

# APPLICATION OF TWO KINETIC METHODS TO EVALUATE THE TRAP ENERGY OF LITHIUM FLUORIDE + SODIUM FLUORIDE THERMOLUMINESCENT PHOSPHOR

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## Abstract

A mixture of equal quantities of powdered LiF and NaF was doped with 0.2% each of Ti, Mg and Mn and heated to obtain a LiF+NaF phosphor. After grinding and sieving, the thermoluminescent phosphor was used to obtain the thermoluminescence characteristics such as the glow curve; the dose-response curve, sensitivity, reproducibility and linearity were all established. The main goal was to introduce two new methods for the calculation of trap energy: the single-peak-differential and single-peak-integration methods, both modifications of the basic method of Randall-Wilkins. The plots used to calculate the trap energy were  $\ln[(d\alpha/dT)/(1-\alpha)]$  vs.  $1/T$  and  $\ln[\ln(1-\alpha)/(T_0-T)]$  vs.  $1/T$ , respectively. These linear plots with slopes of  $(E/k)$  gave trap energies of  $E=0.547$  eV and  $E=0.551$  eV, respectively.

**Keywords:** LiF, NaF, thermoluminescence, trap energy

## Introduction

Many attempts have been made to manufacture suitable thermoluminescent materials based on LiF by using different doping elements such as Eu, Mg, Ti, Al, Mn, etc. [1-5]. The emission spectrum of LiF TLD-100 was detected by Fairchild *et al.* [6].

Thermoluminescence kinetics was first investigated by Randall and Wilkins in 1945 [7]. Thermoluminescence phenomena with very few exceptions are found to obey either first or second-order kinetics. It is essential that the glow curve is used to determine the kinetics, since the area under the curve is considered to be proportional to the number of thermally emitted electrons. An exception is the TL data from a photomultiplier tube which fulfils the condition that for all wavelengths the phototube current is same. The kinetic evaluation using the glow curve is unsatisfactory in the following cases: (i) when the luminescence spectrum changes with temperature, (ii) when the emission occurs in a region where the phototube sensitivity changes rapidly with wavelength, and (iii) when the emission contains more than one component and the glow peaks involve contributions for an undetermined number of emission bands.

The kinetic parameters of LiF TLD-100 have been extensively investigated. Because of the complication of the glow curve, only four prominent peaks were concerned in previous works [8–12]. Fairchild *et al.* [13] used all the peaks of LiF TLD-100 to calculate trap energies and frequency factors. They investigated photon energies in combination with the glow curve peak, and obtained emitted light intensity vs. temperature curves for these photon energies. In the present work, since the dose-response curve is linear, it is possible to use all of the glow curve peaks in a kinetic evaluation. The trap energy of the first and main peak of LiF+NaF crystal is determined by two new methods, assuming first-order kinetics. These, named the single-peak-differential and single-peak-integration methods, are discussed below.

## Experimental

### *Instrumentation*

In the present work, a combination of a Harshaw 2001-A thermoluminescence detector and a 2001-B auto-integrating picoammeter was used. The instrument measures constant or varying low-level current over a wide dynamic range where the absolute value and the time integral are of importance.

### *Sample preparation*

NaF and LiF samples from BDK were mixed in equal proportions. The dopants Eu (as  $\text{Eu}_2\text{O}_3$ ), Ti and Mn (as  $\text{MnCl}_4$ ) were introduced in equal amounts of 0.2%. The doped mixture was placed a furnace at  $600^\circ\text{C}$  and after 10 min the furnace temperature was adjusted to  $900^\circ\text{C}$ . The material was held at that temperature for about half an hour. The temperature was then lowered to  $650^\circ\text{C}$ . After 30 min at  $650^\circ\text{C}$ , the sample was cooled in air to room temperature. The phosphor was then ground, sieved (140–180 mesh) and packed into pyrex capillary tubes (5 mm in length, 1 mm in diameter).

### *Glow and dose-response curves*

The glow curve of this phosphor is shown in Fig. 1. The  $x$  axis denotes the absolute temperature, and the  $y$  axis the amplified total output current of the detector in arbitrary units. The dose-response curve of this sample is given in Fig. 2 in the dose range 0–100 R of the Co-60 gamma radiation source. For all measurements, the same material was used. For every value of the exposure dose, the average of three measurements was used to obtain the dose-response curve. Thus, reproducibility and linearity are achieved.

It is essential that further investigations be carried out on the phosphor characteristics. However, the goal of this work was to introduce two different kinetic methods to calculate the trap energy value of the phosphor.

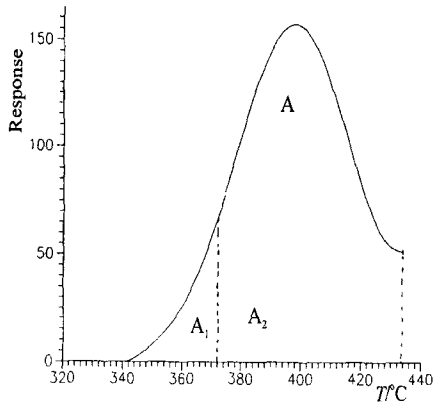


Fig. 1 Glow curve of LiF+NaF phosphor

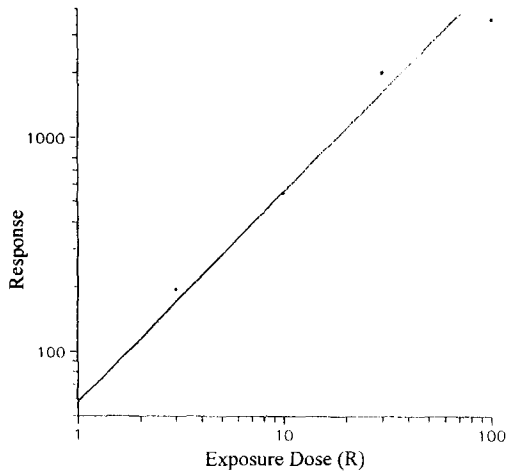


Fig. 2 Dose-response curve of LiF+NaF phosphor

### *Kinetic methods*

#### METHOD 1. Single-peak-differential

Since the method is applied to the single peak of the thermoluminescence glow curve, it is named the single-peak-differential method.

From the Randall-Wilkins [7] thermoluminescence model, light intensity was given for the isothermal experiments as

$$I = C \frac{dn}{dt} \quad (1)$$

where  $n$  is the number of occupied traps at time  $t$  and  $C$  is the proportionality constant. Integration of the equation yields

$$\int_0^n I dt = \int_{n_0}^n C dn \quad (2)$$

where  $n_0$  is the initial number of occupied traps at time zero. The left side of Eq. (2) is the area under the glow curve over the time interval of  $0-t$ . Hence,

$$A_1 = C(n_0 - n) = Cn_0 - Cn = A - A_2 \quad (3)$$

where  $A$  is the total area under the glow curve, and  $A_1$  and  $A_2$  are such that  $A=A_1+A_2$  (Fig. 1). As a result, the area under the glow curve is proportional to the occupied trap number at that moment. From Eq. (3),  $A_2=Cn$  can be derived. Differentiation of the equation leads to

$$\frac{dA_2}{dt} = C \frac{dn}{dt} \quad (4)$$

The equation

$$-\frac{dn}{dt} = pn \quad (5)$$

was given by the Randall-Wilkins model, where  $n$  is the occupied trap number, and  $p$  is the probability. Combination of the Eqs (3) and (4) yields

$$-\frac{dA_2}{dt} = A_2 p \quad (6)$$

In Eq. (3),  $A=A_1+A_2$  is given.  $A_1$  and  $A_2$  are variables and  $A$  is a constant. Differentiating this equation yields.

$$-\frac{dA_2}{dt} = \frac{dA_1}{dt} \quad (7)$$

For a linear heating rate (i.e.  $b=dT/dt$ ) this equation can be modified to

$$b \frac{dA_1}{dT} = (A - A_1)p \quad (8)$$

Division by  $A$  and defining  $A_1/A = \alpha$  results in the equation

$$\frac{b}{A} \frac{dA_1}{dT} = (1 - \alpha)p \quad (9)$$

$dA_1/dT$  can be replaced by  $d\alpha/dT = (1/A) (dA_1/dT)$ . Hence, the equation

$$\frac{d\alpha}{dT} \frac{1}{(1-\alpha)} = \frac{p}{b} \quad (10)$$

can be obtained. Probability  $p$  was given by Randall-Wilkins as

$$p = S_{\text{exp}} \left( -\frac{E}{kT} \right) \quad (11)$$

where  $k$  is the Boltzman constant,  $S$  is the frequency factor,  $E$  is the trap energy, and  $T$  is the absolute temperature of the sample. Therefore, on taking logarithms and combining Eqs (10) and (11), we obtain

$$\ln \left[ \frac{d\alpha}{dT} \frac{1}{(1-\alpha)} \right] = -\frac{E}{kT} + \ln S - \ln b \quad (12)$$

A plot of  $\ln[(d\alpha/dT) 1/(1-\alpha)]$  vs.  $1/T$  yields a straight line with slope  $-E/k$  and y intercept  $(\ln S - \ln b)$ , from which the frequency factor can be calculated when the heating rate is known.

### Calculation of trap energy

After the glow curve has been obtained, the total area and partial areas can be obtained by using a computer program or any of the conventional methods, and the  $\alpha$  values are easily found by dividing the partial area by the total area. The glow curve of the sample LiF+NaF is shown in Fig. 1, the  $\alpha$  values are listed in Table 1 and the  $\alpha$  vs.  $T$  curve is shown in Fig. 3. The  $\alpha$  vs.  $T$  plot is then fitted to a

**Table 1** Data from (LiF + NaF) thermoluminescent phosphor

$T$	$\alpha$	$\ln \left[ \frac{d\alpha}{dT} \frac{1}{(1-\alpha)} \right]$	$\ln \left[ \frac{\ln(1-\alpha)}{(T_0-T)} \right]$	$(1/T) \times 10^5$
379.39	0.18148	-4.08210	-5.25465	264
385.78	0.28002	-3.71303	-4.91377	259
392.17	0.39951	-3.41561	-4.60750	255
398.56	0.53038	-3.14180	-4.33190	251
404.95	0.65901	-2.87330	-4.08416	247
411.34	0.77287	-2.61311	-3.85908	243
417.73	0.86354	-2.39511	-3.65064	239
424.12	0.92919	-2.36840	-3.44597	236

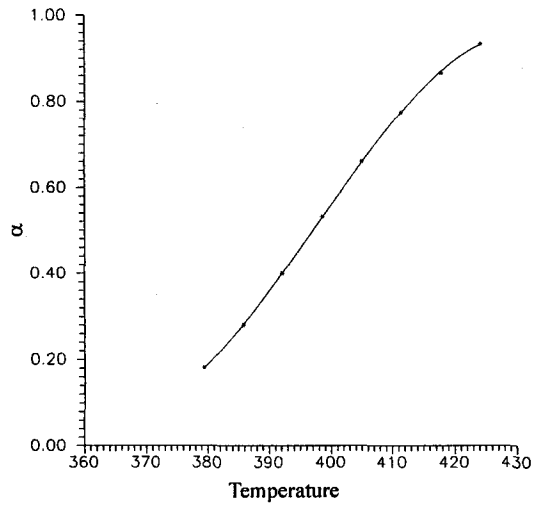


Fig. 3  $\alpha$ - $T$  curve of LiF+NaF phosphor

polynomial. The best fit curve in the interval 379.39–424.12 K is obtained as the third-order equation

$$\alpha(T) = 408.39 - 3.1171T + 0.00788808T^2 - 6.61071 \times 10^{-6}T^3$$

which is the basis of the derivative equation from which the  $d\alpha/dT$  values can be obtained. These are listed together with the calculated values of  $\ln[(d\alpha/dT)/(1-\alpha)]$  in Table 1.

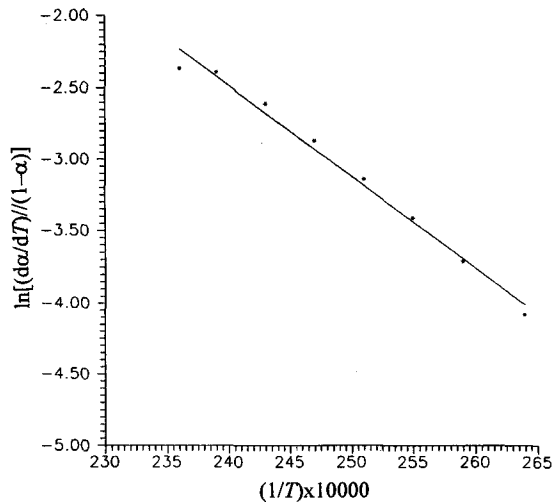


Fig. 4  $\ln[\ln(d\alpha/dT)/(1-\alpha)]$  vs.  $1/T$  plot of LiF+NaF phosphor

The plot of  $\ln[(d\alpha/dT)(1/1-\alpha)]$  vs.  $1/T$  is shown in Fig. 4. The linear function  $y=-6358.26 (1/T)+12.7727$  is obtained from the best fit program. The slope of this line should be equal to  $-E/k$  ( $k=8.61 \times 10^{-5}$  eV/K mol). The trap energy value is obtained *via* the linear fitting program. The slope yields a trap energy of  $E=0.551$  eV.

#### METHOD 2. Single-peak-integration

The luminescence intensity,  $I$ , is known to be proportional to the speed of escape of the electrons from the traps, and the escaping speed is also proportional to both the number of electrons trapped and the probability of escape of electrons from the traps.  $-dn/dt=np$  is valid. For monoenergetic traps, the probability is given by Eq. (11). Thus

$$\int_0^n \frac{dn}{n} = \int_0^t p dt \quad (13)$$

$$\ln \frac{n}{n_0} = p(0 - t)$$

Since  $A_2 = Cn$  and  $A = Cn_0$ , then

$$\frac{A_2}{A} = p(-t) \quad (14)$$

If  $\alpha = A_1/A$  is defined and  $A_2=A-A_1$  (from Fig. 1) is used, we obtain

$$\ln(1 - \alpha) = p(-t) \quad (15)$$

Where a linear heating rate is used,  $T=T_0+bt$  and  $dT=bdT$ , and as a result  $t=T-T_0$  can be substituted into Eq. (15):

$$\ln(1 - \alpha) = \frac{p}{b}(T_0 - T) \quad (16)$$

If it is assumed that the reaction is isothermal in a differential temperature or time interval, it is possible to find a  $p$  value for every temperature and corresponding value of  $\alpha$ . Accordingly,  $p$  values for different temperatures are available. If the probability  $p$  (from Eq. (5)) is substituted into Eq. (16) and logarithms are taken, we get

$$\ln[\ln(1 - \alpha)] = -\frac{E}{kT} + \ln S - \ln b + \ln(T_0 - T) \quad (17)$$

$$\ln \left[ \frac{\ln(1-\alpha)}{(T_0-T)} \right] = -\frac{k}{kT} + \ln \frac{S}{b}$$

When the plot of  $\ln[\ln(1-\alpha)/(T_0-t)]$  vs.  $1/T$  is used from the linear fitting program, the trap energy of the peak can be calculated from the slope of the plot, which is equal to  $-E/k$ . Frequency factor  $S$  can be calculated from the intercept.

### The energy calculation

The plot of  $\ln[\ln(1-\alpha)/(T_0-T)]$  vs.  $1/T$  is shown in Fig. 5. The linear function  $y=-6397.78(1/T)+11.683$  is obtained from the best fit program. The slope yields a trap energy of  $E=0.551$  eV.

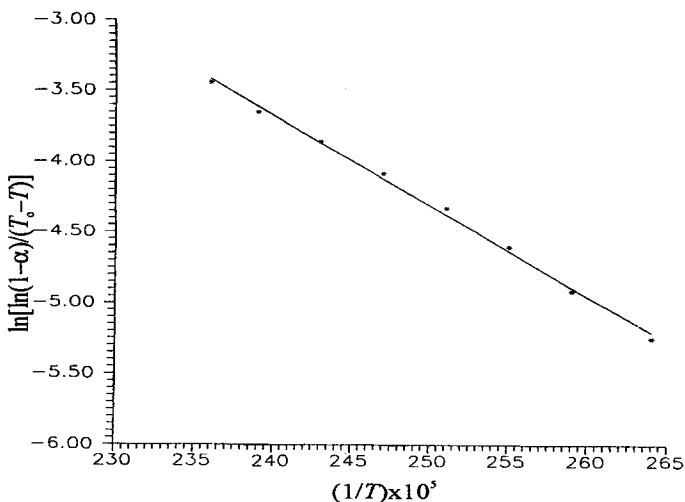


Fig. 5  $\ln[\ln(1-\alpha)/(T_0-T)]$  vs.  $1/T$  plot of LiF+NaF phosphor

## Discussion

The LiF+NaF (0.2% Ti, 0.2% Mg and 0.2% Mn) phosphor displays fairly good sensitivity, reproducibility and linearity; the only disadvantage is that the main peak is located at 125°C, which may cause a deposited dose loss at high room temperature.

The kinetic methods introduced here are applied to the same data to show that the two separate methods can be applied freely to any single glow curve peak without hesitation. The trap energy values obtained with the first and second methods are  $E=0.547$  eV and  $E=0.551$  eV, respectively. These methods basically depend on the Randall-Wilkins theory, in which re-trapping was not recognized. The trap energy values obtained with the two methods are extremely close to



each other. This shows that both methods give reproducible results. These methods are very useful if the peaks of the glow curve are resolved or the glow curve consists of a single peak, since the methods use the total peak. If the adjacent peaks are not resolved, the total area calculation may not be certain since effects are present between the peak areas (number of traps). Thus, the average area [14] is used, as to be seen in Fig. 1.

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