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ISOTHERMAL DECAY OF THE THERMOLUMINESCENCE (TL) GLOW CURVES IN FELDSPAR AT AN AMBIENT TEMPERATURE

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Abstract: Isothermal decay of the TL glow curve has been studied at ambient temperature. Peaks at the low-temperature region of the TL glow curve were isolated by the curve subtraction method. Activation energy and frequency factor parameters of the isolated peaks were calculated taken into account first and second order kinetics. The values of the calculated activation energy vary between 0.7 to 1.1 eV and frequency factor values of the isolated peaks change within the order of 10^9 to $10^{13}s^{-1}$.

Keywords: Feldspar; Isothermal decay; Activation energy; Frequency factor

1. Introduction

Feldspar fraction extracted from sediments has been increasingly investigated for dating of archeological artifacts as well as the age of geological sediments. The main advantage of using feldspars instead of quartz is their higher luminescence brightness and saturation dose, which could extend the range of dating applications. At the same time the luminescence emission of feldspar exhibits large variety due to the huge natural abundance of the mineralogical composition[1]–[3]; the presence of adverse luminescent phenomena like anomalous fading and sensitivity changes; irradiation and thermal history[4]. Investigations were mainly made on natural K-feldspars separated from geological sediments and on pure feldspar minerals. They were devoted to clarifying the luminescence behavior of such materials; to describe the optical bleaching mechanism [5]; to identify traps and recombination centers and to assess a reliable protocol for dating procedures[6], [7]–[9].

Despite these extensive studies of the TL glow curves in feldspars, the exact composition of these glow curves and their kinetics is still an open research question. Specifically, it is not yet known whether the typically broad TL glow curves in feldspars consist of individual narrow TL peaks, or whether they are the result of an underlying continuous distribution of energy levels[7].

With the purpose of contributing to the knowledge of the luminescent mechanisms in feldspars, we present the results of a study of activation energy and frequency factor values on the natural feldspar mineral.

2. Materials and Methods

As a sample, we have taken the feldspar kindly presented by the Institute of Inorganic Chemistry and Catalysis ANAS. Samples were gently crushed and sieved, and the fraction of 100-160 μm of feldspar was used for TL measurement. Hydrochloric acid (1N) was used to remove carbonates and then rinsed with deionized water. Magnetic separation was applied to remove any magnetic inclusions. Any high-density components were separated using heavy liquid Sodium poly-tungsten. Irradiation was performed at ambient temperature with a ^{60}Co gamma source with a dose rate of 3.73 mGy/s. The dose rate of the ^{60}Co source was determined using a Magnette Miniscope MS400 EPR spectrometer using individually packed BioMax alanine dosimetry films with bar code markings (developed by Eastman Kodak Company). For the experiments it, was used both natural and thermally treated feldspar samples in order to compare the changes in radiation sensitivity due to thermal treatment. Thermally treated feldspar was heated at 600ºC for one hour prior to irradiation.

The Harshaw TLD 3500 Manual Reader is used to measure the characteristics of TL samples. TL measurements were performed using a linear heating rate of 20ºC/s from 50ºC to 400ºC. Three aliquots of 5 mg each of the samples were used for each measurement. TL data points represent the average of three different aliquots of the sample. A thin and uniform layer of feldspar grains was laid on the planchet surface in order to get full contact that ensures uniform TL signal from the sample.

A number of experimental methods for evaluating the basic trapping parameters from a TL peak are based on the peak-shape. Peak shape method enables evaluation of 'activation energy" and "frequency factor" using the temperature at the peak maximum (T_m), and the low (T_1) and high (T_2) half-width temperatures (Fig. 1) of the experimental glow curve.

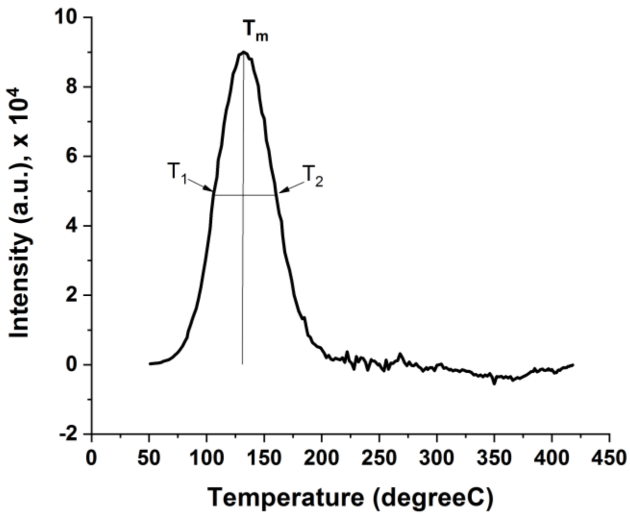

Fig. 1 Isolated TL peak. T_m is a temperature at the peak maximum; T_1 is a temperature at the point of left side half-width; T_2 is a temperature at the point of right side half-width.

The formulas for finding the activation energies by these methods usually contain one of the following factors: (a) $\tau=T_m-T_1$, the half-width at the low-temperature side of the peak, (b) $\delta=T_2-T_m$, the half-width towards the falloff of the glow peak, or (c) $\omega=T_2-T_1$, the total half-width. These formulas were developed and/or systemized by Chen R. [10]. Here are the summarized function and relevant coefficients (Table 1) for the first and second-order kinetics:

$$E = C_\propto \left(\frac{kT_m^2}{\propto}\right) - b_\propto(2kT_m) \quad (1)$$

where k=8.617x10^{-5} eV/K is the Boltzmann constant and α is δ, τ or ω respectively. The values of C_α and b_α for each of the three methods and for first and second-order kinetics are given in Table 1. Note that the order of kinetics of a peak is usually determined by its symmetry factor, defined as

$$\mu = {}^{\delta}/_{\omega} \quad (2)$$

where a characteristic value of μ for the first order peaks is 0.42 and for the second order is 0.52[11].

Table 1 Coefficients appearing in Eq.1 for the various methods at calculating activation energies [11]

	First order			Second order		
	τ	δ	ω	τ	δ	ω
$C_\propto$	1.51	0.976	2.52	1.81	1.71	3.54
$b_\propto$	1.58	0	1	2	0	1

Once the activation energy of a first-order peak is defined, the frequency factor can be determined by using the formula:

$$s = \frac{\beta E}{kT_m^2}\exp(E/kT_m) \qquad (3)$$

where β (K/s) is the constant heating rate.

For the second-order kinetics the formula needs to be written as:

$$s = \frac{\beta E}{kT_m^2(1+\frac{2kT_m}{E})}\exp(E/kT_m) \qquad (4)$$

3. Results and Discussions

The continuum of energy states creates a very broad TL glow curve shown in Figs. 2 and 3. This broad glow curve cannot be analyzed as a single peak, but could possibly be described as the linear combination of many narrower TL peaks, each corresponding to a different but closely located energy level. One possible method of identifying these closely located individual energy states is a subtractive method of analyzing the TL glow curve. For example, Strickertsson [12] examined the TL signals from microclines and identified six overlapping peaks between room temperature and 500°C. This author used the fractional glow technique to estimate the activation energy E as a function of the temperature T_{stop} at which the sample was preheated. Applying T_{stop} –T_{max} method they reported a continuous distribution of energies between E ~1.0 eV at T_{stop} ~70°C and E ~1.7 eV at T_{stop} ~280°C. For higher T_{stop} values between 280°C and 370°C the activation energy E was found to be constant at a value of E ~1.75 eV[12].

In our case, we used isothermal decay method. The TL glow curves of the feldspar samples are obtained using an isothermal cleaning procedure, as follows. Several aliquots of the material are irradiated with a gamma dose of 34.12 Gy, then the aliquot is heated all the way to a high temperature of 450°C and the TL glow curve is obtained. The process is then repeated several times using the remaining part of aliquots after a certain period of time, i.e. after 5 days, 15 days, etc. This procedure produces a series of TL glow curves shown in Fig. 2 and 3, essentially corresponding to a gradual isothermal cleaning process of the overall TL glow curve for this sample.

The comparison of Fig. 2 and Fig.3 shows that heating of feldspar at 600ºC leads to increased sensitivity of the samples upon irradiation for the whole range of glow curve. In general, we observe a sensitivity increase of about five times. Fading of the glow curve is observed at the low-temperature part of the glow curve while it has been kept in a dark at the ambient, constant temperature. After a certain period of time, approximately in 40 to 50 days low-temperature region of the glow curve fades down while the high-temperature part remains unchanged. It is a common phenomenon for the irradiated feldspar and known as an anomalous fading. Explanations of the anomalous fading effect have been based on various proposed models, such as the tunneling model, the localized transition model and a model based on competition with radiationless transitions. Currently, the most accepted explanations of AF are based on quantum mechanical tunneling from the ground state or from the excited state of the trap [13 and references therein].

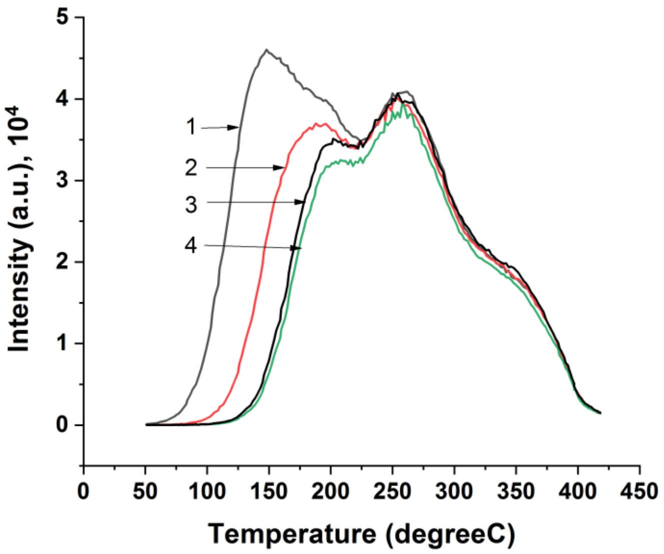

Fig. 2 TL glow curve of unheated natural feldspar irradiated at 34.12 Gy (1); TL glow curve of the same sample after 15 days (2); 22 days (3); and 27 days (4).

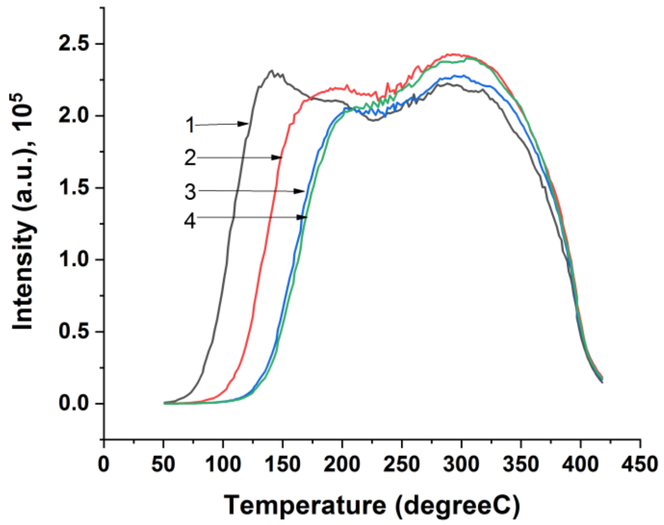

Fig. 3 TL glow curve of natural feldspar heated at 600ºC for one hour and irradiated at 34.12 Gy (1); TL glow curve of the same sample after 5 days (2); 12 days (3); and 40 days (4). Curve (5) represents the isolated peak by subtracting curve (4) from curve (1)

Specifically Figs. 4 and 5 show the results of subtracting the TL glow curve for the two samples. The individual TL glow curves obtained in this subtractive procedure are shown in Figs. 4 and 5.

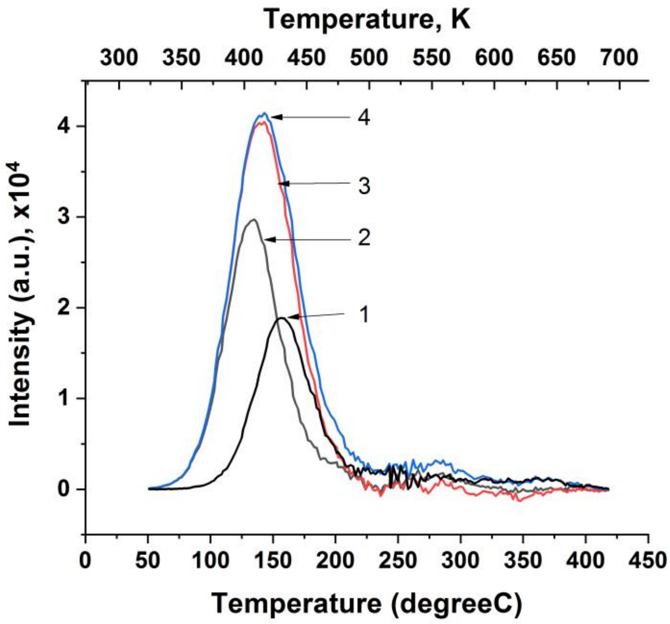

Fig. 4. Isolated glow curves obtained by subtracting method. Curve (1) represents the isolated peak by subtracting glow curve (4) presented in Fig.2 from curve (2) presented in Fig.2, i.e. (1) = Fig 2 curve (2) – Fig.2 curve (4); and subsequently (2) = Fig 2 curve (1) – Fig.2 curve (2); (3) = Fig 2 curve (1) – Fig.2 curve (3); (4) = Fig 2 curve (1) – Fig.2 curve (4)

Table 2 illustrates the major geometric parameters of the isolated peaks for the unheated and irradiated feldspar. The values of μ clearly indicate that all isolated peaks rather belong to second- order kinetics.

Table 2 TL parameters of the isolated peaks for the unheated feldspar irradiated at 34.12 Gy (For the punctuation of the peaks please, refer to Fig.4)

Peak identity	T_m, K	T_1, K	T_2, K	ω	δ	τ	μ
1	429	405	457	52	28	24	0.54
2	408	381	433	52	25	27	0.48
3	414	385	444	59	30	29	0.51
4	414	385	447	62	33	29	0.53

However, in practice, one hardly observes curves with pure first-order or second-order kinetics. Experimental glow curves usually show values somehow in between 0.42 and 0.52 or around them (please, refer to Table 2 and 3). In order to find activation energies by one of the half-width methods, it is suggested [11] to interpolate the constants listed in Table 1 for the first and second-order kinetics. A much more suitable interpolation parameter seems to be μ which is found directly from the geometrical shape of the peak (refer to Tables 2 and 3). We have to write general equations so that, they would give the first-order case for μ=0.42 and for the second-order case μ=0.52. Thus with the parameters of μ given in Table 1 the factors in equation 1 for the interpolated-extrapolated τ method would be

$C_\tau = 1.51 + 3.0 (\mu-0.42)$; $b_\tau = 1.58 + 4.2 (\mu-0.42)$

For the ***δ*** and ***ω*** method coefficients would be

$C_\delta = 0.976 + 7.3 (\mu-0.42)$; $b_\delta = 0$ and

$C_\omega = 2.52 + 10.2 (\mu-0.42)$; $b_\omega = 1$ respectively.

Table 3 Activation energy values of the isolated peaks for the unheated feldspar irradiated at 34.12 Gy (For the punctuation of the peaks please, refer to Fig.4)

Peak identity	E_τ (eV)	E_δ (eV)	E_ω (eV)
1	1.08	1.04	1.06
2	0.77	0.81	0.80
3	0.77	0.80	0.79
4	0.79	0.80	0.80

Frequency factor also easily might be calculated using the formula (3) for the first-order kinetics or for the second-order kinetics by formula (4) [11]. Table 4 illustrates the values of the frequency factors calculated for the peaks listed in Table 3.

Table 4 Calculated frequency factor values of the isolated peaks for the unheated feldspar irradiated at 34.12 Gy (For the punctuation of the peaks please, refer to Fig.4)

Peak identity	Values calculated for τ method		Values calculated for δ method		Values calculated for ω method	
	1st order	2nd order	1st order	2nd order	1st order	2nd order
1	6.64E+12	6.22E+12	2.17E+12	2.02E+12	3.79E+12	3.50E+12
2	3.49E+9	3.20E+9	1.15E+10	1.05E+9	8.51E+9	7.82E+9
3	2.45E+9	2.60E+9	5.94E+9	5.45E+9	4.43E+9	4.07E+9
4	4.43E+9	4.07E+9	5.94E+9	5.45E+9	5.95E+9	5.45E+9

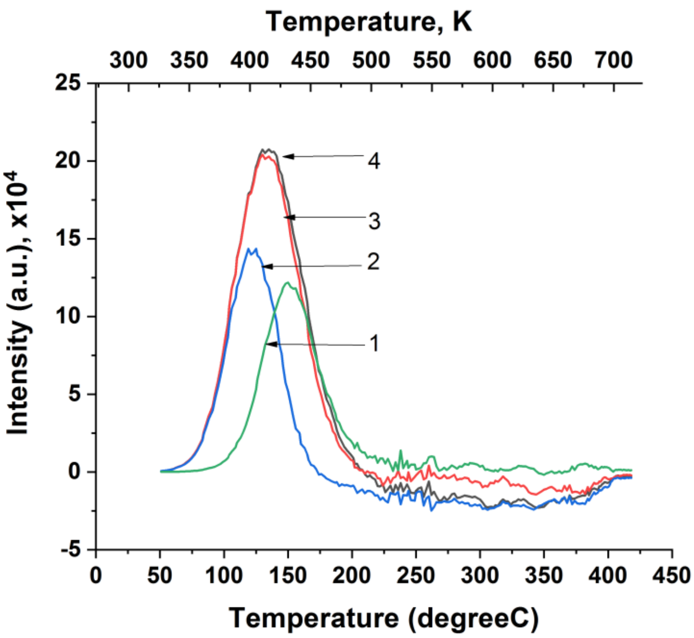

Fig. 5 Isolated glow curves obtained by subtracting method: Curve (1) represents the isolated peak by subtracting glow curve (4) presented in Fig.3 from curve (2) presented in Fig.3, i.e. (1) = Fig 3, curve (2) – Fig.3, curve (4); and subsequently (2)= Fig 3, curve (1) – Fig.3, curve (2); (3)= Fig 3, curve (1) – Fig.3, curve (3); (4) = Fig 3, curve (1) – Fig.3, curve (4)

Table 5 TL parameters of the isolated peaks for the feldspar heated at 600ºC and irradiated at 34.12 Gy (For the punctuation of the peaks please, refer to Fig.5)

Peak identity	T_m, K	T_1, K	T_2, K	ω	δ	τ	μ
1	423	399	448	49	25	24	0.51
2	394	372	419	47	25	22	0.53
3	405	376	437	61	32	29	0.52
4	406	377	439	62	33	29	0.53

Table 6. Activation energy values of the isolated peaks for the feldspar heated at 600°C and irradiated at 34.12 Gy (For the punctuation of the peaks please, refer to Fig.5)

Peak identity	E_τ (eV)	E_δ (eV)	E_ω (eV)
1	1.00	1.01	1.01
2	0.98	0.97	0.98
3	0.75	0.76	0.77
4	0.75	0.77	0.76

Table 7 Calculated frequency factor values of the isolated peaks for the unheated feldspar irradiated at 34.12 Gy (For the punctuation of the peaks please, refer to Fig.4)

Peak identity	Values calculated for τ method		Values calculated for δ method		Values calculated for ω method	
	1st order	2nd order	1st order	2nd order	1st order	2nd order
1	8.81E+13	8.29E+13	2.12E+13	2.12E+13	3.75E+13	3.52E+13
2	2.91E+9	2.67E+9	3.92E+9	3.60E+9	3.92E+9	3.60E+9
3	2.29E+9	2.09E+9	4.16E+9	3.82E+9	3.09E+9	2.83E+9
4	5.03E+12	4.71E+12	2.74E+12	2.56E+12	3.71E+12	3.47E+12

4. Conclusions

Anomalous fading has been considered as an isothermal decay at an ambient temperature. The suggested procedure enables isolate peaks at the low-temperature region of the TL glow curve. An analysis of the values of the symmetry factor suggests that bimolecular mechanisms are based on the kinetics of anomalous fading processes since the values of this parameter vary within 0.52. The values of the calculated activation energy vary between 0.7 to 1.1 eV and frequency factor values of the isolated peaks change within the order of 10^9 to $10^{13} s^{-1}$.

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ИЗОТЕРМИЧЕСКОЕ ЗАТУХАНИЕ КРИВЫХ СВЕЧЕНИЯ ТЛ В ПОЛЕВОМ ШПАТЕ ПРИ ТЕМПЕРАТУРЕ ОКРУЖАЮЩЕЙ СРЕДЫ

С. Мамедов, М. Байрамов, А. Абишов, А. Ахадова

Резюме: Изотермический спад кривой свечения ТЛ изучен при температуре окружающей среды. Пики в области низких температур кривой свечения ТЛ были выделены методом вычитания кривой. Параметры энергии активации и частотного коэффициента рассчитывались с учетом кинетики первого и второго порядка. Значения рассчитанной энергии активации варьируются от 0,7 до 1,1 эВ, а значения частотных коэффициентов изолированных пиков изменяются в пределах от 10^9 до 10^{13} сек$^{-1}$.

Ключевые слова: Полевой шпат; Изотермический распад; Энергия активации; Частотный фактор

ÇÖL ŞPATININ TERMOLUMİNESSENT ŞÜALANMASININ ƏTRAF MÜHİT TEMPERATURUNDA SÖNMƏSİNİN TƏDQİQİ

S. Məmmədov, M. Bayramov, A. Abışov, A. Əhədova

Xülasə: Çöl şpatının termoluminessent şüalanmasının ətraf mühit temperaturunda sönməsi tədqiq edilmişdir. Termoluminessens işıqlanma əyrisinin aşağı temperatur zonasındakı piklər əyrilərin bir-birindən çıxılması metodu ilə ayrılmışdır. Aktivləşmə enerjisinin və tezlik faktorlarının qiymətləri birinci və ikinci tərtib kinetika mexanizmlərinə uyğun olaraq hesablanmışdır. Aktivləşmə enerjisinin qiymətləri 0.7-1.1 eV arasında təyin edilmişdir. Tezlik faktorlarının qiyməti isə 10^9-10^{13} san^{-1} qiymətləri arasında dəyişir.

Açar sözlər: Çöl şpatı; isotermik parçalanma; Aktivləşmə enerjisi; tezlik faktoru