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THERMOLUMINESCENCE BEHAVIOR AND KINETIC ANALYSIS OF QUARTZ UNDER GAMMA IRRADIATION

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This study investigates the luminescence characteristics of quartz samples irradiated with a 60Co gamma source across a dose range of 57 to 570 Gy. Prior to irradiation, the samples were annealed at 650°C for two hours. The thermoluminescence (TL) spectra were measured at a heating rate of 5°C/sec, revealing two primary peaks at approximately 200°C and 320°C. The intermediate peak displayed a shoulder around 150°C. It was observed that the peak temperature maximum (Tm) at 206±2°C remained constant regardless of the irradiation dose. The intensity of the intermediate peak decreased significantly over time, with a lifetime estimated at 8±2 days for most doses and 19±2 days for the highest dose (570 Gy). Dose-response studies showed a linear relationship between the TL intensity and the irradiation dose up to 600 Gy. Comparisons with natural quartz samples indicated significant differences in glow curve shapes and sensitivities. Computerized glow curve deconvolution (CGCD) methods confirmed that the annealed quartz glow curve could be described as a superposition of four first-order kinetic peaks. These findings provide important insights into the stability and behavior of TL signals in quartz, which are crucial for applications in radiation dosimetry and archaeological dating.
Keywords: *Quartz; Isothermal decay, Lifetime; Radiation dosimetry; GlowFit*
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INTRODUCTION

Quartz is widely used in dating and dose reconstruction applications and it requires precise determination of the trap parameters for the intermediate glow peaks in this mineral [1,2]. Investigation of the lifetimes of these peaks is essential for determining the appropriate time frame for conducting retrospective measurements. These intermediate energy level peaks appear in the glow curve within the temperature range of 150–250°C. The intermediate temperature peaks of quartz can be used for dose determination because, due to their relatively short lifetimes, the geological TL signal, i.e., peaks in the higher temperature region, is expected to be weak compared to that produced by artificial radiation. Burnt bricks or roof slabs, which form a significant and integral part of building structures, are widely used in retrospective and emergency dosimetry. As trapped electrons are released by heating, the electrons accumulated over time are released and the TL intensity is canceled by their production.

This research explored the thermoluminescence (TL) properties of quartz [3] identified ten trapping centers with activation energies between 0.62 and 2.96 eV through kinetic analysis of the glow curve. Each glow curve component was tested for linearity. Further analysis using Tm-Tstop and various heating rates (VHR) provided the kinetic parameters, including activation energy (E, eV). The quartz samples' minimum detectable dose (MDD) was determined, and the dosimeter demonstrated good reproducibility. The fading signal was also evaluated over different storage durations.

The TL characteristics and the structural changes in the irradiated quartz were analyzed by examining the crystallinity index through infrared bands of the SiO_4 tetrahedron in the mid-infrared region [4]. Colorless quartz, containing aluminum impurities, turns dark smoky upon exposure to ionizing radiation. The TL glow curve analysis identified four trapping sites with TL peaks at 169, 212, 279, and 370°C. Kinetic parameters, including the order of kinetics, activation energy, and frequency factor, were determined using Chen's peak shape method and the initial rise method. The study discussed the role of $[AlSiO_4/h+]0$ centers (formed when Si^{4+} is replaced by Al^{3+} and charge compensated by a hole) in color development and luminescence, correlating FTIR and TL results. A range of studies have explored the influence of pre-treatment on the thermoluminescent properties of quartz. The glow curves of various quartzes showed glow peaks around 150-170, 190-220 and 290-320°C, which have been reported by several researchers [5,6]. Kitis [7] found that the sensitivity of quartz to heat and irradiation treatments varied, with a significant change in sensitivity occurring at around 10 Gy. Those changes were significant when predose treatment was combined with the heat treatment. This was further explored by [8], who observed that the intensity of glow peaks in synthetic quartz increased between room temperature and 200°C after heat treatments, with good stability above 250°C. The glow-curve of a quartz annealed at 900ºC irradiated to 10 Gy shows three peaks; the main peak at 71 °C and two other peaks at 125°C and 177°C [9]. The center responsible for peak at 177°C is stable at ambient temperature and estimated values for the activation energy and frequency factor of the peak were as ~1.24 eV and ~10^{12} s^{-1} respectively. The intensity of the peak at 177ºC shows sublinear dose dependency in the range 1–300 Gy. Based on the impact of irradiation dose on the peak position authors suggested that the peak follows non-first-order kinetics. The involvement

Cite as: A. Abishov, S. Mammadov, M. Gurbanov, A. Ahadov, A. Ahadova, East Eur. J. Phys. 4, 373 (2024), https://doi.org/10.26565/2312-4334-2024-4-43 of specific defects in the production of thermoluminescence in quartz was highlighted by [10], who identified the $(AlO_4)0$ center and suggested the involvement of H^+ ions. These studies suggest that pre-treatment can significantly impact the thermoluminescent properties of quartz, with specific defects playing a key role in this process.

TL peaks around 150 and 200°C were reported also in [11], while glassy quartz exhibited the second peak at 300°C. TL intensity as a function of heating rate showed a decrease in TL intensity and a shift of TL peaks to higher temperatures due to thermal quenching. Using a computerized glow curve deconvolution program, the glow curve of quartz was resolved into five distinct peaks.

The thermoluminescence (TL) peaks in the intermediate temperature range (350-550 K) of the quartz glow curve are crucial for dose evaluation in both dating and retrospective dosimetry. Despite numerous studies on the TL properties of quartz in this temperature range, there is no consensus on the published values of the trap parameters (thermal activation energy and frequency factor). There is also inconsistency in measurements across different types of quartz and a lack of a consistent progression of trap depth with glow curve temperature.

MATERIALS AND METHODS

Retrospective and emergency dosimetry considers fired bricks and other ceramic products that contain quartz as potential dosimeters. Quartz can be present in the composition of these materials as natural impurities in the raw materials or as fillers to improve the quality of the fired products. In this work we used quartz extracted from fired bricks. The extraction procedure for quartz from intact brick samples involves soaking the sample in dilute hydrofluoric or hydrochloric acid in an ultrasonic bath at room temperature for several hours to loosen the clay matrix. Once softened, the sample is rinsed in distilled water and gently crushed. The crushed sample is then dried, sieved, magnetically separated, and rinsed in acetone. Etched crystals are treated with aluminum chloride, washed, and re-sieved before TL analysis. The quartz fraction with a size of 100-200 μm was used for the experiments. Part of the samples were heated to 650°C for two hours before irradiation. Irradiation was carried out in a gamma irradiator with a dose rate of 0.095 Gy/sec. The dose rate was determined by the electron paramagnetic resonance method using alanine dosimetry using the Magnettech Miniscope MS400 EPR Spectrometer [12]. TL measurements were performed in a Harshaw TLD3500 Manual Reader in a N_2 atmosphere using a Chance Pilkington HA-3 heat- absorbing filter with 80% transmittance response in visible regions (400–700 nm). The methodology of TL measurement is described in previous papers [13,14].

RESULTS AND DISCUSSIONS

Luminescence curves of quartz samples irradiated with a ^{60}Co gamma source in the range of 57 to 570 Gy are shown in Figure 1. Prior to irradiation, the quartz samples were heated at 650°C for two hours. TL spectra were measured at a heating rate of 5°C/sec. Since the TL spectra were taken one day after irradiation, a lower temperature peak in the region of 110°C is not observed. This peak is known to have a short half-life even at room temperature. The spectra clearly show two main peaks, the first at about 200°C and the second at 320°C. The first peak in turn has a shoulder on the left side somewhere around 150°C. The inset in Figure 1 also illustrates the dose dependence of the position of the peak temperature maximum (Tm). The value of Tm is 206±2 °C and is independent of the irradiation dose. As shown below, the intensity of the intermediate peak decreases with time during storage, even at room temperature. It was found that the peak positions remain stable during long-term storage, although the intensity decreases by more than half.

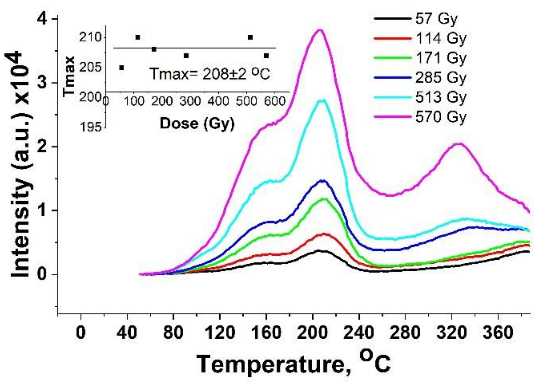

Figure 1. Glow curves of samples heated at 650°C for two hours and irradiated at different doses. The dose dependence of the position of peak maximum temperature (Tm) is given in the inset

The dependence of the temperature at peak maximum ($Tmax$) of a thermoluminescence (TL) glow peak on the radiation dose is a well-known feature in the TL literature. This shift in $Tmax$ with accumulated dose makes it a dynamic experimental parameter. The OTOR model predicts this effect, though it is more commonly explained using the empirical general order kinetics equation. In this framework, the dependence of $Tmax$ on radiation dose is stronger for second-order kinetics and diminishes for first-order kinetics. However, experimental verification of this shift is not consistent, despite extensive TL literature on dose response studies. The OTOR model also forms the basis for the single unit TL peak model, which helps in evaluating kinetic parameters and deconvoluting complex TL glow curves but is not used to explain broader TL effects like dose response and sensitivity variations.

Figure 1 clearly shows that the temperature at peak maximum ($Tmax$) of any TL peak for all studied materials remains constant across different doses, indicating no dependence of $Tmax$ on dose. Regardless of the events during trap filling (irradiation), a certain number of traps are filled with n_0 electrons by the end of irradiation, making the unbleached TL integral correspond to N traps, where $n_0 = N$. After thermal or optical bleaching, some trapped electrons (n_{01}) escape, leaving a portion (N_1) of traps empty. During subsequent TL readout, the number of empty traps is N - N_1. Increasing the duration of thermal or optical bleaching increases the number of empty traps (N - N_1), thus enhancing the probability of re-trapping, which contributes to the shift in $Tmax$ and an increase in kinetic order.

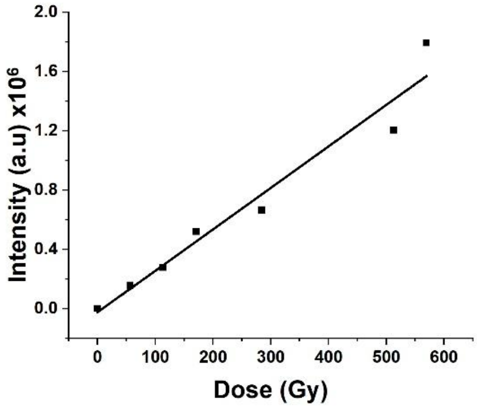

Figure 2. Dose dependence of intermediate temperature TL peaks of quartz heated at 650°C.

The predictions concerning the shift of $Tmax$ as a function of radiation dose has been assessed by [15] using TL peaks derived according to the OTOR phenomenological model, as well as using synthetic TL peaks derived from analytical expressions. It is shown that in the case of non-first-order kinetics, the shift of $Tmax$ as a function of trap emptying is confirmed by experimental results.

Dose dependence of annealed quartz presented in Figure 2. The TL intensity of this glow peak was calculated from the area under the glow curve in the temperature range 180-240°C. Figure 2 shows that the intensity of the glow peak at 206oC shows a linear dependence on the irradiation dose within the dose range up to 600 Gy.

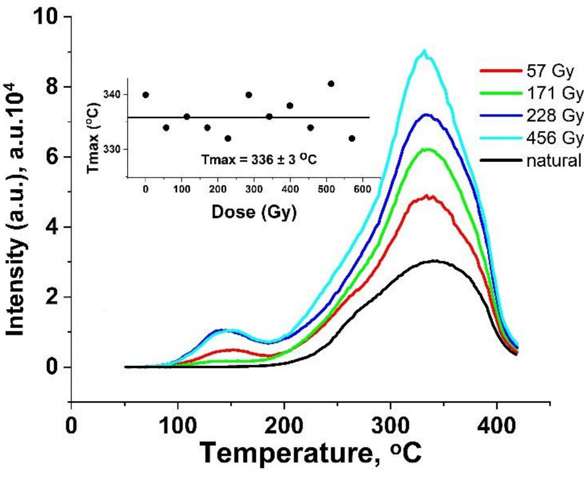

Figure 3. Glow curves of unheated samples irradiated at different doses. The dose dependence of the position of peak maximum temperature (Tm) is given in the inset

For the composition with the annealed quartz, the glow curves of the natural quartz are shown in Fig. 3. Changes in the shape of the glow curve are obvious: firstly, the natural quartz that has not been irradiated shows no peaks in the temperature region up to 250°C and only one broad peak above the 300°C temperature region. Secondly, the sensitivity of the peaks in the intermediate temperature range is several times lower than that of the annealed samples. At the same time, the peak at around 336°C shows no significant shift with increasing irradiation dose, again indicating that this peak or its components most likely follow first order kinetics (see inset in Fig. 3).

Computerized glow curve deconvolution (CGCD) methods were used to determine the number of peaks and kinetic parameters (kinetic orders b, activation energy E and frequency factor s) associated with the thermoluminescence (TL) glow peaks in annealed quartz irradiated at 570 Gy (Fig.4). The results of the CGCD method analysis indicate that the glow curve of quartz annealed at 650ºC can best be described as a superposition of four glow peaks, all of which have first order kinetics. Estimated parameters of four peaks are listed in Table 1.

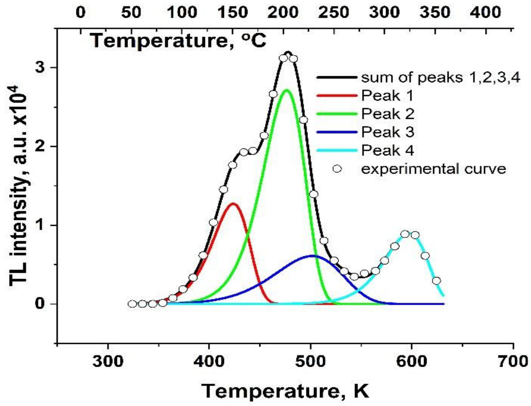

Figure 4. The TL spectrum of quartz deconvoluted into four first-order peaks. The quartz was heated to 650ºC and irradiated with a dose of 570 Gy

Table 1. Kinetic parameters of the four deconvoluted peaks

Peak ID	Tm, K	E, eV	S, s^{-1}
Peak 1	424	0.82	2,70E+9
Peak 2	476	0.91	1.73E+9
Peak 3	502	0.61	0.33E+6
Peal 4	597	1.41	3.69E+11

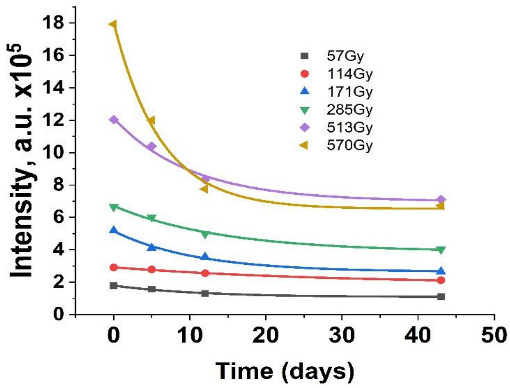

Figure 5. Changes in the TL intensity of intermediate peaks with time at room temperature. Quartz samples were irradiated at different doses

Fading process, which are very important in radiation dosimetry and archaeological dating, of individual TL peaks of this material were also investigated. Each of samples irradiated at 57, 114, 171, 285, 513 and 570 Gy were read after 5, 12 and 43 days. The dose responses of all the glow curves show a similar pattern, with peak temperatures remaining in the same positions. Figure 5 shows the decay of the intermediate peak intensity at room temperature. The experimental data were fitted using the exponential decay function, which allows the lifetime of the responsible center to be estimated at room temperature. For all samples it was estimated to be 8±2 days, except for the sample irradiated at 570 Gy. For these samples the estimated lifetime was 19±2 days.

Quartz luminescence is typically explained phenomenologically, such as through thermoluminescence (TL), where a trapped electron is thermally excited to the conduction band and recombines with a nearby hole in the valence band. However, this explanation does not fully account for the large difference between the band gap energy and the emitted photon energy, often attributed to increased lattice vibrational energy.

Itoh et al. [10] proposed a different, physically-based defect pair model. They explained both optically stimulated luminescence (OSL) and two prominent TL bands (110 °C and 325 °C) through reactions involving defect species created during ionizing irradiation. This model builds on the alkali halide model for luminescence. In quartz, various defect species, especially the aluminum ion (Al^{3+}), play crucial roles. Al^{3+} replaces Si^{4+} in the crystal structure, and charge balance is maintained by interstitial protons or alkali ions like Li^+ and Na+.

When quartz undergoes β or γ ionizing radiation, electron/hole pairs are generated, and interstitial charge-balancing ions are released. For example, as $AlO_4M^+ = AlO_4 + M^+$, where M^+ moves and is captured by defects, forming complexes such as XO_4 + M+ = XO_4/M^+. According to [6], the positively charged [XO_4/M^+] complex can absorb an electron to form a neutral [XO_4/M^+]0, suggested as the source of the 110 °C TL band. Further, the [XO_4/M^+]0 complex may exist in different states, each responsible for different TL bands, such as those at 160 °C and 220 °C.

CONCLUSIONS

This research analyzed the luminescence behavior of quartz samples subjected to gamma irradiation within the range of 57 to 570 Gy. The study revealed that the peak temperature maximum (Tm) of the thermoluminescence (TL) peaks was consistently observed at 206±2°C, regardless of the irradiation dose. Additionally, the intermediate peak intensity exhibited significant decay over time, with lifetimes estimated at 8±2 days for most doses, except for the 570 Gy dose, which showed a longer lifetime of 19±2 days.

The dose-response analysis indicated a linear relationship between the TL intensity of the glow peak at 206°C and the irradiation doses up to 600 Gy. Comparisons with natural quartz samples demonstrated significant differences: natural quartz showed no peaks up to 250°C and only a broad peak above 300°C. The sensitivity of intermediate temperature range peaks in natural quartz was markedly lower than in annealed samples, suggesting distinct kinetic behaviors.

Furthermore, computerized glow curve deconvolution (CGCD) revealed that the glow curve of annealed quartz could be best described as a superposition of four first-order kinetic peaks. These findings underscore the stability and reliability of the 206°C peak in TL studies and highlight the notable differences between natural and annealed quartz. This provides valuable information for applications in radiation dosimetry and archaeological dating.

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ТЕРМОЛЮМІНЕСЦЕНЦІЙНА ПОВЕДІНКА ТА КІНЕТИЧНИЙ АНАЛІЗ КВАРЦУ ПІД ГАММА-ОПРОМІНЕННЯМ

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Це дослідження досліджує характеристики люмінесценції зразків кварцу, опромінених гамма-джерелом 60Co в діапазоні доз від 57 до 570 Гр. Перед опроміненням зразки відпалювали при 650°C протягом двох годин. Спектри термолюмінесценції (TL) вимірювали при швидкості нагріву 5°C/с, виявляючи два первинних піки приблизно при 200°C і 320°C. Проміжний пік показав плече близько 150°C. Було помічено, що пік максимуму температури (Tm) при 206±2°C залишався постійним незалежно від дози опромінення. Інтенсивність проміжного піку значно зменшувалася з часом, причому тривалість життя оцінювалася в 8±2 дні для більшості доз і 19±2 дні для найвищої дози (570 Гр). Дослідження залежності доза-відповідь показали лінійну залежність між інтенсивністю TL і дозою опромінення до 600 Гр. Порівняння із зразками природного кварцу показало значні відмінності у формах кривих світіння та чутливості. Методи комп'ютеризованої деконволюції кривої світіння (CGCD) підтвердили, що криву світіння відпаленого кварцу можна описати як суперпозицію чотирьох кінетичних піків першого порядку. Ці знахідки дають важливу інформацію про стабільність і поведінку сигналів TL у кварці, які мають вирішальне значення для застосування в радіаційній дозиметрії та археологічному датуванні.
Ключові слова: *кварц; ізотермічний розпад, час згасання; радіаційна дозиметрія; GlowFit*