ANALYSIS OF THE BLUE PHOSPHORESCENCE OF X-IRRADIATED ALBITE USING A TL-LIKE PRESENTATION

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Abstract—By analysing the isothermal decay of phosphorescence at various temperatures, the activation energy and pre-exponential factor of the relevant trap, as well as the kinetic order of the process, can be evaluated. Methods of analysis have been suggested, in which $t \times I(t)$ is plotted as function of $\ln(t)$, where t is the time and I the intensity of the phosphorescence. For a single trap this is a peak-shaped curve, which resembles the corresponding thermoluminescence (TL) curve. Previous methods used some features of this peak, such as the maximum and the half intensity points. In practice, however, it might be difficult to evaluate these points accurately. An improved method is suggested, which seeks the best fit of the whole curve to the theoretical expression. This method is applied to the blue phosphorescence of X-irradiated albite.

1. INTRODUCTION

By analysing at various temperatures the phosphorescence (namely the isothermal long-time decay of luminescence) emitted by solids, the kinetic parameters of the relevant traps can be evaluated. If only one trap is involved, and if the depletion of this trap is a first order process, the intensity of the phosphorescence obeys the differential equation:

$$I = -dn/dt = s \cdot n \cdot \exp(-E/kT) \qquad (1)$$

where n (m^{-3}) is the concentration of trapped charge carriers, s (s) is called the frequency factor, E (eV) is the activation energy, k (eV K^{-1}) is the Boltzmann constant and T is the absolute temperature.

Equation (1) can be solved to give the following explicit expression for the intensity of the phosphorescence at a given temperature (T):

$$I(t) = (n_0/\tau)\exp(-t/\tau) \qquad (2)$$

where n_0 is the initial value of n and

$$\tau = s^{-1}\exp(E/kT). \qquad (3)$$

It was found experimentally that in many cases the decay of phosphorescence could be described by the "general order kinetics" equation:

$$I = -dn/dt = s'n^b\exp(-E/kT) \qquad (4)$$

where b is the kinetic order (often $1 \leqslant b \leqslant 2$) and the pre-exponential factor s' has the dimensions of m$^{3(b-1)}$ s^{-1}. This includes the familiar case of second order kinetics ($b = 2$) where the dimensions of s' are m^3 s^{-1}. If one defines a frequency factor $s = s'n_0^{b-1}$

having the units of s^{-1}, the intensity of the phosphorescence as a function of time is given by:

$$I(t) = (n_0/\tau)[1 + (b-1)(t/\tau)]^{-b/(b-1)}, \quad b \neq 1 \qquad (5)$$

where τ is defined by equation (3) above. Equation (5) is obviously not valid for $b = 1$, but it reduces to equation (2) when $b \to 1$.

In this work, we demonstrate a method for evaluating the parameters E, b and s by analysing the phosphorescence. The method is applied to the room temperature phosphorescence of natural albite.

2. THEORY

In order to find the parameters E and s, one should determine τ for several temperatures (in principle, two values of τ would suffice) and plot $\ln(\tau)$ as a function of $1/T$. It should yield a straight line. The values of E and s can than be deduced from the slope of this line and from its intersection with the y-axis, respectively.

A simple method to evaluate τ is to plot $\ln(I)$ vs the time t and find out whether it is a straight line. If this is the case, the kinetic is of first order and τ can be evaluated from the slope. Otherwise, one should plot I vs t on a log–log scale. If equation (5) is valid then for $t \gg \tau$, the curve should turn into a straight line of a slope $-b/(b-1)$. A plot of $(I/I_0)^{-(b-1)/b}$ vs t then yields a straight line of a slope $(b-1)/\tau$, from which τ can be evaluated. This method might be quite cumbersome. Moreover, it is unreliable when several traps are active in the relevant temperature range so that the phosphorescence is the sum of several individual decays. Randall and Wilkins (1945) suggested

the application of the kinetic analysis to a plot of $t \times I(t)$ as a function of $\ln(t)$. Their method was further developed by Visocekas (1978). For a single trap one gets a peak-shaped curve, and for the first order, as well as for the general order, kinetics the maximum of that peak occurs at $\ln(t) = \ln(\tau)$. The activation energy E can be computed by measuring the shift of the peak, D, between two temperatures T_1 and T_2, using the relation $E = DkT_1T_2/(T_1 - T_2)$.

Chen and Kristianpoller (1986) showed that by using the two half-intensity points, in addition to the maximum point, the parameter b can be evaluated. In this work an improved method is presented, which seeks the best fit of the whole curve to the theoretical expression.

2.1. First order kinetics

Let us define $x = \ln(t)$ and $t = \exp(x)$. Equation (2) can be re-written as:

$$I = I_0 \exp[-\exp(x)/\tau] \qquad (6)$$

where $I_0 = n_0/\tau$. Multiplying both sides by t, and using a new variable $y = It$ one gets:

$$y = I_0 \exp(x)\exp[-\exp(x)/\tau]. \qquad (7)$$

For low values of x, $\exp[-\exp(x)/\tau]$ is nearly constant and y increases as $\exp(x)$. At higher values of x the expression $\exp[-\exp(x)/\tau]$, which is a decreasing function of x, dominates. Thus y goes to zero. The maximum of the peak-shaped curve can be found by solving the equation $dy/dx = 0$. The result is:

$$x_m = \ln(\tau). \qquad (8)$$

2.2. General order kinetics

Defining as above $x = \ln(t)$ and $y = It$, equation (5) reduces to

$$y = I_0 \exp(x)[1 + (b-1)(\exp\{x\}/\tau)]^{-b/(b-1)},$$
$$b \neq 1 \qquad (9)$$

which is a peak-shaped curve as well. By setting $dy/dx = 0$ the maximum condition is found again to be $x_m = \ln(\tau)$.

2.3. Methods of kinetic analysis

Since $\tau = \exp(x_m)$ regardless of the order of the kinetics, one can evaluate $\tau(T)$ directly from the peak-shaped curve of $I \times t$ vs $\ln(t)$. Thus, by recording the phosphorescence at two temperatures or more, E and s can be computed from the maxima of the peaks, utilizing the relation.

$$x_m(T) = E/kT - \ln(s). \qquad (10)$$

As for the kinetic order, b, Chen and Kristianpoller (1986) showed that it can be deduced by using the half intensity points x_1 and x_2 which are defined by: $y(x_1) = y(x_2) = y(x_m)/2$ and $x_1 < x_m < x_2$. It was

found that there is a monotonic one-to-one correspondence between b and the shape parameter μ, which is defined by $\mu = (x_2 - x_m)/(x_2 - x_1)$. For example, if $b = 1$, then $\mu \approx 0.4$, and for $b = 2$, $\mu \approx 0.5$. Thus, in principle, by measuring three points of the peak, and the maximum point of the same peak measured at a different heating rate, the three kinetic parameters E, s and b can be evaluated.

In practice, however, it might be difficult to evaluate the three points accurately. Since the x-axis is $\ln(t)$, a long time may be needed in order to reach x_2, or even x_m, resulting in a poor signal-to-noise ratio. For example, let us take the typical values $E = 0.8$ eV, $s = 10^{10}$ s^{-1} and $b = 2$. At room temperature ($T = 300$ K), $t_m = \tau = 2754$ s and $t_2 = \exp(x_2) = 16{,}051$ s. Thus one has to wait 45 min for x_m and about 4.5 h for x_2. The light intensities would be 0.25 and 0.02 of I_0, respectively. At 350 K one has to wait only 33 s and 3.2 min for reaching x_m and x_2 respectively, but the decay is faster and the intensities at these times would be 0.25 and 0.015 of I_0.

2.4. The best fit computer program

A more reliable method is to use many points along the experimental curve and to look for the best fit of the data to equations (7) and (9). The best fit program which we devised for this purpose is a least square optimization procedure based on the following steps.

(1) Check the intensity of the phosphorescence, $I(t)$, at n points of time $t[1]$, $t[2]$, ... $t[n]$.

(2) For $i = 1, \ldots n$ evaluate $x[i] = \ln(t[i])$ and $y_{exp}[i] = I(t[i]) \times t[i]$.

(3) Find values of x_m, y_m and b which minimize the function:

$$F(x_m, y_m, b) = \sum_{i=1}^{n} \left(y_{exp}[i] - y_{th}[i] \right)^2 \qquad (11)$$

where $y_{th}[i]$ is given by equation (7) or (8) with the current values of x_m, y_m and b (y_m is the value of y for x_m).

For the minimization, an iterative computer program was written using the PC turbo-pascal language, which starts from initial values of x_m, y_m and b and proceeds along the following steps.

(1) Calculate $F(x_m, y_m, b)$.

(2) Define $x'_m = x_m - \Delta x_m$, $y'_m = y_m - \Delta y_m$ and $b' = b - \Delta b$ (the procedure for calculating Δx_m, Δy_m and Δb is described below).

(3) If $F(x'_m, y'_m, b') < F(x_m, y_m, b)$ define $x_m = x'_m$, $y_m = y'_m$ and $b = b'$ and go to (1). Otherwise, go to (4).

(4) Define $x'_m = x_m - 0.5\Delta x'_m$, $y'_m = y_m - 0.5\Delta y_m$, $b' = b - 0.5\Delta b$ and go to (3).

The program stops when $[(\partial F/\partial x_m)^2 + (\partial F/\partial y_m)^2 + (\partial F/\partial b)^2]^{1/2}$, namely the size of the gradient, is sufficiently small.

We first tried to evaluate Δx_m, Δy_m and Δb by a revised steepest-descent technique (Cohen, 1981; Chen, 1984) in which

$$\Delta x_m = A\frac{\partial F/\partial x_m}{\Delta}, \quad \Delta y_m = A\frac{\partial F/\partial y_m}{\Delta}, \quad \Delta b = A\frac{\partial F/\partial b}{\Delta} \quad (12)$$

where $\Delta = \partial^2 F/\partial x_m^2 + \partial^2 F/\partial y_m^2 + \partial^2 F/\partial b^2$ and $A \approx 3$. The derivatives of the first and second order were calculated numerically. By applying the method to "synthetic" peaks, it was found that the convergence in y_m is especially slow, to an extent which makes the method impractical. The reason is that $\partial F/\partial y_m$ is much smaller than the other two derivatives, making Δy_m exceptionally small. As a second alternative we tried the following definition:

$$\Delta x_m = B\frac{\partial F/\partial x_m}{\partial^2 F/\partial x_m^2}, \quad \Delta y_m = B\frac{\partial F/\partial y_m}{\partial^2 F/\partial y_m^2},$$

$$\Delta b = B\frac{\partial F/\partial b}{\partial^2 F/\partial b^2}. \quad (13)$$

For F which is a simple quadratic function of x_m, y_m and b, the convergence to the global minimum is achieved in one step for $B = 1$. In our case it was found that for $B = 0.6$, F usually converges quite rapidly to the minimum, as long as the initial values of the parameters are not too far from the optimal values. The best results were achieved by combining the two methods, namely, using equation (13) as long as $F(x'_m, y'_m, b') < F(x_m, y_m, b)$ but resorting to equation (12) (with $A = 2.6$) when the direction of the inequality is reversed. For synthetic peaks, the minimum was achieved after about 30–50 iterations. The final size of the gradient (for y_m normalized to 10) was less than 0.001, but even for gradient sizes of about 1, the values of the parameters differed from the "true" values only by the fifth digit.

3. EXPERIMENTAL

Natural single crystals of the feldspar albite $(NaAlSi_3O_8)$ were used for our measurements. The impurity content of the samples was given elsewhere (Kirsh and Townsend, 1988). The samples were kept in the vacuum and irradiated for 30 min by a tungsten target X-ray tube, which was operated at 30 kVp, 15 mA. The emitted light passed through a Bausch and Lomb grating monochromator followed by an EMI 9659QA photomultiplier. The monochromator was set at a constant wavelength ($\lambda = 450$ nm) and the bandpass was 30 nm, in order to record the intense blue band of albite which was found to extend over the range 400–500 nm. The integrated signal was recorded every 3 s at the beginning of the decay and every 15 s later, and was stored by a microcomputer. In order to improve the signal-to-noise ratio, a further averaging was performed in the course of the data analysis, over periods of 0.5 min, up to 10 min before the end of the measurement. The average noise was deducted from each reading.
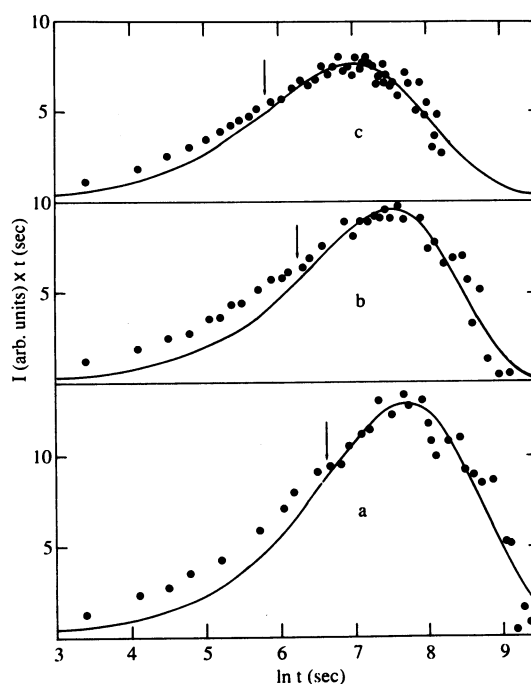

FIG. 1. The best fit of the experimental data to the theoretical equation. The dots represent $I \times t$ vs $\ln(t)$, where t is time and I is the intensity of phosphorescence at $19 \pm 0.5°C$ (a); $23 \pm 0.5°C$ (b); and $28 \pm 0.5°C$ (c). The lines depict equation (9) with the parameters which appear in Table 1. Only points beyond the arrow were taken into account.

4. RESULTS AND DISCUSSION

In Fig. 1, the best fit of the experimental data to the theoretical equations is shown for three temperatures. The dots represent $I \times t$ vs $\ln(t)$, where I is the measured intensity of light and t is the time. The line depicts equation (9) with the parameters which appear in Table 1. Figure 1(a) describes the decay of the phosphorescence at $19 \pm 0.5°C$, for 3.2 h. Figure 1(b) represents the same for the decay at $23 \pm 0.5°C$ for 2.5 h, while Fig. 1(c) covers 1 h of decay at $28 \pm 0.5°C$. In all of these cases, the graph of $\ln(I)$ vs t showed a nearly linear descent after 5–8 min, and a steeper slope for shorter times. Only points beyond the knee-points (indicated by arrows in Fig. 1) were used for the best fit program.

Due to the poor signal-to-noise ratio, which is evidenced by the scattering of the points around the theoretical curve, any attempt to obtain x_m and the half-intensity points without using the best fit program would involve large boundaries of errors.

In Fig. 2 the parameter $\ln \tau (= x_m)$ for each of the three measurements is described against $1000/T$, with

Table 1. The parameters evaluated by the best fit program for the three peaks

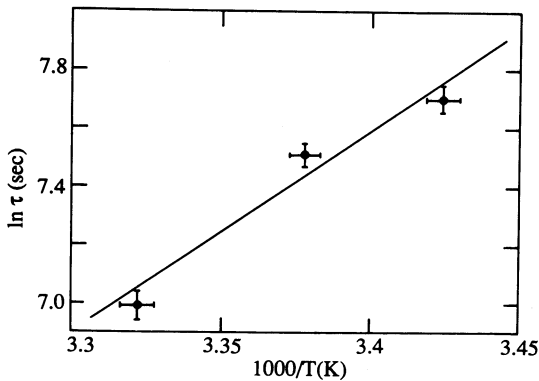| Peak	x_m	y_m	b	T (°C)
a	7.696	12.908	1.167	19
b	7.507	9.643	1.037	23
c	6.987	7.573	1.254	28

FIG. 2. $\ln(\tau)$ $(=x_m)$ against $1000/T$ for the three measurements described in Fig. 1. The error boundaries stem from the reading of the temperature $(\pm 0.5°C)$ and from the uncertainty in the value of x_m. The resulting straight line is described by $\tau = s^{-1}\exp(E/kT)$ with $E = 0.597$ eV and $s = 8.5 \times 10^6\,s^{-1}$.

the error boundaries which stem from the reading of the temperature $(\pm 0.5°C)$ and from the uncertainty in the value of x_m. The resulting straight line corresponds to the following E and s values:

$$E = 0.597(\pm 0.006)\,\text{eV}, s = 8.5 \times 10^6\,s^{-1}.$$

Due to the exponential dependence of s on x_m [equation (10)], s is accurate only within an order of magnitude. In a previous work (Kirsh et al., 1987), the TL of the same sample was analysed, and for the first TL peak the following kinetic parameters were found: $E = 0.60$ eV, $s = 1.1 \times 10^8$ and $b = 1$. The uncertainty in E was estimated to be $\pm 5\%$, while s was accurate up to one order of magnitude. Comparing the results of the kinetic analysis of the TL with phosphorescence, one can see that the E values are in very good agreement, while the s values are within the limits of error.

On the face of it, the analysis of the phosphorescence seems to yield more accurate results than the kinetic analysis of TL. It has to be taken into account,

however, that our analysis here was based on the assumption that there was no overlapping. The fact that the low temperature part of the peak involves a separate decay process is not obvious in that presentation and is shown clearly only on a $\ln(I)$ vs $1/T$ curve. In non-first order cases, it may be more difficult to distinguish between overlapping peaks, especially when the noise is high.

To conclude, we demonstrated the efficiency of the program for synthetic peaks as well as 'pure' experimental ones. However, since the results may be distorted by overlapping, it is recommended that this method be used in addition to the analysis of TL, not independently.

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