

Optical modifications induced by proton irradiation in PM-355 solid state nuclear track detector

M. R. BAIG^a, M. S. AL GARAWI^a, S. MANSOOR ALI^a, S. S. AL-GHAMDI^a, A. KAYANI^b

^aDepartment of Physics and Astronomy, College of Science, P.O BOX 2455 King Saud university Riyadh Saudi Arabia

^bDepartment of Physics, Western Michigan University, Kalamazoo, MI 49008, USA

We report a study on the proton irradiation induced modifications on optical properties of PM-355 solid state nuclear track detector. The samples were irradiated by 6 MV Van de Graaff accelerators at various fluences. The reference as well as irradiated samples were subjected to UV-Visible spectral study, UV-Vis diffuse reflectance spectroscopy and Photoluminescence (PL) spectroscopy. In our study UV-Vis spectra reveals that absorption edge shifted towards longer wavelength region after proton irradiation, and this change is more significant increasing proton fluence. This shift clearly reflects decrease in optical band gap. The samples gradually appears transparent to the visible light and the material changes from transparent to yellowish with the increase in the fluence. It is believed that proton irradiation may induce defects and clusters in the PM-355 due to chain scission and cross linking as observed from PL spectral study.

(Received September 17, 2015; accepted October 28, 2015)

Keywords: Proton irradiation, Optical modification, Band gap, Photoluminescence, Refractive index

1. Introduction

Polymeric materials are an important part of everyday life that is extensively used in a wide variety of industrial, electronic and research applications [1]. Solid State Nuclear Track Detectors (SSNTDs) with the modification of properties are used in different applications, such as detection of ion beam, biological filters, sensors and dosimetry by modifying its properties [2-8]. An allyldiglycol polycarbonate (CR-39) plastic is highly useful for radiation detector due to its ability to record heavy particles [9,10] and the CR-39 and polymer PM-355 (Supergrade PM-355, Pershore Mouldings Ltd., UK) is highly significant, to find diverse applications in physical and modern technological science [11].

Ionizing radiations is one of the important factors that play a major role to modify the physical and chemical properties of solid-state nuclear track detectors (SSNTDs). The irradiation induced chemical changes that could involve the productions of radicals, that may recombine and form polymeric chains. Irradiation of solid-state nuclear track detectors (SSNTDs) primarily leads to intermolecular cross-linking and chain scissions. Some time both processes can coexist and this may depend on the chemical structure of the polymeric material and the conditions of irradiation [12].

In the present investigation, we irradiated PM-355 by 5 MeV protons at different fluences and investigated the modifications induced by protons. These modifications are measured by using different techniques. The techniques which are used to study the changes are UV spectroscopy, diffuse reflectance and photoluminescence (PL) spectroscopy.

2. Experimental details

Ion beam irradiation of PM-355 samples was carried at Western Michigan University's 6 MV Van de Graaff accelerator laboratory. Smaller circular sections of roughly 0.5 cm² size were exposed, to 5 MeV protons with the fluence of 1.0 x 10¹³ ions/cm², 5.0 x 10¹³ ions/cm², and 1.0 x 10¹⁴ ions/cm², 5.0 x 10¹⁴ ions/cm² and 1.0 x 10¹⁵ ions/cm² respectively. The ion beam was allowed to pass through a gold foil to diverge the beam followed by an 8mm diameter circular collimator, which defines the area of the sample to be exposed to the ion beam. Prior to the beam irradiation, an image of the beam on the sample was obtained using photographic film. Charge collected on each sample was measured directly from the floating chamber and integrated to derive the total charge collected. After exposure the samples were left in the scattering chamber at ~10⁻⁶ Torr for 24 hours. The optical measurement were carried out at the physics department of King Soud University, Saudi Arabia

3. Results and Discussion

3.1 UV-Visible spectroscopy

Fig. 1 illustrates the optical absorption spectra of the reference and proton irradiated PM-355 samples with variation of fluence at energy 5 MeV. We notice that the absorption edge shifts from UV towards the visible with the increase of the proton fluence. This shift may be attributed to irradiation-induced defects in the polymeric materials [13-16]. The samples appear gradually yellowish with the increase of the fluence in the visible range. These may be due to the generation of some

chromophoric groups [17] or the formation of free radical that may be trapped within the PM-355 and are responsible for the coloring in the irradiated samples [18] and/or release of gases from the polymeric material during the irradiation

A remarkable change can be observed in the optical absorption spectra of proton irradiated samples compared with the spectra obtained for the reference sample. These changes may be attributed due to the formation of some electronic levels inside the forbidden gap after proton irradiation [19].

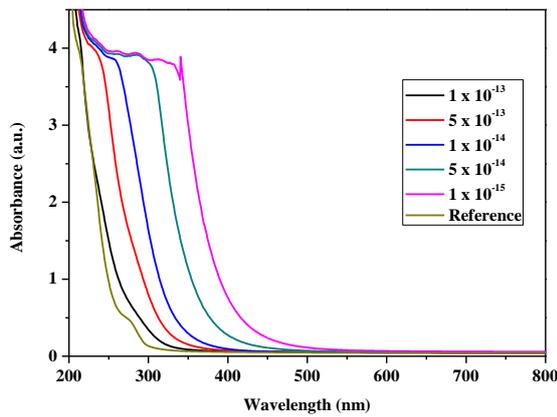


Fig. 1: Absorption spectra of reference and proton irradiated PM-355 with different fluence.

The values of the energy band gaps in any amorphous material is obtained by plotting $(ahv)^2$ as a function of the photon energy ($h\nu$) by extrapolating the linear part of the plot to $h\nu$ axis which gives the optical band gap [20]. The energy band gaps for reference and proton irradiated PM-355 solid state nuclear track detector are shown in Fig. 2.

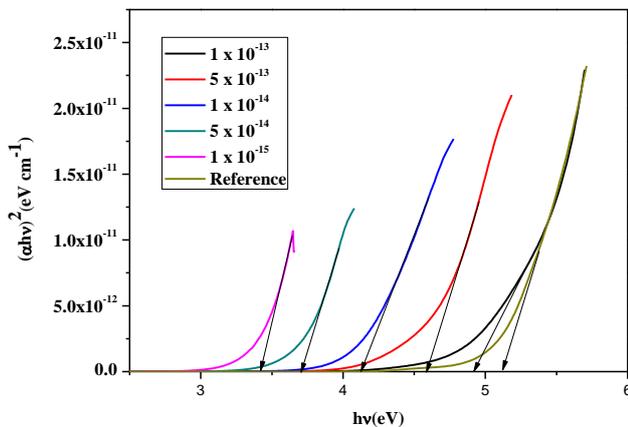


Fig. 2: Tauc plot for calculation of band gap of reference and proton irradiated PM-355 with different fluence.

Fig. 3 shows the variation in energy band gap with proton fluence. A remarkable decrease in the value of

energy band gap can be observed for proton irradiated samples. The energy band gap decreases from 5.12 eV for reference to 3.41 eV for maximum value (1×10^{15} ions/cm²) of proton fluence. This decrease in energy gap may be due to following reason (1) irradiation induce defects, (2) by increasing the number of conjugated bonds and (3) formation of carbon enriched clusters [21]. The decrease in the optical energy gap value means that proton irradiation enhances the electrical conductivity of the PM-355 due to the energy transferred to non-bonding electrons by the proton irradiation. This in turn, may be due to the creation of free radicals or ions inside the conduction band. The creation of free radicals or ions may increase the number of carriers on localized states or the carrier mobility, which will enhance the electrical conductivity of the PM-355 [19].

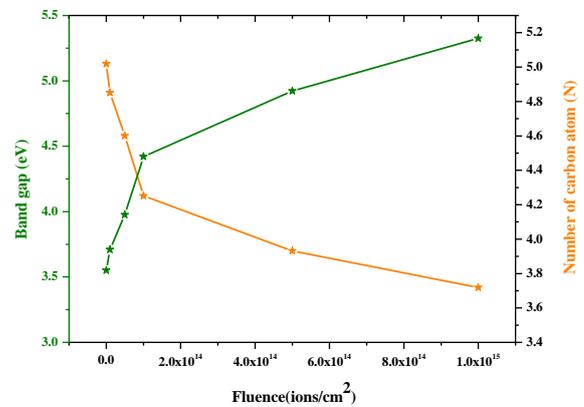


Fig. 3: Variation of optical band gap and number of carbon atoms for reference and proton irradiated PM-355 with different fluence.

One can determine the number of carbon atoms per conjugation length (N) [22]:

$$N = \frac{2\beta\pi}{E_g} \quad (1)$$

Here 2β gives the energy of the band structure of a pair of adjacent π sites. The value of β is considered to be 2.9 eV for $\pi - \pi$ optical transitions in $-C=C-$ structure. The shift of the absorption edge can be endorsed to an increase in conjugation length [23]. It is clearly observed from Figure 3 that the number of carbon atoms (N) in the cluster increase as the fluence of proton increases. This may be increase due to the escape of hydrogen as a result of to the breakage of C-H bonds after irradiation.

3.2 Diffuse reflectance

UV-Vis reflectance spectra of the reference and proton irradiated PM-355 is shown in Figure 4. An obvious red shift in the reflectance edge was observed for proton irradiated sample compared to the reference sample. The relevant increase in the reflectance at

wavelengths greater than 275 nm may be related to the direct bandgap of PM-355 which may be due to the transition of an electron from the valence band to the conduction band. As obtained in the band gap analysis, the band gap decreased by increasing the fluence of protons, which corresponds to the particles size of the PM-355 is increased by increasing the fluence of proton; therefore, this red shift may be related to the quantum confinement effect. This might be due to changes in their morphologies, crystallite size, and surface microstructures of the PM-355 after the proton irradiation.

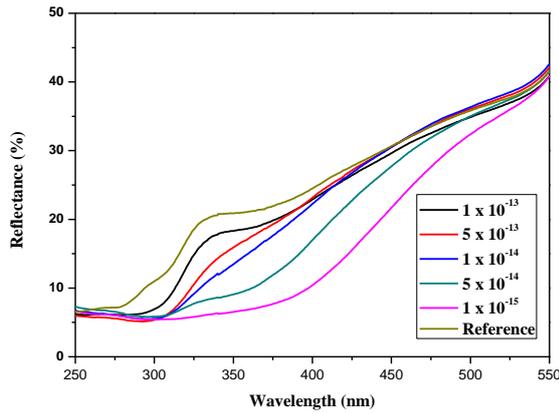


Fig. 4: Reflectance spectra of reference and proton irradiated PM-355 with different fluence.

The results of the diffuse reflectance can be used to obtain for extinction coefficient and the refractive index of the materials. The absorption coefficient can be obtained from [24].

$$\alpha = \frac{(1 - R')^2}{2R'} \quad (2)$$

$$R' = \frac{R}{100} \quad (3)$$

Where R is the reflectance.

In the complex refractive index, $N = n - ik$, n is the refractive index and k is the extinction coefficient. The extinction coefficient is related to the absorption coefficient by

$$k = \frac{\lambda \alpha}{4\pi} \quad (4)$$

By calculating α and then k , the refractive index can be obtained from

$$n = \left(\frac{1 + R}{1 - R} \right) + \sqrt{\frac{4R}{(1 - R)^2} - k^2} \quad (5)$$

The results obtained for the optical properties are presented in Fig. 5 (a, b).

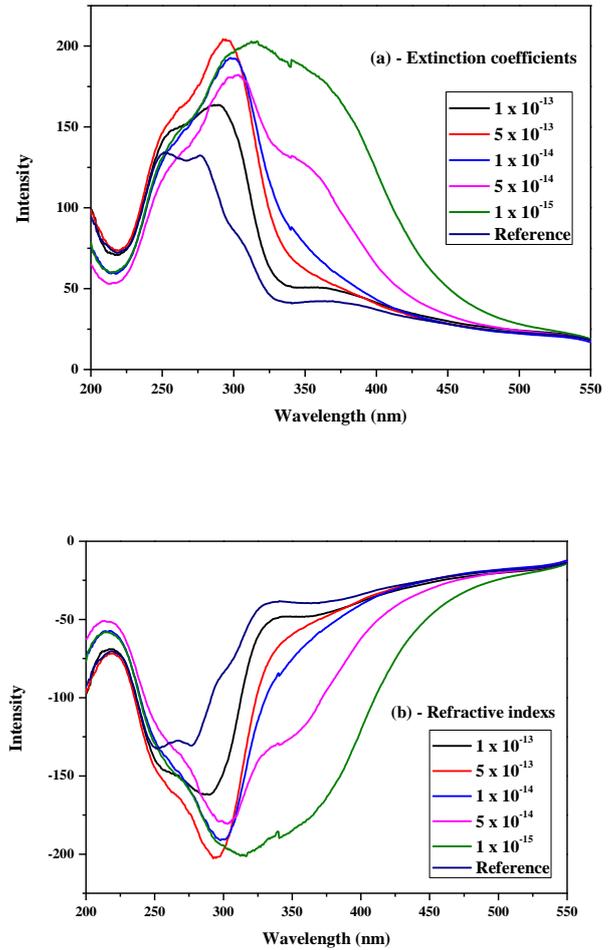


Fig. 5: Behavior of the (a) extinction coefficient and (b) refractive index of reference and proton irradiated PM-355 with different fluences

3.3 Photoluminescence (PL)

The photoluminescence (PL) studies of reference and proton irradiated samples, were carried out in the wavelength range of 350–575 nm. The 325 (3.82 eV) exciting wavelength of a xenon lamp was used as a result of excitation scan for the samples. The PL spectra of reference and proton irradiated PM-355 solid state nuclear track detector are shown in Figure 6. In reference, the peak was observed at 408.61 nm and for proton irradiated samples, the peak was observed at 409.21 for all fluences values. After proton irradiation a new peak was observed at 421.32 nm, this peak became more dominant at 5.0×10^{-15}

10^{13} ions/cm² and by increasing the fluences value this peak merges with the first peak. Thus, a noticeable change was observed in full width at half maximum value of the PL peak of proton irradiated PM-355 with increase in fluence. This may be due to the change in molecular structure and corresponding change in the electronic properties of the polymer. Hence, it is believed that heavy ions irradiation may result in cross linking, degradation of the polymer chains and produce defects and clusters in polymers.

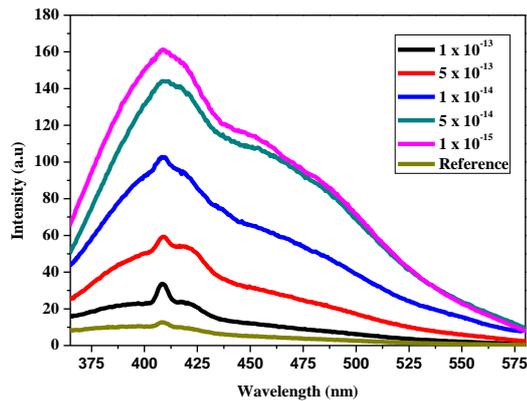


Fig. 6: Photoluminescence spectra of reference and proton irradiated PM-355 with different fluence.

Fig. 7 demonstrates that the PL peak intensity increases with increasing the proton fluences, suggesting that defects concentration increases in the sample after proton irradiation [25]. The overall phenomenon of shift towards longer wavelength regions after irradiation indicates possible cross-linking mechanism inside the polymers [26].

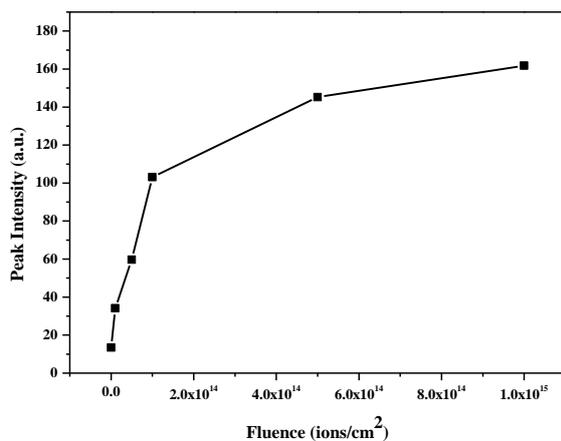


Fig. 7. Variation of PL intensity with different fluence of proton irradiation

4. Conclusions

The optical modification after the proton irradiation of PM- 355 was investigated. PL spectra shows that the intensity of PL increased with increase in proton fluence, which indicates the increase in the defect concentration induced by irradiation. From this experimental study of reference and proton irradiated PM-355, the values of the optical band gap (E_g) are affected with ion fluence as determined from the linear portion of optical spectra, while the number of carbon atoms (N) per conjugated length decreases with the increase in fluence. Thus, these types of polymer track detectors can be used as a dosimeter for proton ion beam.

Acknowledgment

The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for its funding of this research through the Research Group Project No. RG -1436-019.

References

- [1] M. Santosh, B. Dhananjay, A. Mandale, S. Gangal, V. Bhoraskar, *Materials Letters*, **60**(11), 1360 (2006).
- [2] M.F. Zaki, *J. Phys. D* 41 p.175404 (2008).
- [3] Basma A. El-Badry; M. F. Zaki; Tarek M. Hegazy; A. Ahmed Morsy. *Radiation Effects & Defects in Solids*, **163**(10), 821 (2008).
- [4] Basma A. El-Badry, M.F. Zaki, A.M. Abdul-Kader, Tarek M. Hegazy, A. Ahmed Morsy *Vacuum* **83**, 1138 (2009).
- [5] A.M. Abdul-Kader, *Appl. Surf. Sci.* **255** 5016 (2009).
- [6] A.M. Abdul-Kader, A. Turos, R.M. Radwan, A.M. Kelanyl, *Appl. Surf. Sci.* **255**, 7786 (2009).
- [7] A.M. Abdul-Kader; Basma A. El-Badry; M. F. Zaki; Tarek M. Hegazy; Hany M. Hashem, *Philosophical Magazine* **90**(19), 2543 (2010).
- [8] M.F. Zaki and E.K.Elmaghraby., *Journal of Luminescence* **132**, 119 (2012)
- [9] W. Birkholz, C. Winkler, H. Baumbach, Neutron sensitivity of CR-39 SSNTD., *Nucl. Tracks Radiat. Meas.*, **19**, 453 (1991).
- [10] J. Palfalvi, Experiences with CR-39 SSNTD in monitoring neutrons emitted from spent reactor fuel., *Nucl. Tracks Radiat. Meas.*, **19**, 511 (1991).
- [11] M. A. Anan, *Radiation Measurements*, **41**(2), 209 (2006).
- [12] D. Sinha, K.L. Sahoo, U.B. Sinha, T. Swu, A. Chemseddine, D. Fink, *Radiat. Effects Defects Solids*, **159**, 587 (2004),
- [13] S Singh, S. Prasher, *Radiat Meas.*; **40**, 50 (2005).
- [14] PC Kalsi, C. Agarwal, *Radiat Phys Chem* **79**, 844 (2010).
- [15] MF Zakia, AM Abdul-Kader, Nada Afaf, A. El-Badry Basm, *Philos Mag*; **93**, 4276 (2013).

- [16] Z. Lounis-Mokrani, M. Fromm, R. Barillon, A. Chambaudet, M. Allab, *Radiation Measurements* **36**, 615 (2003).
- [17] V Kumar, Y Ali, RG Sonkawadeb, AS. Dhaliwal, *Nucl Instrum Meth B*; **287**, 10 (2012).
- [18] JJ. Grodzinski, Biomedical application of functional polymers. *React Funct Polym*; **39**, 99 (1999).
- [19] AM. Abdul-Kader, *J Nucl Mater*; **435**, 231 (2013).
- [20] Tanu Sharma, Sanjeev Aggarwal, Shyam Kumar, V. K. Mittal, P. C. Kalsi, V. K. Manchanda, *J. Mater Sci.* **42**, 1127 (2007).
- [21] S' iljegovic' M, Kac'arevic' -Popovic' ZM, Bibic' N, Jovanovic' ZM, Maletic' S, Stchakovsky M, et al. *Radiat Phys Chem*; **80**(12), 1378 (2011).
- [22] D Fink, WH Chung, R Klett, A Schmoldt, J Cardoso, R Montiel, et al. *Radiat Effect Defect Solids*; **133**, 193 (1995).
- [23] AM Abdul-Kader, A El-Badry Basma, MF Zaki, M Hegazy Tarek, M Hashem Hany, *Philos Mag*; **90**(19), 2543 (2010).
- [24] D-W Wang, S-L Zhao, Z Xu, C Kong, W Gong, *Org Electron*, **12**, 92 (2011).
- [25] R.A.M. Rizk, A.M. Abdul-Kader, Z.I. Ali., *Vacuum* **83**, 805 (2009).
- [26] K.W. Lee, K.H. Mo, J.W. Jang, C.E. Lee, *J. Korean Phys. Soc.* **47**, 130 (2005)

*Corresponding author email: mrehbaig@ksu.edu.sa,
mansoor_phys@yahoo.com