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Effect of X-ray irradiation on the structure, thermal and mechanical properties of polyester

Samir A. Nouh[1,2,a], Huda A. El-Nabarawy[3], M.M. Abutalib[4], and Radiyah A. Bahareth[4]

[1] Physics Department, Faculty of Science, Taibah University, Al-Madina al Munawarah, Saudi Arabia
[2] Physics Department, Faculty of Science, Ain Shams University, Cairo, Egypt
[3] Clothes and Jewelry Design Department, College of Family Science, Taibah University, Al-Madina al Munawarah, Saudi Arabia
[4] Physics Department, College of Science (Girls Branch), King Abdulaziz University, Jeddah, Saudi Arabia

Abstract. Samples from sheets of the polymeric material polyester have been exposed to X-rays from a 50 kV X-ray tube in the dose range 10–100 kGy. The resultant effect of X-rays has been investigated using different techniques such as X-ray diffraction XRD, thermogravimetric analysis TGA, differential thermal analysis DTA and stress-strain measurements. The results indicate that the polyester decomposes in one weight loss stage. Also, the X-ray irradiation in the dose range 30–100 kGy led to a more compact structure of polyester, which resulted in an improvement in its thermal stability. The variation of transition temperatures with the X-ray dose has been determined using DTA. The polyester thermograms were characterized by the appearance of an endothermic peak due to the melting of the crystalline phase. The melting temperature of the polymer T_m was investigated to probe the crystalline domains of the polymer. At the dose range 30–100 kGy, the defect generated destroys the crystalline structure, thus reducing the melting temperature. In addition, the stress-strain measurements indicate that the X-ray irradiation at the same dose range 30–100 kGy yields crosslinked polyester of high resilience that is suitable for manufacturing protective clothes that reduce heat stress.

1 Introduction

Clothing materials are the last line of defense protecting the human body from exposure to any potential hazards. Because of this fact, protective clothing is designed as necessary personal protective equipment for many professionals. Currently, widely used protective clothing is made of barrier textile materials that strongly affect the transport of heat generated by wearers, resulting in heat stress and low work efficiency. Polyester has many desirable characteristics that allowed it to achieve its present status as one of the important commercial polymers that fit these requirements. In spite of its enormous technical and economic importance, polyester still has some problems that alter its properties, such as poor thermal stability. This may be due to the structure defects that may be formed during the polymerization process. Therefore, obtaining crosslinked polyester is required. Crosslinked polyester will reduce heat stress and improve comfort performance for wearers. Thus, the irradiation of polyester is a useful technology to induce suitable modifications in it [1,2]. In par-

ticular, it is an important way to achieve some desired improvements that promise many applications in a wide range of industrial fields [3,4]. Irradiation of polymers destroys the initial structure by way of crosslinking, free radical formation, irreversible bond cleavages, etc., that result in the fragmentation of molecules and formation of saturated and unsaturated groups [5]. All these processes introduce defects inside the material that are responsible for change in the physical properties of the material [6–9]. The radiation induced modifications in the physical properties of polymers have already been widely reported [10–14]. The available literature was reviewed to determine the nature and extent of information on the thermal decomposition products and the toxicity of the combustion products of polyester materials used in consumer applications such as textiles. This literature review is limited. Hence, the aim of the present study is not only to obtain information concerning the interaction of 50 kV X-rays with polyester but also to study the possibility of improving its thermal stability to be suitable candidate for clothing industry.

[a] e-mail: samin273@gmail.com

2 Experimental

2.1 Samples

The polyester polymer used in this study is a 178 μm thick sheet manufactured by Eastman Kodak Company, Rochester, NewYork.

2.2 Irradiation facilities

The polyester samples of dimensions 1.5×1.5 cm and 178 μm thickness were irradiated with different X-ray doses, 10, 30, 50, 80 and 100 kGy. The X-ray irradiation was carried out using an Oxford Instrument XF5011 50 kV X-ray tube with a molybdenum target, which produced a maximum 1 mA current. The same instrument was used in previous work [15–17].

2.3 Analysis of the irradiated samples

The X-ray diffraction measurements were carried out with a Philips powder diffractometer type PW 1373 goniometer. The diffractometer was equipped with a graphite monochromator crystal. The wavelength of the X-rays was 1.5405 A$^\circ$ and the diffraction patterns were recorded in the 2θ range (10°–40°) with scanning speed of 2 degrees per minute.

Thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were performed on irradiated and non-irradiated polyester samples using the TGA and DTA apparatus model Shimadzu-50 with platinum cells. α-Al$_2$O$_3$ was used as a reference material for DTA measurements. Thermal experiments were carried out on all samples at a heating rate of 10 $^\circ$C/min with nitrogen as a carrier gas at a flow rate of 30 mL/min.

The mechanical measurements were carried out using Testometric M350–5 Ax with 5 kN load cell, at room temperature. Dumbbell-shaped samples of standard dimensions (50 mm long with a neck of 27 mm and width of 3 mm) were placed between the jaws and the load was applied at a rate of 50 mm/min until failure occurred. Five pieces of the same sample were used and the results were averaged for each data point.

3 Results and discussion

3.1 X-ray diffraction

In order to study the effect of X-ray irradiation on the degree of ordering of the polyester, X-ray diffraction measurements were carried out. Several investigations have shown that practically all crystalline polymers contain amorphous regions. The existence of amorphous regions leads to the appearance of characteristic amorphous halos in the diffraction pattern. Figure 1 shows the X-ray diffraction patterns of the non-irradiated and X-ray irradiated polyester samples. From the figure we see that the
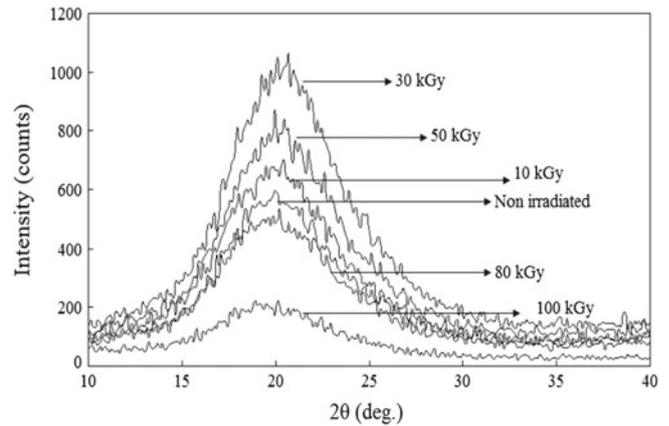

Fig. 1. X-ray diffraction patterns of the non-irradiated and X-ray irradiated polyester samples.
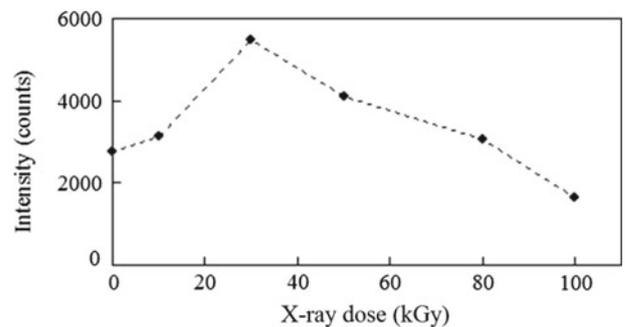

Fig. 2. Variation of the integral intensity I for polyester samples, with the X-ray dose.

X-ray diffraction patterns of the samples are characterized by halos extending in the 2θ range 10°–30° with maximum of the peak at 20°. The profile of the halos shows that the polyester is a partly crystalline polymer with a dominant amorphous phase. The spectra of all samples were fitted with a Lorentz function. Thereby the integral intensities I (area) of the main diffraction peak were extracted and are represented in Figure 2 as a function of the X-ray dose. The integral intensity shows an increase up to a maximum value around the 30 kGy irradiated sample, followed by a decrease on increasing the X-ray dose up to 100 kGy.

Since the halo's width at the half of maximal intensity ΔW is inversely proportional to the crystallite size, approximate indicative values of ΔW were calculated using the Scherrer equation:

$$L = (0.89\lambda)/(\Delta W \cos\theta),$$

where ΔW is the peak's width at the half of maximal intensity and λ is the wavelength of the X-rays. The obtained values are plotted in Figure 3 as a function of the X-ray dose. The peak's half width exhibited an opposite trend to that of the integral intensity, where it shows a decrease until a minimum value for a dose of 30 kGy, indicating an increase in the crystallite size, followed by an increase on increasing the X-ray dose up to 100 kGy.
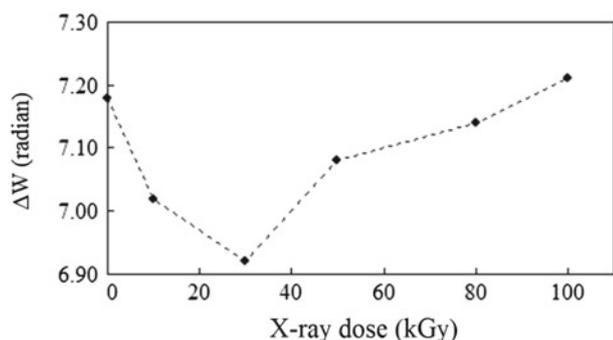
Fig. 3. Variation of the halo's width at the half of maximal intensity ΔW for polyester samples, with the X-ray dose.

Fig. 5. Variation of the onset temperature of decomposition T_o with the X-ray dose.

The increase in integral intensity indicates an increase in the crystallinity (ordering character) of polyester samples which can be attributed to degradation induced by X-ray irradiation. This degradation reduces the number of entanglements per molecule, thus increasing chain mobility. The increase in mobility permits some molecules to re-crystallize because crystalline state is a thermodynamic stable state [18]. On the other hand, at the dose range 30–100 kGy in which the integral intensity decreases denotes a decrease in the amount of crystalline phase in the samples, indicating that the crystalline structure has been destroyed due to crosslinking.

3.2 Thermal analysis techniques

3.2.1 TGA

TGA was performed on polyester samples in the temperature range from room temperature up to 500 °C, at a heating rate of 10 °C/min. Figure 4 shows the TGA thermograms for the non-irradiated and irradiated polyester samples. It is clear from the figure that the polyester polymer decomposes in one main breakdown stage. Using the TGA thermograms, the values of onset temperature of
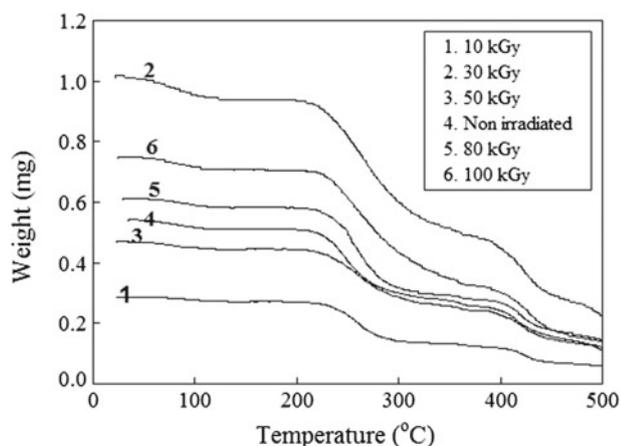
decomposition T_o, the temperature at which the decomposition starts, were calculated. Figure 5 shows the variation of T_o with the X-ray dose. The figure shows that T_o decreases until a minimum value around the 30 kGy irradiated sample due to degradation (i.e., preferentially chain scission) followed by an increase with increase in X-ray dose up to 100 kGy, due to the crosslinking process. At the dose range 30–100 kGy, the free radicals formed due to scission will often chemically react in various ways, sometimes at slow reaction rates. The free radicals can recombine forming the crosslinks.

3.2.2 DTA

DTA was performed in the temperature range from room temperature up to 400 °C at a heating rate of 10 °C/min, the obtained thermograms are shown in Figure 6. The polyester samples are characterized by the appearance of an endothermic peak at the melting temperature T_m. The values of these melting temperatures could be calculated and the variation of T_m with the X-ray dose is shown in Figure 7. The figure shows that T_m increases up to a maximum value around 30 kGy and then decreases with increase in X-ray dose up to 100 kGy. Usually the increase in melting temperature of polymer is attributed to the

Fig. 4. TGA thermograms of the non-irradiated and irradiated polyester samples, measured in the temperature range from room temperature up to 500 °C, at a heating rate of 10 °C/min.
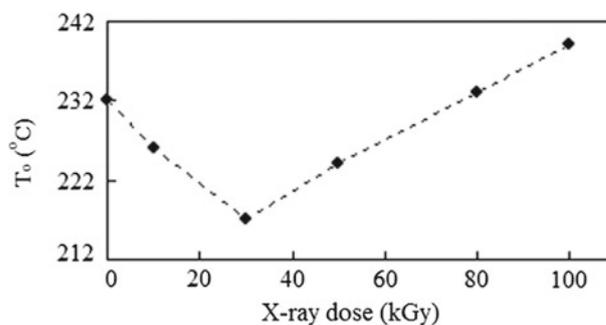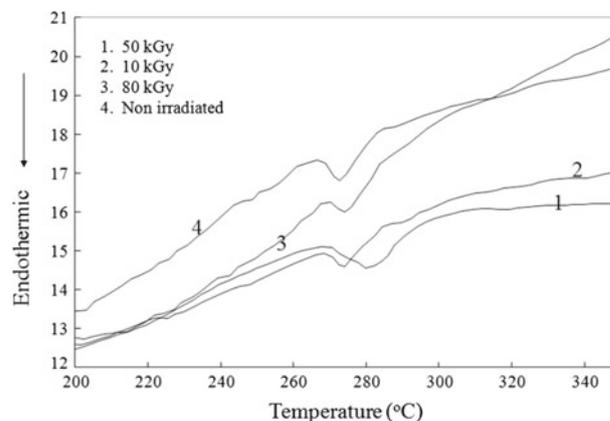

Fig. 6. DTA thermograms of the non-irradiated and irradiated polyester samples, measured in the temperature range from room temperature up to 400 °C, at a heating rate of 10 °C/min.
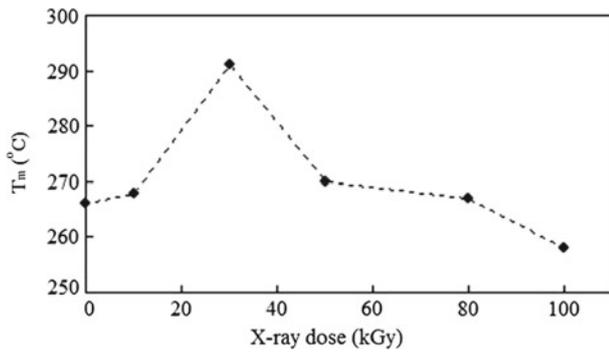
Fig. 7. Variation of the melting temperature T_m with the X-ray dose.

crosslinking. The apparent discrepancy between the dependence of T_o and T_m on dose results from the fact that T_m is sensing the crystalline domains of the polymer. It is possible to speculate that at low doses, the thickness of crystalline structures (lamellae) is increased. At higher doses, defects generation splits the crystals depressing the melting temperature. For such doses, the decrease of the polymer length contributes also to the shift of T_m toward lower temperatures. Similar results were obtained by Nasef et al. [19] when they studied the electron beam irradiation effects on partially fluorinated polymer films, where they investigated that the crosslinking inhibits the

crystallization and this is coupled with gradual decease in T_m with the irradiation dose. Also, the results are in agreement with those obtained in our previous work when we studied the effect of neutron irradiation on the thermal properties of cellulose nitrate [20]. In addition, Mishra et al. [21] investigated that the chain-scissioning leads to decrease in the strength of the poly(ethylene terephthalate) polymer thus decreasing its ability to withstand high temperatures.

3.3 Mechanical properties

A set of stress-strain curves for irradiated and non-irradiated polyester samples were measured and are given in Figure 8. Those curves were obtained by continuously measuring the force developed as the sample is elongated at a constant rate of extension. Generally, the strain increases on increasing the stress due to the increase in the flexibility of the chain in the macromolecules.
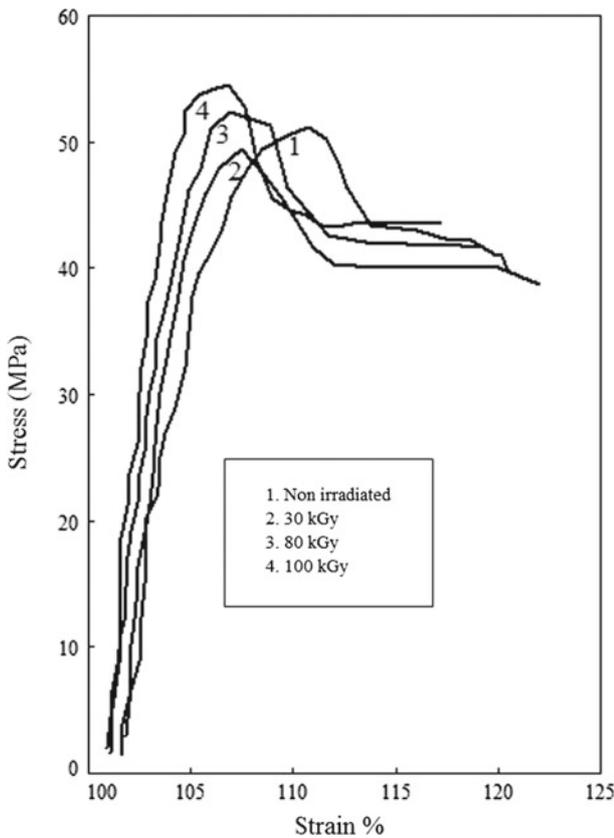

Fig. 8. Stress-strain set for the non-irradiated and X-ray irradiated polyester samples.
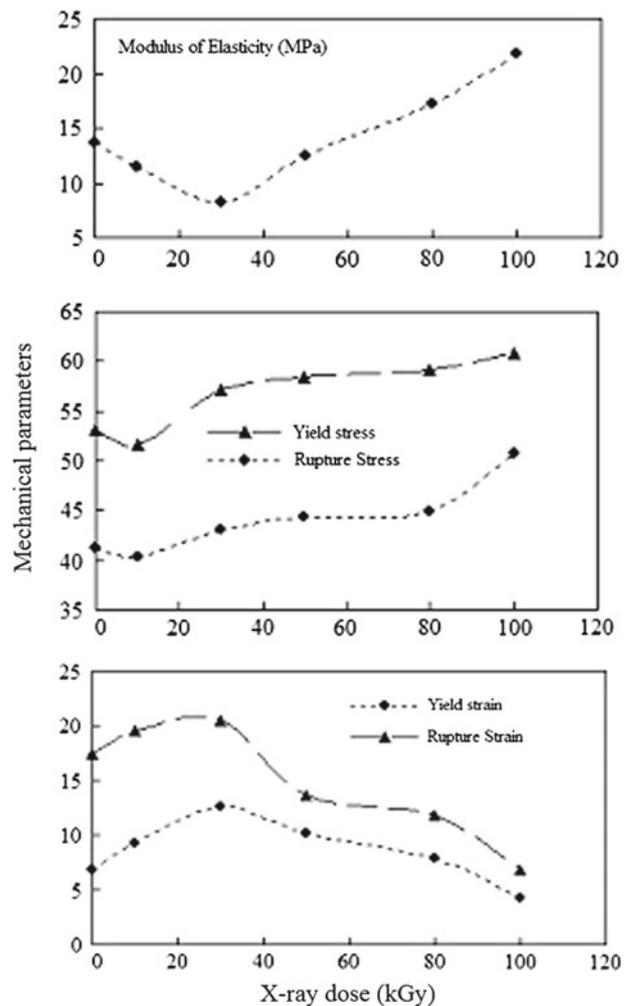

Fig. 9. Variation of Young's modulus, yield stress σ_y, yield strain ε_y, rupture stress σ_f and rupture strain ε_f with the X-ray dose.

Values of the Young's modulus E were calculated and are plotted in Figure 9 as a function of the X-ray dose. It is clear that the Young's modulus decreases until a minimum value around 30 kGy. Above 30 and up to 100 kGy, it increases. The decrease in elastic modules indicates that the sample has become more flexible which simply results from the decrease in interatomic force constants. Also, irradiation with X-rays up to 30 kGy tends to allow the onset of rather localized rotational motions in many parts of the polymer molecules, and these motions are reflected in a decrease in the elastic modules.

The stress-strain curves shown in Figure 8 serve to define several useful quantities including yield stress σ_y and yield strain ε_y (the stress and strain corresponding to a peak on the stress-strain curve), rupture stress σ_f (the stress corresponding to the fracture point) and rupture strain ε_f (elongation at the break).

The variation of σ_y, ε_y, σ_f and ε_f with the X-ray dose is shown in Figure 9. It is clear that σ_y and σ_f exhibited the same trend with the X-ray dose, as they decreased with increasing the dose up to 10 kGy, then increases with increasing the dose up to 100 kGy. Almost an opposite trend could be observed by ε_y and ε_f. The increase in yield stress may be attributed to the fact that high stresses enhance the flow mechanism by increasing the mobility of the macromolecular chains to yield higher flexibility. Also, the dose range in which σ_y and σ_f decreases, the changes can be attributed to a degradation mechanism in which the standard chains and a great number of chain ends weaken and the material may become softer. On increasing the dose above 30 and up to 100 kGy, crosslinking takes place.

4 Conclusion

The X-ray irradiation of polyester polymer leads to chain scission followed by crosslinking and as a result there are changes in its structural, thermal and mechanical properties.

Polyester samples irradiated at the dose range 30–100 kGy were characterized by dominate amorphous regions that give polymer resilience. Thus, the polyester may be a suitable candidate for industrial applications requiring its bending without breaking.

The X-ray irradiation in the dose range 30–100 kGy leads to a more compact structure of polyester, which results in an increase in its thermal stability. This enhances the scope of polyester in manufacturing protective clothes that reduce heat stress.

The results of the stress-strain test indicated that, at the X-ray dose 10–30 kGy, the standard chains and a great number of chain ends weaken and the material may become softer. Also the decrease in elastic modules indicated that the sample has become more flexible which simply results from the decrease in inter-atomic force constants.

References

1. M. Parul, C. Keshav, K. Saurabh, Malaysian Polym. J. **5**, 55 (2010)
2. R.C. Ramola, N. Ambika, S. Anju, C. Subhash, J.M. Rana, R.G. Sonkawade, D. Kanjilal, J. Appl. Polym. Sci. **121**, 3014 (2011)
3. R. Mishra, S. Tripathy, K. Dwivedi, D. Khathing, S. Ghosh, M. Muller, D. Fink, Radiat. Meas. **37**, 247 (2003)
4. A. Adla, V. Buschmell, H. Fuess, C. Trautmann, Nucl. Instr. Methods B **185**, 210 (2001)
5. M. Magida, J. Appl. Polym. Sci. **125**, 3184 (2012)
6. R. Nathawat, A. Kumar, V. Kulshrestha, Y.K. Vijay, T. Kobayashi, D. Kanjilal, Nucl. Instr. Methods B **266**, 4749 (2008)
7. Z.L. Zhou, A. Eisenberg, J. Polym. Sci. Phys. Ed. **21**, 595 (1983)
8. M. Aubin, R.E. Prud'homme, Macromolecules **13**, 365 (1980)
9. B. Bodmann, U. Hoim, Nucl. Instr. Methods B **185**, 299 (2001)
10. A. Belafrites, A. Nourreddine, D. Mouhssine, A. Nachab, A. Boucenna, Radiat. Meas. **39**, 241 (2005)
11. M.H. Abdel-Salam, S.A. Nouh, Y.E. Radwan, S.S. Fouad, Mater. Chem. Phys. **127**, 305 (2011)
12. S.A. Nouh. A. Abdelnaby, P.J. Sellin, Radiat. Meas. **42**, 1655 (2007)
13. A. Srivastava, T.V. Singh, S. Mule, C.R. Rajan, S. Ponrathnam, Nucl. Instr. Methods B **192**, 402 (2002)
14. P.C. Kalsi, C. Agarwal, Radiat. Eff. Defects Solids **162**, 25 (2007)
15. S.A. Nouh, R.A. Bahareth, Radiat. Eff. Defects Solids **167**, 229 (2012)
16. F.A. Boroumand, M. Zhu, J.L. Keddie, P.J. Sellin, Appl. Phys. Lett. **91**, 91 (2007)
17. S.A. Nouh, S. Bahmmam, Radiat. Eff. Defects Solids **167**, 102 (2012)
18. Z. Zhudi, Y. Wenxue, C. Xinfang, Radiat. Phys. Chem. **65**, 173 (2002)
19. M. Nasef, M. Dahlan, M. Khairal, Nucl. Instr. Methods B **201**, 604 (2003)
20. S.A. Nouh, T.M. Hegazy, Radiat. Meas. **41**, 17 (2006)
21. R. Mishra, S.P. Tripathy, K.K. Dwivedi, D.T. Khathing, S. Ghosh, M. Muller, D. Fink, Radiat. Eff. Defects Solids **153**, 257 (2001)