





ISOTHERMAL DECAY ANALYSIS OF THERMOLUMINESCENCE PEAKS OF QUARTZ FOR KINETIC PARAMETER DETERMINATION

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This study delves into the intricacies of isothermal decay analysis applied to thermoluminescence (TL) peaks, focusing on determining kinetic parameters. The study challenges the conformity of the trap responsible for the ITL signals to first, second, or general-order kinetics, supported by the non-conforming decay pattern and the inference of two overlapping first-order TL peaks. This work enhances the understanding of TL peaks and establishes a reliable methodology for characterizing luminescence mechanisms in materials, contributing to advancements in luminescence dosimetry research. These observations lead to the conclusion that the TL data originates from more than one trap, and based on existing literature, it is inferred that there are two overlapping first-order TL peaks. The investigation involves the consideration of isothermal decay data at distinct temperatures ($T = 250, 260, 270, 280, \text{ and } 290^\circ\text{C}$) and explores challenges associated with achieving precise linear fits for different kinetic order values (b). The nature of decay is interpreted based on the monomolecular theory, suggesting adherence to a first-order process. ITL curves were deconvoluted into two exponential decay curves. The slopes of the regression lines provide activation energy (E) values for curve1 and curve2, respectively: $E_1 = 0.99 \pm 0.16 \text{ eV}$ and $E_2 = 1.32 \pm 0.18 \text{ eV}$. The frequency factor (s) is determined from the intercept of the regression line: $s_1 = 1.32 \times 10^8 \text{ s}^{-1}$ and $s_2 = 1.77 \times 10^{12} \text{ s}^{-1}$.

Keywords: *Isothermal decay; Quartz; Activation energy; Frequency factor*

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INTRODUCTION

Natural minerals are increasingly vital in contemporary science and technology, with many displaying thermoluminescence (TL) characteristics that contribute to our understanding of damage and safety processes in radiation incidents. Among these minerals, quartz is a crucial, cost-effective, and abundant material with numerous advantages for research in radiation, environmental, and clinical radiological applications [1]. When irradiated grains of quartz undergo heating from room temperature to elevated levels, they exhibit various glow curves. These curves depend on chemical composition, impurity types and concentrations, defects, geological origin, irradiation, sensitization, and other experimental conditions [2], [3].

Numerous TL glow peaks within the temperature range of 333–753 K have been reported by various authors for diverse quartz samples [4]–[6]. According to these studies, high-temperature TL peaks demonstrate greater stability post-irradiation than low-temperature peaks, which decay more rapidly due to shorter lifetimes. Despite the diverse capabilities demonstrated by natural quartz, a comprehensive understanding of its detailed irradiation response, defect production and distribution, and thermoluminescence mechanism remains elusive. The challenge arises from the difficulty in comparing TL measurements across different studies, as quartz samples from various origins, conditions, and impurities may exhibit inconsistencies. Therefore, this study explores the TL characteristics and defect production of naturally occurring quartz subjected to high gamma doses (8 kGy).

Luminescence-based measurements in retrospective dosimetry entail assessing the charge stored in localized defect states through external stimuli like heat or light. In thermoluminescence (TL), the exclusive mechanism for stimulation is heat energy. Isothermal signals, termed phosphorescence or isothermal TL (ITL), are employed to estimate the equivalent dose (D_e) and determine trap parameters such as thermal and optical trap depths (in units of eV), frequency factor (in units of s^{-1}), as well as thermal assistance and thermal-quenching energies. Therefore, a comprehensive understanding of the characteristics and origins of isothermal signals, ITL, is crucial. Signals originating from a constant flux of stimulation energy are anticipated to exhibit a consistent, often exponential, decay pattern.

Current interest in the thermoluminescence of quartz obtained from building materials such as mortar and concrete, especially for dose reconstruction purposes, requires accurate determination of this mineral's thermoluminescence parameters associated with intermediate luminescence peaks [7], [8]. The isothermal TL signal from deep traps holds the potential for retrospective dosimetry [7]. Recently, there have been indications that the high-temperature TL signal (325°C) demonstrates significantly higher dose saturation compared to OSL. Consequently, efforts have been made to utilize isothermal TL at 310 and 320°C to develop single-aliquot dose measurement methods.

This study aims to present the findings of an isothermal TL investigation, evaluating various parameters essential for describing the TL process in quartz. The objective is to contribute to understanding natural quartz's luminescence mechanisms. These parameters include the activation energy (E) for TL traps, also known as trap depth, the frequency factor (s), and the order of kinetics (b) of the TL process.

MATERIALS AND METHODS

The quartz samples employed in this experiment were obtained from beach sand through traditional chemical separation methods. The sand underwent sieving to isolate grain size fractions ranging from 80 to 120 μm . Subsequently, this grain size fraction underwent hydrochloric acid (HCl) treatment, separation through heavy liquids, and etching in a 40% hydrofluoric acid (HF) solution. The precipitated fluorides were dissolved using HCl. Before subsequent irradiation, the samples were heated to 600°C for one hour to eliminate residual thermoluminescence (TL) centers. The irradiation occurred at an ambient temperature using a ^{60}Co source, with dose levels reaching 8 MGy.

In a standard isothermal decay experiment, the established procedure entails rapidly heating the irradiated sample to a specified temperature and maintaining it for a predetermined duration. The quartz grains were affixed to an aluminum disc of 0.1 mm thickness using silicone spray for measurement purposes. Isothermal TL (ITL) measurements were conducted using a Harshaw 3500 manual reader, holding the aliquots for 50 s at a constant temperature. The preheating was executed at a rate of 2°C s⁻¹ in a nitrogen (N₂) atmosphere, and the ITL curves were recorded immediately upon reaching the measurement temperature. Under these conditions, we observed monotonically decreasing ITL signals that exhibited no detectable disturbance due to thermal lag. Any significant thermal lag would have manifested as an initial rise to a maximum before subsequent decay [9]. The emitted light, termed phosphorescence decay, is observed over a period, enabling the evaluation of the decay rate of trapped electrons. Graphs depicting the correlation between thermoluminescence (TL) intensity and time at a constant temperature are known as isothermal decay curves.

Garlick and Gibson showcased the methodology of analyzing isothermal decay within the framework of first-order kinetics [10]. When scrutinizing isothermal decay curves at a specific temperature (T_i) for TL peaks following first-order kinetics, the resultant graphs exhibit an exponential relationship with time, as depicted by the Equation:

$$I_t = I_0 \exp\left(-s \exp\left(-\frac{E}{kT_i}\right) t\right), \quad (1)$$

where

I_0 = initial TL intensity, I_t = the TL intensity at time t , s = effective frequency factor, E = activation energy, T = temperature of isothermal decay.

This Equation signifies that a plot of $\ln(I)$ against time will exhibit a linear relationship for peaks governed by first-order kinetics. Furthermore, the slope of this linear graph will be determined by:

$$\text{slope} = m_i = -s \exp\left(-\frac{E}{kT_i}\right), \quad (2)$$

Taking the natural logarithm of the equation yields:

$$(\text{slope}) = \ln s - \frac{E}{kT_i}. \quad (3)$$

The graph depicting $\ln(\text{slope})$ versus $1/kT$ is expected to be a straight line with a slope equal to $-E$ and a Y-intercept corresponding to $\ln(s)$.

Equations describing the thermoluminescence processes have been provided by Randall–Wilkins for first order, Garlick–Gibson for second order, and May–Partridge for general order kinetics [11]:

$$I(t) = -\frac{dn}{dt} = n \exp\left(-\frac{E}{kT}\right), \quad (4a)$$

$$I(t) = -\frac{dn}{dt} = \frac{n^2}{N} \exp\left(-\frac{E}{kT}\right), \quad (4b)$$

$$I(t) = -\frac{dn}{dt} = n^b s' \exp\left(-\frac{E}{kT}\right), \quad (4c)$$

Where n is the trapped charged population.

These equations provide a method for calculating E . In this context, applying isothermal analysis allows determining the kinetics order, denoted as b . By keeping the temperature constant and integrating the general-order equation (4c) with respect to time (t), the following expression is derived:

$$I_t = I_0 \left[1 + s' n_0^{b-1} (b-1) t \exp\left(-\frac{E}{kT}\right) \right]^{\frac{b}{1-b}}, \quad (5)$$

Where I_0 and n_0 represent the initial TL intensity and the initial concentration of trapped charges, respectively, I_t is the TL intensity at time t . By rearranging Equation (5), we obtain:

$$I_0 = s' n_0^b \exp\left(-\frac{E}{kT}\right), \quad (6)$$

where

$s' = s/N$ = effective frequency factor, N is the number of traps.

n_0 = initial trapped charged population.

This Equation suggests that a plot of the quantity against time should exhibit a linear trend when an appropriate value of b is determined. Various isothermal decay temperatures produce a series of straight lines with different slopes.

RESULTS AND DISCUSSIONS

Figure 1 illustrates the given data corresponding to five distinct temperatures: T = 250, 260, 270, 280, and 290°C. As previously detailed, the isothermal decay curves for thermoluminescence (TL) peaks conforming to first-order kinetics follow exponential time functions. According to [12], a plot of ln(I) against time (t) will exhibit a linear correlation for first-order kinetics peaks, with the slope of the line determined by equation (3). A plot of ln(|slope|) versus 1/kT is anticipated to display a linear pattern, with a slope equal to -E and a y-intercept equal to ln s if the provided isothermal TL data aligns with first-order kinetics. Initially, we calculate ln (TL) for each isothermal curve and plot ln (TL) against time.

Subsequently, regression lines are computed for the plot with T=250°C in Figure 2. Figure 2 depicts the plot of ln(TL) against time (t), with T=250°C representing the temperature while recording isothermal decay curves. First-order kinetics can be ruled out by inspecting the ln (TL) graph against time, as shown in Figure 2. The resultant plots reveal a nonlinearity, indicating that the data does not conform to first-order kinetics. If we reformulate Equation (5), the isothermal decay curves of TL peaks corresponding to general order kinetics with the kinetic order parameter denoted as "b" will be characterized as follows:

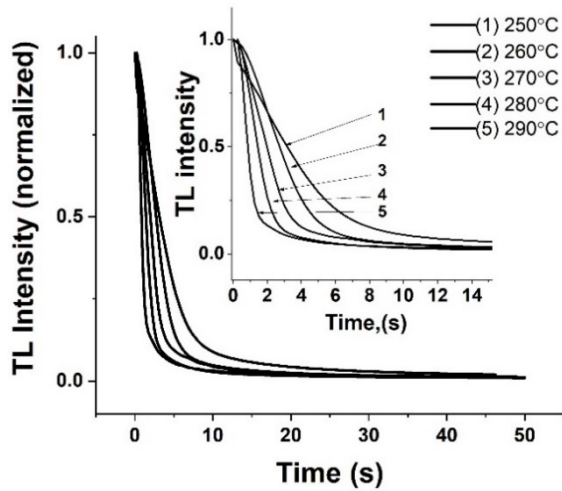


Figure 1. Isothermal TL decay curves of quartz at different temperatures. Quartz irradiated at 8MGy. Inserting is a magnified part of the spectrum from 0 to 14 s

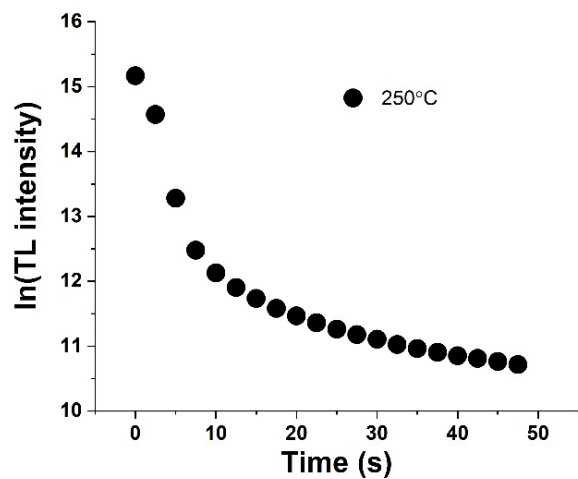


Figure 2 The isothermal decay curves on the semi-log scale for the isothermal decay curve of quartz at 250°C

$$\left(\frac{I_t}{I_0}\right)^{\frac{1-b}{b}} = 1 + s'n_0^{b-1} (b - 1) \exp\left(-\frac{E}{kT}\right) \tag{7}$$

This Equation suggests that a graph of the quantity $(I_t / I_0)^{(1-b)/b}$ against time t should form a straight line when an appropriate value of b is identified. After determining the value of b, we will plot $(I_t / I_0)^{(1-b)/b}$ against time t for the five different decay temperatures, resulting in a set of straight lines with a slope (m) given by the formula:

$$m = s'n_0^{b-1} (b - 1) \exp\left(-\frac{E}{kT}\right) \tag{8}$$

The activation energy E and the effective frequency factor $s'' = s'n_0^{b-1}$ will be determined from the slope and intercept of the plot of ln(m) versus 1/ kT.

Figure 3 depicts the quantities $(I_t / I_0)^{(1-b)/b}$ for the isothermal decay data at T = 260°C, considering four different values of the kinetic-order parameter (b = 1.9, 2.0, 2.1, and 2.2) as a function of time t. It is evident that none of the four graphs yield satisfactory linear fits.

This situation emphasizes a potential challenge when dealing with isothermal decay data: attaining a precise estimation of the optimal linear fit might prove challenging due to subtle graph variations for different values of b. The computed values of R suggest that the graphs corresponding to different values of b do not provide an accurate linear fit, affirming the consistency of the provided TL data with second-order kinetics. A parallel analysis has been applied to all other four isothermal decay datasets, yielding the same results.

The observed decay in the current investigation is elucidated through the monomolecular (first-order) superposition theory. This type of decay results from the overlay of exponentials associated with different traps and is mathematically represented by the Equation [13]:

$$I_t = I_{01} \exp(-P_1t) + I_{02} \exp(-P_2t) + \dots$$

where I_{0n} is the phosphorescence intensity due to electrons in the traps of energy E_n , $P_n = s \exp(-E_n/kT)$ is the probability of an electron escaping from a trap, k is the Boltzmann constant, and s is the escape frequency factor. Consequently, each decay curve can be dissected into a series of exponentials using the "unraveling" procedure, enabling the calculation of E values corresponding to each exponential.

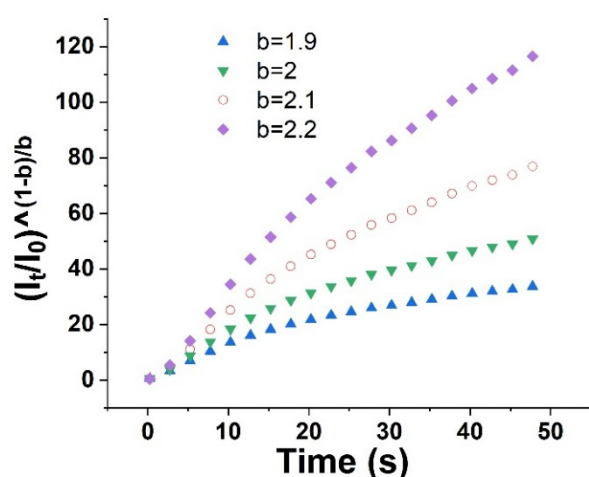


Figure 3. Isothermal decay data at a temperature of 260°C calculated for several values of kinetic order b as a function of time

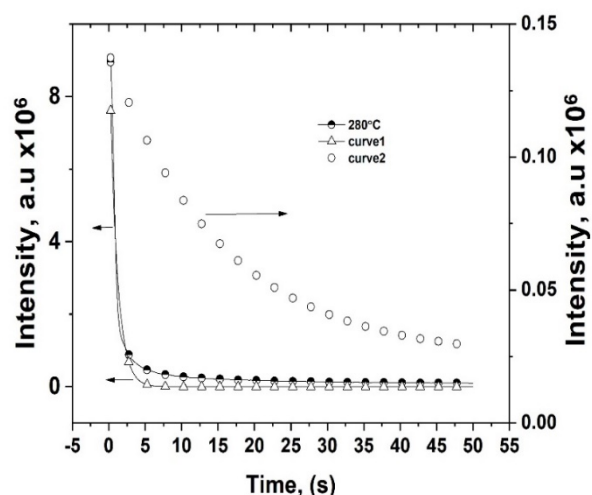


Figure 4. Isothermal decay data for the 280°C deconvoluted into two exponential decay curves

It is observed that each decay curve can be decomposed into two exponentials, as illustrated in the isothermal decay curve at 20°C presented in Fig. 4. For the first curve, $I_1 = 4.84634E6$ and $P_1 = 0.96471$, while for the second curve, $I_2 = 114707$ and $P_2 = 0.06435$. The nature of decay can thus be interpreted based on the monomolecular theory, suggesting that the luminescence kinetics adhere to a first-order process. The consideration of first-order kinetics is supported by inspecting the linearity in the $\ln(\text{TL curve1})$ and $\ln(\text{TL curve2})$ plots against time, as depicted in Figure 5. The resulting plots for curve1 and curve2 demonstrate linearity, indicating that the data conforms to first-order kinetics.

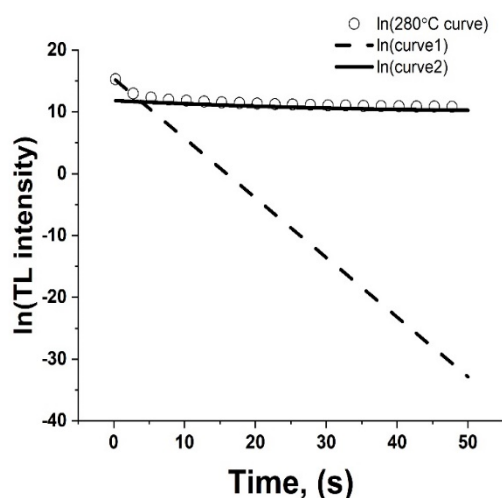


Figure 5. The isothermal decay curves on the semilog scale for the isothermal decay curve of quartz at 280°C and the two deconvoluted curves 1 and 2

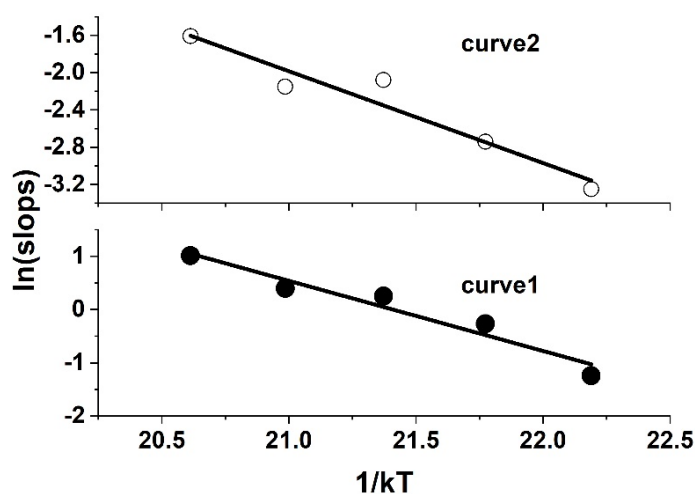


Figure 6. The $\ln(\text{slope})$ versus $1/kT$ graph to determine E for TL data of convoluted curves 1 and 2

In the subsequent step, we compile the slopes of these linear graphs in Table 1 and compute the natural logarithm of the slopes, denoted as $\ln(\text{slope})$, for all five ITL curves corresponding to the temperatures $T = 250, 260, 270, 280,$ and 290°C . A graph in Figure 6 depicts the $\ln(\text{slope})$ of curve 1 and curve 2 against $1/kT$, where T represents the temperature (in Kelvin) while recording isothermal decay curves.

Table 1. The slopes of linear isothermal graphs and their natural logarithms $\ln(\text{slope})$

Temperature $^\circ\text{C}$	$1/kT$ (eV^{-1})	Curve1		Curve2	
		slope (s^{-1})	$\ln(\text{slope})$	slope (s^{-1})	$\ln(\text{slope})$
250	22.19	0.2888	-1.24202	0.0388	-3.24934
260	21.77	0.76471	-0.26826	0.06455	-2.74032
270	21.37	1.28707	0.25237	0.12493	-2.08
280	20.99	1.48454	0.3951	0.11639	-2.15081
290	20.61	2.75118	1.01203	0.20012	-1.60884

The slope of the regression line provides the activation energy E , and interceptions for curve1 and curve2 subsequently are:

$$E1=0.99\pm 0.16 \text{ eV}; \text{intersept1} = 18.7\pm 3.4 \text{ and}$$

$$E1=1.32\pm 0.18 \text{ eV}; \text{intersept1} = 28.2\pm 4.2$$

The frequency factor s can be found from the intercept of the regression line:

$$\text{intersept1} = \ln(s1)=18.7; s1=\exp(18.7) = 1.32\times 10^8 \text{ s}^{-1} \text{ and}$$

$$\text{intersept2} = \ln(s2)=28.2; s2=\exp(28.2) = 1.77\times 10^{12} \text{ s}^{-1}$$

As reported in the literature, most natural sedimentary quartz grains exhibit two thermo-luminescence (TL) peaks, at 325 and 375 °C, when the grains are heated between 300 and 400 °C at a rate of 20 °C/s [14] and their luminescence is observed with blue and near UV color glass filters in front of the photomultiplier tube. Previous studies have shown that at a heating rate of 5 °C/s, the peaks occur at 305 and 350 °C, respectively [6]. Our observations also lead to the conclusion that the ITL data described in Figure 1 originates from more than one trap, and based on existing literature, it is inferred that there are two overlapping first-order TL peaks.

CONCLUSIONS

Investigating isothermal decay analysis of thermoluminescence (TL) peaks has provided valuable insights into the kinetic parameters governing this luminescent phenomenon. The challenges associated with achieving precise linear fits for different kinetic order values (b) underscore the intricacies of the analysis. In summary, it can be inferred that the trap responsible for the ITL signals at 250, 260, 270, 280, and 290°C does not conform to first, second, or general order kinetics. This deduction is supported by: (a) The decay pattern of the ITL signal recorded at 250, 260, 270, 280, and 290°C deviates from the behavior described by Eq. (5) for b values ranging from 1 to 2 (refer to Fig. 2 and 3). (b) These observations lead to the conclusion that the TL data depicted in Fig. 4 originates from more than one trap, and based on existing literature, it is inferred that there are two overlapping first-order TL peaks.

This thorough analysis contributes to the understanding of TL peaks and establishes a robust methodology for characterizing luminescence mechanisms in materials. The consistent application of these analytical techniques to isothermal decay data across various temperatures enhances the reliability and applicability of our findings. In summary, our study advances the understanding of kinetic parameters in TL peaks and provides a foundation for future research in luminescence dosimetry.

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**АНАЛІЗ ІЗОТЕРМІЧНОГО РОЗПАДУ ПІКІВ ТЕРМОЛЮМІНЕСЦЕНЦІІ КВАРЦУ
ДЛЯ ВИЗНАЧЕННЯ КІНЕТИЧНИХ ПАРАМЕТРІВ****Сахіб Мамедов, Муслім Гурбанов, Акшин Абішов, Ахмад Ахадов***Інститут радіаційних проблем Міністерства науки і освіти Азербайджану,
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Це дослідження заглиблюється в тонкощі аналізу ізотермічного розпаду, застосованого до піків термолюмінесценції (TL), зосереджуючись на визначенні кінетичних параметрів. Дослідження ставить під сумнів відповідність пастки, відповідальної за сигнали ІТЛ, кінетиці першого, другого чи загального порядку, що підтверджується невідповідною схемою розпаду та висновком про два перекриваються піки TL першого порядку. Ця робота покращує розуміння піків TL і встановлює надійну методологію для характеристики механізмів люмінесценції в матеріалах, сприяючи прогресу в дослідженнях люмінесцентної дозиметрії. Ці спостереження приводять до висновку, що дані TL походять від більш ніж однієї пастки, і на основі існуючої літератури робиться висновок про наявність двох перекриваючих піків TL першого порядку. Дослідження передбачає розгляд ізотермічних даних розпаду при різних температурах ($T = 250, 260, 270, 280$ і 290°C) і досліджує проблеми, пов'язані з досягненням точних лінійних відповідностей для різних значень кінетичного порядку (b). Природа розпаду інтерпретується на основі мономолекулярної теорії, яка передбачає дотримання процесу першого порядку. Криві ІТЛ були розведені на дві експоненціальні криві розпаду. Нахили ліній регресії забезпечують значення енергії активації (E) для кривої 1 і кривої 2 відповідно: $E_1 = 0.99 \pm 0.16$ eV і $E_2 = 1.32 \pm 0.18$ eV. Коefіцієнт частоти (s) визначається з точки перетину лінії регресії: $s_1 = 1.32 \times 10^8 \text{ c}^{-1}$ та $s_2 = 1.77 \times 10^{12} \text{ c}^{-1}$.

Ключові слова: *ізотермічний розпад; кварц; енергія активації; частотний фактор*