

SINGLE PEAK DIFFERENTIAL THERMOLUMINESCENCE METHOD FOR CALCULATION OF THE TRAP ENERGIES

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ABSTRACT

The energy level of the traps of natural calcium fluoride sample is calculated using a single thermoluminescence glow curve peak by new non-isothermal kinetic method. The plot of $\ln \left(\frac{da}{dT} \frac{1}{1-a} \right)$ versus $\frac{1}{T}$ yields a straight line with a slope of $-\frac{E}{k}$, where E is the trap energy k , is the Boltzman constant, "a" is the fraction of the total occupied trap number. The frequency factor S can be calculated from y intercept which is equal to $\ln(Sxb)$ where b is the constant heating rate.

The trap energy value of the main glow curve peak of the natural calcium fluoride is calculated as 0.64 eV by using single peak differential thermoluminescence method.

ÖZET

Tabii kalsiyum florürün tuzak enerjilerini tayin için yeni bir değişen sıcaklık metodu uygulanmıştır. Bu metoda göre $\ln \left(\frac{da}{dT} \frac{1}{1-a} \right)$ bağıntısını $1/T$ nin fonksiyonu olarak gösteren grafik bir doğru denklemi vermekte ve bu doğrunun eğiminin $(-\frac{E}{k})$ değerine eşit olması özelliğinden E tuzak enerjisi tayin edilebilmektedir. Kalsiyum florürün ana piki için $E = 0.64$ eV değeri bulunmuştur.

DEFINATION OF THE METHOD

Since the method applied should be used for a single peak of the thermoluminescence glow curve (monoenergetic traps) is named as "Single Peak Differential Method"¹.

As known from Randall-Wilkins² thermoluminescence model light intensity was given for isothermal experiments as

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

where n is the number of the occupied traps at time t and C is the proportionality constant. Integration of this equation, if n_0 is the initial number of occupied traps at time zero

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

The left side of the equation 2 is the area under the glow curve in the time interval of $(0 - t)$. So

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

is obtained by abbreviating A as the whole area under the glow curve peak and A_2 as the area completing the A_1 to the A value as shown in Figure-1. As a result the area under the glow curve peak is proportional to the occupied trap number at that moment. From the equation 3

$A_2 = Cn$ can be derived. Differentiating the equation

$$\frac{dA_2}{dt} = C \frac{dn}{dt} \quad \text{is obtained} \quad 4$$

$$\text{Since } - \frac{dn}{dt} = pn \quad 5$$

was given by Randall-Wilkins model if n was the occupied trap number, p was the probability. Combination of the equation 3, 4 and 5 yields

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

As seen from Figure-1

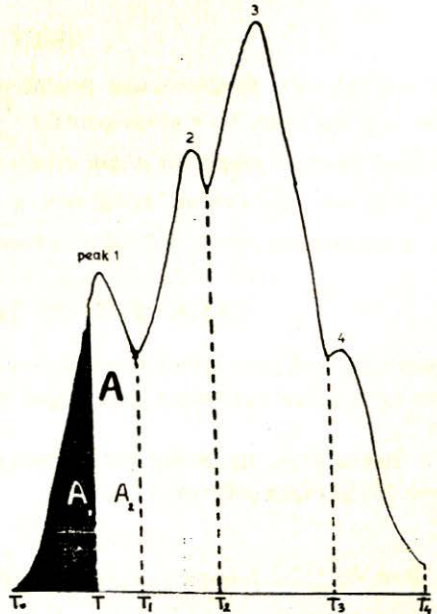


Figure - 1

$A = A_1 + A_2$ is given. A_1 and A_2 variables and A is constant so differentiation of this equation yields

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

For the linear heating rates this equation can be modified (by using $\frac{dT}{dt} = b$ equation) as

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

dividing by A and defining $\frac{A_1}{A} = a$

$$\frac{b}{A} \frac{dA_1}{dT} = (1 - a) p \quad \text{is obtained} \quad 9$$

Since "a" was defined as $a = \frac{A_1}{A}$ differential of the equation can be obtained as

$$\frac{da}{dT} = \frac{1}{A} \frac{dA_1}{dT}$$

The value of $\frac{dA_1}{dT}$ can be derived and place into equation 8

$$\frac{da}{dT} \frac{1}{(1 - a)} = \frac{p}{b} \quad \text{can be obtained} \quad 10$$

Probability p was given by Randall-Wilkins as

$$p = S \exp\left(-\frac{E}{kT}\right)$$

where k is the Boltzmann constant, S is the Frequency factor E is the trap energy, T is the absolute temperature of the sample. Having natural logarithm of the equation 10

$$\ln\left(\frac{da}{dT} \frac{1}{(1 - a)}\right) = -\frac{E}{kT} + \ln S - \ln b \quad \text{is obtained} \quad 11$$

The plot of $\ln\left(\frac{da}{dT} \frac{1}{(1 - a)}\right)$ versus $\frac{1}{T}$ yields a straight line having a slope of (E/k) and y intercept which is equal to $(\ln S - \ln b)$.

APPLICATION OF THE METHOD

The data obtained from the main peak of the glow curve of the natural calcium fluoride phosphore (numbered 18 blue) which is shown in Figure-2 is tabulated in Table-1 which contains the heights measured from the curve and the areas (A_1) calculated by Library program 10 of TI-58 or 59 calculator. "a" values can be calculated dividing partial areas A_1 by the whole area under the glow curve peak.

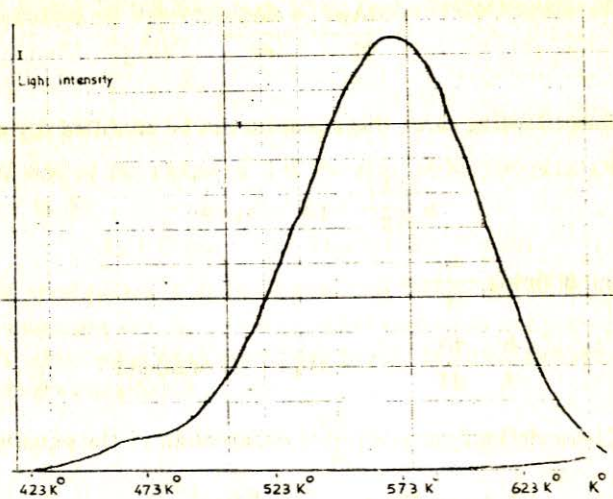


Figure - 2

Table: 1
 (a - T) Data Obtained From The Main Peak of The Glow Curve Of
 The Natural CALCIUM FLUORITE (No: 18, Blue)

$b = 2.36 \text{ C}^\circ/\text{sec}$ $T_0 = 459.95 \text{ K}^\circ$ $T_m = 546.91 \text{ K}^\circ$					
T K ^o	a	(1/T) 10 ⁵	Area	I (mm)	$\text{Ln} \left(\frac{da}{dT} \times \frac{1}{(1-a)} \right)$
459.95	0.00000	217.41	00000.90	000.0	
474.45	0.02247	210.77	243.96	23	
488.94	0.06341	204.52	688.4	41	
496.19	0.09513	201.54	1032.8	54	
503.43	0.13528	198.64	1468.6	66	- 4.984
517.93	0.24207	193.08	2628	94	- 4.466
525.17	0.30952	190.41	3360.25	108	- 4.245
533.42	0.38514	187.82	4181.2	117	- 4.029
539.67	0.46495	185.29	5047.58	122	- 3.859
546.91	0.54734	182.85	5942	124	- 3.681
554.16	0.62914	180.45	6830.1	121	- 3.510
561.41	0.70709	178.12	7676.3	110	- 3.344
568.65	0.77654	175.85	8430.3	98	
575.9	0.83725	173.64	9089.4	83	
583.14	0.88733	171.48	9632.2	67	
590.39	0.92674	169.38	10060.95	51	
619.38	1.00000	161.45	10856.28	10.5	

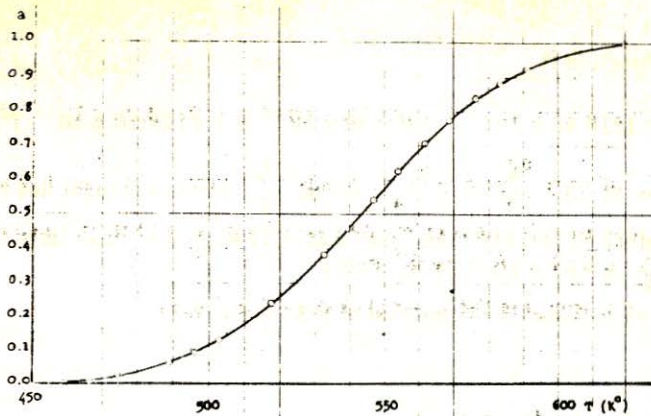


Figure - 3

The plot of "a" versus T is shown in Figure-3. $a = F(T)$ function should be defined to calculate the da/dT values for the different temperature values. In this work it is thought to fit this curve to a polynomial in the third order in the interval of "a" value as shown below.

$$a = A + BT + CT^2 + DT^3 \quad 12$$

Substituting the values of T_1, T_2, T_3, T_4 and corresponding values of a_1, a_2, a_3, a_4 into this function, the linear equation of

$$\begin{aligned} a_1 &= A + BT_1 + CT_1^2 + DT_1^3 \\ a_2 &= A + BT_2 + CT_2^2 + DT_2^3 \\ a_3 &= A + BT_3 + CT_3^2 + DT_3^3 \\ a_4 &= A + BT_4 + CT_4^2 + DT_4^3 \end{aligned} \quad 13$$

is obtained.

From this equation the coefficients of A, B, C, D, can be defined in an interval of $(a_1 - a_4)$. So the function of a $F(T)$ and so the derivative function da/dT can be obtained.

RESULTS

In the interval of $0.13528 \leq a \leq 0.38514$ the $a(F(T))$ function is

$$a = 80.67 - 438.48 \times 10^{-3} T + 776.89 \times 10^{-6} T^2 - 444.30 \times 10^{-9} T^3$$

and derivative function is

$$\frac{da}{dT} = 438.48 \times 10^{-3} + 1552.78 \times 10^{-6} T - 1332.90 \times 10^{-9} T^2$$

In the interval of $0.38514 \leq a \leq 0.70709$ the function $a(F(T))$ is

$$a = 217.47 - 1216.40 \times 10^{-3} T - 2251.66 \times 10^{-6} T^2 - 1376.40 \times 10^{-9} T^3$$

and derivative function is

$$\frac{da}{dT} = 1216.40 \times 10^{-3} + 4503.32 \times 10^{-6} T + 4129.20 \times 10^{-9} T^2$$

The values of $\ln \left(\frac{da}{dT} \times \frac{1}{1-a} \right)$ versus $\frac{1}{T}$ yields a straight line as seen in Figure-4. The slope of this line is calculated as -7436.68 and then, since this value is equal to $-\frac{E}{k}$ ($k 8.61 \times 10^{-5} \text{ eV/K}^\circ \text{ mol.}$)

$E = 0.64 \text{ eV}$ is found in the interval of $0.24 \leq a \leq 0.71$.

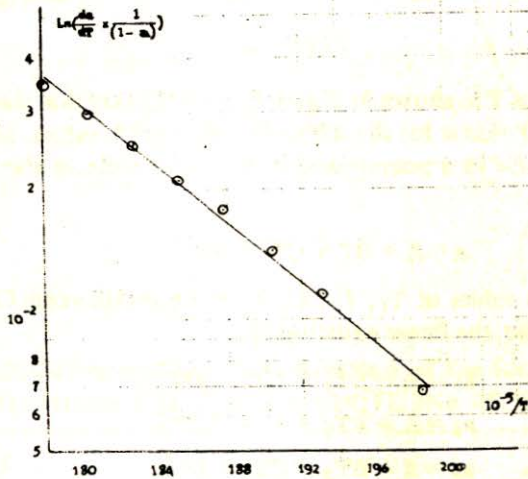


Figure - 4

DISCUSSION

This method is applied to natural calcium fluorite phosphore together with other two method. One of them is Garlick-Gibson³ method which yields 0.64 eV trap energy value. This value fits the result obtained by that method. The second method is "Single Peak Integration Method"⁴ which is also introduced together with the method used in that work. 0.54 eV trap energy value is obtained by that second method.

Although the application of that method takes a long time but it is most believable since substantial part of the peak is used.

REFERENCES

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