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

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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

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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

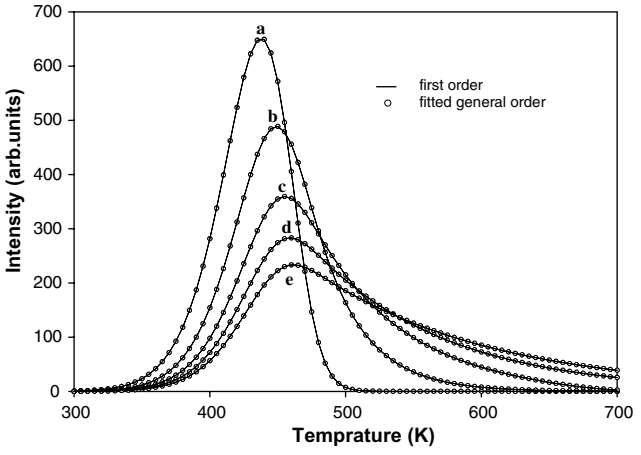

Fig. 1. Fitting of first-order model with exponential distribution of activation energies and kinetics parameters of $E_0 = 0.63$ eV, $n_0 = 8.5 \times 10^4$ cm^{-3}, $s = 4.4 \times 10^6$ s^{-1} and (a) $\sigma = 0.01$, (b) $\sigma = 0.05$, (c) $\sigma = 0.1$, (d) $\sigma = 0.15$ and (e) $\sigma = 0.2$ 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.