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SPECTROSCOPIC STUDY OF Γ-IRRADIATION ON CR-39 POLYMER

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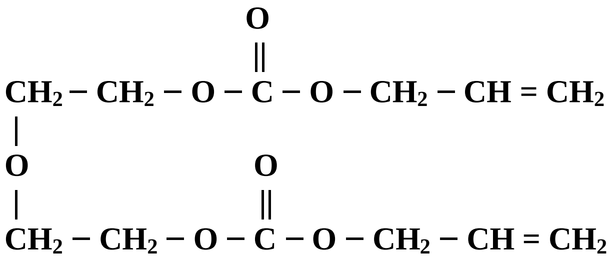
ABSTRACT: Gamma ray irradiation-induced modification in CR-39 polymer has been investigated using UV visible spectroscopy and FTIR spectroscopy. In the present work the Urbach energy has been calculated using Urvach edge method also the direct and indirect energy band gap in virgin and γ-irradiated CR-39 polymer samples were calculated. The decrease in optical energy band gap with increasing irradiation has been discussed on the basis of irradiation-induced modification in CR-39 polymer. The correlation between optical energy band gap and the number of carbon atom in a cluster with modified Tauc's equation has been discussed. The FTIR spectra show appreciable change due to irradiation indicating that this polymer is not chemically stable.

INTRODUCTION

The polyallyldiglycol carbonate (commercial name CR-39) is an amorphous polymer consisting of short polyallyl chains joined by links containing carbonates and diethyleneglycol groups into a dense three-dimensional network with an initiating monomer unit as given below [1].



$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad \mathbf{O} \\ \qquad\qquad\qquad\qquad\quad \| \\ \mathbf{CH_2-CH_2-O-C-O-CH_2-CH=CH_2} \\ | \\ \mathbf{O} \qquad\qquad\qquad\qquad\quad \mathbf{O} \\ | \qquad\qquad\qquad\qquad\quad\; \| \\ \mathbf{CH_2-CH_2-O-C-O-CH_2-CH=CH_2} \end{array}$$

CR-39 polymer is colorless and optically transparent to the visible light and almost completely opaque in infrared and ultraviolet regions of the spectrum. The applications of CR-39 include up-to-date studies in nuclear and fission physics; cosmic ray studies and astrophysics; alpha- and neutron-dosimetry; uranium prospection and radon-emanation measurements; space vehicles, as well as search for super heavy elements. Besides many other applications in optical devices, it finds significant applicability in fission-related studies. In such studies, the polymer gets exposed to high doses of neutrons, beta and gamma radiations [2, 3].

EXPERIMENTAL DETAIL AND ANALYTICAL TECHNIQUES

CR-39 polymer sheets of thickness 250μm were brought from Good Fellow U.K. (United Kingdom) and were used without any further treatment. Five polymer samples of size $(2\times1)\ \mathrm{cm}^2$ each were cut from the commercially available sheet. One sample was kept as virgin and the other four samples were irradiated at UGC-DAE CSR, Kolkata Centre, using 1.25MeV gamma radiation source of ^{60}Co in the high-vacuum $(2\times10^{-6}$ Torr) radiation chamber (in the form of a cylindrical chamber of 14 cm length and 10 cm diameter with dose rate 4 kGy/h and source strength 2KCurie or 74 GBq). The virgin sample was kept for reference and the other four samples were exposed for 125, 250, 375 and 500 hours respectively to achieve the doses of 500, 1000, 1500 and 2000 kGy.

The irradiated samples were characterized by analytical techniques namely UV-VIS spectroscopy and FTIR spectroscopy to observe the modifications in CR-39 polymer by **γ**-radiation.

1. Optical response (UV-VIS) spectroscopy: The UV–visible absorption spectra of virgin and **γ**-irradiated CR-39 polymer samples were recorded using UV–visible spectrophotometer (JASCO, V-570) in the wavelength range of 190–900 nm by mounting the samples in the integrating sphere assembly attached with the spectrophotometer, keeping air as the reference.

2. Chemical study (FTIR): Fourier transform infrared (FTIR) spectra of virgin and **γ**-irradiated CR-39 polymer samples were recorded in transmission mode using Perkin Elmer FTIR spectrophotometer (Model 1720) in the range 400 to 4000 cm^{-1}. The scanning rate was 2 cm^{-1} s^{-1} with an average of 21 scans per sample. The infrared double beam spectrophotometer instrument plots intensities versus wave number. The spectrum of air was also taken as the reference spectrum for all spectra of polymer samples.

RESULTS AND DISCUSSION

The following are the results of UV-visible spectroscopy and FTIR spectroscopy for virgin and **γ**-irradiated CR-39 polymer. The results are discussed below.

Optical properties*:* The UV-Visible absorption spectra of virgin and gamma irradiated (500 to 2000 kGy) CR-39 polymer samples are shown in Fig.1. From the UV-Visible absorption spectra we observe the shift of absorption edge towards the longer wavelength as well as the broadening of the absorption peak with increasing gamma dose. This shift of absorption edge and the broadening of absorption peak may be considered due to the formation of extended systems of conjugate bonds i.e. possible formation of carbon clusters [4].

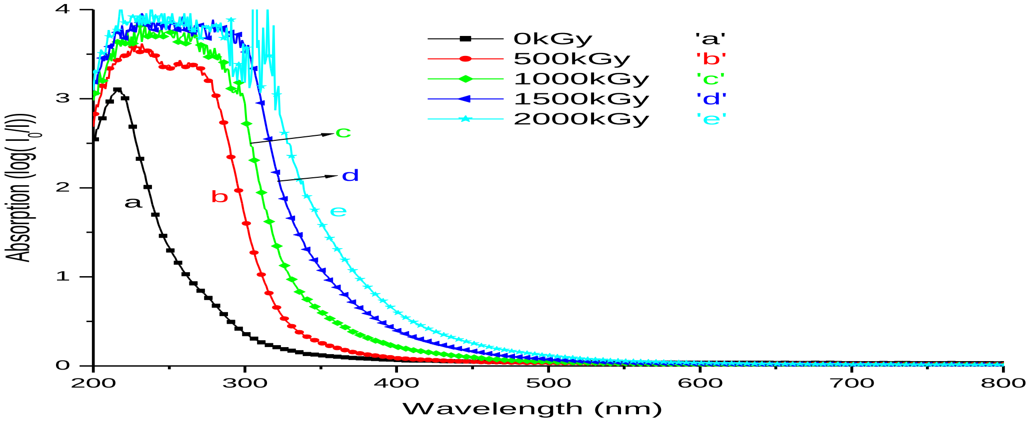


Fig. 1 Absorption vs. wavelength for (a) virgin and gamma irradiated (b) 500kGy (c) 1000kGy (d) 1500kGy (e) 2000kGy, CR-39 polymer samples

The optical absorption coefficient (α) was calculated from the absorbance (A) by using the following formula [5]

$$\alpha(\nu) = \frac{A}{l} \dots\dots\dots\dots\dots\dots..(1)$$

Where l is the thickness of the sample in cm.

Urbach energy: The absorption coefficient near the band edge for non-crystalline materials shows an exponential dependence on the photon energy ($h\nu$ following the Urbach formula [6]

$$\alpha(\nu) = \alpha_0 exp\left(\frac{h\nu}{E_u}\right) \dots\dots\dots...(2)$$

where α_0 is a constant, ν is the frequency of radiation and h is the Planck's constant. E_u is the energy interpreted as the width of the tail of localized states in the forbidden band gap, the thermal vibrations in the lattice are considered as the origin of this energy [7].

Taking natural log on both of the sides of eq^n (2) and then differentiating it with respect to photon's energy ($h\nu$, we get,

$$\frac{d\{ln(\alpha)\}}{d(h\nu)} = \frac{1}{E_u} \dots\dots\dots\dots\dots\dots\dots (3)$$

The eq. (3) shows that $\frac{d\{ln(\alpha)\}}{d(h\nu)}$ is the slope of the curve given by eq. (2) and is equal to the reciprocal of E_u. Therefore the logarithm of the absorption coefficient $\alpha(\nu)$ was plotted as a function of the photon energy ($h\nu$ for virgin and γ-irradiated CR-39 polymer samples (Fig. 2) and the values of Urbach energy (E_u were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of these curves. The results of Urbach energy for virgin and **γ**-irradiated CR-39 polymer samples are presented in table 1.

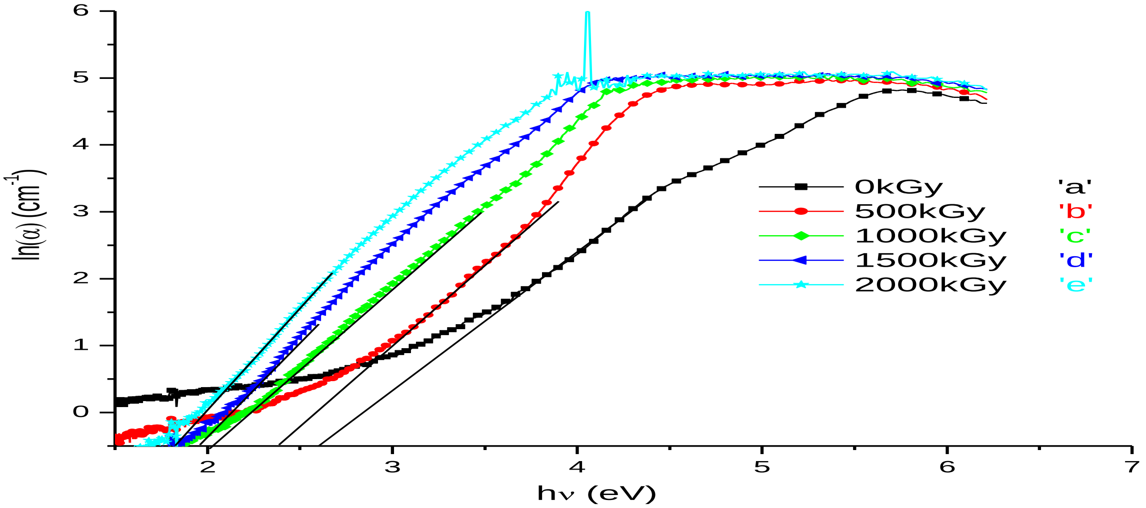


Fig.2 Dependence of natural logarithm of α on photon energy (hν) for (a) virgin and gamma irradiated (b) 500kGy (c) 1000kGy (d) 1500kGy (e) 2000kGy, CR-39 polymer samples

The value of Urbach energy is found to be decreased with increasing gamma dose in CR-39 polymer from 0.47eV for virgin sample to 0.33eV for the sample irradiated at the highest dose of 2000kGy. This decrease in Urbach energy may be attributed to the decrease in the crystalline nature of the polymer [4].

The above mentioned relation given in eq. (3) was first proposed by Urbach [6] to describe the absorption edge in alkali halide crystals. Also, this relation has been found to be valid for many amorphous materials. Equation (2) was modified to a more general form by Davis and Mott [8].

$$\alpha(\nu) = \frac{B(h\nu - E_g)^n}{h\nu} \dots\dots\dots\dots\dots\dots.. (4)$$

where the factor B depends on the transition probability and may be assumed to be a constant within the optical frequency range, $\alpha(\nu)$ is the absorption coefficient at frequency ν, E_g is the value of the optical energy band gap between the valence band and conduction band, n is index which characterizes the electronic transition can assume different values, i.e. 2 for indirect allowed transitions, 3 for indirect forbidden transitions, 0.5 for direct allowed transitions and 1.5 for direct forbidden transitions, respectively.

DETERMINATION OF DIRECT AND INDIRECT ENERGY BAND GAPS

Table 1. Urbach energy, energy band gap and carbon atoms in a cluster for virgin and gamma irradiated CR-39 polymer samples

γ-radiation dose (kGy)	Urbach's energy (eV)	Energy band gap (eV)		Carbon atoms (N) in a cluster	
		Direct	Indirect	Direct	Indirect
0	0.47	5.07±0.02	3.54±0.04	□4	□5
$5\text{x}10^2$	0.42	4.05±0.01	3.47±0.08	□5	□5
$1.0\text{x}10^3$	0.42	3.88±0.08	3.31±0.03	□5	□6
$1.5\text{x}10^3$	0.35	3.73±0.01	2.85±0.02	□5	□6
$2.0\text{x}10^3$	0.33	3.50±0.09	2.53±0.03	□5	□7

For the determination of direct and indirect energy band gap, $(\alpha h\nu)^2 \wedge (\alpha h\nu)^{\frac{1}{2}}$ were plotted separately as a function of photon energy $(h\nu)$ [9, 10] taking into account the linear portion of the fundamental absorption edge of the UV-Visible spectra (curves 'a' to 'e' in Fig.1)**.** Such plots have been shown in Fig.3 and 4, respectively. From the intercept of the best fit lines on $h\nu$ axis, direct and indirect energy gaps were calculated for virgin and γ-irradiated CR-39 polymer samples and the results are presented in table 1.

The magnitude of standard errors is maximum up to ~ 4%. This, in turn, clearly indicates the simultaneous existence of direct and indirect energy band gaps in CR-39 polymer. This simultaneous existence of direct and indirect energy band gaps in CR-39 polymer may be due to the presence of different regions in the polymer.

For some regions the top of the valence band and the bottom of the conduction band may occur at the same value of momentum and for some other regions they may occur at different values of momentum, thus justifying the simultaneous existence of direct and indirect energy band gaps.

The decrease in the direct and indirect energy band gaps is found to be about 31% and 28.5%, respectively. This decrease in direct and indirect energy band gaps may be attributed to the creation of electronic disorder which becomes prominent with increasing γ-radiation dose. Furthermore, the values of indirect energy band gap are found to be lower than the corresponding values of direct energy band gap. The plots for direct energy band gap and indirect energy band gap versus dose are shown in Fig. 5.

The value of direct energy band gap is found to decrease from 5.07eV for virgin sample to 3.5 eV for the sample irradiated at the highest dose of 2000kGy. Similarly, the value of indirect energy band gap is found to decrease from 3.54eV for virgin sample to 2.53 eV for the sample irradiated at the highest dose of 2000kGy.

CARBON ATOMS IN A CLUSTER

The number of carbon atoms (N) in a cluster is correlated to the optical energy band gap (E_g) determined with the modified Tauc's equation [5, 11].

$$N = \frac{2\pi\beta}{E_g} \dots\dots\dots\dots\dots\dots\dots\dots (5)$$

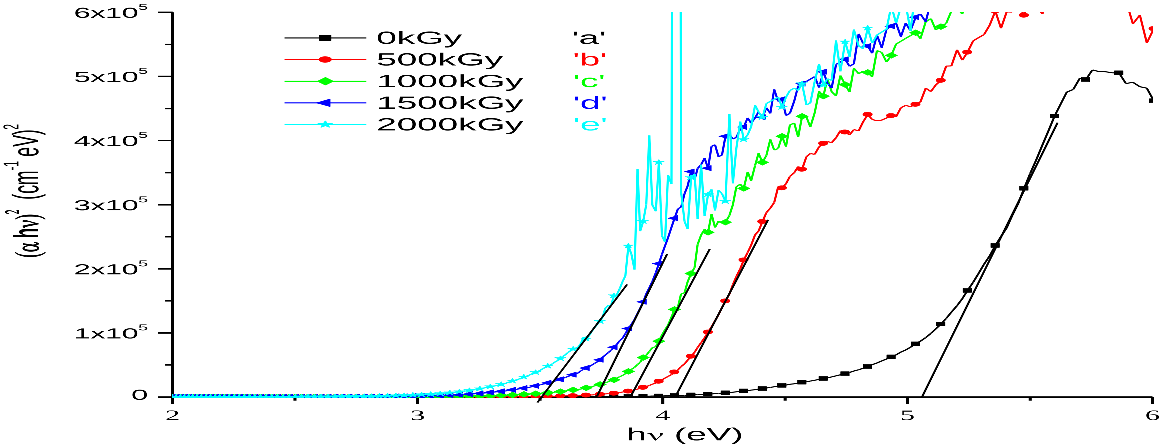


Fig.3 Plots for indirect energy band gap (eV) in (a) virgin and gamma irradiated (b) 500kGy (c) 1000kGy (d) 1500kGy (e) 2000kGy, CR-39 polymer samples

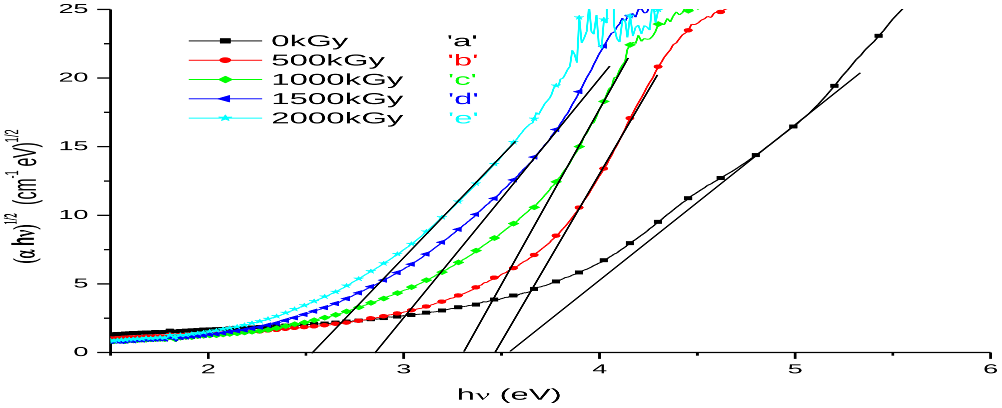


Fig. 4 plots for indirect energy band gap (eV) in (a) virgin and gamma irradiated (b) 500kGy (c) 1000kGy (d) 1500kGy (e) 2000kGy, CR-39 polymer samples

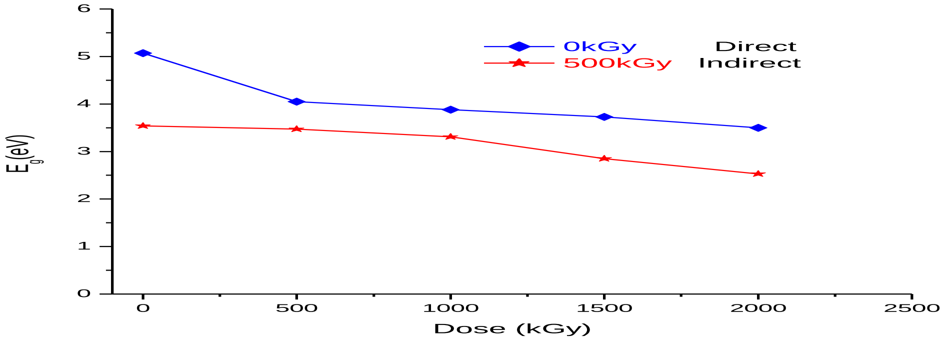


Fig.5 Variation of direct energy band gap and indirect energy band gap with dose.

Fourier Transforms Infrared (FTIR) analysis

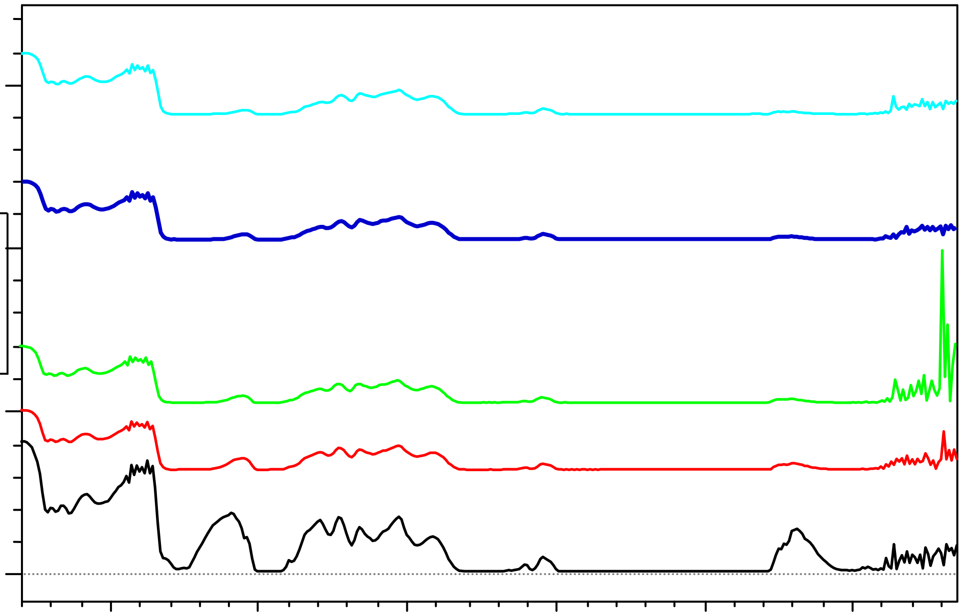


Fig. 6 FTIR spectra of (a) virgin and γ-irradiated (b) 500 kGy (c) 1000 kGy (d) 1500 kGy (e) 2000 kGy, CR-39 polymer samples

FTIR spectroscopy allows the identification of different absorption bands [12-15]. Fig. 6 shows the FTIR spectra of virgin and γ-irradiated CR-39 polymer samples indicating the changes produced by γ-irradiation. In the virgin sample (Fig.6a), there is a band at 1581 cm^{-1} which is assigned to –C=C- vibrations [16]. The bands at 2217 and 2756 cm^{-1} are due to CO vibration and –C-H- deformation vibration respectively, the band at 3079cm^{-1} is due to stretching vibration of unsaturated =CH. Furthermore, the absorbance was found to remain constant in the frequency range of about 780cm^{-1} to 1500cm^{-1}. It is observed from the FTIR spectra that there is a reduction in the absorption intensity of all characteristic bands of the γ-irradiated CR-39 polymer samples (Fig. 6, b-e). But this reduction in intensity is almost constant for allγ-irradiated samples at doses 500, 1000, 1500, 2000kGy. This reduction in intensity of all characteristic bands may be attributed to the breakage of chemical bonds. This may also be due to the probable elimination of low molecular gases as a result of γ-irradiation. This indicates about the initiation of chain scissioning in CR-39 polymer sample at 500kGy which becomes insignificant with increasing γ-radiation dose.

CONCLUSIONS

Modifications in CR-39 polymer samples under γ-radiation source of Co^{60} were studied by means of UV-VIS and FTIR.

The following conclusions have been drawn from the obtained results:

- The existence of peaks in absorbance spectra, their shifting and broadening as a result of gamma irradiation was discussed. Urbach energy (E_u) and energy band gap (E_g) were calculated from the optical absorption spectra. The Urbach energy was found to decrease with increasing γ-radiation dose. The values of indirect energy band gap are found to be lower than the corresponding values of direct energy band gap in virgin as well as in γ-irradiated CR-39 polymer samples. The analysis also indicates that the energy band gap (E_g) decreases with increasing γ-radiation dose.
- The FTIR spectra showed the degradation of CR-39 polymer after γ-irradiation.

REFERENCES

1. Lakhwant Singh, Kawaljeet Singh Samra, Ravinder Singh, Nuclear Instruments and Methods in Physics Research B 255 (2007) 350–356.a
2. S. A. Nouh, M. R. Atta, W. M. El-Melleegy, Rad. Eff. And Def. in Solids, 159 (8) (2004) 461-474.
3. P. C. Kalsi, K. D. S. Mudher, A. K. Pandey, R. H. Iyer, Thermochimica Acta 254(1995) 331-336.
4. M. F. Zaki, J. Phys. D: Appl. Phys. 41 (2008) 175404-175408.
5. S.K. Raghuvanshi, Bashir Ahmad, Siddhartha, A.K. Srivastava, J.B.M. Krishna, M.A. Wahab, Nuclear Instruments and Methods in Physics Research B 271 (2012) 44–47
6. F. Urbach, Phys. Rev. 92, (1953) 1324.
7. M. D. Migahed, H. M. Zidan, Current Applied Physics 6 (2006) 91-96.
8. N. F. Mott, E. A. Davies, Electronic Processes in Non-Crystalline Materials Clarendon Press, Oxford, 1979.
9. F. Yakaphanoglu, M. Arslam, M. Kucukislamoglu, M. Zengin, Solar Energy 79 (2005**)** 96-100.
10. A. V. Kokate, U. B. Suryavanshi, C. H. Bhosale, Solar Energy 80 (2006) 156-160.
11. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall Inc., NJ, USA, (1994).
12. Yasir Ali, Vijay Kumar, R.G. Sonkawade, A.S. Dhaliwal, Vacuum 90 (2013) 59-64
13. M. A. Malek, C. S. Chong FTIR study of H_2O in polyaalyl diglycol carbonate, Vibrational Spectroscopy 24 (2000) 181-184.
14. Lounis- Mokrani, M. Fromm, R. Barillon, A. Chabaudet, M. Allab, Radia. Measur. 36 (2003) 615-620.
15. Ambika Negi, Anju Semwal, Subhash Chandra, R.V. Hariwal, R.G. Sonkawade, D. Kanjilal, J.M.S. Rana, R.C. Ramola, Radiation Measurements 46 (2011) 127-132.
16. Surinder Singh, Sangeeta Prasher, Nucl. Instr. and Meth. In Phys. Res. B 222(2004)518–524.
17. D. Fink, W. H. Chung, R. Klett, A. Schmoldt, J. Cardoso, R. Montiel, M.H. Vazquer, L. Wang, F. Hosoi, H. Omichi, P. Goppelt-Langer, Radiat. Eff. Def. Solids, 133 (1995) 193- 208.