose bismuth-based alumino-borosilicate glass system for demonstrating the nature and impact of radiation damage on the glass structure as a result of interaction with SHI.

In this paper, working on a concept that the radiation-induced disorder is much easily absorbed in the heavily disordered structure of an amorphous materials such as glass, we present swift heavy ion beam interaction of two borosilicate glass systems BBiSA [B_2O_3 (45%)- Bi_2O_3 (20%)- Al_2O_3 (10%)- SiO_2 (25%)] and BBiSA [B_2O_3 (40%)- Bi_2O_3 (25%)- Al_2O_3 (10%)- SiO_2 (25%)] using 180 MeV Ag^{14+} and 50 MeV Li^{3+} ions at different fluences rates ranging from 10^{12} ions/cm² to 10^{14} ions/cm². For this purpose, thin films of each glass system were synthesized using quartz as a substrate. To characterize the thin films, analysis of the samples has been done using X-ray diffraction, UV-visible, and IR spectroscopy. Also, the present investigations are carried out to compare the influence of Li^{3+} ion beam

TABLE 1: Chemical composition (mole fraction) of the glass samples used in this work.

Sample code	Bi_2O_3	Al_2O_3	B_2O_3	SiO_2
BBiSA	20	10	45	25
BBiSB	25	10	40	25

of energy 50 MeV on structural and optical properties of bismuth-based borosilicate glass system with Ag^{14+} ion of 180 MeV on the either glass system.

2. Experimental

2.1. Sample Preparation. Bismuth based alumino-borosilicate glasses containing B_2O_3 , Bi_2O_3 , Al_2O_3 , and SiO_2 have been synthesized from LR grade reagents in amount sufficient to produce 75 gm glass. The composition along with the sample label is given in Table 1. Appropriate amounts of chemicals were weighed by using an electric balance with an accuracy of 0.001 gm. The weighed samples were ball milled in acetone medium for 90 minutes. The mixed powder was kept overnight for drying. The dried mixture was then melted in alumina crucible of 120 mL capacity in a temperature range of 1300–1350°C using high temperature resistance furnace. The temperature of the mixture was raised slowly to ensure homogeneity of the mixture. Finally the melt was cast into preheated graphite mould of the dimensions 12×12×45 mm³. The sample was annealed for three hours at 300°C in muffle furnace. The glass samples thus formed were hard and dark brown in color.

2.2. Thin Film Preparation and Irradiation. Since the energy of the heavy ions is of the order of few MeV and higher so these impinging ions due to their large range (typically a few tens of micrometer or larger) do not get embedded in the thin substrates used as target such as thin films. It is therefore always preferred and advisable to use thin film samples for better understanding of interaction of SHI with matter as the elastic collision effects causing collision cascade can be safely neglected, and the effect of the embedded ion does not come into picture [33, 34]. In the present case, glass thin films of thickness 300 nm were deposited on quartz glass slide (1 cm × 1 cm) substrate by electron beam gun evaporation of the glass prepared. The pressure during evaporation was 10^{-6} Torr, and the distance from the source to substrate was 135 mm. The thickness of the film being deposited was monitored by quartz crystal monitor.

2.3. Irradiation Procedure. The irradiations were performed at the 15 UD pelletron tandem accelerator at Inter University Accelerator Centre, New Delhi, using Li^{3+} and Ag^{14+} ions of energies of 50 and 180 MeV, respectively. To ensure uniform irradiation, the beam was made incident upon the samples in the scanning mode. The selected zone of the beam area was 1 cm by 1 cm. The expected ranges of the films allowed the ions to cross the whole thickness of the films giving rise to

TABLE 2: Showing the fluence ranges and the values of optical band gap and Urbach of samples of BBiSA and BBiSB series irradiated with Ag^{14+} and Li ion.

Fluence (ions cm^{-2})	Ag^{14+} ion irradiated				Li^{3+} ion irradiated				
	BBiSA series		BBiSB series		BBiSA series		BBiSB series		
	E_g (eV)	ΔE (eV)	E_g (eV)	ΔE (eV)	E_g (eV)	ΔE (eV)	E_g (eV)	ΔE (eV)	ΔE (eV)
0	2.84	1.91	2.06	2.78	0	2.84	1.91	2.06	2.78
1×10^{12}	2.47	2.79	1.16	2.89	5×10^{12}	2.82	2.67	1.93	2.82
5×10^{12}	1.71	2.82	1.12	2.90	1×10^{13}	2.50	2.79	1.82	2.83
1×10^{13}	1.55	2.84	1.05	2.93	5×10^{13}	2.36	2.90	1.66	2.87
3×10^{13}	1.49	2.89	1.01	2.99	1×10^{14}	2.28	2.85	1.58	2.99

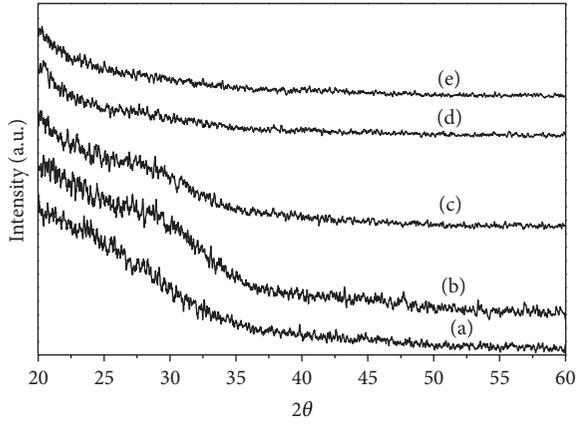


FIGURE 1: The X-ray diffraction patterns of the Ag^{14+} ion-irradiated BBiSA glass thin films: (a) unirradiated; (b) 1×10^{12} ions/ cm^2 ; (c) 5×10^{12} ions/ cm^2 ; (d) 1×10^{13} ions/ cm^2 ; (e) 3×10^{13} ions/ cm^2 .

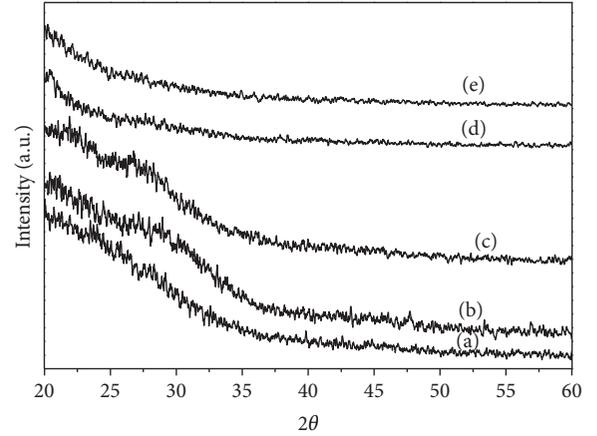


FIGURE 2: The X-ray diffraction patterns of the Li^{3+} ion-irradiated glass thin films of BBiSA series: (a) unirradiated; (b) 5×10^{12} ions/ cm^2 ; (c) 1×10^{13} ions/ cm^2 ; (d) 5×10^{13} ions/ cm^2 ; (e) 1×10^{14} ions/ cm^2 .

homogeneous damage in the bulk. Irradiation has been made at four fluences between 10^{12} to 10^{14} ions/ cm^2 .

The nature and extent of radiation damage, or in other words, structural and optical modifications in glass thin films irradiated with Li^{3+} and Ag^{14+} ions, have been characterized by X-ray diffraction (Bruker Axs diffractometer), Fourier transform infrared (FTIR-8400S Shimadzu, Japan), and UV-visible spectroscopy (Hitachi UV-300). Table 2 represents the fluence ranges to which the samples of the series BBiSA and BBiSB were exposed with Ag ion and Li ion.

3. Results and Discussion

The color of thin films has been found to transform from light brown to dark brown with the increase in the ion fluence. The change was more pronounced for both the glass systems in case of Ag ion as compared to Li ion. This is because the higher electronic energy losses of Ag^{14+} ion in the borosilicate glass thin films is assumed to be responsible for the modification of the properties of glass thin films. The more the electronic energy deposited in the material, the more change in the structural units takes place thereby, leading to the formation of internal defects such

as color centers as observed in the present case. Also it has been observed that irradiation of ordinary borate, silicate, and phosphate glasses can induce numerous changes in the physical properties of glass and especially related to visible coloration, and for this reason the defect centers causing this are often referred to as color centers [35, 36]. The changes induced in other spectroscopic properties due to ion irradiation have been analyzed, and results are discussed below.

3.1. XRD Spectra

3.1.1. BBiSA Glass. XRD data recorded for Ag^{14+} and Li^{3+} ions as shown in Figures 1 and 2 does not show any peaks due to crystalline structure and shows a characteristic broad peak of amorphous structure for all the specimens of the composition BBiSA.

3.1.2. BBiSB Glass. For the glass thin films of BBiSB series (Figures 3 and 4), the absence of Bragg's peak in the pristine sample confirms the amorphous nature of the sample. A broad hump appearing at $2\theta = 25^\circ - 30^\circ$ in pristine sample

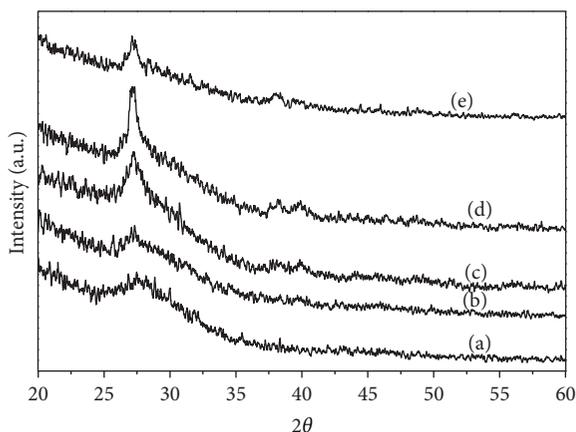


FIGURE 3: The X-ray diffraction patterns of the Ag^{14+} ion-irradiated glass thin films for BBiSB samples: (a) unirradiated; (b) 1×10^{12} ions/cm²; (c) 5×10^{12} ions/cm²; (d) 1×10^{13} ions/cm²; (e) 3×10^{13} ions/cm².

is characterized by the presence of the borate groups in the glass [37]. Initially at a fluence of 1×10^{12} ions/cm², no visible change is observed in the XRD spectra of the thin film samples. But as the fluence is increased from 10^{12} to 10^{13} ions/cm² in either case for Li^{3+} ion and Ag^{14+} ion, this characteristic region at $2\theta = 25^\circ - 30^\circ$ becomes prominent and shows an increase in intensity. At lower fluence, the increase in the intensity of the peak is due to the fact that the energy transferred from the excited electronic system to the lattice results in a sudden and sharp increase in temperature in the irradiated cylindrical zone for a very short time ($< 10^{-15}$ s). This leads to the local heating known as thermal spike, resulting from energy and momentum transfer from the excited electrons to the lattice in the track. Hence, due to the incident fluence, the local electronic temperature rises which results in the nucleation of crystalline phase in the glass matrix which is of Al_2SiO_5 (JCPDS card no. 22-0018) [4, 38]. But on further irradiation, it is observed that intensity of diffraction peak decreases for the films irradiated with the fluence of 3×10^{13} ions cm⁻². The decrease of peak intensity is due to reduction in crystallinity of the borosilicate glass thin film. In this case the sample is amorphized as a consequence of cascade quenching with SHI irradiation [39, 40]. Also it is observed that as compared to Li^{3+} ion, the region is more prominent in case of Ag^{14+} ion for the same sample (BBiSB). It can be therefore be concluded that the increasing width of the XRD peak with increased fluence of Ag^{14+} ion-irradiated BBiSB thin films can be attributed to the lattice damage caused during ion irradiation because of the higher rate of electronic energy loss of Ag^{14+} ion.

3.2. Optical Studies. The optical absorption spectra of all the samples of BBiSA series and BBiSB series glass thin film samples are recorded in the wavelength region of 200–900 nm. The values of optical band gap (E_g) were determined by

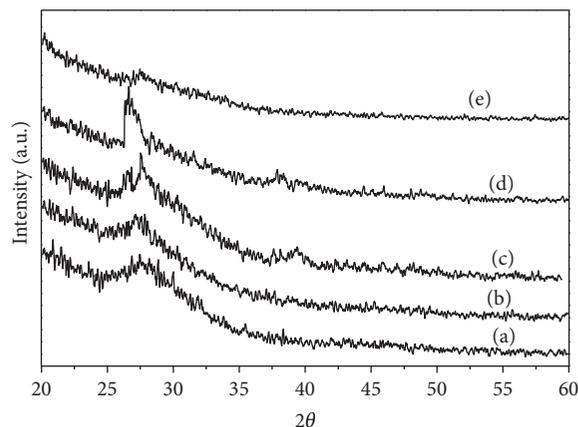


FIGURE 4: The X-ray diffraction patterns of the Li^{3+} ion-irradiated glass thin films for BBiSB series: (a) unirradiated; (b) 5×10^{12} ions/cm²; (c) 1×10^{13} ions/cm²; (d) 5×10^{13} ions/cm²; (e) 1×10^{14} ions/cm².

extrapolation of the best linear fit from the absorption band edge and measuring the intercept value in $h\nu$ -axis. ΔE is the Urbach energy and is determined from the inverse of the slope of the plots $\ln(\alpha)$ versus $h\nu$ [41–45].

3.2.1. Before Irradiation (Effect of Composition). The optical absorption spectrum of the unirradiated base glass thin film for BBiSA series and BBiSB series is shown in the Figures 5 and 6, respectively. The unirradiated parent borosilicate glass thin film for both the series, that is, BBiSA and BBiSB reveals strong UV absorption extending from 325 to 370 nm. As the thin film is grown on quartz glass substrate, it cannot show a band prior to 245 nm, since the glass substrate itself has an absorption band edge around 300 nm. The ultraviolet charge transfer bands of high intensity which are observed here before irradiation could be attributed to the presence of unavoidable trace iron impurities in the raw materials used for glass preparation and mainly due to Fe^{3+} ions [46]. In addition to the impurities, the visible transmittance of the samples also depends on bismuth content and as observed decreases when bismuth content increases. Figures 5 and 6 show that the absorption wavelength shifts towards red from 300 to 375 nm. The value of optical band gap, E_g , given in Table 2 decreases from 2.84 to 2.06 eV for BBiSA and BBiSB, respectively, as the content of Bi_2O_3 increases from 20 to 25 mol percent. The decrease in band gap before irradiation with increase in Bi_2O_3 can be explained on the basis of the structural changes which are taking place within the glass system. Increase in Bi_2O_3 is related to a progressive increase in the molecular weight and concentration of nonbridging oxygen (NBO), which results in the decrease in bridging oxygen (BO). Since nonbridging oxygen is bonded to only one framework cation and bridging oxygen is bonded to two network cations, so with the addition of Bi_2O_3 , wavelength shift towards red and E_g decreases [47]. Many workers [48] have shown even when traces of Bi^{3+} ions are added in borate

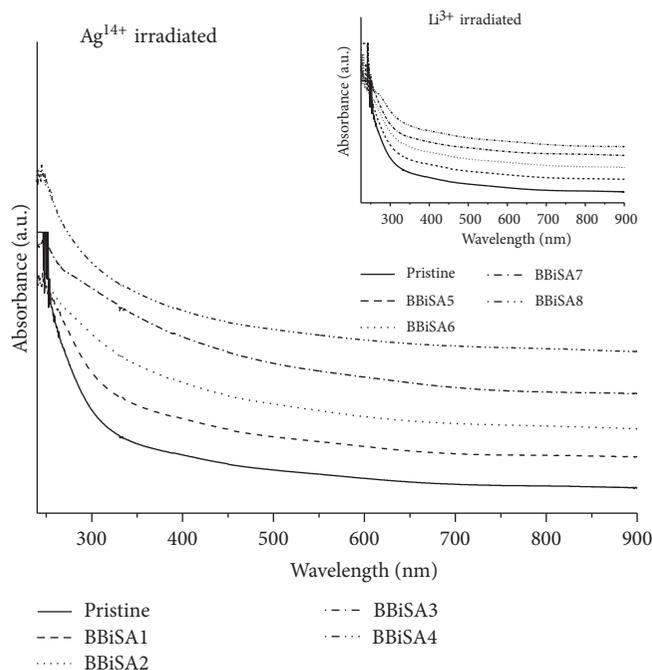


FIGURE 5: Showing the UV-Vis spectra of BBiSA-series glass thin film samples before and after irradiation with Ag^{14+} ion. Inset: UV-Vis spectra of the same glass samples irradiated with Li^{3+} .

and phosphate glasses, a UV peak is observed, and the transition of this peak was related to $^1\text{S}_0\text{-}^3\text{P}_1$. It can be concluded from above results that UV absorption band appearing in unirradiated parent bismuth alumino-borosilicate glass film (BBiSA and BBiSB) is due to absorption by bismuth ions and also due to the presence of unavoidable trace iron impurities in the raw materials for glass preparation [49, 50].

3.2.2. After Irradiation. The mobility gap and Urbach energies of bismuth alumino-borosilicate glass thin films before and after fluence variation from 10^{12} ions/cm² to 10^{14} ions/cm² are listed in Table 2 for Ag ion and Li ion.

BBiSA Glass Thin Films. The UV-Vis spectra recorded for the Ag^{14+} ion and Li^{3+} ion beam irradiated for BBiSA-series glass thin film samples are shown in Figure 5. From the analysis of optical absorption spectra, it is found that optical absorption edge is not sharply defined indicating the amorphous nature of the prepared BBiSA glass thin film samples. For all irradiation doses the optical band decreases after irradiation. The decrease in E_g with the increase in fluence indicates that structural changes are taking place in the glass system, and such similar variations were observed in some bismuth borate glasses [51, 52]. In the present glass it is observed that the fundamental absorption edge and cutoff wavelength shift towards red with the increase in incident ion beam fluence. The change in the absorption band or shift to lower energy is related to the formation of

nonbridging oxygen (NBO) which binds excited electrons less tightly than bridging oxygen (BO). The interaction of glass with swift heavy ion beam resulted in the breaking up of three-dimensional network leading to the transformation of this BO to nonbridging oxygen which does not participate in the network [53–55]. The decrease in E_g with increase in fluence corresponding with the red shift suggests that nonbridging oxygen (NBO) ions are increasing. These NBO ions contribute to valence band maximum. Increase in the concentration of NBO ions results in shifting of valence band maximum to higher energies thereby, reducing the band gap. This trend indicates that the top of the valence band and the bottom of the conduction band are modified to various extent with increasing ion fluence. Further, ion irradiation produces point defects such as vacancies and interstitials, causing lattice damage. Hence, the reduction in energy gap with increasing ion fluence may arise due to the effect of band tailing, owing to the defects produced during irradiation [56]. The variations in band gap energy of BBiSA are found to be larger in case of Ag ion where electronic excitation density is high.

BBiSB Series. The optical band gap (E_g), calculated from the absorption edge of the UV spectra of the BBiSB glass samples in 200–900 nm region varied from 2.06 to 1.01 eV for pristine and various irradiated samples, respectively. Further, it can be observed that there is higher decrease in band gap of the glass samples when irradiated with Ag^{14+} ion (Table 2) as compared to that with Li^{3+} ion of same fluence (BBiSB2 and

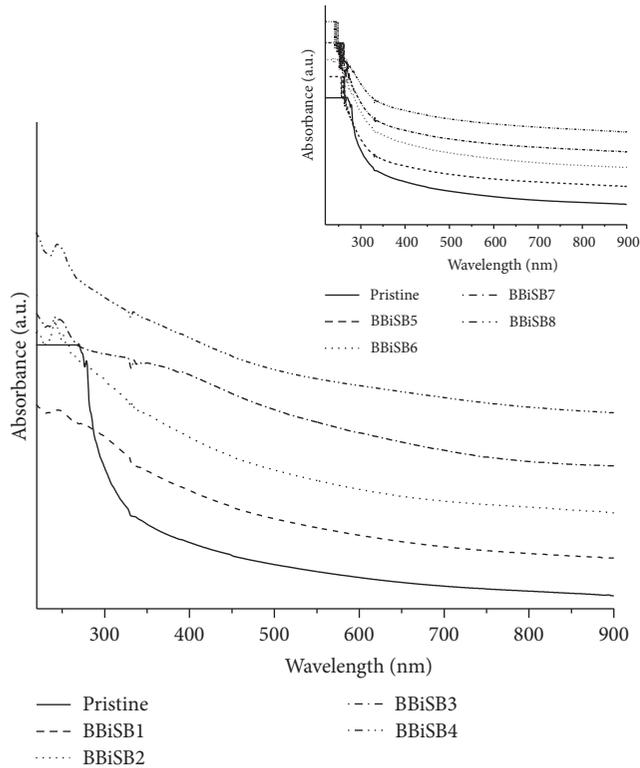


FIGURE 6: Showing the UV-Vis spectra of BBiSB-glass series thin film samples before and after irradiation with Ag^{14+} ion. Inset: UV-Vis spectra of the same glass samples irradiated with Li^{3+} .

BBiSB5; BBiSB3 and BBiSB4). This can be attributed to the fact that higher electronic energy losses of Ag^{14+} ion have resulted in a highly cross linked network thus decreasing the optical mobility gap and causing densification of the glass structure. Decreasing band gap indicates a compaction of the glass network after irradiation. Radiation compaction includes displacements, electronic defects, and breaks in the B–O bonds allowing the structure to relax and fill the large interstices in the interconnected network of boron and oxygen atoms [57]. This result is further supported by the shifting of absorption band towards higher wavelength and is attributed to the increasing number of nonbridging oxygen (NBO) atoms after breaking.

Urbach energy, which corresponds to the width of localized states, is used to characterize the degree of disorder in amorphous and crystalline systems. Materials with larger Urbach energy would have greater tendency to convert weak bonds into defects [58]. The values of ΔE of the present glass system lie in the range 1.91–2.89 eV (BBiSA series) and 2.78–2.99 eV (BBiSB series). The increase in Urbach energy (Table 2) shows that the disorder in the glass structure increases resulting in the even more amorphicity of the glass samples [59]. This emphasizes the fact that the due to high energy, SHIs have caused the damage to the glass network structure.

3.2.3. *Effect of SHI Beam on Refractive Index.* Refractive index of these glasses has been calculated using the relation proposed by Dimitrov and Sakka [60] as following:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1 - \sqrt{E_g}}{20}. \quad (1)$$

The graphical representation of the variation of refractive index as a function of increasing fluence of Ag^{14+} ion and Li^{3+} ion is given in Figures 7 and 8.

It can be seen from Figure 7 that as the fluence of the incident Ag^{14+} beam is increased from 10^{12} ions/cm² to 10^{14} ions/cm², the refractive index of the glass thin film both in case of BBiSA and BBiSB series also increases. This is also true in the either case for both Li ion (Figure 8). The increase in the refractive index may be due to the atomic displacements or ionization that resulted from the collision of SHI with the glass which probably caused the material alterations or changes in the internal structure in the glass [61]. Irradiation of the glass thin film sample with high-energy SHI increases the polarizability of the ionic bonds of bridging oxygen. This leads to a higher refractive index value [62].

The refractive index of the glass is related to glass density as well [63]. The increase in the refractive index signifies that the density of the glass thin film samples has also increased with the increasing fluence. The incident high-energy beam causes compaction in the structure of B_2O_3 by breaking the bonds between the trigonal elements allowing the formation of the different ring configuration. This results in a compact glass structure leading to increase in the density and consequently observed increase in the refractive index [64]. Since it was not possible to measure the density of thin films by immersing it in a medium, following Archimedes principle, as it would have caused the stripping of the film from the substrate, so in the present case density of the thin film samples was not calculated. However, an increase in refractive index do indicates the increase in density of thin films with increasing fluence.

3.3. *FTIR Spectra.* An FTIR spectrum is studied in the present case to investigate the structural changes induced in glass thin film samples before and after irradiation with SHI. The changes have been estimated from the relative increase or decrease in the intensity of the bands associated to the functional groups present in the thin film samples. Figures 9 and 10 show infrared absorption spectra for BBiSA glass thin films irradiated with Ag and Li ion, respectively. Figures 11 and 12 represent the IR spectra of Ag ion and Li irradiated samples of BBiSB series.

3.3.1. *Origin of IR Spectra (Before Irradiation).* For BBiSA series (Figures 9 and 10), the glass samples and the absorption bands appear at around ~519, 617, 725, 811, 963, 1183, and 1496 cm⁻¹ in the pristine glass thin film sample. The weak band observed at 519 cm⁻¹ can be assigned together due to vibrations of BO_4 tetrahedral and due to Bi–O vibrations [65]. The strong band at 617 cm⁻¹ is due to the bending vibration of B–O–B linkages of BO_3 units [66]. Another small

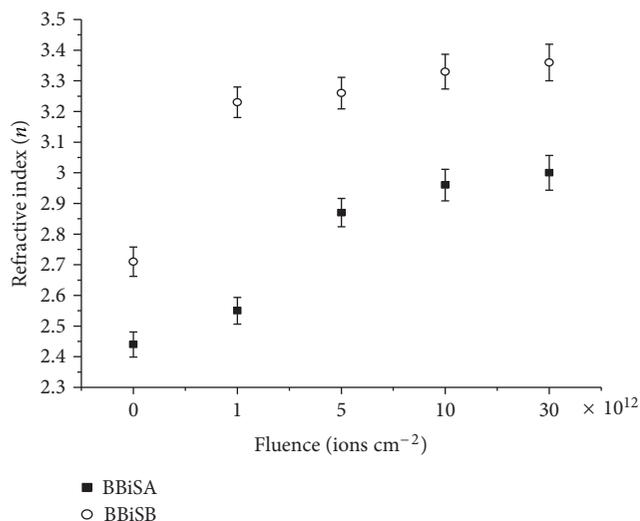


FIGURE 7: Shows variation of refractive index for BBiSA and BBiSB glass thin film samples as a function of increasing fluence for Ag^{14+} ion.

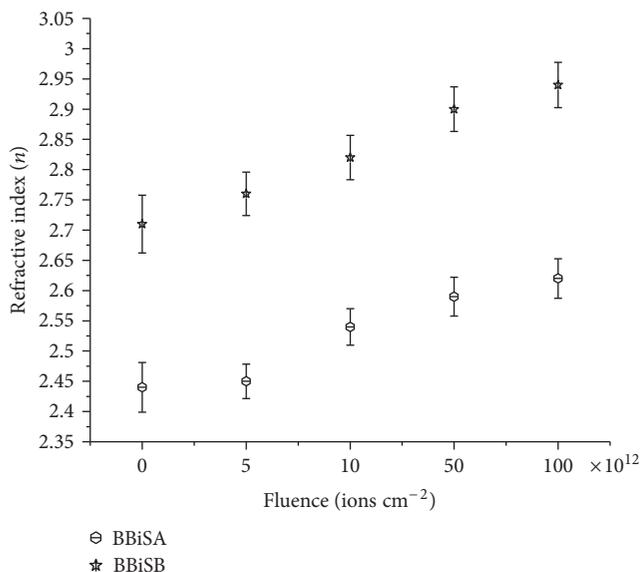


FIGURE 8: Shows variation of refractive index for BBiSA and BBiSB glass thin film samples as a function of increasing fluence for Li^+ ion.

band at around 811 cm^{-1} can be related to the symmetrical stretching vibration of the Bi–O bonds in the (BiO_3) groups [67]. The addition of Bi_2O_3 transforms the structure of B_2O_3 from boroxol groups to the formation of BO_4 tetrahedral and presents mainly as tetra borate and diborate groups which are characterized by the appearance of an infrared absorption band at 963 cm^{-1} and a shoulder at 1000 cm^{-1} .

In increasing the bismuth content from 20 to 25 mol percent in BBiSB series, this band shows a decrease in

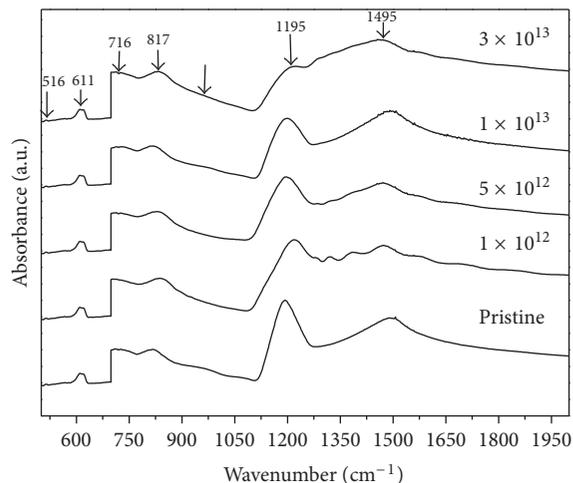


FIGURE 9: Showing the FTIR spectra of Ag^{14+} -irradiated samples for BBiSA series.

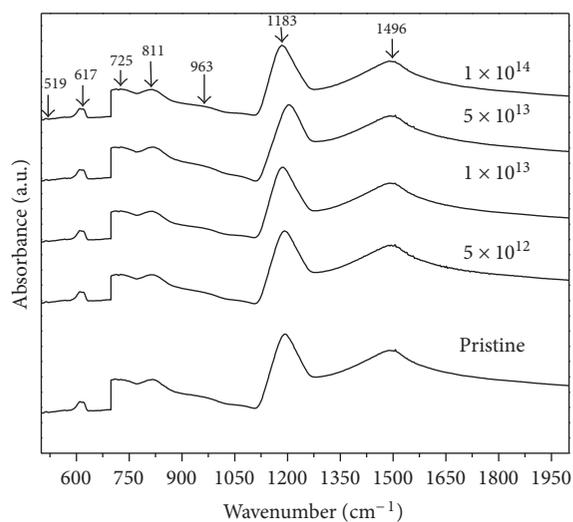


FIGURE 10: Showing the FTIR spectra of Li^{3+} -irradiated samples for BBiSA series.

intensity which indicates that the addition of Bi_2O_3 causes decrease of (BO_4) units as shown in Figures 11 and 12. The rest of the bands extending from nearly 2200 to 4000 cm^{-1} are due to OH and B–OH vibrations including the characteristic near-infrared absorption bands to water [68]. The bands at about 1183 cm^{-1} can be attributed to the combined stretching vibrations of Si–O–Si and B–O–B network of tetrahedral structural units consisting of borate and silicate groups [69]. The intensity of this band increases with the increase of the bismuth content indicating that the distorted (BiO_6) groups may induce a high influence on the boron network in these glasses. The existence of band at about 725 cm^{-1} is attributed to the presence of some super structural borate

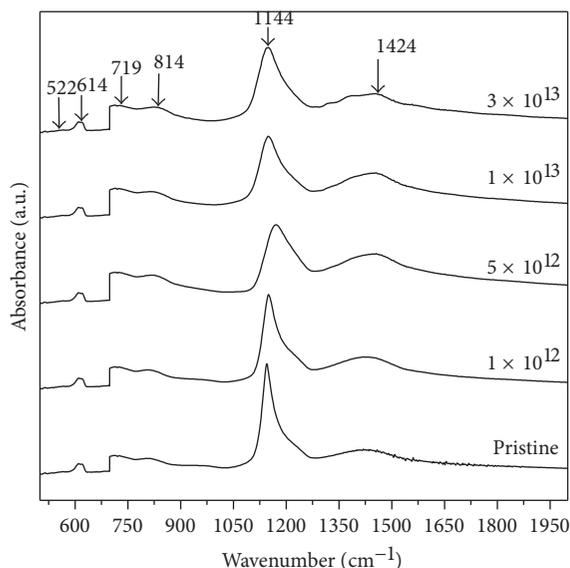


FIGURE 11: Showing the FTIR spectra of Ag^{14+} -irradiated samples for BBiSB series.

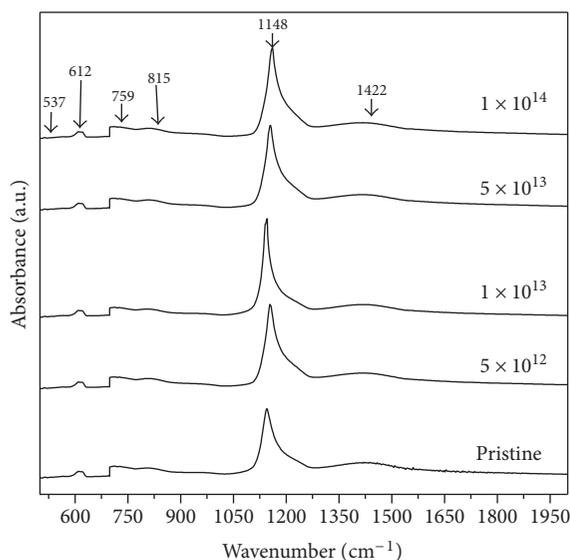


FIGURE 12: Showing the FTIR spectra of Li^{3+} -irradiated samples for BBiSB series.

units [70]. Also the absorption bands due to AlO_4 or AlO_6 groups are located at same position of borate groups. Thus the absorption band near 680 cm^{-1} is assumed with to be combined vibration of AlO_6 groups and the vibrations of bridging oxygen between trigonal boron atoms. The band at 1183 cm^{-1} could also be due to superposition of many small adjacent bonds which are observed between 1200

and 1400 cm^{-1} . The bands at about 516 and 817 cm^{-1} in Figure 9 indicate the presence of (BiO_6) octahedral and (BiO_3) polyhedron units, respectively. Therefore, the network of BBiSA and BBiSB glasses is built up by both (BiO_6) octahedral and (BiO_3) polyhedron units. The band observed around at 700 cm^{-1} is due to the B–O–B bending vibration of (BO_3) triangles. The intensity and position of this band change slightly with increasing of Bi_2O_3 content.

3.3.2. Effect of SHI on IR Spectra. The comparative investigations of the FTIR spectra with Li^{3+} and Ag^{14+} ion reveal that on subjecting the glasses to SHI the relative intensity of the main and near-infrared absorption bands shows an overall decrease, and their positions are generally shifted to longer wave number. Secondly, no new bonds appear in the IR spectra of the either glass series. The results are more pronounced in the case of Ag^{14+} ion rather than in the Li^{3+} ion which is due to higher energy losses of Ag^{14+} ion.

4. Conclusions

Borosilicate glass thin films of two different compositions were prepared using electron gun evaporation method to study the modification induced by 180 MeV Ag^{14+} and 50 MeV Li^{3+} ions in their structural and optical properties. XRD analysis shows that with the increase in the fluence, the characteristic peak of the borate glasses becomes more prominent for one of the compositions (BBiSB) while the other composition remains nearly unaffected. This indicates that at low fluence, the film quality is improved and roughness is reduced due to the strain relaxation between the atoms of the material. But at higher fluence, the disordering in the structure of the films is observed. UV-Vis spectroscopy indicated that irradiated films show a decrease in the band gap which is due to the creation of loosely bound NBO's in the glass structure. However, there was an increase in the refractive index for the either composition which is attributed to the atomic displacements or ionization that resulted from the collision of SHI with the glass. The infrared absorption spectra of all the glasses resemble in some general features the same absorption spectra usually observed from borate glasses but the positions of the absorption bands are different due to the abundance of the heavy metal bismuth oxide (Bi_2O_3). For the same ion beam irradiation, BBiSA series gets influenced to higher extent compared with BBiSB series, which may be due to the high bismuth concentration in BBiSB series. The effect of Ag^{14+} ion beam on either glass is more compared with Li^{3+} ion. This is due to the greater electronic energy loss for Ag ion as compared to Li^{3+} ion beam.

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