MYSTERIES OF LiF TLD RESPONSE FOLLOWING HIGH IONISATION DENSITY IRRADIATION: NANODOSIMETRY AND TRACK STRUCTURE THEORY, DOSE RESPONSE AND GLOW CURVE SHAPES

Y. Horowitz^{1,*}, E. Fuks¹, H. Datz², L. Oster³, J. Livingstone⁴ and A. Rosenfeld⁴

¹Physics Department, Ben Gurion University, Beersheva, Israel

²Radiation Safety Division, Soreq Nuclear Research Center, Yavne, Israel

³Physics Unit, Sami Shamoon College of Engineering, Beersheva, Israel

⁴Center for Medical Radiation Physics, University of Wollongong, Wollongong, Australia

*Corresponding author: yigal@bgu.ac.il

Received September 2 2010, revised October 20 2010, accepted October 21 2010

Three outstanding effects of ionisation density on the thermoluminescence (TL) mechanisms giving rise to the glow peaks of LiF:Mg,Ti (TLD-100) are currently under investigation: (1) the dependence of the heavy charged particle (HCP) relative efficiency with increasing ionisation density and the effectiveness of its modelling by track structure theory (TST), (2) the behaviour of the TL efficiency, $f(D)$, as a function of photon energy and dose. These studies are intended to promote the development of a firm theoretical basis for the evaluation of relative TL efficiencies to assist in their application in mixed radiation fields. And (3) the shape of composite peak 5 in the glow curve for various HCP types and energies and following high-dose electron irradiation, i.e. the ratio of the intensity of peak 5a to peak 5. Peak 5a is a low-temperature satellite of peak 5 arising from electron-hole capture in a spatially correlated trapping centre/luminescent centre (TC/LC) complex that has been suggested to possess a potential as a solid-state nanodosimeter due to the preferential electron/hole population of the TC/LC at high ionisation density. It is concluded that (1) the predictions of TST are very strongly dependent on the choice of photon energy used in the determination of $f(D)$; (2) modified TST employing calculated values of $f(D)$ at 2 keV is in agreement with 5-MeV alpha particle experimental results for composite peak 5 but underestimates the 1.5-MeV proton relative efficiencies. Both the proton and alpha particle relative TL efficiencies of the high-temperature TL (HTTL) peaks 7 and 8 are underestimated by an order of magnitude suggesting that the HTTL efficiencies are affected by other factors in addition to radial electron dose; (3) the dose-response supralinearity of peaks 7 and 8 change rapidly with photon energy: this behaviour is explained in the framework of the unified interaction model as due to a very strong dependence on photon energy of the relative intensity of localised recombination and (4) the increased width and decrease in $T_{\max}$ of composite peak 5 as a function of ionisation density is due to the greater relative intensity of peak 5a (a low-temperature component of peak 5 arising from two-energy transfer events, which leads to localised recombination).

INTRODUCTION

Many of the effects of high ionisation density (HID) on the TL of LiF:Mg,Ti are due to the spatial correlation/coupling of the trapping centres (TCs) and luminescent centre (LCs) giving rise to composite glow peak 5 and, possibly, other major glow peaks. A direct consequence of this spatial correlation is that the TL arises from a mixture of geminate recombination between locally trapped electron-hole (e-h) pairs and delocalised recombination mediated by charge carrier migration in the conduction and valence bands⁽¹⁾. This complexity gives rise to several interesting features: (1) The dependence of the dose-response supralinearity of composite peak 5 on photon/electron energy, which has been successfully modelled in the framework of the unified interaction model (UNIM)⁽²⁾; (2) the increased width and reduction in $T_{\max}$ of composite peak 5 as a function of heavy charged particle (HCP) mass

and energy, which is due to an increase in the relative intensity of peak 5a to peak 5 with increasing ionisation density. Peak 5a, a low-temperature component of composite peak 5, is believed to arise from joint e-h capture in the TC/LC molecular complex and this 'two-energy-transfer' event is preferred at HID compared with the 'single-energy transfer' event giving rise to peak 5 (electron capture only)⁽³⁾. It has been suggested that the ratio 5a/5 can provide a nanodosimetric measurement of average ionisation density in the 'nanoscopic' volume comprising the TC/LC molecular complex giving rise to peaks 5a and 5⁽⁴⁾; (3) the decrease in the relative efficiency following HID/HCP irradiation, which has been modelled by track structure theory (TST) with some degree of success⁽⁵⁾. However, the TST premise that the radiation action of HCPs is exclusively due to the dose delivered by the secondary electrons liberated by

the HCP slowing down has never been subjected to a stringent test. Recent work on alpha particle-induced TL following F band excitation⁽⁶⁾ and calculations of the relative efficiency of HCP-induced HTTL⁽⁷⁾ casts doubt on this postulate and on the validity/accuracy of TST modelling. These ionisation-density-induced phenomena still pose a formidable and continuing challenge to the understanding of the effects of ionisation density on the TL mechanisms in LiF:Mg,Ti.

TRACK STRUCTURE THEORY

TST assumes that HCP-induced TL is governed solely by the action of the secondary electrons and higher order electrons created by the slowing down of the HCP in the medium. The possible effects of HCP-induced defects/displacements due to nuclear collisions are ignored. Following the calculation of the electron radial dose by analytical or Monte Carlo methods, all that is required is some form of a transfer function [i.e. the normalised TL dose–response, $f(D)$] which relates electron dose to TL intensity. Some applications of TST have used values of $f(D)$ generated by ^{60}Co gamma rays or high-energy X rays⁽⁸⁾ and have claimed excellent agreement between calculations and experiment over a wide range of ions and energies. However, this approach does not consider the gross mismatch between the secondary electron spectrum generated by low-energy HCPs and gamma rays. For example, the maximum electron energy ejected by a 5-MeV alpha particle is a few kiloelectron volt compared with the hundreds of kiloelectron volt secondary electron energy generated by Compton scattering in the interaction of ^{60}Co gamma rays. This difference is especially important in the TL of LiF:Mg,Ti since $f(D)$ is different for ^{60}Co gamma rays and low-energy gamma rays due to the dependence of the supralinearity on gamma ray energy. The maximum value of $f(D)$ following ^{60}Co irradiation is $\sim 3\text{--}4$ ⁽⁵⁾ decreasing to ~ 1.5 using 10-keV synchrotron photons⁽⁹⁾. Gamboa deBuen *et al.*⁽¹⁰⁾ have also measured $f(D)_{\text{max}}$ of 1.7 ± 0.1 using 20 kV_p X rays of 8.1-keV effective energy. Modified TST (MTST)^(11, 12) emphasises the importance of matching the energy spectra of the secondary electrons generated by the test photon/electron radiation used to generate $f(D)$ and the HCPs. The importance of the radial distribution of electron spectra (not only the dose) has also been recognised in the extension of ‘average-track’ TST models⁽¹³⁾. No free parameters are used in MTST modelling contrary to the approach employed in microdosimetric TST, which involves a ‘target’ of variable dimensions⁽¹⁴⁾. In MTST, the relative HCP-to-gamma efficiency

$\eta_{\text{HCP},\gamma}$ is then given by

$$\eta_{\text{HCP},\gamma} = \eta_{\delta,\gamma} \times \frac{w_{\gamma} \int_0^{R_{\text{max}}} \int_0^{r_{\text{max}}} f_{\delta}(D) D(r, z) 2\pi r dr dz}{w_{\text{HCP}} \int_0^{R_{\text{max}}} \int_0^{r_{\text{max}}} D(r, Z, E) 2\pi r dr dz}, \quad (1)$$

where $\eta_{\delta,\gamma}$ is the relative TL response of the HCP secondary electrons to the ^{60}Co reference gamma radiation electrons. For composite peak 5 in LiF:Mg,Ti at low dose, this is usually taken equal to unity. w_{γ} and w_{HCP} are the mean energies required to produce an e–h pair by the gamma and HCP radiation, respectively. In LiF these have been estimated⁽¹¹⁾ at 33.97 eV and 36.0 eV, respectively based on a model suggested by Klein⁽¹⁵⁾. The uncertainty in the ratio $w_{\gamma}/w_{\text{HCP}}$ although estimated to be of the order of 10 % is still significantly smaller than other uncertainties involved in the calculation of relative HCP TL efficiencies. $D(r, Z, E)$ is the microscopic radial dose distribution around the HCP path. R_{max} and r_{max} are the maximum axial and radial penetration distances reached in the radiation absorption stage by the charge carriers emitted during the HCP slowing down and $f_{\delta}(D)$ is the experimentally measured normalised dose–response function (the TL efficiency) defined as

$$f_{\delta}(D) = \frac{F(D)/D}{F(D^*)/D^*}, \quad (2)$$

where $f(D)$ is the TL signal intensity and D^* is the dose in the linear-low-dose region. It deserves mention that MTST dose not assume that the relative TL efficiency depends only on the radiation absorption stage⁽¹⁶⁾ since it employs values of $f_{\delta}(D)$ (the TL efficiency), which depend on and include the recombination/heating stage of the TL process.

Monte Carlo calculations of $D(r)$ have been carried out in condensed phase LiF⁽¹⁷⁾ for 4-MeV and 5-MeV alpha particles and 1.43-MeV protons in a track segment approach (Figures 1 and 2). In addition, both η and $f_{\delta}(D)$ have been measured under identical experimental protocols for these HCPs^(17, 18), which justifies a careful comparison of TST calculations and the experimental values shown in Table 1⁽¹⁹⁾. A compilation of recent experimental data for a wider variety of ions and energies is also available⁽²⁰⁾.

The values of η for peaks 7 and 8 shown in Table 1 are approximately 1 order of magnitude greater than those of peak 5 and are certainly a manifestation of the very high supralinearity of the dose–response of these peaks as first pointed out by Waligorski and Katz⁽²¹⁾ and abundantly obvious from inspection of eqn (1) and the glow curves shown in Figures 3 and 4. Massillon *et al.*⁽¹⁸⁾ have measured values of $f(D)_{\text{max}}$ of 31 ± 8 and 207 ± 52

Figure 1. Monte Carlo calculated values of $D(r)$ for 4-MeV He ions in condensed phase LiF (reproduced from Avila⁽¹⁶⁾ with permission).

Figure 2. Monte Carlo calculated values of $D(r)$ for 1.43-MeV protons in condensed phase LiF (reproduced from Avila⁽¹⁶⁾ with permission).

for peaks 7 and 8 following ^{60}Co irradiation (1.25 MeV). These very high values of $f(D)_{\text{max}}$ are unprecedented and have been theoretically predicted using the UNIM⁽²⁾ as due to near negligible relative

Table 1. Experimental values of η .

1.43-MeV protons			4.9-MeV alpha particles		
Peak 5	Peak 7	Peak 8	Peak 5	Peak 7	Peak 8
0.3	4 ± 1.5	4 ± 1.5	0.12	1–2	1–2

Figure 3. Glow curves induced by 5-MeV alpha particles and $^{90}\text{Sr}/^{90}\text{Y}$ beta rays.

intensities of localised recombination. In addition to the greatly increased relative intensity of the HTTL following irradiation by HCPs, peak 5 is somewhat broader following alpha particle irradiation and the temperature of maximum TL intensity (T_{max}) is shifted downwards in temperature by $\sim 5^\circ\text{C}$ from 208°C to 203°C when a glow peak heating rate of 1°C s^{-1} is employed (Figure 3). In addition, the shoulder on the low-temperature side of composite peak 5 (attributed to peak 4) following gamma/electron irradiation at low dose is not observed following alpha particle irradiation suggesting a reduced relative intensity of peak 4 in the alpha-induced glow curves. As predicted by TST, the alpha particle and proton-induced glow curves begin to appear similar to the gamma/electron-induced glow curves only at very high gamma/electron irradiation levels of dose, i.e. 100 Gy and beyond (Figure 5).

As previously mentioned, MTST requires the matching in energy of the secondary electron spectra generated by the HCP and the test radiation used to generate $f(D)$. The maximum energy of HCP ejected secondary electrons, E_{max} , is given by

$$E_{\text{max}} = \left\{ \frac{(4m_e)}{(M_{\text{HCP}})} \right\} E_{\text{HCP}}, \quad (3)$$

where m_e , M_{HCP} are the masses of the electron and HCP, respectively and E_{HCP} is the energy of the HCP. It follows that E_{max} is ~ 2.4 and ~ 3.3 keV for 5-MeV

Figure 4. Glow curve induced by 1.5-MeV protons (reproduced from Avila⁽¹⁶⁾ with permission).

Figure 5. Glow curves following 100-keV X-ray irradiation as a function of dose (reproduced from Livingstone *et al.*⁽²⁾).

alpha particles and 1.43-MeV protons, respectively. The average electron energy can be expected to be $\sim 50\%$ of these maximum values. MTST thus requires the measurement of $f(D)$ at photon/electron energies of $\sim 1\text{--}2$ keV. This is a formidable experimental undertaking because the shallow penetration of these very soft radiations (especially in the case of electrons) makes surface effects of the irradiated samples of critical importance. Indeed it has been recommended that the annealing procedures be carried out in vacuum or an inert atmosphere in order to minimise surface effects⁽²²⁾. Ultra-soft X

rays are a more attractive possibility than electrons, however, the half-thickness for absorption of 1.5-keV X rays of $\sim 1.7\text{ }\mu\text{m}$ in LiF still demands carefully controlled annealing procedures in an inert atmosphere. Folkard *et al.*⁽²³⁾ reported $f(D)$ of 1.3 ± 0.1 at 60 Gy surface dose for peak 5 following 1.5-keV X-ray irradiation. Since the average dose in the irradiated volume is considerably less, at ~ 15 Gy, this value is considerably higher than the measurements carried out at 8.1-keV effective energy and 10 keV, which resulted in $f(D) \sim 1$ at this level of dose. Annealing carried out in air and readout at a constant temperature of 240°C for 16 s in contrast with the slow-linear heating rate protocols described herein are sufficient reasons to explain the discrepancy. The approach at this stage has been to construct the ultra-low electron energy $f(D)$ by extrapolation of experimentally measured $f(D)$ data from the higher energies using the UNIM⁽⁵⁾.

THE UNIM

Basic concepts

The basic premise of the UNIM is that the linear response at low dose arises from geminate recombination in a localised entity. For gamma rays and electrons, the localised entity is a coupled/spatially correlated TC and LC. The localised recombination process is unaffected by conduction band-mediated competitive processes. The dependence on dose of the delocalised conduction-band-mediated luminescence recombination gives rise to the supralinearity. At higher dose levels, the average of the distance distribution between occupied/active neighbouring TC/LC entities decreases, and the luminescence recombination efficiency increases due to the greater probability of charge carrier migration between neighbouring TC/LC complexes without interception by the competitive centres (CCs). In addition, if the CCs during irradiation capture charge of the same sign as the TCs, and are not depopulated before the peak 5 traps during glow curve heating (so-called deep traps), their 'competitive efficiency' is decreased as the dose level increases since an occupied CC no longer serves as an active CC for the charge carrier liberated by the TC.

Mathematical formulation

In the UNIM, the TL signal intensity is given by

$$F(D) = ksn_e + (1 - ks)n_e \sum_{i=1}^{i=4} \int_{r_0}^{R_{\max}} g(r_h, R) e^{-R_i/\lambda} \times P_i(n_{LC}, R_i) dR_i. \quad (4)$$

Configuration states after irradiation

Figure 6. TC/LC complex configurations following irradiation.

The first-term represents the contribution from localised (geminate) recombination. The second term estimates the increased TL intensity at high dose levels due to conduction band-mediated recombination in the presence of competitive processes. n_e is the number density (cm^{-3}) of occupied TCs and its dose dependence is given by $N_e[1 - \exp(-\beta_{\text{TC}} D)]$ as demonstrated by optical absorption studies, where β_{TC} is the dose filling constant of the TC and N_e is the total number density of available TCs. k is the relative probability of geminate/localised recombination in the surround of the TC/LC complex not subject to competitive processes and s is the fraction of TC/LC complexes, which have captured an e-h pair following irradiation. Following irradiation, The TC/LC complex can exist in four different trapping configurations as shown in Figure 6. r_o is the distance between the paired TC and LC and is some measure of the average distance over which geminate recombination can occur. $g(r_h, R_i)$ is an approximate three-dimensional solid angle factor between two neighbouring TC/LC pairs so that

$$g(r_h, R) \approx \frac{\pi r_h^2}{4\pi R^2}, \quad (5)$$

$S_{\text{LC}} = \pi r_h^2$ is the cross section for capture of an electron by the hole-occupied LC. R_i is the distance

between neighbouring TC/LC pairs: λ , the mean free path of the electrons between the TC/LC pairs, is an increasing function of dose [due to the filling (de-activation)] of the competitors with increasing dose and its dose dependence for gamma rays is given by

$$\lambda_g = \lambda_o \exp(\beta_{\text{cc}} D) \quad \text{where } \lambda_o = (N_{\text{cc}} S_{\text{cc}})^{-1}, \quad (6)$$

where β_{cc} is the dose filling constant of the CC, N_{cc} is the total number density of available CCs and S_{cc} is the cross section for charge carrier capture by the CC. $P_i(n_{\text{LC}}, R_i) dR_i$ is the i th nearest-neighbour distance probability distribution function, which have been calculated elsewhere^(2, 5).

At low dose, in the linear part of the dose response, the second term describing the increased efficiency due to nearest-neighbour interactions is vanishingly small due to the competitive processes, so that

$$F(D^*) \sim k s n_e(D^*). \quad (7)$$

The normalised TL dose-response, $f(D)$, or relative

TL efficiency is then given by

$$f(D) = \{[n_c(D)/D]/[n_c(D^*)/D^*]\}\{1 + ([1 - ks]/(ks))[I_1 + I_2 + I_3]\} \quad (8)$$

where

$$I_i = \int g(r_h, R_i) \exp(-R_i/\lambda) P_i(n_{LC}, R_i) dR_i. \quad (9)$$

There are nine parameters in the UNIM (β_{TC} , β_{LC} , β_{cc} , ks , r_o , S_{LC} , λ_o , N_{LC} and β_{RD} , where β_{RD} is a recent addition⁽²⁾, which allows the modelling of the effects of radiation damage via destruction of LCs at high levels of dose.

Previous applications of the UNIM have demonstrated its capability to quantitatively describe several of the important characteristics of the TL mechanisms giving rise to the supralinearity of composite peak 5 in TLD-100^(5, 24). For example: (1) the dependence of the supralinearity on ionisation density, (2) the required dose dependence of the recombination stage CC, (3) the dependence of supralinearity on recombination temperature and (4) HCP-induced TL fluence response.

Measurements of $f(D)$ as a function of photon energy: extrapolation to 2 keV

Experimental measurements of $f(D)$ have been carried out at 1.25 MeV⁽¹⁸⁾, ~500 keV ($^{90}\text{Sr}/^{90}\text{Y}$ beta rays)^(6, 25), 100-keV X rays⁽²⁾ and 8.1-keV effective energy X rays⁽¹⁰⁾. The experimental results for peaks 5, 7 (7a+7) and 8 and fits to $f(D)$ using the UNIM are shown in Figure 7. The UNIM parameters used for the fits to peaks 5, 7 and 8 are shown in Table 2. The dose response of peaks 7 and 8 required values of the dose filling constants different from those used for peak 5 in order to accommodate the higher values of $D_{\max}$ (the level of dose where $f(D)_{\max}$ occurs) for these peaks⁽²⁾. In addition, the dose filling constants for peaks 7 and 8 at the various photon/electron energies require somewhat different values. This is probably a reflection of the fact that peaks 7 and 8 are, in fact, composite peaks. Peaks 7 and 8 show a strong dependence of $f(D)_{\max}$ on photon energy over the entire range of photon energies unlike peak 5 for which $f(D)_{\max}$ is approximately constant from 100 keV to 1.25 MeV (Figure 8). It is interesting to note (although perhaps coincidental) that the extrapolation to extremely low photon energies converges on the same value of $f(D)$ of ~0.4 at 0.1 keV for all the peaks. Based on this extrapolation Figure 8 indicates that the supralinearity of peaks 5, 7 and 8 should disappear at photon energies of ~2, 0.7 and

0.4 keV, respectively. The energy dependence of $f(D)$ was obtained for all the glow peaks by variation in the localised recombination parameter (ks) as shown in Figure 9.

The well-behaved dependence of $f(D)_{\max}$ and ks on photon energy allows calculation of $f(D)$ at 2 keV by extrapolation of the values of ks as shown in Figures 7 and 8 and the use of the parameters shown in Table 2. The calculated values of $f(D)$ are shown in Figure 10 and yield values of $f(D)_{\max}$ =1.0, 1.35 and 2.3 for peaks 5, 7 and 8, respectively.

MTST CALCULATION OF η FOR 1.43-MEV PROTONS AND 5-MEVALPHA PARTICLES

Using the values of $f(D)$ shown in Figure 10 allows the calculation of η for peaks 5, 7 and 8 for 1.43 MeV protons (Figure 11) and 5.0 MeV alpha particles (Figure 12). In addition, are shown the values of η calculated using the values of $f(D)$ measured at photon/electron energies of 1.25 MeV, 100 and 8.1 keV. Several points are worthy of emphasis:

- (1) The calculated values of η for both the protons and the alpha particles vary by a factor of ~3, ~38 and ~145 for peaks 5, 7 and 8 depending on the photon energy used to generate $f(D)$. This convincingly demonstrates that any claimed agreement (or disagreement for that matter) between TST and experiment is arbitrary and unjustified unless one uses the correctly matched photon energy to generate $f(D)$ as postulated by MTST.
- (2) The experimental value of η for the 5-MeV alpha particles of 0.12 is in good agreement with the low photon energy (2 keV) calculated value of 0.13. The calculated value is less satisfactory for the protons, which underestimates the experimental value by ~50 %.

For peaks 7 and 8, there are very large discrepancies between the calculated values and experimental values using values of $f(D)$ appropriate to low photon energies. This indicates that there are significant unresolved problems in the application of TST to the calculation of relative HCP TL efficiencies for the HTTL peaks. The problem may be due to enhanced creation and participation of defects created by HCP nuclear scattering in the TL mechanisms of peaks 7 and 8 and to a lesser extent peak 5. Another possibility is that the extrapolation of $f(D)$ to low photon energies is incorrect. To resolve this latter possibility, experimental measurements of $f(D)$ generated by 2-keV photons are required.

Figure 7. Experimental measurements of $f(D)$ as a function of photon energy with UNIM fits: (a) peak 5, (b) peak 7 and (c) peak 8.

Table 2. UNIM parameters: 8-keV X-ray dose response.

Parameter	Glow peak				
	4	5	6	7	8
$\beta_{TC} (10^{-3} \text{ Gy}^{-1})$	1.1	1.1	0.5	0.5	0.2
$\beta_{LC} (10^{-3} \text{ Gy}^{-1})$	9.0	9.0	4.0	9.0	4.0
$\beta_{cc} (10^{-3} \text{ Gy}^{-1})$	0.1	0.1	0.1	0.1	0.1
ks	0.14	0.285	0.06	0.125	0.055
$r_o (\text{\AA})$	20	20	20	20	20
$S_{LC} (10^{-16} \text{ m}^2)$	9.6	9.6	9.6	9.6	9.6
$\lambda_o (\text{\AA})$	475	475	475	475	475
$N_{LC} (10^{22} \text{ m}^{-3})$	1.95	1.95	1.95	1.95	1.95
$\beta_{RD} (10^{-3} \text{ Gy}^{-1})$	0.5	0.1	0.02	0.02	0.02

Figure 8. Dependence of $f(D)_{\max}$ on photon energy for peaks 5, 7, 8.

THE SHAPE OF COMPOSITE PEAK 5 AS A FUNCTION OF HCP TYPE AND ENERGY

Composite peak 5 [believed to arise from a TC/LC configuration based on $\text{Mg}^{++}\text{Li}_{\text{vac}}$ trimers (the TC)

coupled to $\text{Ti}(\text{OH})_n$ (the LC)] consists of the main peak 5, a low-temperature satellite (peak 5a) and a high-temperature satellite (peak 5b). Following low ionisation density (LID) irradiation, peak 5 appears at a temperature of maximum intensity, $T_{\max}$, of

$\sim 208^\circ\text{C}$ when the sample is naturally cooled following the 400°C pre-irradiation annealing and then heated at a linear heating rate of 1°C s^{-1} . By natural, cooling is usually meant removal of the samples from the annealing oven at the end of the pre-irradiation anneal. The sample temperature

Figure 9. Dependence of the localisation parameter (ks) on the photon energy employed to measure $f(D)$.

decreases approximately exponentially and the cooling rate will be mainly determined by the mass and heat capacity of the sample holder. The average cooling rate is $\sim 1000^\circ\text{C h}^{-1}$. Peak 5a and Peak 5b

Figure 11. 1.43-MeV proton relative TL efficiencies as a function of photon energy used to determine $f(D)$.

Figure 10. Calculated values of $f(D)$ at a photon energy of 2 keV: (a) peak 5, (b) peak 7 and (c) peak 8.

appear at values of $T_{\max}$ of $\sim 196^\circ\text{C}$ and $\sim 224^\circ\text{C}$, respectively. The relative intensity of peak 5a induced by (LID) $^{90}\text{Sr}/^{90}\text{Y}$ radiation in naturally cooled materials is $\sim 0.04 \pm 0.02$ [1 standard deviation (SD)] and has proven difficult to measure reproducibly even with carefully controlled annealing, readout and deconvolution protocols due to its low intensity and strong overlap with peaks 4 and 5. Following HID irradiation, the relative intensity of 5a/5 increases to a value of ~ 0.3 for 5-MeV alpha particles (Figure 13). Peak 5b is readily observed only at high LID dose levels or following HCP irradiation. The effect of ionisation density on the shape of composite peak 5 is quite subtle. For low energy (~ 1 MeV/amu) alpha particles, the $T_{\max}$ of composite peak 5 is shifted to lower temperatures by $\sim 5^\circ\text{C}$ and the width of the peak is increased.

Figure 12. 5-MeV alpha particle relative TL efficiencies as a function of photon energy used to determine $f(D)$.

The shoulder on the low-temperature side of peak 5 (due to peak 4) is no longer observed. This behaviour can be interpreted as due to an increased intensity of peak 5a relative to peaks 4 and 5 following HID irradiation. The deconvolution analysis into component glow peaks shown in Figure 13 is based on this hypothesis and is supported by $T_m - T_{\text{stop}}$ measurements⁽²⁶⁾.

THE PEAK 5A IONISATION DENSITY-DEPENDENT NANODOSEMETER

It has been previously demonstrated that peak 5a arises from geminate recombination between a locally trapped e-h (a ‘two-energy transfer event’ in microdosimetric terminology⁽²⁷⁾ in a TC/LC complex of ~ 2 nm dimensions⁽¹⁾. Peak 5 on the other hand results from delocalised recombination arising from a singly trapped electron in the TC/LC complex (a ‘single-energy transfer’ event) and peak 4 from a ‘singly trapped hole’ in the same complex (Figure 6). Localised recombination via tunnelling is a well-known phenomenon in luminescence mechanisms and is usually described in the terminology of ‘donor-acceptor pairs’ in which the probability of recombination is strongly dependent on the distance between the donor and the acceptor. In the geminate recombination mechanism responsible for peak 5a, delocalised charge carrier traffic in the conduction band/valence band is not involved, whereas the opposite is true for peaks 4 and 5 in which the recombination mechanism is completely delocalised. The TC giving rise to composite peak 5 is associated with a 4 eV optical absorption band and very strong conversion of peak 5a to peak 4 following 4 eV optical excitation and stepped ($I_m - T_{\text{stop}}$) annealing is the primary experimental evidence supporting the

Figure 13. Deconvoluted glow curves following alpha particle and beta irradiation in ‘rapidly cooled’ material. Note the increased relative intensity of peak 5a in the alpha glow curve.

above hypothesis for the TL absorption mechanisms giving rise to composite peak 5⁽³⁾. Due to the ‘two-energy transfer event’ nature of peak 5a it is expected on purely statistical grounds that its relative intensity following HID irradiation would be increased relative to the same ratio following LID radiation due to the very high levels of dose (ionisation density) in the HCP track⁽²⁸⁾. Model calculations of the ratio of peak 5a/5 following proton and alpha particle irradiation using a track structure approach have been carried out demonstrating enhanced intensity of peak 5a following HCP irradiation due to full population of TCs and LCs and de-activation of CCs at high ionisation density⁽²⁸⁾. The relative intensity of peak 5a to peak 5 thus represents a measure of ionisation density in a volume of nanometre dimensions (corresponding to the approximate size of the TC/LC complex), which may be correlatable with radiation damage in certain biological systems due to its conceptual similarity to the radiation-induced mechanisms of

‘single-strand breaks’ and ‘double-strand breaks’ in DNA⁽²⁷⁾. Realisation of the potential of this ‘solid-state nanodosimeter’ has, however, previously been hampered by the low intensity of peak 5a relative to peak 5 of 0.04 ± 0.02 (1 SD) following LID irradiation in samples, which are naturally cooled following the 400°C pre-irradiation annealing.

THE EFFECT OF SLOW COOLING

The properties of a modified LiF:Mg,Ti (TLD-100) material in which the relative intensity of peak 5a is significantly increased have been recently described^(29, 30). The sample is prepared using a slow/linear/programmer-controlled cooling rate of 100°C h^{-1} to room temperature following the 400°C/1 h pre-irradiation annealing. Slow cooling decreases the intensity of peak 5 and increases the relative intensity of peak 5a resulting in increased values of the ratio 5a/5 (Figures 14 and 15). Note the shift in T_{max} of composite peak 5 to lower temperatures and the lack of a low-temperature shoulder in the slow-cooled glow curve, reminiscent of the behaviour following HID irradiation in naturally cooled material and again, indicative of an increased presence of peak 5a. This behaviour arises since different rates of cooling ensure different equilibrium concentrations of dipoles ($\text{Mg}^{++}\text{Li}_{\text{vac}}$), dimers, trimers, clusters and precipitates⁽³¹⁾. The broadening of composite peak 5 at slow cooling rates was previously reported by Bos *et al.*⁽³²⁾. The former carried out a systematic study on the effect of cooling rate and reported an activation energy of 1.95 eV at a cooling rate of $1000^\circ\text{C h}^{-1}$ decreasing to 1.8 eV at 60°C h^{-1} . They suggested that the broadening of peak 5 was due to increased Mg precipitate phases bringing about a perturbation in the crystal potential and a distortion of the band gap in the vicinity of the precipitate particles. This hypothesis, although plausible, has yet to be supported by

Figure 14. Effect of slow cooling following irradiation by 6-MV photons.

Figure 15. Effect of cooling rate on the ratio of 5a/5 following $^{90}\text{Y}/^{90}\text{Sr}$ irradiation: (a) slow cooling and (b) rapid cooling.

ancillary experimental evidence. Slow cooling and improved deconvolution procedures have significantly increased the precision of measurement of the ratio of peak 5a/5 as will be described in the following.

Experimental details

Four samples of LiF:Mg,Ti (TLD-100) 3 mm × 3 mm × 0.89 mm chips (Batch S-4453) were irradiated in a variety of radiation fields. The batch sensitivity was measured by irradiation of 10 chips with ^{137}Cs gamma rays (661 keV) at the Israeli Secondary Standards Dosimetry Laboratory (ISSDL) at the Soreq Nuclear Research Center. The ISSDL dosimetry has been calibrated via the Primary Standards Dosimetry Laboratory at the Physikalisch-Technische Bundesanstalt and undergoes annual postal intercomparisons at the International Atomic Energy Agency. The SD of the composite peak 5-sensitivity for the 10 chips was measured to be 6 % and this was assumed to be representative of the entire batch. Glow curve readout was carried out on a Harshaw 3500 manual reader at a heating rate of 1°C s^{-1} from an initial temperature of 50°C to a maximum temperature of 375°C . After irradiation, each TLD was post-irradiation annealed at $155^\circ\text{C}/6\text{s}$ to remove the low-temperature component of the glow curves thereby simplifying the deconvolution procedure. The temperature stability of the readout procedure has been measured to be $\pm 2^\circ\text{C}$ by repeated measurements of the maximum temperature of composite peak 5 following $^{90}\text{Sr}/^{90}\text{Y}$ irradiation. The chips were pre-irradiation annealed in air at 400°C for 1 h followed by a rapid non-linear cool down in ~ 20 min to room temperature achieved by removing the TLDs from the annealing oven or by slow cooling in the oven to room temperature with a constant cooling rate of 100°C h^{-1} determined by a programmer/controller. The readout procedure was carried out in a flow of high-purity N_2 gas following passage through a dehydrator.

Glow curve analysis

The relative intensity of glow peak 5a was determined by computerised glow curve deconvolution using peak shape parameters (Table 3) based on first-order kinetics and deduced from ancillary studies using 4 and 5 eV optical excitation, which create nearly 'single-peak' glow curves for peaks 4 and 5⁽³³⁾. These studies resulted in activation energies of 1.9, 2.3 and 2.15 eV for peaks 4, 5a and 5, respectively. The uncertainty in these values is estimated to be ± 0.1 eV for peaks 4 and 5 and ± 0.2 eV for peak 5a. The activation energies of 1.9 and 2.15 eV for peaks 4 and 5, respectively, are in good agreement with the range of values reported in the

Table 3. Glow peak parameters: first-order kinetic analysis.

Glow peak	T_{max} ($^\circ\text{C}$)	Activation energy (eV)
2	119	1.10
3	162	1.15
4	182	1.90
5a	196	2.30
5	208	2.15
5b	224	2.25
6	242	2.1
7a	258	2.00
7	275	2.00
8	300–310	2.00
9	320–330	2.8
10	348	2.8

literature. Satisfactory fits to the glow curves in both naturally cooled and slow-cooled materials were obtained using these activation energies, which were kept constant for all the analyses. The relative intensity of peak 5a is not very sensitive to the value of the activation energy of peak 5a, e.g. using a value of 2.15 eV instead of 2.3 eV changes the 5a/5 ratio following HCP irradiation by $\sim 10\%$. The values of T_{max} were allowed to vary but only within the $\pm 2^\circ\text{C}$ corresponding to the temperature stability/reproducibility of the readout procedure. This point deserves emphasis. If the value of T_{max} of peak 5 used for the analysis of the HCP-induced glow curves is allowed to vary freely, the chi-squared minimisation procedure will invariably converge on a value of T_{max} of peak 5 corresponding to the experimentally measured T_{max} of composite peak 5. This will then invariably lead to a loss in the correlation between peak 5a and ionisation density as was reported by Brandan *et al.*⁽³⁴⁾ in the various deconvolution protocols employed in that investigation in which 'the curves were displaced in order to overlap the positions of their peak 5'. The deconvolution procedure used herein is based on the hypothesis that peak 5 does not shift in temperature as a function of ionisation density and that the experimentally observed shift in the T_{max} of composite peak 5 is due to the increased relative intensity of peak 5a, which 'pulls' the T_{max} of composite peak 5 downward in temperature. This procedure reveals a robust correlation of the intensity of peak 5a with ionisation density and has been successful in leading to improved precision of measurement of the 5a/5 ratio in both types of materials and was found to produce satisfactory fits to the experimental glow curve data with 'integral figure of merit' values no worse than $\sim 5\%$. The ratio of peak 5a/5 deduced from the deconvolution procedure is, however, quite sensitive to the chosen temperature difference between peaks 5a and 5. The subtraction procedure employed to determine the peak shape parameters of peak 5a

MYSTERIES OF LiF TLD RESPONSE

Table 4. Ratio of peak 5a to peak 5 as a function of ionisation density and cooling rate.

Radiation	Energy (MeV)	(LET) _{ave} (keV μm^{-1} in water)	Fluence/dose (cm^{-2}) (Gy)	Cooling rate (K h^{-1})		Increase in 5a/5 ratio due to slow cooling
				100	1000	
[e ⁻] Sr/Y ⁺	~0.5	~5.6 ^a	0.5	0.13 $\pm$ 0.02	0.04 $\pm$ 0.02	3.2
[e ⁻]	1500 $\times 10^{-6}$	10		0.95 $\pm$ 0.2		
[e ⁻]	1000 $\times 10^{-6}$	13		1.02 $\pm$ 0.09		
[e ⁻]	500 $\times 10^{-6}$	19.5		1.12 $\pm$ 0.07		
[e ⁻]	100 $\times 10^{-6}$	30		1.27 $\pm$ 0.07		
[e ⁻] ^a	100–1500 $\times 10^{-6}$ (no significant variation with energy detected)				0.61 $\pm$ 0.08	
X rays ^b	0.069		1.0		0.35 $\pm$ 0.05	
X rays ^b	0.153		1.0	0.20 $\pm$ 0.015		
X rays ^b	0.040		1.0	0.19 $\pm$ 0.014	0.089 $\pm$ 0.027	2.1
X rays ^c	0.028		0.4	0.18 $\pm$ 0.020		
X rays ^c	0.097		1.0		0.10 $\pm$ 0.016	
X rays ^c	0.097		250		0.07 $\pm$ 0.03	
X rays ^d	0.1		1.0		0.12 $\pm$ 0.04	
Protons ^c	4.5	9	10 ⁹	0.27 $\pm$ 0.036	0.14 $\pm$ 0.057	1.9
Deuterons ^c	4.5	15	10 ⁹	0.31 $\pm$ 0.11	0.10 $\pm$ 0.02	3.1
Protons ^c	2.6	13	1.26 $\times 10^{10}$	0.54 $\pm$ 0.18	0.08 $\pm$ 0.03	6.8
Protons ^c	1.3	22	10 ⁹	0.43 $\pm$ 0.016	0.096 $\pm$ 0.027	4.5
Deuterons ^c	1.7	30	10 ⁹	0.58 $\pm$ 0.12	0.23 $\pm$ 0.05	2.5
Alpha ^c	7.5	67	10 ⁹	0.35 $\pm$ 0.08	0.12 $\pm$ 0.03	2.9
Alpha ^c	2.0	150	10 ⁹	0.69 $\pm$ 0.14	0.37 $\pm$ 0.14	1.9
Cu ^{+3e}	20.6	406	4 $\times 10^8$	0.78 $\pm$ 0.13	0.33 $\pm$ 0.095	2.4
I ^{+10e}	82.5	711	2.3 $\times 10^9$	0.60 $\pm$ 0.08	0.27 $\pm$ 0.08	2.2
I ^{+10e}	20.7		4 $\times 10^9$	0.80 $\pm$ 0.04	0.35 $\pm$ 0.07	2.3

^aElectron gun: Tel Aviv University.

^bXRAD 320 X-ray tube: Westmead Millenium Institute, Sydney Australia.

^c5-MeV Singletron (high-voltage engineering) Radiological Research Accelerator Facility: Columbia University, USA

^dEuropean Synchrotron Radiation Facility, Grenoble, Switzerland: FWHM of the energy spectrum=70 keV.

^e10-MVANTARES Tandem: Australian National Science and Technology Organization, Sydney, Australia.

+ ⁹⁰Sr/⁹⁰Y source: Ben Gurion University, Israel.

Figure 16. Glow curve following 4.5-MeV proton irradiation in 'slow-cooled' material.

Figure 17. Glow curve following 7.5-MeV alpha particle irradiation in 'slow-cooled' material.

Figure 18. Glow curve following 1.7-MeV deuteron irradiation in 'slow-cooled' material.

does not determine the $T_{\max}$ of peak 5a to better than $\pm 2^\circ\text{C}$. For the results shown in Table 4, $\Delta T_{\max(5a \rightarrow 5)}$ was kept constant at 12°C . Allowing $\Delta T_{5a \rightarrow 5}$ to vary by $\pm 1\text{--}2^\circ\text{C}$ in either direction changes the values of $5a/5$ significantly, but the trend and magnitude of the increase of $5a/5$ with increasing ionisation density/LET is maintained. The temperature 'jitter' in the value of $T_{\max}$ of composite peak 5 of 2°C and the uncertainty in the temperature difference between peaks 5a and 5 are thus the major factors in determining the precision

of measurement of the ratio of peak 5a/5 induced by the various radiation fields.

RESULTS

Table 4 summarises the experimentally measured peak 5a to peak 5 relative intensities in a large variety of LID and HID radiation fields including (1) $^{90}\text{Sr}/^{90}\text{Y}$ beta rays (2) 0.1–1.5-keV monoenergetic electrons, (3) X rays, (4) protons and deuterons, (5) He ions and (6) Cu and I ions. Representative

Figure 19. Glow curve following 2-MeV alpha particle irradiation in 'slow-cooled' material.

Figure 20. Glow curve following 20.6-MeV Cu ion irradiation in 'slow-cooled' material.

glow curves are shown in Figures 16–21 in slow-cooled materials. The ratio of the intensities of peak 5a to peak 5 is increased in the slow-cooled samples compared with the naturally cooled samples by a factor of ~ 3 with the notable exception of the results for the low-energy proton irradiations, which show an even greater increase. This increase results in significantly improved precision in the measurement of $5a/5$ with a SD averaged over all the radiation fields of 15 % compared with 25 % for the naturally cooled samples. The peak $5a/5$ ratio in the

slow-cooled material for the various radiation fields is shown in Figure 22 plotted against LET, which serves as a rough indicator of ionisation density. The data for each radiation species clearly show an increase in the peak $5a/5$ ratio with decreasing particle energy (increasing ionisation density). The value of the $5a/5$ ratio for the very heavy ions (Cu and I) is somewhat lower than expected and may indicate the role of defect production due to enhanced nuclear scattering in the efficiency of the luminescence mechanisms. Although track structure

Figure 21. Glow curve following 1.5-keV electron irradiation in 'slow-cooled' material.

Figure 22. $5a/5$ ratios as a function of LET for various radiation fields.

model calculation^(35,36) can describe the basic underlying mechanisms leading to increased values of $5a/5$ following HCP irradiation, the many unknowns preclude at this stage of knowledge detailed here modelling of these experimental results. Nonetheless, since the HCPs studied herein produce secondary electrons of maximum energy of a few kiloelectron volt the $5a/5$ values induced by low-energy electrons might be expected to reflect this fact and lead to values close to those following HCP irradiation. At least three issues, however, complicate this expectation. The first is the radial dose distribution in the HCP tracks, which varies by ~ 10 orders of magnitude from the track 'core' to the periphery of the

track, thereby leading to radial distributions of the TC, LC and CC occupation probabilities very different from those following the low-dose electron irradiation. The second, as previously mentioned, is the possibility of enhanced defect production due to nuclear scattering following HCP irradiation. And, the third is the possibility of surface effects influencing the TL mechanism following irradiation by low-energy electrons in samples annealed in air⁽³⁷⁾. Studies using ultra-soft synchrotron X rays in both nitrogen and air-annealed samples are planned in order to resolve the latter possibility.

CONCLUSIONS

Values of η calculated by TST strongly depend on the choice of photon energy employed to measure the TL efficiency, $f(D)$. This supports the postulate of MTST that the calculation of η should be carried out using $f(D)$ measured with a secondary electron spectrum as similar as possible in energy to the secondary electron spectrum generated by the HCP. Calculations of η for 1.43-MeV protons and 5-MeV alpha particles using theoretically estimated values of $f(D)$ appropriate to 2-keV electrons yield mixed results. Good agreement is obtained for the alpha particles, less so for the protons and very large discrepancies of an order of magnitude for the peaks comprising the HTTL. This suggests that additional defects due to nuclear scattering or other factors (e.g. dose rate, local microscopic heating, ...) may be influencing the HCP relative TL efficiency. The dose response

supralinearity of peaks 7 and 8 show a very strong dependence on photon energy, especially peak 8 for which $f(D)_{\max}$ decreases by ~ 2 orders of magnitude when measured at 1.25 MeV compared with a few kiloelectron volt. This behaviour can be interpreted in the framework of the UNIM by a very strong dependence of the relative intensity of localised recombination on photon energy compared with peak 5. The microscopic/physical reasons underlying this strong dependence are as yet unknown.

The shape of composite peak 5 is dependent on ionisation density due to enhanced localised recombination at high ionisation density, which results in an increase in the relative intensity of a low-temperature satellite, peak 5a. The increased relative intensity of peak 5a in the HID-induced glow curves broadens composite peak 5 and ‘pulls’ the value of $T_{\max}$ of composite peak 5 to slightly lower temperatures. The ratio of peak 5a to peak 5, determined by computerised glow curve analysis is found to increase by ~ 1 order of magnitude from the glow curves induced by LID radiation fields to the HID radiation fields. The systematic increase in the ratio of 5a/5 by ~ 1 order of magnitude with increasing ionisation density demonstrates the viability of the concept of the peak 5a/5 nanodosimeter. The precision of measurement depends on strictly applied protocols both in the preparation/annealing protocols of the material and in the deconvolution analysis since the ratio of peak 5a/5 is strongly dependent on the chosen temperature difference between peaks 5a and 5. The results shown above are, therefore, not easily transferable to other measurement modalities and should not be attempted to be reproduced unless great care is taken to reproduce all the readout and analysis and experimental conditions. These results are primarily intended to demonstrate the concept and potential of a solid-state nanodosimeter based on existing LiF:Mg,Ti materials. Further work is necessary to improve the reproducibility of the heat transfer to the sample during readout in order to improve the precision in the appearance of $T_{\max}$ of peak 5 from $\pm 2^\circ\text{C}$ to $\sim \pm 0.5^\circ\text{C}$. Such an improvement would be expected to profoundly improve the precision of measurement of the 5a/5 ionisation density-dependent nanodosimetric signal.

FUNDING

This publication was supported in part by grant no. P41 EB002033-13, Radiological Research Accelerator Facility (RARAF) from the National Institutes of Health/National Institute of Biomedical Imaging and Bioengineering (NIBIB) and supported in part by The Australian Institute of Nuclear Science and Engineering—proposal no. 5268.

REFERENCES

1. Horowitz, Y. S., Oster, L., Biderman, S. and Einav, Y. *Localised transitions in the thermoluminescence of LiF:Mg,Ti: potential for nanoscale dosimetry*. J. Phys. D Appl. Phys. **36**, 446–459 (2003).
2. Livingstone, J., Horowitz, Y. S., Oster, L., Datz, H., Lerch, M., Rosenfeld, A. and Horowitz, A. *Experimental investigation of the 100 keV X-ray dose response of the high temperature thermoluminescence in LiF:Mg,Ti (TLD-100): theoretical interpretation using the Unified Interaction Model*. Radiat. Prot. Dosim. **138**, 320–332 (2010).
3. Weizman, Y., Horowitz, Y. S. and Oster, L. *Investigation of the composite structure of peak 5 in the thermoluminescent glow curve of LiF:Mg,Ti (TLD-100) using optical bleaching*. J. Phys. D Appl. Phys. **32**, 2118–2127 (1999).
4. Fuks, E., Horowitz, Y. S., Horowitz, A., Oster, L., Marino, S., Rainer, M., Rosenfeld, A. and Datz, H. *Thermoluminescence solid state nanodosimetry—the peak 5a/5 dosimeter*. In: The 15th International Symposium on Microdosimetry, Verona, Italy (2009). Radiat. Prot. Dosim., in press.
5. Horowitz, Y. S. *A unified and comprehensive theory of the TL dose response of thermoluminescent systems applied to LiF:Mg,Ti*. In: Microdosimetric Response of Physical and Biological Systems To Low- and High-Let Radiations: Theory and Applications to Dosimetry. Horowitz, Y. S., Ed. Elsevier Press (2006).
6. Weiss, D., Horowitz, Y. S. and Oster, L. *Ionisation density effects following F-centre optical excitation in LiF:Mg,Ti (TLD-100): analysis via track structure theory*. J. Phys. D Appl. Phys. **42**, 085113–085123 (2009).
7. Livingstone, J., Rosenfeld, A., Horowitz, Y. S., Oster, L., Datz, H., Brett, C. and McCallum, J. *Track structure microdosimetric calculation of relative glow peak intensities following 5 MeV He irradiation of LiF:Mg,Ti (TLD-100)*. In: 19th Annual Meeting Australian Institute of Physics, Melbourne (2010).
8. Geiß, O. B., Kramer, M. and Kraft, G. *Efficiency of thermoluminescent detectors to heavy charged particles*. Nucl. Instrum. Methods **B142**, 592–598 (1998).
9. Nariyama, N., Tanaka, S., Yoshizawa, M., Hirayama, H., Ban, S., Nakashima, H., Namito, Y. and Nakane, Y. *Responses of LiF TLDs to 10–40 keV monoenergetic photons from synchrotron radiation*. Radiat. Prot. Dosim. **49**, 451–457 (1993).
10. Gamboa de Buen, I., Buenfil, A. E., Ruiz, C. G., Rodriguez-Villafuerte, M., Flores, A. and Brandan, M. E. *Thermoluminescent response and relative efficiency of TLD-100 exposed to low energy X-rays*. Phys. Med. Biol. **43**, 2073–2083 (1998).
11. Kalef-Ezra, J. and Horowitz, Y. S. *Heavy charged particle thermoluminescence dosimetry: track structure theory and experiments*. Int. J. Appl. Radiat. Isot. **33**, 1085–1100 (1982).
12. Avila, O. and Brandan, M. E. *Influence of $f\delta(D)$ on modified track structure efficiency calculations*. Radiat. Prot. Dosim. **100**, 163–166 (2002).
13. Cucinotta, F. A., Katz, R. and Wilson, J. W. *Radial distribution of electron spectra from high-energy ions*. Radiat. Environ. Biophys. **37**, 259–265 (1998).

14. Horowitz, Y. S. and Olko, P. *The effects of ionisation density on the thermoluminescence response (efficiency) of LiF:Mg,Ti and LiF:Mg,Cu,P*. Radiat. Prot. Dosim. **109**, 331–348 (2004).
15. Klein, C. A. *Bandgap dependence and related features of radiation ionization energies in semiconductors*. J. Appl. Phys. **19**, 2029–2038 (1968).
16. Avila, O., Gamboa-deBuen, I. and Brandan, M. E. *Study of the energy deposition in LiF by heavy charged particle irradiation and its relation to the thermoluminescent efficiency of the material*. J. Phys. D Appl. Phys. **32**, 1175–1181 (1999).
17. Avila, O. *Deposito de Energia en LiF irradiacion con particulas cardagas pesadas y su relacion con la respuesta termoluminiscente del material*. PhD thesis, Ensanada, Mexico (2000).
18. Massillon, J. L. G., Gamboa deBuen, I. and Brandan, M. E. *Onset of supralinear response in TLD-100 exposed to ⁶⁰Co gamma rays*. J. Phys. D Appl. Phys. **39**, 262–268 (2006).
19. Avila, O., Rodriguez-Villafuerte, M., Gamboa-deBuen, I., Aviles, P., Estrada, P., Buenfil, A. E., Ruiz-Trejo, C., Gonzales, P., Brandan, M. E. and Horowitz, Y. S. *On the correct measurement of relative heavy charged particles to gamma thermoluminescent efficiencies*. Radiat. Prot. Dosim. **100**, 87–90 (2002).
20. Berger, T. and Hajek, M. *TL-efficiency-overview and experimental results over the years*. Radiat. Meas. **43**, 146–156 (2008).
21. Waligorski, M. P. R. and Katz, R. *Supralinearity of peak 5 and 6 in TLD-700*. Nucl. Instrum. Methods **175**, 48–50 (1980).
22. Carrillo, R. E., Pearson, D. W., DeLuca, P. M. Jr. and Mackay, J. F. *Thermoluminescent response of lithium fluoride (TLD-100) to monoenergetic photons beams of 600, 730, 900 and 1500 eV*. Radiat. Prot. Dosim. **47**, 519–523 (1993).
23. Folkard, M., Roper, M. J. and Michael, B. D. *Measurement and analysis of supralinearity in LiF TLD-100 irradiated by 1.5 keV X-rays*. Phys. Med. Biol. **34**, 707–715 (1989).
24. Horowitz, Y. S. *Theory of thermoluminescence dose response: The Unified Interaction Model*. Nucl. Instrum. Methods **B184**, 68–84 (2001).
25. Datz, H. PhD thesis, Ben Gurion University of the Negev, Israel (2010).
26. Horowitz, Y. S., Sattinger, D., Yossian, D., Brandan, M. E., Buenfil, A. E., Gamboa-deBuen, I., Rodriguez-Villafuerte, M. and Ruiz, C. G. *Ionisation density effects in the thermoluminescence of TLD-100: computerised Tm-Tstop glow curve analysis*. Radiat. Prot. Dosim. **84**, 239–242 (1999).
27. Rossi, H. H. and Zaider, M. *Microdosimetry and Its Applications*. Springer-Verlag (1996).
28. Oster, L., Horowitz, Y. S. and Biderman, S. *The concept of a quasi-tissue-equivalent nanodosimeter based on the glow peak 5a/5 ratio in LiF:Mg,Ti (TLD-100)*. Australas. Phys. Eng. Sci. Med. **26**, 78–83 (2003).
29. Fuks, E., Horowitz, Y. S. and Oster, L. *Investigation of the properties of composite glow peak 5 in slow-cooled TLD-100*. Radiat. Meas. **43**, 249–253 (2008).
30. Fuks, E., Horowitz, Y. S., Oster, L., Belaish, Y. and Ben Shahr, B. *The effects of ionisation density on the glow curve structure of LiF:Mg,Ti (TLD-100): the behaviour of composite peak 5 in 'slow-cooled' material*. Radiat. Prot. Dosim. **126**, 194–197 (2007).
31. Taylor, G. C. and Lilley, E. *Effect of clustering and precipitation on thermoluminescence in LiF(TLD-100) crystals*. J. Phys. D Appl. Phys. **15**, 1235–1276 (1982).
32. Bos, A. J. J., Vijverberg, R. N. M., Pijters, T. M. and McKeever, S. W. S. *Effects of cooling and heating rate on trapping parameters in LiF:Mg,Ti crystals*. J. Phys. D Appl. Phys. **25**, 1249–1257 (1992).
33. Horowitz, Y. S., Fuks, E., Oster, L., Podpalov, L., Belaish, Y. and Ben Shahr, B. *Advanced multi-stage deconvolution applied to composite glow peak 5 in LiF:Mg,Ti (TLD-100)*. Radiat. Prot. Dosim. **126**, 322–325 (2007).
34. Brandan, M-E., Angeles, O. and Mercado-Urbe, H. *Phenomenological study of the ionisation density dependence of TLD-100 peak 5a*. Radiat. Prot. Dosim. **119**, 29–32 (2006).
35. Horowitz, Y. S., Belaish, Y. and Oster, L. *Theories of TL systems, failures, successes, conflicts, trends: insights into possible future materials and techniques*. Radiat. Prot. Dosim. **119**, 124–129 (2006).
36. Horowitz, Y. S., Sattinger, D. and Avila, O. *Track structure approach to the calculation of peak 5a to peak (TLD-100) relative intensities following heavy charged particle irradiations*. Radiat. Prot. Dosim. **119**, 45–48 (2006).
37. Lasky, J. B. and Moran, P. R. *Thermoluminescent response of LiF(TLD-100) to 5–30 keV electrons and the effect of annealing in various atmospheres*. Phys. Med. Biol. **22**, 852–862 (1977).