The analysis of thermoluminescent glow peaks of CaF_2 : Dy (TLD-200) after β-irradiation

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Abstract
Variable dose (VD), $T_m - T_{stop}$, initial rise (IR), variable heating rate (VHR), peak shape (PS) and computerized glow curve deconvolution (CGCD) methods are used to determine the number of peaks, the order of kinetics (b), the activation energy (E_a) and attempt-to-escape frequency (s) associated with the glow peaks in CaF_2 : Dy (TLD-200) after β-irradiation between the dose level 0.1 and 110 Gy. The $T_m - T_{stop}$ procedure indicates that the glow curve of this crystal consists of at least nine glow peaks. The dose variation experiment indicates that seven of them, namely peaks 1–6 and 8, are of first-order kinetics and peaks 7 and 9 are of general-order kinetics. However, the $T_m - T_{stop}$ procedure and the CGCD method have indicated that peak 6 has general-order kinetics too. The activation energy found with the IR, VHR, PS and CGCD methods for peak 4 yield very close values. For all other peaks, there is no agreement between the results of all the applied methods. This work also indicates that the post-irradiation annealing and the heating rate have pronounced effects on the evaluated kinetic parameters of all glow peaks.

1. Introduction

Calcium fluoride singly doped with dysprosium is an important TLD material which is commercially available as TLD-200 from the Harshaw Chemical Company [1]. The sensitivity of this material is approximately 30 times higher than that of TLD-100. Therefore, it has found widespread use in the field of environmental and personnel radiation dosimetry due to its high sensitivity, despite some problems associated with batch-to-batch fluctuations, anomalous fading, complex glow curve structure and its poor energy response resulting from its high effective atomic number compared with tissue. Binder and Cameron [2] have studied its glow curve behaviour as well as the dosimetric properties. They have observed that its glow curve structure consists of a group of four

low temperature peaks (known as I–IV) which considerably overlap near approximately 120˚C, 140˚C, 200˚C and 240˚C, and two higher temperature peaks (V and VI) near 340˚C and 400˚C at a heating rate of $6˚C\,s^{-1}$. It has been found that all the studied peaks in the glow curve of this material grow at different rates with exposure. Compared to the vast literature on CaF_2 : Mn, CaF_2 : Tm, $CaSO_4$: Dy, LiF : Mg : Ti (TLD-100) and some other thermoluminescent materials, relatively little work has been done on the CaF_2 : Dy (TLD-200) crystal [3–5]. A survey of the literature has indicated that very few studies on the thermoluminescence (TL) properties and defect structure of CaF_2 : Dy dosimeter have been carried out [6, 7]. Especially, there have been only few systematic published studies [8–11], of kinetic parameters associated with the TL peaks in this material. Merz and Pershan [8, 9] estimated the E_a and s parameters for the major peaks appearing below

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350 K, and Yazici and Öztürk [10, 11] analysed the kinetic parameters of well-isolated glow peak 6 as a function of the duration of post-irradiation annealing at 145°C. The latter study has shown that all kinetic parameters (E_a, s and b) are significantly influenced by the post-irradiation annealing time at this temperature. No similar analysis is available for the other dosimetric peaks above room temperature.

The dosimetric characteristics of any TL material mainly depend on the sensitivity, energy response and the kinetic parameters quantitatively describing the trapping–emitting centres responsible for the TL emission. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. For example, the simultaneous estimation of the dose rate and the time elapsed since exposure are closely related to the position of the trapping levels within the band gap, and therefore it is necessary to have a good knowledge of these parameters. There are various methods for evaluating the trapping parameters from TL glow curves [12]. When one of the glow peaks is highly isolated from the others, the experimental methods such as initial rise, various heating rates, and peak shape methods are suitable methods to determine them. However, in most materials, the glow curve consists of several overlapping peaks, which is also the case in CaF$_2$: Dy. When more than one glow peak is present in the glow curve, there are essentially two ways to obtain these parameters: the first is to isolate each individual TL peak from the others using partial thermal annealing treatment and the other is to make a complete glow curve analysis using deconvolution [13]. Some difficulty arises in the first method due to the problems in isolating the peak of interest without any loss of intensity. The major attractive feature of the deconvolution technique is the simultaneous determination of kinetic parameters of all peaks with no thermal treatment. However, the deconvolution method has also its disadvantages as compared to the classical methods in some cases, especially when the structure of the glow curve is very complex. Therefore, different methods along with the deconvolution method have been used to determine the kinetic parameters of CaF$_2$: Dy (TLD-200) due to some difficulties in interpreting the deconvolution results. These are (i) the variable dose (VD) method; (ii) the T_m−T_{stop} method; (iii) the initial rise (IR) method; (iv) the variable heating rate (VHR) method; (v) the peak shape (PS) method; (vi) the computerized glow curve deconvolution (CGCD) technique. These methods were described elsewhere [12–16] in detail and, therefore, are not reviewed in this study. The CGCD analysis was performed using the GLOCANIN program, which is based on the least square minimization procedure. It was developed at the Reactor Institute at Delft, The Netherlands [17]. At the end of the deconvolution, the goodness of fit is tested by an FOM (figure of merit) [18].

2. Experimental procedures

The samples used in this study were CaF$_2$: Dy (TLD-200) crystal chips (3.2 mm × 3.2 mm × 0.89 mm) obtained from the former company known as Harshaw Chemical Company, Ohio, USA. The samples were annealed at 500 ± 1°C for 30 min through the experiments to erase any residual information before the subsequent irradiation and then cooled

in air at approximately 75°C min^{-1} to room temperature. All annealing treatments were carried out with a specially designed microprocessor-controlled electrical oven, which is able to control the temperature to within ±1.0°C. All irradiations were performed immediately after the standard annealing at room temperature with β-rays from a ^{90}Sr–^{90}Y source ($\approx$0.02 Gy s^{-1}). The irradiation equipment was an additional part of the 9010 Optical Dating System. The samples were irradiated to various dose levels between $\approx$0.1 and $\approx$110 Gy during the variable dose method. The irradiated samples were read out in an N$_2$ atmosphere with a Harshaw QS 3500 manual type reader that is interfaced to a PC where the TL signals were studied and analysed. A standard clean glass filter was always installed in the reader. Glow curves were measured using a platinum planchet at a linear heating rate of 1°C s^{-1}. The time duration between irradiation and the TL reading was always kept constant at about 1 min. For the variable heating rate method, heating rates were varied from 1°C s^{-1} to 7°C s^{-1}. At each experimental measurement, four chips were read out. Each chip was read out twice and the second readout is considered to be the background of the reader plus chip; this was subtracted from the first one and all of the analyses have been carried out after the subtraction.

3. Results

As mentioned previously, published studies [19–22] showed that the determination of E_a and s mainly depends on the prior knowledge of b and the exact number of glow peaks in the glow curve. Therefore, to find the order of kinetics of each individual glow peak, the variable dose method was first used. Some of the selected glow curves after different dose levels are shown in figure 1. In TL theory, for first-order kinetics, peak temperatures of the glow peaks are expected to change only with the heating rate. Hence, for a constant heating rate, the peak maximum should not be affected by other experimental parameters and should thus be fairly constant within the limit of experimental errors. However, for general-order kinetics below the trap saturation points {n_0 (concentration of trapped electrons) < N_t (concentration of traps)}, the peak temperatures are shifted to the lower temperature side with increasing dose levels. It is seen from figure 1 that the peak temperature of some glow peaks (i.e. peaks 1–6 and 8) in the glow curve of CaF$_2$: Dy are within the experimental error of ±2°C for the various dose levels. However, the peak temperature of peaks 7 and 9 are shifting to the low temperature side with increasing dose levels and this point clearly indicates that peaks 7 and 9 are of general-order and the others have first-order kinetics. However, this is not so for peak 6 and this property is clearly demonstrated in our previously published paper [10]. Although there is no shift in the peak temperature of this peak with increasing dose levels, the CGCD, peak-shape and isothermal decay methods have indicated that this peak has general order kinetics. (For a discussion on this possibility see, for example, [16, p 32].)

A typical analysed TL glow curve from 2 min irradiated ($\approx$2.4 Gy) TLD-200 crystal is shown in figure 2 along with the components obtained from CGCD. A careful investigation of this figure indicates that its glow curve structure is described by a linear combination of at least seven glow peaks between room
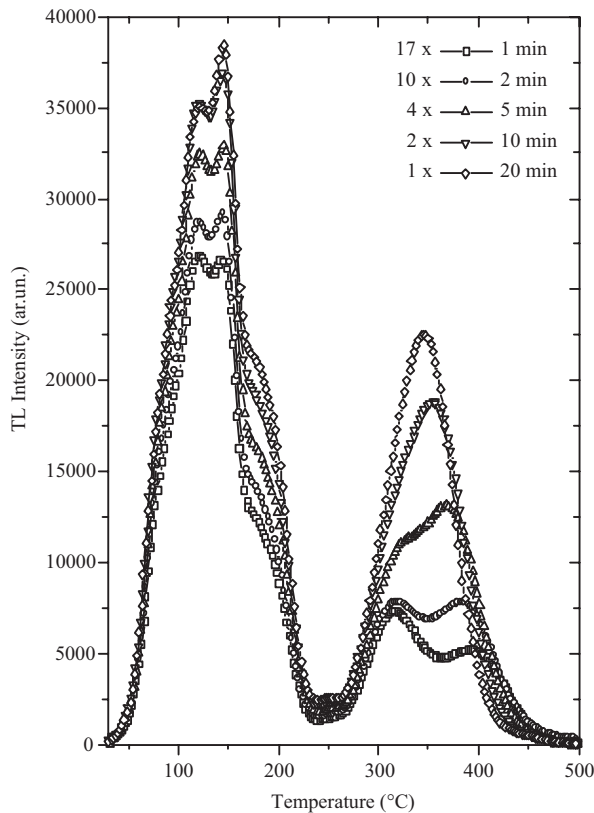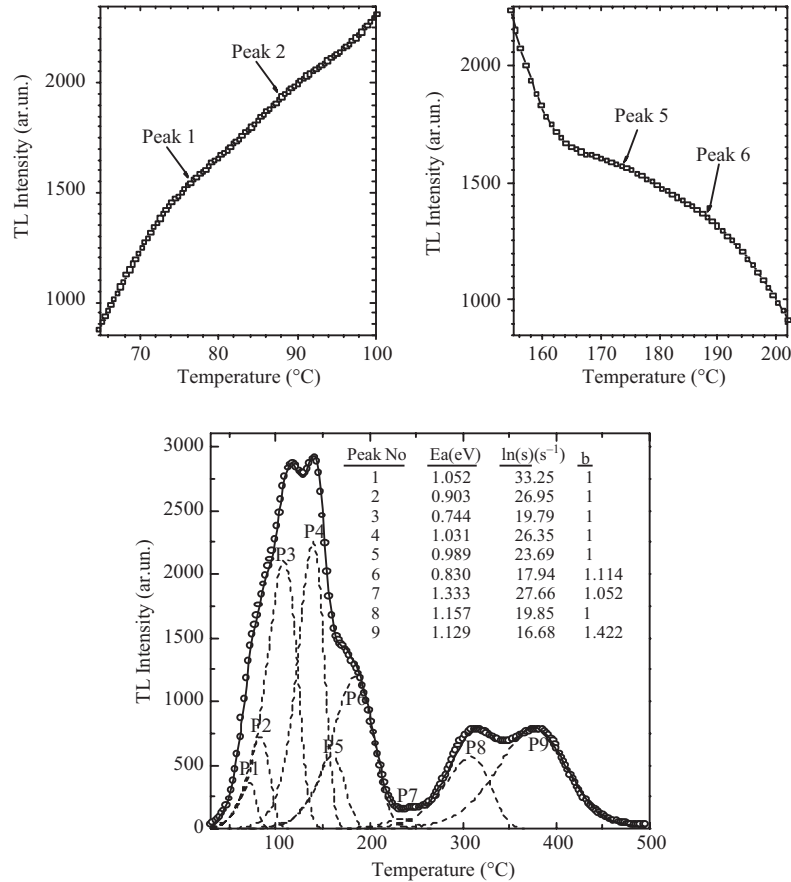
Figure 1. The glow curve of TLD-200 measured after various dose levels (at a heating rate $\beta = 1°C\,s^{-1}$). Doses were varied using different irradiation times at a rate of $0.02\,Gy\,s^{-1}$. In all figures, open circles represent the experimental points.

temperature and 250°C, when the glow curve is immediately recorded after irradiation, and that a best fit was always obtained by assuming that the first five peaks are of first-order kinetics and the others (peak 6 and 7) are of general-order kinetics. Two higher temperature glow peaks above 250°C are clearly seen in the glow curve, the first one with first-order kinetics and the second one with general-order kinetics.

The order of kinetics for the various peaks in the glow curve was also tested with the T_m-T_{stop} procedure. Here, an irradiated sample is heated at a linear heating rate to a temperature T_{stop} corresponding to a point on the low temperature tail of the first peak. The sample is then cooled down quickly to room temperature and then re-heated at the same rate to record all of the remaining glow curve, and the position of the peak temperature T_m is noted. The heating rate used was $1°C\,s^{-1}$ and the dose level was $\approx 6\,Gy$. The process is repeated several times on the same annealed/irradiated sample at a different T_{stop} values and four measurements were taken within each 10°C region. Some of the selected glow curves after the T_m-T_{stop} procedure are shown in figure 3. As seen in this figure, the peak temperatures of some glow peaks (i.e. peaks 3, 4, 6 and 9) are easily obtained from the glow curves without any CGCD whereas the others are not. Therefore, all the glow curves were also analysed by the CGCD method and their peak temperatures were determined. Some of the analysed glow curves are shown in figure 4. The number of peaks and their kinetic parameters are also shown in this figure. The following comment on the deconvolution method should

be made. According to many experienced researchers, the results obtained by the CGCD method, in some cases, seem to be unreliable. It has previously been mentioned [10] that the CGCD method is a very popular method to evaluate the kinetic parameters of glow peaks from the glow curves. However, since during the curve fitting procedures the whole curve is utilized in the analysis, rather than just a few points on the glow curve, it is apparent that if the number of data points used in the analyses is increased, the potential for accurate determination of the kinetic parameters is better. However, this advantage of the CGCD method may be undermined in complex glow curves. One may get a local (not global) minimum of the least square function which may yield erroneous kinetic parameters as the computerized fitting routine attempts to define the 'best-fit' to the numerical data. As a result, many possible sets of parameters could be assigned to the same glow curve and, therefore, they would not be acceptable from a physical point of view. Thus, many researchers have recommended using the results of some classical methods as initial estimating parameters in the computer program to obtain reliable and physically acceptable data. This would increase the chance of reaching a global minimum of the relevant objective function. Nevertheless, according to the results obtained in this work it is necessary to state that even this is not enough to guarantee that the CGCD method yields the 'real' parameters. A further study on this subject is required. Therefore, the peak temperatures found by CGCD in some cases may be different from the real values and it may be due to the insufficiency of CGCD.

A plot of T_m against T_{stop} shows a stepwise curve after the T_m-T_{stop} procedure. This method allows one to estimate the number of peaks and each plateau region indicates the approximate position of an individual peak. A gradual rise of T_m at the end of the plateau region is an indication that the TL kinetics have an order higher than one. Peaks with first-order TL kinetics show a sharp rise to the next flat region. However, in the case of overlapping peaks, this sharp rise can be slightly smoothed out. Figure 5 shows the plots of the T_m-T_{stop} curve obtained with this method. It reveals at least seven flat and two slightly rising regions. At the end of each plateau, there are always rising parts and this raises a question whether all glow peaks in the glow curve structure of TLD-200 have general-order kinetics. However, when the regions of peaks 6 and 9 are closely checked, it is observed that there is no plateau region but rather, a slight increase at the beginning and then a quick increase at the end. Thus, the general-order glow peaks do not have a plateau, which is clearly observed from figure 5. On the other hand, the other peaks always have either a narrow or wide flat regions and, therefore, the rising parts at the end of each flat region do not indicate any non-first-order glow peak(s). It appears to be due to highly overlapping glow peaks around this region and this is also clearly observed from the analysed glow curves. Another interesting result obtained in this work is that the obtained peak temperatures found by the CGCD method are always lower than those obtained from the maxima in the glow curve. When the individual glow peak is highly isolated from its neighbours, the obtained peak temperatures are close to each other. So far, the observations support the assertion that the glow curve of TLD-200 is composed of at least nine glow peaks between room temperature and 500°C under all the dose levels studied

Figure 2. A typical analysed glow curve of CaF$_2$: Dy (TLD-200) measured after $\approx$2.4 Gy irradiation at room temperature. The glow curve was measured by heating the sample to 500°C at a rate of 1°C s^{-1}.

between 0.1 and 110 Gy, and peaks 6, 7 and 9 have general-order whereas the others have first-order kinetics.

The IR method was also employed after T_m–T_{stop} measurements. According to this method, at the beginning of the TL glow peak, the concentration of trapped electrons n_0 changes by only a small amount with temperature and thus it can be regarded as constant, so that the first- and general-order TL equations are simplified as $I(T) \propto A \exp(-E_a/kT)$, where A is a constant and the TL intensity is independent of the order of kinetics. Therefore, a plot of $\ln(I)$ versus $1/T$ would yield a straight line with a slope of $-E_a/kT$, from which E_a can readily be calculated. This method can be used only in the initial region of the TL signal up to $\sim$10% of its peak maximum (I_m). However, the intensity at the beginning of each peak is very low and, especially when the glow curve is composed of several glow peaks, the obtained values of activation energies may not reflect the actual values. Therefore, in many cases, the high-level glow peaks were used, and in order to reduce the inaccuracies in E_a due to high levels of the signal used, the methods introduced by Christodoulides [23] and Singh *et al* [24] were used. The calculated values of the activation energy for each heating profile in the T_m–T_{stop} experiments are shown in figure 6. As shown in this figure, there are high up or down changes between 40°C and 70°C and this could be due to an overlapping of peaks 1–3 around this region. After the complete annihilation of peaks 1 and 2 from the glow curve when $T_{stop} > 85$°C, the high fluctuations in the calculated

activation energy are reduced and it becomes nearly constant around 1.12 ± 0.03 eV which is believed to give the activation energy of peak 3. Beyond 110°C, after a slow increase, the E_a values become constant again near 1.16 ± 0.02 eV, which gives the E_a value of peak 4 up to 135°C. At the end of the flat region of peak 4, the calculated value of E_a starts to increase and reaches another plateau region near 1.31 ± 0.04 eV up to 160°C. This region can be considered to give the value of E_a of peak 5. After the complete vanishing of peak 5, the calculated values of the activation energies were continuously increased between 1.32 and 1.44 eV up to 210°C. No flat regions were noticed around this region. At the end of this region, another plateau was again obtained near 1.44 ± 0.03 eV up to 225°C and it was deduced that this flat region gives the activation energy of peak 7 by the IR method. When this peak completely disappears, the calculated activation energy quickly increases from 1.44 to 1.73 ± 0.05 eV which gives the E_a value of peak 8. The calculated activation energies around this region (240°C $\leqslant T_{stop} \leqslant$ 320°C) were again highly unstable, with an initial increase followed by a decrease with increasing stopping temperatures. Therefore, this result again raises the question of whether this peak has general-order kinetics. According to the results of the VD method, it appears to have first-order kinetics but its peak temperature after the T_m–T_{stop} experiment increases from 308°C to 318°C and this result also indicates that it should have general-order kinetics, as peak 6. Finally, when peak 8 completely disappears from the glow curve around
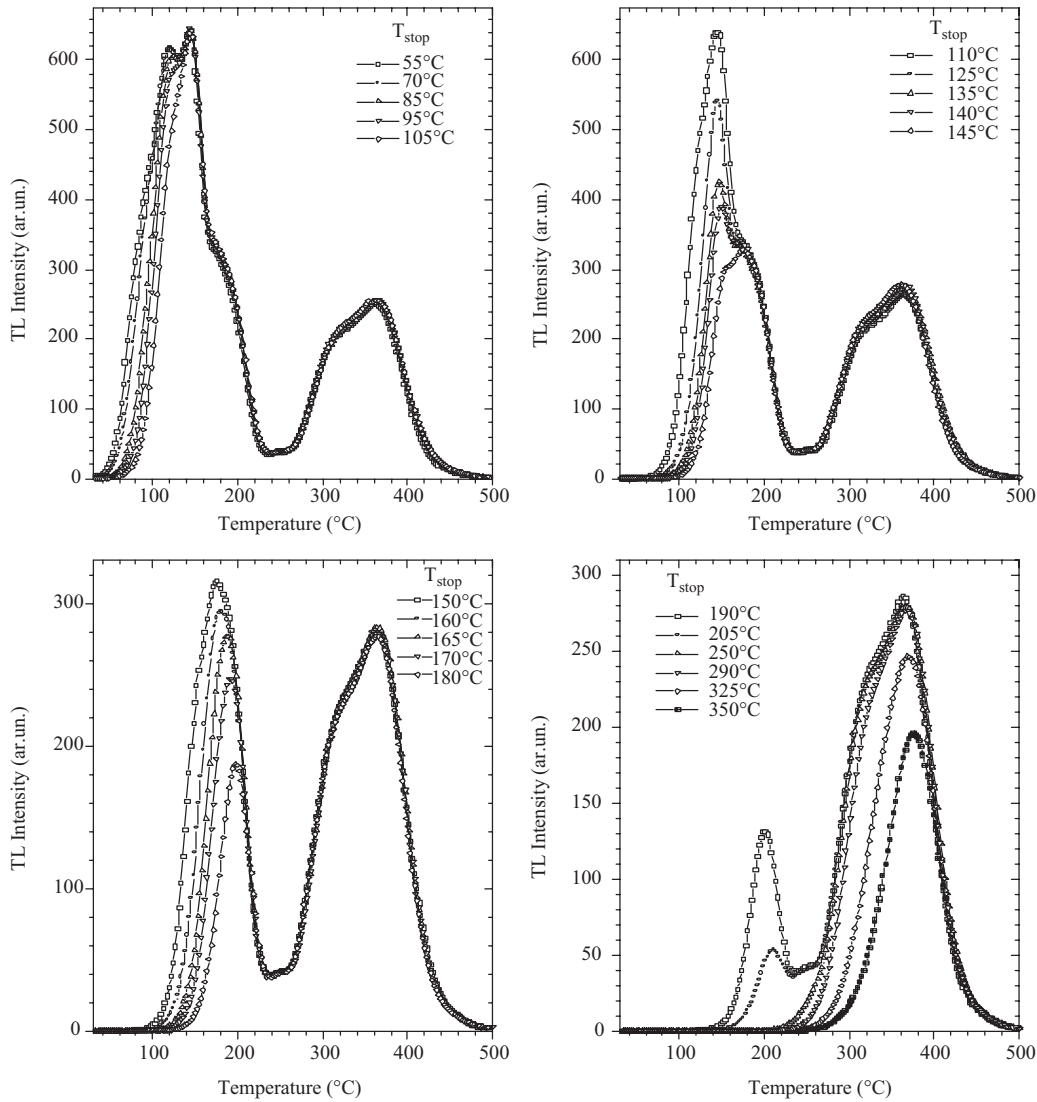
Figure 3. Some of the selected glow curves of TLD-200 after different T_{stop} temperatures at a heating rate $\beta = 1°C\,s^{-1}$. Dose levels are always adjusted to ≈ 6 Gy.

330°C, the calculated activation energies of peak 9 always decrease from 1.7 ± 0.03 to 1.5 ± 0.03 eV with increasing stopping temperatures. This behaviour is completely opposite to that of peak 6 and it means that when the number of empty traps is increased, the calculated values of activation energies decrease.

Another method which was used to determine the kinetic parameters in this work is the variable heating rate method. This is based on the shift of the temperature at the maximum (T_m) to higher temperatures when the heating rate is increased. A plot of $\ln(T_m^2/\beta)$ against $1/(T_m)$, where β is the given heating rate, should give a straight line of slope E_a/k. Extrapolating to $1/T_m = 0$, a value for $\ln(sk/E_a)$ is obtained from which s can be calculated by inserting the value of E_a/k from the slope. However, a difficulty arises in the case of highly overlapping glow peaks, since, then, the apparent maxima of the measured glow curve may not coincide with the actual peak maxima of the individual glow peaks. Indeed, when the observed peak temperature or that determined by the CGCD method are compared after the T_m–T_{stop} procedure (figure 5),

it is seen that there are some differences between them for some peaks. Therefore, the determined kinetic parameters by this method may not reflect the real values. To overcome this problem, in some cases, the thermal cleaning method was first used to clean the low temperature peaks with a minimum loss in the intensity of the main peak in question. In this respect, the maximum temperatures of peaks 3, 4, 8 and 9 are easily distinguishable from the other peaks. Thus, the activation energies of these peaks were calculated by the VHR method after determination of their peak temperatures by choosing their directly read maxima from the glow curves. The maximum temperature of peak 6 is obtained after its isolation from the other peaks by the thermal cleaning method. The activation energy of peak 5 was calculated after the determination of its peak temperature by the CGCD method. A set of measured and then normalized glow curves at different heating rates is shown in figures 7(*a*)–(*c*). Note that figure 7(*a*) was recorded without any thermal manipulation whereas figure 7(*c*) was recorded after a thermal cleaning at 170°C (dose level = 6 Gy in both figures). Figure 7(*b*) was recorded after the application of a
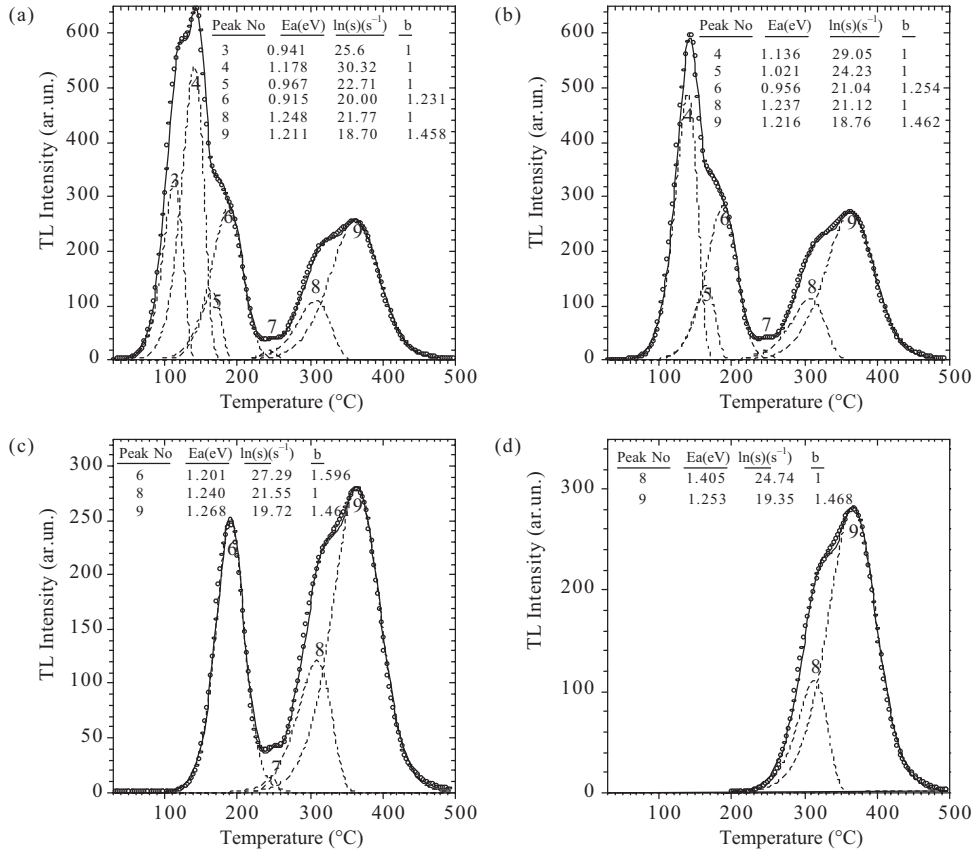
Figure 4. CGCD analysed glow curves of TLD-200 following post-irradiation annealing at different temperatures: (*a*) $T_{stop} = 90°C$; (*b*) $T_{stop} = 120°C$; (*c*) $T_{stop} = 170°C$; (*d*) $T_{stop} = 220°C$.

dose level of 3.6 Gy followed by a thermal cleaning at 90°C. Another important point that has to be taken into consideration to avoid large errors in the kinetic parameter determination by the VHR method is the temperature lag (TLA) between the heating element and the thermoluminescent sample during the TL readout in readers using contact heating. To avoid this problem, a simple method has recently been proposed by Kitis and Tuyn [25] to correct for the TLA and to determine the exact peak temperatures after different heating rates by using the equation

$$T_m^j = T_m^i - C \ln \left(\frac{\beta_i}{\beta_j} \right).$$

Here, T_m^j and T_m^i are the maximum temperatures of a glow peak with heating rates β_j and β_i, respectively, and C is a constant, which is initially evaluated by using two very low heating rates where the TLA can be considered as negligible. In order to find C, low heating rates below $1°C\,s^{-1}$ are preferable. However, the TLD reader used in this work cannot use heating rates below $1°C\,s^{-1}$, therefore, two intermediate heating rates of $1°C\,s^{-1}$ and $2°C\,s^{-1}$ were used to calculate the constant C and then the peak temperatures were corrected by TLA. The curves in figure 7(*d*) correspond to the peak maximum positions corrected for the TLA. The calculated kinetic parameters from the slopes and intercepts are given in table 1. The VHR method was not applied to peaks 1, 2 and 7 because of the large error involved in the T_m determination of these peaks at any heating rate, which is more than $\pm2°C$, owing to the impossibility of resolving it from the main peaks. Therefore, they were not

studied by the VHR method in this work. All the glow curves were also analysed by the CGCD method, but it was observed that although glow curve analysis yields consistent fit results for all heating rates, the results do not generally agree with each other. Figure 8 shows two of the analysed glow curves by the CGCD method recorded at different heating rates.

In addition to this consideration, a comparison between the data obtained by the IR, VHR and CGCD methods indicates that the results are significantly different from each other, especially the results of the CGCD method, when compared with others. A good way to check which of the results is better, is to apply the PS method to some of the isolated, or partially isolated glow peaks. In this respect, the peaks 6 and 9 are more suitable for isolation from the others. First, let us assume that the results obtained by the IR and VHR methods yield more or less correct values because they are independent of the shape of the peak. In contrast, the CGCD and the PS methods depend on the same features of the peak, namely the shape and full width at half maximum (FWHM). As a consequence, the PS method should give results similar to those obtained by the CGCD method. Therefore, the modified PS method of Chen [26] was used to evaluate the kinetic parameters of peaks 6 and 9 after their separation from the low temperature peaks. The activation energy was determined by the following equations:

$$E_\tau = [1.51 + 3(\mu_g - 0.42)]\frac{kT_m^2}{\tau}$$
$$- [1.58 + 4.2(\mu_g - 0.42)]2kT_m,$$
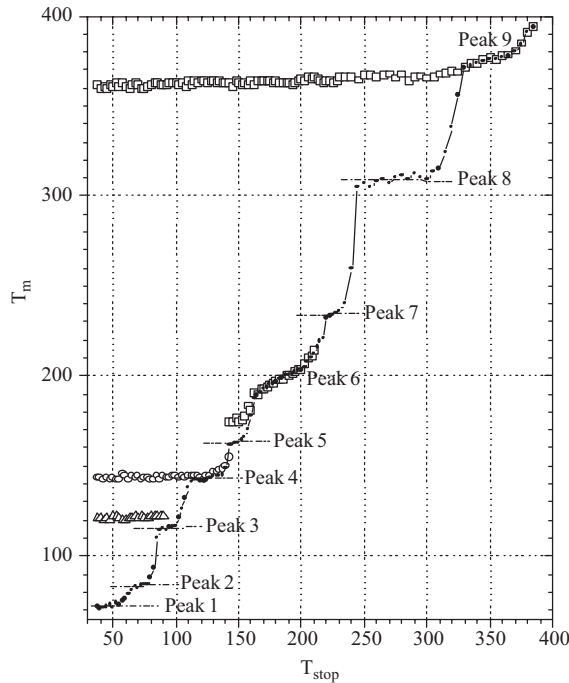
Figure 5. A T_m–T_{stop} plot for thermoluminescence from CaF$_2$: Dy (TLD-200). Solid circles represent the evaluated T_m values by CGCD method and the other symbols represent the maximum temperatures obtained from directly observed maxima during the T_m–T_{stop} procedure. The flat regions indicate the approximate position of the individual glow peaks and the slight slopes at the end of some flat region indicates highly overlapping glow peaks rather than non-first-order kinetics. Note that each experimental point is the average of four measurements.
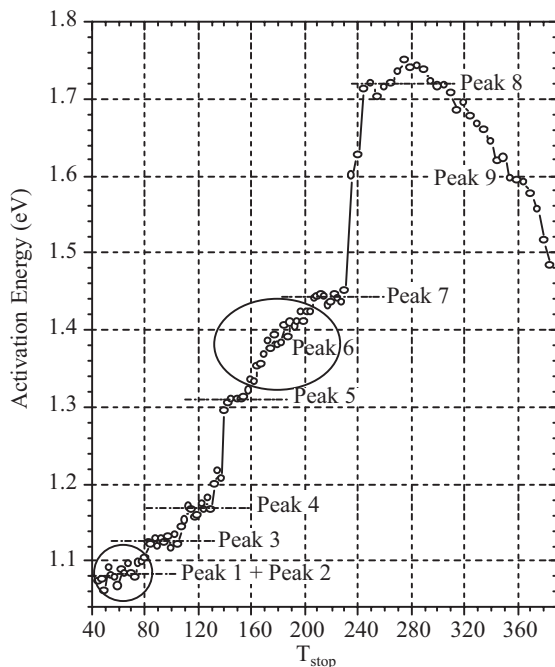
Figure 6. The activation energy (E_a) resulting from the IR method after T_m–T_{stop} procedure. Note that each experimental point is the average of at least four measurements.

$$E_\delta = [0.976 + 7.3(\mu_g - 0.42)]\frac{kT_m^2}{\delta},$$

$$E_\omega = [2.52 + 10.2(\mu_g - 0.42)]\frac{kT_m^2}{\omega} - 2kT_m,$$

where T_m is the peak temperature, $\omega = T_2 - T_1$ is the FWHM, $\delta = T_2 - T_m$ is the half width on the high-temperature side of the maximum, $\tau = T_m - T_1$ is the half width on the low-temperature side of the maximum (T_1 and T_2 are, respectively, the low and high half-maximum temperatures), and $\mu_g = \delta/\omega$ is the geometric factor (PS parameter). After determination of the activation energy and the order of kinetics, the effective frequency factor s can, in general, be estimated using the relation

$$s = \frac{\beta E_a}{kT_m^2}\exp\left(-\frac{E_a}{kT_m}\right)\left[1 + (b-1)\frac{2kT_m}{E}\right]^{b/(b-1)}.$$

In this method, the kinetic order is estimated by means of the geometric factor μ_g; the calculated μ_g values for peaks 6 and 9 are given in table 2 along with the other parameters by using the PS methods. Chen has found that μ_g changes with the order of kinetics b from 0.42 to 0.52, where these two limits correspond to first- and second-order kinetics, respectively. In this case, μ_g was found to be ≈ 0.469 for the isolated glow peak 6 after annealing at 168°C, which gives a kinetic order of about ≈ 1.45. However, as seen from figure 3, when the annealing temperature is increased, the peak temperature of peak 6 shifts to the higher temperature side and the symmetry factor of this peak increases from 0.469 to 0.485, which corresponds to an increase of the kinetic order b. This result implies that the apparent kinetic parameters of peak 6 are dependent on post-irradiation annealing temperatures; the variations of the evaluated kinetic parameters by the PS and CGCD methods are clearly shown in figure 9. On the other hand, after the complete isolation of peak 9 from peak 8, its kinetic parameters become nearly constant, where E_a is around 1.5 ± 0.025 eV, $\ln(s)$ is around 23.4 ± 0.7 s^{-1}, and b is around 1.58 ± 0.03 according to both the PS and CGCD methods. So far, this study has demonstrated that all the kinetic parameters were dependent on the different heat treatments after the irradiation.

4. Conclusion

The results in this work indicate that the glow curve of CaF$_2$: Dy (TLD-200) after β-irradiation between 0.1 and 110 Gy in the temperature range from 300 to 773 K can be best described as a superposition of nine glow peaks. Dose variation experiments indicate that seven of them, namely peaks 1–6 and 8, are of first-order kinetics, and peaks 7 and 9 are of general-order kinetics. On the other hand, the T_m–T_{stop} and CGCD methods have indicated that peak 6 also has general-order kinetics. The activation energy found with the IR, VHR and CGCD methods for peak 4 yield very close values whereas the results of IR and VHR are in agreement for peaks 3 and 5. For all other peaks, there is no agreement between the results of all the applied methods. However, when the stopping temperature increases, the results of IR, PS and CGCD are closer to each other for peaks 7–9 (see table 3).

The kinetic parameters of TLD-200 were also analysed by the CGCD method after different heating rates and it was
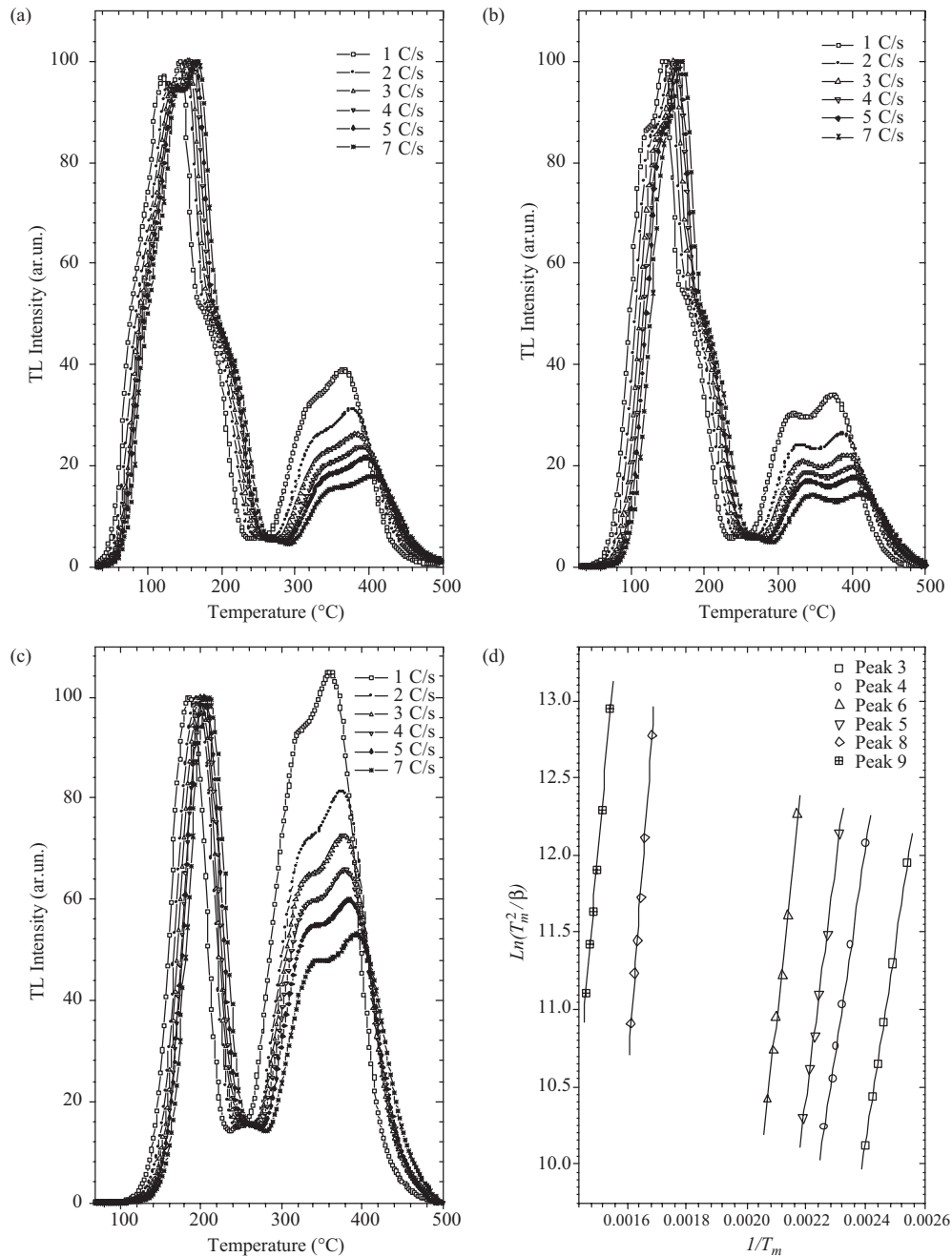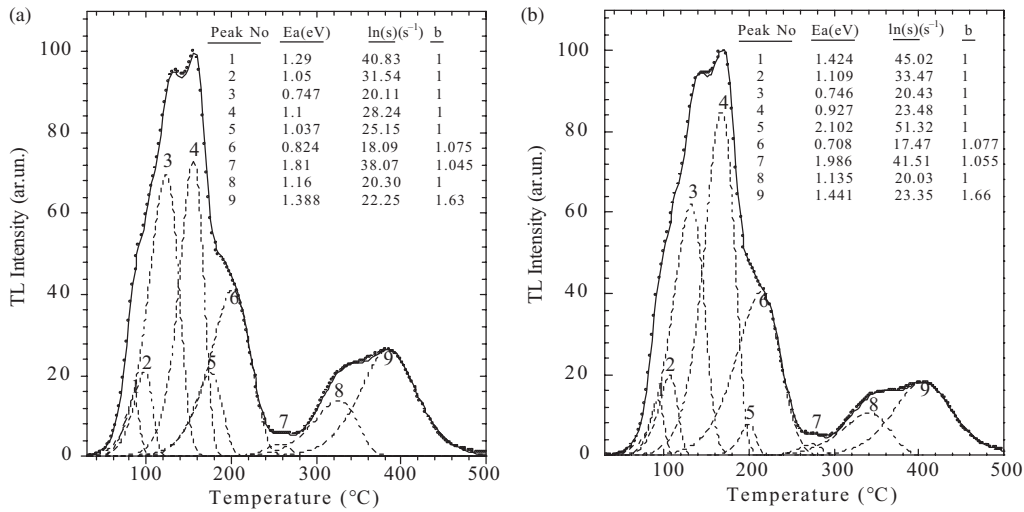
Figure 7. Some of the selected and then normalized glow curves of TLD-200 measured at various heating rates from $1\,°C\,s^{-1}$ to $7\,°C\,s^{-1}$. The glow curves in (*a*) immediately measured after β-irradiation to a dose level of 6 Gy, (*b*) measured after β-irradiation to a dose level 3.6 Gy following the application of post-irradiation annealing at $T_{stop} = 90\,°C$, (*c*) measured after β-irradiation to a dose level of 6 Gy following the application of post-irradiation annealing at $T_{stop} = 170\,°C$. (*d*) Variable heating rate plots of $\ln(T_m^2/\beta)$ against $1/T_m$. The curves were drawn after the application of TLA.

Table 1. The values of the activation energy E_a (eV) and frequency factor s (s^{-1}) of peaks 3–6, 8 and 9 of CaF$_2$: Dy (TLD-200) determined by the VHR method. At each heating rate, four samples were measured and the values shown are their averages.

	Peak 3	Peak 4	Peak 5	Peak 6	Peak 8	Peak 9
E_a (eV)	1.11 ± 0.04	1.18 ± 0.02	1.36 ± 0.05	1.55 ± 0.03	2.35 ± 0.06	1.95 ± 0.05
s (s^{-1})	$1.12 \pm 1 \times 10^9$	$9.67 \pm 1.5 \times 10^8$	$3.91 \pm 5 \times 10^{10}$	$4.67 \pm 2 \times 10^{11}$	$2.24 \pm 3 \times 10^{14}$	$3.51 \pm 4 \times 10^9$

observed that they are not constant. It is clearly seen from figure 7 that the heating rate is one of the most important experimental parameters that adversely affects the intensities of some glow peaks (i.e. peaks 5, 8 and 9) of TLD-200.

Therefore, a small change in the intensities of these peaks should affect the kinetic parameters of all glow peaks evaluated by CGCD. Another important and more interesting result was observed in the behaviour of dosimetric peaks 5. As the heating

Figure 8(a) inset table:

Peak No	Ea(eV)	ln(s)(s⁻¹)	b
1	1.29	40.83	1
2	1.05	31.54	1
3	0.747	20.11	1
4	1.1	28.24	1
5	1.037	25.15	1
6	0.824	18.09	1.075
7	1.81	38.07	1.045
8	1.16	20.30	1
9	1.388	22.25	1.63

Figure 8(b) inset table:

Peak No	Ea(eV)	ln(s)(s⁻¹)	b
1	1.424	45.02	1
2	1.109	33.47	1
3	0.746	20.43	1
4	0.927	23.48	1
5	2.102	51.32	1
6	0.708	17.47	1.077
7	1.986	41.51	1.055
8	1.135	20.03	1
9	1.441	23.35	1.66

Figure 8. Deconvoluted glow curves of $CaF_2 : Dy$ (TLD-200) obtained at a heating rate of (*a*) $3°C\,s^{-1}$ and (*b*) $7°C\,s^{-1}$ following β-irradiation to a dose level of 6 Gy.

Table 2. Evaluated kinetic parameters of glow peaks 6 and 9 of $CaF_2 : Dy$ (TLD-200) by the PS and CGCD methods after post-irradiation annealing at 168°C, 185°C, 355°C and 380°C. The given values are the averages of four different samples each, treated in the same experimental procedure.

T_{stop} (°C)	μ_g	b	E_τ (eV)	$\ln(s)$ (s⁻1)	E_δ (eV)	$\ln(s)$ (s⁻¹)	E_ω (eV)	$\ln(s)$ (s⁻¹)	b_{fit}	E_{fit} (eV)
					Peak 6					
168	0.469 ± 0.01	1.43	1.21 ± 0.04	27.45 ± 1	1.15 ± 0.04	25.85 ± 1	1.13 ± 0.04	25.5 ± 1	1.53	1.19 ± 0.03
185	0.475 ± 0.01	1.49	1.50 ± 0.04	34.35 ± 1	1.41 ± 0.04	32.24 ± 1	1.42 ± 0.04	32.46 ± 1	1.72	1.46 ± 0.03
					Peak 9					
355	0.483 ± 0.01	1.58	1.48 ± 0.02	23.27 ± 0.4	1.52 ± 0.02	24.12 ± 0.4	1.51 ± 0.02	23.85 ± 0.4	1.57	1.49 ± 0.01
380	0.480 ± 0.01	1.55	1.48 ± 0.02	22.77 ± 0.4	1.53 ± 0.02	23.7 ± 0.4	1.52 ± 0.02	23.39 ± 0.4	1.61	1.50 ± 0.01
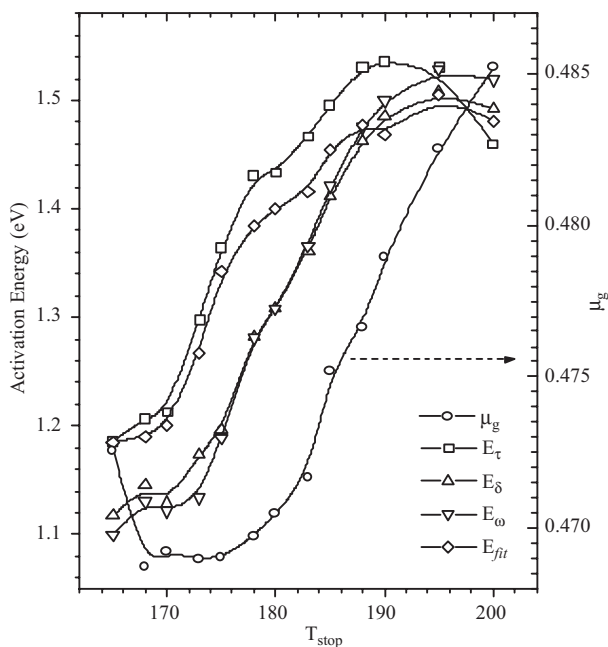
Figure 9. The activation energy E_a of peak 6 determined by PS and CGCD methods versus T_{stop} at a linear heating rate of $1°C\,s^{-1}$. The points shown are the average values of the E_a of four different measurements treated with the same experimental procedure. Lines are the fits to guide the eye.

rate increases, the intensity of this peak quickly decreases and it completely vanishes from the glow curve when the heating rate is above $15°C\,s^{-1}$. This property should be taken into consideration in dosimetric investigations.

It is also seen from the analysed glow curves that the evaluated values of the activation energies of low temperature peaks between room temperature and 250°C by the IR and CGCD methods continuously increase with increasing stopping temperatures and reach the calculated values by the VHR method. Thus, the values of kinetic parameters determined by the VHR method are seen to be more reliable than the determined values of the IR, PS and CGCD methods, since the last procedures often give rise to ambiguous results due to highly overlapping peaks in the glow curve. Additionally, the initial rise method gives values of E_a, 1–25% lower than those obtained by the VHR method. This fact has already been analysed by Wintle [27] who has shown that this discrepancy might be caused by non-radiative transitions in the luminescent centres which could lead to a computation of an apparent energy differing from the real one by an amount W. Thus, what one gets is $(E_a - W)$ instead of E_a.

This work also indicates that the post-irradiation annealing has pronounced effects on the evaluated kinetic parameters of glow peaks of $CaF_2 : Dy$. Variations in the kinetic parameters and also peak temperatures as a result of annealing are not expected to occur for alkali halide crystals, but it is

Table 3. The values of the activation energy E_a (eV) of glow peaks of CaF$_2$: Dy (TLD-200) determined by different methods.

Methods	P1	P2	P3	P4	P5	P6	P7	P8	P9
IR	1.08 ± 0.02	1.08 ± 0.02	1.12 ± 0.03	1.16 ± 0.02	1.31 ± 0.04	1.32–1.44 ± 0.03	1.44 ± 0.03	1.73 ± 0.05	1.50 ± 0.03
VHR	—	—	1.11 ± 0.04	1.18 ± 0.02	1.36 ± 0.05	1.55 ± 0.03	—	2.35 ± 0.06	1.95 ± 0.05
CGCD[a]	1.05 ± 0.07	0.9 ± 0.1	0.75 ± 0.05	1.03 ± 0.04	0.99 ± 0.06	0.83 ± 0.04	1.33 ± 0.05	1.16 ± 0.03	1.13 ± 0.02
PS	—	—	—	—	—	1.3 ± 0.2	—	—	1.5 ± 0.03

[a] The present values were obtained after irradiation of the sample up to 2.4 Gy at room temperature and then its glow curve was measured by heating at a rate of 1°C s^{-1}.

a general property of rare earth doped CaF$_2$ crystals [19]. The variations in the measured trapping parameters as a function of annealing time could have several interpretations. One possible explanation for the change of the value of kinetic parameters with post-annealing temperature is that the variation in the emission spectrum with temperature, self-absorption, thermal quenching and application of a high heating rate are some possibilities for causing distortions in the glow curve shape which in turn have an effect on the evaluated kinetic parameters of rare earth doped alkali halide crystals. Additionally, a distribution of activation energies and frequency factors may cause a variation of the estimated kinetic parameters.

Acknowledgment

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