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Thermoluminescence kinetic analysis of basaltic rocks using a generalized model for exponential distribution of activation energies

M. Zahedifar *, P. Rezaeian, S. Harooni

Physics Department, University of Kashan, P.O. Box 8731751167, Kashan, Iran

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Abstract

A new general order Thermoluminescence (TL) model for exponential distribution of activation energies has been presented. In the proposed model an effective kinetic-order has been introduced as an additional adjustable parameter. This makes it possible to take the re-trapping into account and would give a better estimate of the activation energy compared with the first order kinetics model. The proposed model has been applied to the basaltic rocks from central zone of Iran. The obtained results show that the proposed model gives a better fit to the experimental peaks compared to the first order model.

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Keywords: Thermoluminescence; Continuous trap; Exponential; General order

1. Introduction

Continuous distribution of activation energies of thermoluminescence (TL) glow peaks was presented by Randall and Wilkins [1]. They assumed both uniform and exponential distributions of activation energies and showed a time dependence of t^{-1} for phosphorescence decay. Their studies on exponential distribution of $\alpha \cdot \exp(-\alpha E)$ for trapping states resulted in phosphorescence decay low of $t^{-(\alpha kT+1)}$, where k is Boltzman's constant. Gaussian shape distribution of activation energies was investigated by Medlin [2] who proposed an isothermal decay law for TL peaks and obtained information about level width and other peak parameters. Hornyak and Franklin [3] developed a theoretical model for isothermal decay of a TL peak having Gaussian shape distribution and took into account the re-trapping during the annealing process. They also presented an analytical expression for the case of linearly increasing temperature for initial rise region of TL glow peak. Hornyak and Chen [4] assumed first-order kinetics and a continuous distribution of trapping states with uniform distribution over a finite range of ΔE and obtained an equation for TL intensity $I(T)$ for the case of constant linear heating rate. Kitis and Gomez-Ros [5] expressed the aforementioned equation in terms of the intensity and temperature of the peak maximum (which can easily be estimated from the experimental glow peak). In this study a new expression describing the TL intensity $I(T)$ with exponential shape distribution has been presented. This distribution function for activation energies is usually used for fitting of experimental glow curves [6]. Introducing the effective kinetic order in this model as an additional adjustable parameter in curve fitting procedure, makes it possible to estimate the kinetic parameters more accurately compared to the first-order model. The proposed model were applied to TL kinetic analysis of basaltic rocks from central zone of Iran. This type of rocks are usually used

* Corresponding author. Tel.: +98 361 5552935; fax: +98 361 5552930.
E-mail address: zhdfr@kashanu.ac.ir (M. Zahedifar).

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in luminescence dating [7]. Results show that the glow peaks obtained from our proposed model with high values of effective kinetic-order make a better fit to glow peaks of basaltic samples as compared to the first-order model.

2. First order model

Using first order of kinetics and a linear heating profile $T(t) = T_0 + \beta t$ (in which β, T_0 and t are heating rate, initial temperature and time of anneal, respectively), the intensity $I(T)$ of the glow peak with continuous distribution of trapping centers given by $n(E)$ is [8]:

$$I(T) = \int_{E_0}^{\infty} n(E)s \cdot \exp(-E/kT).\exp\left[-\frac{s}{\beta}\int_{T_0}^{T}\exp(-E/kT')\,dT'\right]dE, \quad (1)$$

where s is the frequency factor, E is the energy of the trap and k is the Boltzman's constant.

3. Proposed model

The equation describing the TL intensity of a glow peak with general order of kinetics and a single activation energy of E is [9]:

$$I(T) = n_0 s \cdot \exp(-E/kT)\left[\frac{s}{\beta}(b-1)\int_{T_0}^{T}\exp(-E/kT')\,dT' + 1\right]^{-b/(b-1)}, \quad (2)$$

where n_0 is the initial concentration of trapped carriers, s is the pre-exponential factor with dimension of (s^{-1}), T_0 is the initial temperature and b is the order of kinetics which takes the values between 1 (dominant recombination) and 2 (dominant retrapping). The parameter b is related to the symmetry factor of the glow peak (defined as $(T_2 - T_m)/(T_2 - T_1)$ where T_m is the maximum temperature and T_1 and T_2 the lower and higher half intensity temperatures) such that increasing the kinetic order from 1 to 2 causes the symmetry factor to increase from 0.42 to 0.52. Eq. (2) can be transformed in order to describe a general-order glow peak with an exponential shape distribution of activation energies as follows:

$$I(T) = \int_{E_0}^{\infty}\frac{sn_0}{\sigma}\exp\left(-\frac{E-E_0}{\sigma}\right) \times \exp(-E/kT)\left[\frac{s}{\beta}(b-1)\int_{T_0}^{T}\exp(-E/kT')\,dT' + 1\right]^{-b/(b-1)} dE \quad (3)$$

in which n_0 and s are defined as in Eq. (1), E_0 is the shallowest energy level in the continuous energy distribution and σ is a parameter describing the width of the distribution and b is defined as effective kinetic order. As will be discussed, the effective kinetic order which introduces the retrapping in a complicated manner, should not be related to the symmetry factor as pointed out for a glow peak with a single activation energy. The integral entered in Eq. (3) cannot be solved in an analytical form. For numerical calculation of the TL intensity, the integral $\int_{T_0}^{T}\exp(-E/kT')\,dT'$ was expressed in terms of second order exponential integral, $E_2(-E/kT)$ [10] and the remaining integral over energy were solved by the Gauss method.

4. Synthetic glow curves and comparisons

It is evident that we cannot reduce the proposed general-order model given by Eq. (3) to the first-order model when b is equal to one. Thus Eq. (3) which describes the general-order glow peaks with exponential distributions of activation energies, was fitted to the first-order model. As will be shown, lowering the value of the effective kinetic order in the proposed model causes the kinetic parameters to approach to those of the first-order model. We have produced a program for curve fitting using the Levenberg–Marquart algorithm based on non-linear least square method. For testing the goodness of fit, the figure of merit (FOM) has been used[11].

$$\mathrm{FOM} = \sum_{j_f}^{j_l}\frac{100[y_i - y(x_i)]}{A} \quad (4)$$

in which j_f and j_l are the numbers of first and the last temperature interval (ΔT) used for curve fitting, y_i is the intensity in the interval obtained from first-order model (Eq. (1)) and $y(x_i)$, the intensity expected from Eq. (3) and A, the total area of fitted glow peak between j_f and j_l. In Fig. 1 the synthetic glow peaks which have been produced using first-order model with exponential distribution function, are shown with solid lines. Open circles show the fitted general-order peaks given by Eq. (3) with $b = 1.001$. The

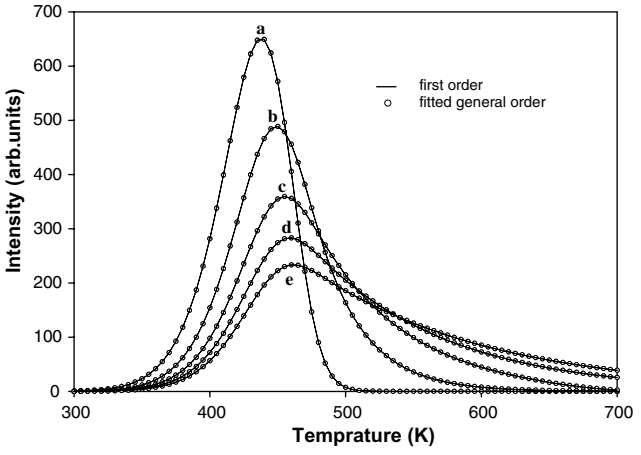

Fig. 1. Fitting of first-order model with exponential distribution of activation energies and kinetics parameters of $E_0 = 0.63$ eV, $n_0 = 8.5 \times 10^4$ cm^{-3}, $s = 4.4 \times 10^6$ s^{-1} and (a) $\sigma = 0.01$, (b) $\sigma = 0.05$, (c) $\sigma = 0.1$, (d) $\sigma = 0.15$ and (e) $\sigma = 0.2$ eV (solid lines) to the proposed model with effective kinetic order of 1.001 (open circles). As can be observed in this limiting case, our proposed model give entirely the same results compared to the first-order model.

developed program was used for curve fitting process. The obtained values for FOM were 0.0061, 0.0023, 0.0019, 0.0055, 0.0016 for glow peaks (a), (b), (c), (d) and (e), respectively. Considering the FOM values, it indicated that Eq. (3) by approaching the effective kinetic order to one, will result entirely the same glow peaks compared to the first-order model. The effect of increasing of effective kinetic order b on the peak shape has been shown in Fig. 2(a), (b) and (c). It is evident that both the effective kinetic order and the width of the energy distribution cause the descending part of the glow peaks shift to higher temperatures. For clarifying the role of effective kinetic order in proposed model compared to the kinetic order in the usual general order model, the variation of symmetry factor with parameter σ for different values of effective kinetic order b is presented in Fig. 3. It is observed that in the limiting cases of narrow energy distribution (low values of σ) the relation between effective kinetic order and symmetry factor is the same as discussed above. But increasing the parameter σ causes the symmetry factor to shift to higher values for each specified value of b. Furthermore, the results obtained from the proposed model with different values of b get close to each other for high values of σ. This shows that the results obtained from the proposed model approach the results of first order model for glow peaks bearing high values of energy width.

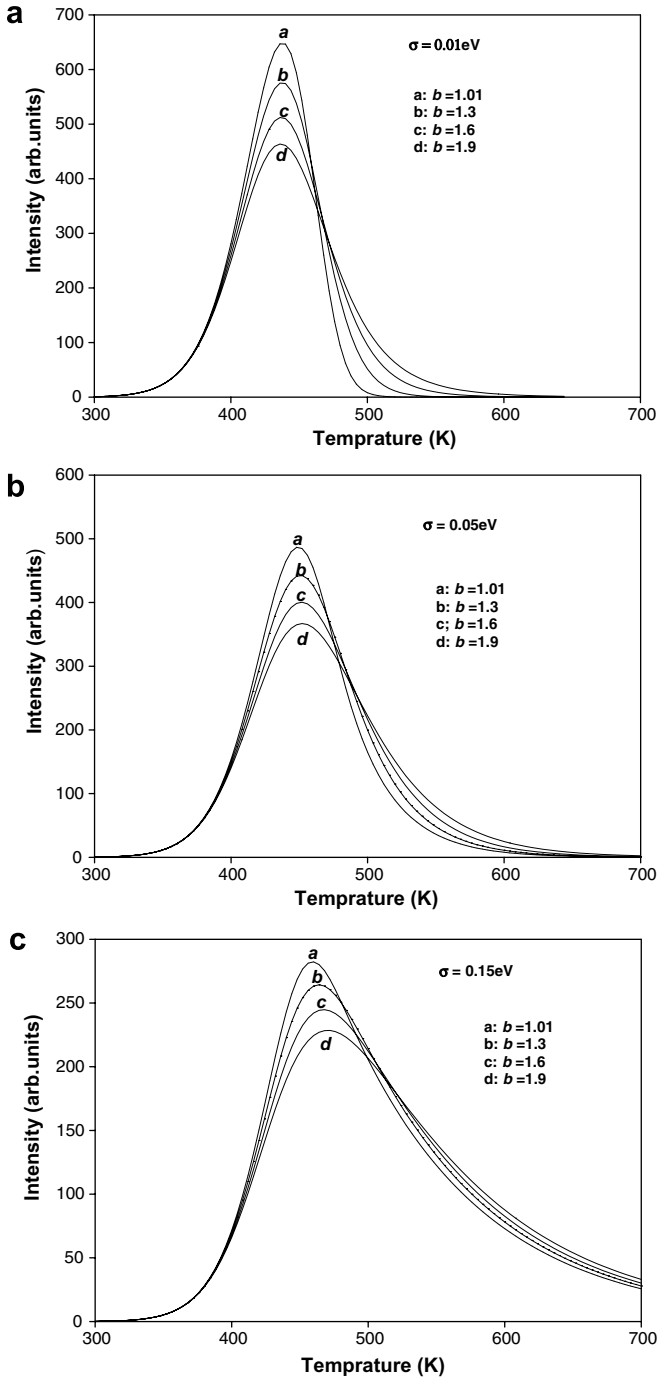

Fig. 2. Glow peaks produced using the proposed model with the same kinetic parameters as in Fig. 1 and (a) $\sigma = 0.01$ eV, (b) $\sigma = 0.05$ eV and (c) $\sigma = 0.15$ eV and different values of effective kinetic order, b. As is evident, increasing of b causes the descending part of the glow peaks to shift to higher temperatures compared to the first order model.

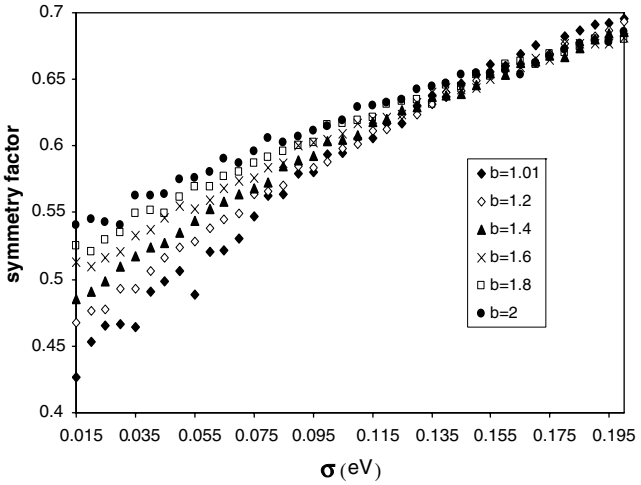

Fig. 3. Variation of symmetry factor with the width of energy distribution σ for different values of effective kinetic order b. As is evident, with approaching the parameter σ to zero (which corresponds to single activation energy) the expected relation between symmetry factor and b appears. Increasing of σ results in higher values for symmetry factor, but for higher values of σ the symmetry factor is approximately the same for different values of b.

5. Experiment

Basaltic samples from central zone of Iran were characterized by X-ray diffraction (XRD) and electron probe microanalyser (EPMA) model JXA-8800R with the acceleration voltage of 15 kV and beam current of 15 nA. The main components were detected in the microcrystalline phase of samples were plagioclase feldspar (40%), pyroxene (32%), pumplleyite (15%), chlorite (5%), amphiobole (5%) and Cr-spinel (3%) (which is similar to Cr-spinels of mid-ocean basalts). Field, petrography, mineral chemistry by EPMA and geochemistry show the signs of spilitization of pillow lavas. A pre-irradiation anneal at 500 °C for

15 min. was applied in order to remove the TL signals accumulated due to natural irradiations over the geological times. The TL signal of basaltic rocks were studied after irradiation with ^{60}Co source from which the sample received 100 Gy Gamma dose. TL measurements were carried out using TL reader model 4500 from Harshaw. Samples were milled to mesh size about 1 μm.

All the TL measurements were performed using a linear heating rate of 3 °C/s. It is known that plagioclase feldspar in volcanic rocks is the most sensitive element [6]. In our sample because of the most abundant of this mineral, we expect it to be the phosphor with main contribution in the whole TL glow curve. Fig. 4(a) shows the total glow curve of this basaltic sample. Thermal bleaching method was used in order to record the TL glow curve of high temperature peak (Fig. 4(b)). The glow curve, including both main peak and low temperature peak was obtained by subtracting the ascending part of high temperature peak from the total glow curve. By using the proposed model and our developed algorithm, the first and second peaks of basaltic sample were separated. As is shown in Fig. 4, in addition to the main broad peak (c) which matches well with the proposed exponential distribution of trapping states with effective kinetic order of 1.69, $\sigma = 0.14$ eV and $E_0 = 1.08$ eV, there is a low intensity peak (d) at about 570 K which obeys simple first-order model with single activation energy of 1.44 eV and frequency factor of 2×10^{12} s^{-1}. Fig. 5 shows the glow curves of the basaltic sample recorded after post irradiation anneal up to T_{stop} in a range 80 °C–220 °C. As can be seen, with increasing the T_{stop}, the main glow peak at about 180 °C moves continuously towards higher temperature. The peak area which indicates the population of trapping states and the maximum intensity decrease, while the high temperature part of the glow peak remains unaffected. This indicates that the broad peak of this sample obeys continuous energy distribution. Increasing the pre-

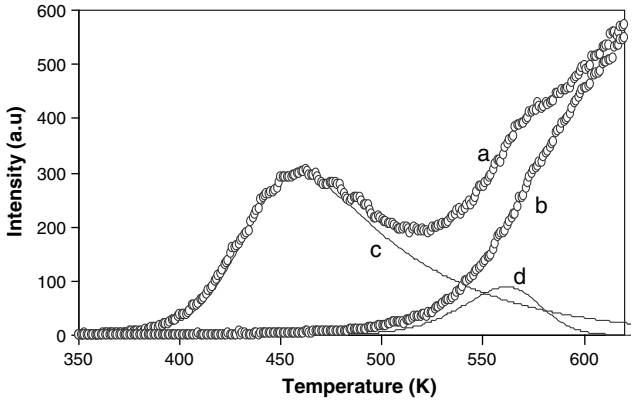

Fig. 4. Glow curve of basaltic sample after receiving of 100 Gy gamma dose. The total glow curve (a) and the initial rise region of high temperature peak (b) which has obtained after thermal bleaching of lower temperature peaks are shown with open circles. By subtracting the curves (a) and (b) the glow curve including the two lower temperature peaks were obtained. Finally with application of our developed deconvolution procedure, the main peak (c) and a low intensity peak (d) were obtained.

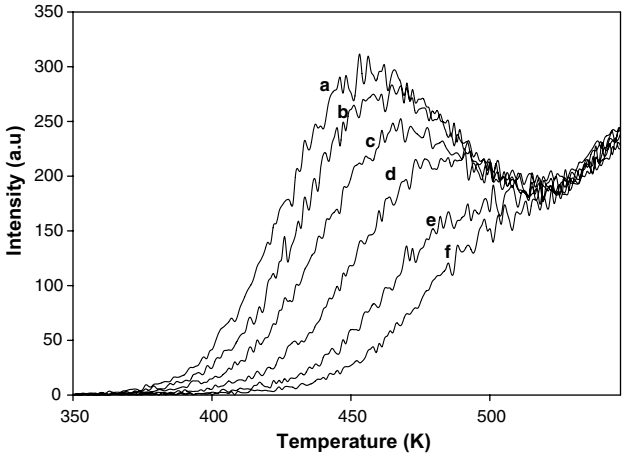

Fig. 5. The main glow peak of the basaltic rock recorded for different values of T_{stop} of 80 °C, 140 °C, 160 °C, 180 °C, 200 °C and 220 °C for peaks (a), (b), (c), (d), (e), (f), respectively. As can be seen, increasing of T_{stop} causes the whole peak to shift continuously to higher temperatures.

heat temperature (T_{stop}), causes emptying the shallower energy levels in the continuous energy distribution. Therefore cooling the phosphor followed by subsequent recording the glow curve results in shift the initial rise region of the glow peak to higher temperatures while the high temperature tail remains unchanged. Therefore we expect that the parameter E_0 (the edge of continuous energy distribution near to conduction band) to shift to higher values with increasing the T_{stop}. The same procedure of obtaining the kinetics parameters as discussed for Fig. 4 were applied for determination of kinetic parameters of the main glow peaks recorded following different values of T_{stop}. All the main glow peaks obtained followed by pre-heating up to different T_{stop} were fitted well with our proposed general-order model for continuous trap distribution. Table 1 shows that by increasing of T_{stop}, the parameter E_0, the effective kinetic order and the width of the glow peak σ shift to higher values. Also the basaltic sample obeys the proposed model with high value of effective kinetic order, such that increasing in T_{stop} causes the effective kinetic order b approach to higher limiting value of 2. These results can be explained as following: increasing the T_{stop}causes the initial rise region of the main glow peak to shift towards higher temperatures and the intensity of the peak maximum to decrease,while the declining part remains unchanged. This effect is in agreement with increasing the values of symmetry

Table 1
Kinetic parameters of the main glow peak of the basaltic sample with different values of T_{stop} using our proposed model for glow curve fitting

T_{stop}	E_0 (eV)	σ (eV)	s (s^{-1})	b
80	1.166	0.230	1.0e13	1.669
140	1.230	0.240	3.3e13	1.700
160	1.249	0.260	3.6e13	1.760
180	1.283	0.340	3.7e13	1.770
200	1.315	0.400	3.9e13	1.800
220	1.350	0.440	4.2e13	1.830

factor, effective kinetic order b and the parameter σ as were mentioned in Fig. 2(a), (b), (c) and Fig. 3.

6. Discussion

Most of the previous works on curve fitting and determining of kinetic parameters of TL glow peaks with continuous distribution of trapping states have been carried out using first order model. The basic assumption in this model is to ignore the re-trapping, i.e. after thermally excitation of charge carriers to conduction band, all of them go under radiative recombination. For a trap possessing single activation energy, re-trapping has a clear meaning, but for a continuous energy distribution, this effect is more complicated. Once the re-trapping is allowed, the free carriers can be re-trapped at any energy level in continuous distributed trapping states, but not necessarily at the same energy level at which they are thermally excited. Thus we speak of effective kinetic order for whole the energy range over which the trapping states are distributed. Although, increasing the effective kinetic order from value one shows that the re-trapping cannot be ignored, but the basis for this parameter is mainly empirical rather than physical. Consideration of effective kinetic order as an additional adjustable parameter, makes it possible to achieve lower FOM value, therefore obtaining more accurate values for trapping parameters [12]. It should be noted that the symmetry factor, μ_g which for a single activation energy changes from 0.42 (first order kinetics) to 0.52 (second-order kinetics), in the case of continuous trap distribution will lose its usual meaning as discussed in Fig. 3. As can be seen in Fig. 3, only for small values of level width, the above definition for μ_g remains valid and increasing the width of trap distribution cause broadening of high temperature half ($T_2 - T_m$) of the glow peaks. Increasing of effective kinetic order results in the same effect as can be seen in Fig. 2(a), (b) and (c). Thus for glow peaks of basaltic rocks with exponential distribution of trapping states and effective kinetic order significantly greater than one, a first order model in which re-trapping is assumed to be negligible, will result in higher level width compared to the width obtained from proposed model in which the re-trapping has been taken into account. Thus for trapping states with effective kinetic order greater than one, the more accurate kinetic parameters are those which are obtained using the proposed general order model. It is worth noting that parameter b cannot considerably affect the shape of the glow peak for higher values of level width (Fig. 3) and it is expected that by increasing the value of level width, the results obtained for kinetic parameters by using general order model approach to the results obtained from first order model.

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